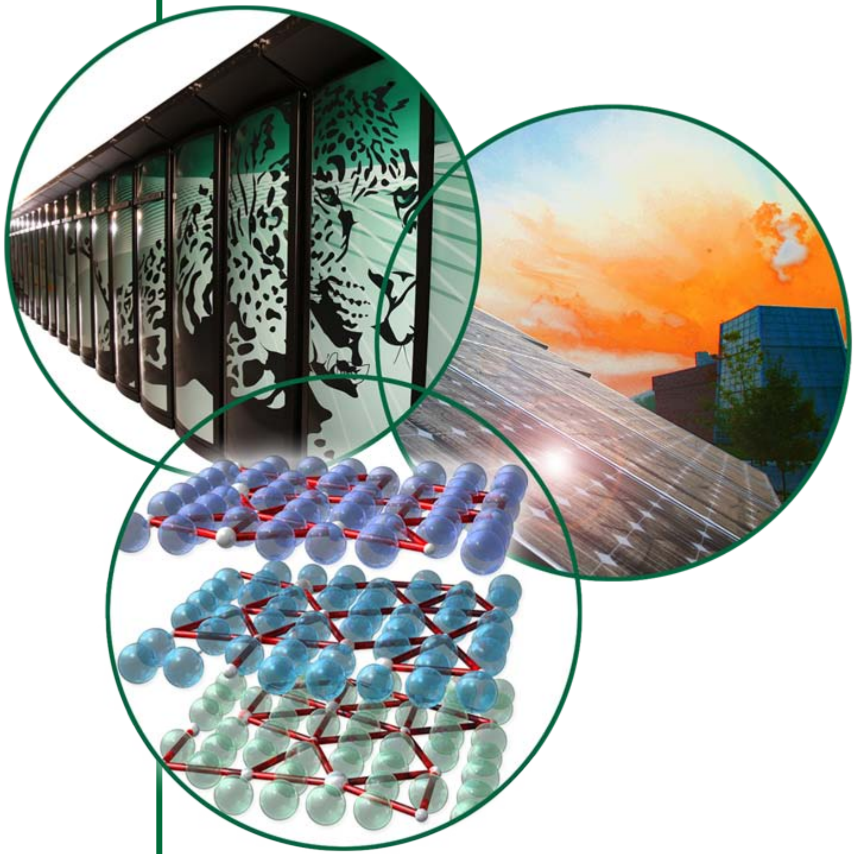
Quasielastic Neutron Scattering



Ken Herwig

Deputy Director
Neutron Scattering Science Division
Oak Ridge National Laboratory

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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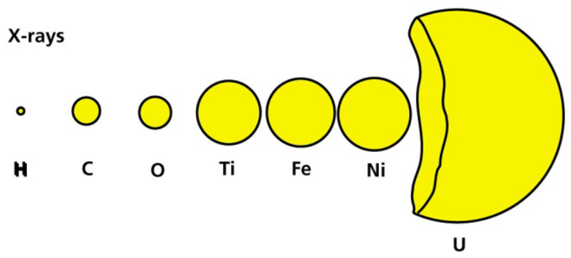
OUTLINE

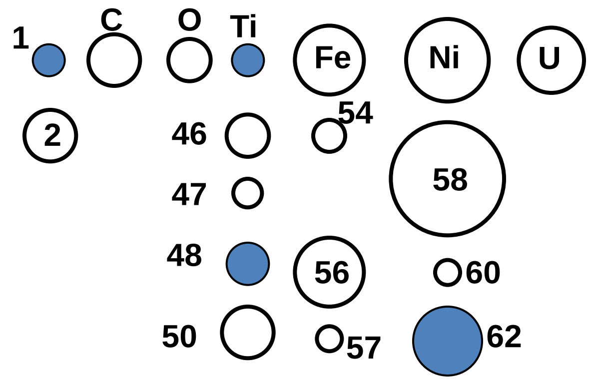
- Background – the incoherent scattering cross section of H
- Neutrons and QENS
- Experiment Design
- Connection to Molecular Dynamics Simulations
- The Elastic Incoherent Structure Factor (EISF)
- The Role of Instrumentation
- Restricted Diffusion Example – Tethered Molecules
- References and Summary

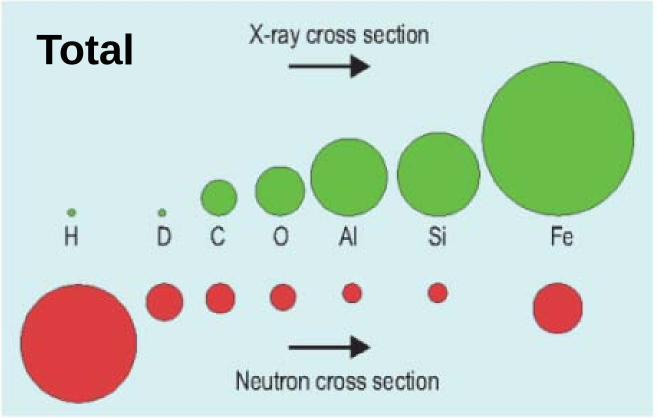
Incoherent and Coherent Scattering

- Origin – incoherent scattering arises when there is a random variability in the scattering lengths of atoms in your sample – can arise from the presence of different isotopes or from isotopes with non-zero nuclear spin and the relative orientation of nuclear spin with nuclear spin
- 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.
  – 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)

Neutrons and the Large Incoherent Cross-section of H



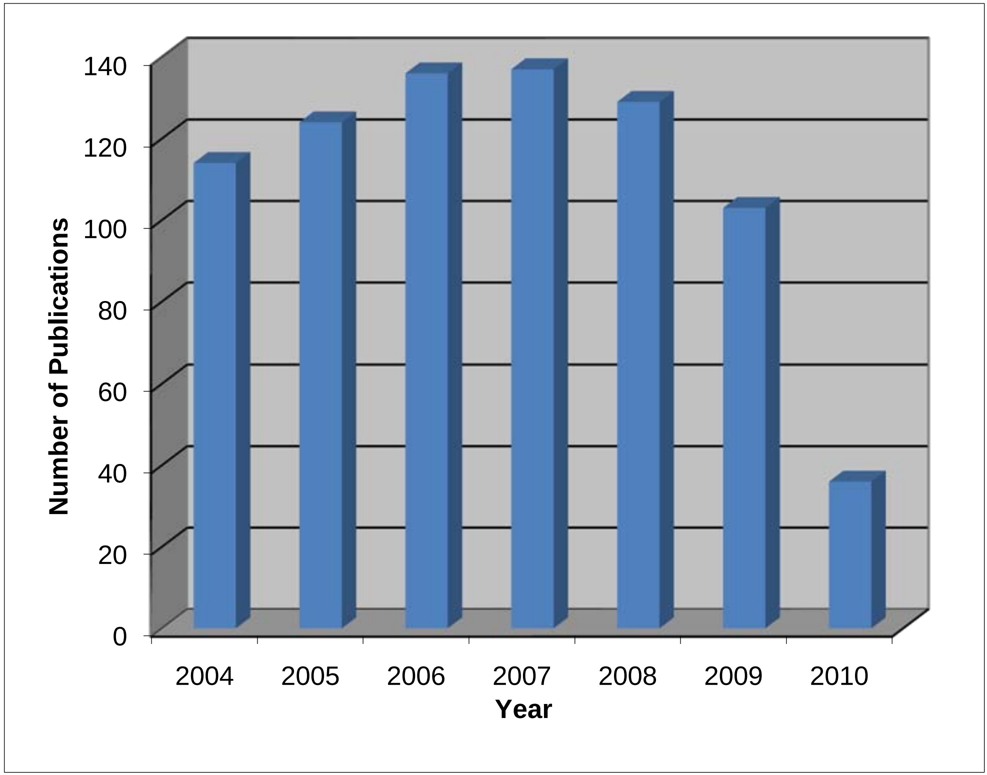




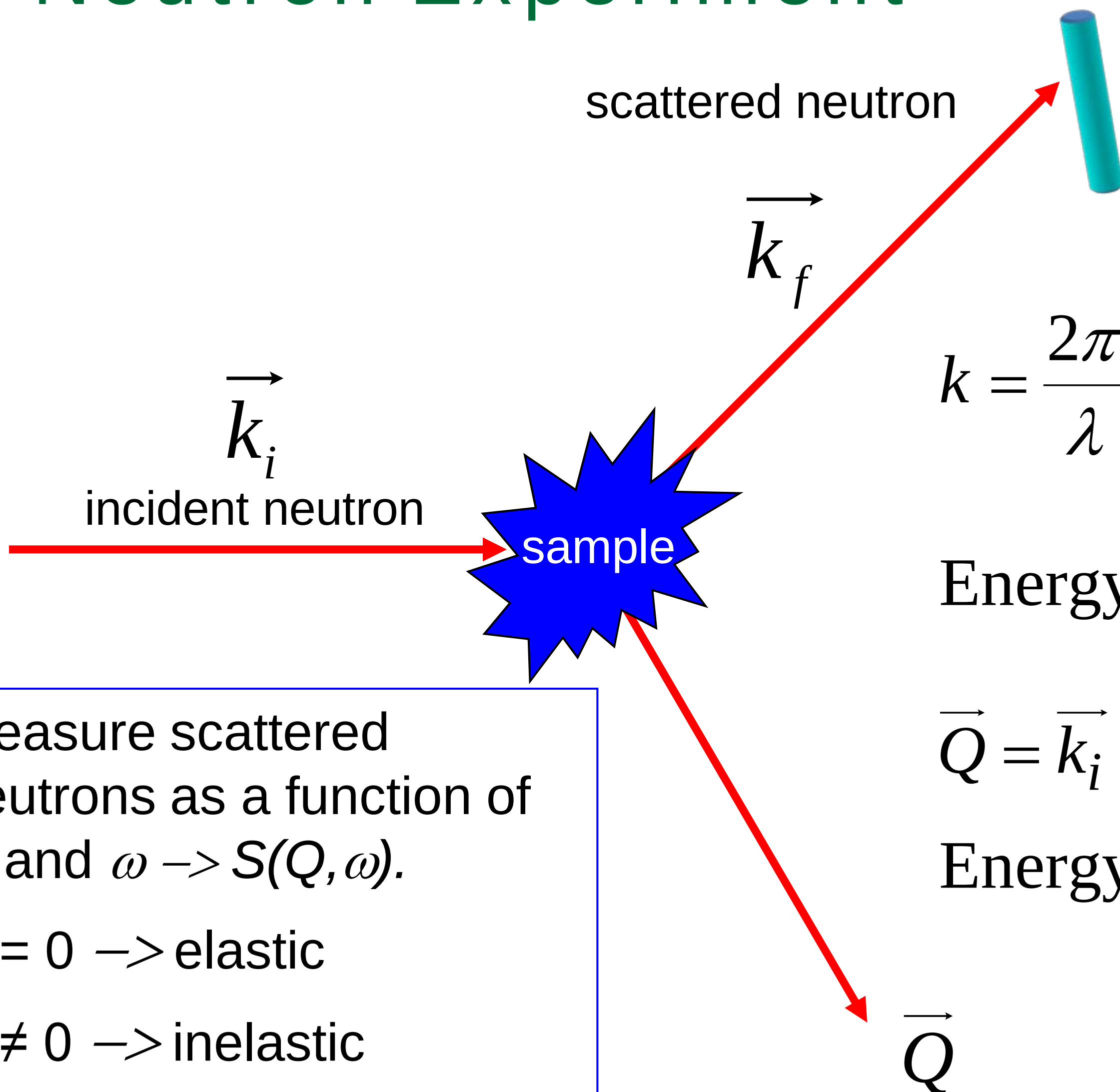
- Isotopic sensitivity – random nuclear cross-section with element and isotope
  - H-D contrast, light element sensitivity in presence of heavy elements
  - H large incoherent cross-section – self-correlation function
- Magnetic moment
- Wavelength and energy match excitations in condensed matter (Geometry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

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

- Applicable to wide range of science areas
  - Biology – dynamic transition in proteins, hydration water
  - Chemistry – complex fluids, ionic liquids, porous media, surface interactions, water at interfaces, clays
  - Materials science – hydrogen storage, fuel cells, polymers
- Probes true “diffusive” motions
- Range of analytic function models
  - Useful for systematic comparisons
- Close ties to theory – particularly Molecular Dynamics simulations
- Complementary
  - Light spectroscopy, NMR, dielectric relaxation
- Unique: Answers Questions you cannot address in other ways.



A Neutron Experiment



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

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

$$\overrightarrow{Q} = \overrightarrow{k_i} - \overrightarrow{k_f}$$

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

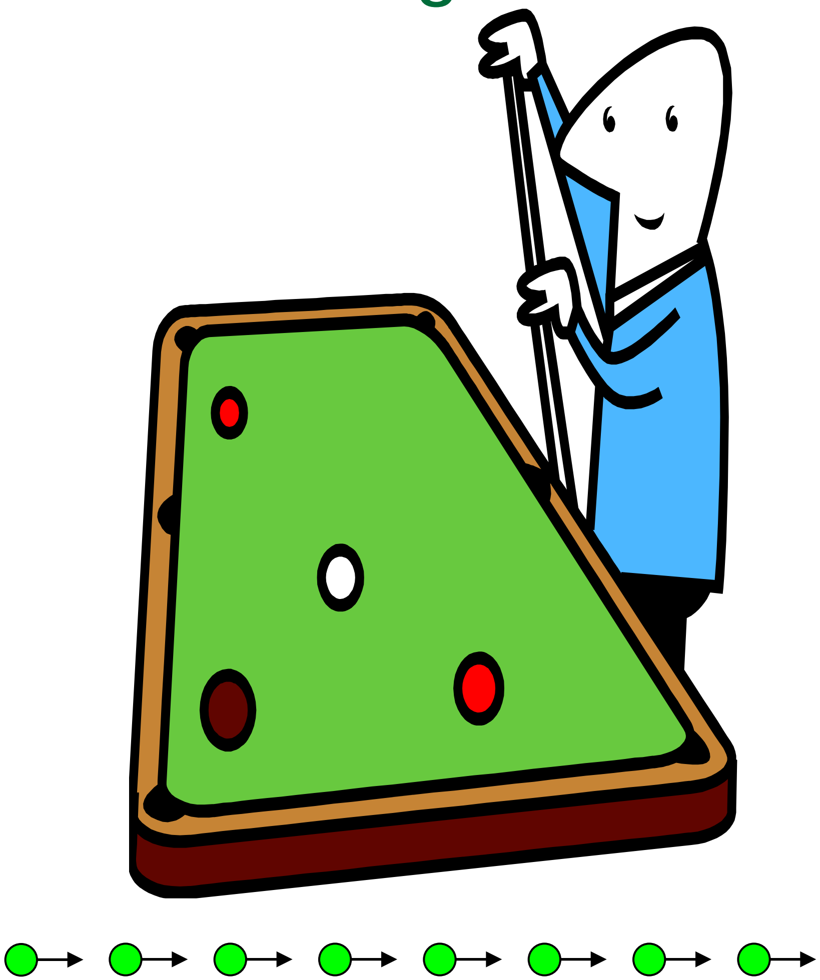
Measure scattered neutrons as a function of Q and ω –> $S(Q,\omega)$.

$\omega = 0$ –> elastic

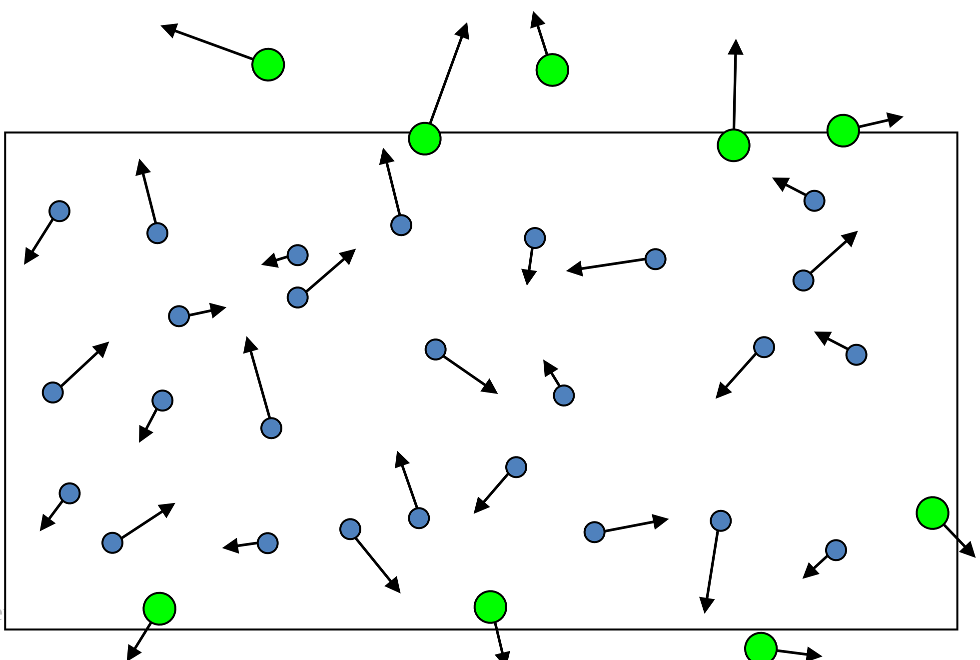
$\omega \neq 0$ –> inelastic

ω near 0 –> quasielastic

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 $\omega = 0$
- Low-Q – typically less than 5 Å^{-1}



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})

$$\Sigma = n\sigma$$

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)

An Example – Water

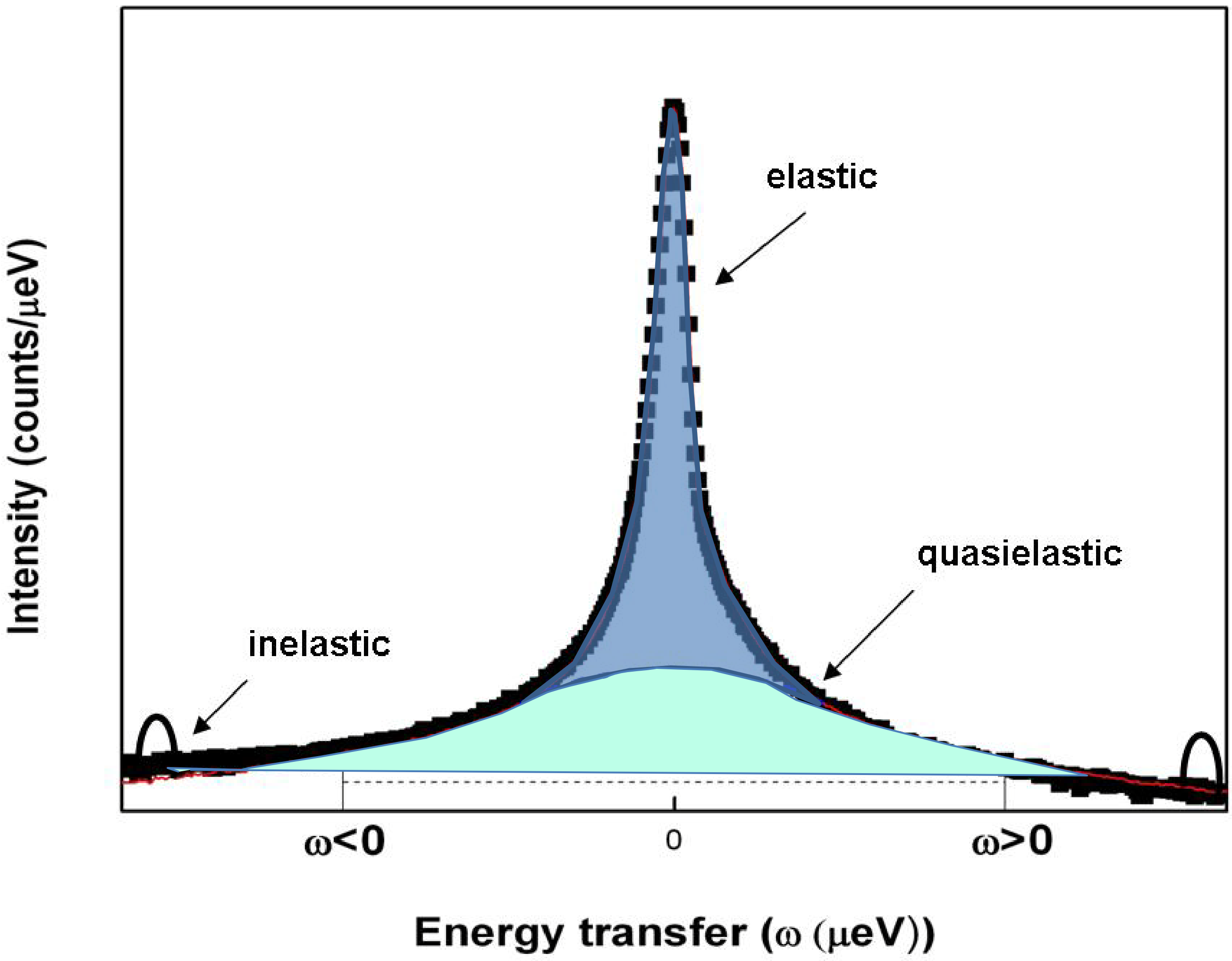
$$n = \frac{1\,\mathrm{gm}}{\mathrm{cm}^3} \times \frac{1\,\mathrm{mole}}{18\mathrm{gm}} \times \frac{6.02\times10^{23}}{\mathrm{mole}} = \frac{3.34\times10^{22}}{\mathrm{cm}^3}$$

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

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

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

QENS Spectra



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

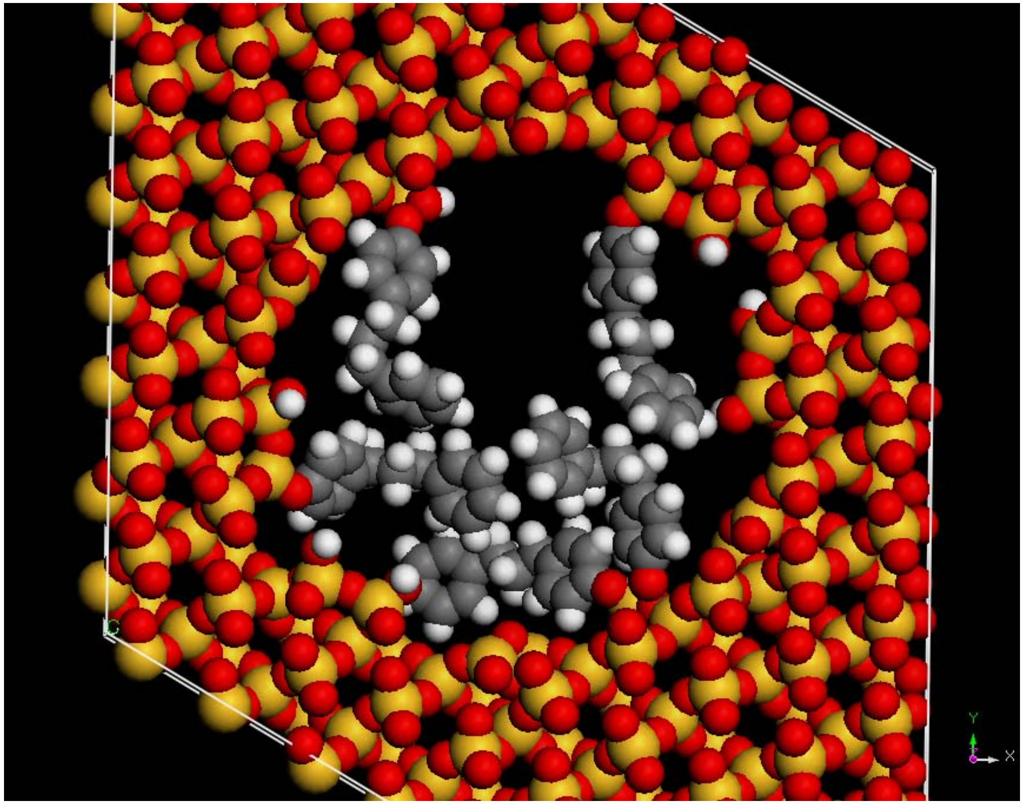
$$I_{inc}(\mathbf{Q},t) = \frac{1}{N}\sum_i \left\langle \exp\{i\mathbf{Q}\bullet\mathbf{R}_i(t)\}\exp\{-i\mathbf{Q}\bullet\mathbf{R}_i(0)\}\right\rangle$$

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

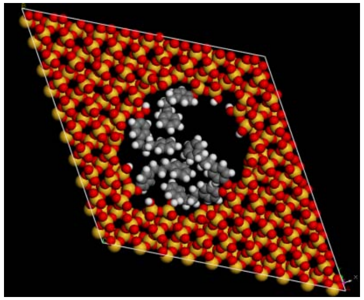
$$S_{inc}(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_{inc}(\mathbf{Q},t))\exp(-i\omega t)dt$$

QENS and Molecular Dynamics Simulations

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

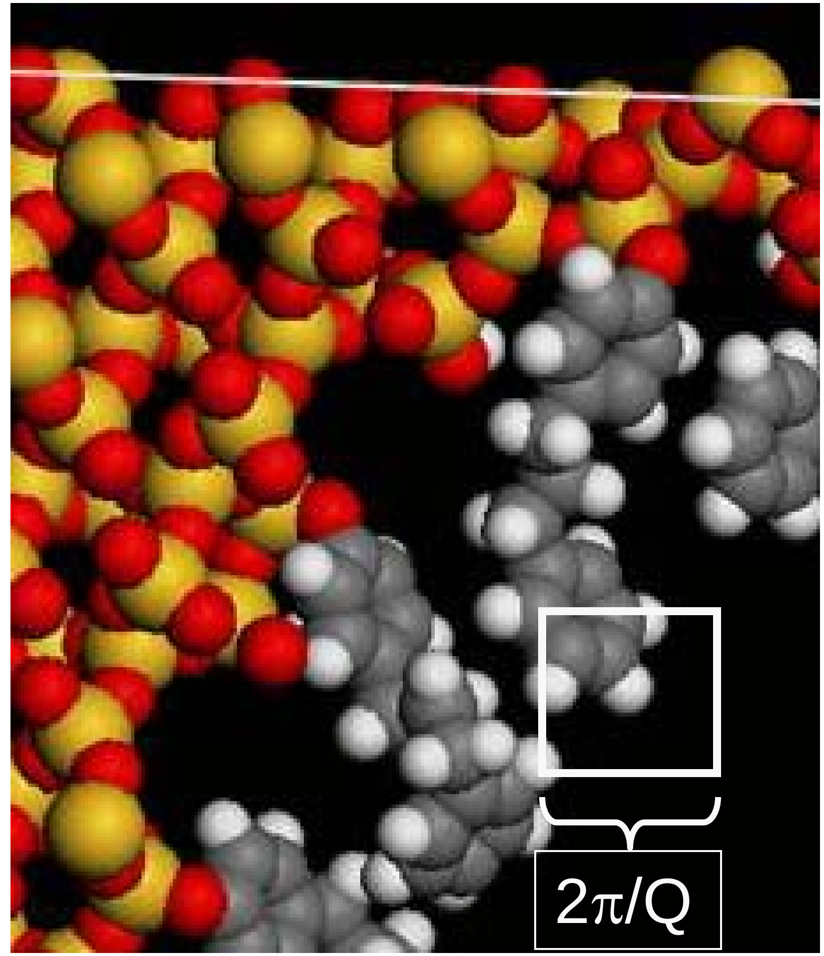


1,3 diphenylpropane tethered to the pore surface of MCM-41



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



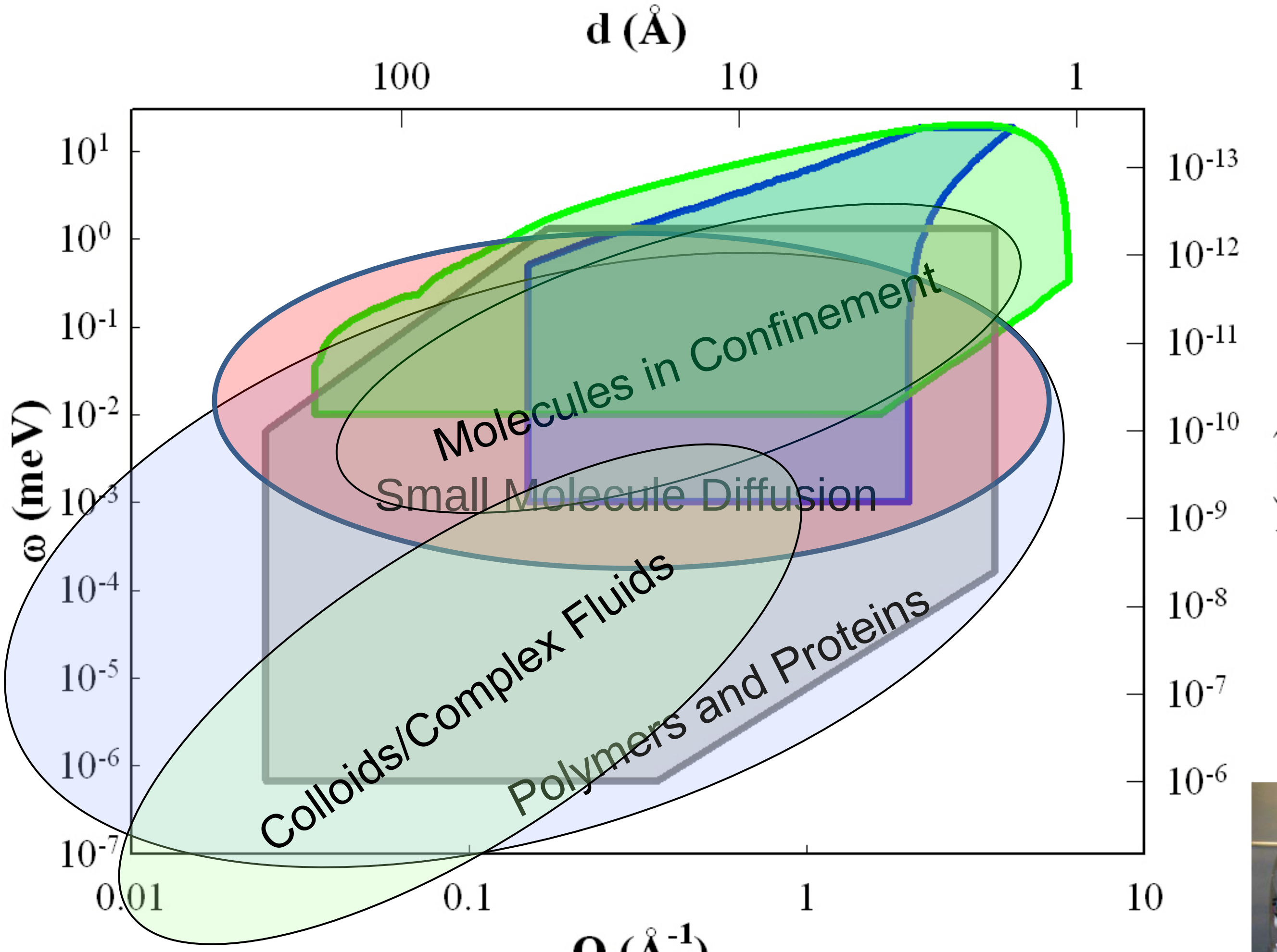
QENS and Neutron Scattering Instruments

- 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



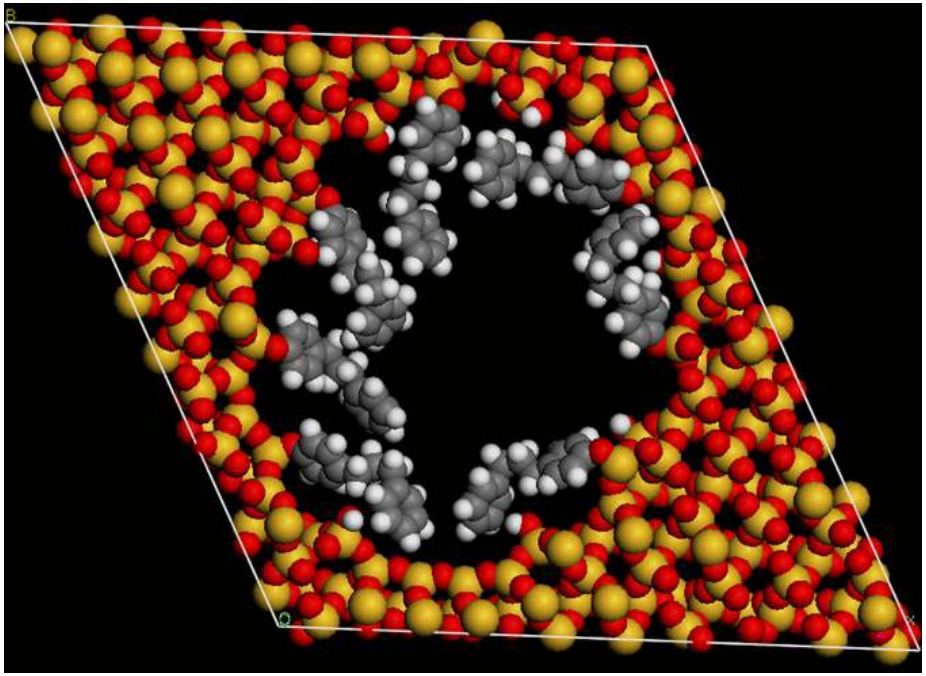
Backscattering

Cold Neutron Chopper

Neutron Spin Echo

BaSiS - SNS Near Backscattering Spectrometer

Restricted Diffusion – Tethered Molecules



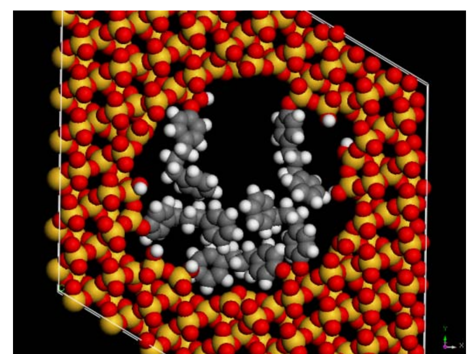
Samples – typical 0.7 g

240 K < T < 340 K

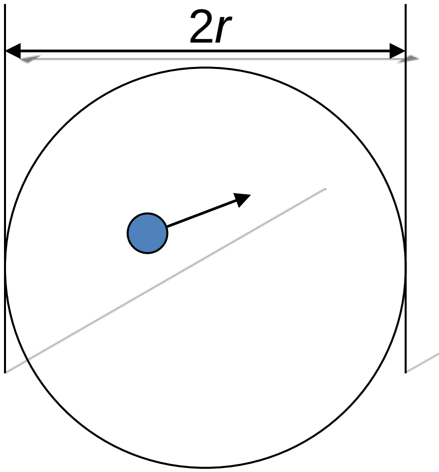
Simple Fit – Lorentzian + δ

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)

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



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

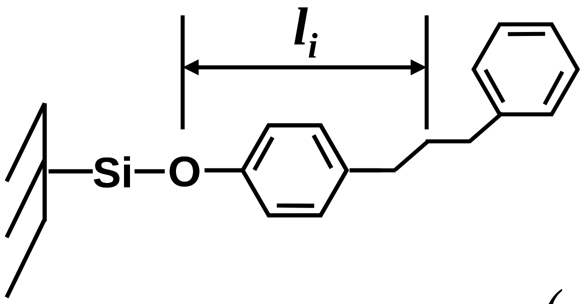


$$S_s(Q,\omega,r,D) = A_0^0(Qr)\delta(\omega) + \frac{1}{\pi}\sum_{(l.n)\neq(0,0)}(2l+1)A_n^l(Qr)\frac{\left(x_n^l\right)^2 D/r^2}{\left[\left(x_n^l\right)^2 D/r^2\right]^2+\omega^2}$$

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

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

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



DPP

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

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

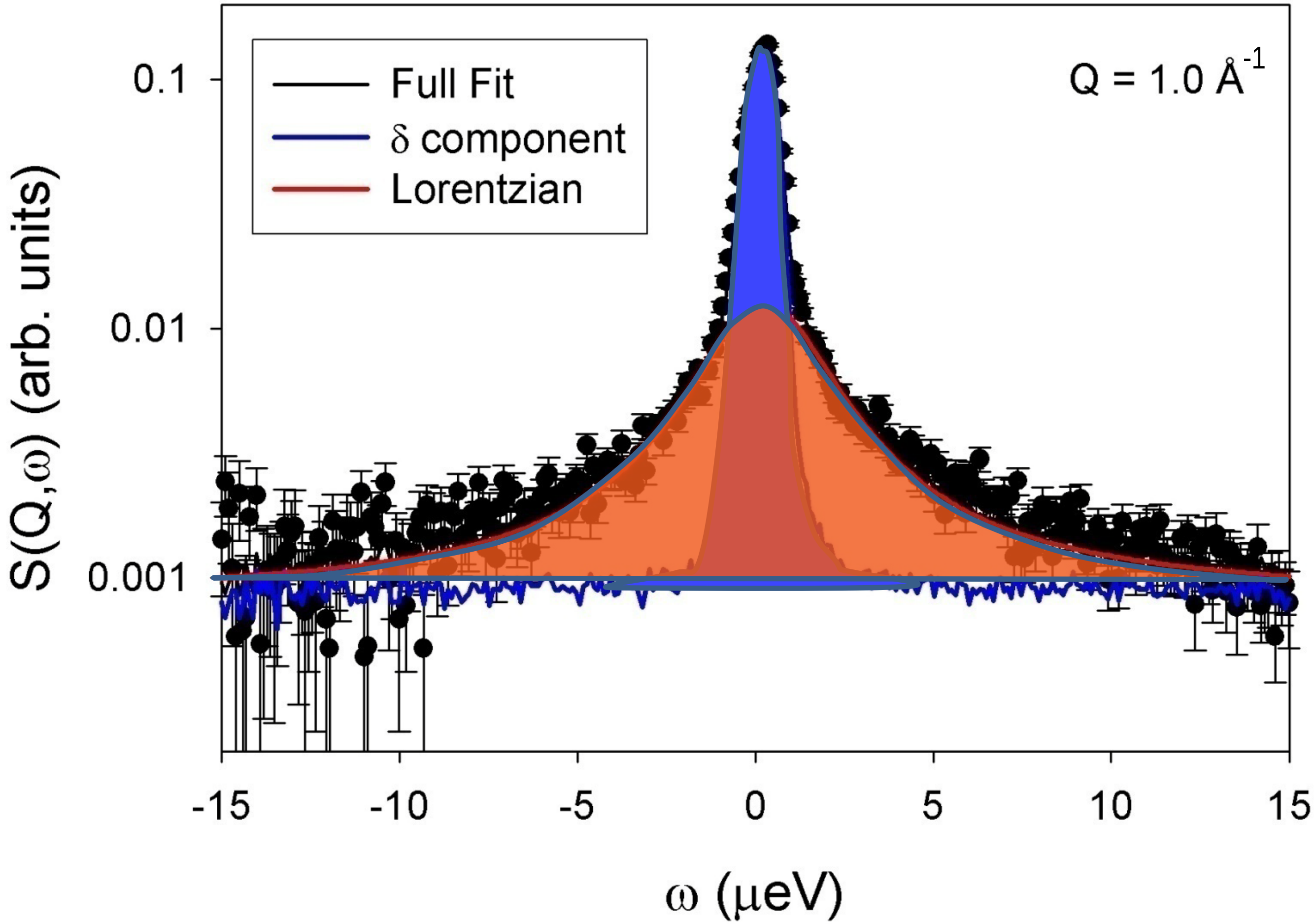
$$EISF(Q) = (1 - f_m) + f_m \times \frac{1}{15} \sum_{i=1}^{15} \left[\frac{3 j_1(QR_i)}{QR_i} \right]^2$$

Fits to Data

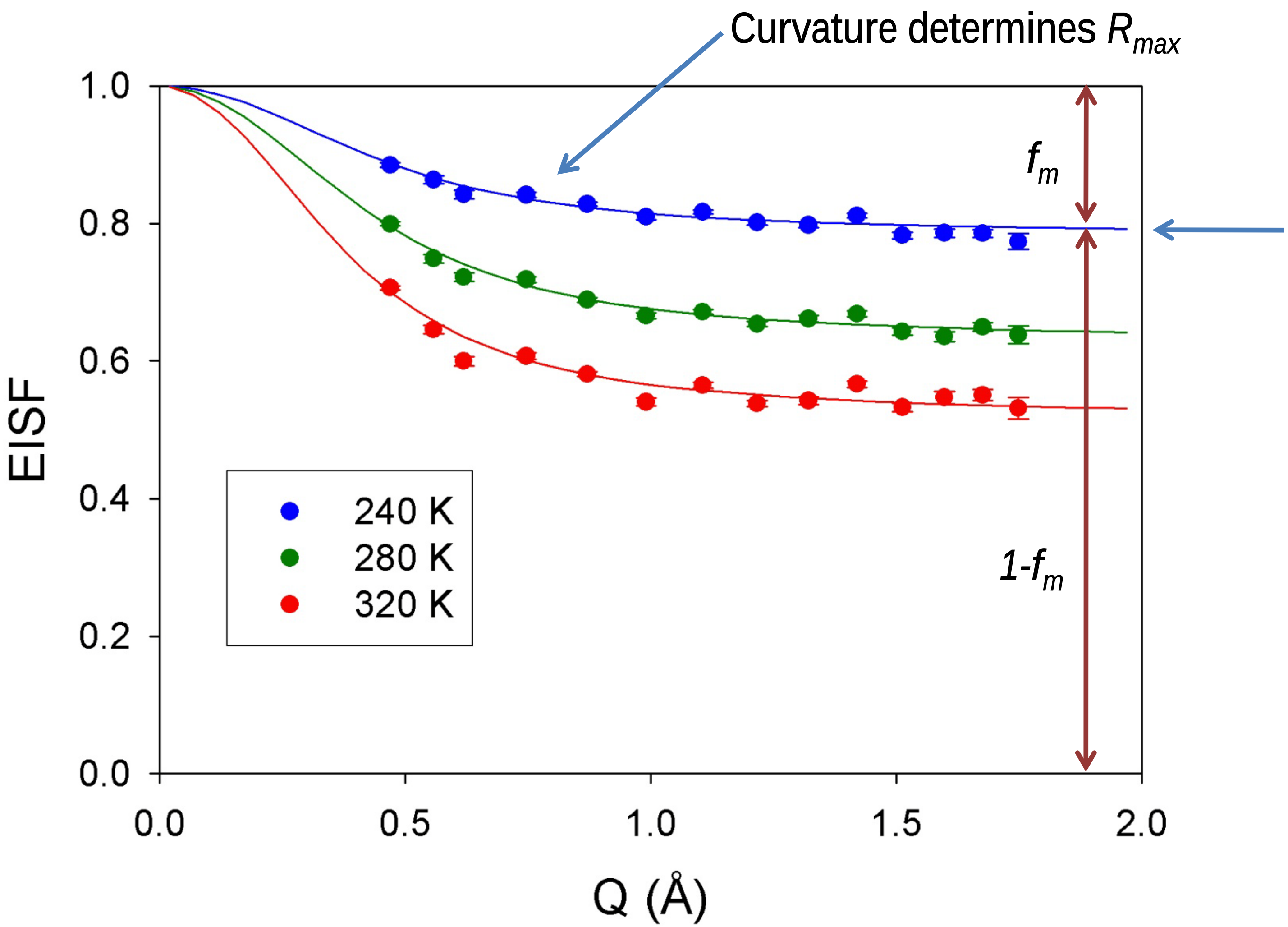
$$S(Q,\omega) = A(Q)\delta(\omega) + (1 - A(Q)) \times Lorentzian$$

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

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

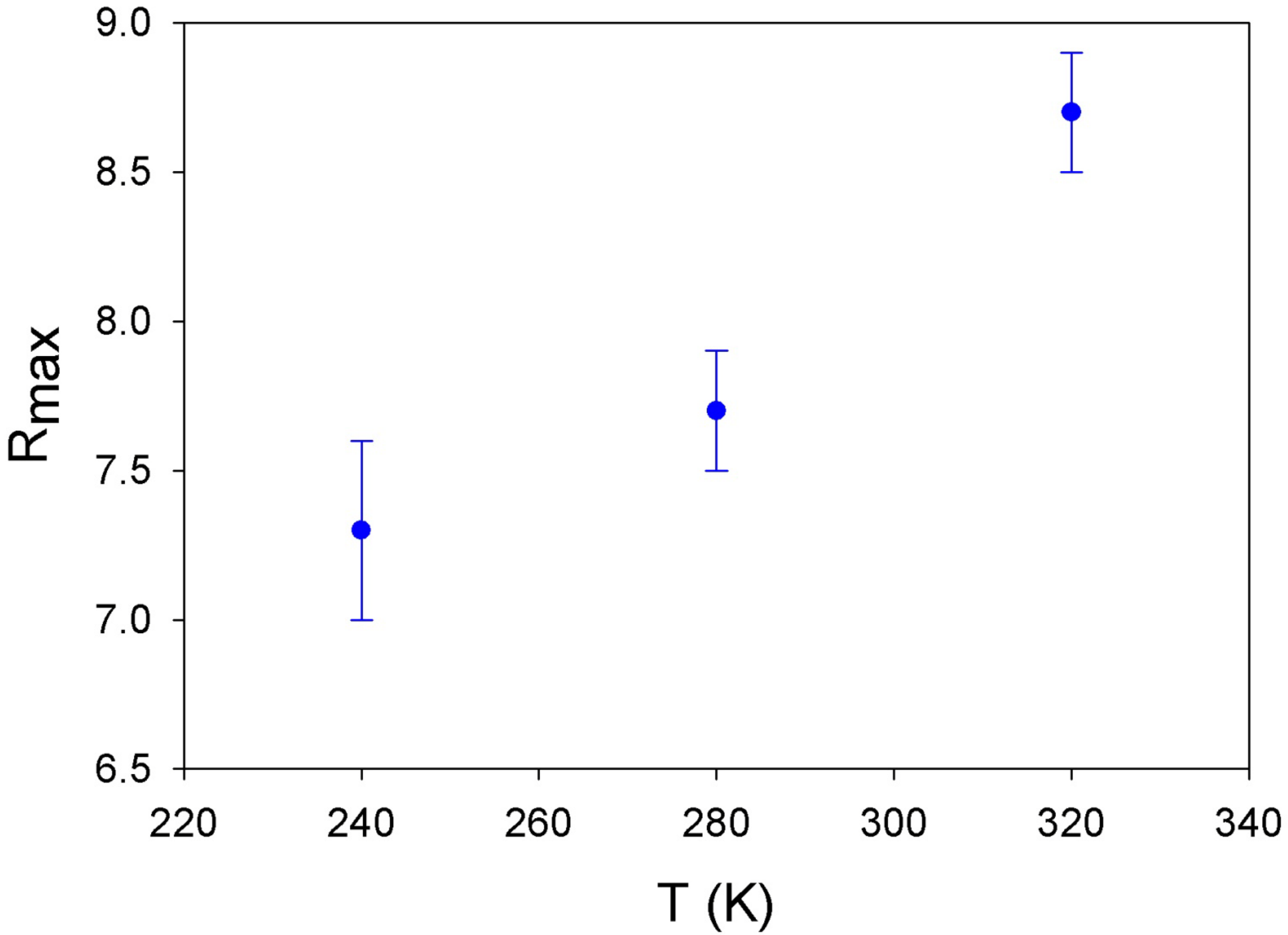


EISF – 29.6 Å radius DPP sample, saturation

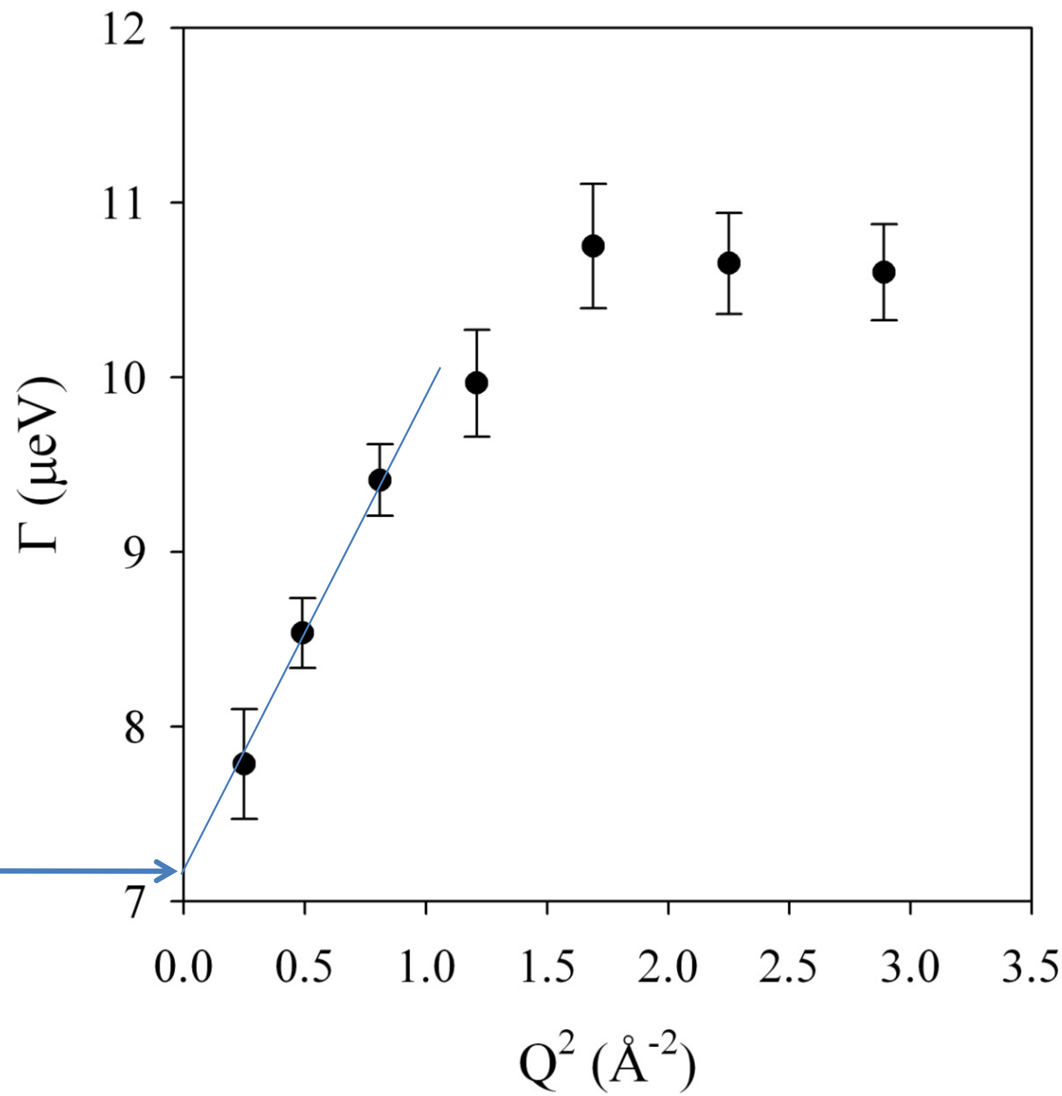


Non-zero asymptote implies immobile H-atoms *(on the time scale of this instrument)*

29.6 Å radius DPP sample, saturation

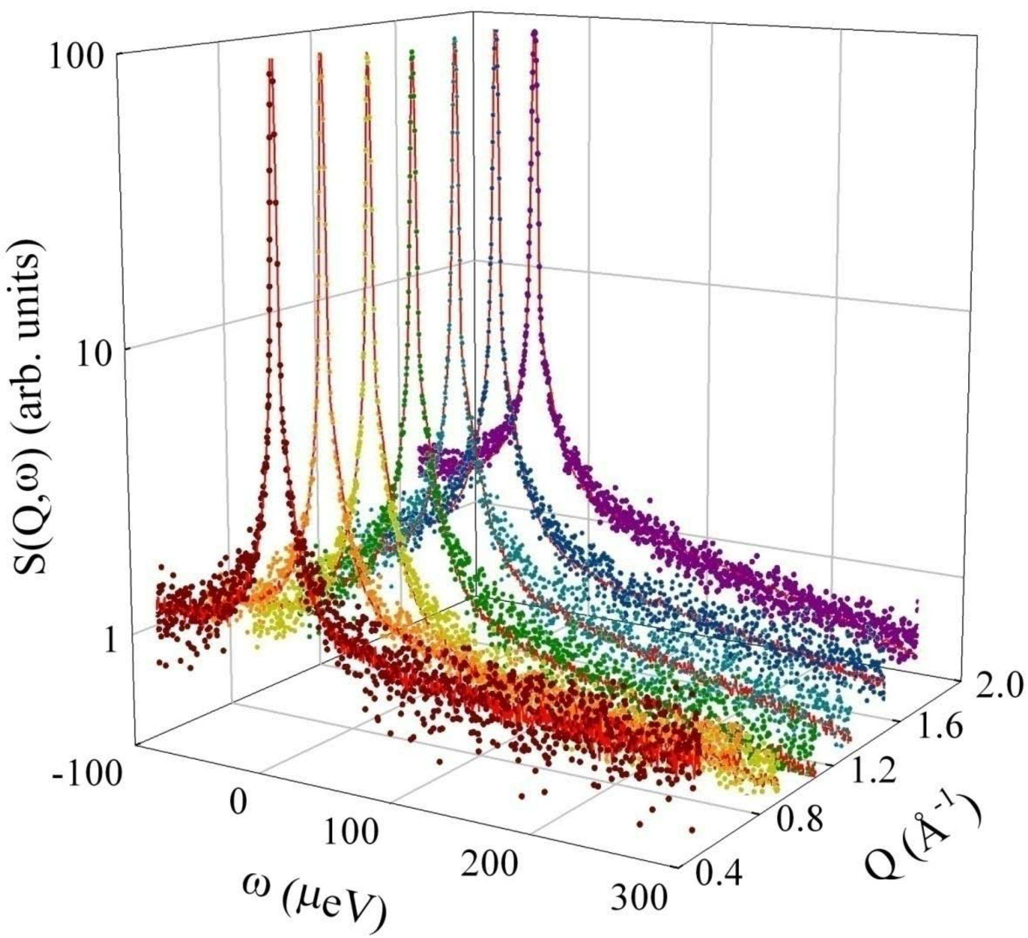


Lorentzian Γ(Q)

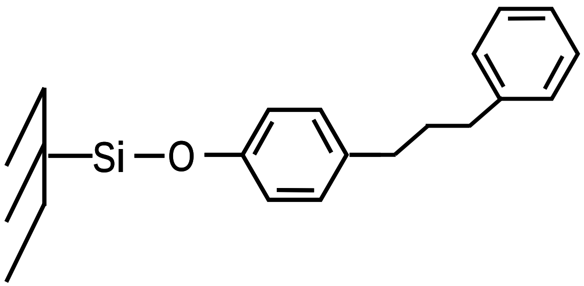


Non-zero intercept
Implies restricted/confined diffusion

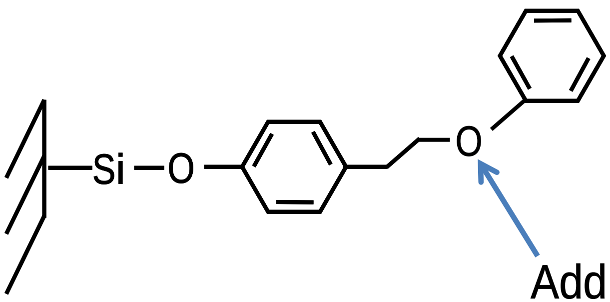
DPP – 29.6 Å diameter pores – 370 K (BaSiS - SNS) – Beyond the EISF – Fitting the Model to the Full Data Set



Detailed Fits



DPP

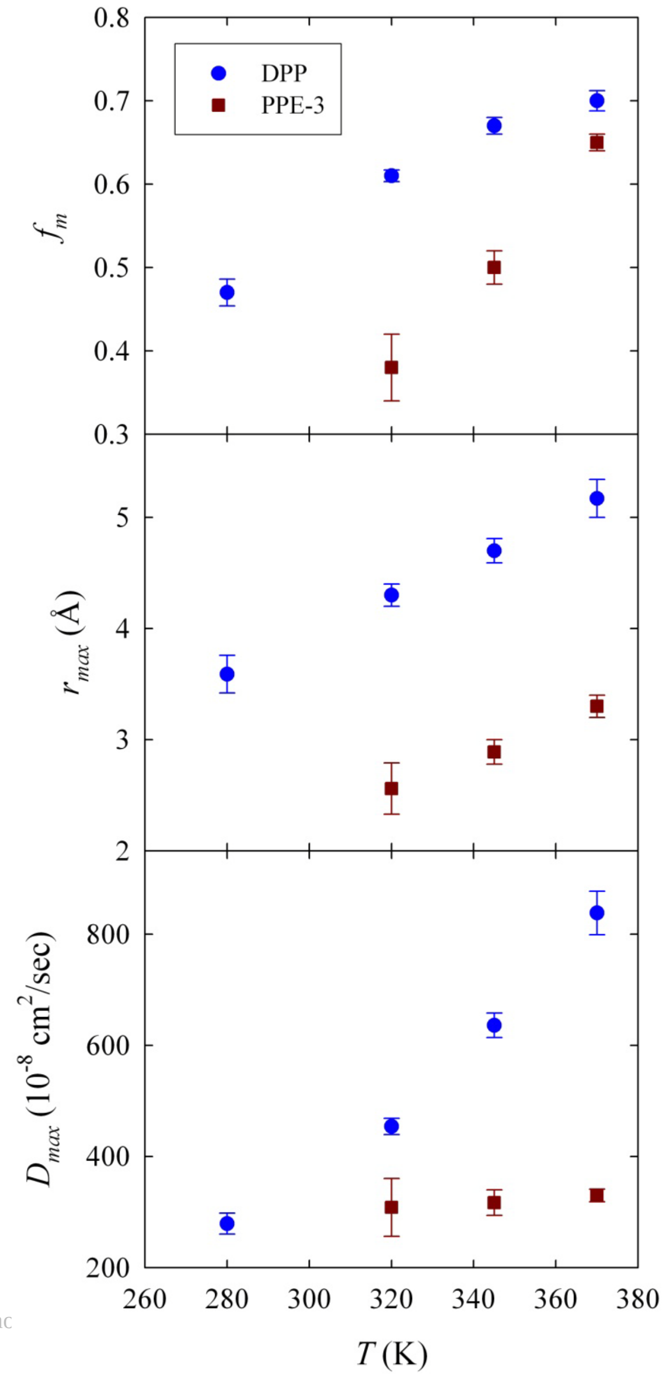


PPE3

Additional H-bond interaction

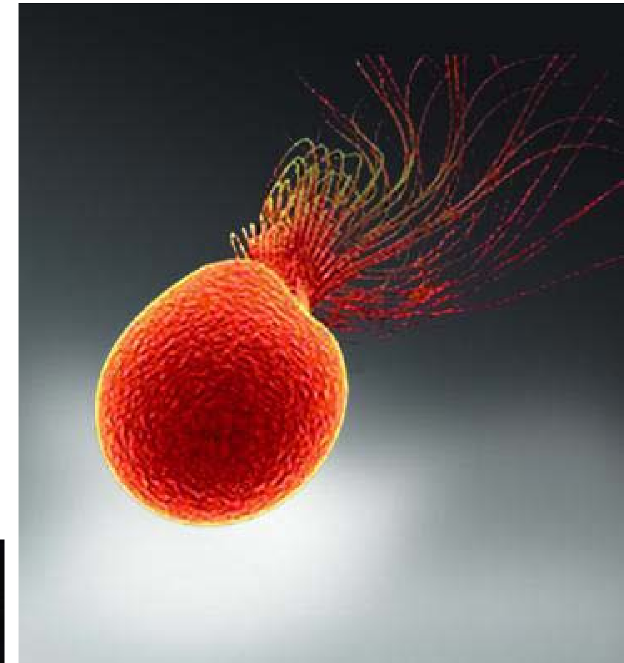
$$S_{DPP}(Q,\omega) = \sum_{i=1}^{15} S_s(Q,\omega,R_i,D_i)$$

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

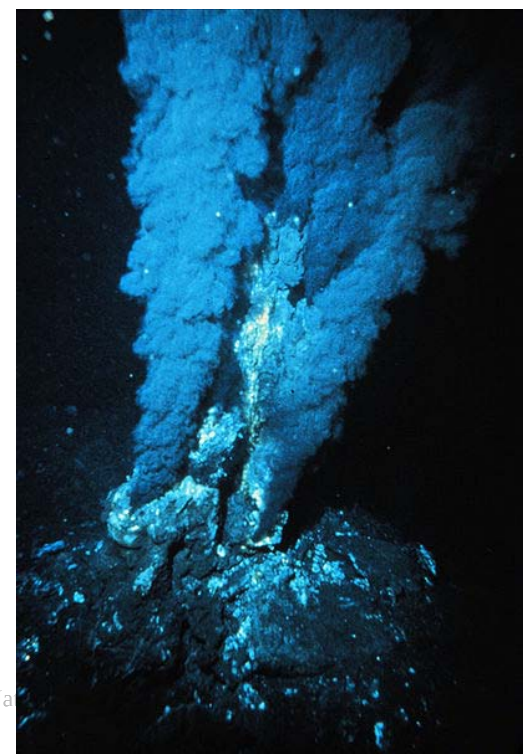


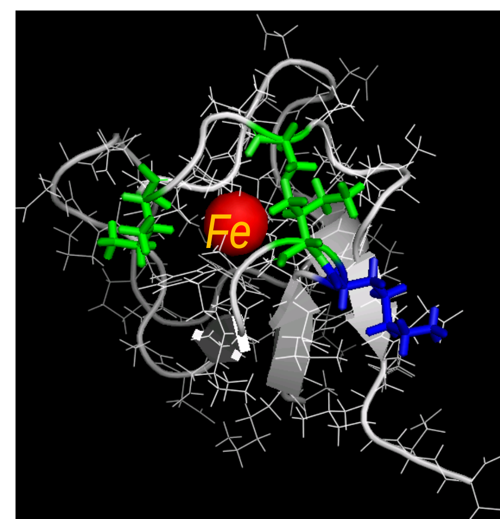
Thermophilic Rubredoxin – a small protein

- *Pyrococcus furiosus* - a sulfur-metabolizing bacteria found in super-heated deep sea vents
- RdPf – small iron-sulfur protein
  - 53 amino acids
  - Stable for days in boiling water
  - Fe tetrahedrally coordinated to the sulfurs of four Cysteines
  - Electron transfer protein
  - Structure studied by both x-ray and neutron

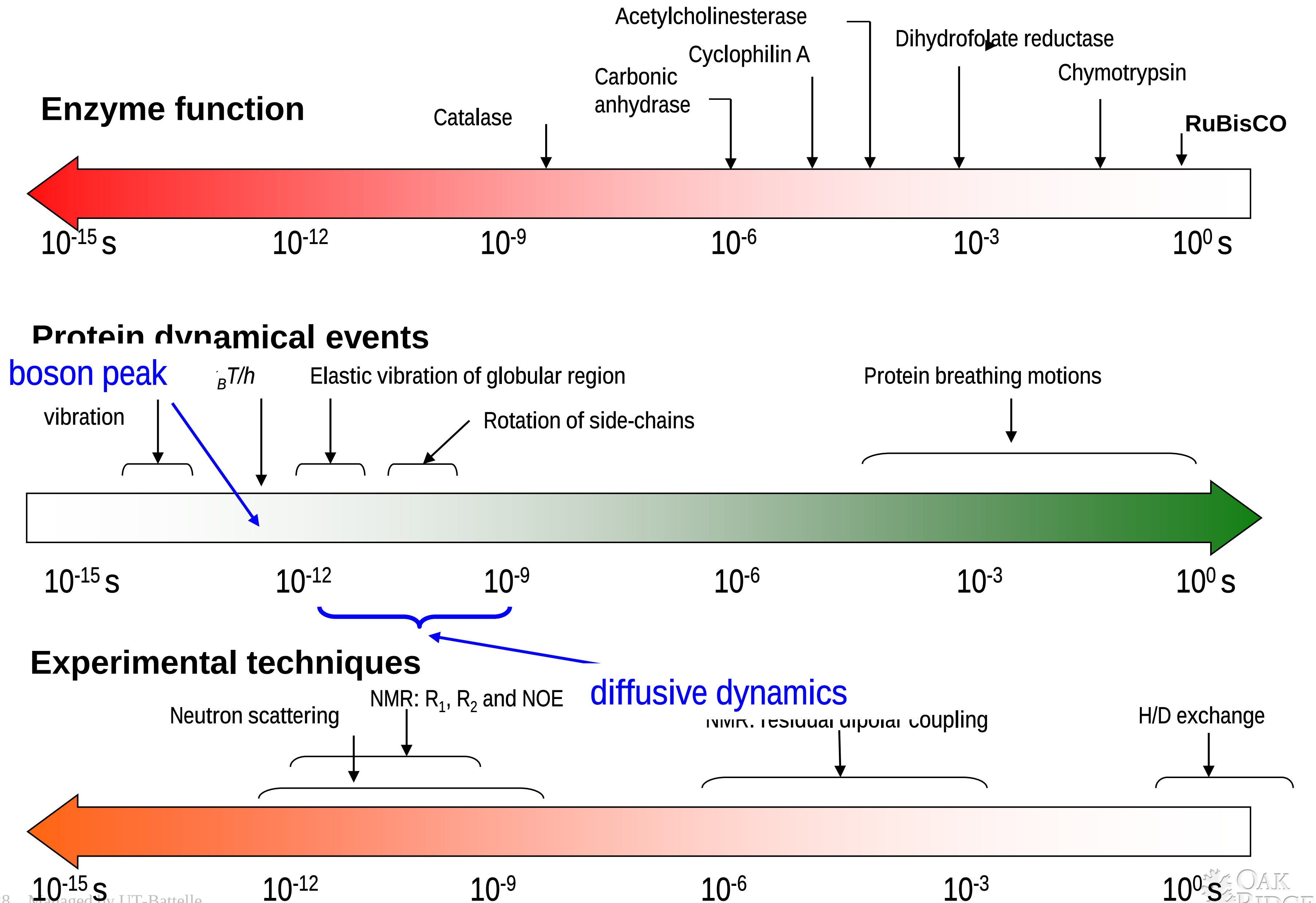


Lawrence Livermore National Laboratory – Hydrogen Fuel production





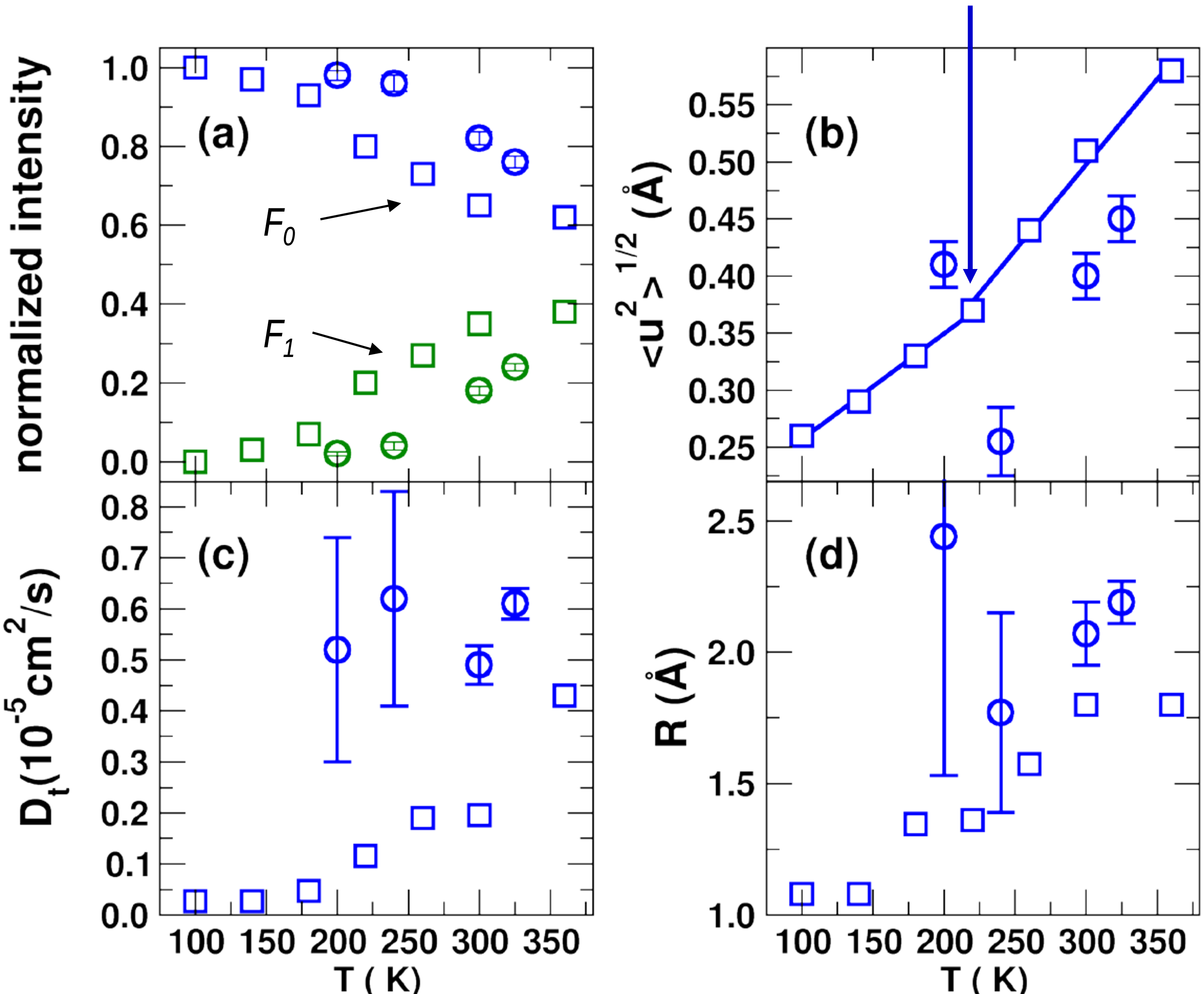
Time Scales

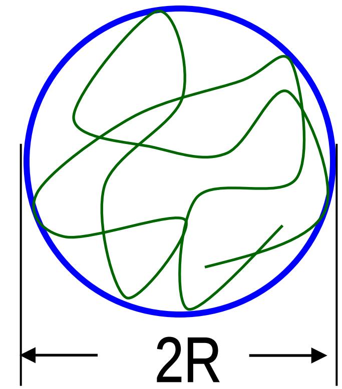


Enzyme function
Catalase
Carbonic anhydrase
Cyclophilin A
Acetylcholinesterase
Dihydrofolate reductase
Chymotrypsin
RuBisCO
10^{-15} s
10^{-12}
10^{-9}
10^{-6}
10^{-3}
10^{0} s
Protein dynamical events
boson peak
vibration
$_BT/h$
Elastic vibration of globular region
Rotation of side-chains
Protein breathing motions
10^{-15} s
10^{-12}
10^{-9}
10^{-6}
10^{-3}
10^{0} s
Experimental techniques
diffusive dynamics
Neutron scattering
NMR: R_1, R_2 and NOE
NMR: residual dipolar coupling
H/D exchange
10^{-15} s
10^{-12}
10^{-9}
10^{-6}
10^{-3}
10^{0} s

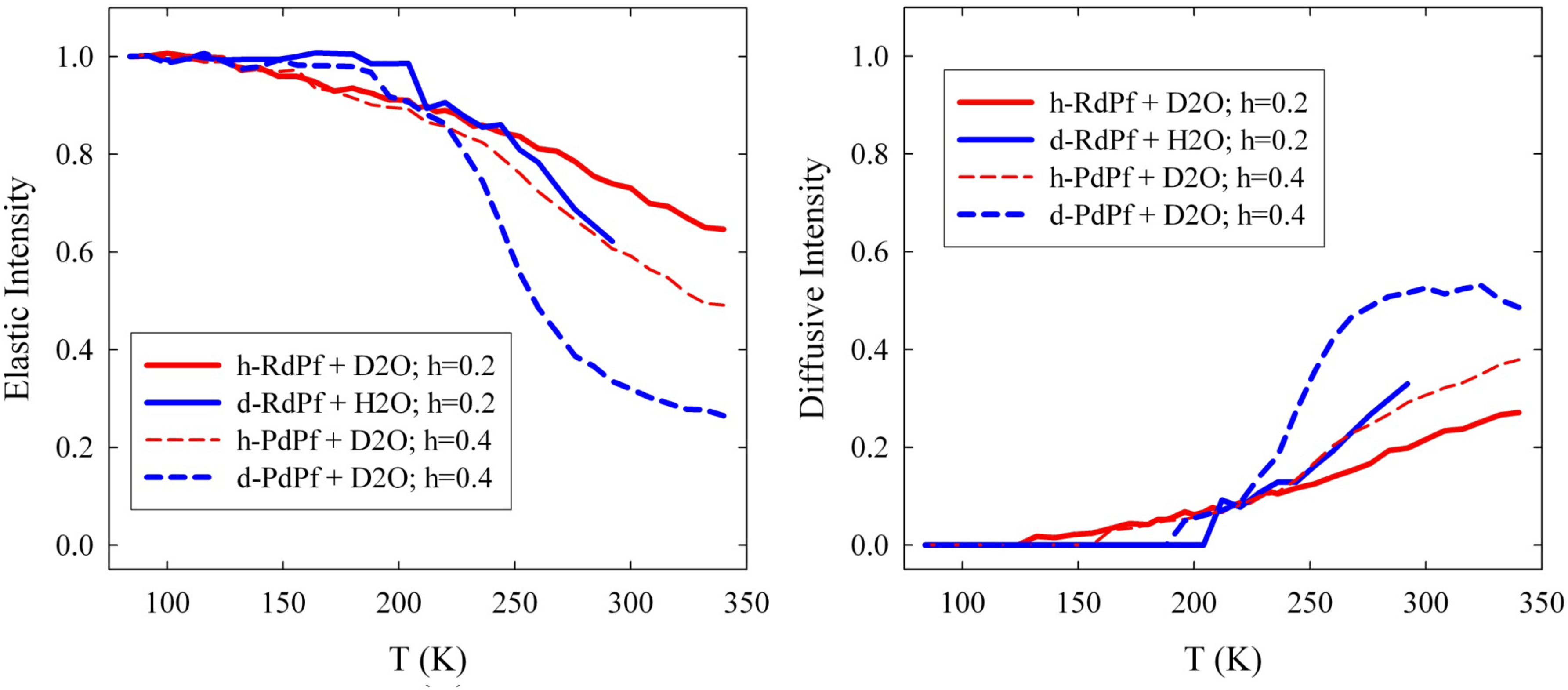
QENS and MD

Dynamic Transition T ≈ 220 K

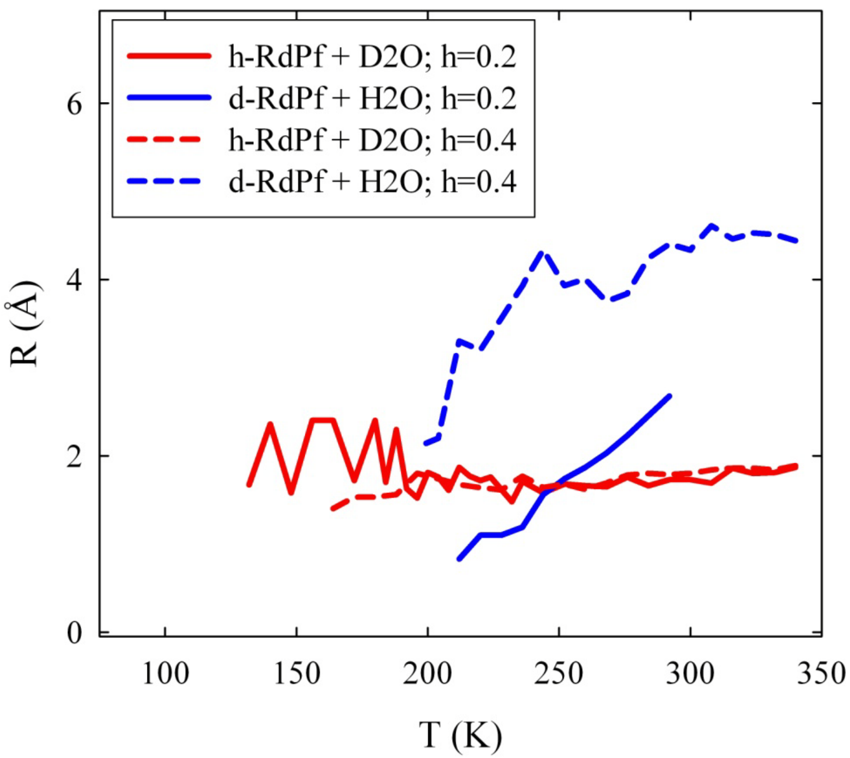


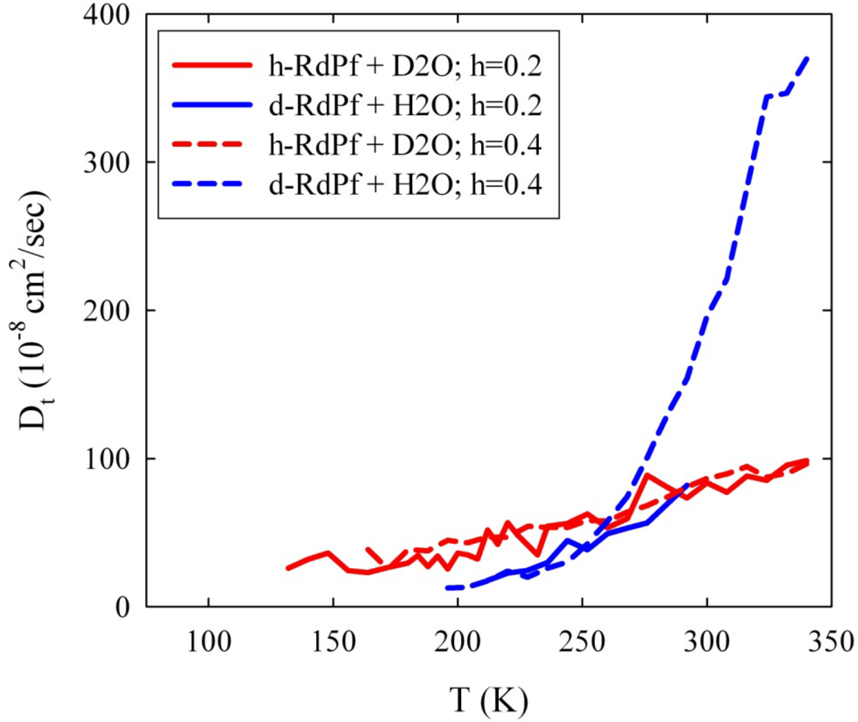


Rubredoxin and water (hydration study on Basis (166 data sets in 4 days)



Diffusive Motions





- Protein exhibits diffusive motions below dynamic transition T
- Both Water and Protein exhibit enhanced dynamics at dynamic transition T
- At high-hydration, 0.4 gm water/gm protein, water dynamics strongly decouples from protein time and length scales by about 270 K
- More water – more protein dynamics

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