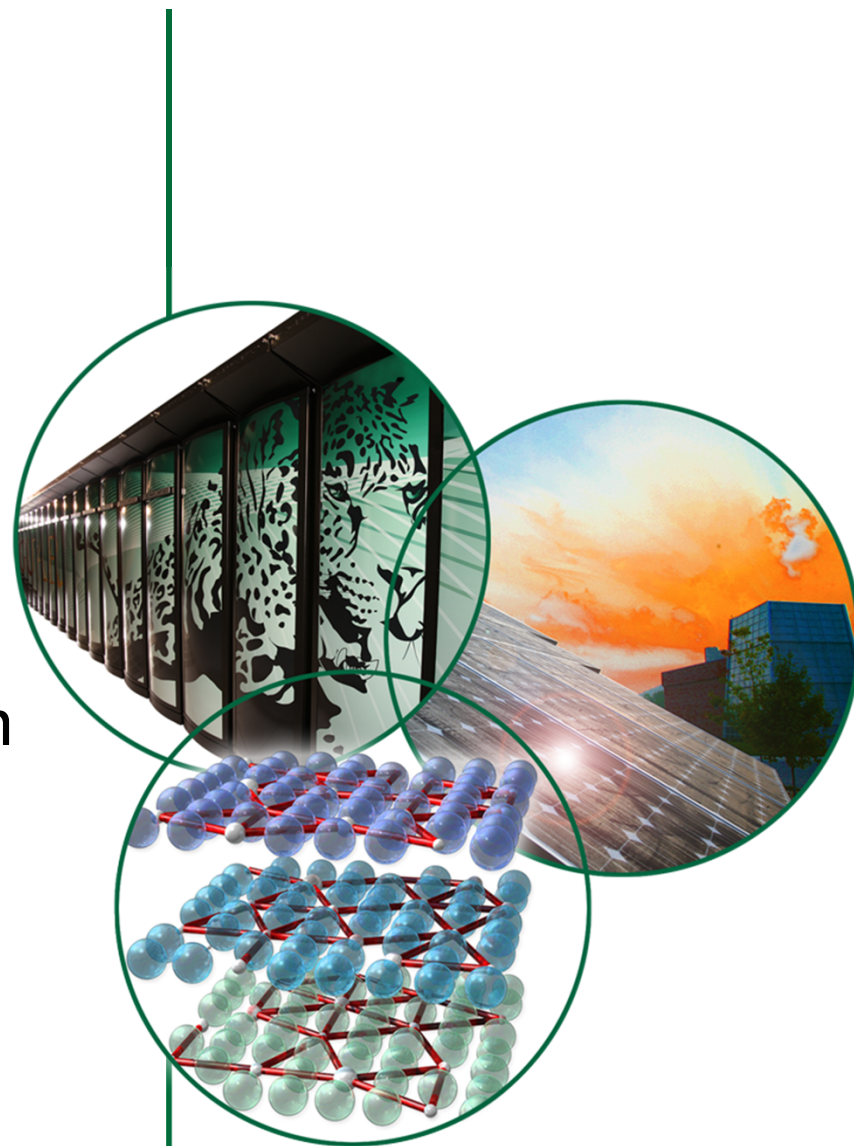


Quasielastic Neutron Scattering

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August 19, 2013



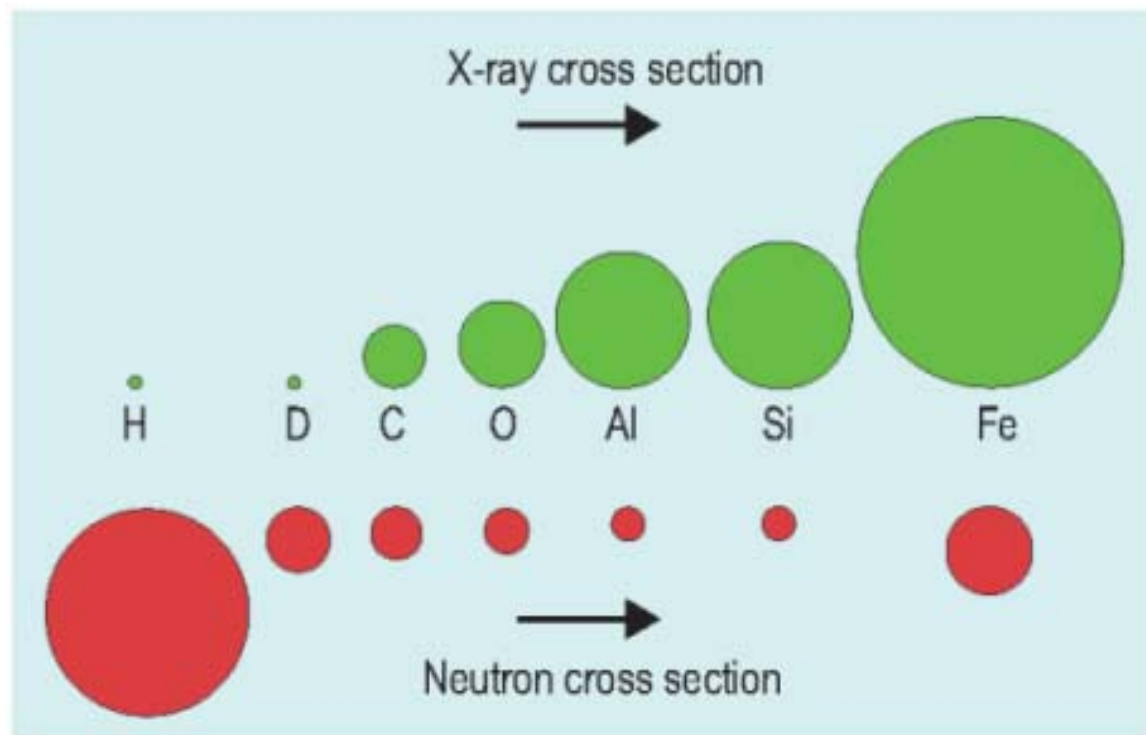
OUTLINE

- 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)
 - “Theory of Thermal Neutron Scattering”, W. Marshall and S. W. Lovesey, Oxford University Press (1971). (out of print)

Neutron Properties – H is our friend!

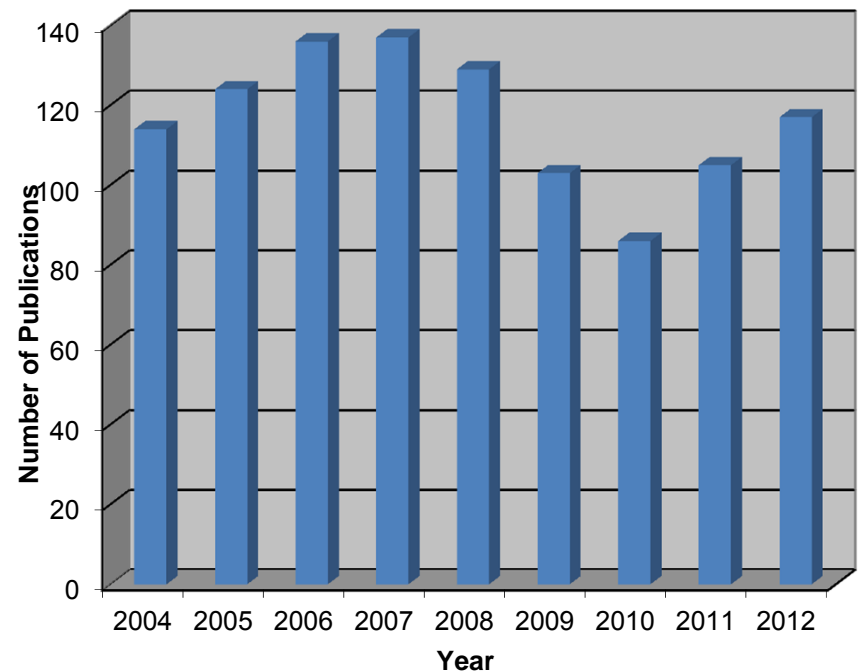


- Isotopic sensitivity of H
 - H has a large incoherent neutron scattering cross-section
 - H and D have opposite signed scattering lengths
 - D has a much smaller cross section
- The signal from samples with H are often dominated by the incoherent scattering from H
- The Q and ω ranges probed in QENS experiments is well-suited to the “self” part of the dynamic structure factor

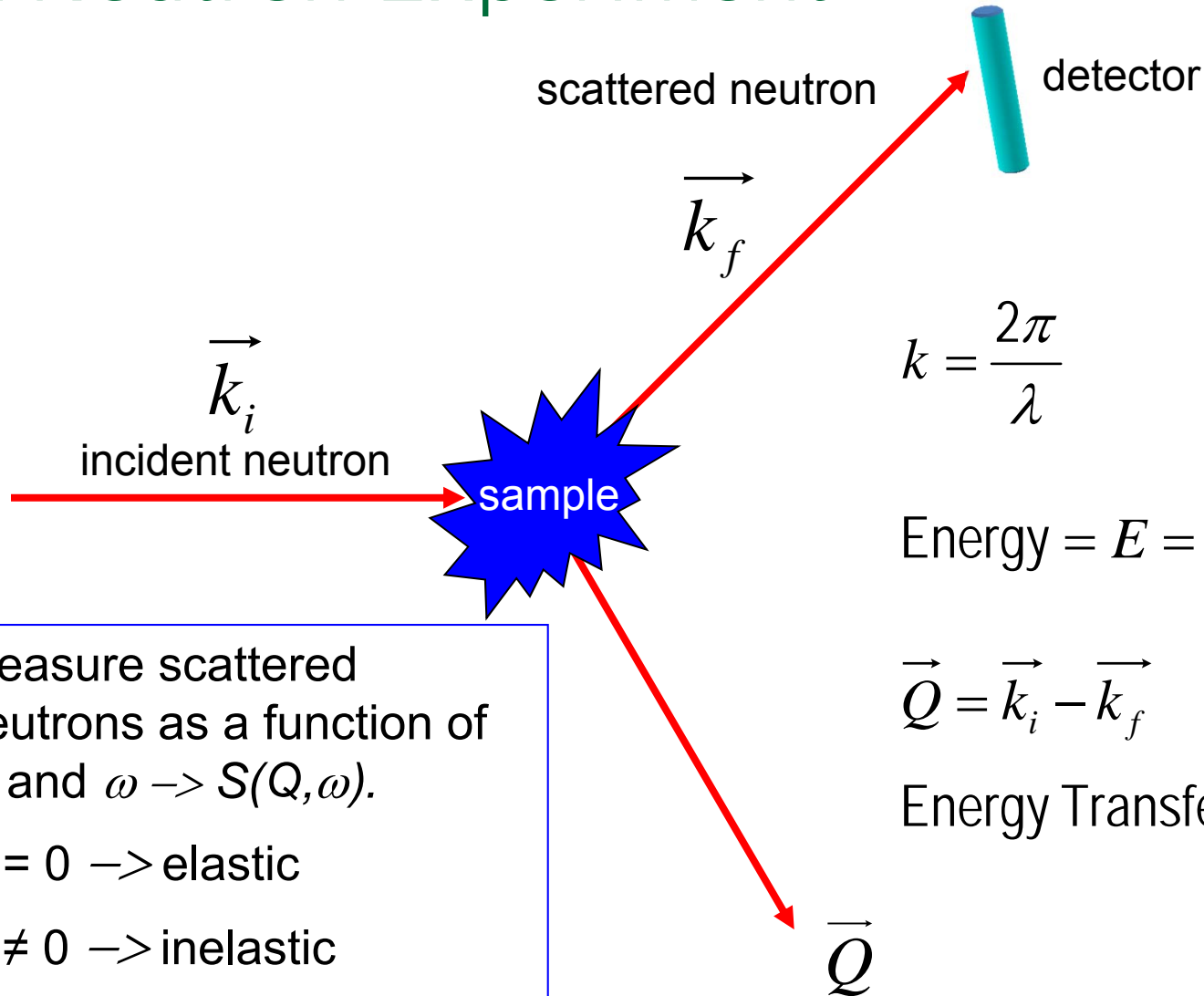
Quasi-elastic Neutron Scattering (Why Should I Care?)

- 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

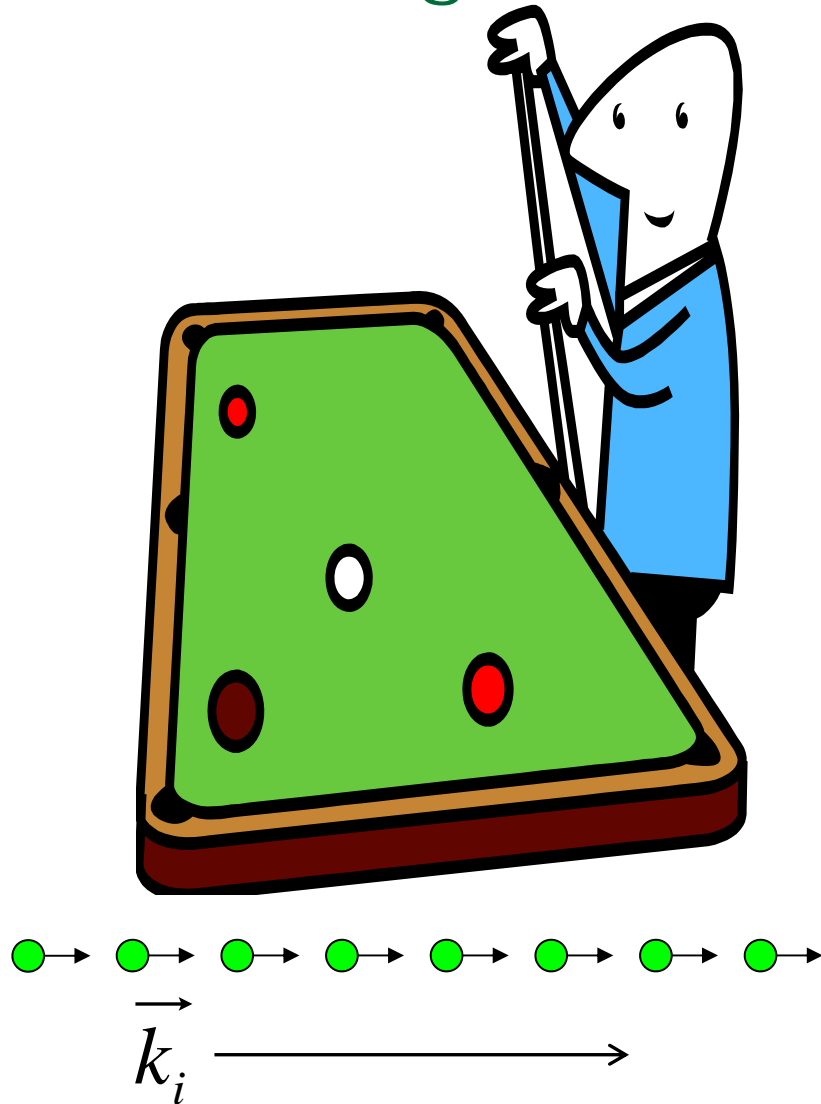
Neutrons AND (QENS OR quasi-elastic OR quasielastic)



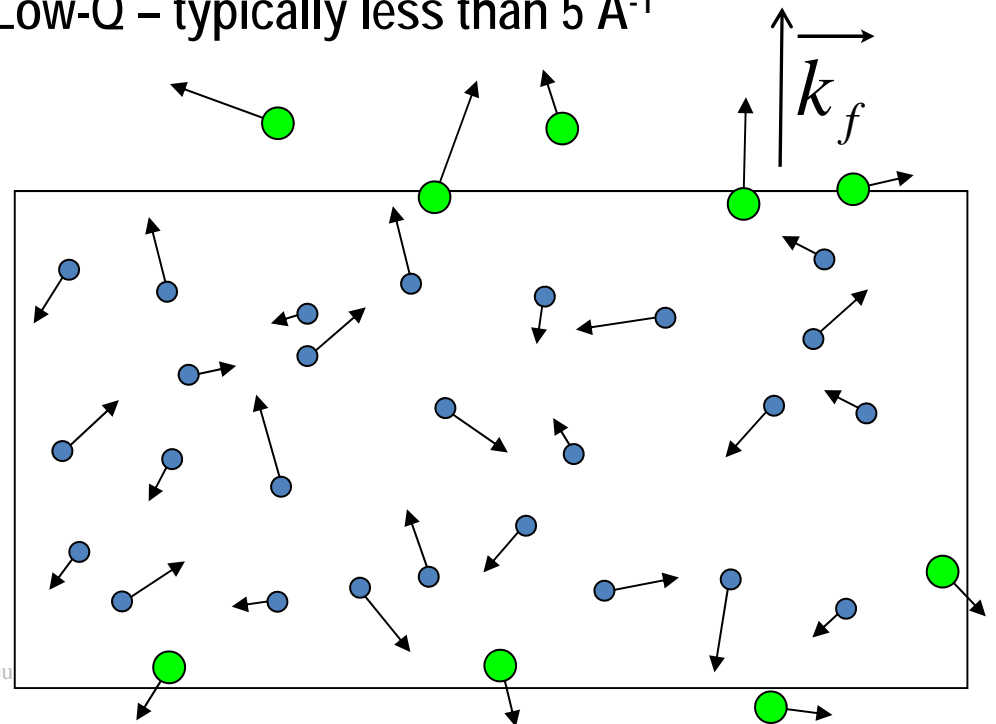
A Neutron Experiment



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 \AA^{-1}



Experiment Design

- σ is the microscopic cross section (bn/atom) 10^{-24} cm²/atom
- n is the number density (atom/cm³)
- 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 cm² beam
(BaSiS, HFBS, CNCS, DCS)***

An Example – Water

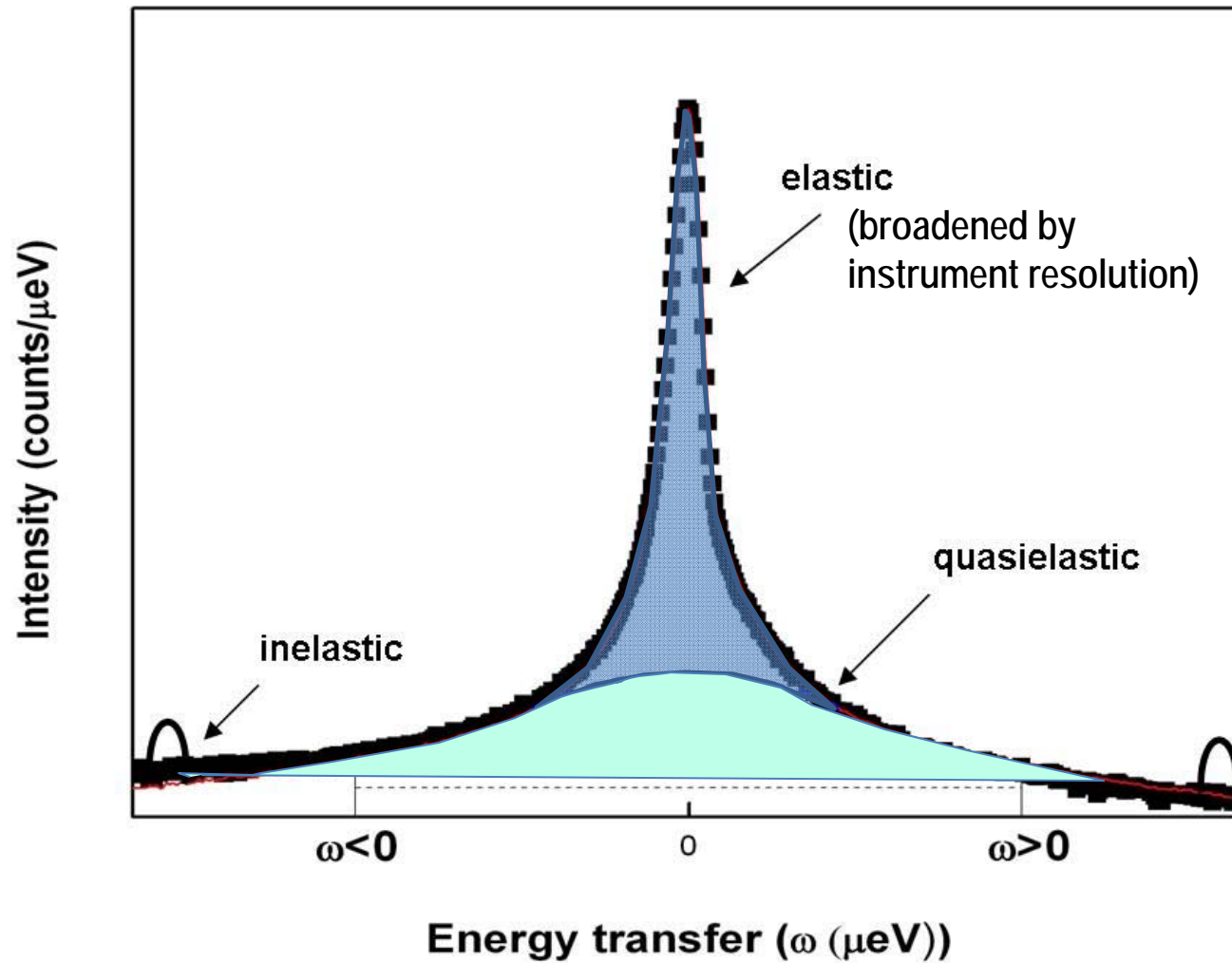
$$n = \frac{1 \text{ gm}}{\text{cm}^3} \times \frac{1 \text{ mole}}{18 \text{ gm}} \times \frac{6.02 \times 10^{23}}{\text{mole}} = \frac{3.34 \times 10^{22}}{\text{cm}^3}$$

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

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

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

QENS Spectra



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

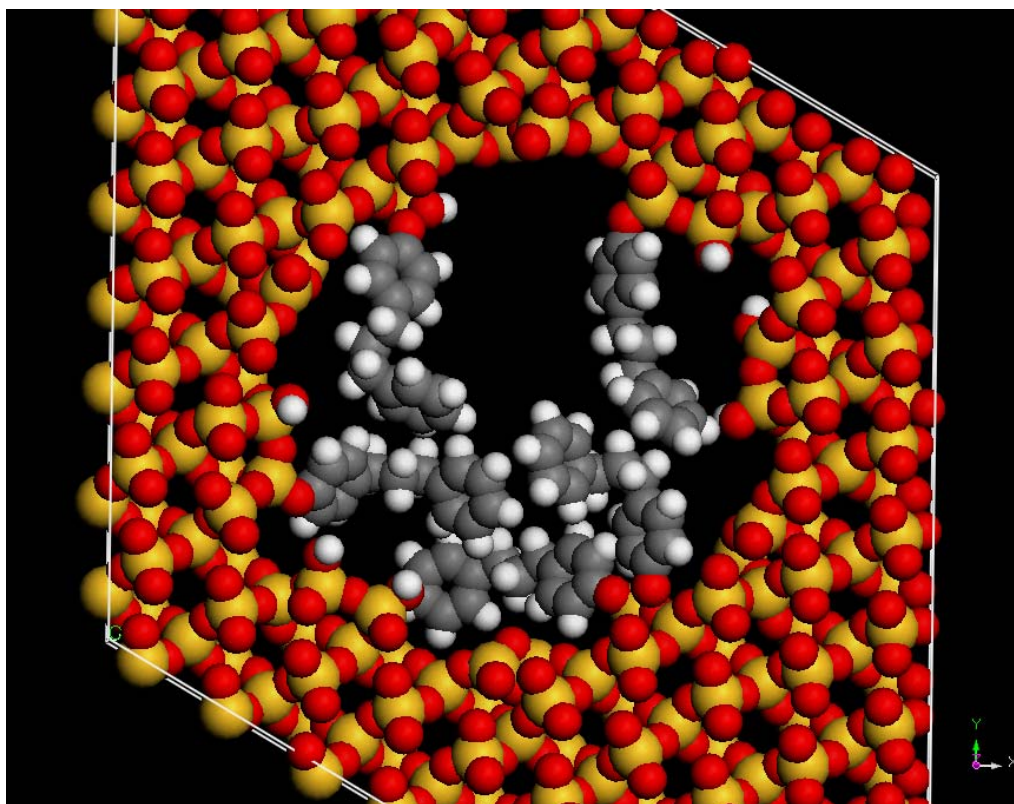
$$I_{inc}(\mathbf{Q}, t) = \frac{1}{N} \sum_i \langle \exp\{i\mathbf{Q} \cdot \mathbf{R}_i(t)\} \exp\{-i\mathbf{Q} \cdot \mathbf{R}_i(0)\} \rangle$$

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

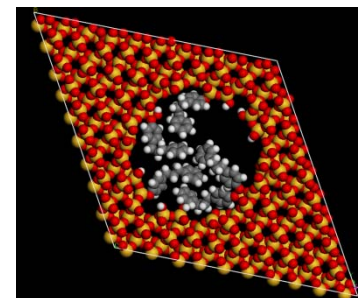
$$S_{inc}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{inc}(\mathbf{Q}, t) \exp(-i\omega t) dt$$

QENS and Molecular Dynamics Simulations

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



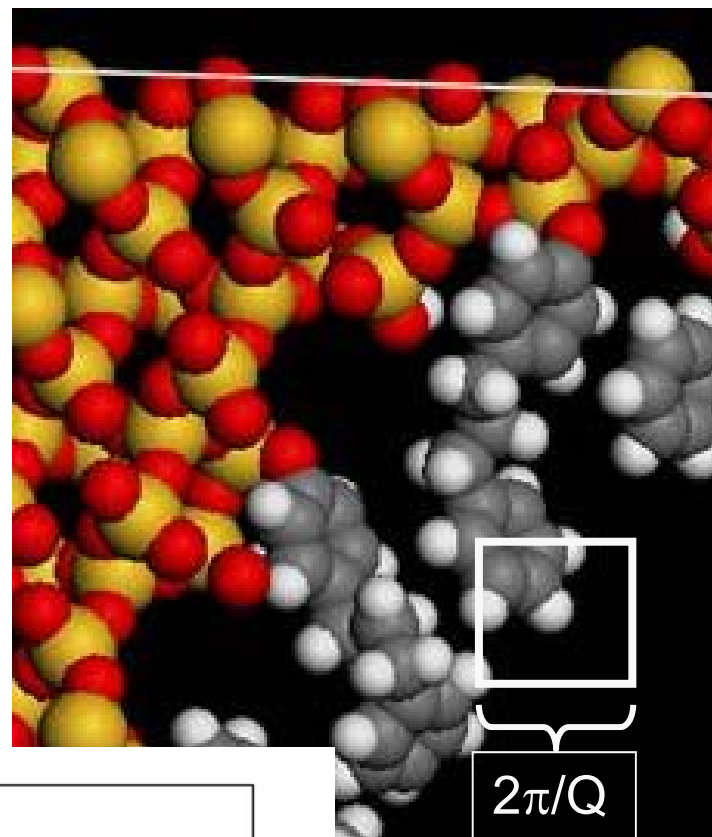
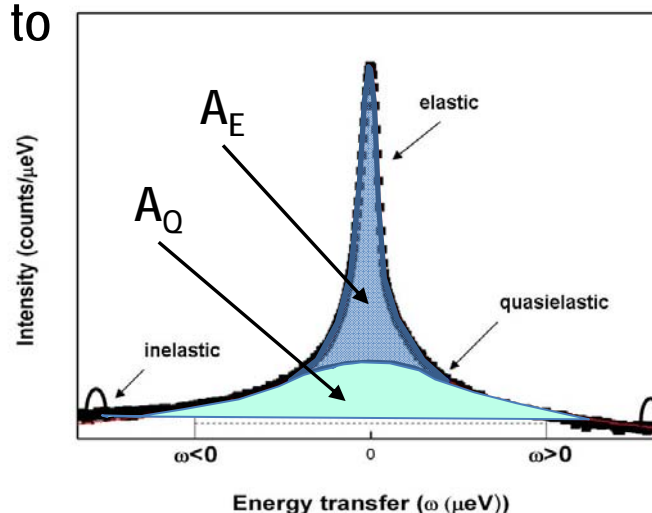
**1,3 diphenylpropane
tethered to the pore
surface of MCM-41**



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

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



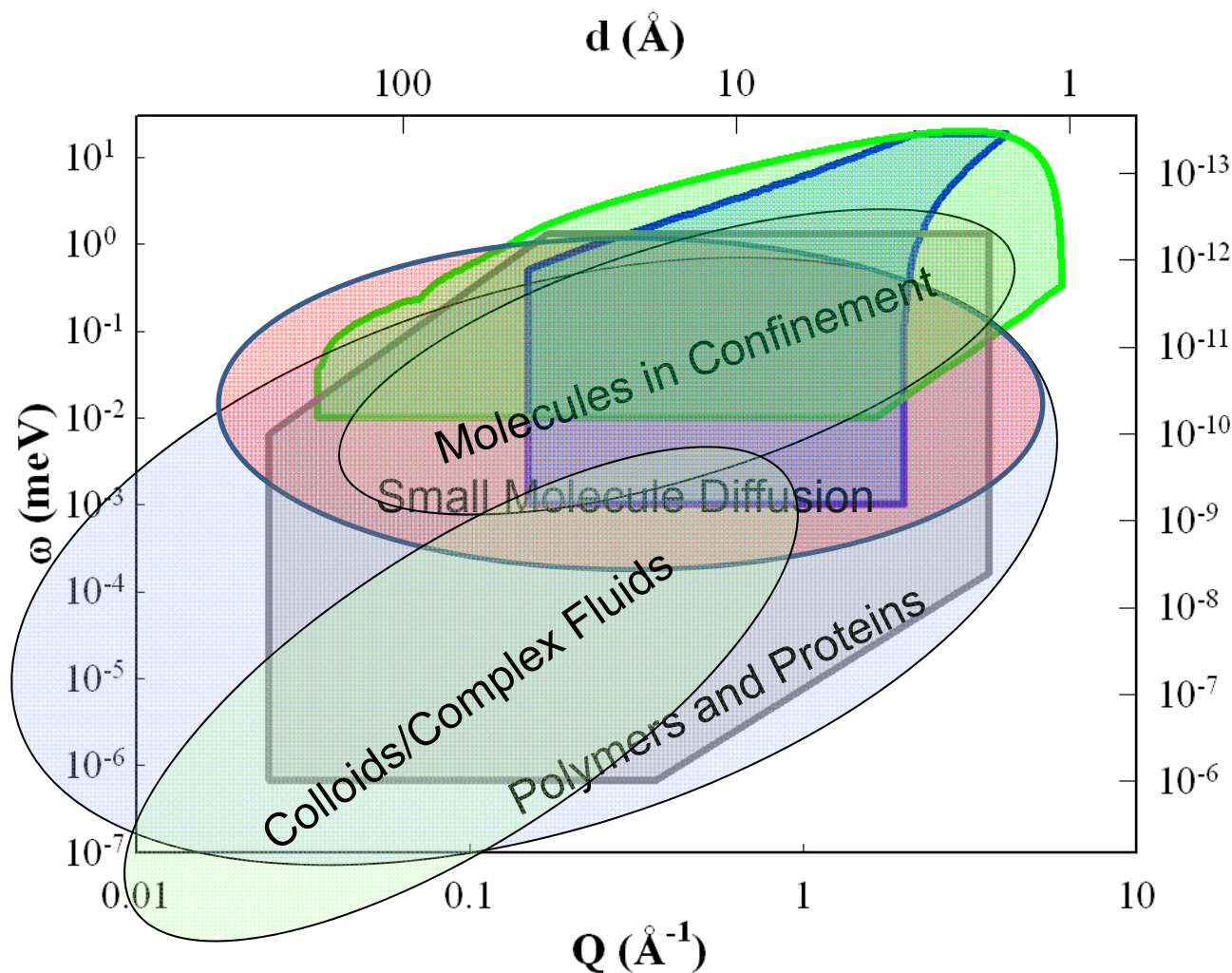
QENS and Neutron Scattering Instruments

- Probe Diffusive Motions
 - Length scales set by Q , $0.1 \text{ \AA}^{-1} < Q < 3.7 \text{ \AA}^{-1}$, $60 \text{ \AA} > d > 1.7 \text{ \AA}$.
 - 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 λ limits Q)
 - Incident neutron wavelengths typically 4 \AA to 12 \AA (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 (f to 400 nsec)
- Trade-offs
 - Resolution/count rate
 - Flexibility
 - Dynamic range
 - Neutron λ vs Q
 - large λ \rightarrow high resolution \rightarrow long times/slow motions
 - large λ \rightarrow limited Q-range, limited length scales

The High-Resolution Neutron Spectrometer Landscape



● Backscattering

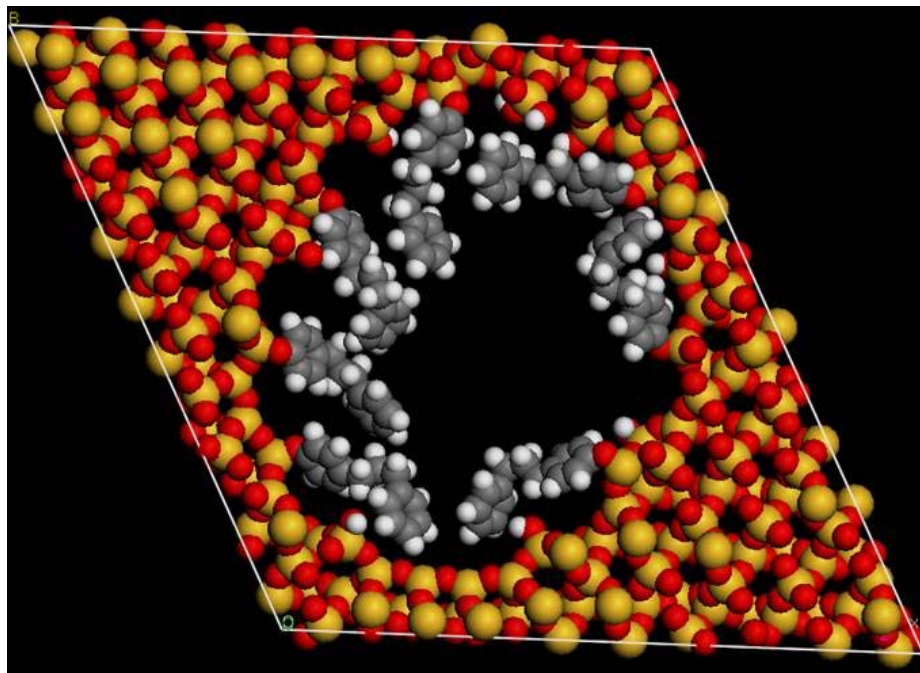


● Cold Neutron Chopper

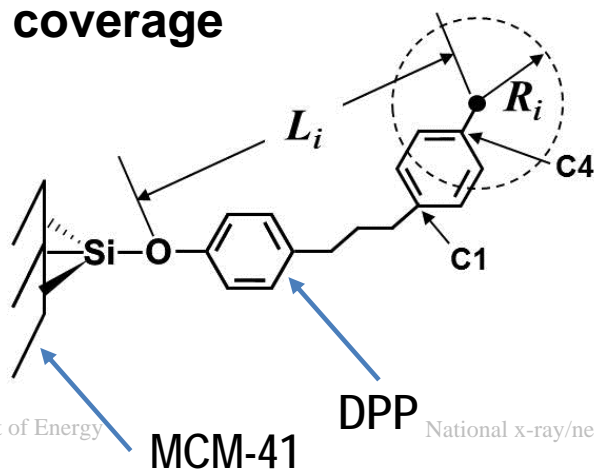


● Neutron Spin Echo

Restricted Diffusion – Tethered Molecules



**MCM-41 (2.9 nm pore diameter)
high DPP coverage**

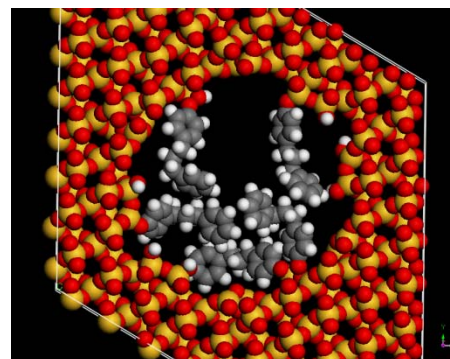


Samples – typical 0.7 g

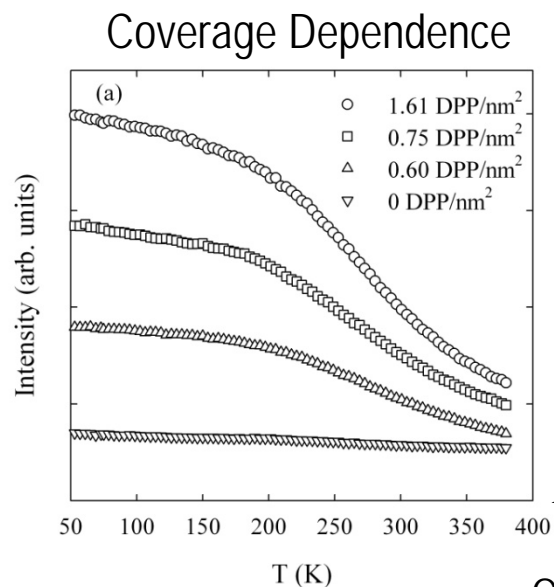
240 K < T < 340 K

Simple Fit – Lorentzian + δ

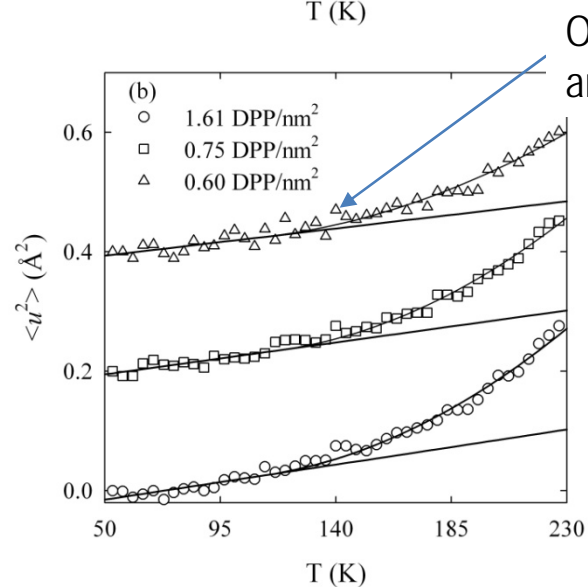
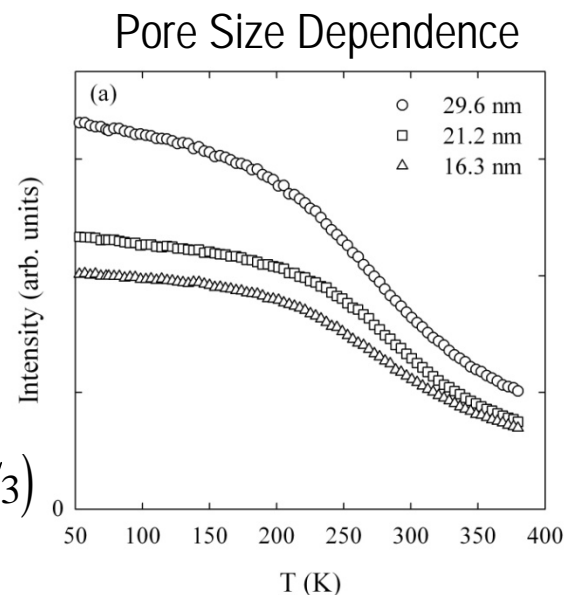
Pore Diameter (nm)	Coverage (molecules/nm ²)
1.6	0.85 (saturation)
2.1	1.04 (saturation)
3.0	0.60 0.75 1.61 (saturation)



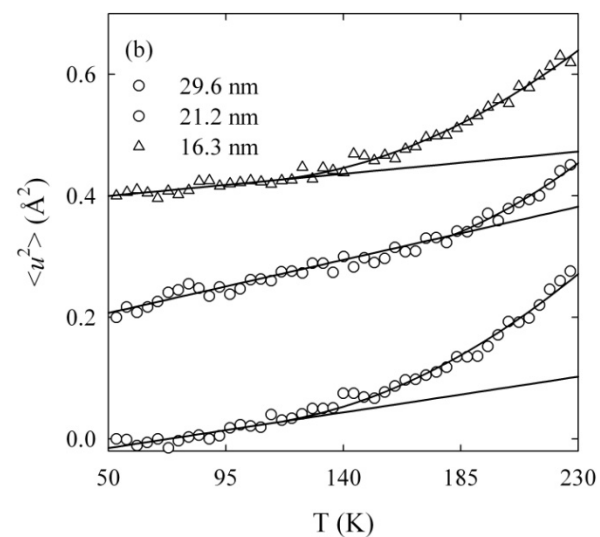
Elastic Scans – Fixed Window Scans



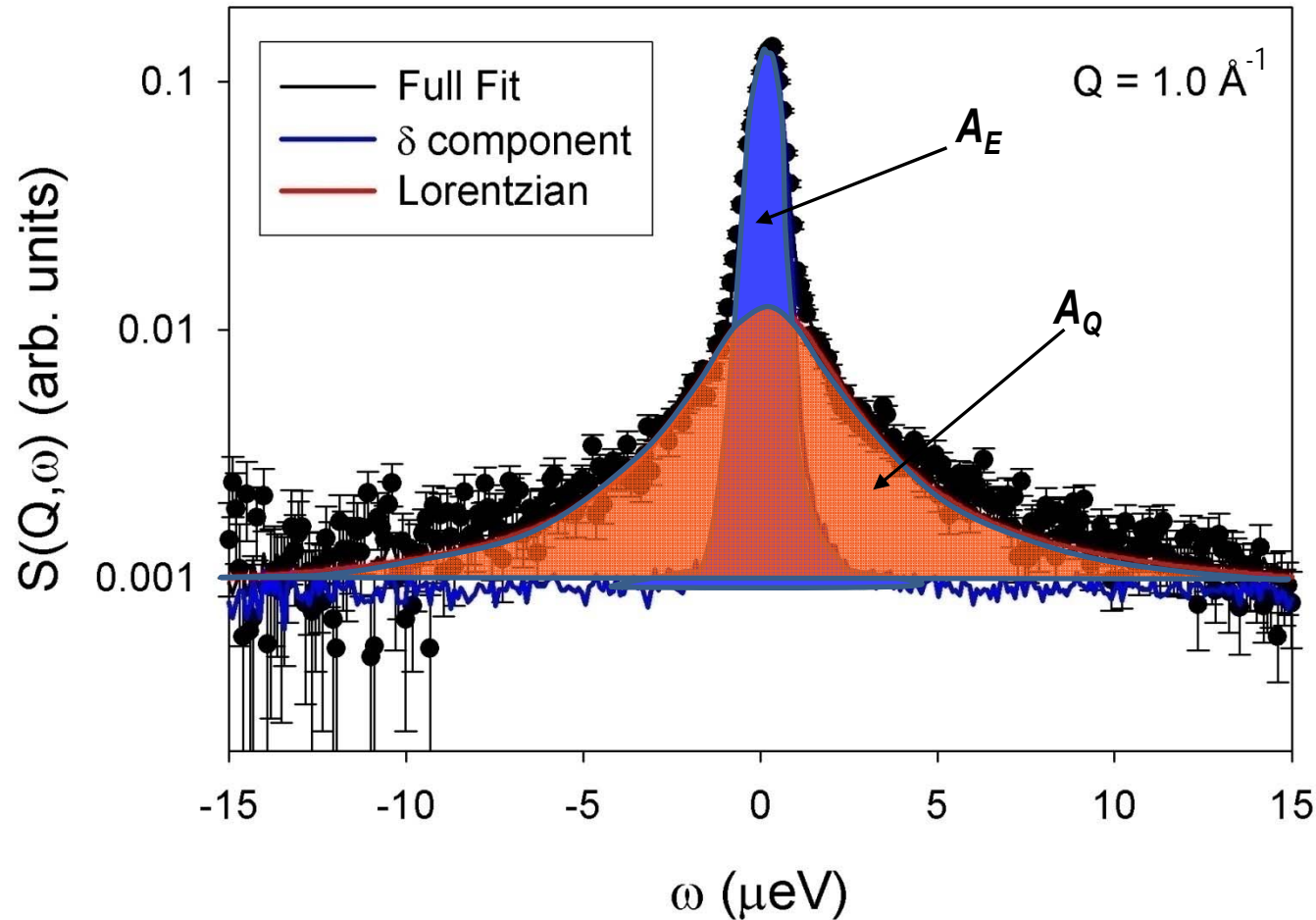
$$I(Q) = I(0) \exp(-Q^2 \langle u^2 \rangle / 3)$$



Onset of diffusive and anharmonic motion

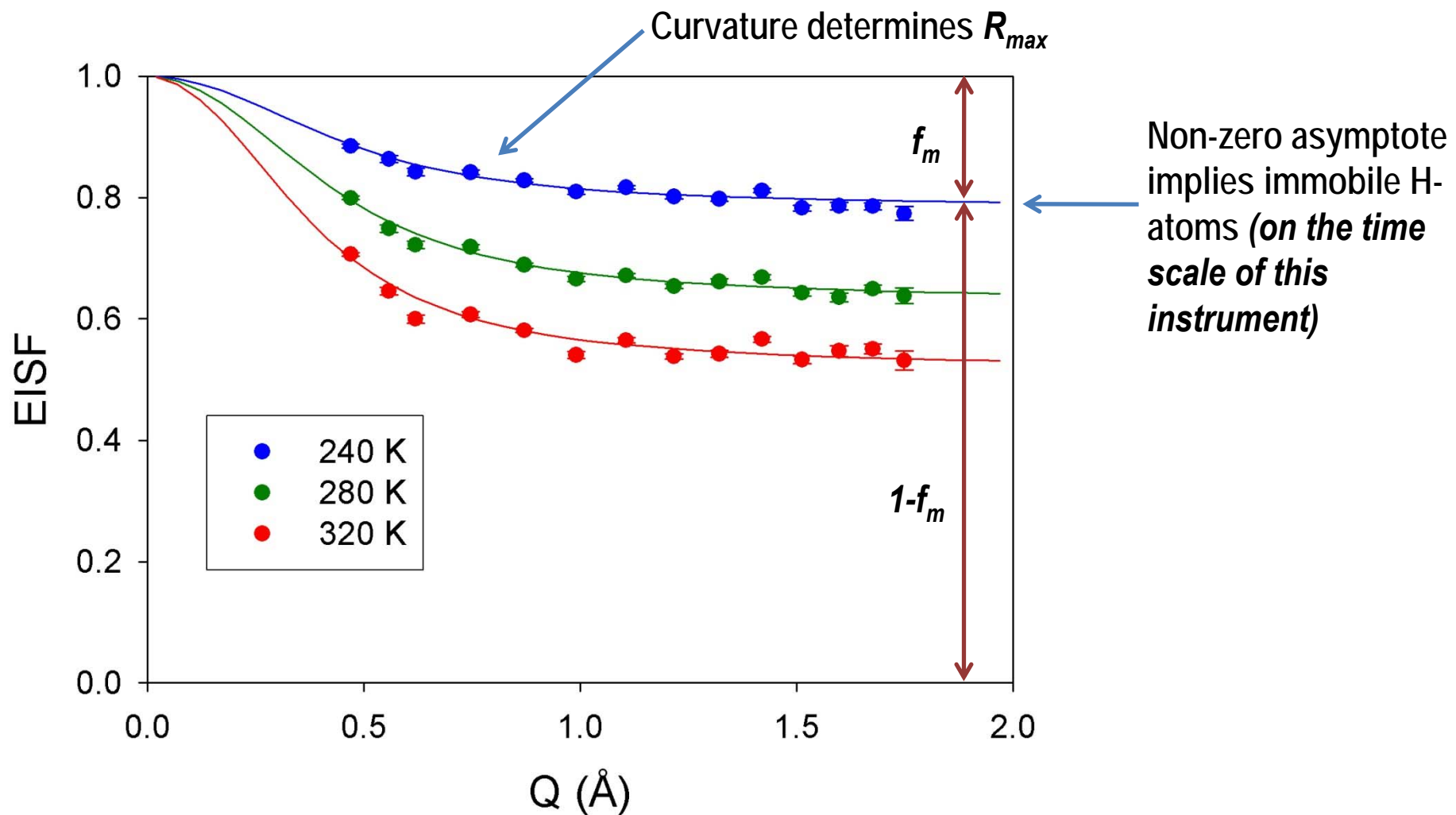


Simple Fit to data (HFBS – NCNR) 30 Å diameter pore, 320 K, $Q = 1 \text{ Å}^{-1}$

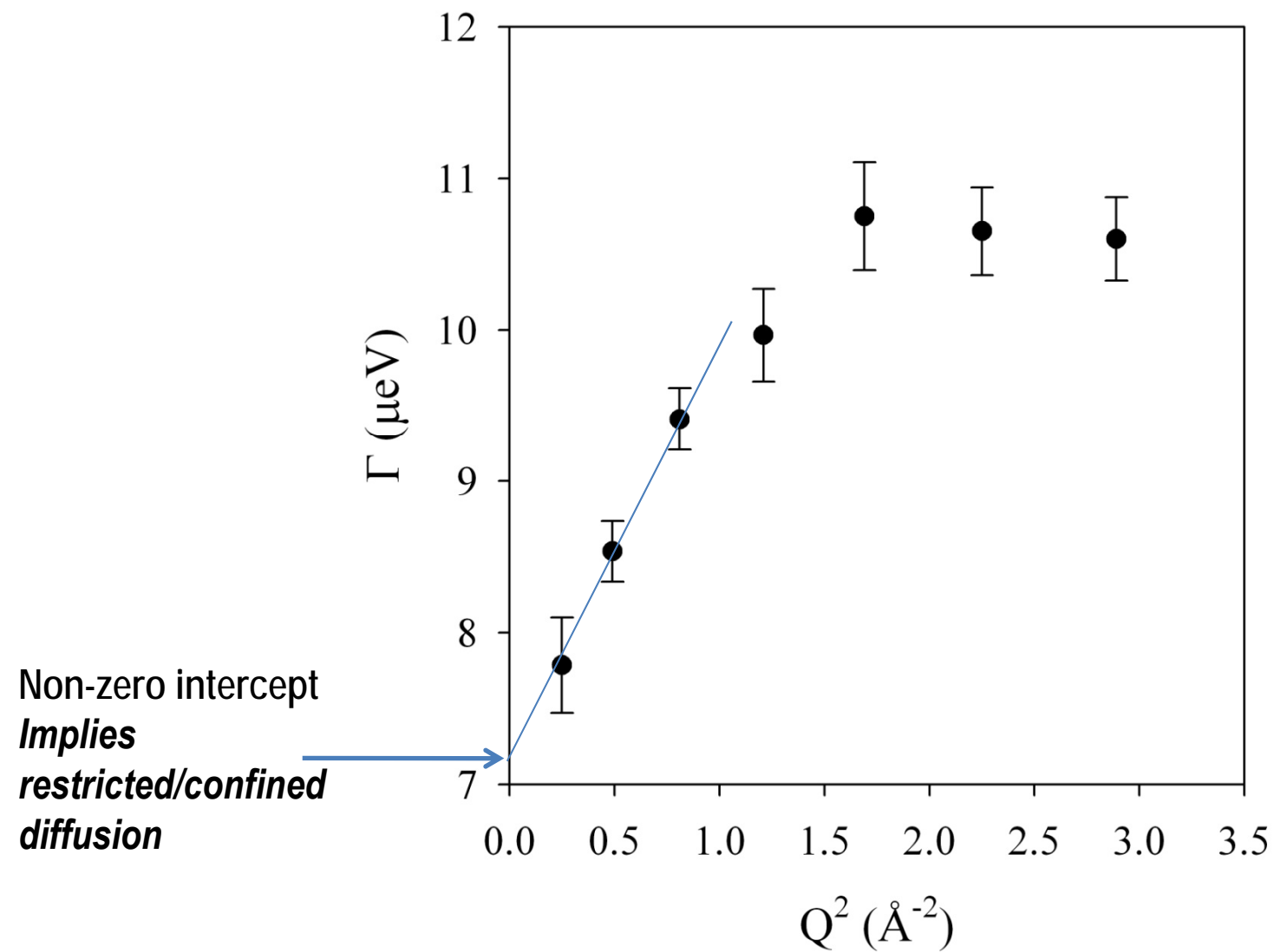


$$EISF = \frac{A_E}{A_E + A_Q}$$

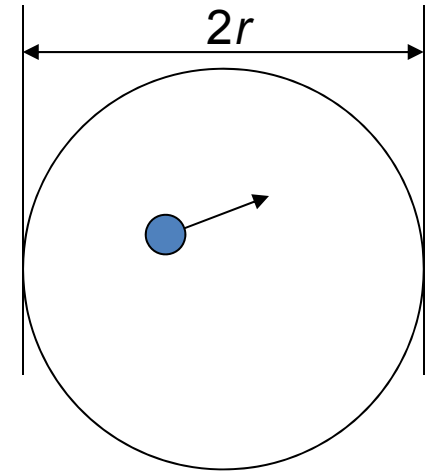
EISF – 30 Å DPP sample, saturation



Lorentzian $\Gamma(Q)$



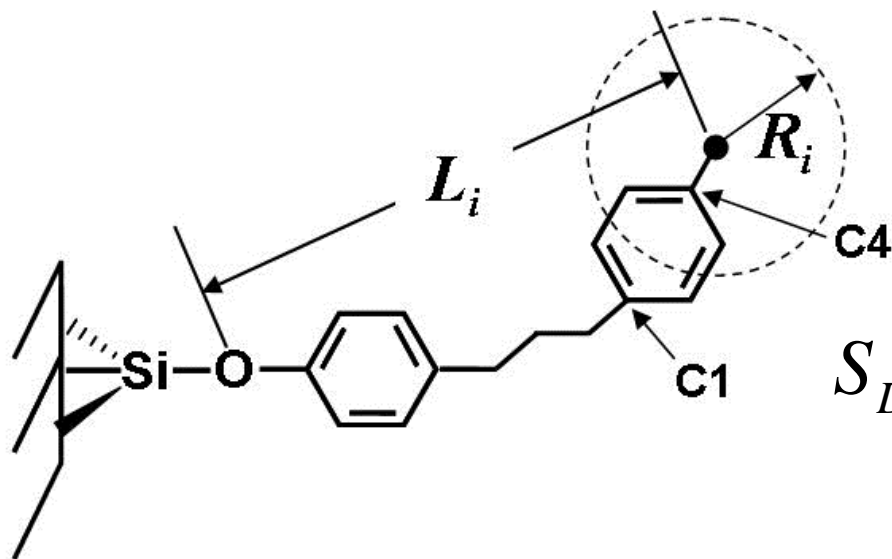
Simple Analytical Model – e.g. Diffusion in a Sphere



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

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

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



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

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

Fits to Data

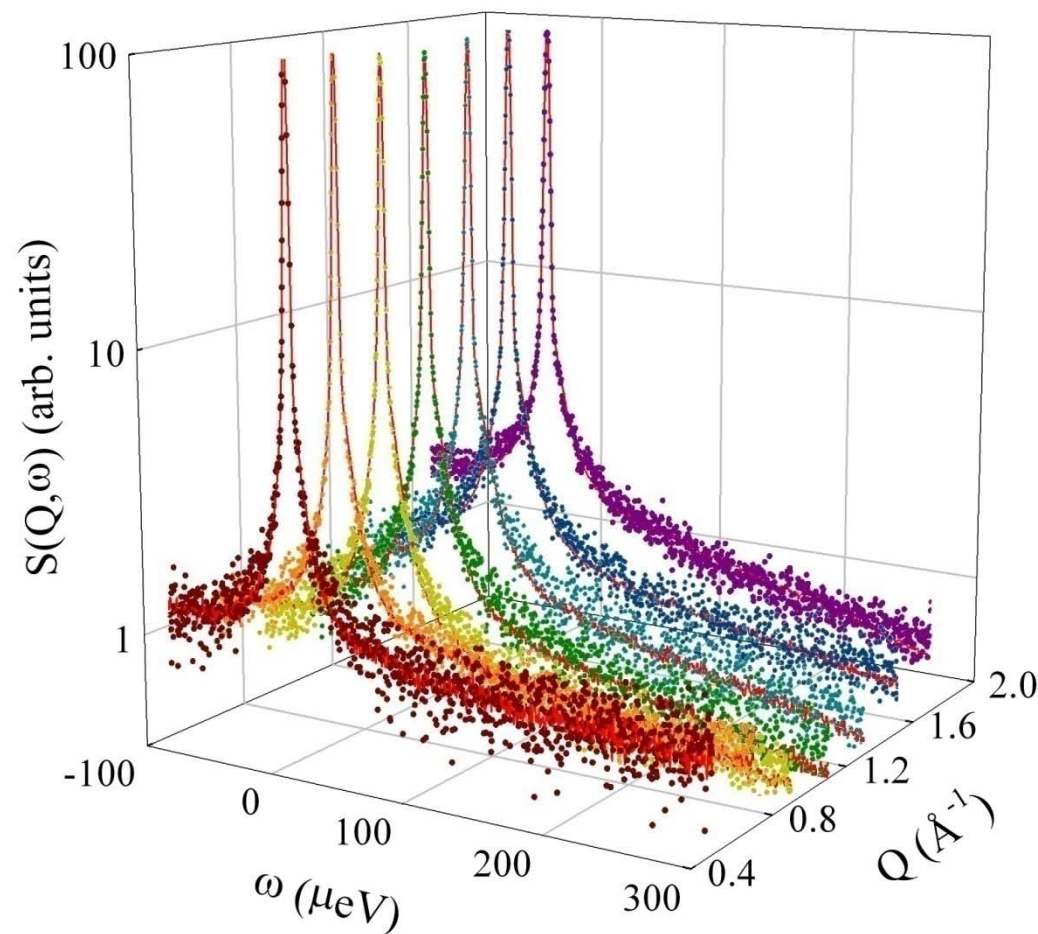
$$S(Q, \omega) = \left(C_0(Q) + C_1(Q) e^{-Q^2 \langle u^2 \rangle / 3} \right) \delta(\omega) + C_2 e^{-Q^2 \langle u^2 \rangle / 3} \sum_{i=1}^{15} S_s(Q, \omega, R_i, D_i)$$

MCM-41

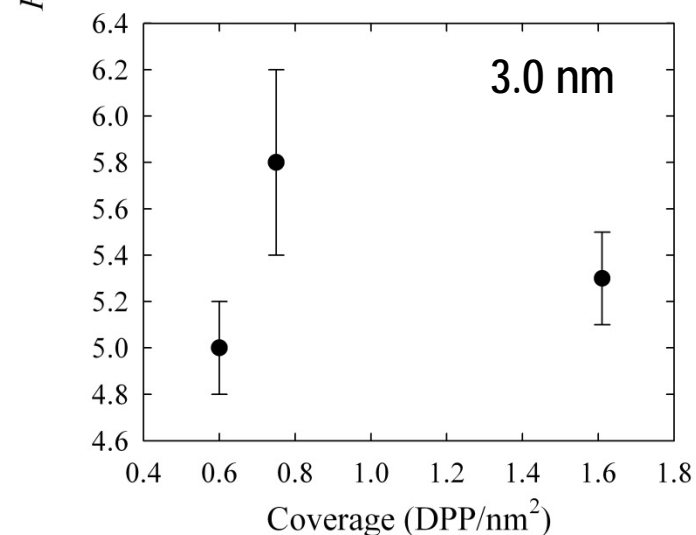
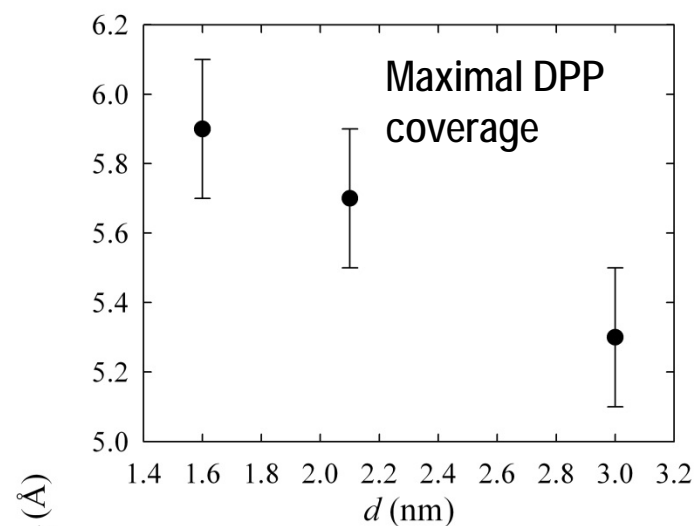
$$f_m = \frac{C_2}{C_1 + C_2}$$

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

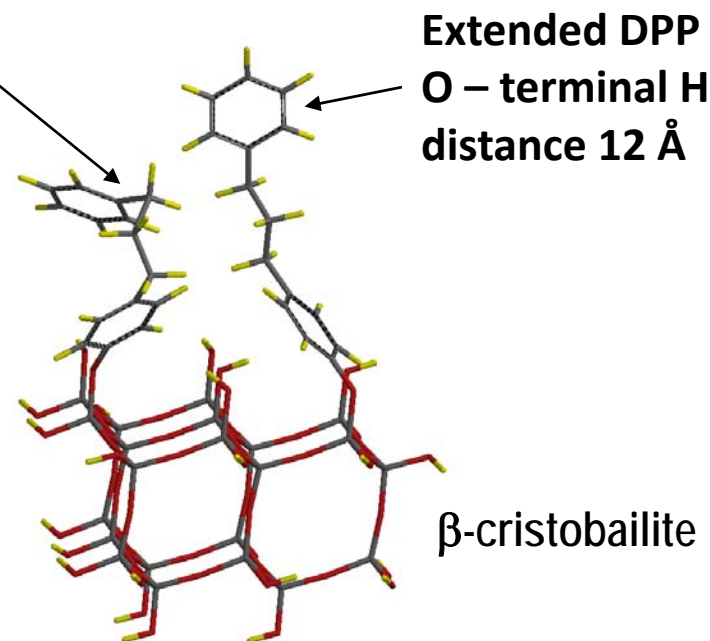
DPP – 29 Å diameter pores – 370 K (BaSiS - SNS) – Beyond the EISF – Fitting the Model to the Full Data Set



R_M – How extended is the motion?

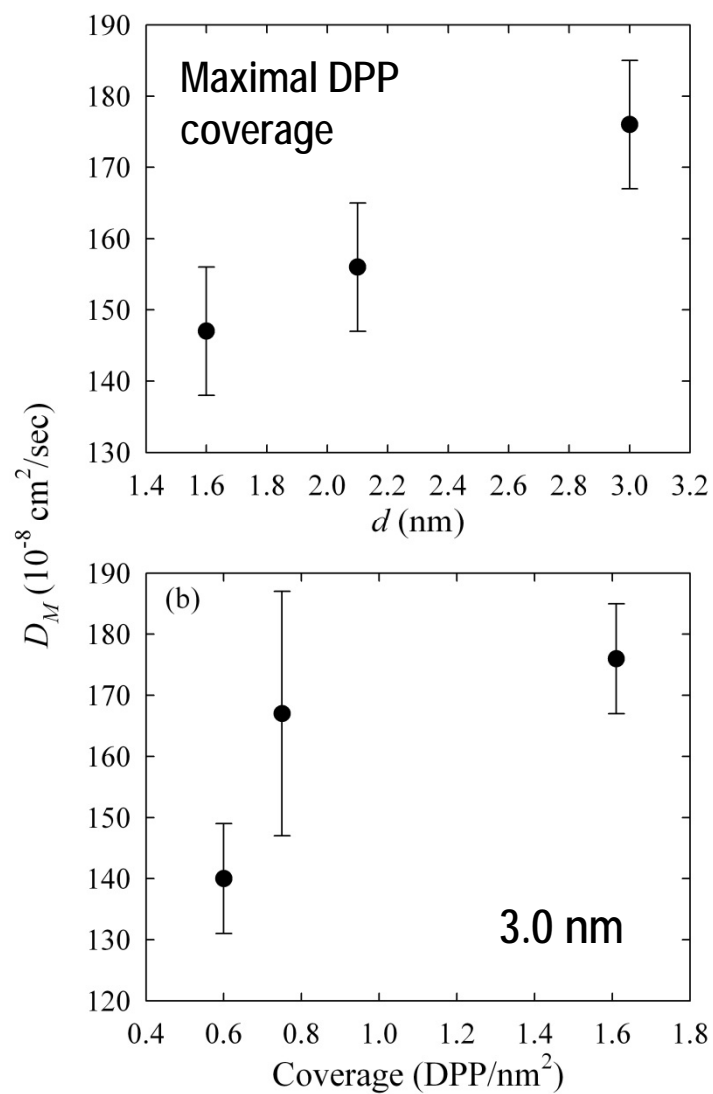


Partially folded
DPP
O – terminal H
distance 5.9 Å



- 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

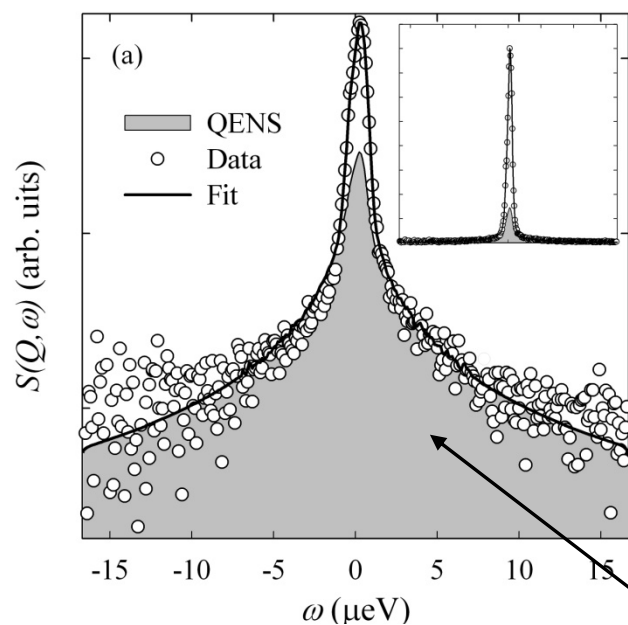
D_M – How fast is the motion?



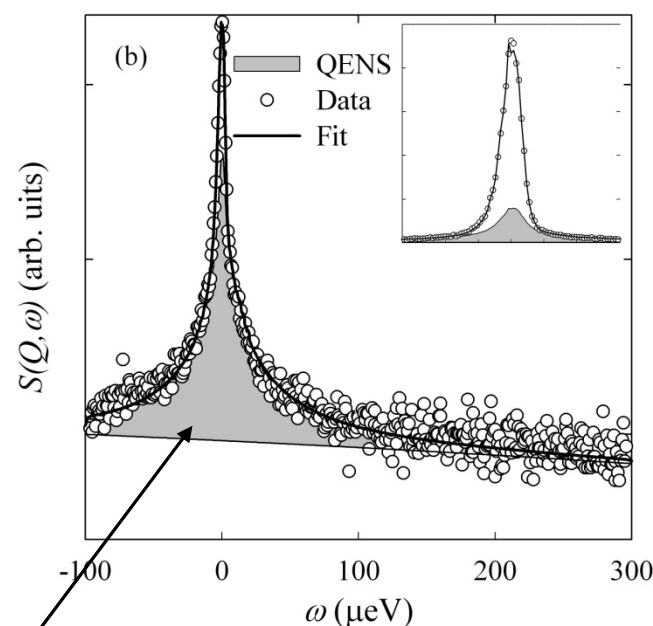
- D_M increases with pore diameter while the radius decreases
 - Diffusion in the pore volume depends on how crowded it is
- D_M increases with surface coverage in large pores
 - More molecules are forced into the more open volume of the pore and away from the pore surface

Two Instruments – Two Resolutions – Two Dynamic Ranges – 3.0 nm 320 K

HFBS ($1\text{ }\mu\text{eV}$, $\pm 17.5\text{ }\mu\text{eV}$)



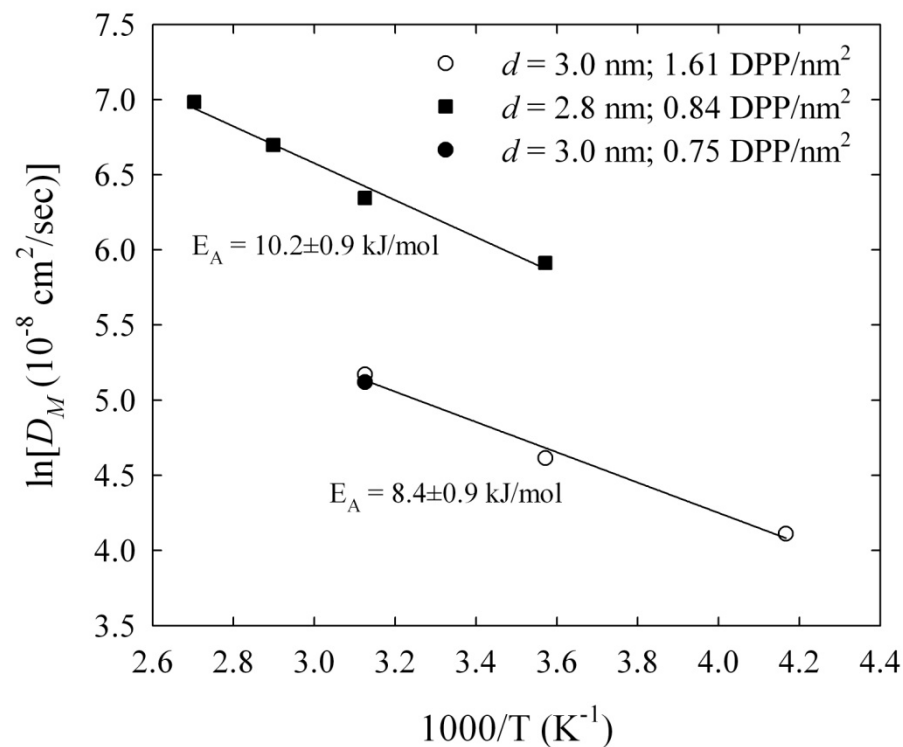
BaSiS ($3\text{ }\mu\text{eV}$, -100 to 300 μeV)



QENS

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

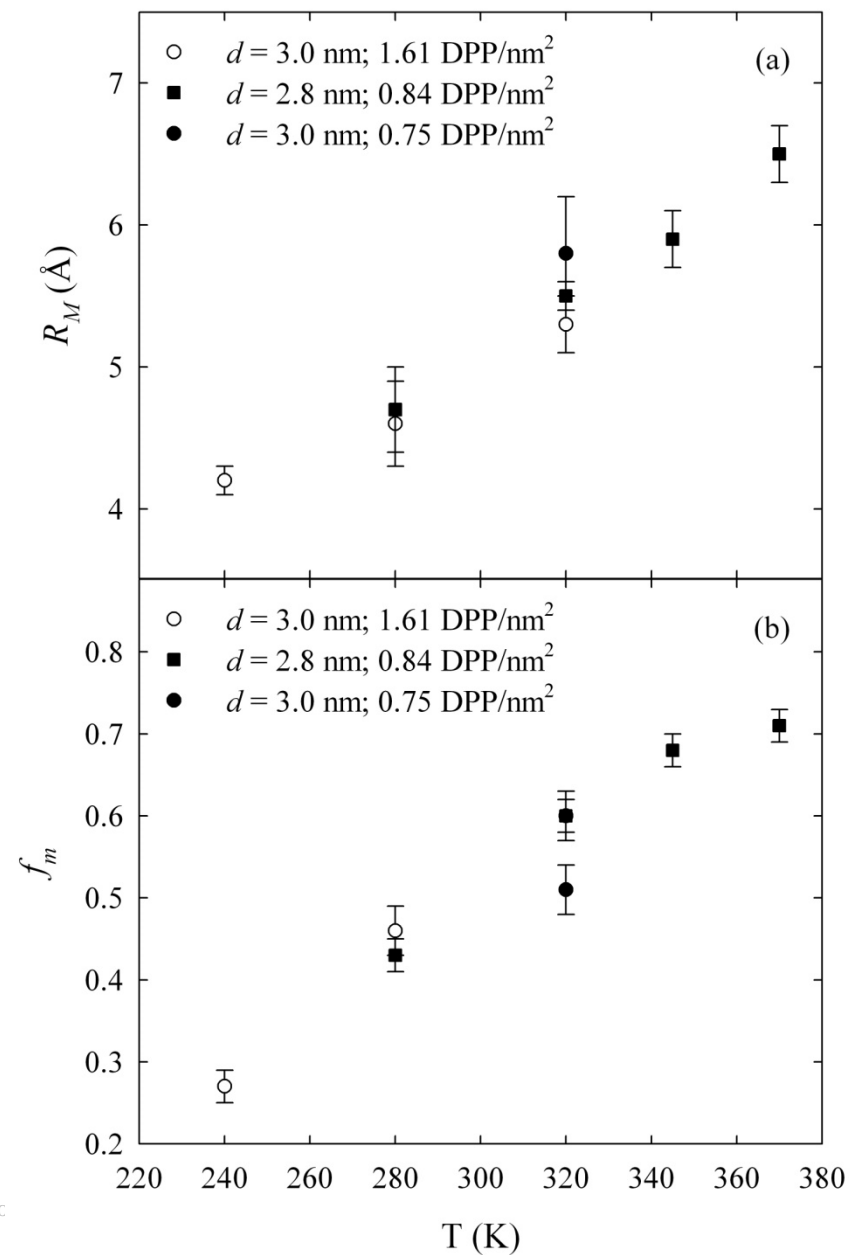
Two Instruments



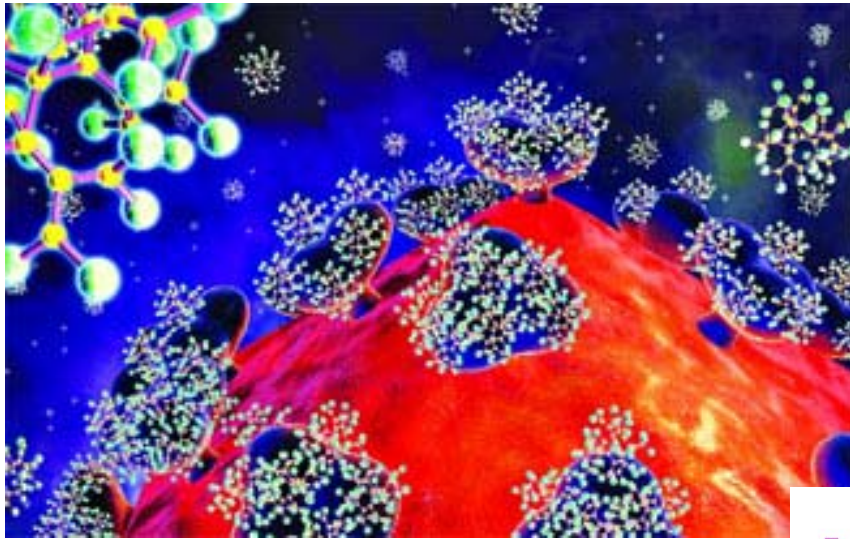
Dynamics

- Similar activation energies
- Different magnitudes

Geometry – nearly identical –
determined by intensity measurements



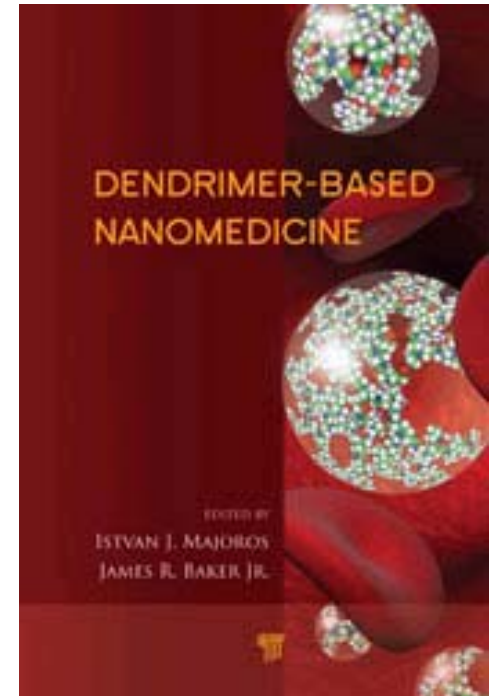
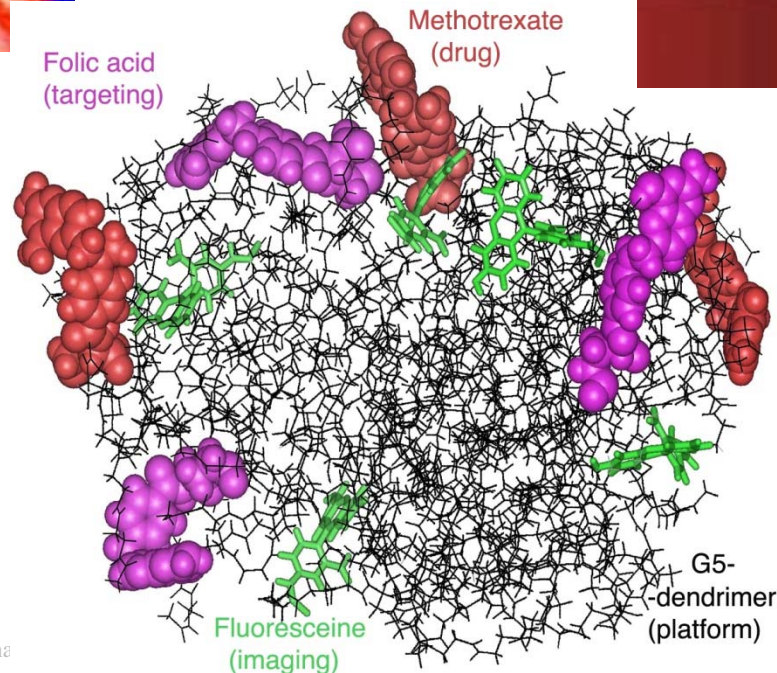
Example 2: Dendrimers – Colloidal Polymer – pH responsive



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

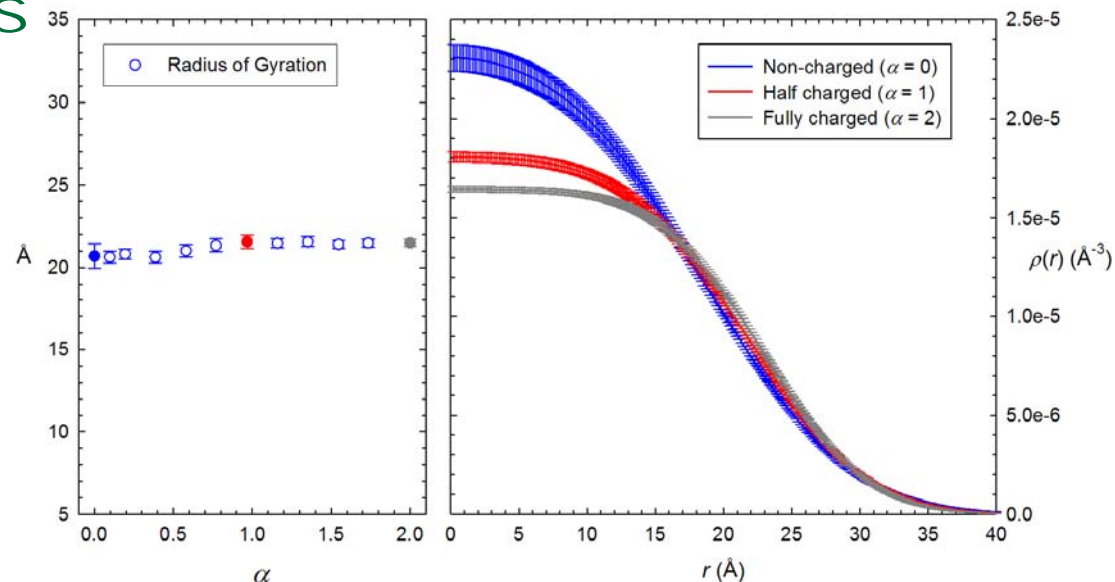
“Trojan horse” – folic acid adsorbed by cancer cell delivering the anti-cancer drug as well

James R. Baker Jr., Univ. of Michigan Health Sciences Press Release



SANS Results – Global Size Constant, Redistribution of Mass

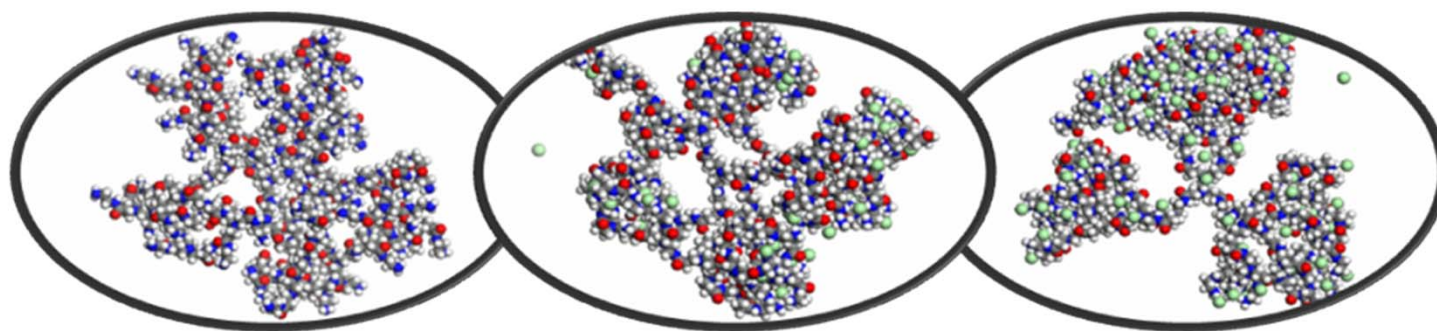
Samples: 0.05 gm protonated dendrimer in 1 ml deuterated solvent



Molecular Dynamics Simulations

Basic

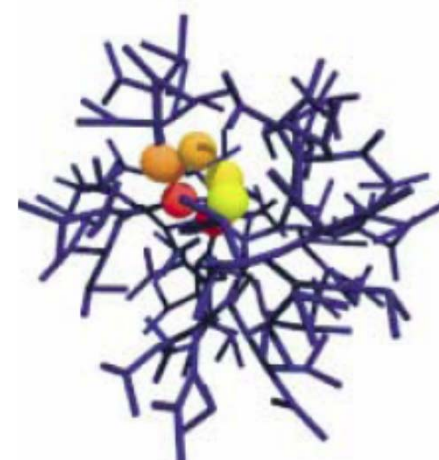
Acidic



High pH

Neutral pH

Low pH



Methodology

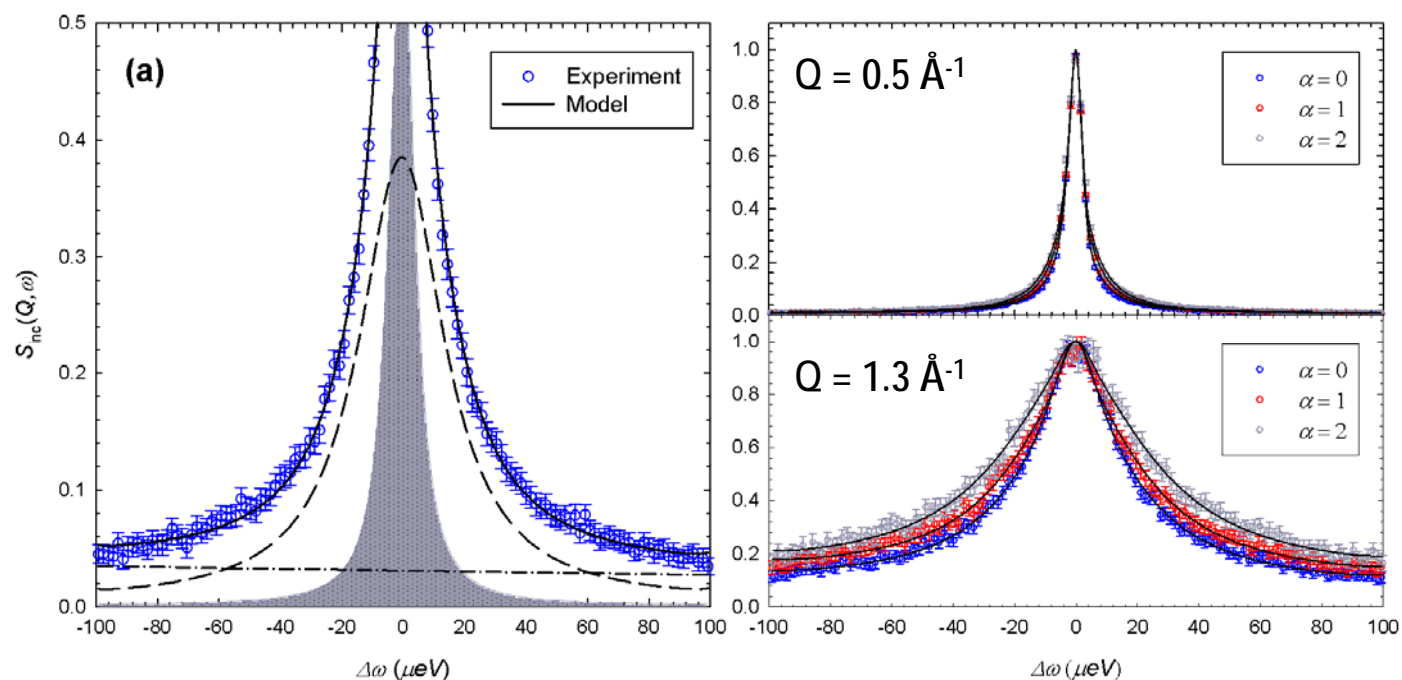
- Determine center-of-mass translational motion with pulsed field-gradient spin echo NMR
 - Could have been determined directly from QENS measurement but this tied down parameter set
- Measure (dendrimer + deuterated solvent) – (deuterated solvent) -> dendrimer signal
- Vary pH to charge dendrimer amines ($\alpha = 0$ (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

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

Localized Motion of Dendrimer Arms

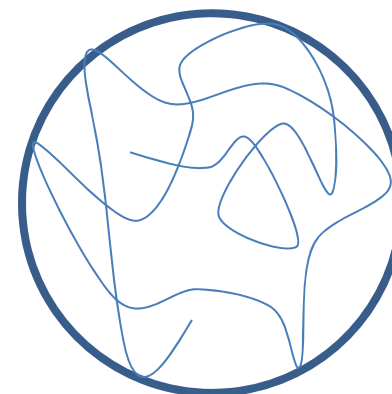


Localized motion modeled as Diffusion in a Sphere

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

$R \sim 2.8 \text{ \AA}$, α independent

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



Localized motion increases as amines are charged!

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).

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