Neutron Scattering and Diffraction Studies of Fluids and Fluid-Solid Interactions

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Outline

Role of Fluids in Geochemical Processes

Homogeneous Fluids

Fluids Under Confinement

Fluids at Surfaces

Opportunities

Focus on Applications

Role of Fluids in Geochemical Processes

Geologic fluids (gases, liquids, and supercritical solutions) act as reaction media, reactants, and carriers of energy and matter in the natural environment.

Fluid interactions at stable mineral surfaces control – precipitation and growth; colloidal dispersion & agglomeration; catalysis of aqueous solutions; contaminant adsorption; nanoparticle assembly

Mineral-fluid reaction processes are rate-limited by exchange at interfaces (e.g. mineral surfaces, grain boundaries, porous reaction zones), and contribute significantly to global geochemical cycles

Fluid Properties and Behavior

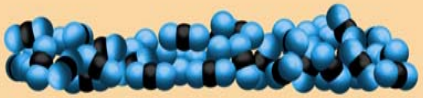
- **THERMOPHYSICAL:** Density, Expansivity, Compressibility,
  Phase Behavior - e.g. freezing/melting,
  vaporization/condensation, criticality
  Thermodynamic - e.g dielectric constant,
  heat capacity, entropy, enthalpy
- **TRANSPORT:** Diffusivity - e.g. H_2O self-diffusion, ionic
  Viscosity; Shear; Conductance
- **INTERACTIONS:** Adsorption/Layering, Wetting, H-Bonding;
  Solvent structure; ion-water; ion-ion
- **DYNAMICAL:** Motion - trans-, rot-, vibra-, librational

Many of these can be interrogated with X-rays, neutrons, NMR, IR
Molecular-level simulations crucial

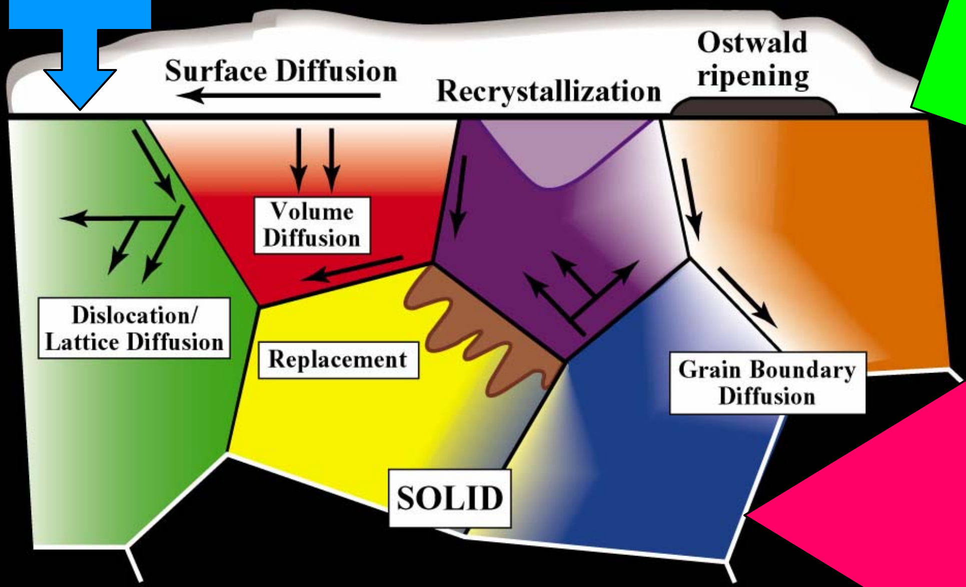
Complex Fluids - Confinement - Interfaces

Metal chloride-H_2O interaction

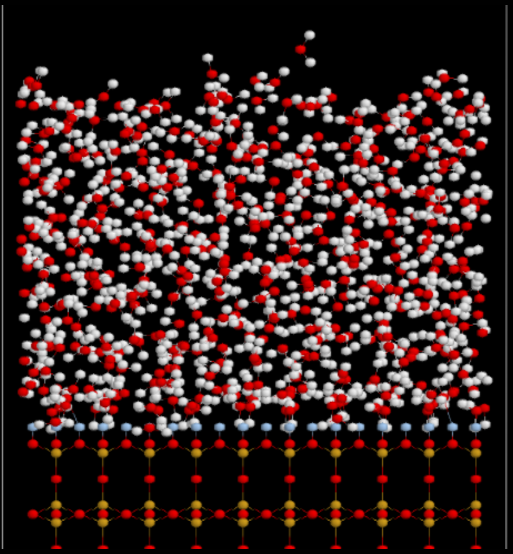
CO_2 on graphite



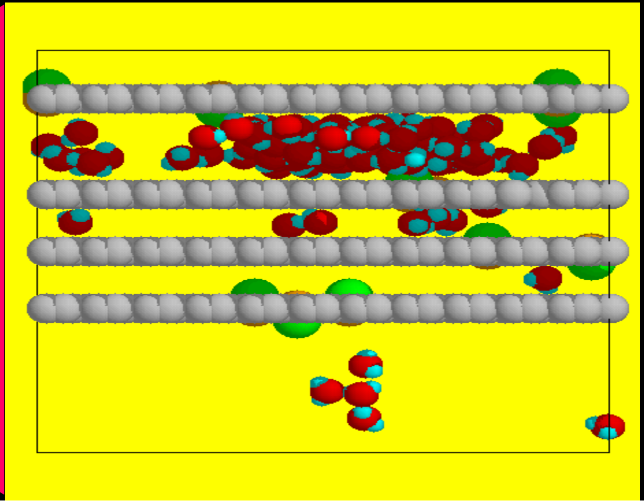
Gaseous or Aqueous System



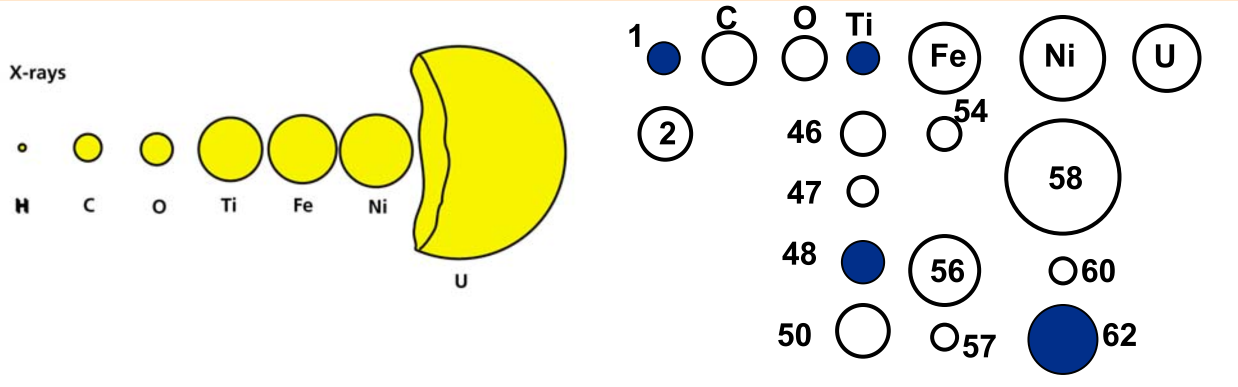
H_2O on SiO_2 surface

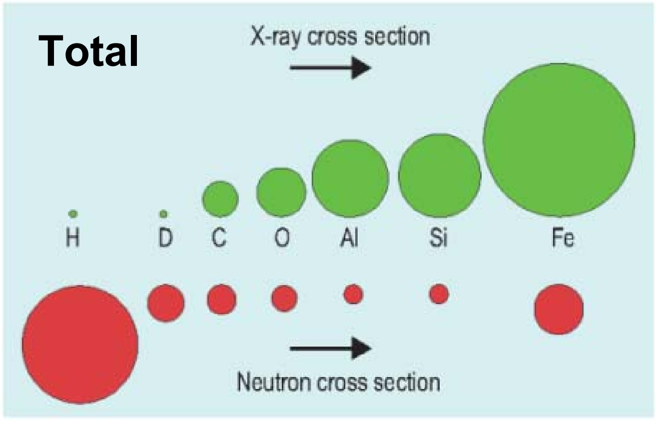


H_2O dynamics in slit pores



Why Neutrons: Hydrogen is the Key





- 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

1 meV = 11.6 K = 8.01 cm^{-1} = 0.1 kJ/mole = 2.42 x 10^{11} Hz ~ 10^{-12} sec

Neutron Methods Applicable for Studying Fluids and Fluid-Solid Interactions

Neutron Diffraction

Neutron Diffraction with Isotope Substitution (NDIS)

Small-Angle Neutron Diffraction (SANS)

Neutron Reflectivity

Inelastic & Quasielastic Neutron Scattering

Neutron Spin-Echo

Homogeneous Fluids

What is the molecular nature of hydrogen bonding in hydrogenous fluids?

How does structure and bonding environment change with increasing temperature and pressure?

What is the extent of perturbations to hydrogen bonding and structure due to dissolved constituents?

How are dynamics influenced by solutes and/or an increase in temperature and pressure?

Key Features of Homogeneous Fluids

Complex intermolecular interactions observed in C-O-H-N-S fluids:
H_2O, CO_2, H_2, H_2S, N_2, CH_4, etc.

Water is the best general solvent due to its molecular structure and distribution of electric charge

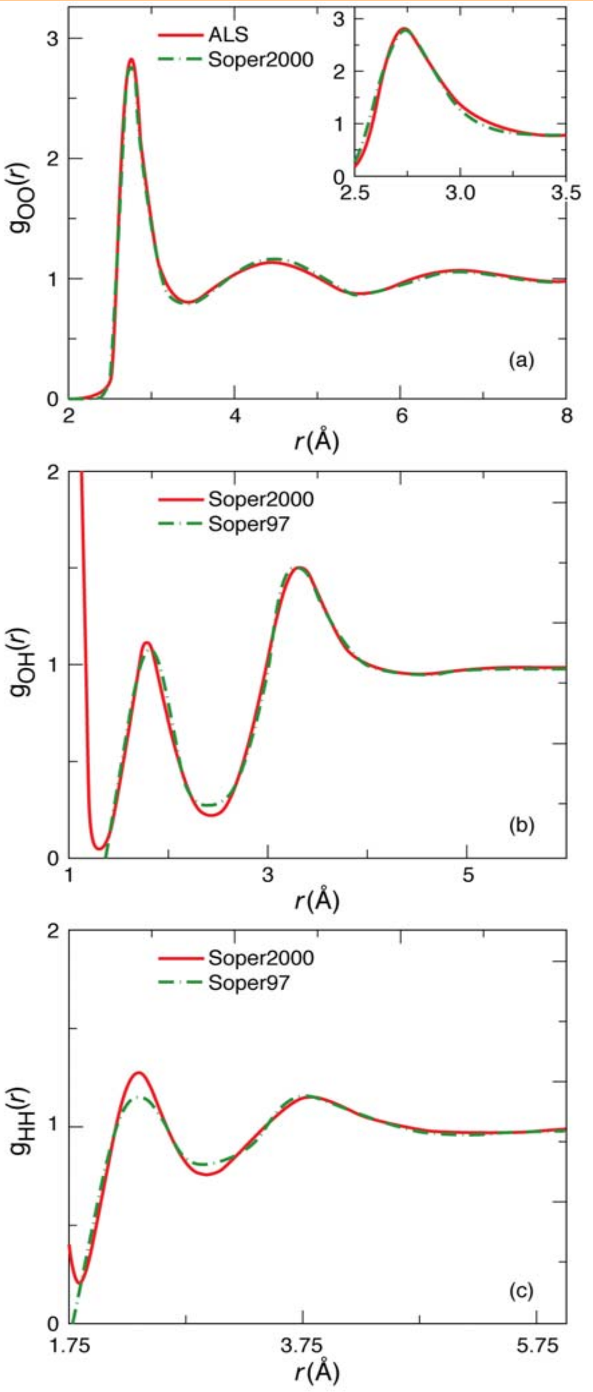
Solute-solute and solute-solvent reactions lead to:
complexation, binding, local ordering; clustering

Features probed by scattering:
interatomic distances; coordination numbers; extent of local ordering around a particular atom; orientation (tilt angle)

Local structure divided into several parts:
contact distance, nearest neighbor distance; end of short range order

Water: The Premier Geo-Fluid

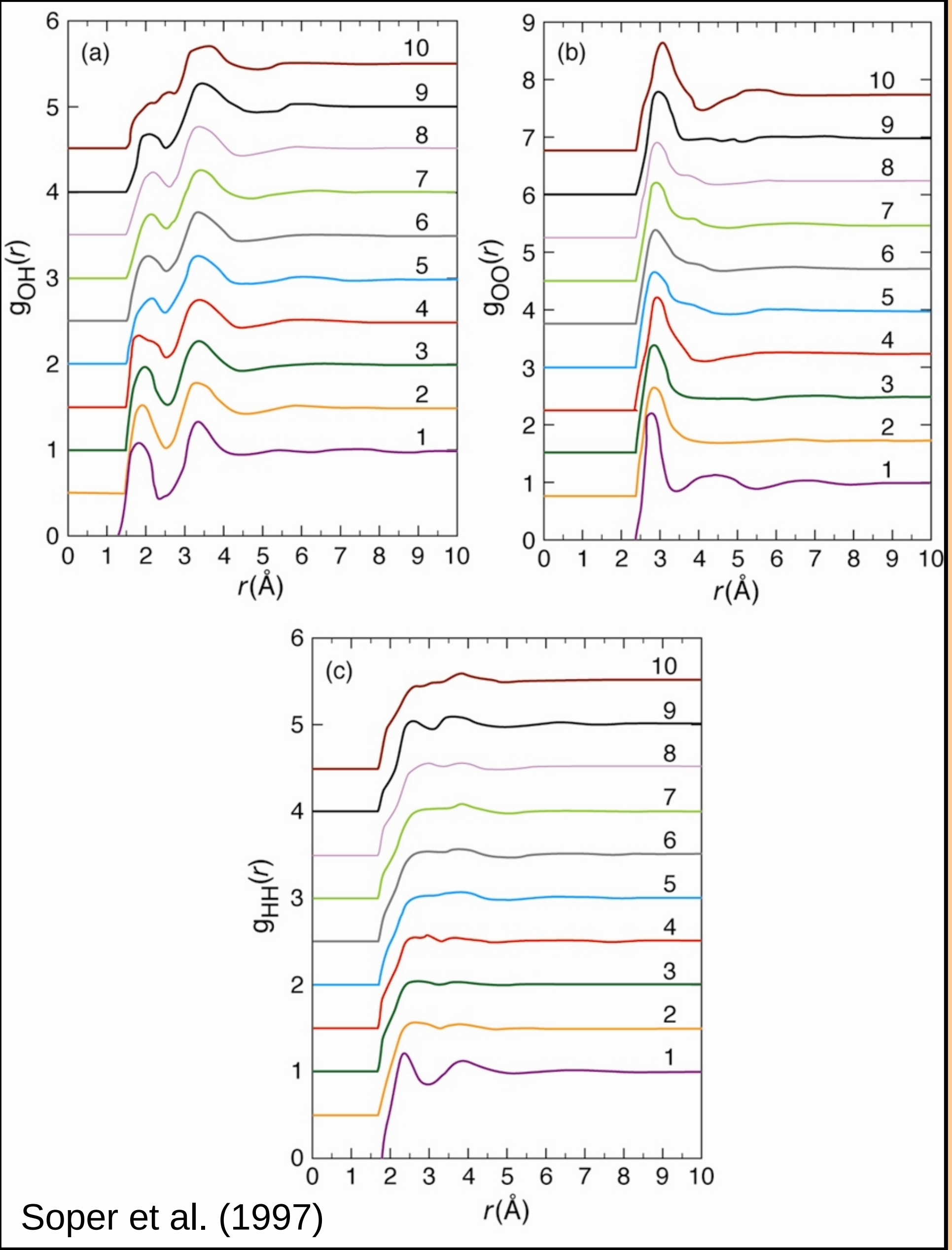
- The structure of fluid water includes nanoscale features (hydrogen-bond networks).
    - - Affects solvation; solute structures; solute interactions
- H/D substitution is the best method for determining water structure.
- Data analysis is complicated by inelastic scattering from H.
    - - Uncertainty in data analysis leads to controversial interpretations
- NDIS reveals atom-atom interactions;
    - - O-O; O-H; H-H distribution functions
- Structural data on O-O from X-ray scattering
- Estimate atom-atom coordination number;
    - - integrate the distribution function
- Molecular geometry - on average tetrahedral, but may consist of a mixed species- i.e. 2 H-bonded and tetrahedral (Nilsson and others)



Head-Gordon & Hura (2002)

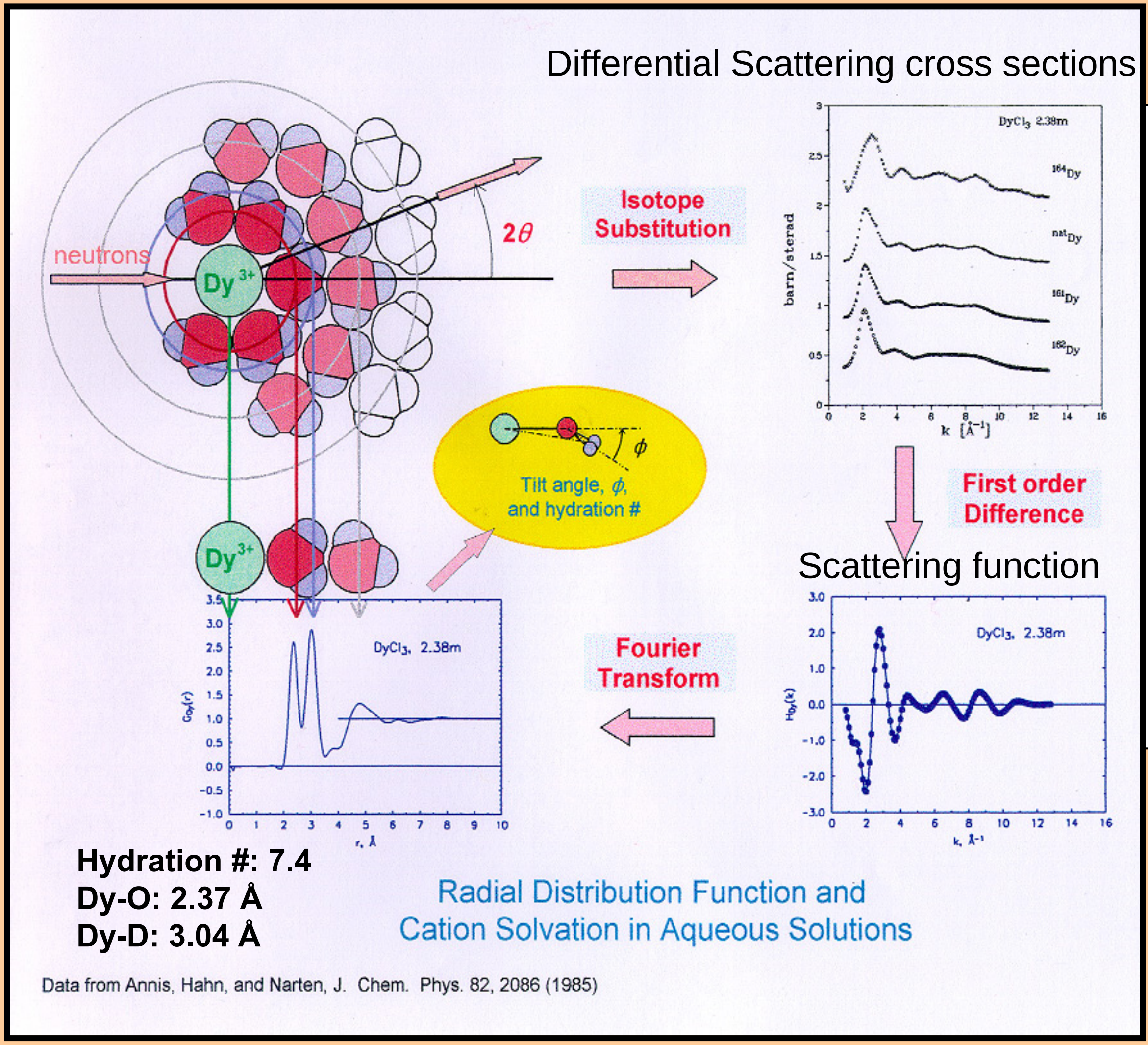
Water at Elevated P & T

- At ambient T, liquid water is ‘fragile’
- When compressed, number of H bonds per water molecule not altered appreciably compared to ambient P
- H bonds do become bent and are weaker energetically
- Significant effect on O-O separation with increasing P where 2nd peak in $g_{OO}(r)$ is diminished.
- 1st peak position shifts to larger *r* values with increasing T functions
- O-H and H-H peaks tend to broaden and become less distinct with increase in T
- Above critical point no distinct O-H site correlation peak preserved
- 1st O-O correlation peak stays sharp, but is less intense and does broaden
- H-bonding reduced but still present near the critical temperature and density, but space-filled percolating H-bonded network dominant at ambient T & P collapses.



Soper et al. (1997)

Neutron Diffraction with Isotopic Substitution (NDIS) for Determining Hydration/Complexation Structure



Hydration #: 7.4
Dy-O: 2.37 Å
Dy-D: 3.04 Å

Radial Distribution Function and Cation Solvation in Aqueous Solutions

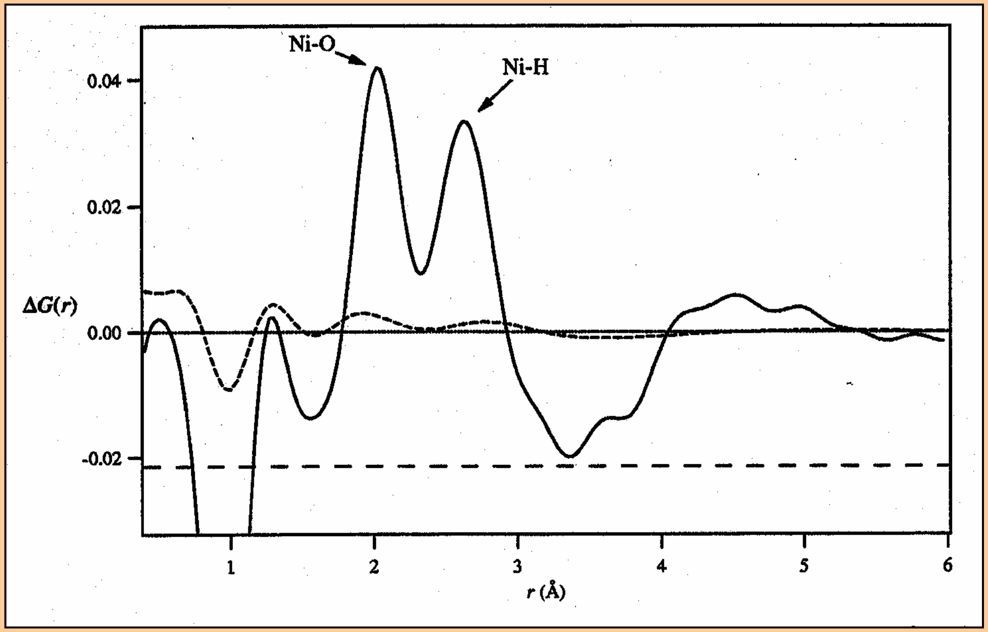
Data from Annis, Hahn, and Narten, J. Chem. Phys. 82, 2086 (1985)

Match T,p,m for two solutions
- **D_2O to minimize corrections**
- **Differ in metal isotope**
- **Special sample environment needed (null scattering); Ti-Zr cell**

Difference gives local (short range) environment
- **High stability needed**
- **S/N dependent on system**

Structural Results from Neutron Scattering from $NiCl_2$

Fourier transform of Ni difference function; ^{62}Ni and ^{nat}Ni isotopes used



Results at 298K for $NiCl_2$ at 3.87m.

Coord. N ≈ 6, $r_{Ni-O} \approx 2.05$ Å, $r_{Ni-H} \approx 2.67$ Å

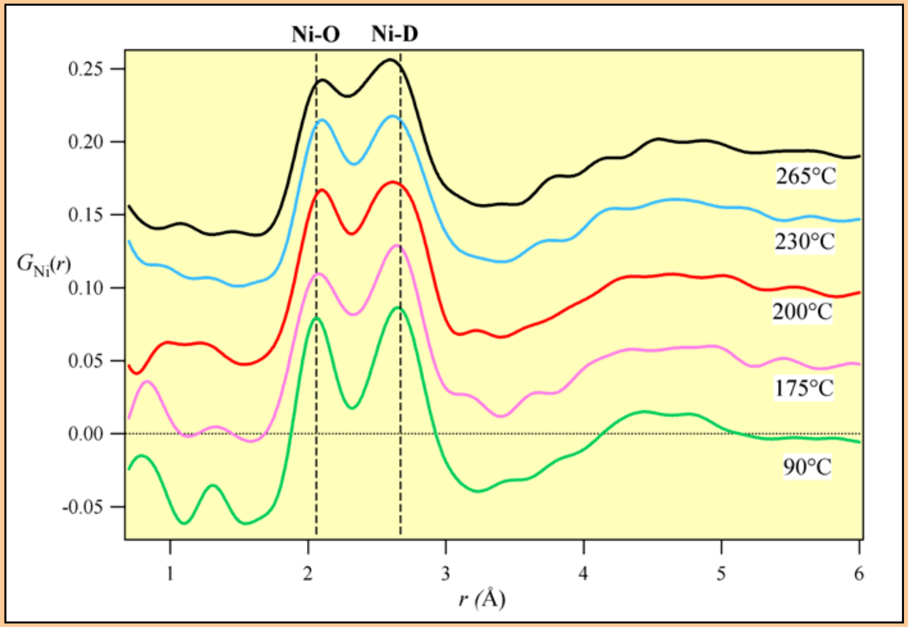
From Badyal et al., *J. Neutron Res*., 2002.

Results at higher temperatures for $NiCl_2$ ($Ti_{62}Zr_{32}$ cell)

Increasing temperature leads to:

Apparent broadening and shift inward of hydration peaks; no discernable ion association.

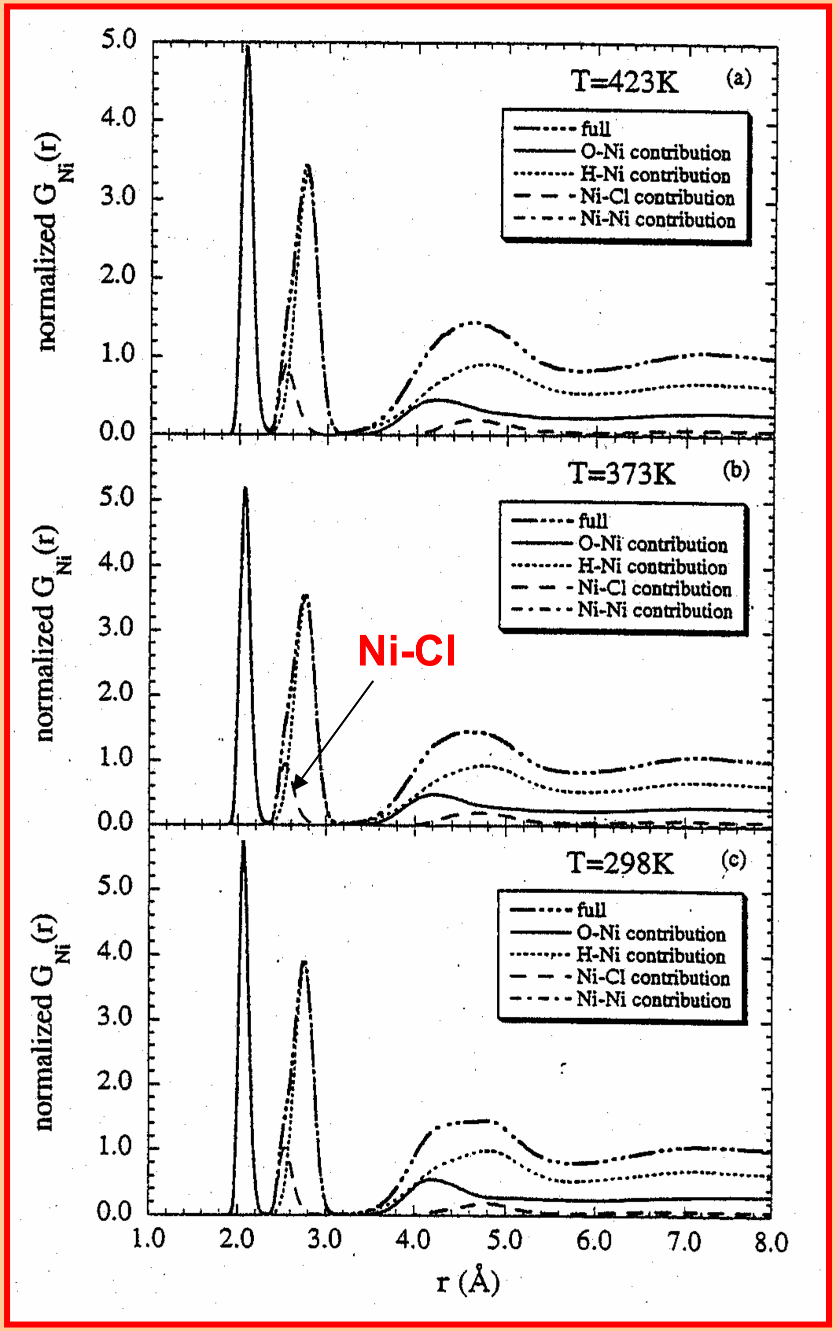
From Badyal et al., *J. Chem. Phys*. 2003



Simulation Results

- All partial structure factors g_{ij} resolved
- Direct comparison with $G_{Ni}(r)$ from experiment
  - Simulation shows chloride complex
  - Coord. #: Ni-O = 4.5, Ni-Cl =1.5
  - Peak positions agree with experiment
  - Nearly independent of temperature
- Ni-Cl shoulder in G(r) unresolved in experiment
- N(Ni-O) = 4.5 disagrees with experiment
  - Experiment affected by possible H/D mismatch
  - Simulation dependent on model potentials (reparameterize?)

SPC/E H_2O; L-J for Ni and Cl ions



Results from Chialvo and Simonson, *Mol. Phys*. 2002

Fluids-Solid Interactions

How are phase behavior and fluid structure influenced?

Can we determine the directions and time-dependence of atomic motion?

Can we tell whether the motions are periodic?

Fluids in pores or fractures; at surfaces

Why Study Fluids in Confined Geometries

They are very common in nature and engineering environments (chemical, oil and gas, pharmaceutical industries, catalysis).

Their properties are very different from bulk counterparts (due to finite size effects, varying dimensionality, surface forces).

Dynamics of fluids are affected dramatically by confinement (e.g. mobility of confined water – pore size, shape, distribution, connectivity.

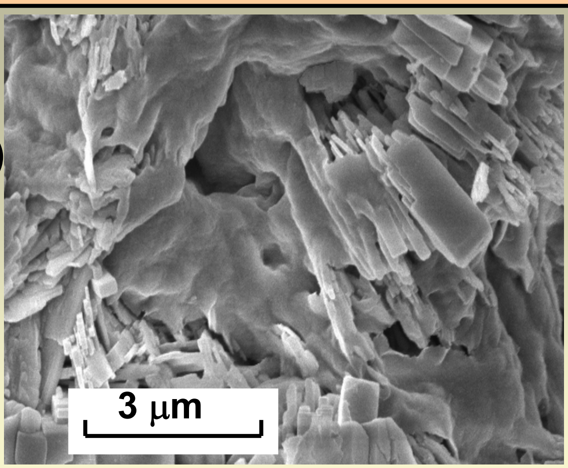
Interrogation of molecular mobility and transport is key to understanding the initiation and sustainability of reactions.

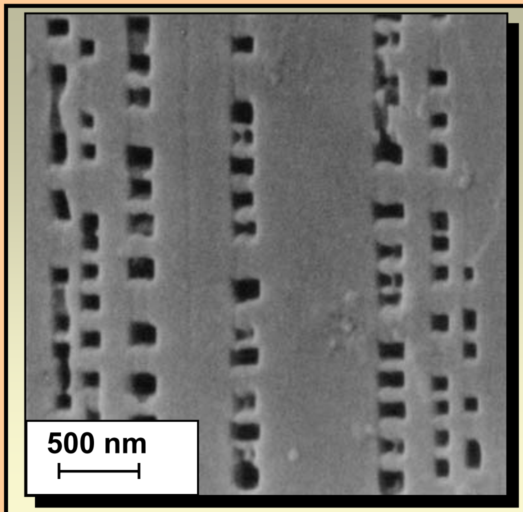
Aqueous solutions form due to interaction with the matrix

Flow, diffusion and selective adsorption of fluids are important in natural systems (e.g. oil and gas migration, soils and groundwater, geological CO_2 sequestration, waste disposal).

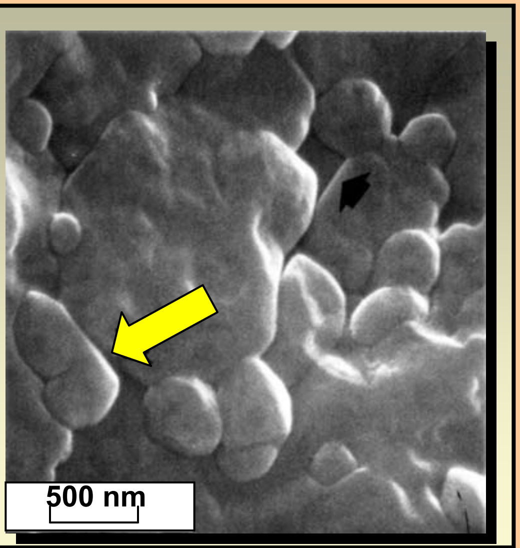
Microstructures in Nature

(a) **Sodium-clinoptilolite (~4-8 Å pores)**

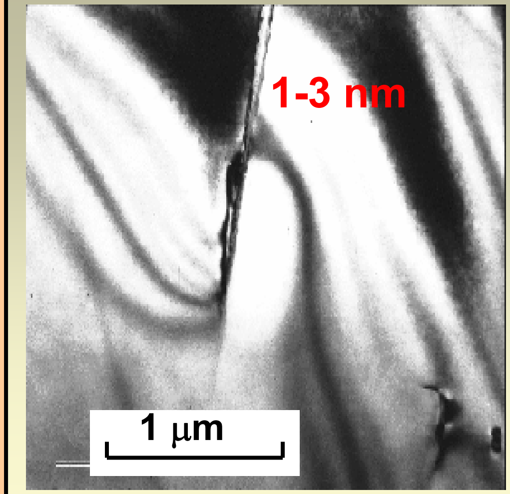




(b) **Weathered Feldspar**



(c) **Quartz with Micro-capillaries**



(d) **Microcrack in Quartz**

How Do We Interrogate Dynamical Behavior?

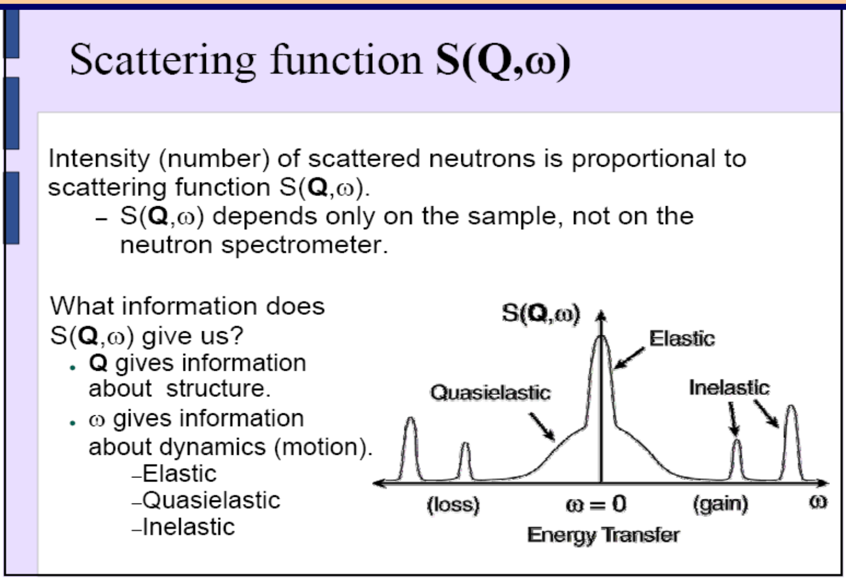
The advantages of QuasiElastic Neutron Scattering (QENS):

Time scale: 10^{-12} to 10^{-9} s: a good match for diffusive motions.

Length scale: Å to nanometers; the nature of motions can be probed through Q-dependence of the signal.

Huge incoherent neutron scattering cross-section of H dwarfs scattering contribution from other atoms in the system.

Highly penetrating, non-destructive probe. (molecular behavior in bulk samples)



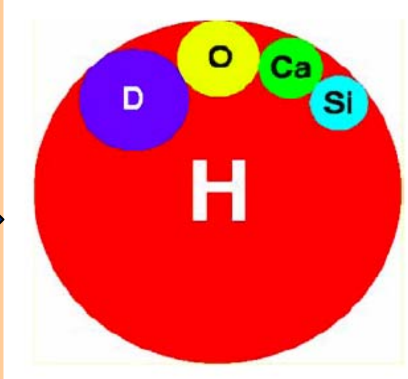
Scattering function S(**Q**,ω)

Intensity (number) of scattered neutrons is proportional to scattering function S(**Q**,ω).

- S(**Q**,ω) depends only on the sample, not on the neutron spectrometer.

What information does S(**Q**,ω) give us?

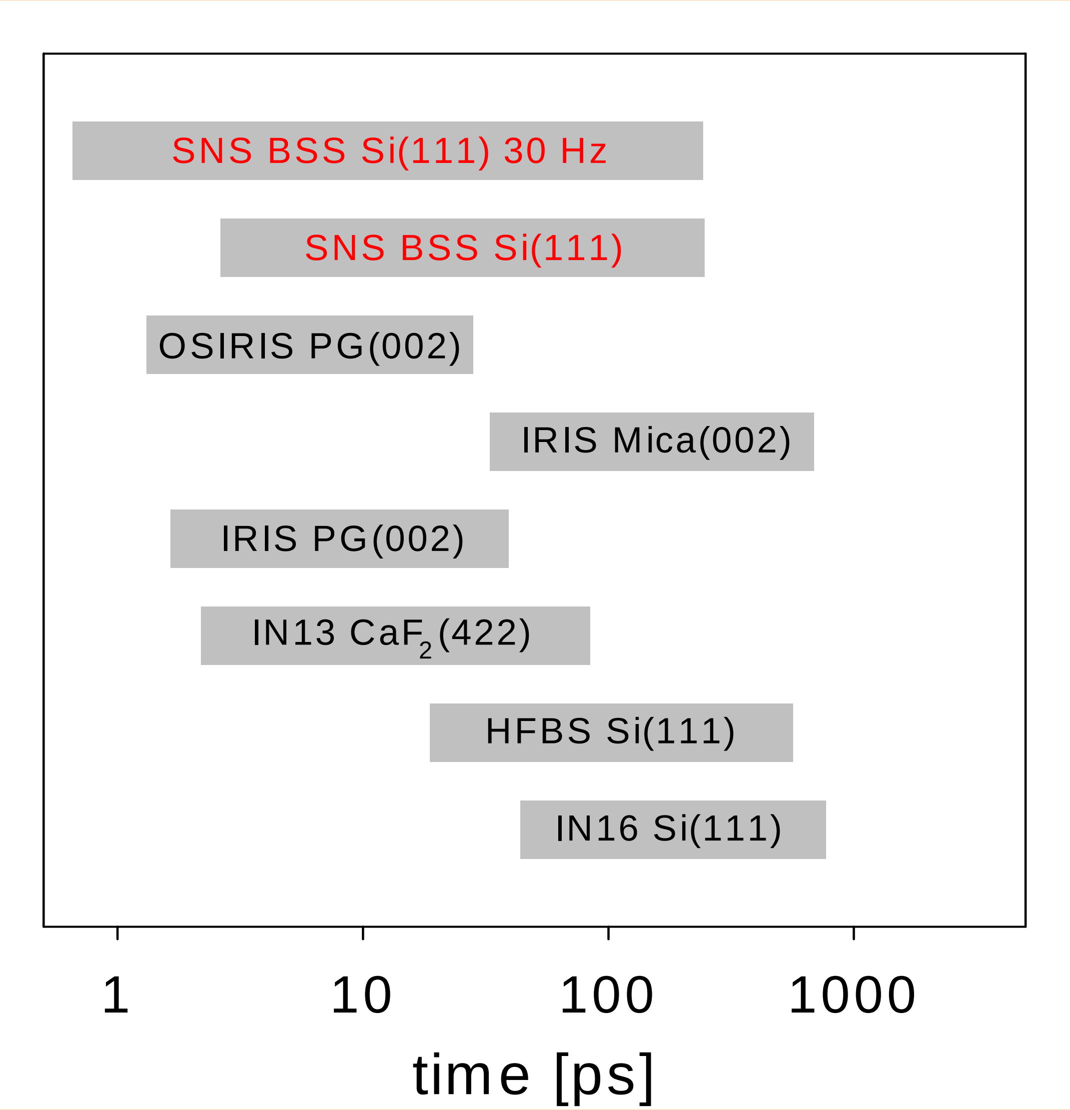
- **Q** gives information about structure.
- ω gives information about dynamics (motion).
  - Elastic
  - Quasielastic
  - Inelastic



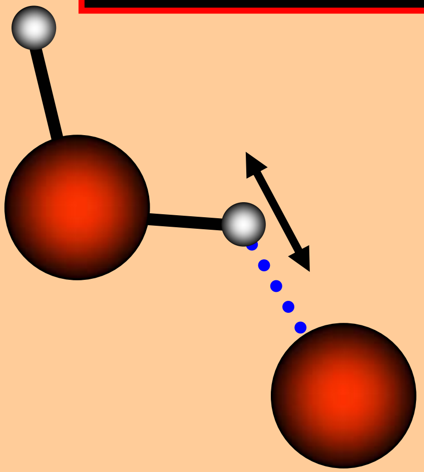
Jump distance,
Residence time between jumps
Diffusion rate

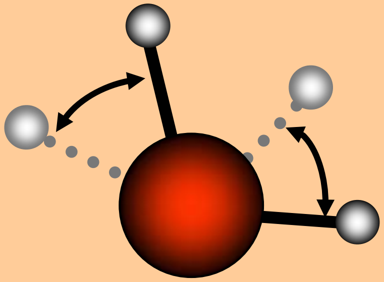
Time Scales Probed by Backscatter Instruments

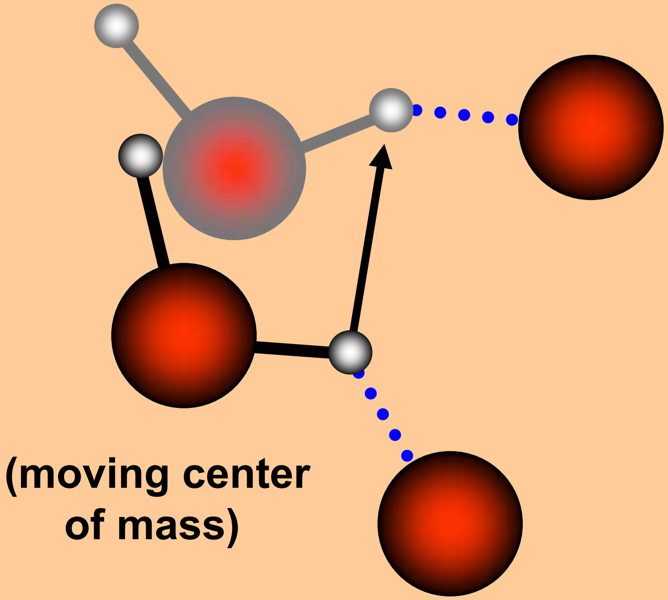
High energy resolution, dynamic range, and intensity. Also inelastic capabilities, high Q resolution...



Molecular Motions







Vibration

(harmonic oscillation)

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

Debye-Waller Factor

(too fast for QENS)

Reorientation

(isotropic rotation)

τ_r

Rotational Correlation Time

r_g

Radius of Gyration

Jump Translational

D_t

Translational Diffusion Constant

τ_o

Residence Time

L

Mean Jump Distance

Dynamic Structure Factor

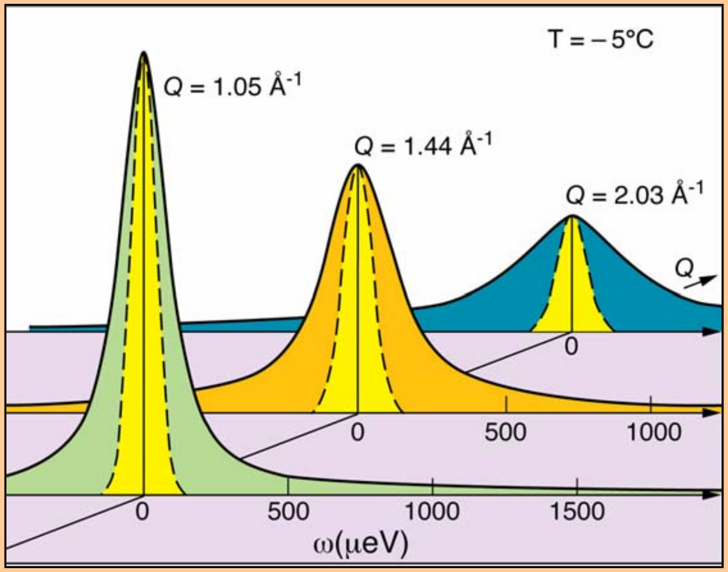
$$S(Q,\omega) = \mathrm{e}^{-\langle u^2 \rangle Q^2/3}\; R(Q,\omega) \otimes T(Q,\omega)$$

from Fourier transform of intermed. struct. factor;
time dependent correlation function

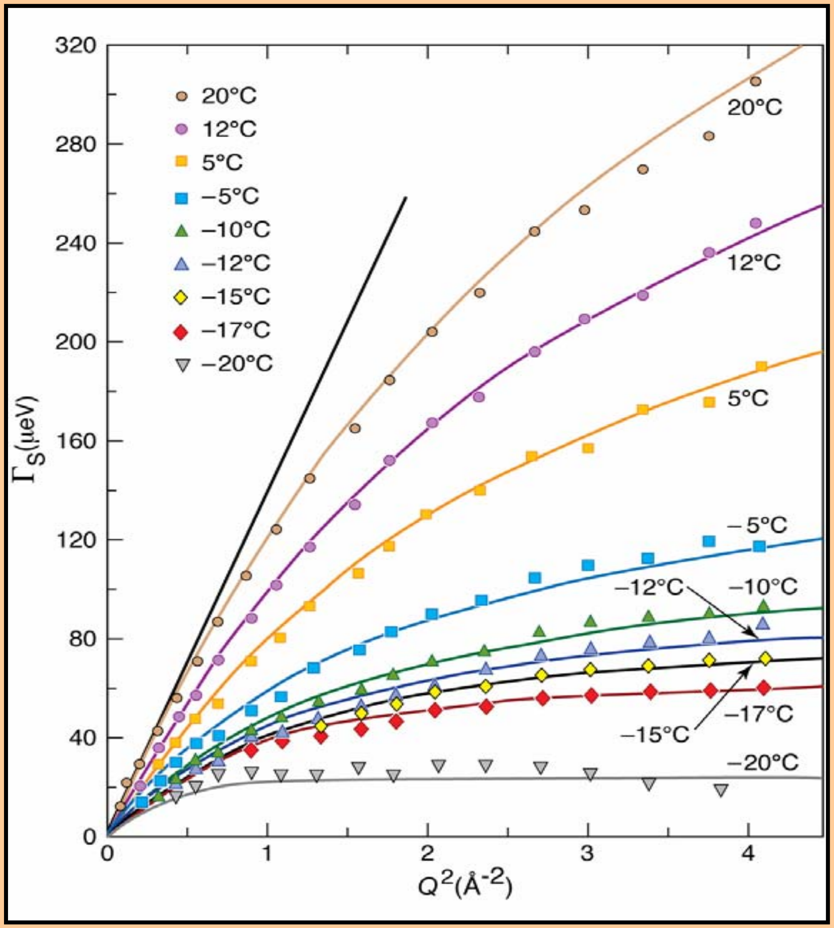
Self-Correlation (probability of particle position)
Assumes decoupling of rot. & trans

Supercooled Water

Data from Teixeira et al. (1985)



Quasielastic incoherent spectra



- **Translational Motion**

$$T(Q,\omega)=\frac{1}{\pi}\;\frac{\Gamma(Q)}{\Gamma^2(Q)+\omega^2}$$

- **Jump Diffusion**

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

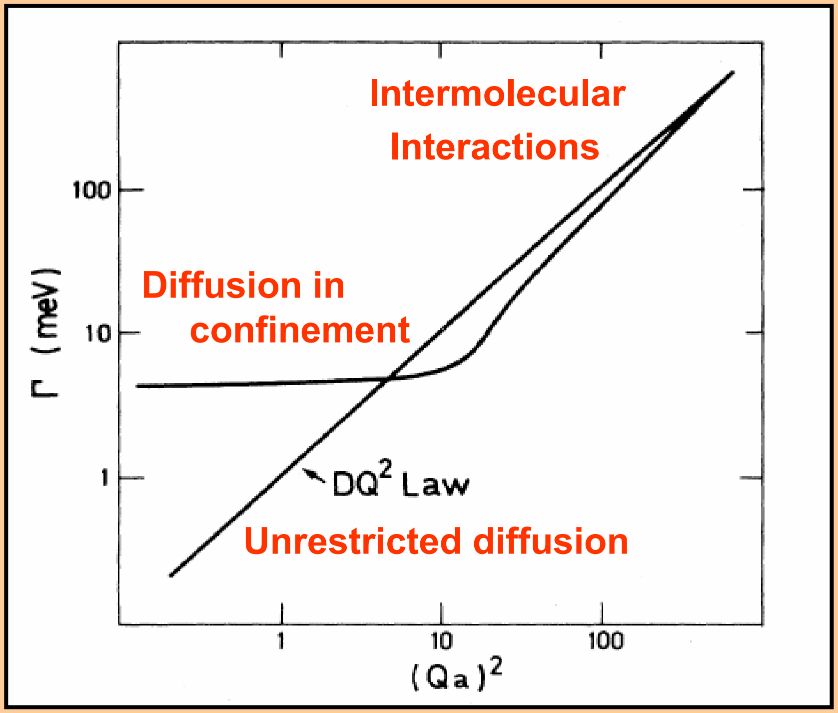
Behavior of supercooled water relevant to freezing/melting transitions in confined water

Good example of translational jump diffusion

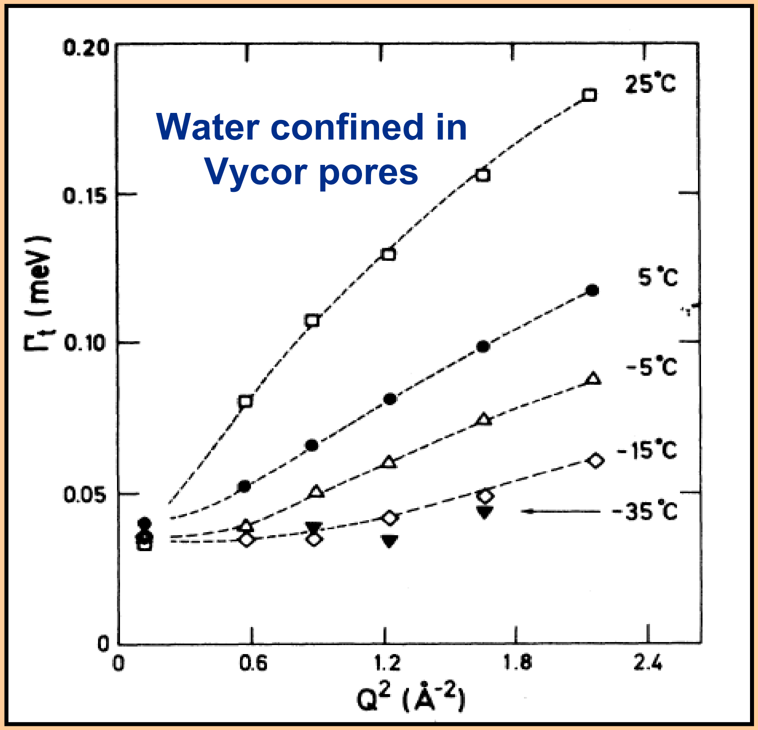
Γ (HWHM) is Q-dependent

Low Q: $\Gamma = \hbar D_T Q^2$; High Q, $\Gamma = \hbar/\tau_O$

DIFFUSION IN CONFINEMENT



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



Bellissent-Funel et al., Phys. Rev. E **51**, 4558 (1995).

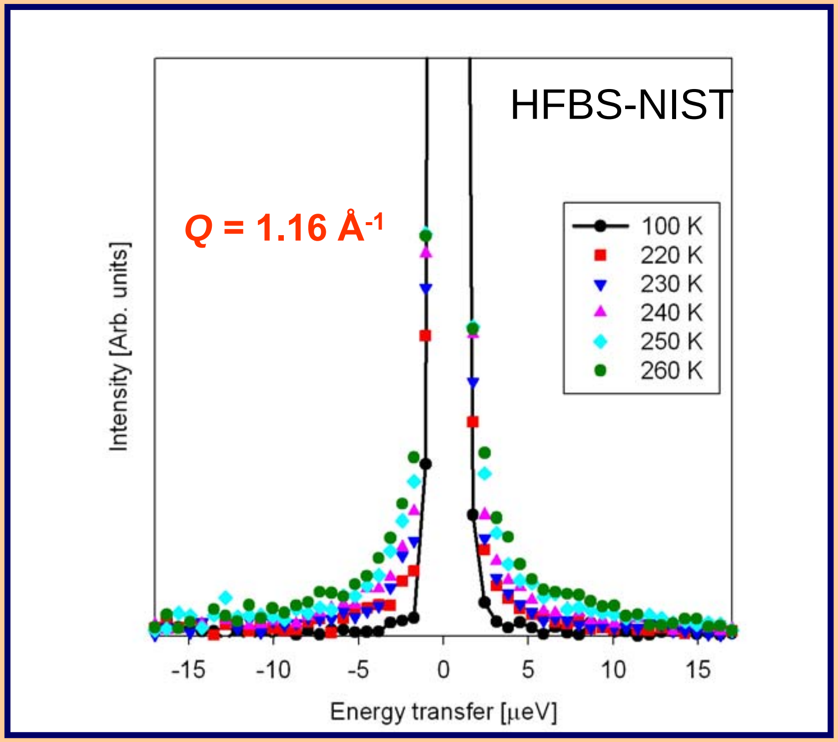
What Changes:

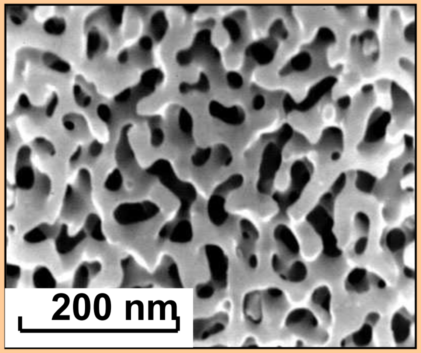
Not much at high Q where $\Gamma = \hbar/\tau_o$; dynamics defined by intermolecular interactions

Low Q, $\Gamma \neq DQ^2$ dependence because diffusing molecules cannot penetrate the borders of the pore.

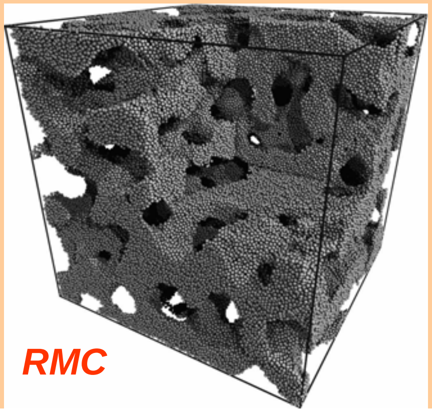
Deduce pore size from position of flat curve!

Confined Aqueous Solution: $CaCl_2$ – H_2O in Vycor Pore Glass





~40 nm



RMC

Typical temperature dependence of QENS data:

The width of the QENS signal tends to grow as the temperature is increased: shorter relaxation times (faster diffusion).

The relative intensity of the QENS signal tends to increase as the temperature is increased: more molecules become mobile on the time scale of the measurement.

At sufficiently low temperature, only elastic signal (representing the instrument resolution) is present.

Mamontov and Cole, Phys. Chem. Chem. Phys. (2006)

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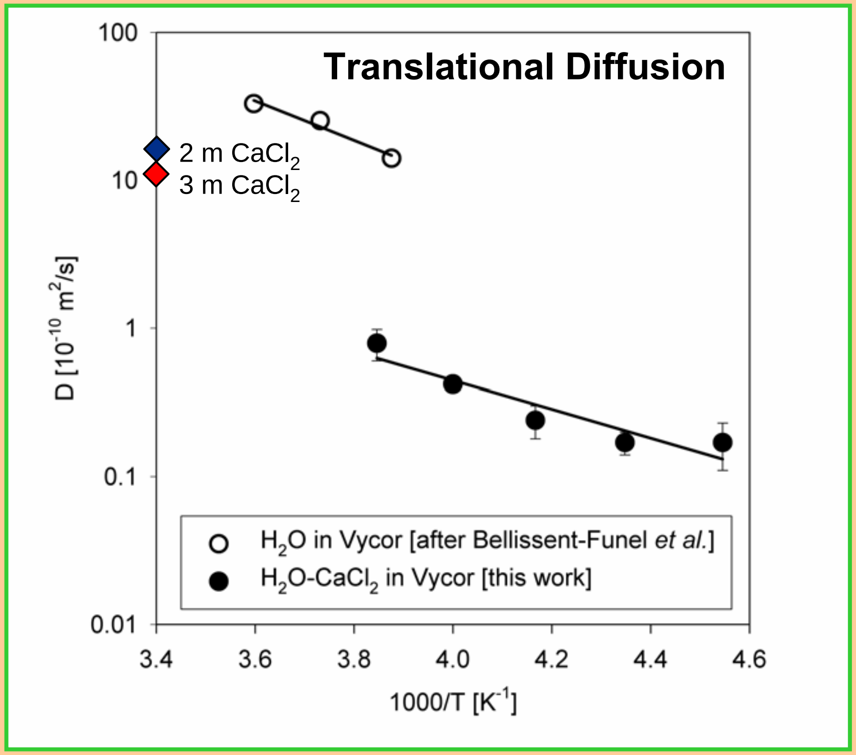

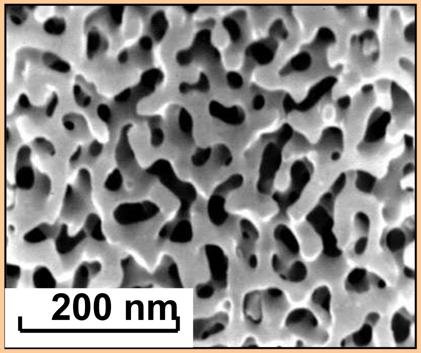

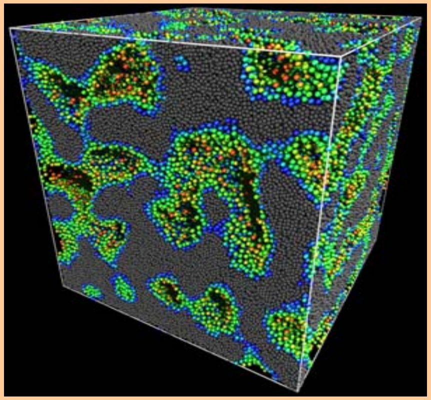

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Mamontov and Cole, Phys. Chem. Chem. Phys. (2006)

Typical Dynamical Effects of Confinement

- QENS broadening remains finite at low *Q*: the confining radius can be deduced.
- Translational dynamics slows down by 1-2 orders of magnitude, depending on the pore size.
- Reorientational dynamics slows down much less, usually by a factor of 1-2.

Key Issues for Confined Geo-Fluids

What is the impact of different modes of molecular-scale confinement (e.g. channels, pores, surface roughness, interconnectivity) on the properties (e.g. dynamical, thermophysical) of fluids (e.g. gaseous, aqueous, nonaqueous)?

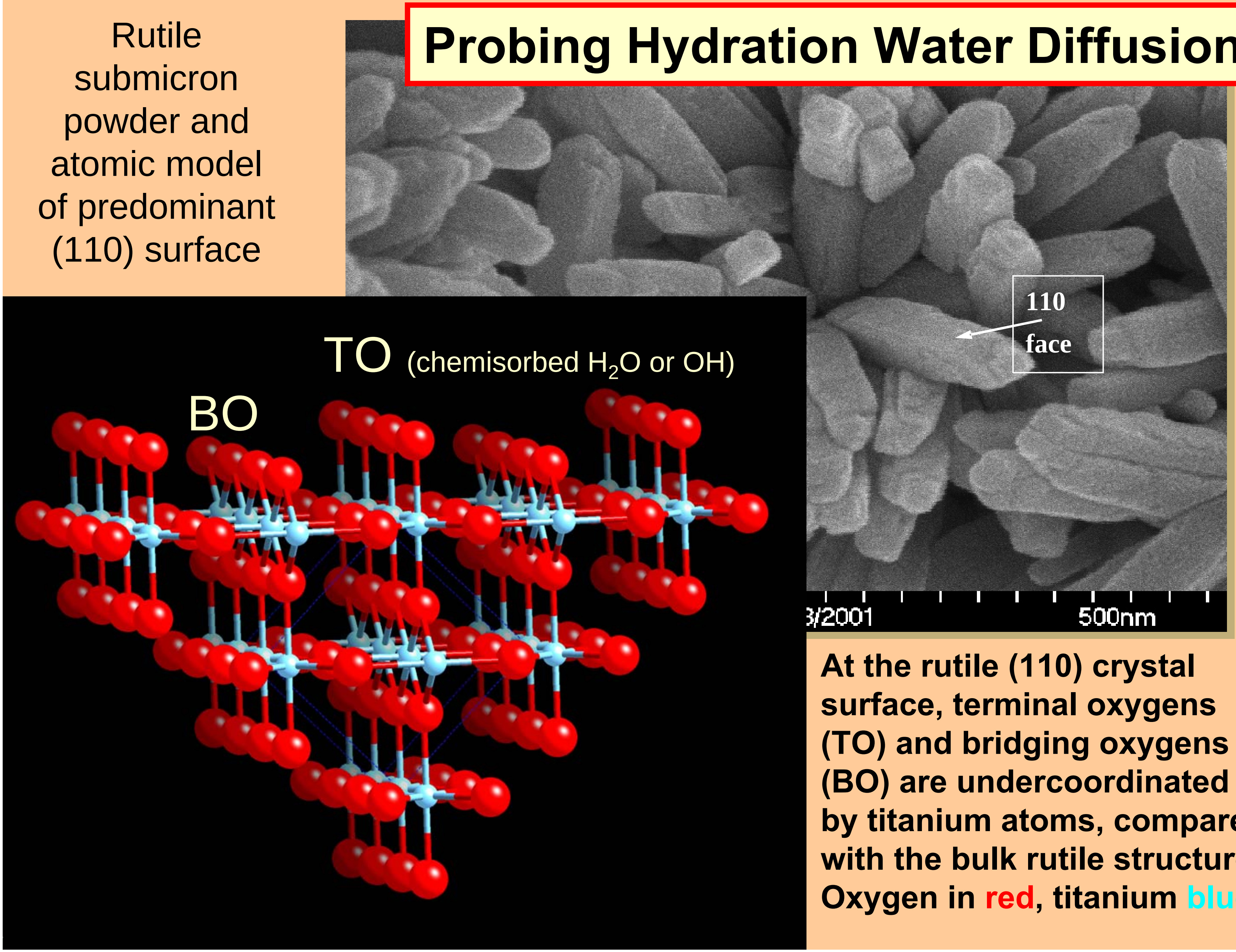
How does confinement influence the extent of reactivity between fluids and the pore walls, channels or fractures ?

How do we assess the impact of macroscopic phenomena (e.g. fluid flow, stress) on molecular scale behavior resulting from confinement, and adequately scale up to “real world” scenarios?

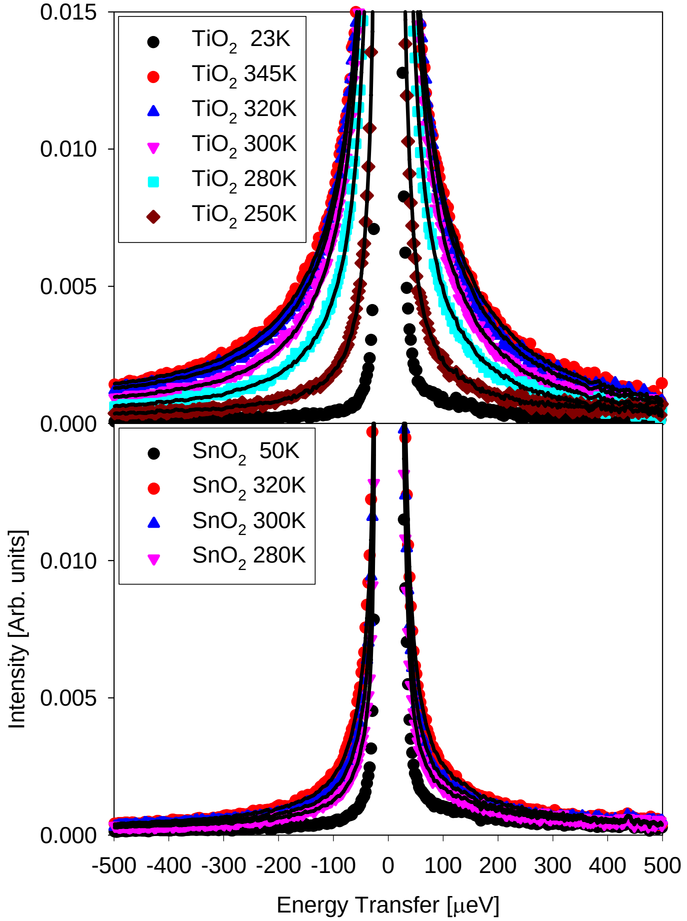
Fluids at Solid Surfaces

Probing Hydration Water Diffusion

Rutile submicron powder and atomic model of predominant (110) surface

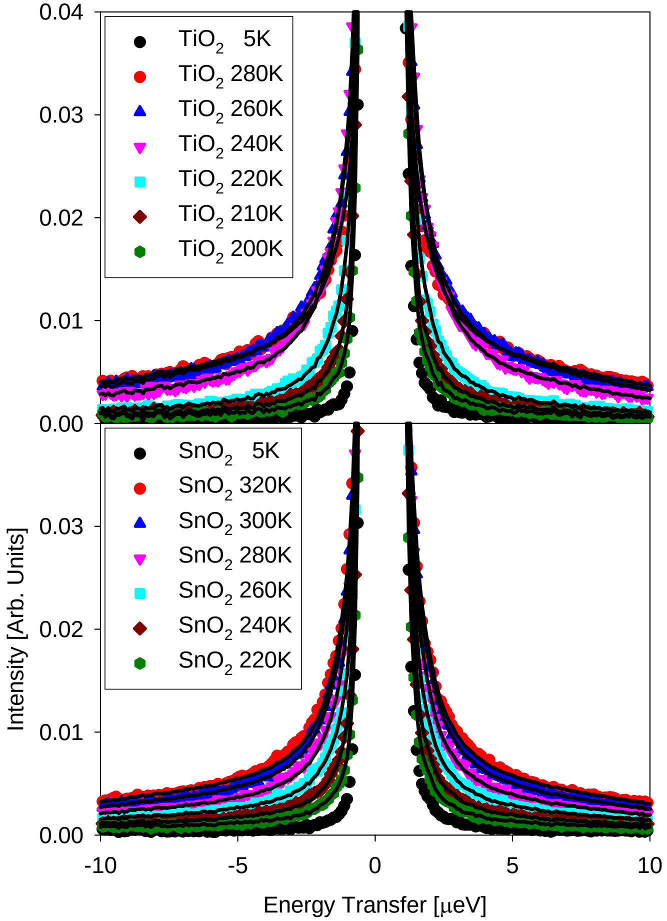


At the rutile (110) crystal surface, terminal oxygens (TO) and bridging oxygens (BO) are undercoordinated by titanium atoms, compared with the bulk rutile structure. Oxygen in red, titanium blue.



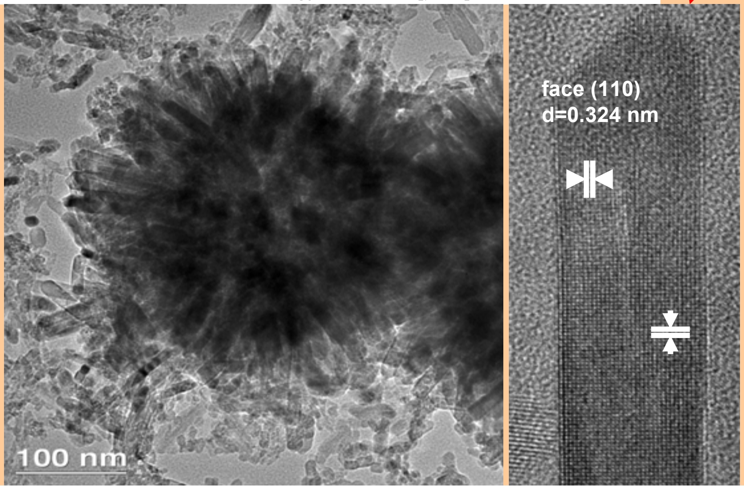
NIST Disk Chopper quasielestic neutron spectrum (QENS) from rutile and cassiterite nano-particles hydrated at ~70% RH at 298K

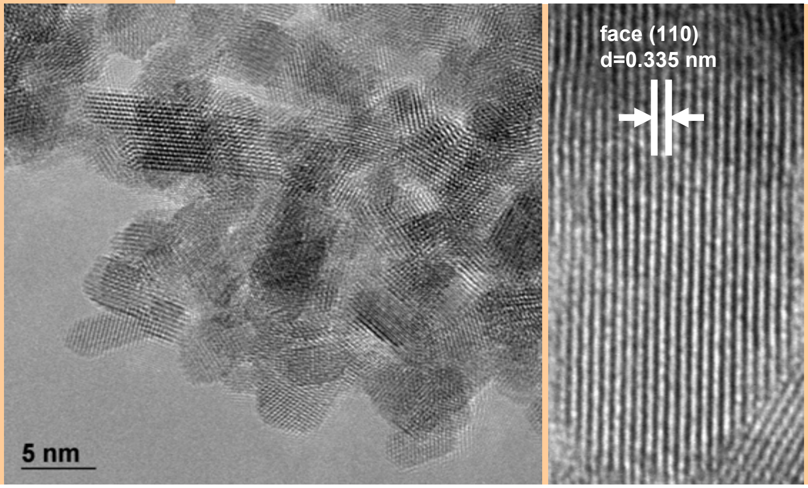
NIST Backscatter QENS same nanoparticles

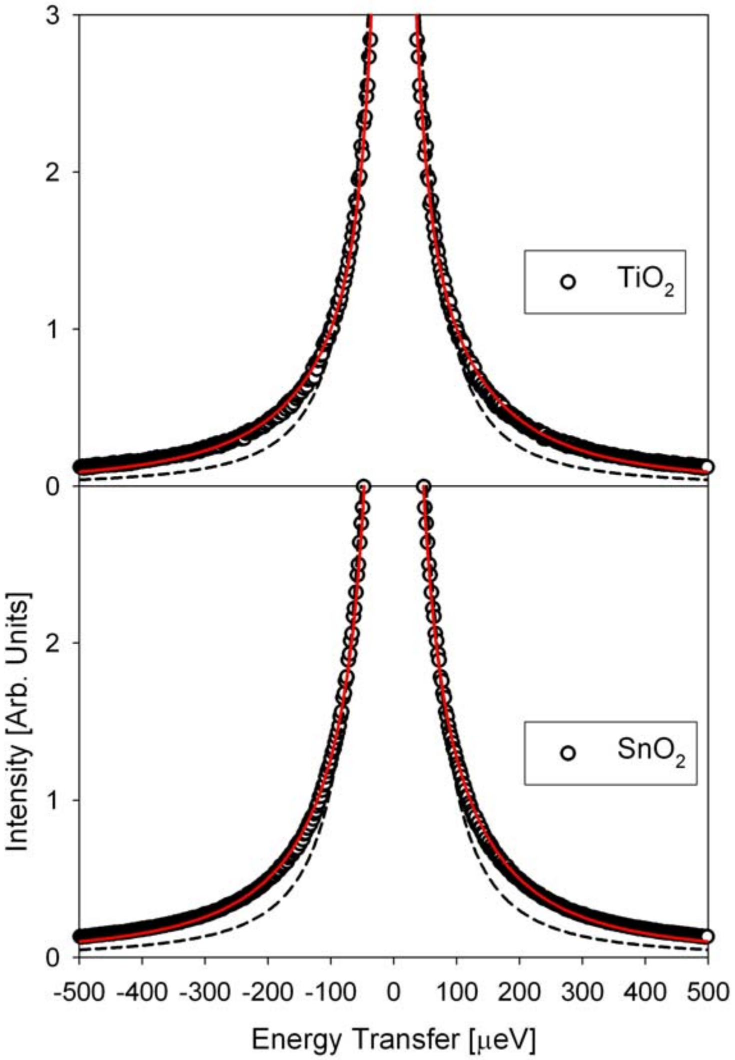


TiO_2, 188m²/g

SnO_2, 155m²/g



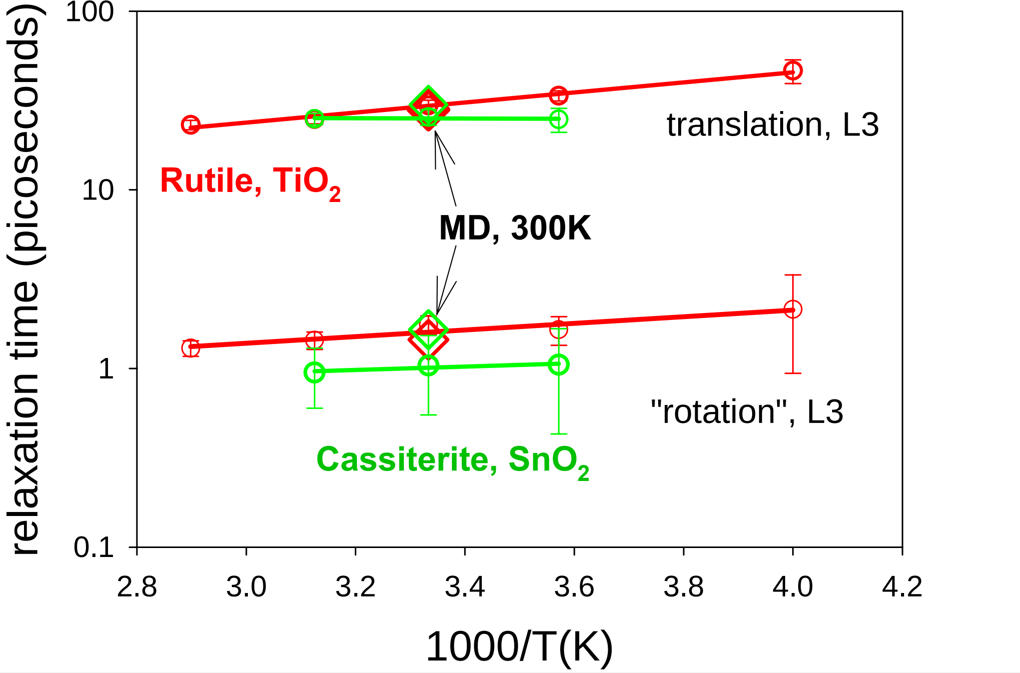




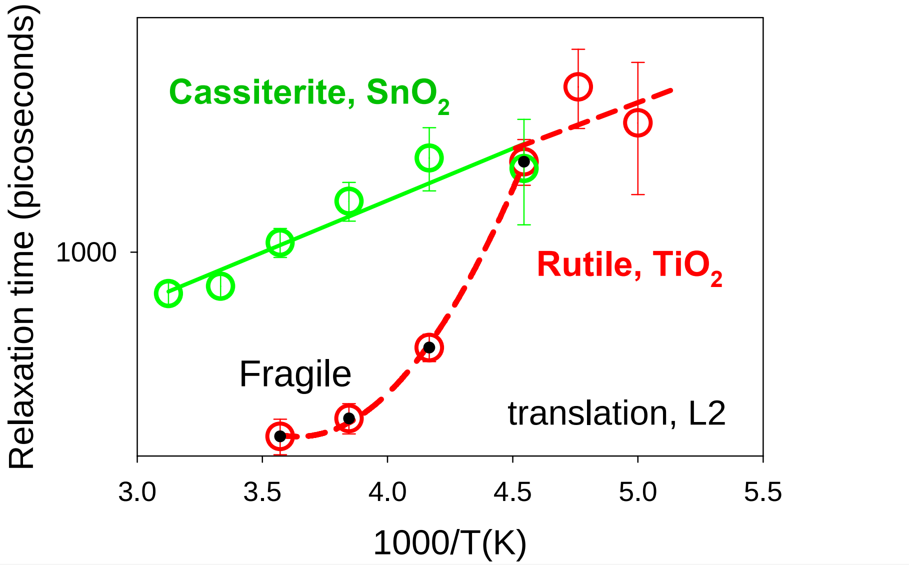
Fit of *MD simulated* QENS 300K energy transfer spectrum to one (dashed) and two (red) components

Mamontov et al. (accepted) JPC

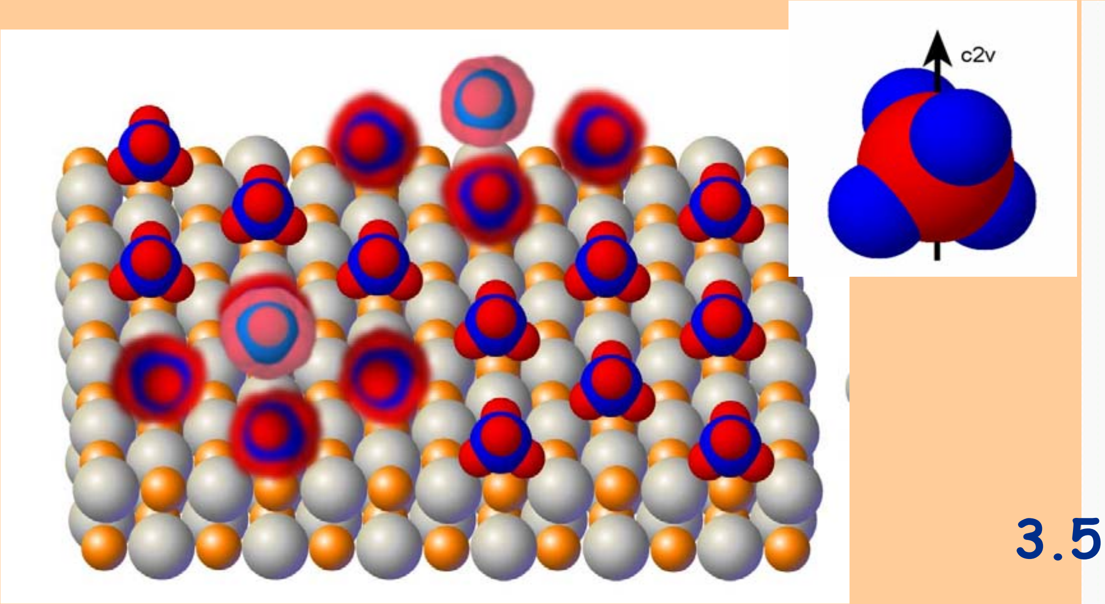
Fit of QENS energy transfer spectrum from Disk Chopper Spectrometer (NIST)

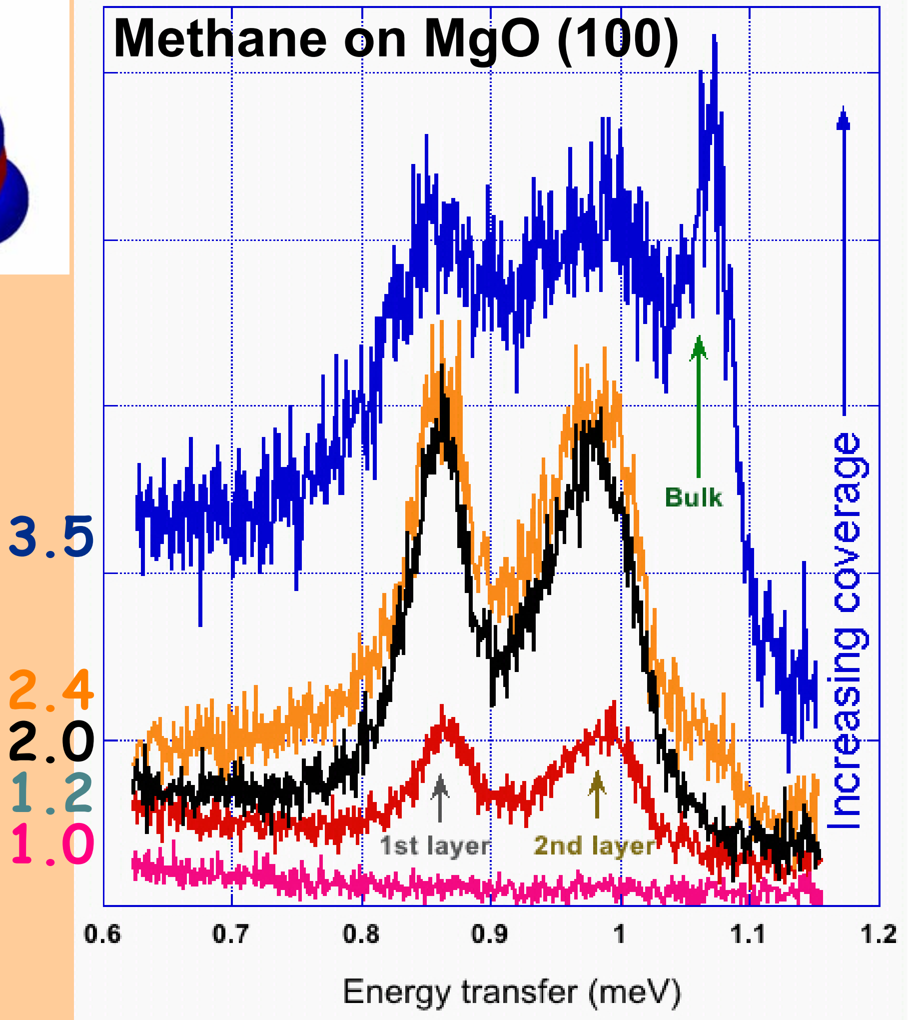


Fit of QENS energy transfer spectrum from NIST Backscatter spectrometer



Example of Rotational Motion Using INS





INS is a powerful method to gauge the barrier to rotation and the evolution of PES as the thickness of a molecular film on nanoparticle surface changes.

J.Z.Larese, D. Martin, CJ Carlile, M Adams
ORNL, UTK, ISIS, Univ. Madrid, ILL

Research Opportunities

Neutron diffraction and scattering have contributed to our molecular level understanding of complex fluids and fluid – solid interactions

We still do not have a complete understanding of the mechanisms that give rise of the molecular features of water and other simple hydrogenous fluids – hydrogen bonding?

Effects of extreme conditions still a wide open area of research

Interaction of complex fluids with geological interfaces virtually uncharted territory

Gaps still exist between experimental observations and molecular dynamic simulations

Good news: next generation sources; new beam lines and access to advanced computational facilities

Why? - New Tools for Neutrons and Nano-Science

Unique tools and capabilities:

- World's absolute best neutron scattering capabilities are provided by the Spallation Neutron Source and the newly upgraded High-Flux Isotope Reactor

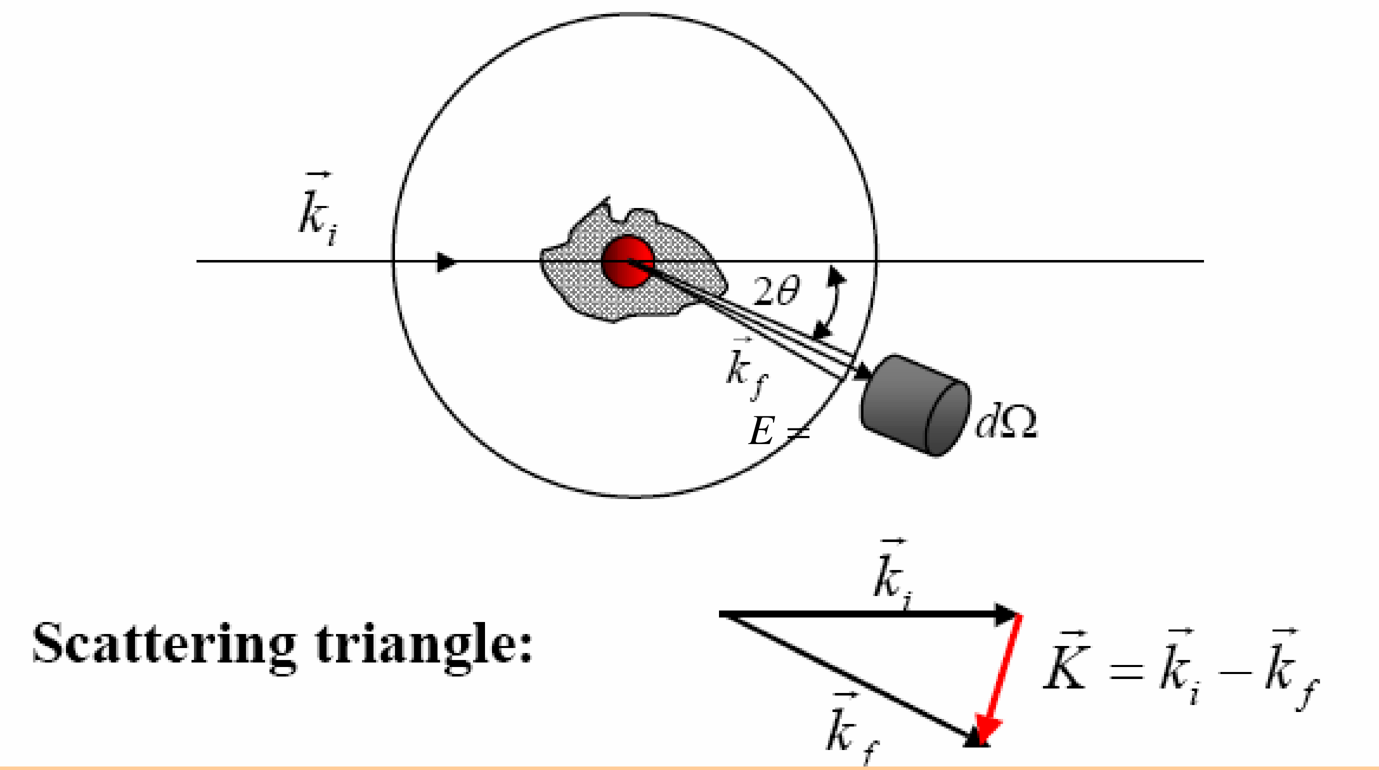
Scientific focus areas:

- Nanoscale materials related to polymers, macromolecular systems, exotic crystals, complex oxides, and other nanostructured materials
- Scientific theory/modeling/simulation, building on the outstanding ORNL materials sciences program


Center for Nanophase Materials Sciences

Supporting Slides

Inelastic Scattering



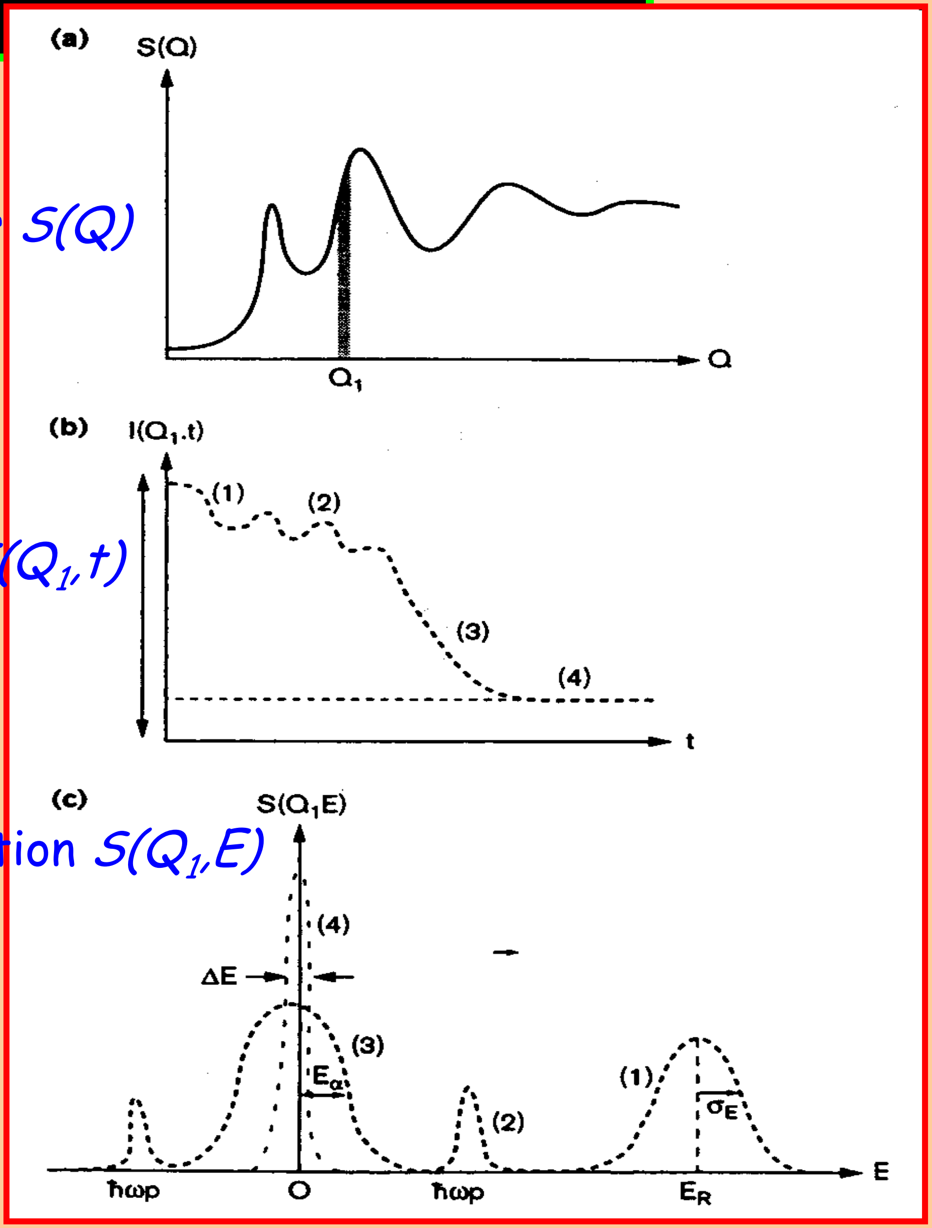
Scattering triangle:

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

Energy transfer:

$$E = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m} \neq 0, \mathit{in\ general}$$

Dynamical Regimes Probed by Inelastic Neutron Scattering



structure factor $S(Q)$

intermediate-scattering function $I(Q_1,t)$

scattering function $S(Q_1,E)$

The numbers denote

- *(1) recoil ,*
- *(2) one-phonon,*
- *(3) quasielastic*
- *(4) elastic*

scattering regimes

Intermediate Scattering Function and $S(Q,\omega)$

Intermediate Scattering Function

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

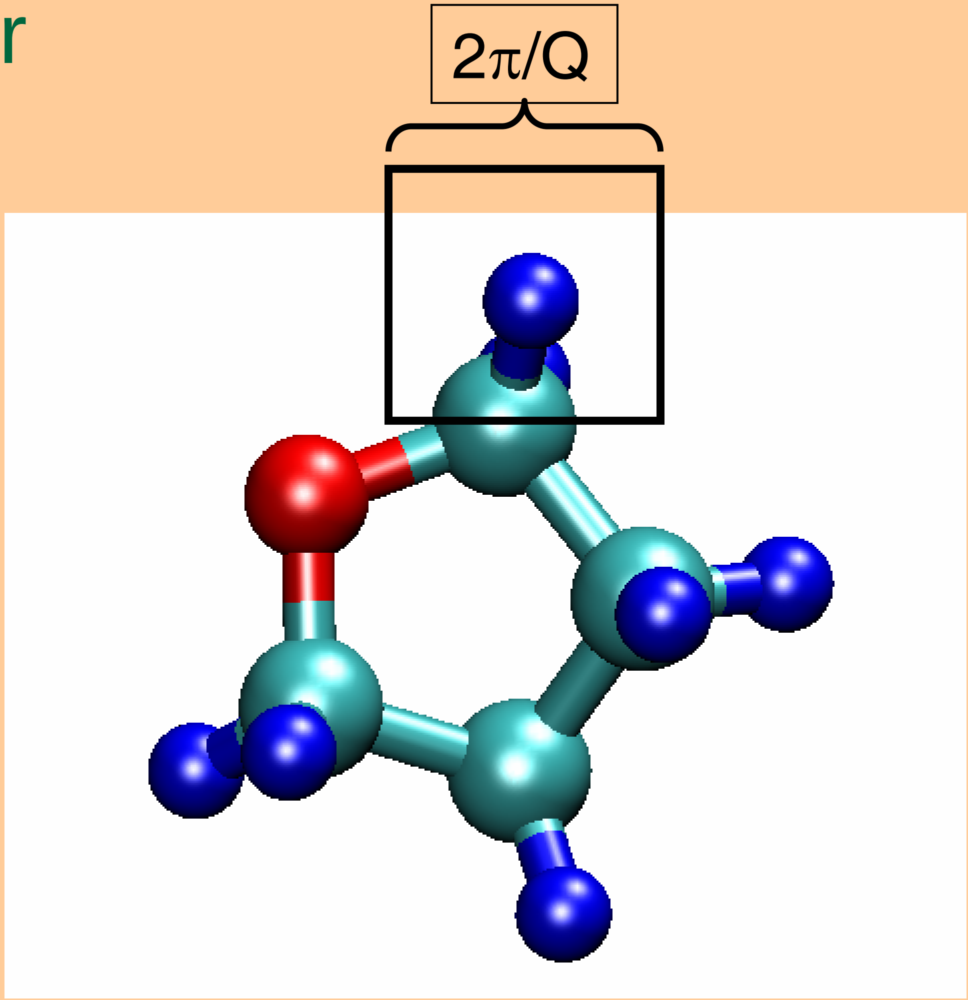
$$I_{inc}(\mathbf{Q},t)=\frac{1}{N}\sum_i \left\langle \exp\{i\mathbf{Q}\bullet\mathbf{R}_i(t)\}\exp\{-i\mathbf{Q}\bullet\mathbf{R}_i(0)\}\right\rangle$$

$S_{inc}(Q,\omega)$ [Dynamic Structure Factor] **– Fourier transform of** ***$I_{inc}(Q,t)$***

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

The EISF – Elastic Incoherent Structure Factor

- **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.**



THF (C_4H_8O)

Role of Instrumentation

- **Currently about 25 neutron scattering instruments in the world useful for QNS (approximately 5 in the U. S.)**
- **13 new instruments are on the horizon**
  - **3 new instruments at the SNS – Backscattering (2.5 μeV), CNCS (10 – 100 μeV), NSE (t to 1 μsec, ω ~0.7 neV)**
  - **3 FRM-II – Munich, Germany**
  - **1 ISIS – Rutherford-Appleton Laboratory, UK**
  - **1 ILL – rebuild of IN16**
  - **5 JPARC (including 3 spin echo)**
- **Trade-offs**
  - **Resolution/count rate**
  - **Flexibility**
  - **Dynamic range**

SNS Backscattering