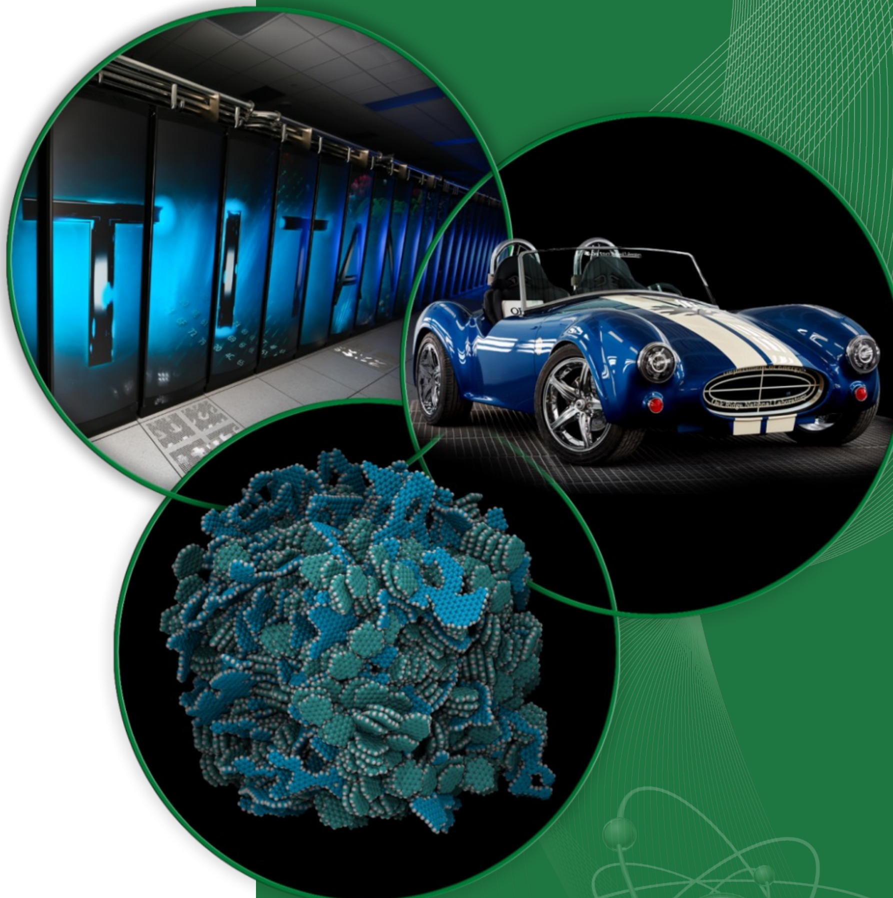
Quasi-Elastic Neutron Scattering



Niina Jalarvo

Overview

INTRO to QENS

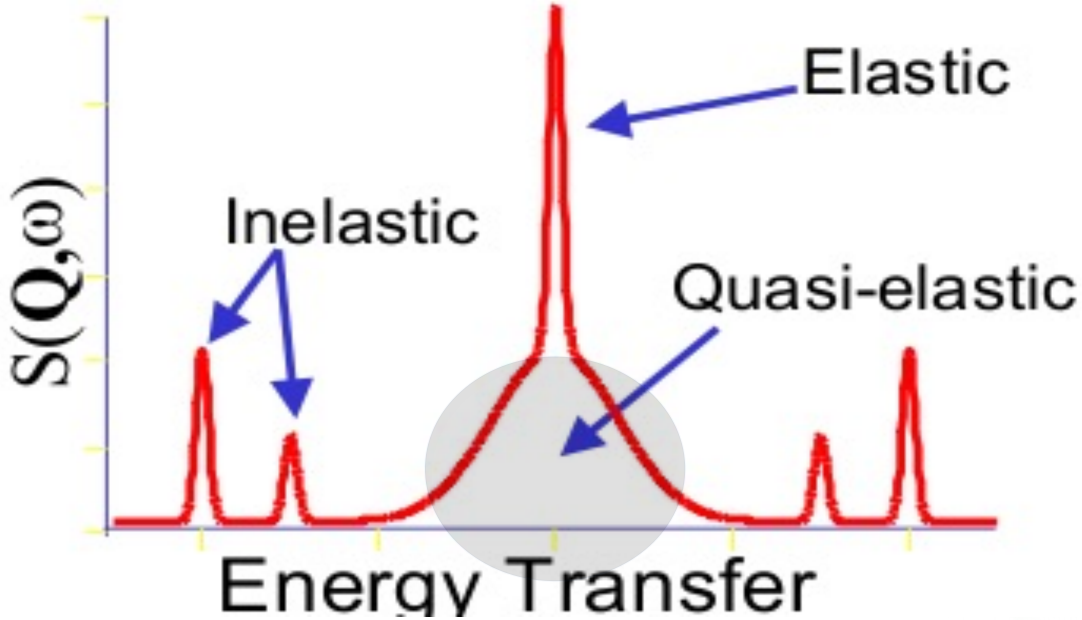
QENS Theory

QENS Instruments

Science Examples

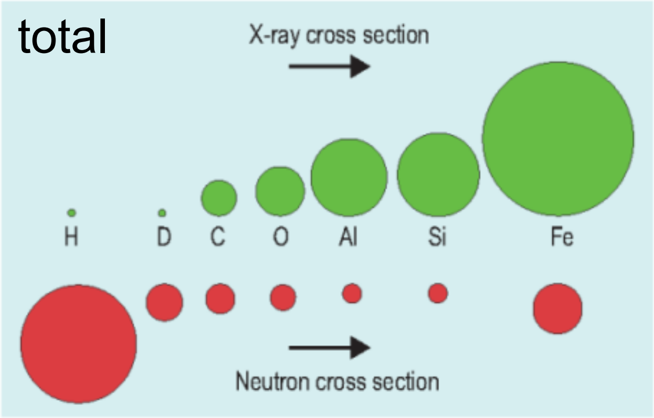
What is QENS

Quasi Elastic Neutron Scattering QENS



- Quasi elastic neutron scattering is a limiting case of inelastic neutron scattering
- Doppler type of broadening of the elastic line due to a small energy transfer between the neutrons and the atoms in the sample

Neutron-Material Interaction



- **Cross section (σ)** – Area related to the probability that a neutron will interact with a nucleus in a particular way (*e.g.* scattering or absorption)
- Light element sensitivity in presence of heavy elements
- Systems containing a reasonable proportion of H atoms, scattering from H tends to dominate
- Isotopic sensitivity
  - H-D contrast, H large incoherent cross-section
    - Use of deuteration/selective deuteration to suppress incoherent scattering
- Thermal neutron wavelengths (few Å's) are comparable to interatomic and intermolecular distances
- Thermal neutron energies (few meV's) comparable to energies of excitation in materials

  => vibrations, librations, reorientations, diffusion, and relaxational processes can be observed

What is QENS used for

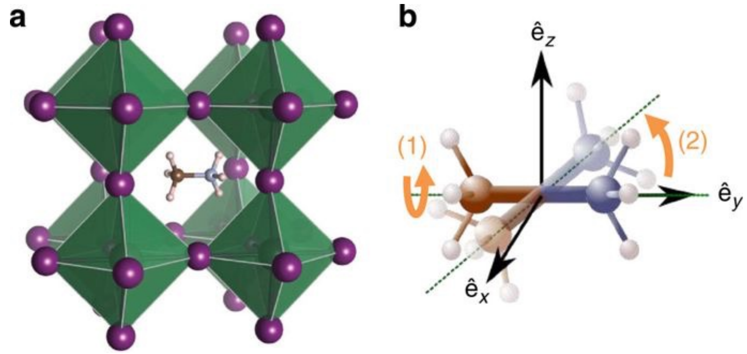
Probes slow dynamics

- Translational diffusion
- Molecular reorientations
- Relaxation processes

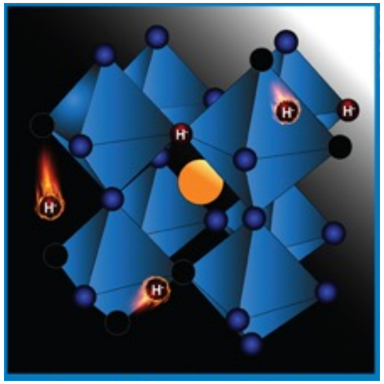
Applicable to wide range of scientific topics

- ***Materials science***: fuel cells, batteries, hydrogen storage,
- ***Soft Matter***: polymer nanocomposites and blends, organic photovoltaics, polymer electrolytes
- ***Biology***: hydration water, dynamics of proteins
- ***Chemistry***: water interfaces, ionic liquids, clays, porous media, complex fluids, surface interactions

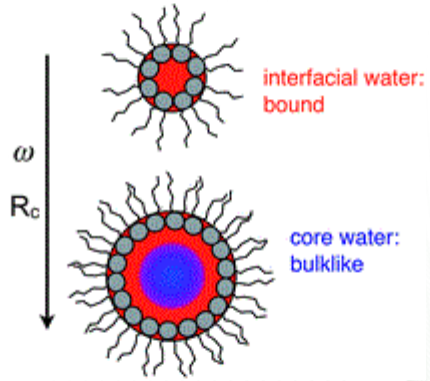
Results are comparable to Molecular Dynamics simulations



Nature Communications 6, 7124 (2015)



Journal of Physical Chemistry C, 123, 2019 (2019).



Soft Matter, 7, 12, 5745-5755 (2011)

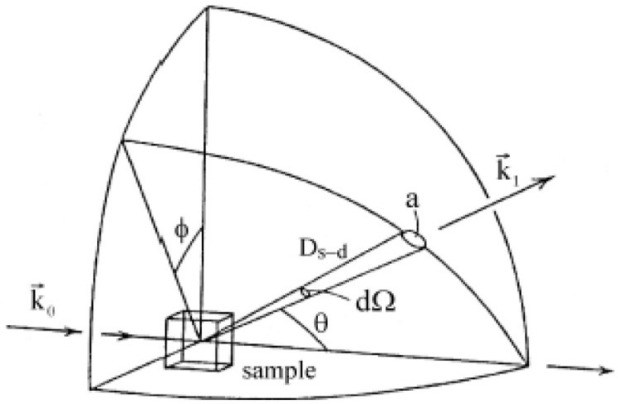
QENS theory

Scattering Function S(Q,ω)

The quantity measured in a neutron scattering experiment is the double differential cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{k_f}{k_i}\frac{\sigma}{4\pi}S(\mathbf{Q},\omega)$$

that gives the proportion of neutrons with an incident energy E_0 scattered into a solid angle element $d\Omega$ with an energy between E_1 and E_1+dE_1.



Double differential cross-section:

$$\frac{\partial^2\sigma}{\partial\Omega\delta E} = \left(\frac{\partial^2\sigma}{\partial\Omega\delta E}\right)_{incoh} + \left(\frac{\partial^2\sigma}{\partial\Omega\delta E}\right)_{coh}$$

σ = cross-section
Ω = solid angle, and
E = energy transfer($E = \hbar\omega$)

COHERENT SCATTERING: Scattered neutron waves from the different nuclei have **DEFINITE** relative phases (interference)

- Collective excitation from periodic samples (quasielastic)
- Structure

INCOHERENT SCATTERING: Scattered neutron waves from the different nuclei have **RANDOM** relative phases (no interference)

- Single particle dynamics (quasielastic)
- Vibrational modes from inelastic spectra

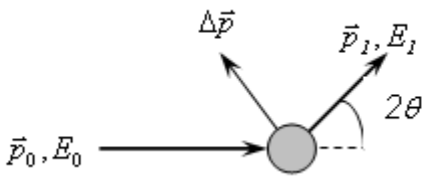
$$\frac{\partial^2\sigma}{\partial\Omega\delta E} = \left(\frac{\partial^2\sigma}{\partial\Omega\delta E}\right)_{incoh} = \frac{1}{4\pi N}\frac{\vec{k_f}}{\vec{k_i}}[\sigma_{incoh}S_{incoh}(Q,E)]$$

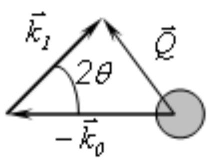
Scattering Kinematics

The collision of two objects (e.g. neutron and sample atom) can be described in terms of momentum and energy conservation.

Neutron scattering events are described by means of energy and momentum transfer.

$$\hbar\vec{Q} = \hbar\vec{k}_1 - \hbar\vec{k}_0$$
$$\hbar\omega = E_1 - E_0$$

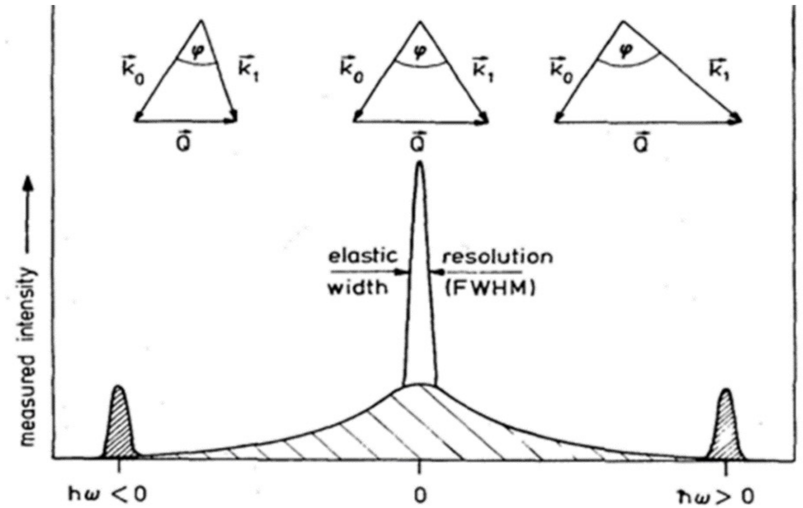




$\hbar\omega = 0$ ⟶ **ELASTIC** scattering

$\hbar\omega \neq 0$ ⟶ **INELASTIC** scattering

$\hbar\omega \approx 0$ ⟶ **QUASIELASTIC** scattering

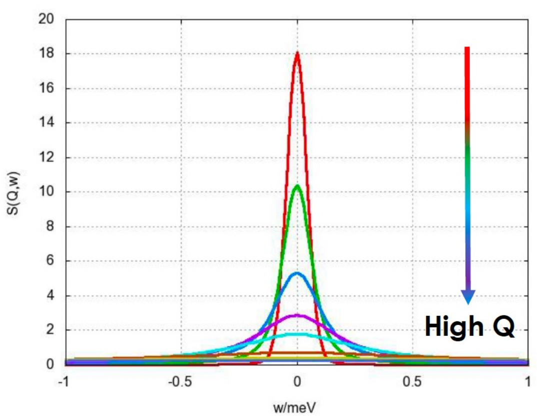


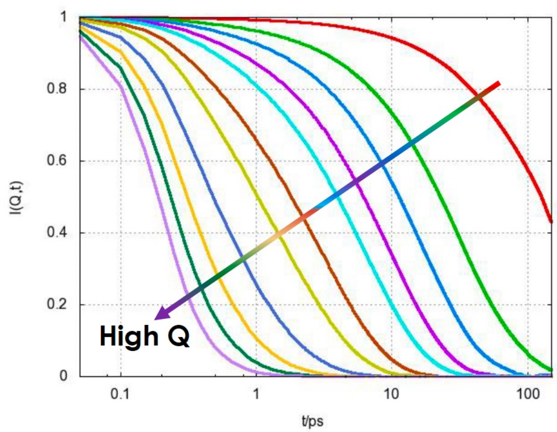
QENS Data Analysis

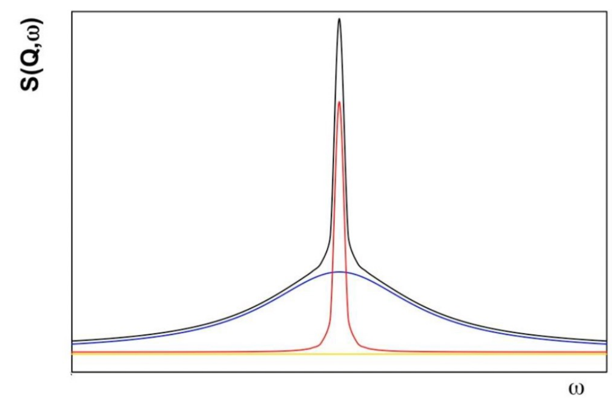
$$S_{QE}(Q,E) = \underbrace{[p_1(Q)\delta(E)}_{\text{Elastic}} + \underbrace{(1-p_1(Q))S_{incoh}(Q,E)}_{\text{Quasielastic}}] \otimes \underbrace{R(Q,E)}_{\text{Resolution}} + \underbrace{B(Q,E)}_{\text{Inelastic}}$$

$$S_{incoh}(Q,E) \equiv S_{QE}(Q,E)$$

$$S_{QE}(Q,E) = \frac{1}{\pi}\frac{DQ^2}{E^2+(DQ^2)^2} \xrightarrow{\text{FT}^{-1}\text{ in time}} I_s(Q,t) = \exp(-DQ^2t) \xrightarrow{\text{FT}^{-1}\text{ in space}} G_s(r,t) = (4\pi Dt)^{-3/2}\exp(-r^2/4Dt)$$







- ❑ Intermediate scattering function, $I_{inc}(Q,t)$ can be obtained from a molecular dynamic simulation

Elastic intensity → Debye-Waller factor: Vibrational amplitudes

Elastic intensity, **Quasielastic intensity** → A_0 = EISF (ratio elastic/total): Geometry of motion

Quasielastic broadening → Width: Characteristic time scale / diffusion

Incoherent vs Coherent Neutron Scattering

Different atoms and isotopes have different coherent and incoherent scattering cross sections

Element	σ_{coh} (barns)	σ_{inc} (barns)
Hydrogen (H)	1.8	79.9
Deuterium (D)	5.6	2.0
Carbon (C)	5.6	0.001
Oxygen (O)	4.232	0

If the scattered neutron waves from the different nuclei have RANDOM relative phases (no interference)
=> *IN*COHERENT SCATTERING

If the scattered neutron waves from the different nuclei have definite relative phases, they can interfere
=> COHERENT SCATTERING

DYNAMICS

Protonated sample to observe single particle dynamics (quasielastic) and for the inelastic spectrum to weight hydrogen vibrations.

STRUCTURE

Deuterated sample to obtain structure and collective excitations.

Deuteration can help to **suppress** dynamics of particular groups

QENS - Incoherent and Coherent Scattering

- Large proportion of QENS experiments focus on dynamics of hydrogenous samples

$$S(Q,\varpi) = S_{inc}\,(Q,\varpi) + S_{coh}\,(Q,\varpi)$$

No information about structure
Dominated by H dynamics

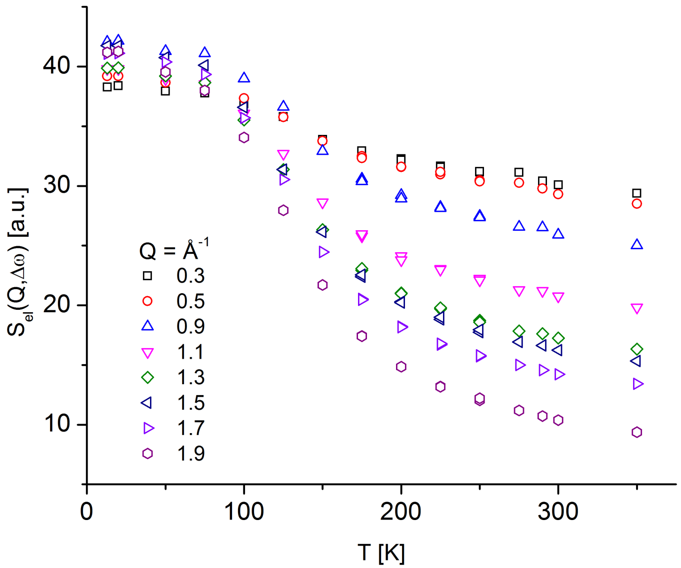
Contaminates QENS signal (Bragg peaks)

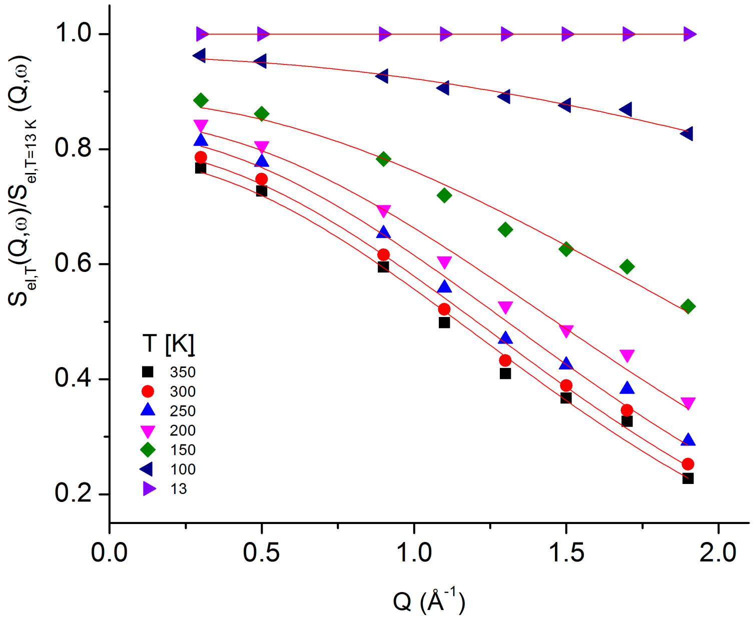
- Coherent QENS signal observable e.g. oxide ion diffusion
- Mixed coherent and incoherent QENS signal e.g. lithium or sodium diffusion

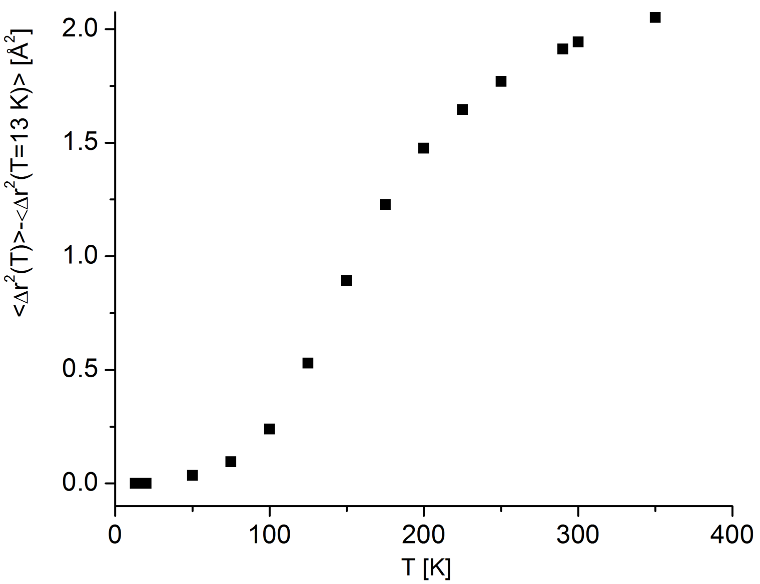
Elastic Window Scan

- Elastic intensity scan as a function of temperature is a typical approach to estimate dynamic transitions.
- Resembles a DSC scan, i.e. locate transition temperature at which the dynamics enter the time window of the neutron spectrometer.
- Derive MSD using Gaussian approximation

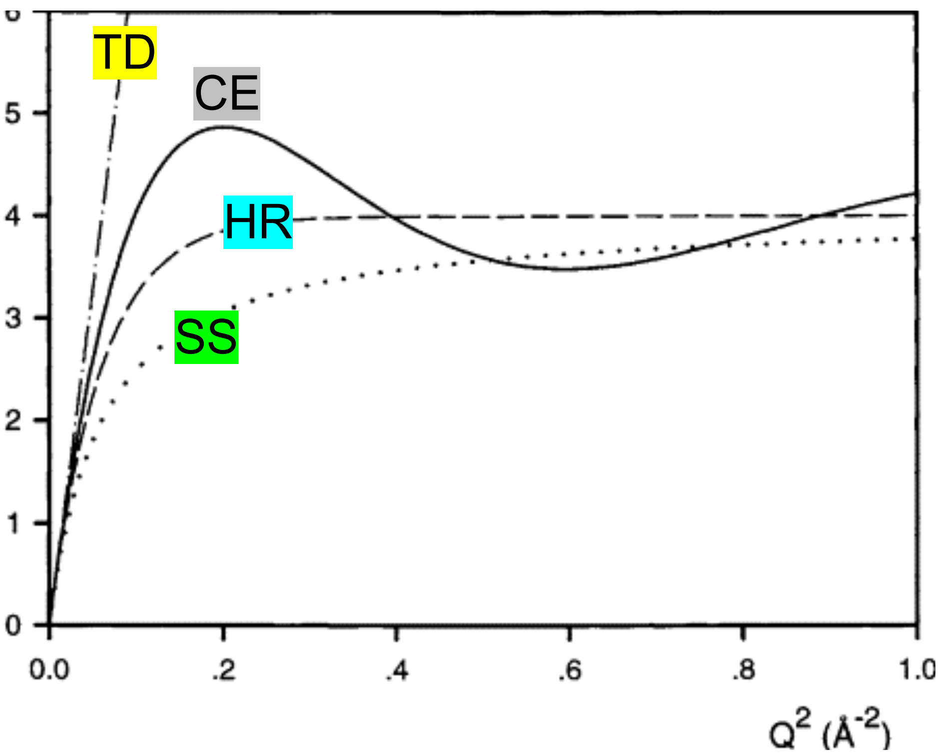
$$S_{el}(Q,\omega) = A * e^{-Q^2\langle r^2 \rangle/3}$$

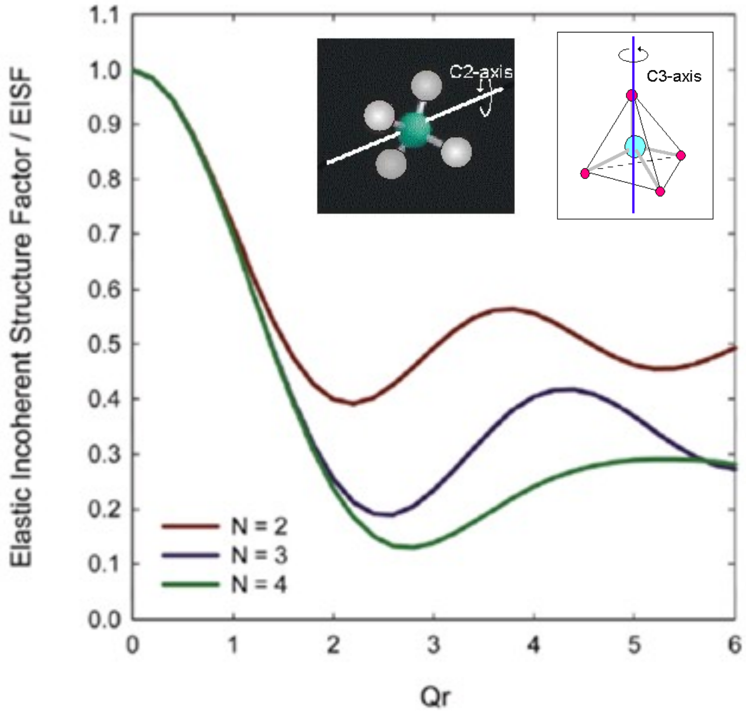






QENS diffusion models





- (TD) Translational Diffusion following Fick's law
- (CE) Chudley-Elliot -model, jump diffusion on a lattice
- (SS) Singwi-Sjölander -model, alternation between oscillatory motion and directed motion
- (HR) Hall-Ross –model, jump diffusion within a restricted volume

Spatially restricted diffusion

- Jumps between 2, 3, … n sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder

Angular dependency gives access to fundamental processes

QENS Instruments

QENS Instruments

Currently about 20 QENS spectrometers in the world (in the U. S., Germany, France, Switzerland, U.K. Japan and Australia)

Backscattering Spectrometers

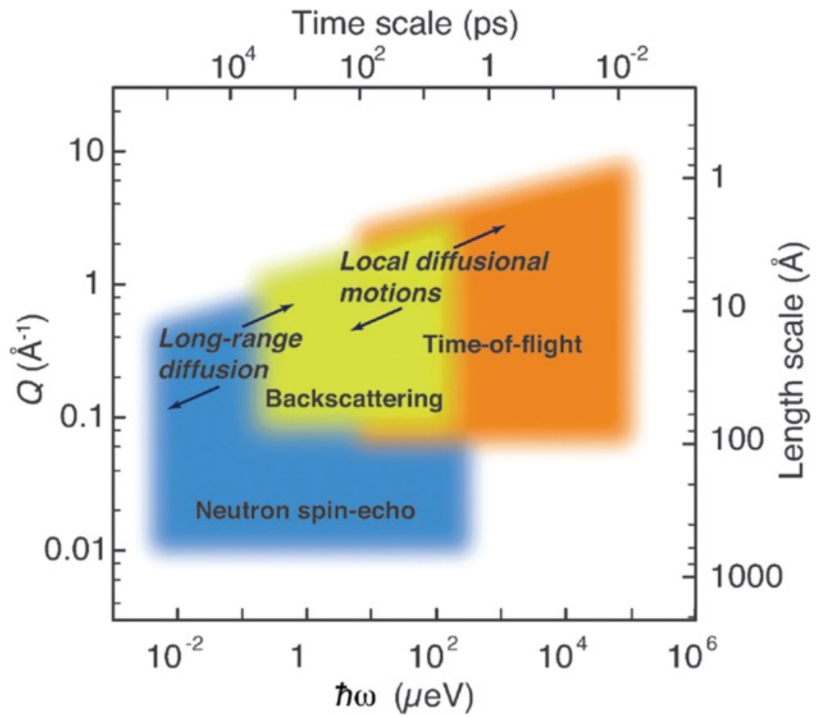
- High energy resolution
  - Resolution determined by the instrument (final energy of neutrons fixed)
  - Access to slower dynamics on nanosecond to picosecond time scale
  - Dynamic range limited

Time-of-Fligth Spectrometers

- Lower energy resolution
  - Resolution can be varied by changing the energy of incoming neutrons
  - Access to dynamics on picosecond time scale
  - Larger dynamic range accessible

QENS and Neutron Scattering Instruments

- Dynamics in sample measurable
  - length scales set by Q range
    - $Q = 2\pi/d$
    - $0.1\ Å^{-1} < Q < 4\ Å^{-1} \rightarrow\ 60\ Å > d > 1.6\ Å$
  - Time scales set by the elastic energy resolution
    - higher resolution → longer times/slower motion (ns time scales accessible)
    - lower resolution → shorter times/faster motion (ps time scales accessible)
- interchange
  - dynamic range / resolution / count rate
  - Neutron λ vs Q
    - large λ –> high resolution -> long times/slow motions
    - large λ –> limited Q-range, limited length scales



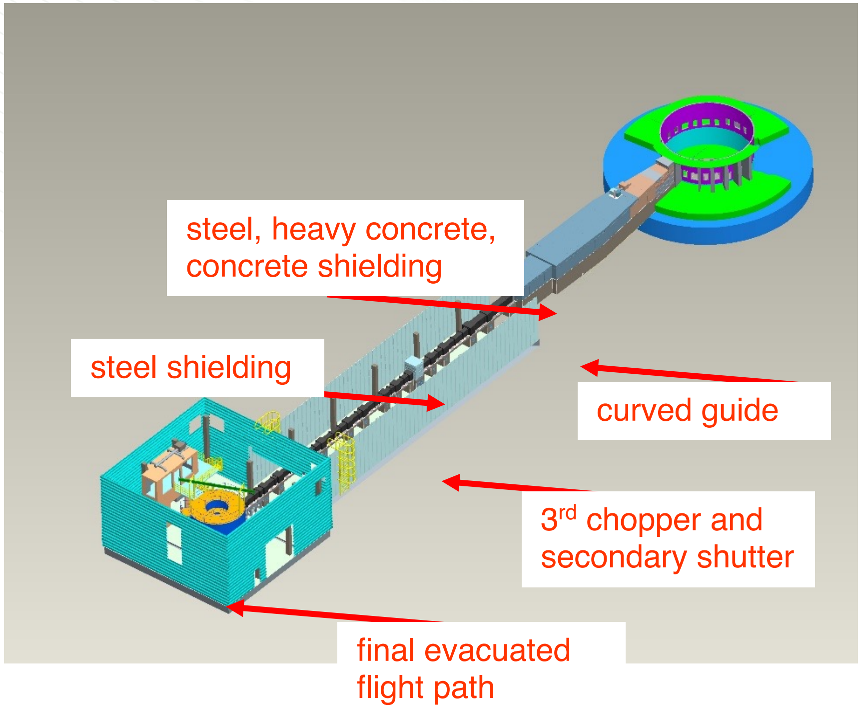
M. Karlsson, Phys. Chem. Chem. Phys., 2015, **17**, 26.

OAK RIDGE National Laboratory

BASIS backscattering spectrometer at SNS

BASIS overview

BAckscattering SIlicon Spectrometer is a high-energy resolution, wide-dynamic range inverted geometry neutron spectrometer built on BL2 and facing a decoupled supercritical hydrogen, centerline-poisoned moderator



- Incident Flight Path - 84 m moderator-sample position
  - Curved Guide: 10 cm wide x 12 cm tall, 1000 m radius of curvature, line-of-sight at 31 m
  - Straight Guide: 10 cm wide x 12 cm tall
  - Converging Funnel: last 7.7 m; exit 3.25 cm x 3.25 cm, stops 27.5 cm from sample
- Chopper System

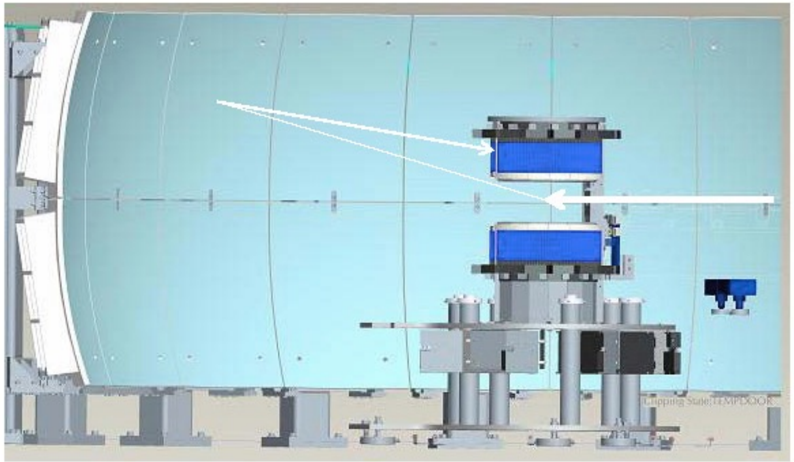
  - 3 bandwidth/frame overlap choppers at 7, 9.25 and 50 m

  - Operation at 60 (standard), 30, 20, 15, 12, or 10 Hz

  - Bandwidth (full choppers transmission) of about 0.5 Å at 60 Hz

OAK RIDGE National Laboratory

Instrument Specifications



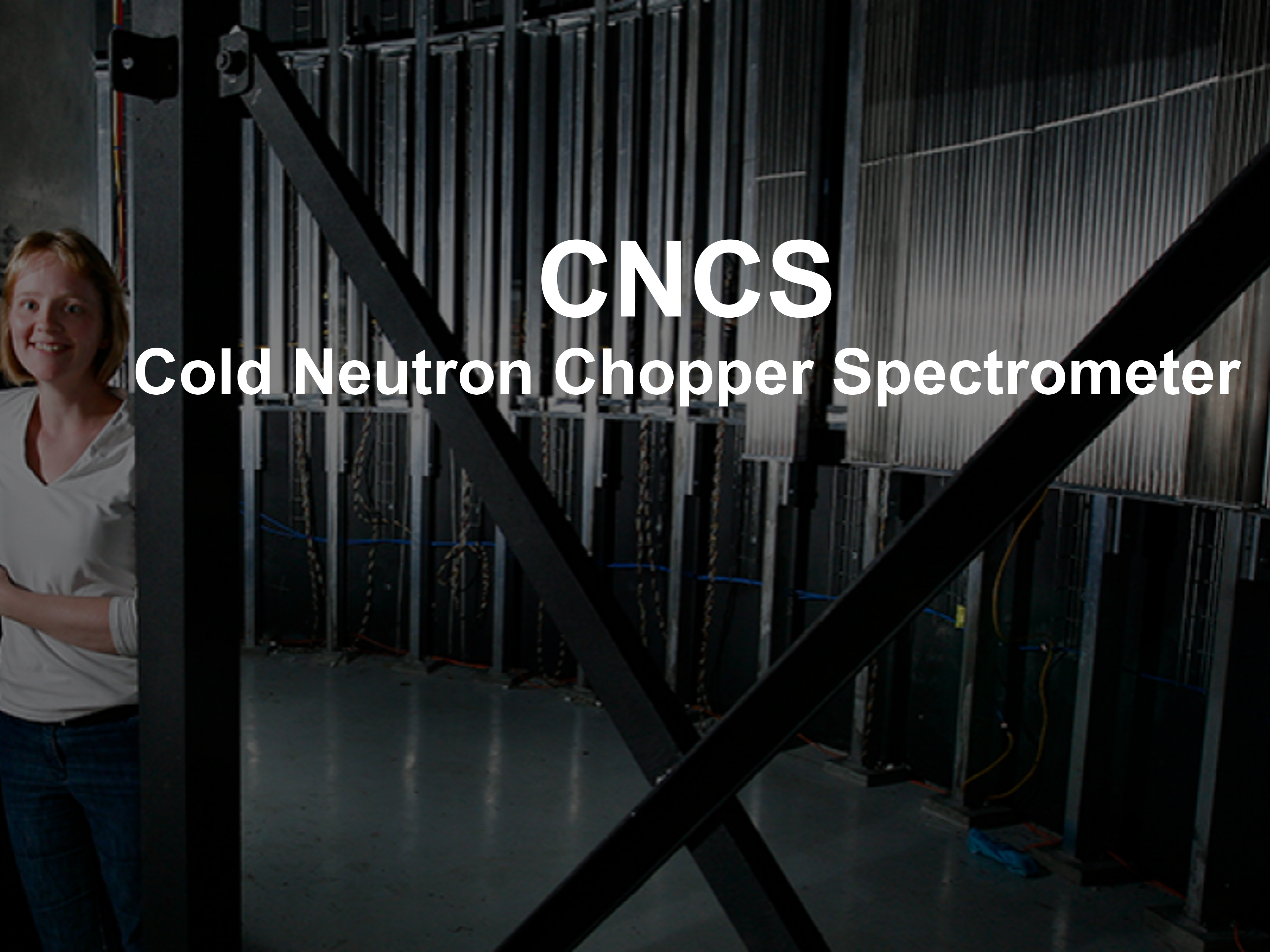
	Si111	Si311
Elastic energy	2.08 meV	7.63 meV
Bandwidth 60 Hz 30 Hz	 ±100 μeV ±200 μeV	 ±660 μeV ±1700 μeV
Elastic resolution (HWHM)	3.6 μeV	15 μeV
Q range (elastic)	0.2 $Å^{-1}$ < Q < 2.0 $Å^{-1}$	0.4 $Å^{-1}$ < Q < 3.8 $Å^{-1}$

- Radial Collimator – restricts analyzer view of the sample
- Final Evacuated Flight Path - 2.5 m sample - analyzer, ~ 2.23 m analyzer – detector
- Detector Choice – LPSD ^{3}He tubes

OAK RIDGE National Laboratory

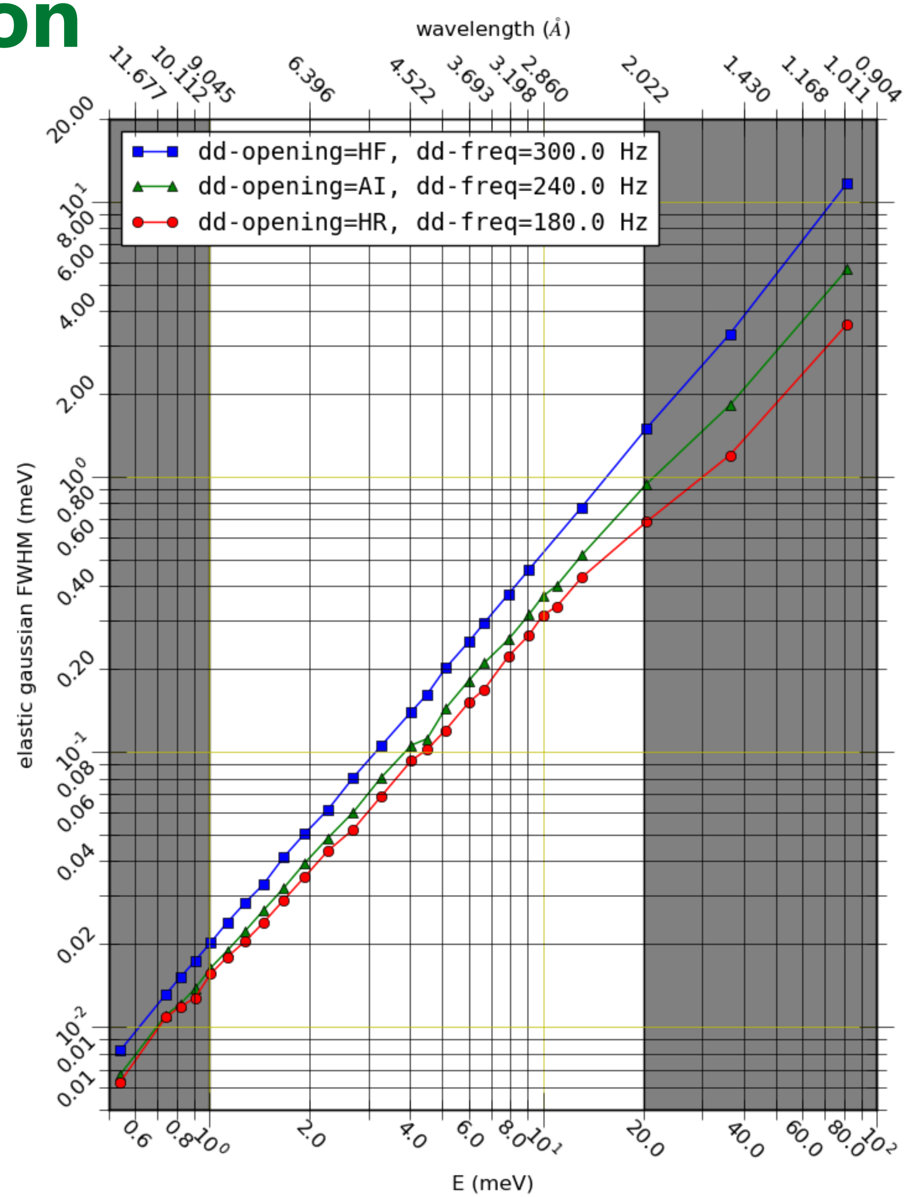
CNCS

Cold Neutron Chopper Spectrometer

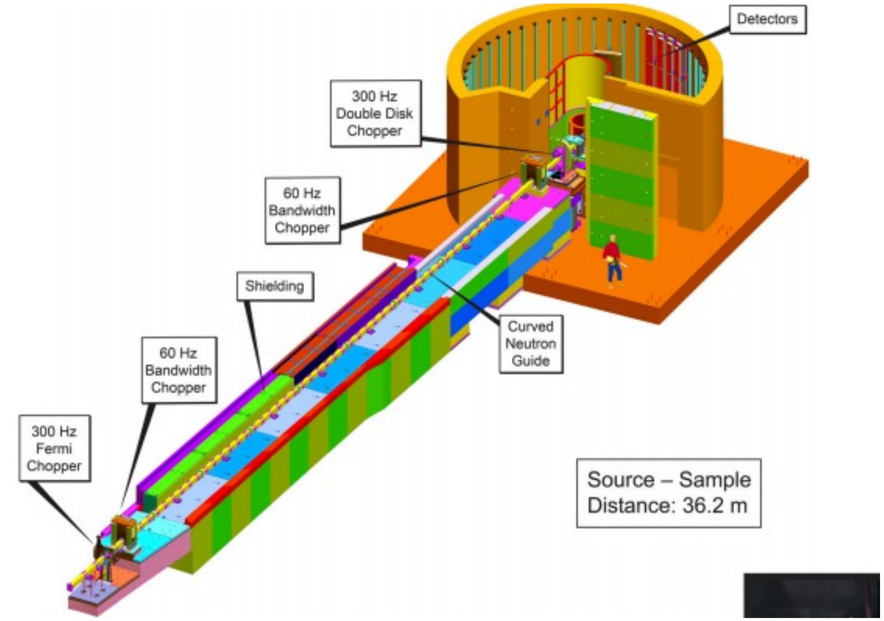


Instrument Description

- direct-geometry, multi-chopper inelastic / QENS spectrometer designed to provide flexibility in the choice of energy resolution
  - best at low incident energies (2 to 50 meV).
  - typical experiments use energy resolutions between 10 and 500 μeV.



Specifications

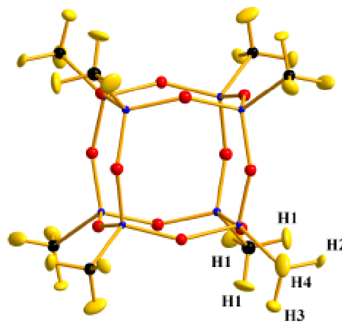


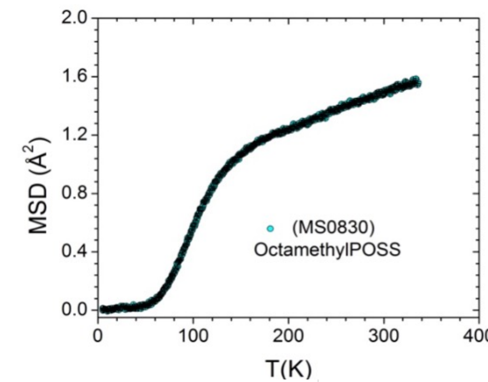
Source-sample distance	36.2 m
Sample-detector distance	3.5 m
Angular coverage	Horizontally:−50° – +140° Vertically:±16°
Energy resolution	10 – 500 μeV
Incident energy range	0.5 – 80 meV
Momentum transfer range	0.05 – 10 Â−1

QENS - Science examples

Science Example 1: Molecular Reorientations

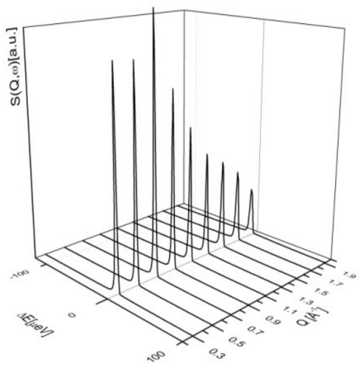
- Polyoligosilsesquioxane (POSS) Ligand Dynamics
- How do ligand dynamics contribute to the functionalities

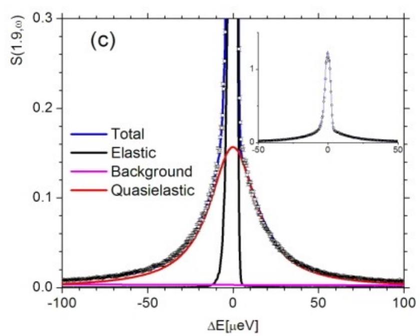


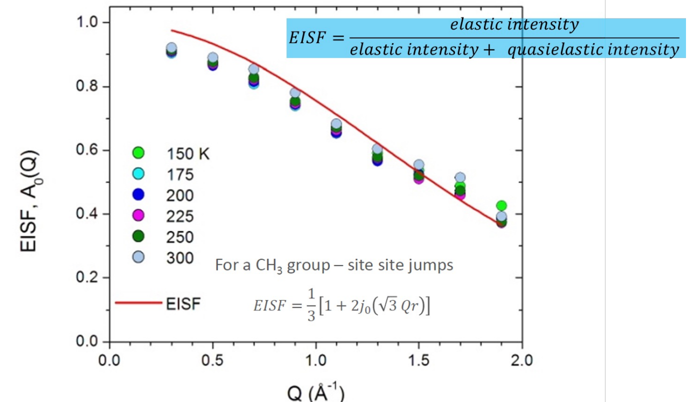


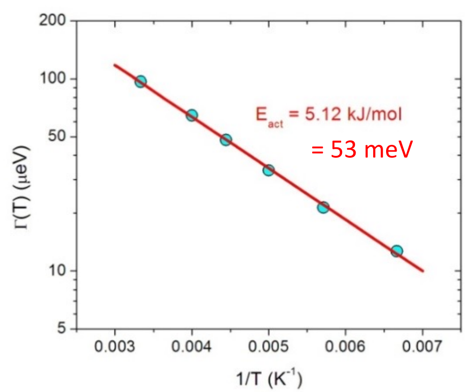
Octamethyl POSS @ BASIS

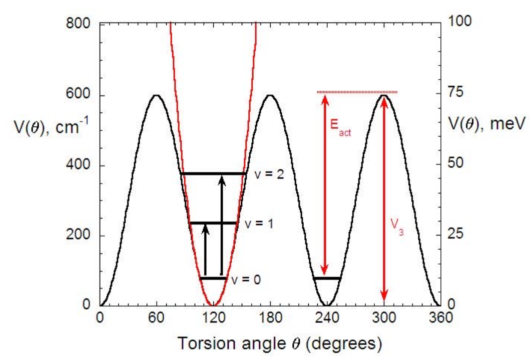
$$S(Q,\omega) = f\left[p_0\delta(\omega) + \sum_{i=1}^{n} p_i \frac{1}{\pi}\frac{\Delta_i(Q)}{\omega^2 + \Delta_i^2}\right] \otimes R(Q,\omega) + B$$











Barrier for methyl rotation

$$V(\theta) = \frac{V_3}{2}(1 - cos3\theta)$$

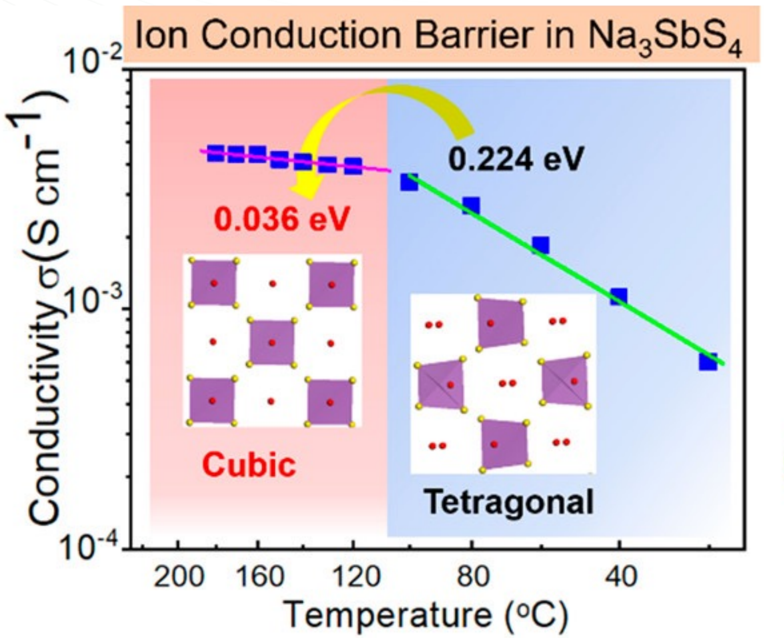
$$H\psi_n(\theta) = E_n\psi_n(\theta)$$

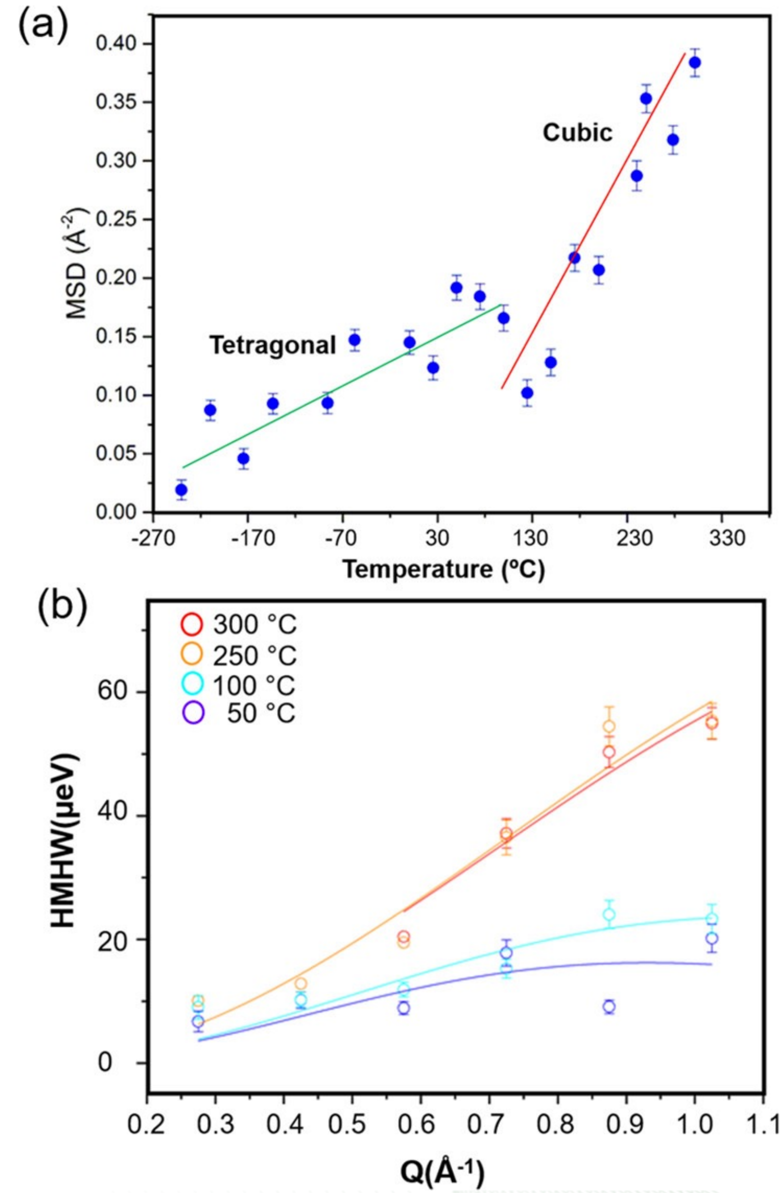
-> V_3 = 74.4 meV (7.18 kJ/mol)

Jalarvo N., *et al*, *Journal of Physical Chemistry C*, **118,** 10, 5579-5592 (2014)

Science Example 2: Superionic Conductors

- Inorganic Na-ion superionic conductors play a vital role in all-solid-state Na batteries that operate at RT
- fundamental understanding of the Na-ion diffusion mechanisms in Na_3SbS_4 with different crystal structures (e.g., tetragonal and cubic) from QENS
- The high degree of symmetry in cubic Na_3SbS_4 leads to less interatomic correlations between Na and S(Sb) atoms, a shorter jump distance (2.85 Å), and a larger diffusion coefficient.

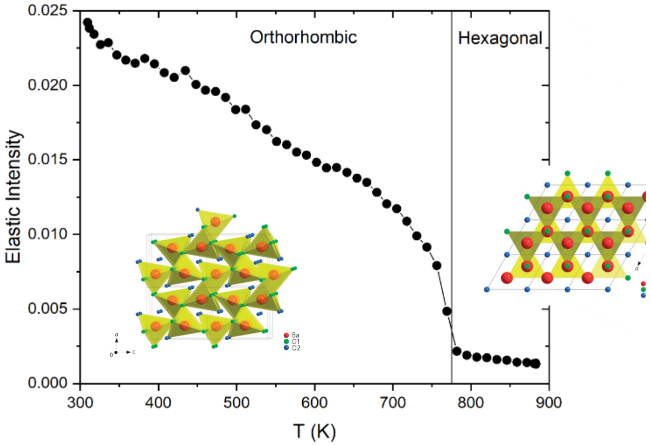


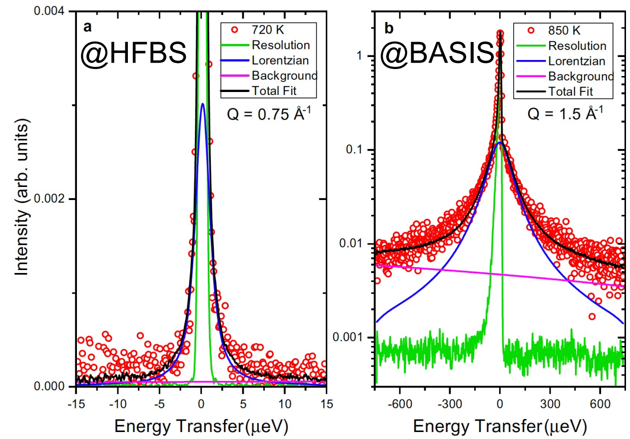


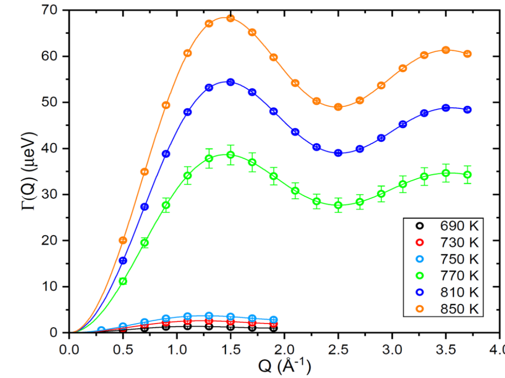
Zhang Q., *et al, Chem. Mater.* 2020, 32, 6, 2264–2271

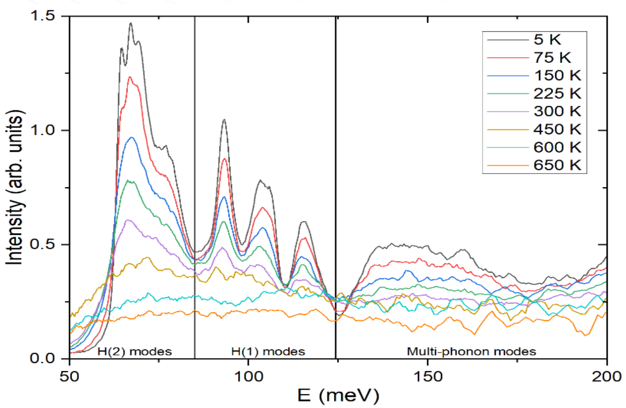
Science Example 3: Metal hydride dynamics

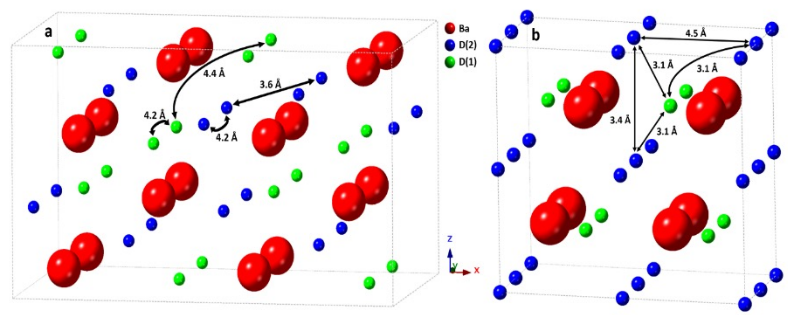
BaH_2 @ BASIS, HFBS and VISION





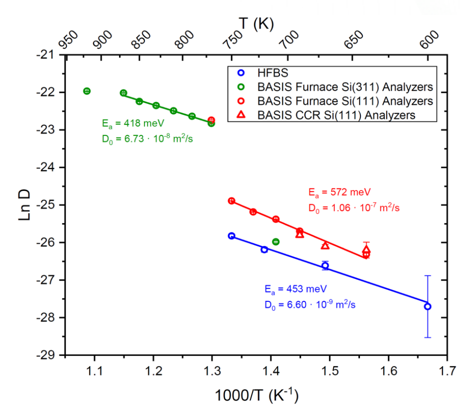






Orthorhombic Phase
D(1)-D(1) and D(2)-D(2) type jumps

Hexagonal Phase
D(1)-D(2) type jumps



Different hydrogen sites produce distinct vibrational modes

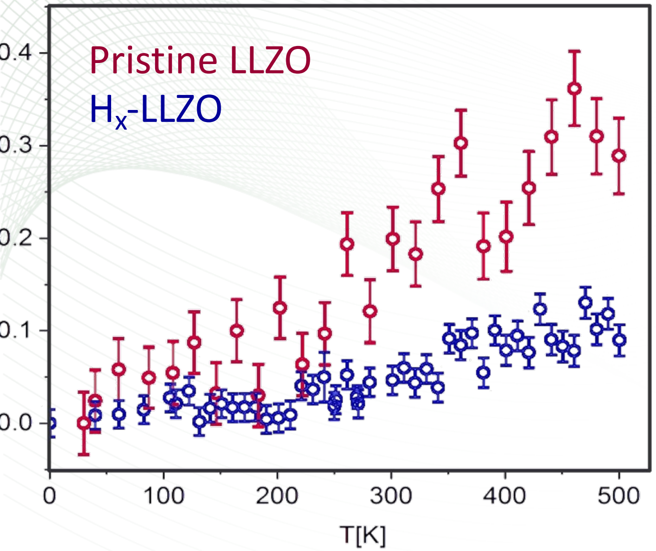
Softening of modes

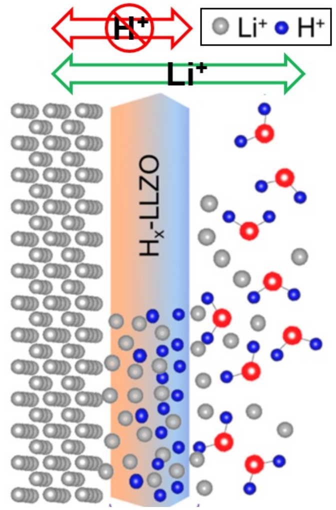
H(1) and H(2) behave similarly with temperature

- Modes merge with background at 600 K
  - Hydrogen releases and begins diffusing
  - Same temperature as onset of observable QENS diffusion

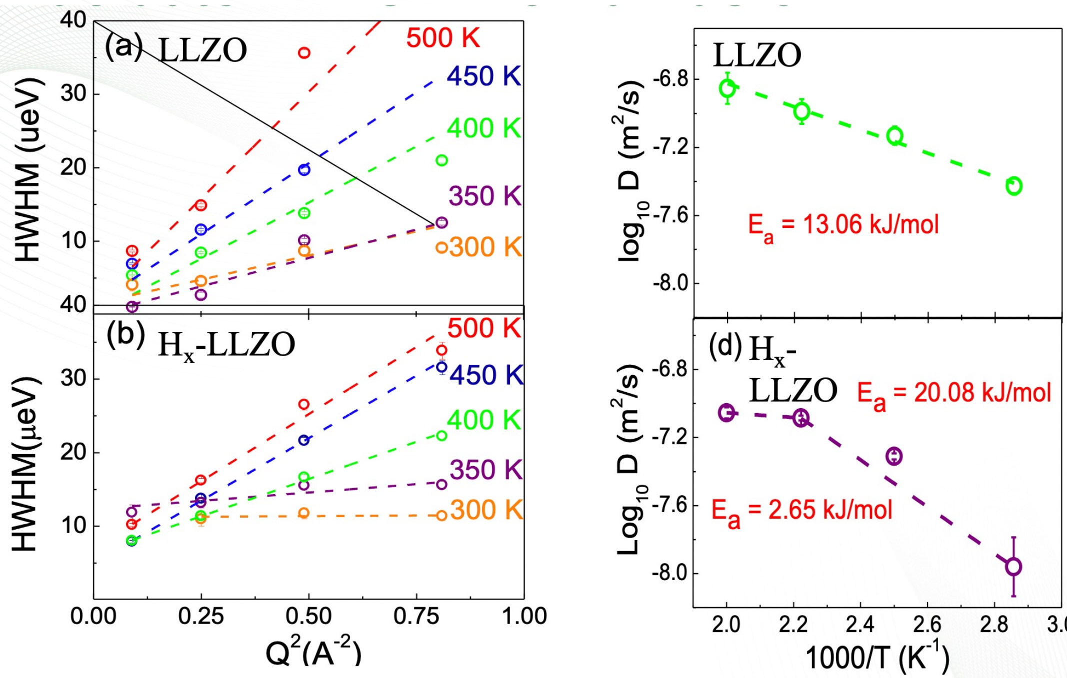
Novak E., *et al. Scientific Reports,* **12,** 6794 (2022).

Science example 4: Elucidate Li^+ vs H^+ ion diffusion





H^+ ions were found to be immobile while Li^+ ion maintained a desired mobility in the solid electrolyte $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$

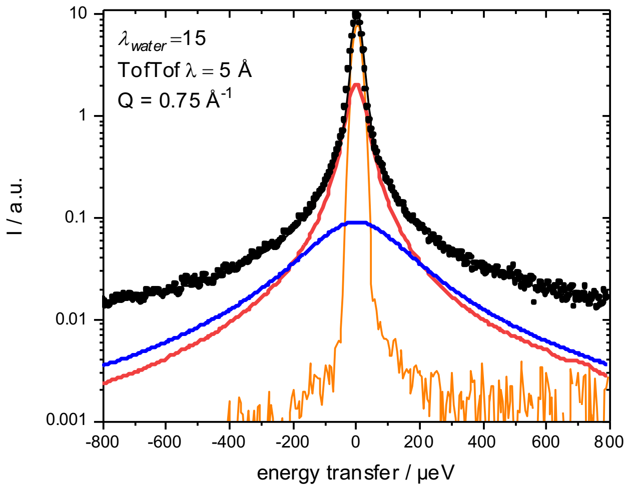


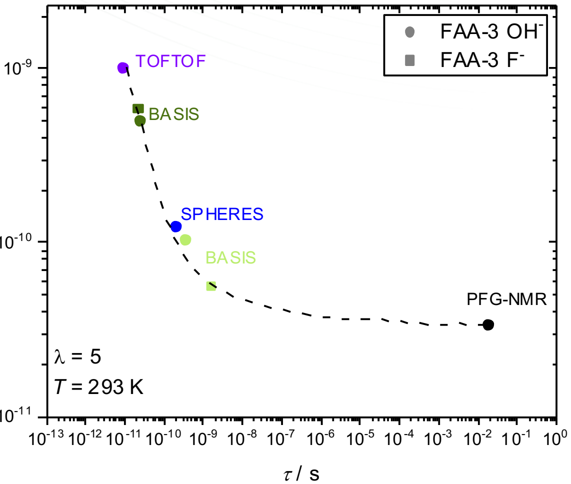
- ❑ Li+ ions show good ion mobility in the structure, the H+ ions are immobile at RT.
- ❑ Inactivity of H+ ions should contribute to the interfacial stability of LLZO being used as a protection layer for Li-metal in aqueous Li batteries.
- ❑ This work provides a new method to probe diffusion behavior of different ions in solids that contain multiple mobile ion species

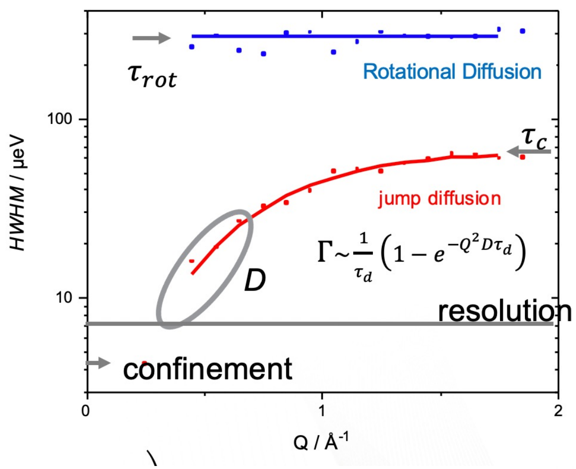
Xiaoming Liu, *et al*, *Energy & Environmental Science*, **12,** 3, 945-951 (2019).

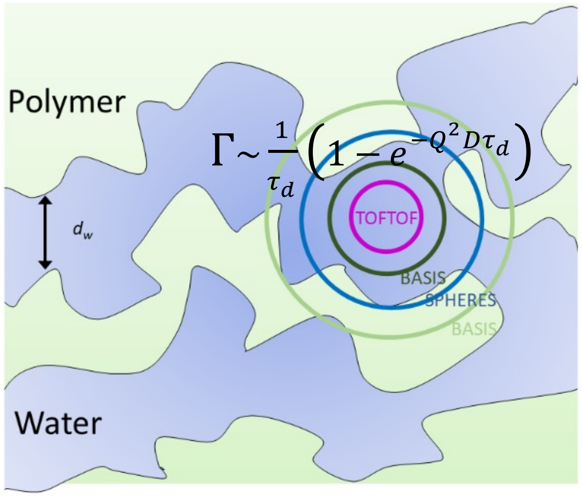
Science Example 5: Water Dynamics in Anion Exchange Membranes

- Ionic conductivity and water transport are key properties for applications
  - Depends on water content
- Water transport in AEM multiscale problem
  - Investigation of transport in multiple time- and length scales for structure – function insight







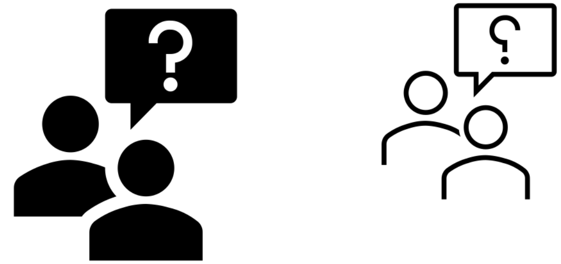


J. Melchior, *et al*, Journal of Membrane Science 586, Pages 240-247 (2019)

Summary:

- QENS is a unique technique to measure diffusive dynamics providing exclusive information about the geometry of the diffusion
  - accessible through Q-dependence
  - Large range of time scales available depending of the selected QENS instrument (sub-picosecond < t < nanosecond (μsec for NSE)
  - Hydrogen sensitivity
- Instrument selection is a critical decision
  - resolution to match the time scale of the diffusion process
  - Q range to match the diffusion length scale
- Suitable technique to study dynamics in large variety of materials and science problems.

- Questions?



- Literature:
  - Quasielastic Neutron Scattering, M. Bee (Bristol, Adam Hilger, 1988).
  - Quasielastic Neutron Scattering and Solid State Diffusion, R. Hempelmann (2000).

NXS Lecture - Niina Jalarvo:
“Quasi-elastic Neutron Scattering”