An Introduction to Quasielastic Neutron Scattering (QNS)

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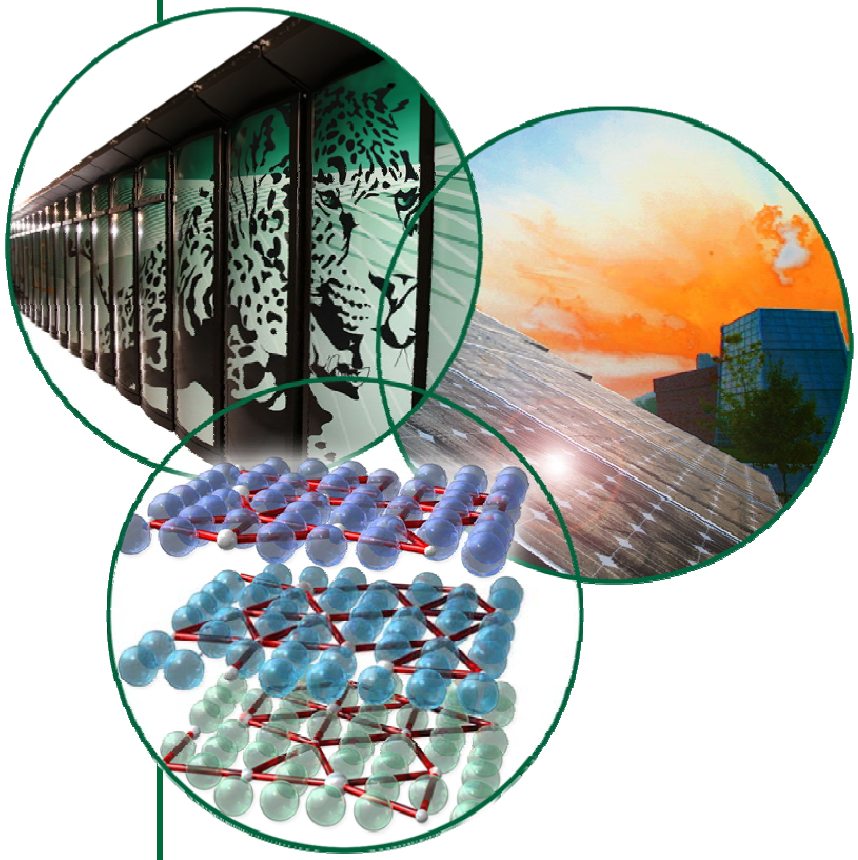

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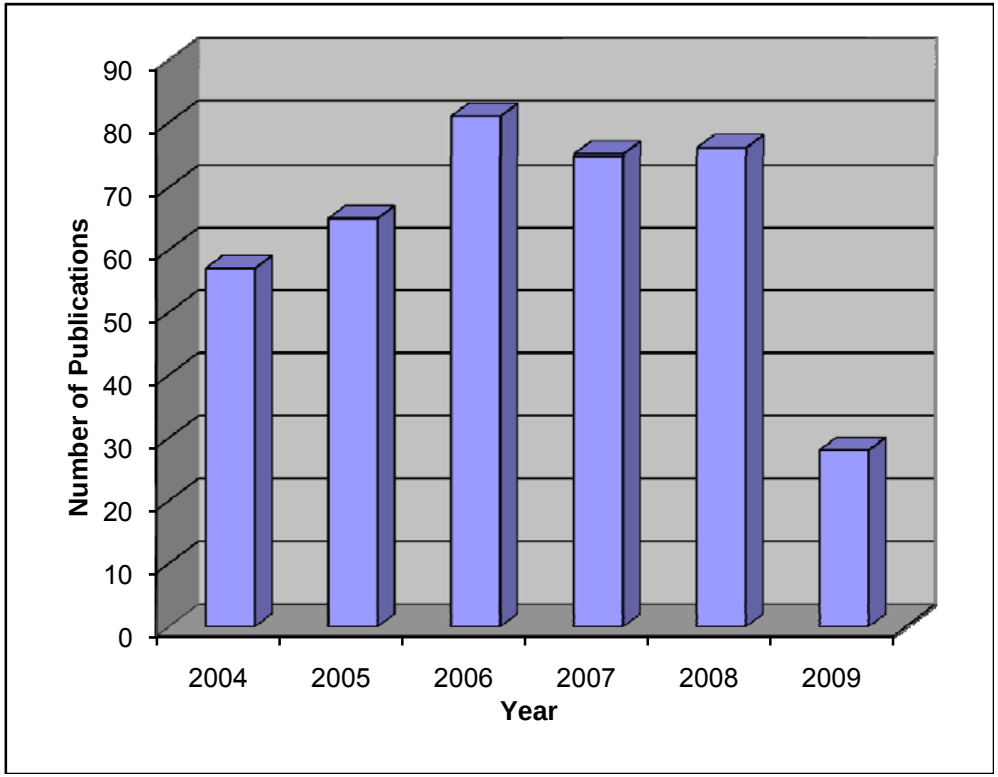
OUTLINE

- Background
- Neutrons and QENS
- Connection to Molecular Dynamics Simulations
- The Elastic Incoherent Structure Factor (EISF)
- The Role of Instrumentation
- Restricted Diffusion Examples
- Experiment Design – an example
- Water - Excel Spread Sheet – an illustration
- Recent Applications
- References and Summary

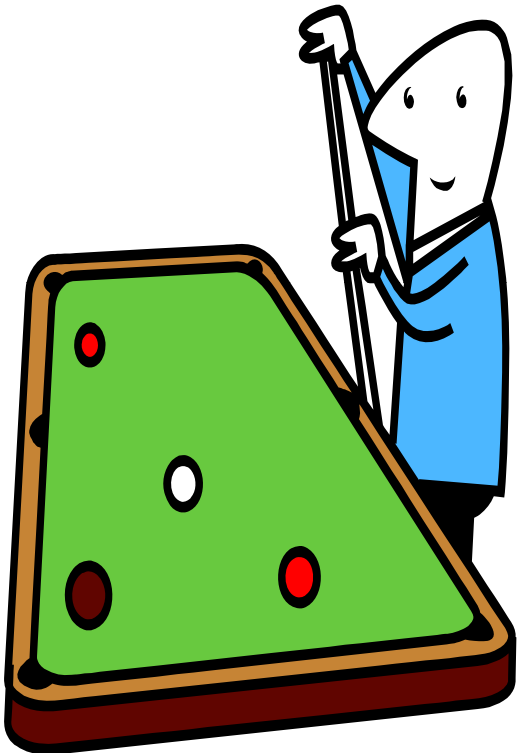
Background (Why Should I Care?)

- 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

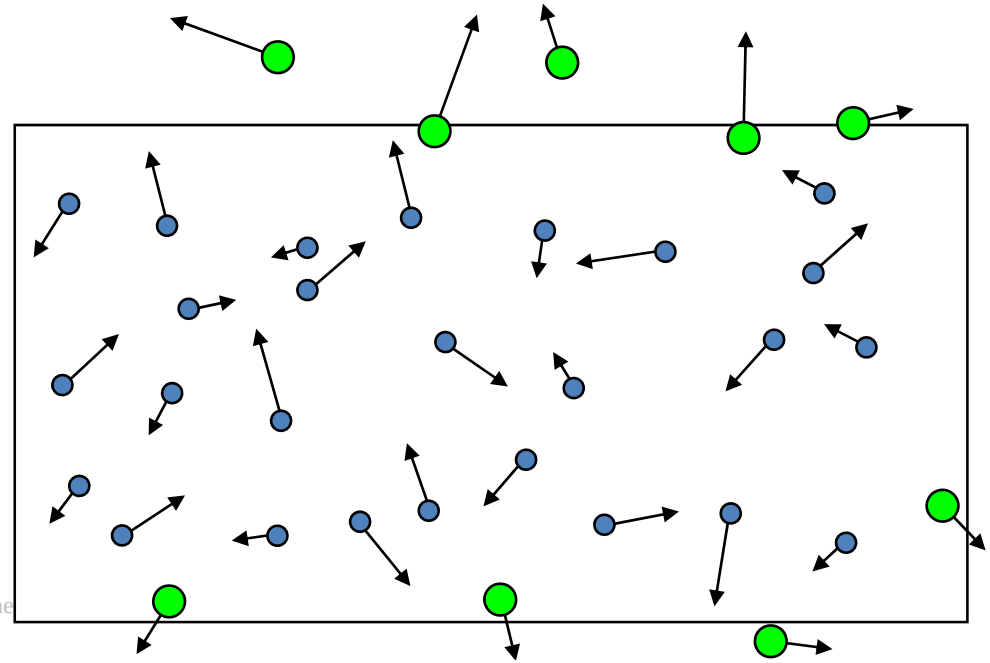


Quasi-Elastic Neutron Scattering

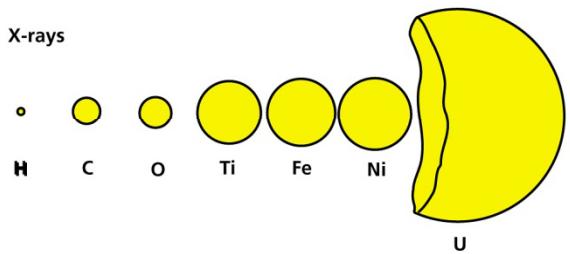
- Neutron exchanges small amount of energy with atoms in the sample

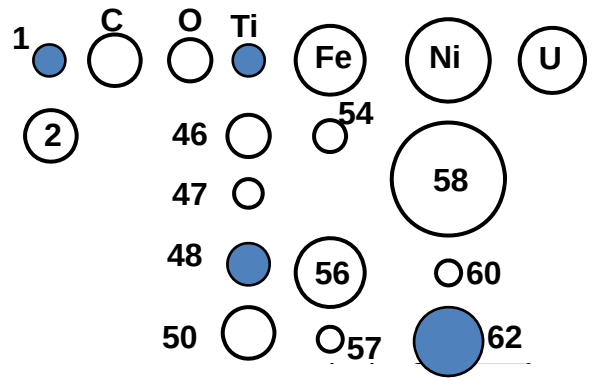


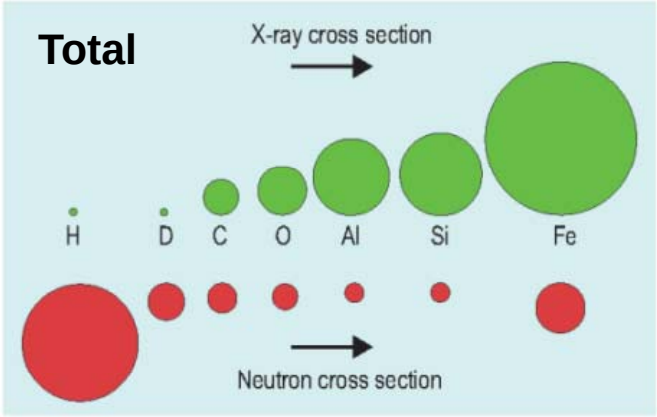
Doppler Effect



Neutrons, QENS, and the Large Incoherent Cross-section of H

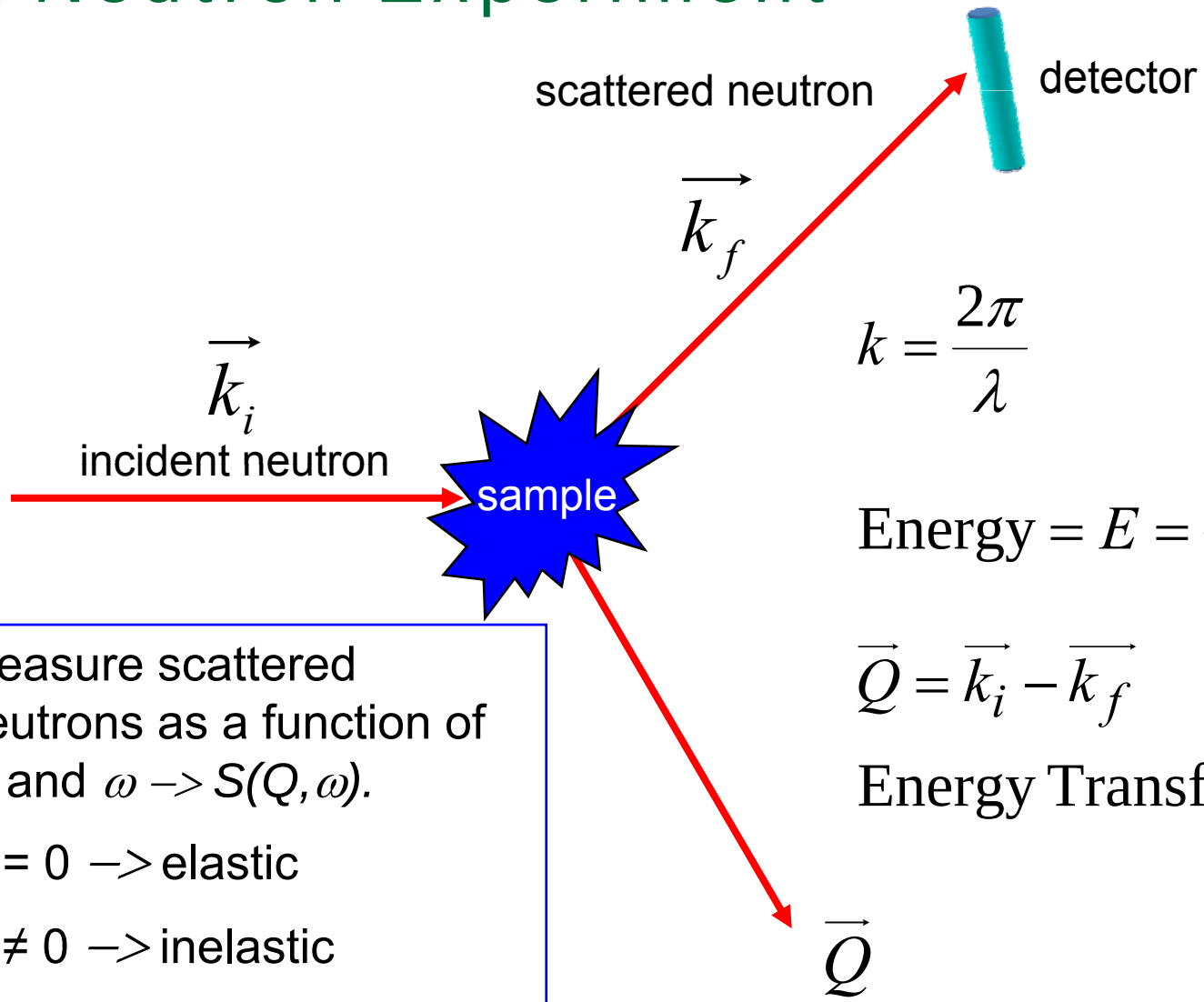






- Isotopic sensitivity – random nuclear cross-section with element and isotope
  - H-D contrast, light element sensitivity in presence of heavy elements
  - H large incoherent cross-section – self-correlation function
- Magnetic moment
- Wavelength and energy match excitations in condensed matter (Geometry and time): **Where** are the atoms and **how** do they move?
  - neutrons $\lambda \sim$ Å; E ~ meV; spectroscopy – no selection rules
  - x-rays $\lambda \sim$ Å; E ~ keV
  - light $\lambda \sim$ 1000 Å; E ~ eV
- Small absorption cross section – can penetrate sample cells

A Neutron Experiment



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

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

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

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

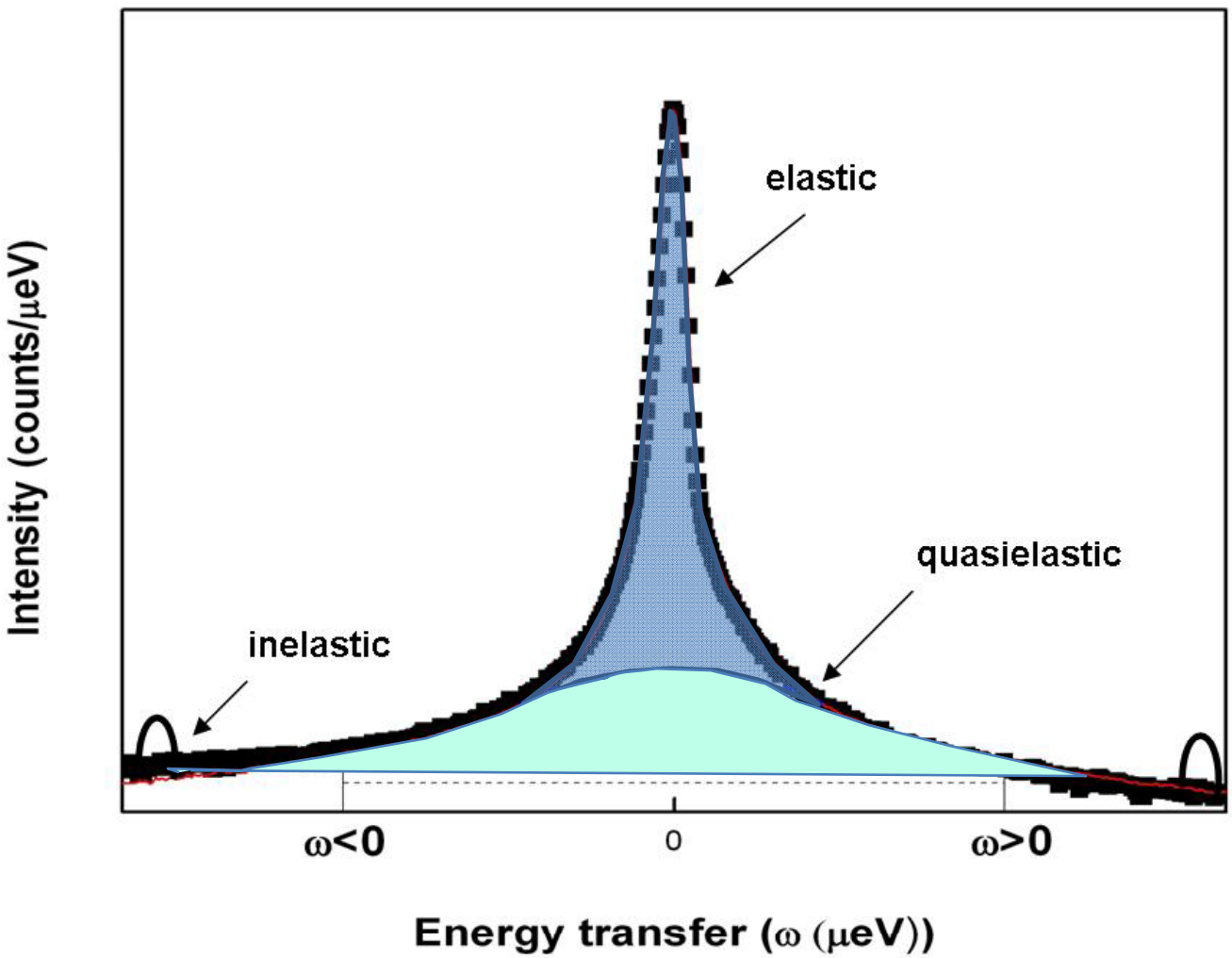
Measure scattered neutrons as a function of Q and ω –> $S(Q,\omega)$.

$\omega = 0$ –> elastic

$\omega \neq 0$ –> inelastic

ω near 0 –> quasielastic

QENS Spectra



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

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

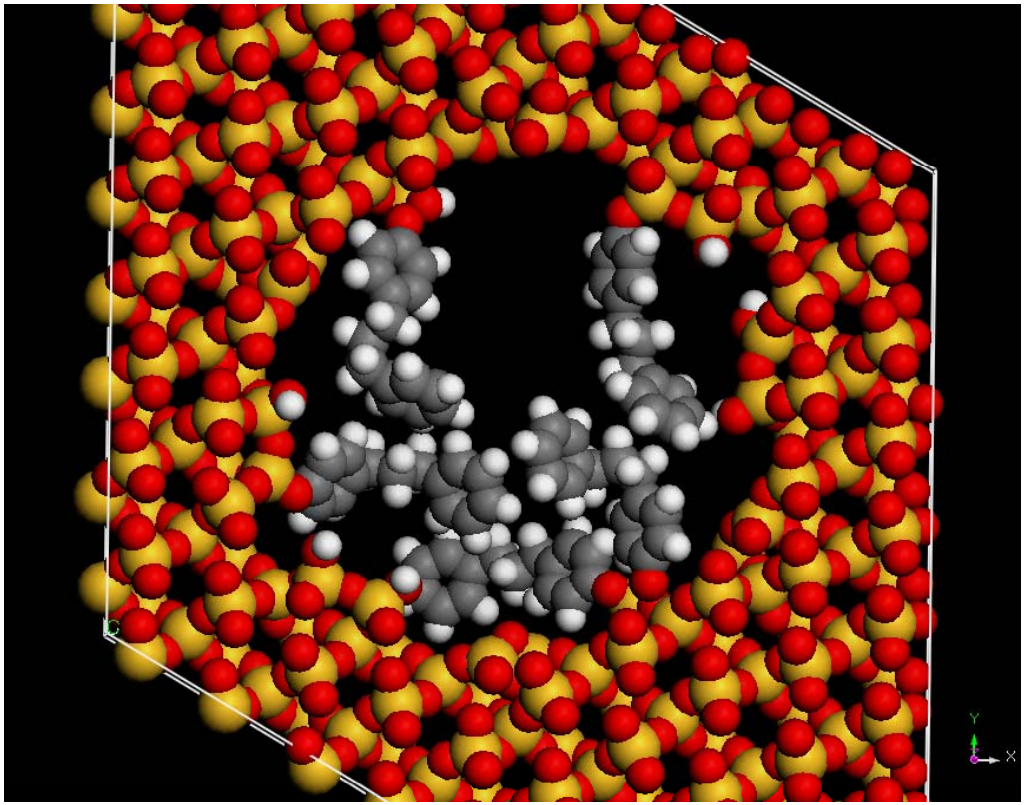
$$I_{inc}(\mathbf{Q},t) = \frac{1}{N}\sum_i \left\langle \exp\{i\mathbf{Q}\bullet\mathbf{R}_i(t)\}\exp\{-i\mathbf{Q}\bullet\mathbf{R}_i(0)\}\right\rangle$$

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

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

QENS and Molecular Dynamics Simulations

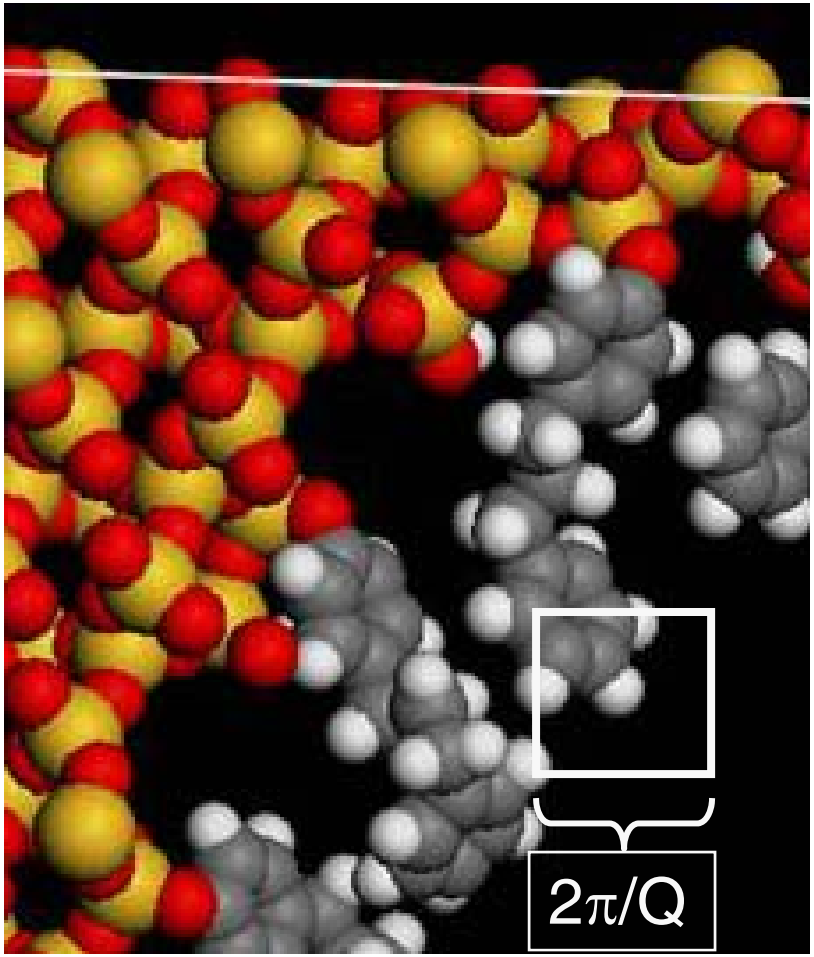
- Same atomic coordinates used in classical MD are all that is needed to calculate $I_{inc}(Q,t)$



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



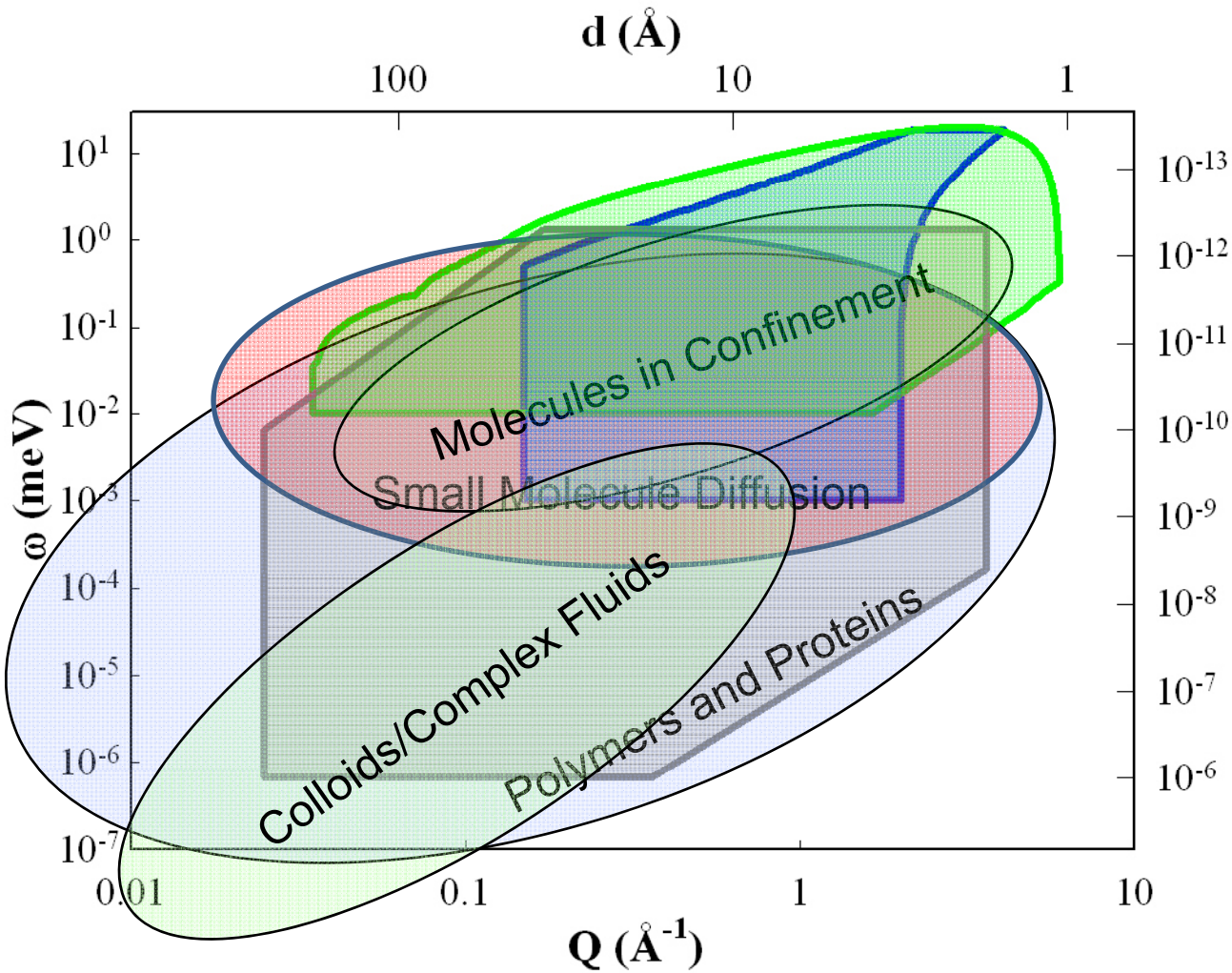
QENS and Neutron Scattering Instruments

- 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 to100 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 (approximately 5 in the U. S.)
- U.S. instruments – <u>Opportunity is Good- Competition is Strong</u>
  - NIST Center for Neutron Research
    - Disc Chopper Spectrometer
    - High Flux Backscattering Spectrometer
    - Neutron Spin Echo
  - Lujan – Los Alamos National Laboratory
    - Rebuild of QENS instrument from IPNS
  - 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 λ vs Q (
    - large λ –> high resolution -> long times/slow motions
    - large λ –> limited Q-range, limited length scales

The Neutron Spectrometer Landscape



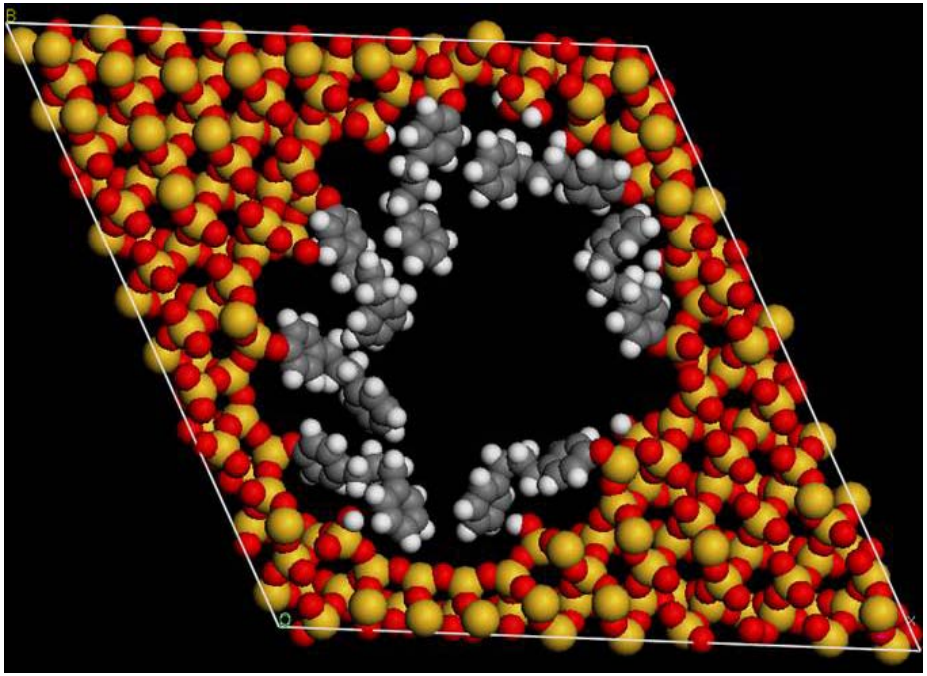
● Backscattering

● Cold Neutron Chopper

● Neutron Spin Echo

BaSiS - SNS Near Backscattering Spectrometer

Restricted Diffusion – Tethered Molecules



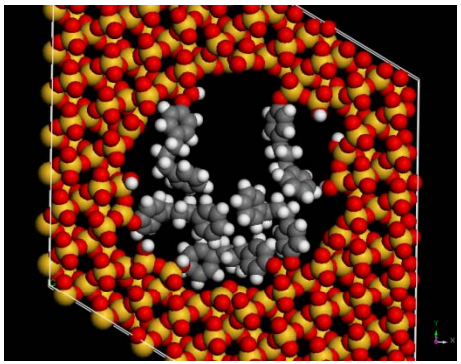
MCM-41 (2.9 nm pore diameter)
high DPP coverage

Samples – typical 0.7 g

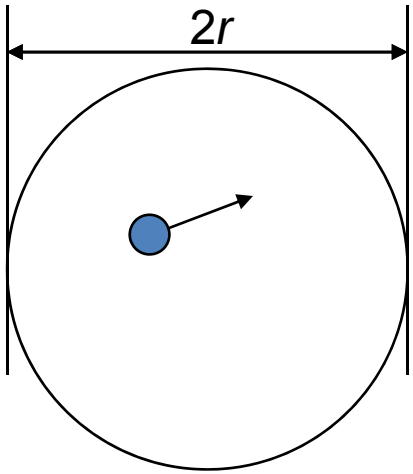
240 K < T < 340 K

Simple Fit – Lorentzian + δ

Pore Radius (nm)	Coverage (molecules/nm^2)
1.63	0.85 (saturation)
2.12	1.04 (saturation)
2.96	0.60 0.75 1.61 (saturation)



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

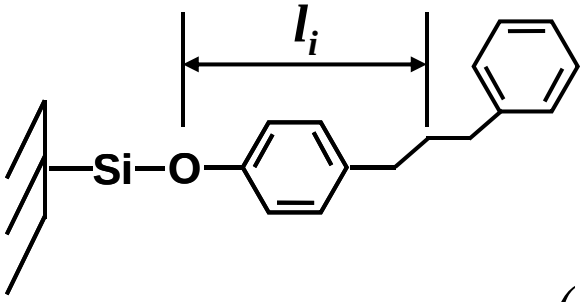


$$S_s(Q,\omega,r,D) = A_0^0(Qr)\delta(\omega) + \frac{1}{\pi}\sum_{(l.n)\neq(0,0)}(2l+1)A_n^l(Qr)\frac{\left(x_n^l\right)^2 D / r^2}{\left[\left(x_n^l\right)^2 D / r^2\right]^2 + \omega^2}$$

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

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

Sum over H-atoms



DPP

$$R_i = R_{\max} \times \frac{l_i}{l_{natom}}$$

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

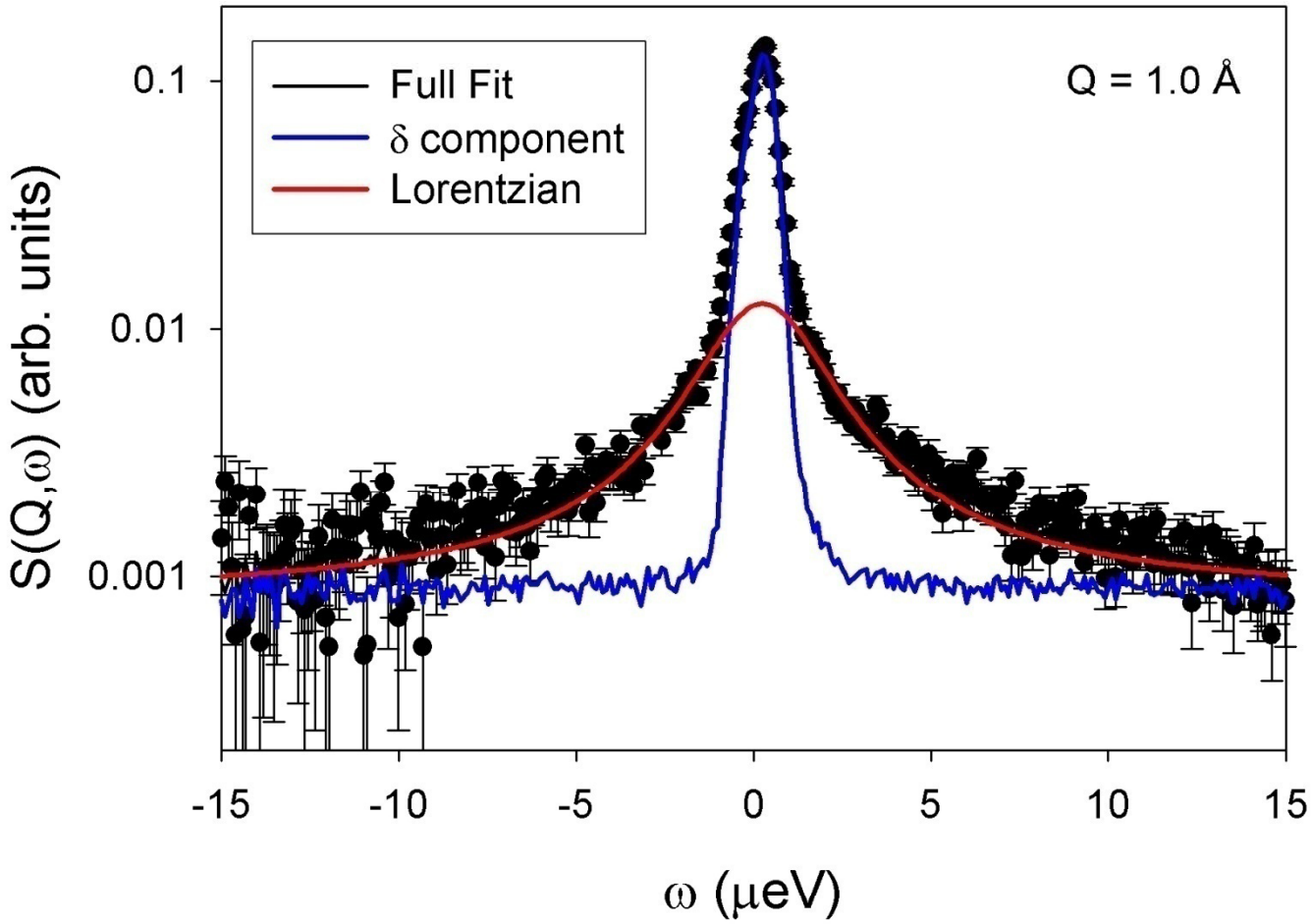
$$EISF(Q) = (1-f_m) + f_m \times \frac{1}{15}\sum_{i=1}^{15}\left[\frac{3j_1(QR_i)}{QR_i}\right]^2$$

Fits to Data

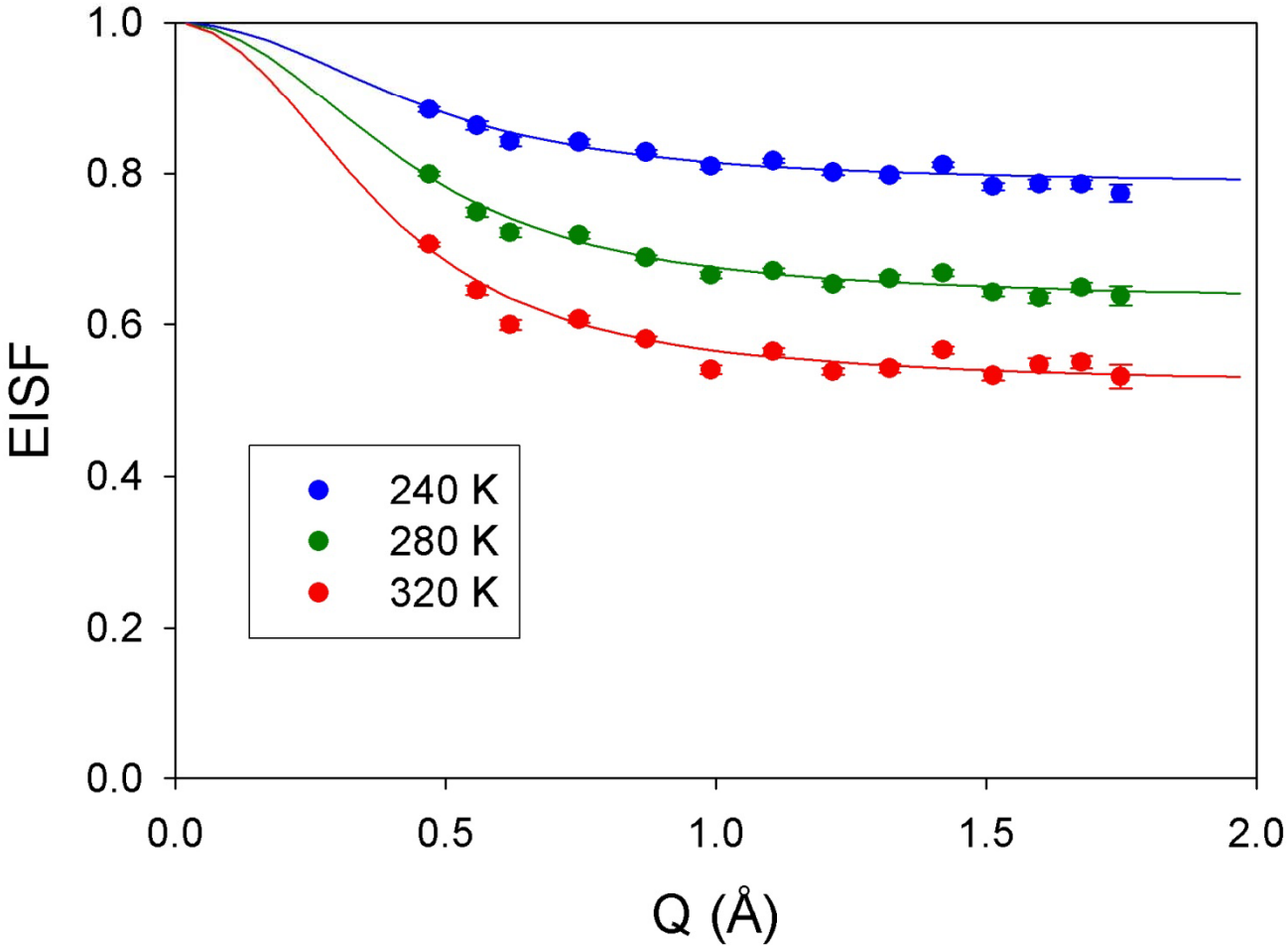
$$S(Q,\omega) = A(Q)\delta(\omega) + (1-A(Q)) \times Lorentzian$$

$$EISF(Q) = A(Q)$$

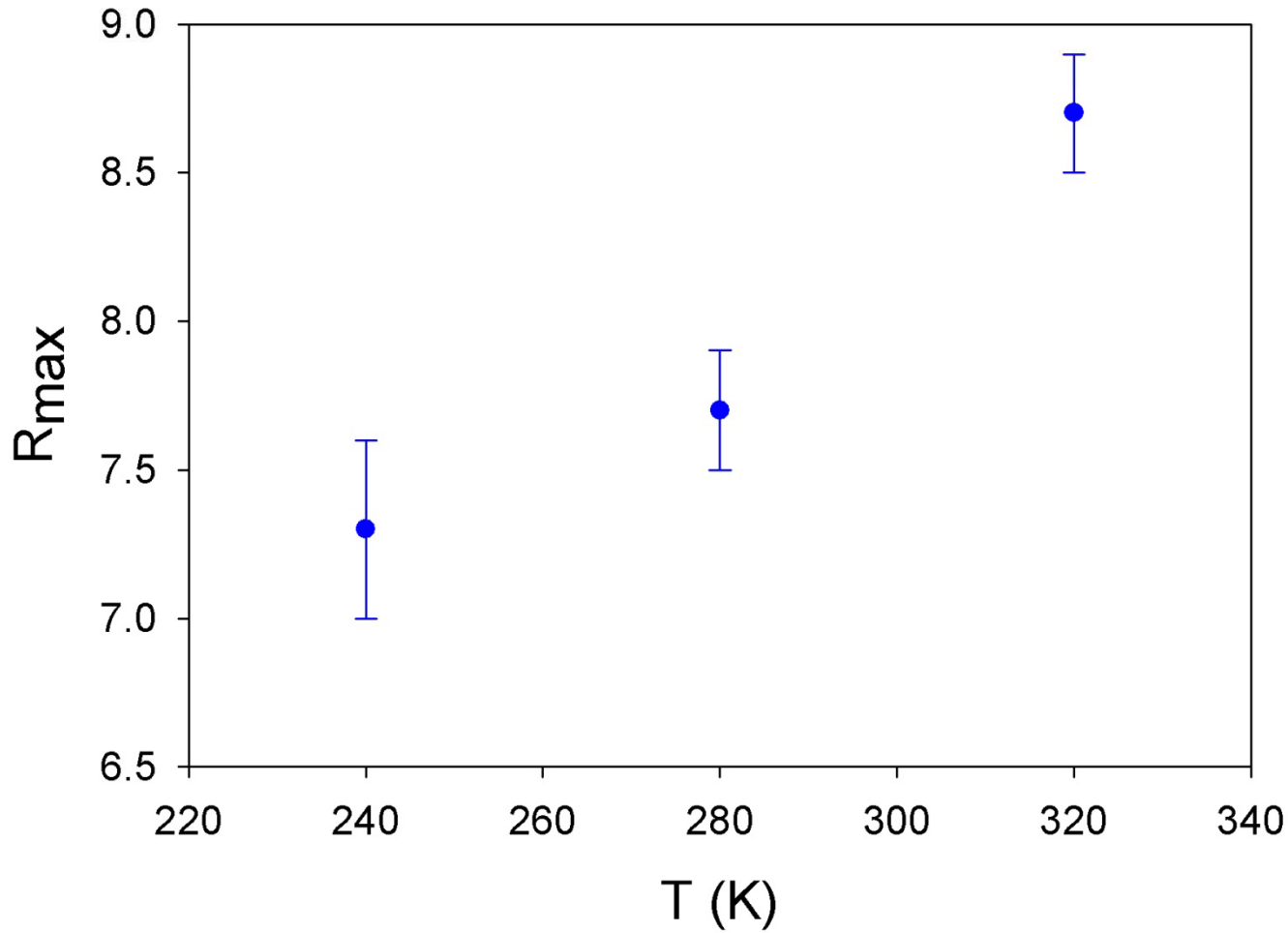
Fit to data (HFBS – NCNR) 29.6 Å diameter pore, 320 K, Q = 1 Å^{-1}



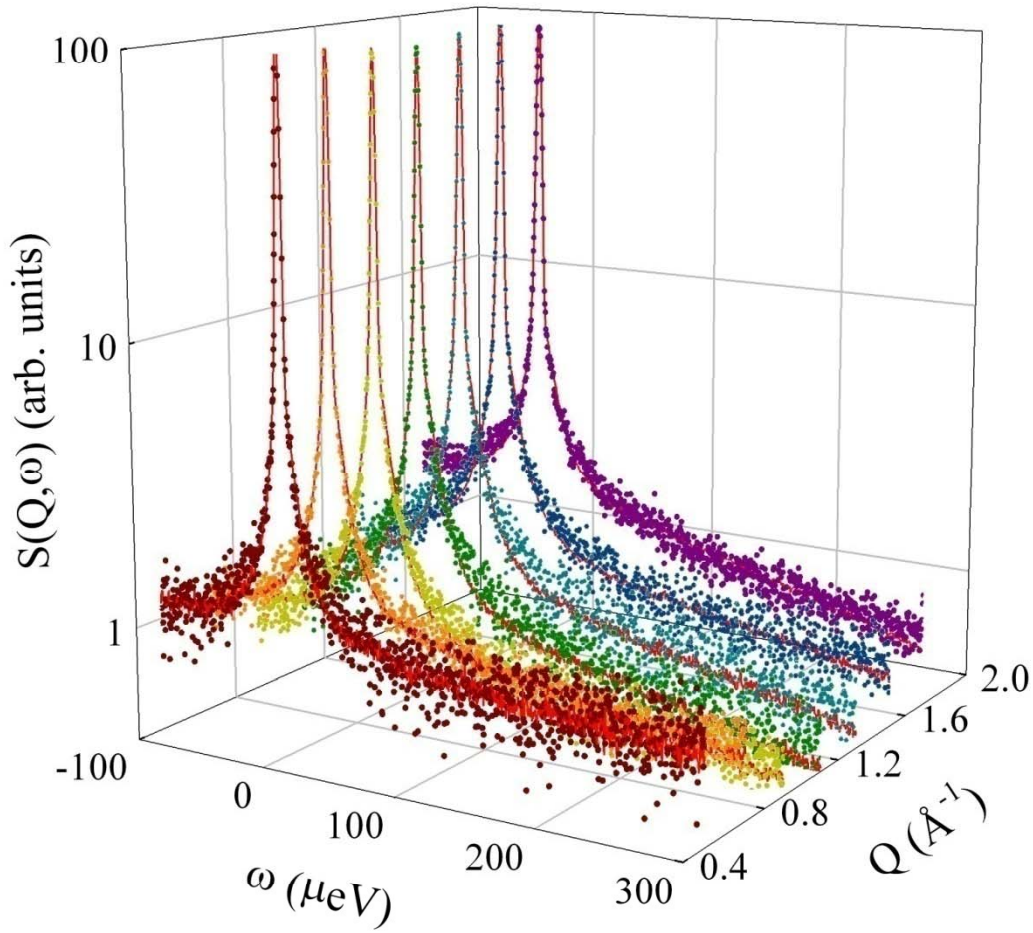
EISF – 29.6 Å radius DPP sample, saturation



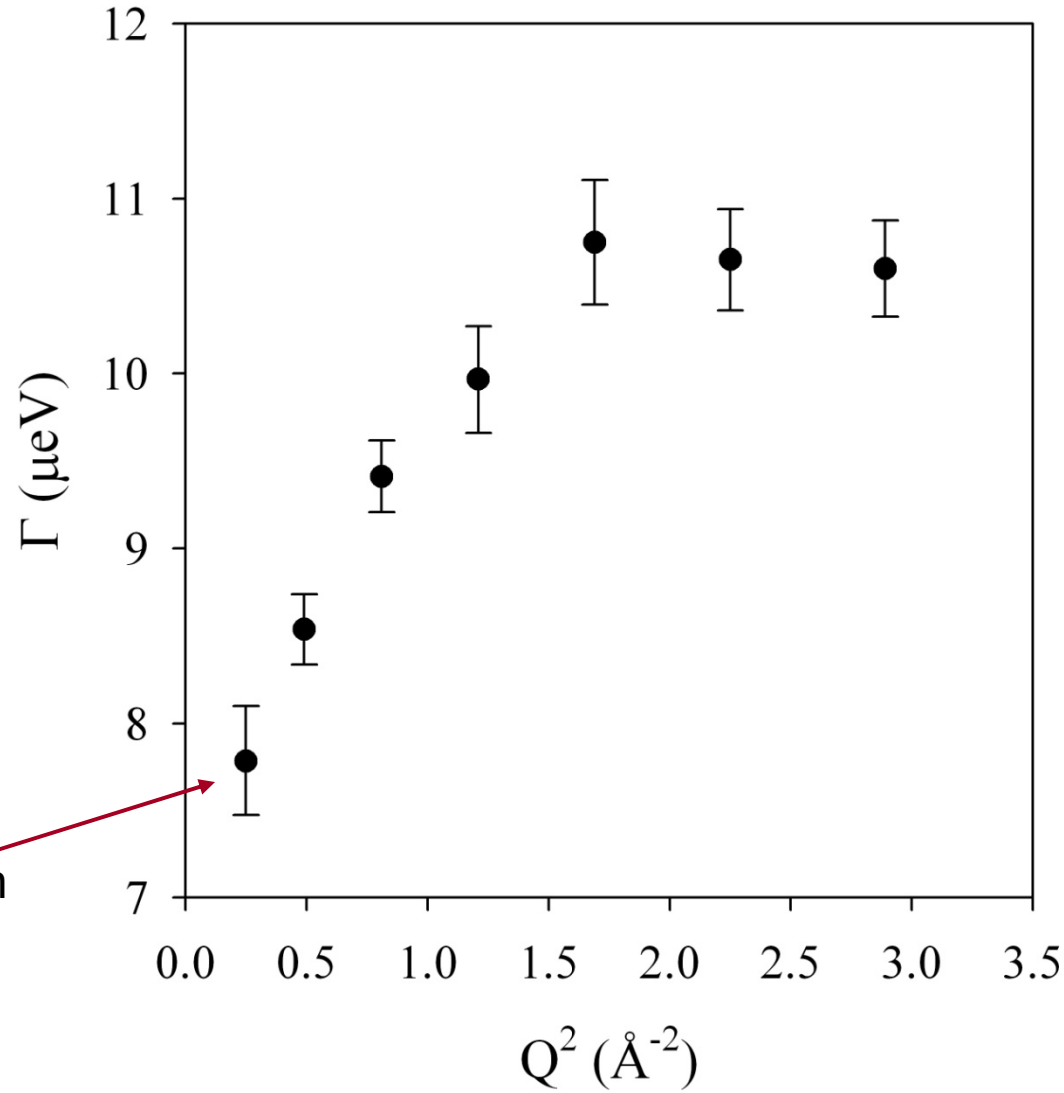
29.6 Å radius DPP sample, saturation



DPP – 29.6 Å diameter pores – 370 K (BaSiS - SNS)

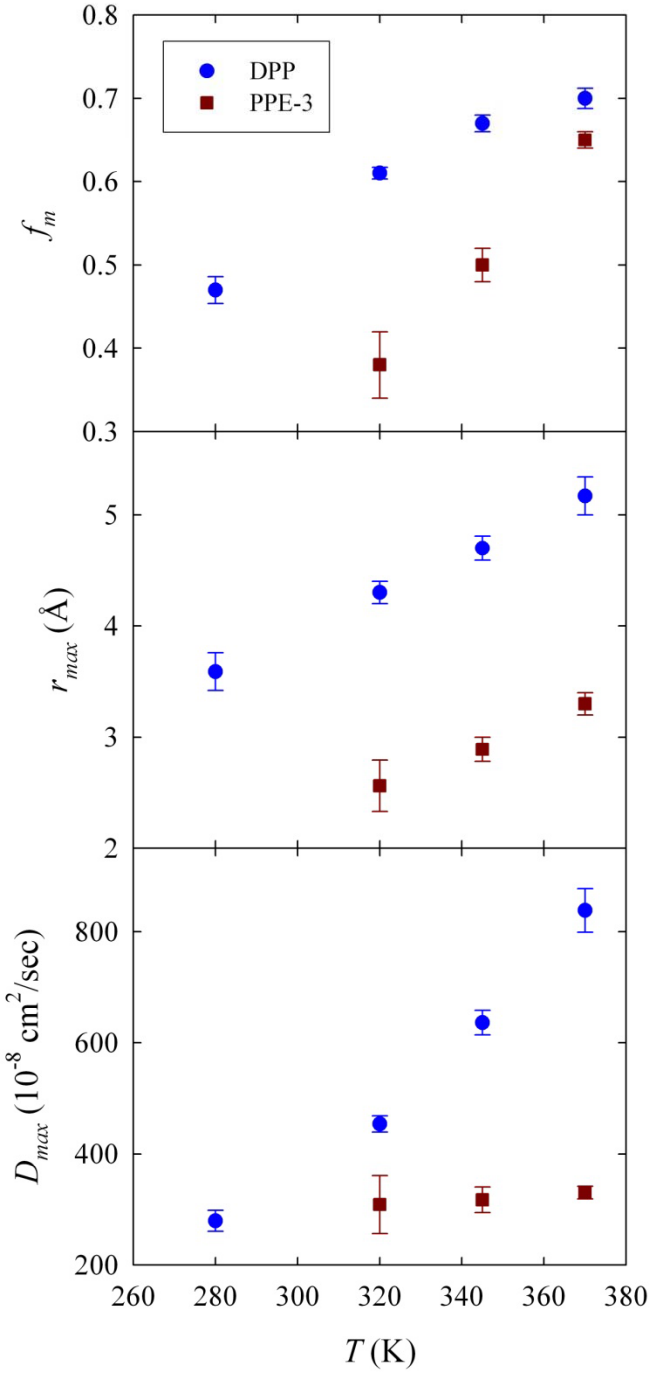


Lorentzian Γ(Q)



Non-zero intercept
–> restricted motion

Detailed Fits



Experiment Design

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

$$\Sigma = n\sigma$$

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

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

- Good rule of thumb is $T = 0.9$
  - 5 – 15 mmole H-atoms for 10 cm^2 sample (BaSiS, HFBS, CNCS, DCS)

An Example – Water

$$n = \frac{1\,\text{gm}}{\text{cm}^3} \times \frac{1\,\text{mole}}{18\text{gm}} \times \frac{6.02\times10^{23}}{\text{mole}} = \frac{3.34\times10^{22}}{\text{cm}^3}$$

$$\sigma = 2\times80\,10^{-24}\ \text{cm}^2$$

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

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

Models

- Rotation on the Surface of a Sphere

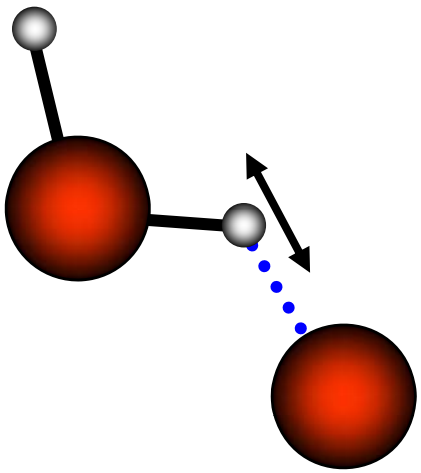
$$R(Q,\omega) = j_0^2(Qa)\delta(Qa) + \frac{1}{\pi}\sum_{l=1}^{\infty}(2l+1)j_l^2(Qa)\frac{l(l+1)D_r}{\left(l(l+1)D_r\right)^2+\omega^2}$$

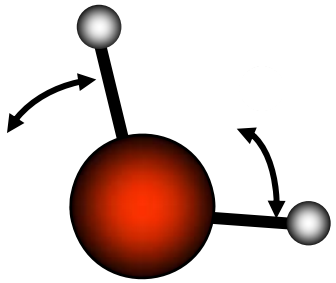
- Translational Motion

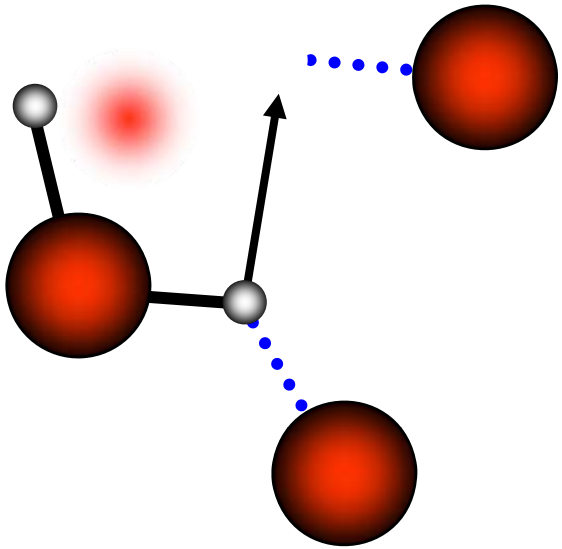
- Jump Diffusion

$$\Gamma(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0} \text{ and } D_t = \frac{L^2}{6\tau_0}$$

Excel Spread Sheet Model







Oscillation

$\langle u^2 \rangle^{1/2}$

Debye-Waller

Isotropic Rotation

τ_r

Rotational Correlation Time

r_g

Radius of Gyration

Jump Translational

D_t

Translational Diffusion Constant

τ_t

Residence Time

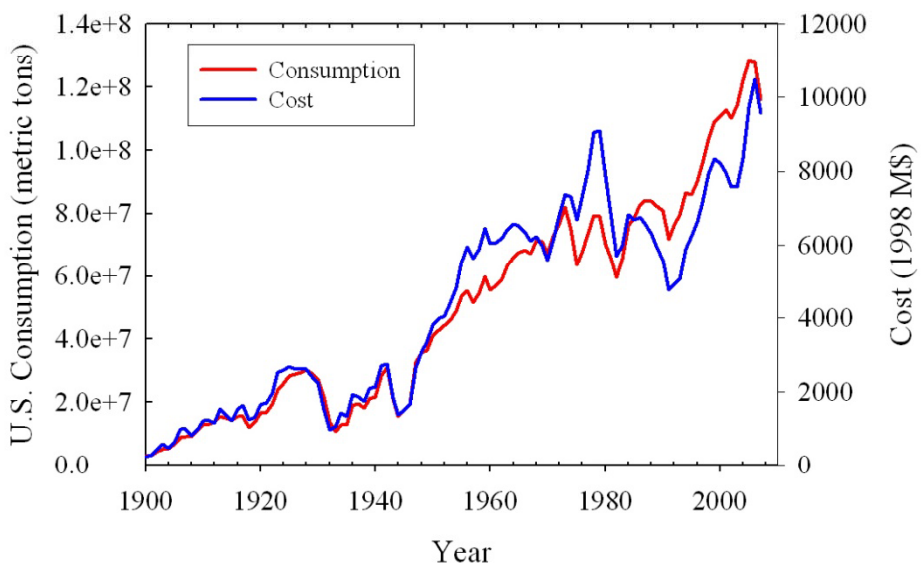
l

Mean Jump Distance

$$S(Q,\omega) = \mathrm{e}^{-\langle u^2 \rangle Q^2/3}\, T(Q,\omega) \otimes R(Q,\omega)$$

The nature of water in cement

- Massive economic impact of cement
  - 2007 United States Geological Survey
    - U.S. consumption – 115,900,000 tons, ~4% of World-wide consumption
    - U.S. value $105/ton ~ $12B
  - SNS used ~3600 metric tons of cement during construction



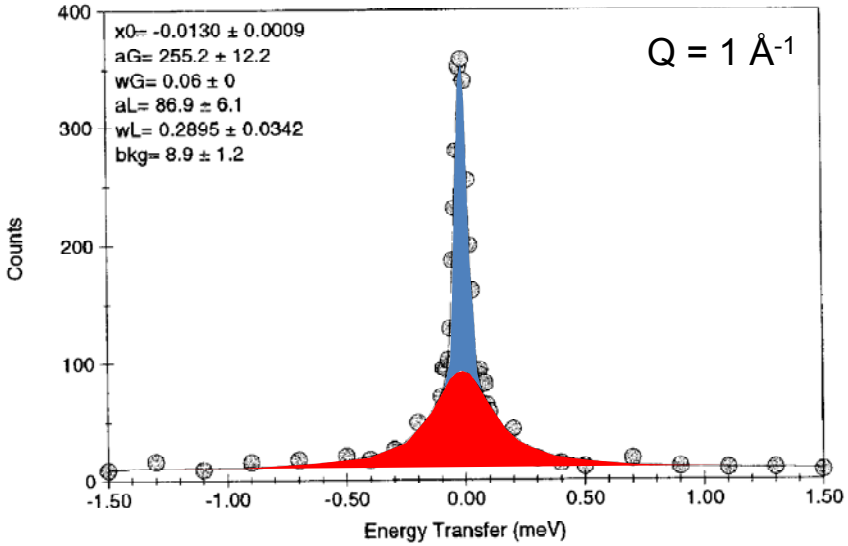
U.S. Geological Survey data

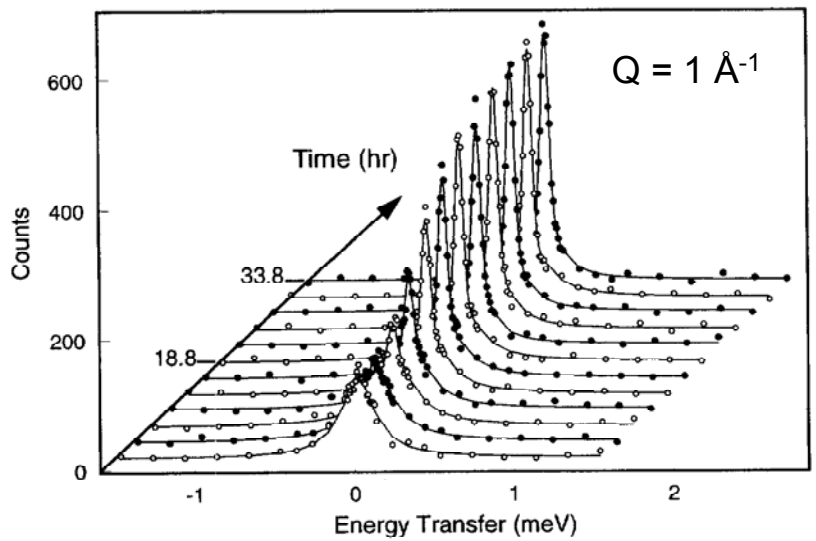
Three Gorges Dam
Wikipedia image – Christoph Filnkößl

Water in tri-Calcium Silicate (Ca_3SiO_5)

- Ordinary Portland Cement is formed of a variety of silicates with one majority phase being tri-Calcium Silicate (C_3S)
- When mixed with water
  - Initial period of rapid reaction ~few minutes
  - Induction period when hydration proceeds far slower ~few hours
  - Rate of reaction increases again and cement hardens
- 1998 – QENS used to explore the relative amount of bound water in cement paste
  - R. Berliner, et al., Cement and Concrete Research 28, 231-243 (1998)
  - A. J. Allen, et al., J. Mater. Res. 19, 3242-3254 (1998)

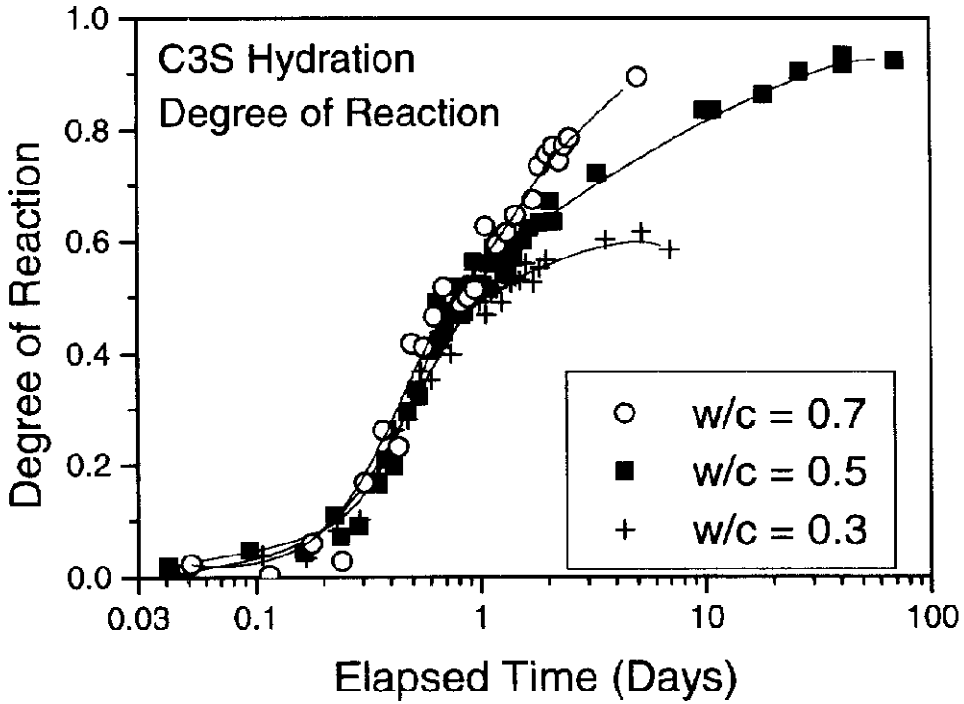
QENS spectra (60 μeV FWHM resolution)





- Bound Water Index (BWI) = Elastic Intensity/Sum of Elastic and Quasielastic
- BWI can be related to the degree of reaction (the fractional amount of cement consumed)
- Water-to-Cement ratio (by mass) (w/c)

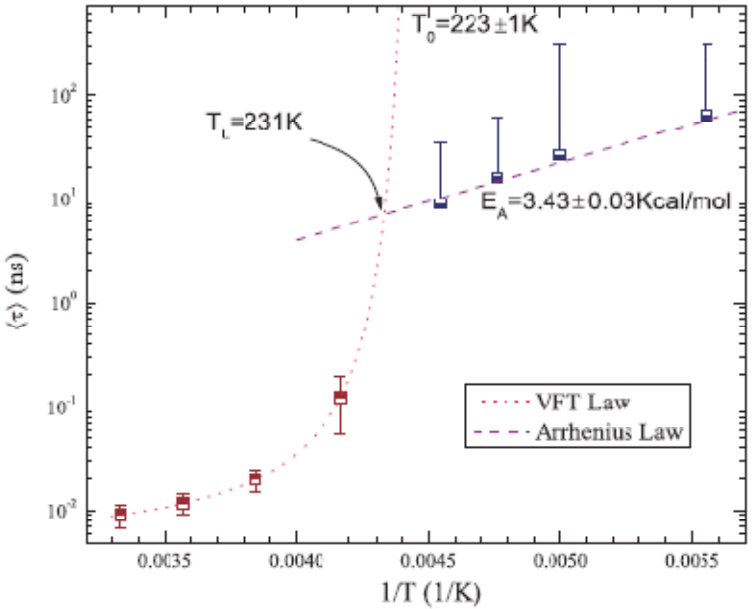
Modeling



- t < 15 hr
  - Little dependence on water to cement ratio
  - Degree of reaction is consistent with interfacial growth between two separate phases with constant nucleation with a plate or needle product morphology OR diffusion limited growth with no nucleation and plate product morphology
- t > 15 hr
  - Higher degree of reaction occurs if more water is present
  - Modeling consistent with a core of unreacted C_3S surrounded by shell that controls the diffusion of water to the interior

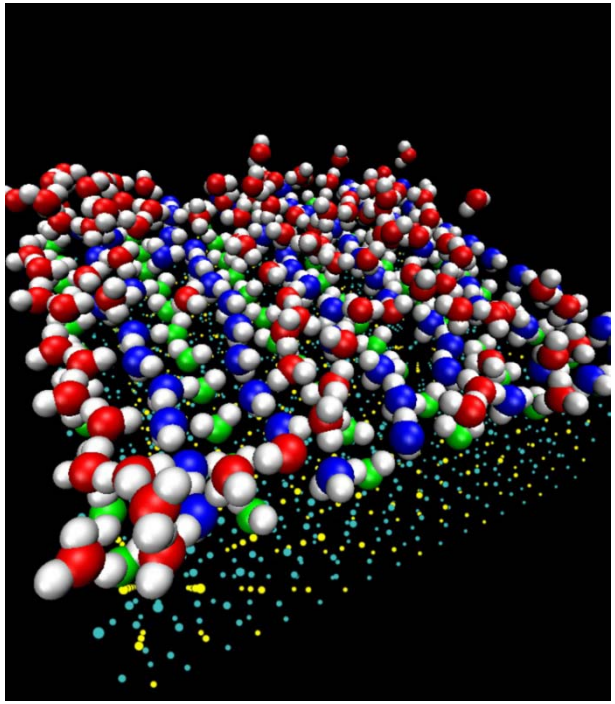
After 1998

- Initial studies followed by many publications (> 20)
  - Details of the water motion
  - Studies with additives – accelerants/retardants
  - Recent high-resolution study of water in aged cement (8 days) on BaSiS at the SNS by group of S.-H. Chen – part of this groups pursuit of the dynamics of water in a variety of confined geometries

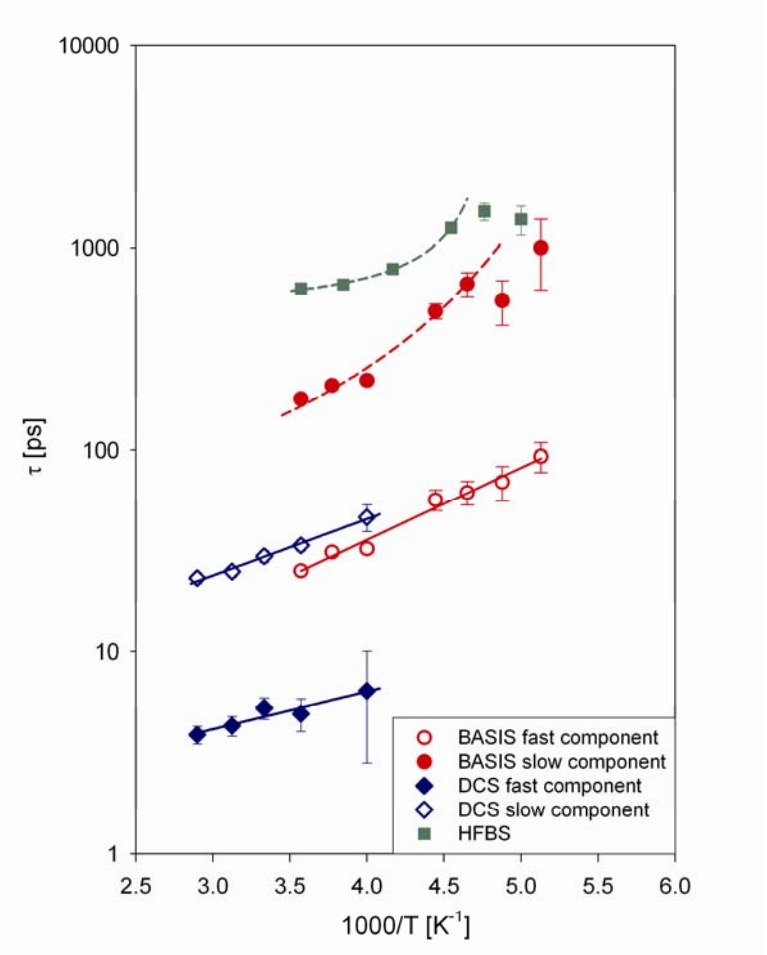


Y. Zhang, M. Lagi, F. Ridi, E. Fratini, P. Baglioni, E. Mamontov, and S.-H. Chen, J. Phys.: Condens. Matter 20, art. 502101, (2008).

Nanoparticle Surfaces – the role of adsorbed water



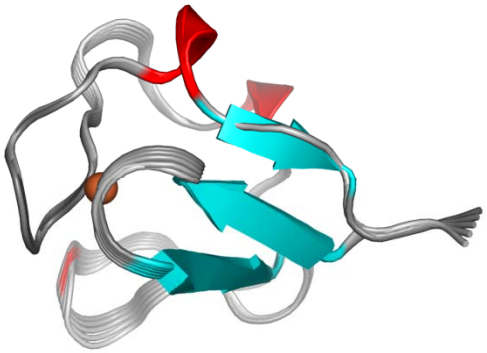
Molecular Dynamics Simulation
Green – innermost
Blue – intermediate
Red - outermost

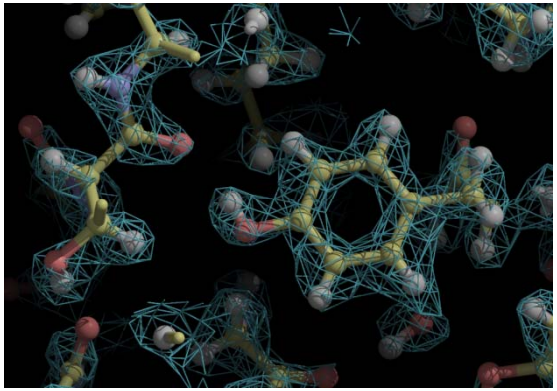


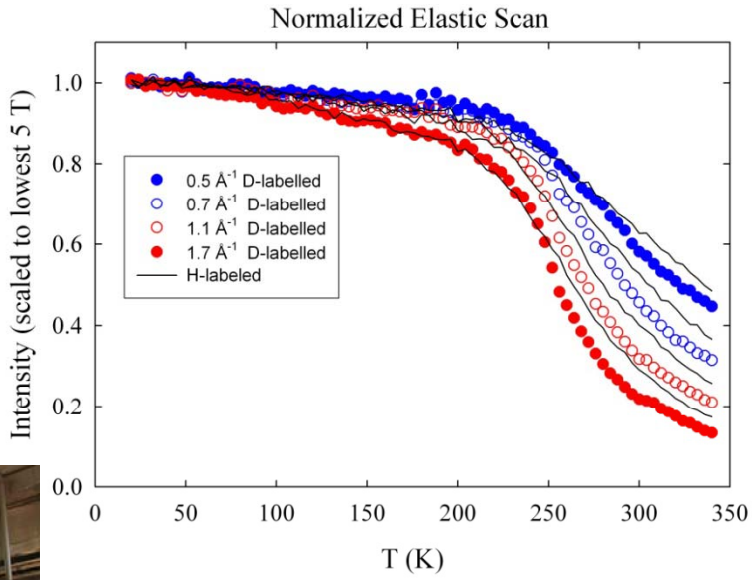
- Slowest motion – translational jumps of fully H-bonded H_2O in intermediate layer
- Faster component - localized motion of H_2O in all layers
- Fastest component – motion of outermost H_2O (3 bonds on average)

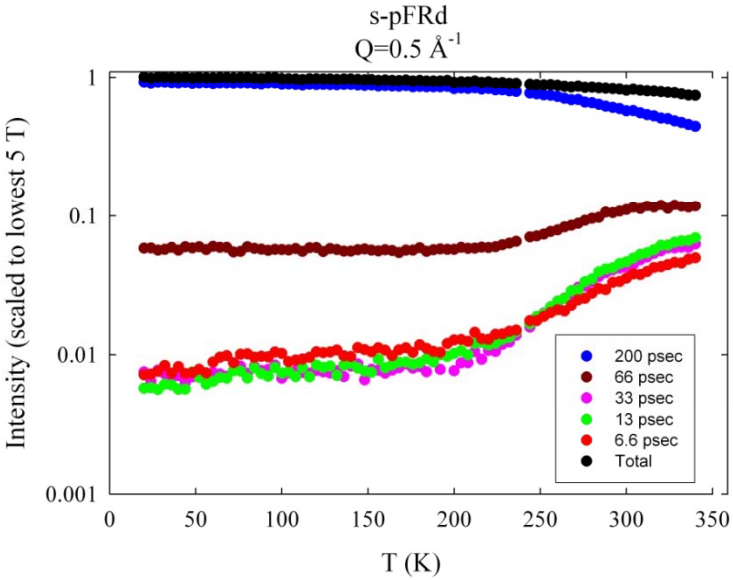
E. Mamontov, et al., J. Phys. Chem. D **112**, 12334 (2008).

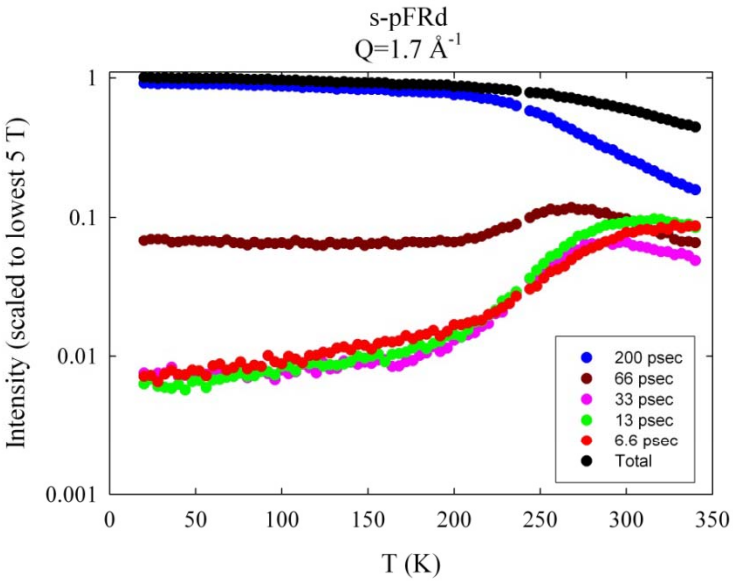
Rubredoxin-hyperthermophile - 16 min. data sets on BaSiS – December 2008



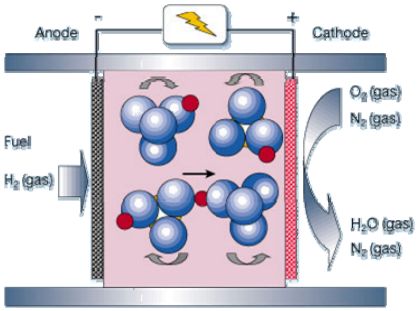


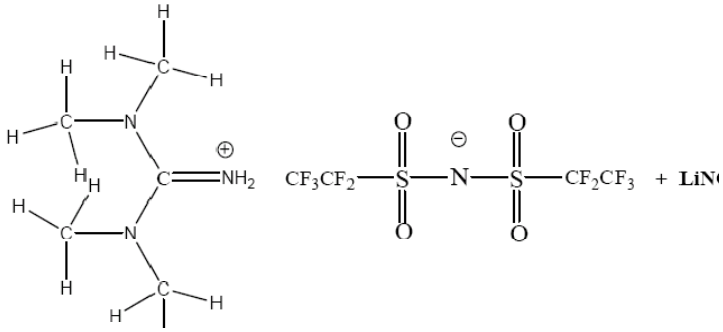


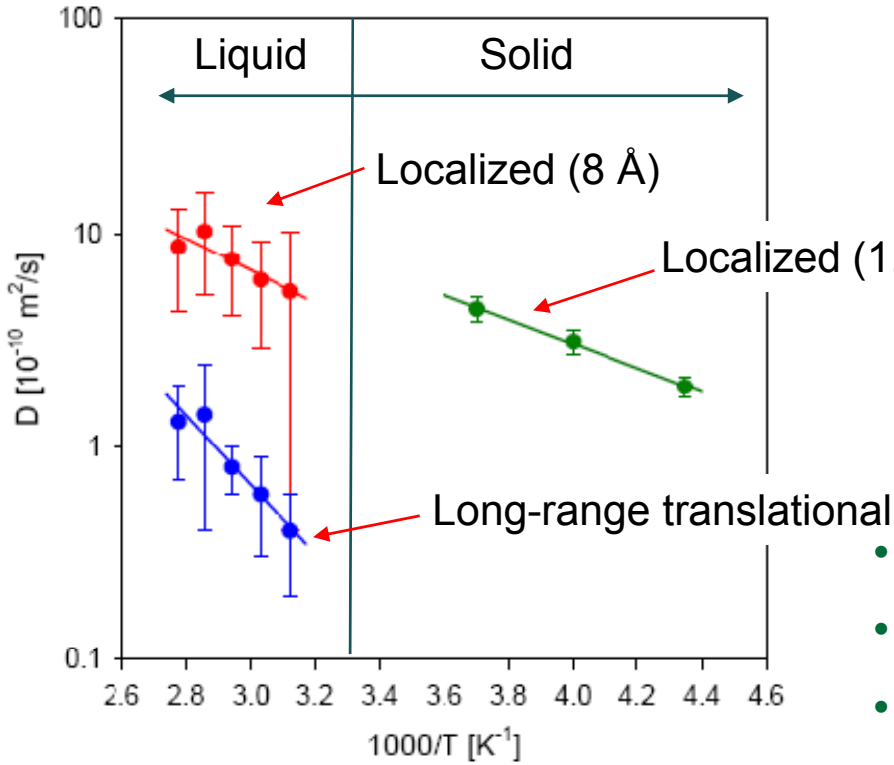




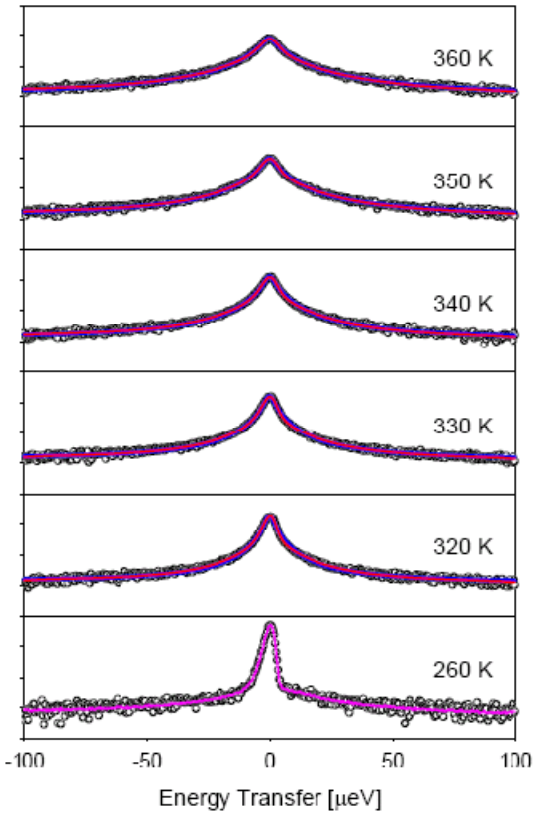
Protic Ionic Liquids – microscopic understanding of molecular mobility







Q = 0.7 Å^{-1}



- Methyl rotations T > 100 K
- Localized motion of amine group in solid
- Fast localized motion in liquid phase
- Slowest long-range translation in liquid phase associated with long-range proton transfer

E. Mamontov, et al., J. Phys. Chem. B **113**, 156-169 (2009).

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

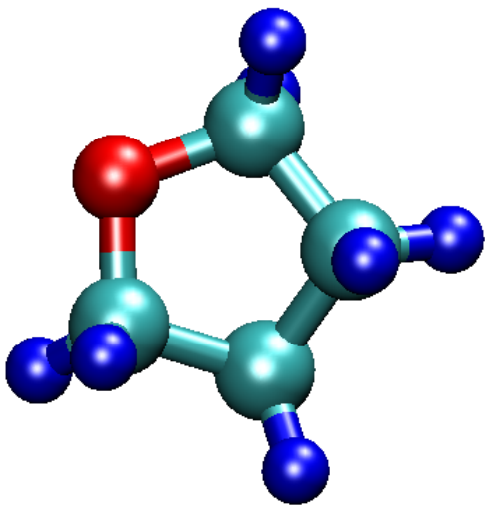
- Classic Papers
  - L. Van Hove
    - Phys. Rev. 95, 249 (1954)
    - Phys. Rev. 95, 1374 (1954)
  - V. F. Sears
    - Canadian J. Phys. 44, 867 (1966)
    - Canadian J. Phys. 44, 1279 (1966)
    - Canadian J. Phys. 44, 1299 (1966)
  - G. H. Vineyard
    - Phys. Rev. 110, 999 (1958)
  - S. Chandrasekhar
    - "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

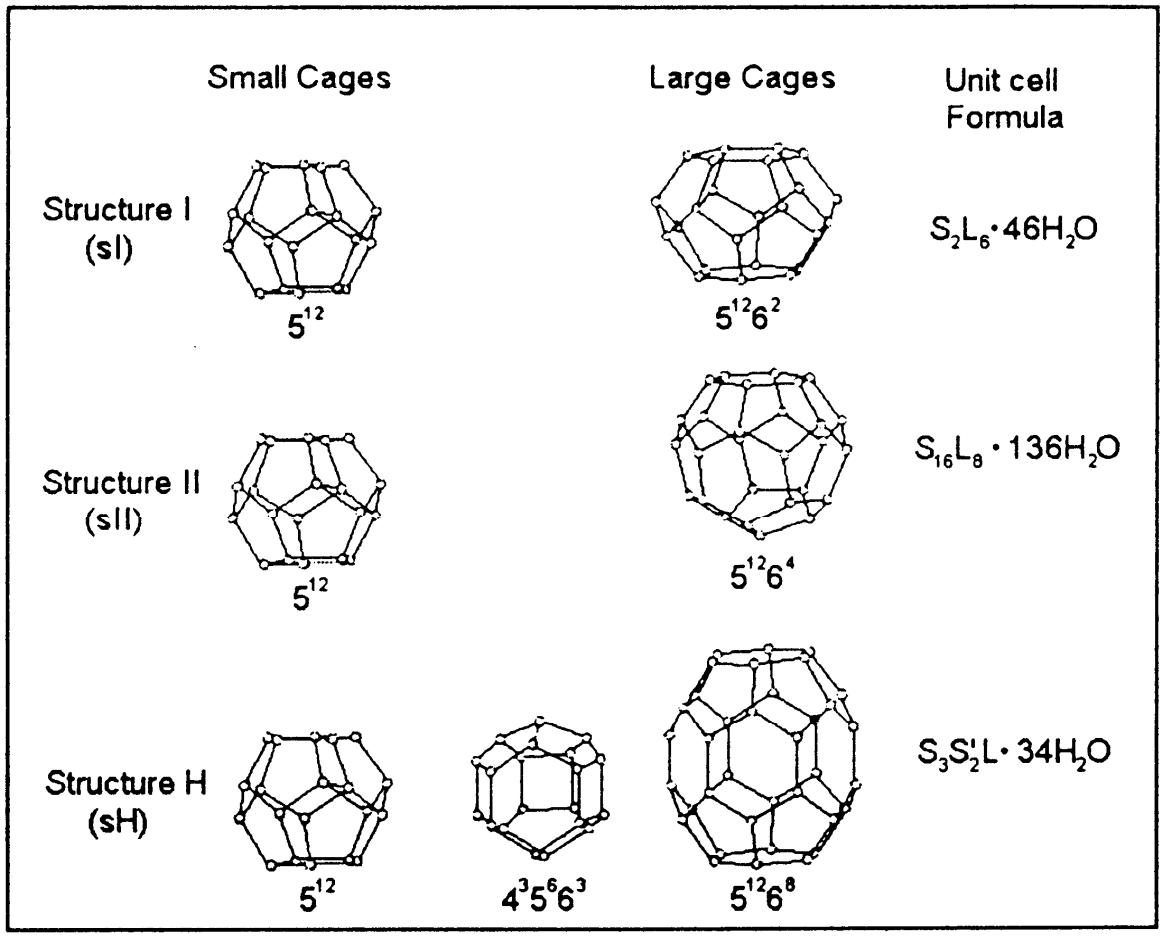
- QENS is an excellent technique to measure diffusive dynamics
  - Length scales/geometry accessible through Q-dependence
  - Many analytic models form a framework for comparison
  - Large range of time scales (sub-picosecond < t < nanosecond (μsec for NSE)
  - H-atom sensitivity
- Instrument selection 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

Backup Material More Examples

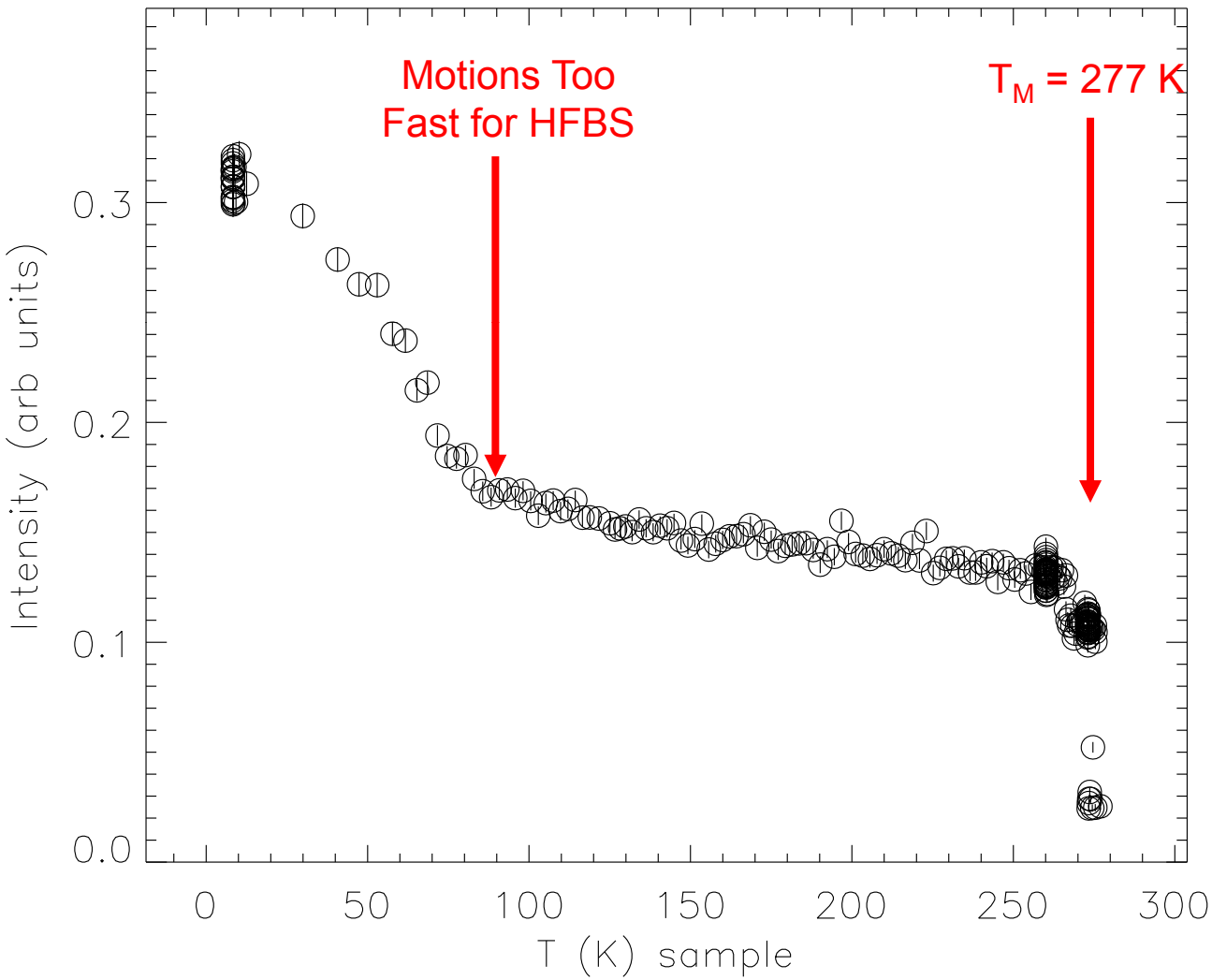
Examples – THF Clathrate Hydrate



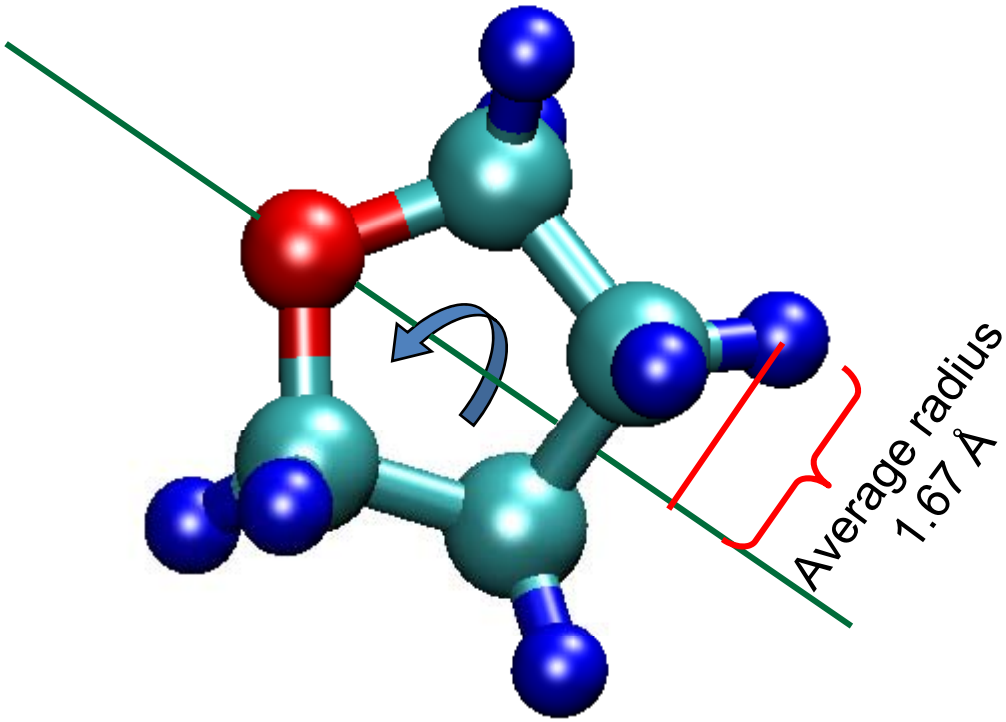
- Structure II
  - Cubic
  - Large Cages 5.9 Å - 6.9 Å
  - Avg. radius 4.73 Å

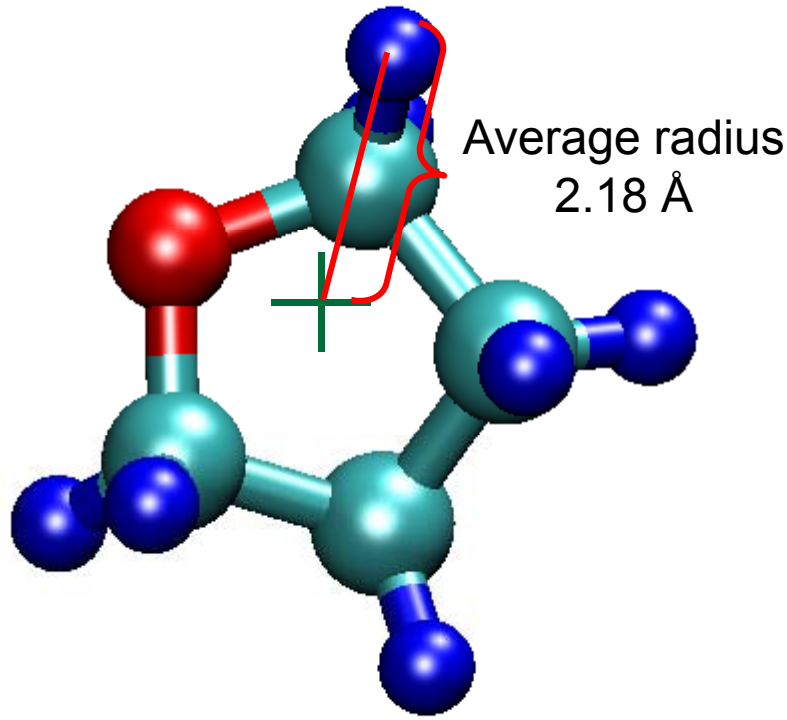


Elastic Scan (Fixed Window Scan)



Rotational models





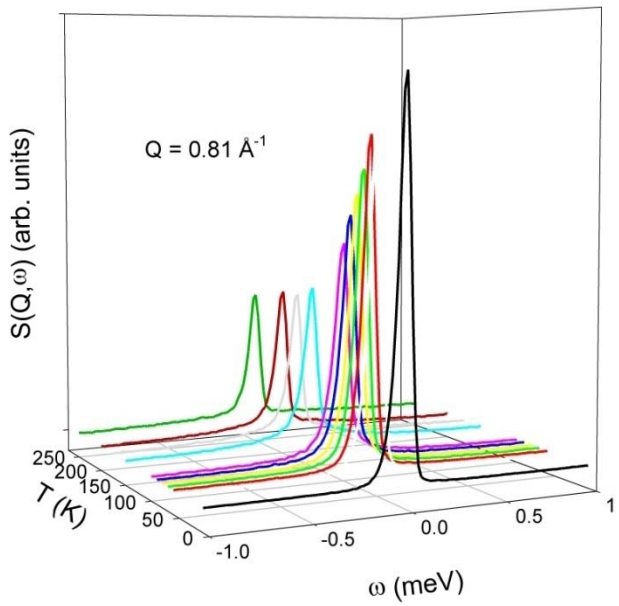
Uniaxial Rotation (powder avg. of motion in a circle)

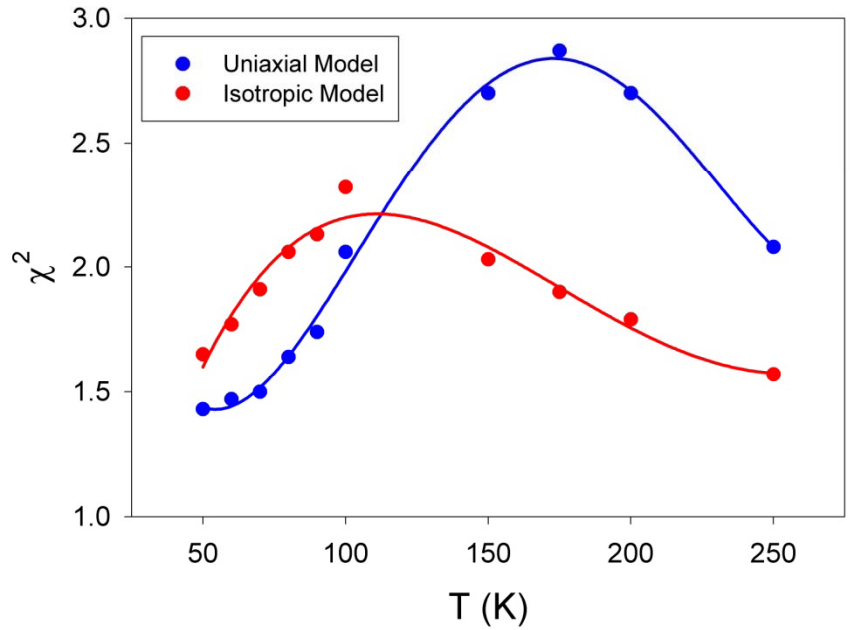
Isotropic Rotation (motion on surface of a sphere)

$$S(Q,\omega) = A_0\delta(\omega) + \sum_{l=1}^{N-1} A_l(Q)\frac{1}{\pi}\frac{\tau_l}{1+\omega^2\tau_l^2}$$

$$S(Q,\omega) = A_0\delta(\omega) + \sum_{l=1}^{\infty} A_l(Q)\frac{1}{\pi}\frac{\tau_l}{1+\omega^2\tau_l^2}$$

Two temperature regimes

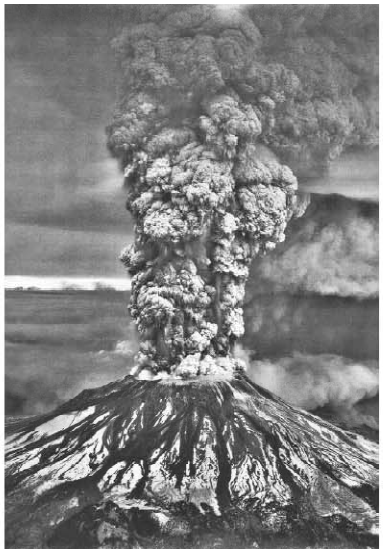


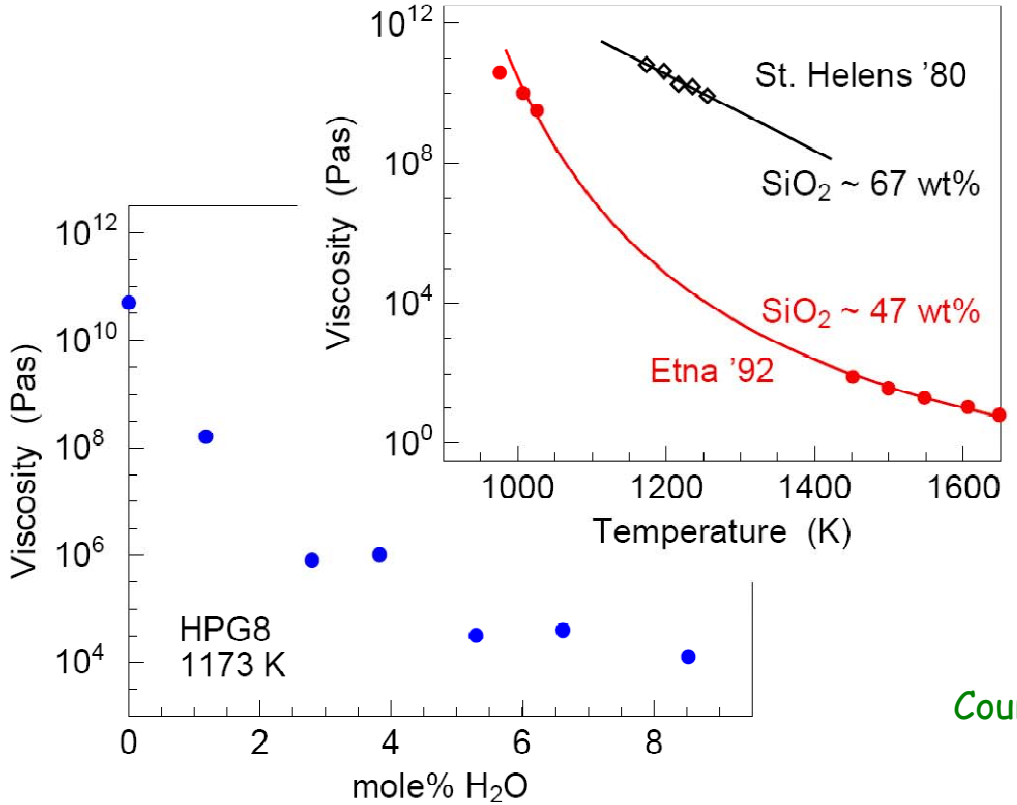


- As T increases
  - Q-dependence of intensity varies
  - Motions become faster
- T < 100 K – more restricted motion – uniaxial rotation
- T > 100 K – uniform diffusion in approximately spherical geometry
- Activated process: 1.8 kJ/mole (< 100 K), 2.8 kJ/mole (T >100K)

Backup Material - Some Examples – courtesy D. A. Neuman (QENS – 2006 talk)

Silica Melts – a Model System for Lava





Courtesy of Florian Kargl

SiO_2 + Na_2O, K_2O, Al_2O_3, Fe_2O_3, CaO, MgO ...

effusive (flow) or explosive (fragmentation) eruption:

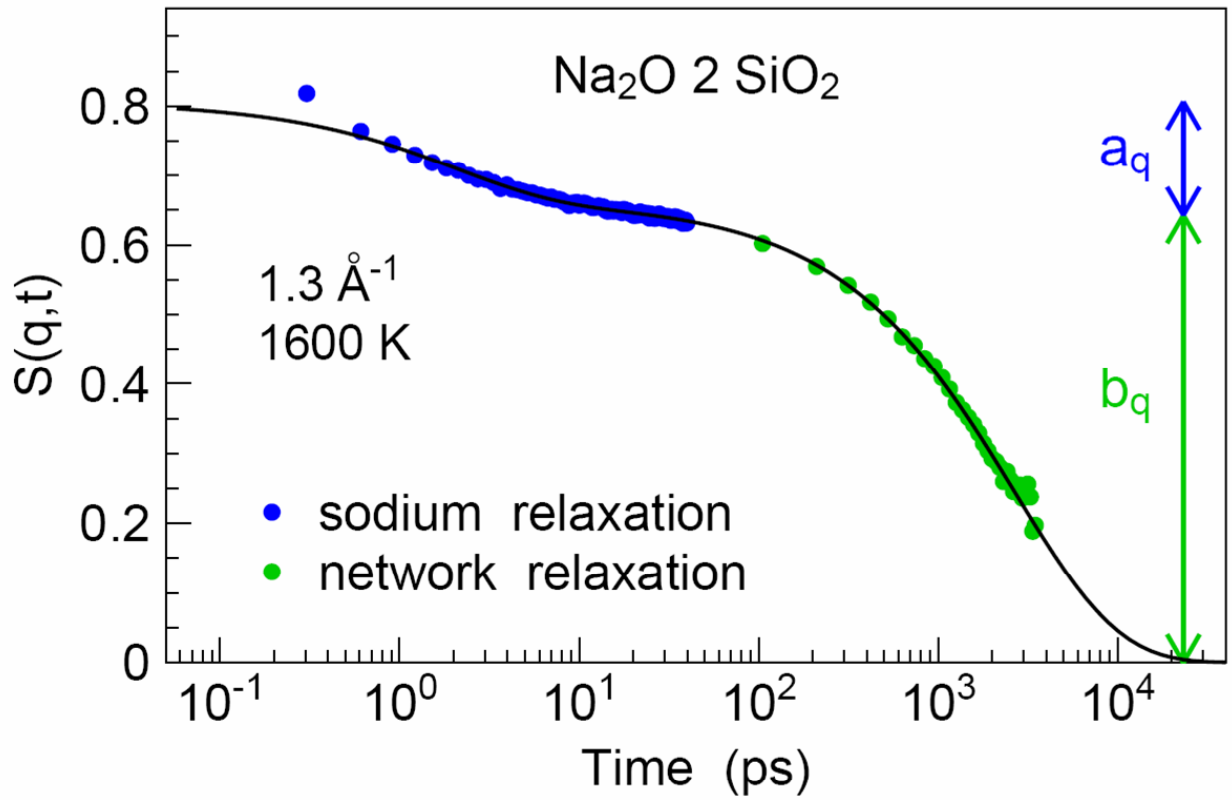
– H_2O content in magma chamber (up to ≈15 mole%)

– viscosity of the anhydrous silicate melt (composition)

Silica Melts

fast sodium relaxation on picosecond time scale
=> sodium diffusion (IN5)

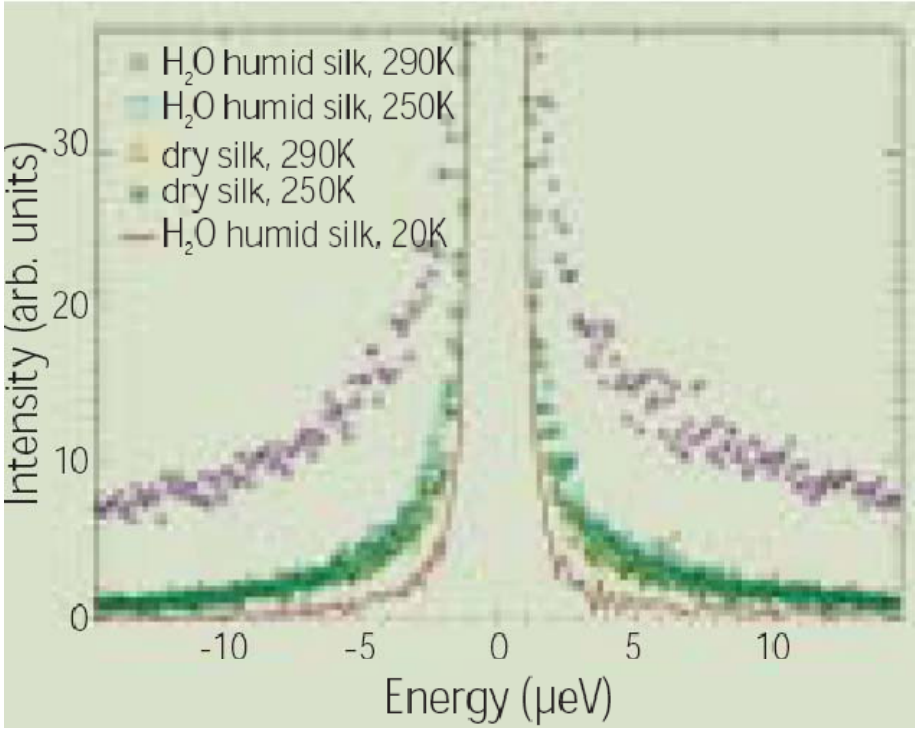
Si-O network relaxation on nanosecond time scale
=> viscous flow (HFBS)



A. Meyer, H. Schober, D. B. Dingwell, Europhys. Lett. **59**, 708 (2002)

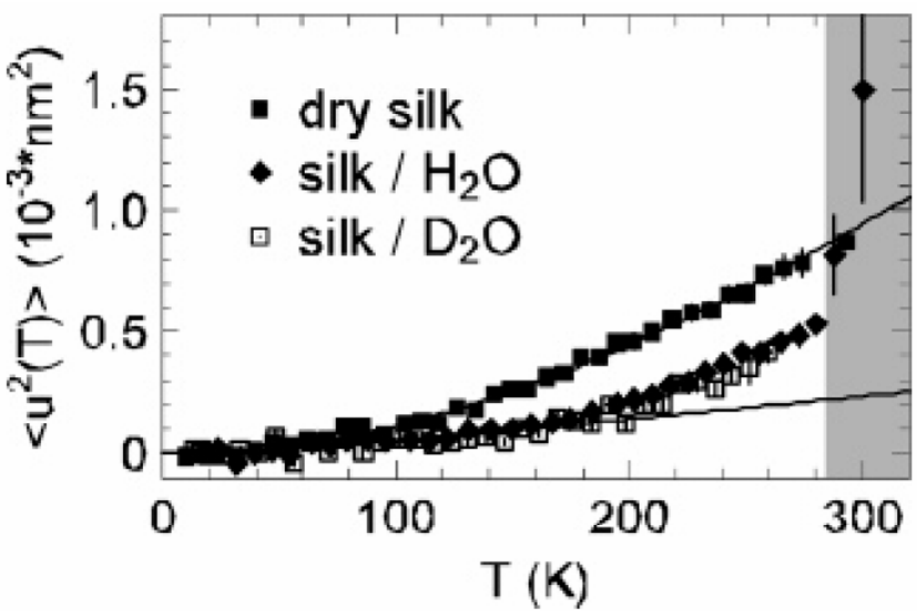
Spider Silk and Water

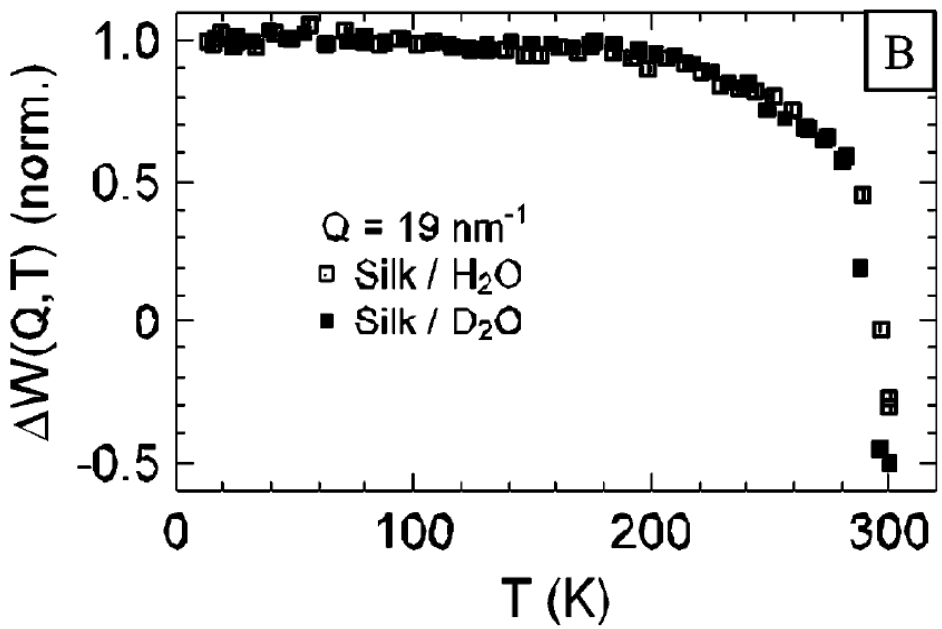
Spider dragline silk possesses outstanding mechanical properties. It is spun at ambient temperature and pressure using water as a solvent. It is therefore crucial to understand the role of adsorbed water to spider silk.



T. Seydel, M. Koza, D. Sapede, C. Riekel, T. Forsyth, F. Vollrath, ILL annual report, **58** (2003).

Spider Silk





The mobility of the polymer chains is enhanced by the presence of water.

D. Sapede, T. Seydel, V.T. Forsyth, M.M. Koza, R. Schweins, F. Vollrath, and C. Riekel, Macromolecules **38**, 8447 (2005).

Data from IN16