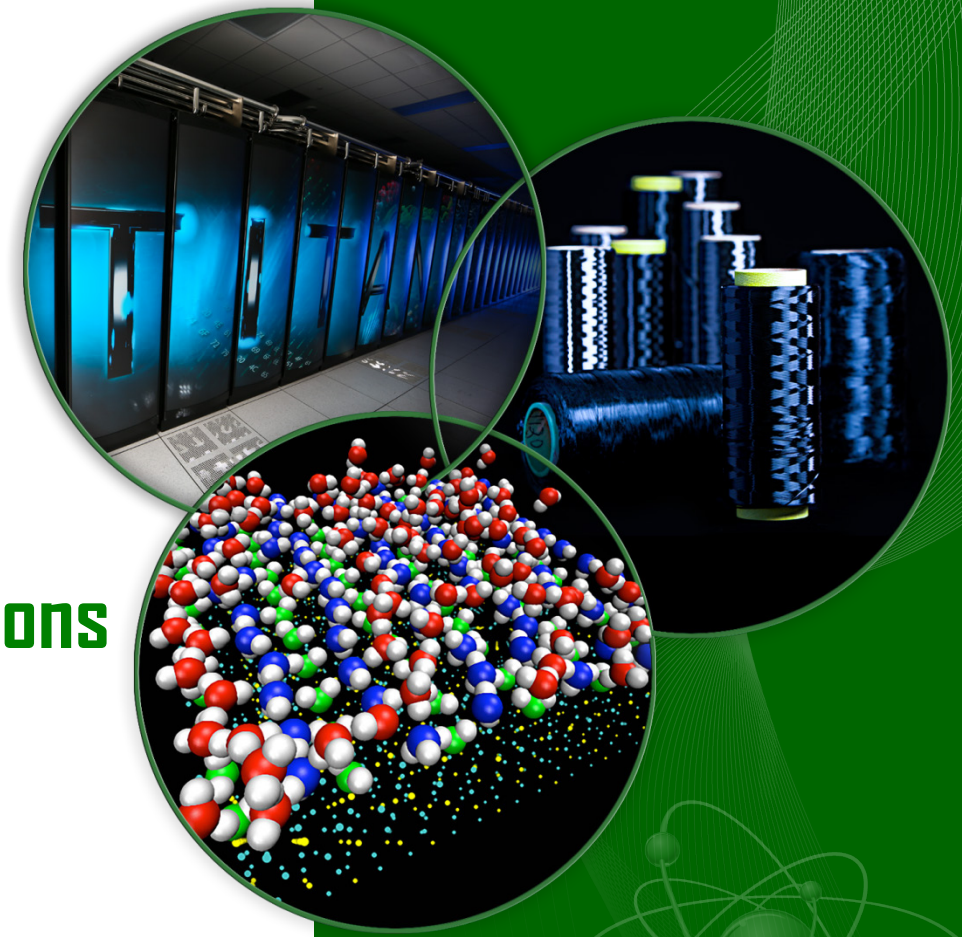
Modeling of Quasi Elastic Neutron Scattering with Molecular Dynamics Simulations



The neutron lifecycle talks

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ORNL is managed by UT-Battelle
for the US Department of Energy

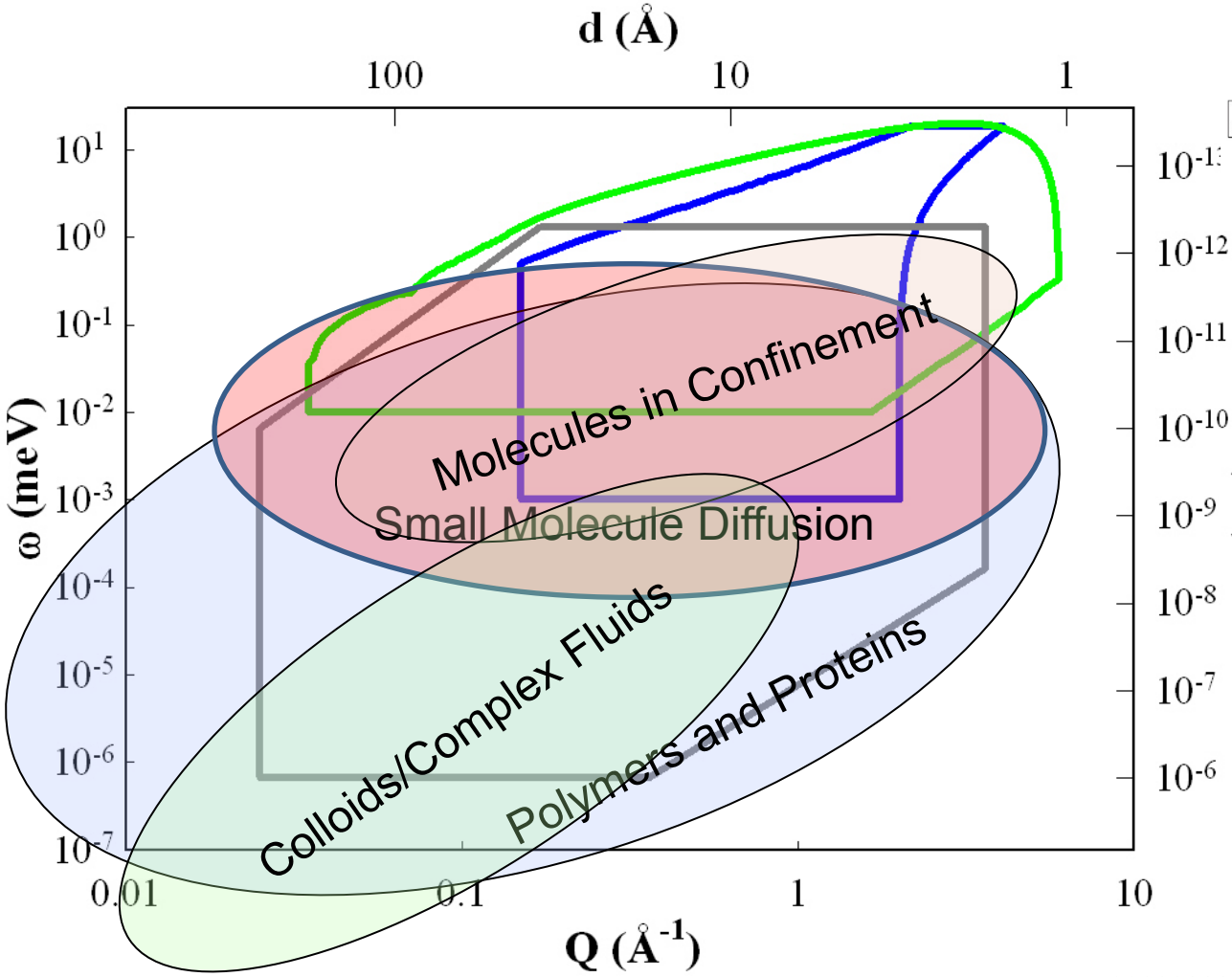
OAK RIDGE National Laboratory

Overview

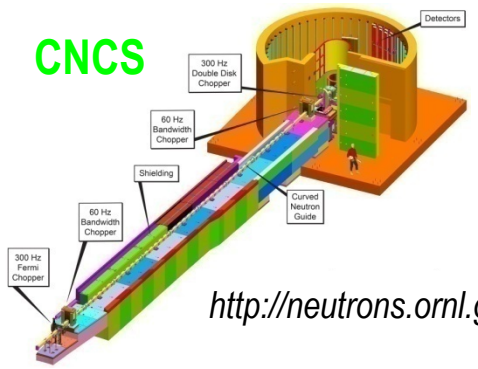
- Spectrometers at SNS measuring Quasi Elastic Neutron Scattering
- What is Quasi Elastic Neutron Scattering ?
- Connection with classical self-diffusion and molecular dynamics simulations
- Simulations complementing experiments
- Experiments refining a simulation force-field

Spectrometers at SNS measuring QENS

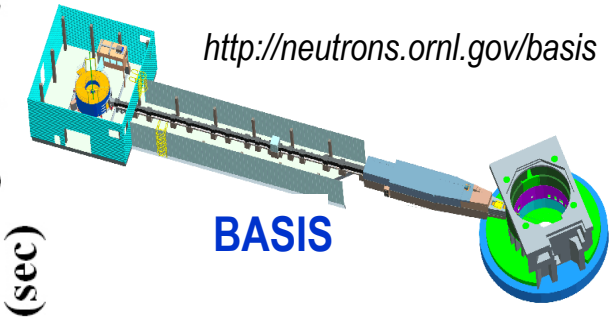
QENS Spectrometers at SNS



CNCS

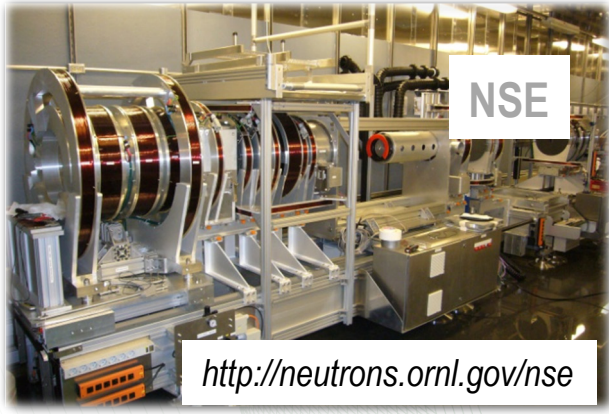


http://neutrons.ornl.gov/cncs



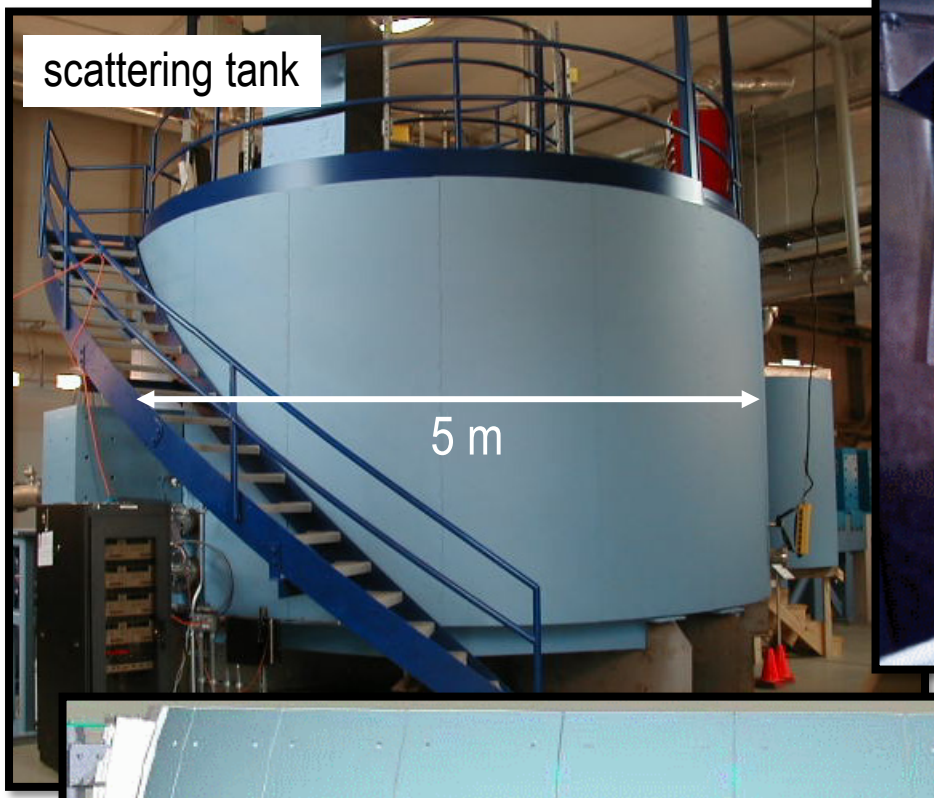
http://neutrons.ornl.gov/basis

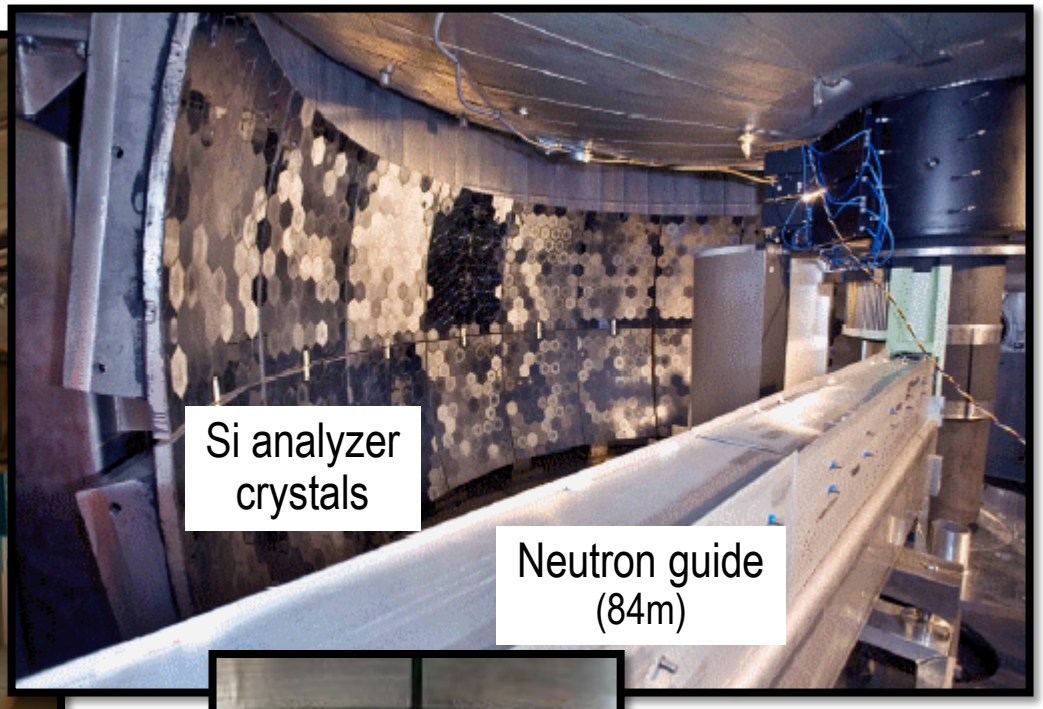
BASIS

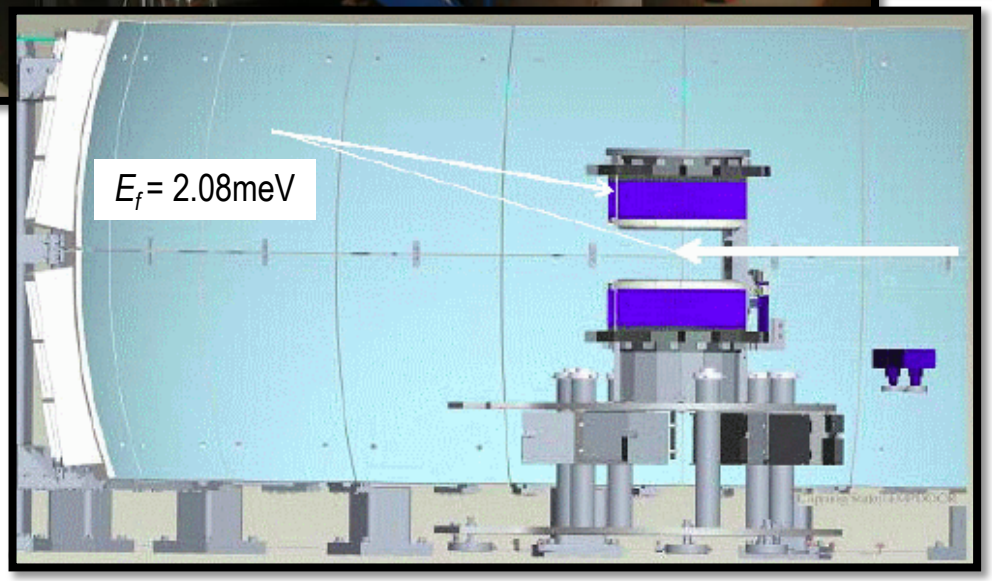


http://neutrons.ornl.gov/nse

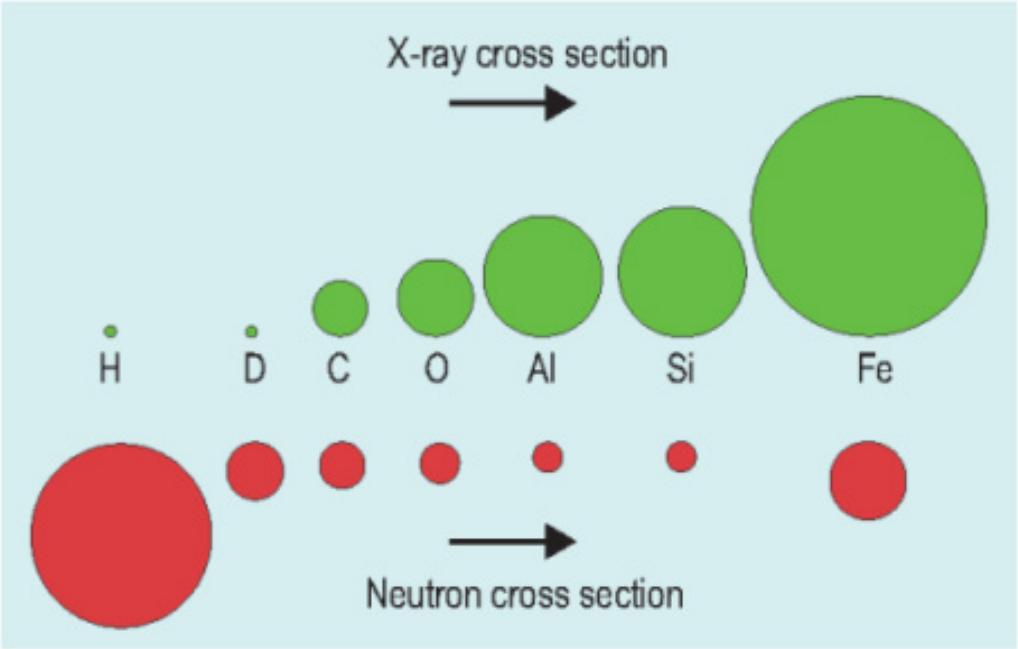
BASIS – Backscattering Spectrometer







QENS is most sensitive to Hydrogen

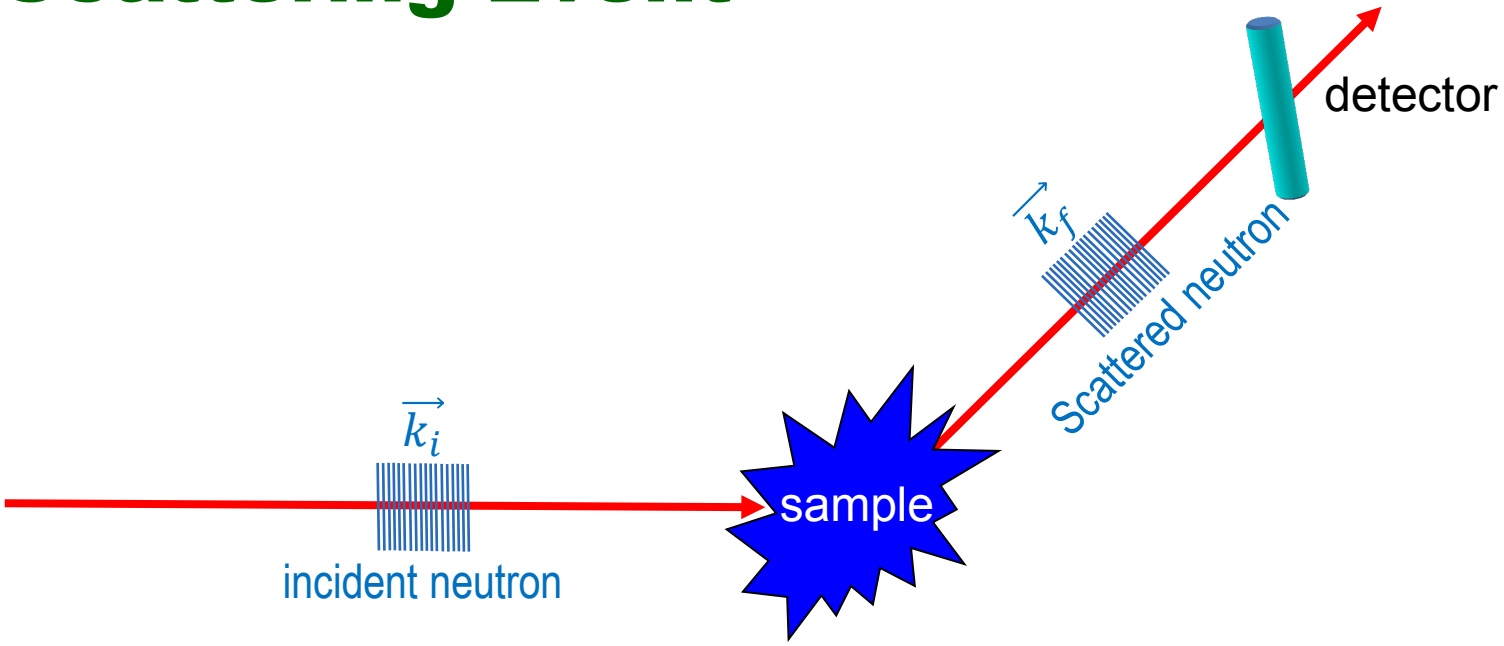


Materials rich in hydrogen?

- Water!
- Biological molecules (proteins, DNA, RNA, drugs,...)
- Polymers
- Porous materials storing hydrogen fuel

What is QENS ?

The Scattering Event



Momentum transfer $\vec{Q} = \vec{k_i} - \vec{k_f}$

Energy transfer $E = K_i - K_f$

Elastic: $E = 0$

Quasi elastic: $E \ll K_i$

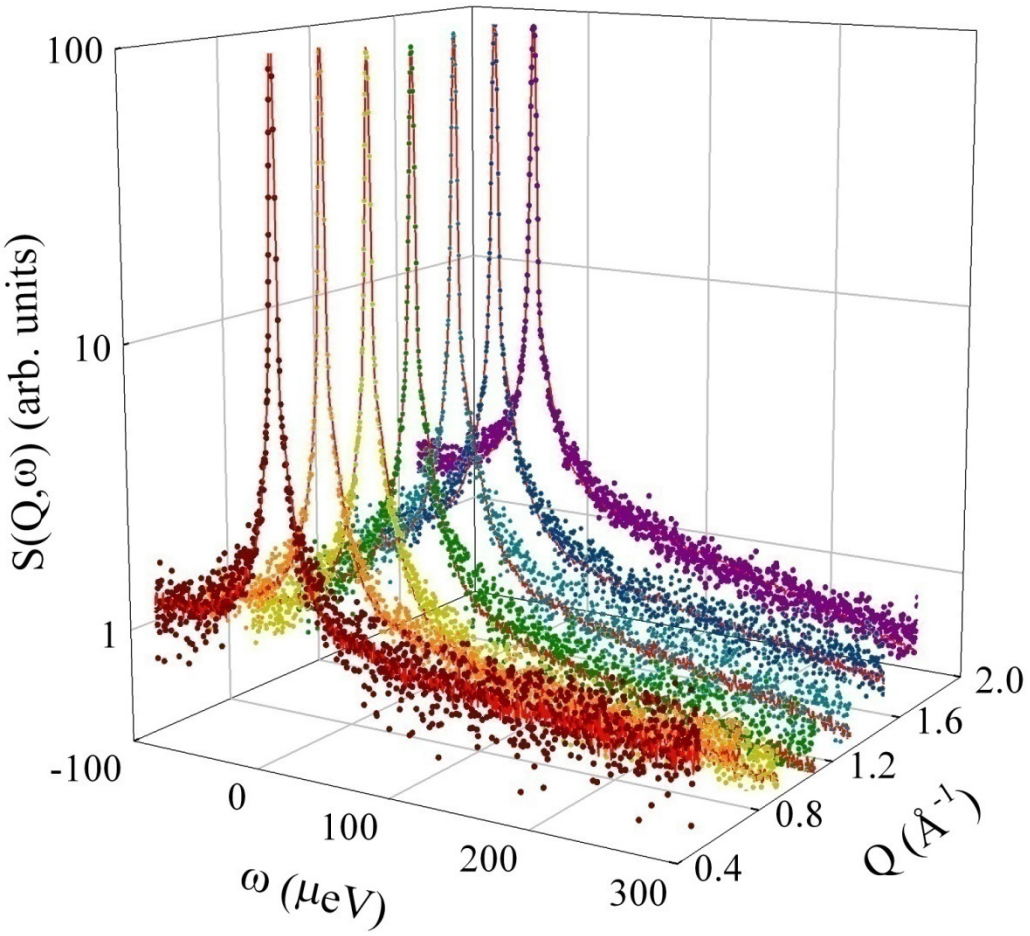
Inelastic: $E \geq K_i$

Quasi elastic means “almost elastic collision”

Typical QENS Spectra

Intensity is presented as:

- Energy dependent ($E = \hbar\omega$)
- Sliced in momentum transfer Q

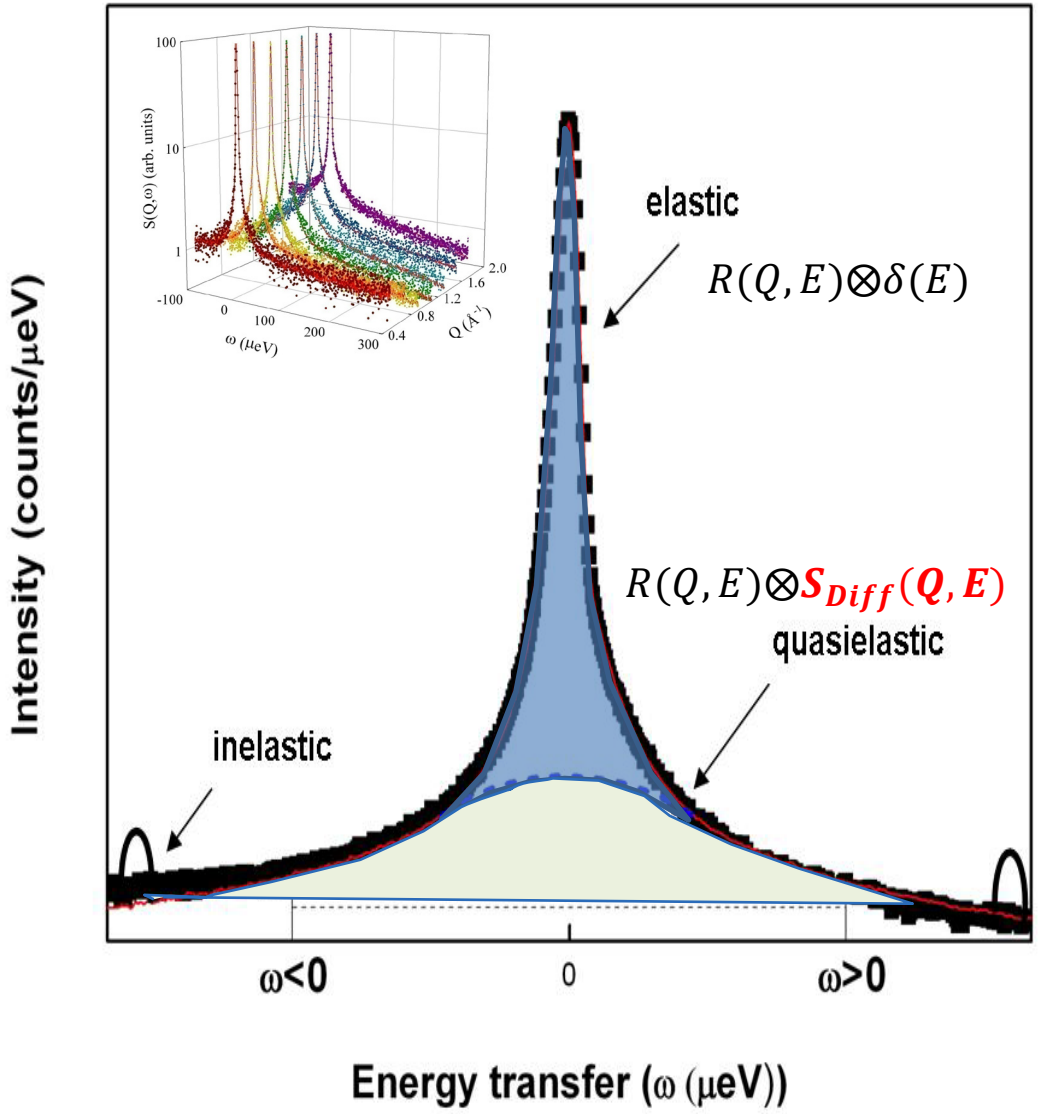


The Shape of the QENS Peak

Two contributions shape the peak:

1. **elastic scattering**
2. **self-diffusion**

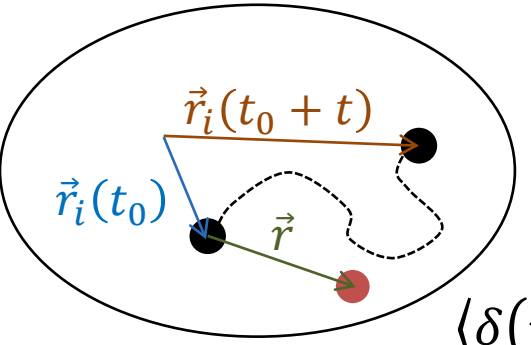
Goal: extricate the self-diffusion term



The *broadening* of the peak contains the information about diffusion in the sample

Connection with classical self-diffusion and simulations

From Diffusion to QENS spectra



What is the probability of finding classical particle ***i*** at position $\vec{r}_i(t_0) + \vec{r}$ at time $t_0 + t$ if the particle was at position $\vec{r}_i(t_0)$ at time t_0?

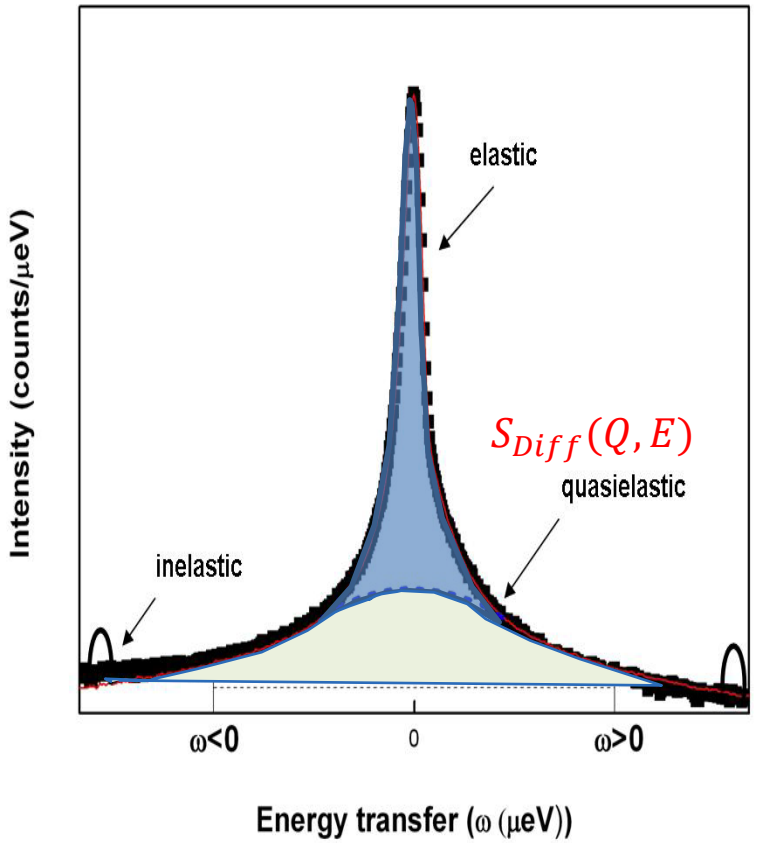
$$\left\langle \delta\left(\vec{r} + \vec{r}_i(t_0) - \vec{r}_i(t_0+t)\right)\right\rangle_{t_0}$$

Fourier ⇩ *transform* ($\vec{r} \rightarrow \vec{Q}$)

$$I(Q,t) = \left\langle \sum_i (b_i{}^{inc})^2 \, e^{i\vec{Q}[\vec{r}_i(t+t_0)-\vec{r}_i(t_0)]} \right\rangle_{t_0,\Omega_{\vec{Q}}}$$

Fourier ⇩ *transform* ($t \rightarrow E$)

$$S_{Diff}(Q,E)$$



We calculate $I(Q,t)$ from the simulations

Simulations complement experiments

Why care about simulations?

We **know**…

where the atoms have been….

where they are now…..

and where they will be.

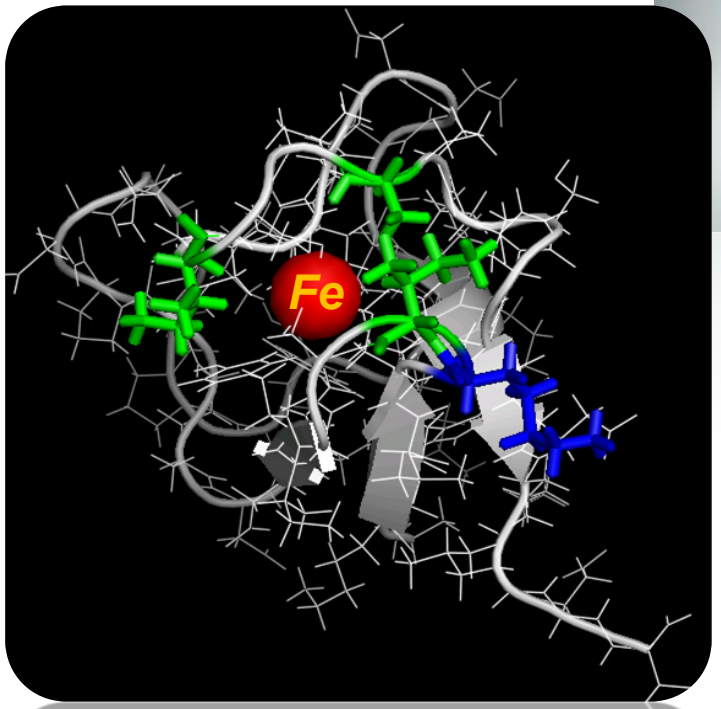
…while QENS data informs on motions **averaged** for all scatterers

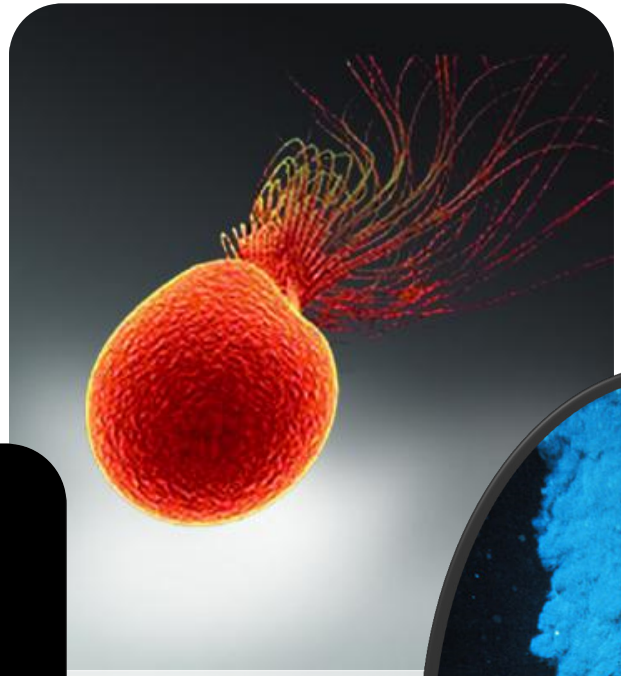
The way to go:

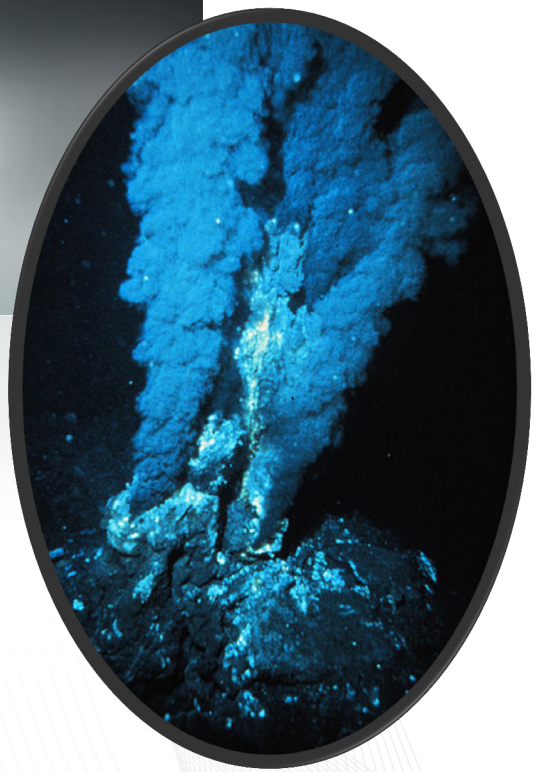
1. First, make sure the simulation produces the same QENS than the experiment
2. Then, go dig deep in the simulation for atomistic details

Thermophilic Rubredoxin

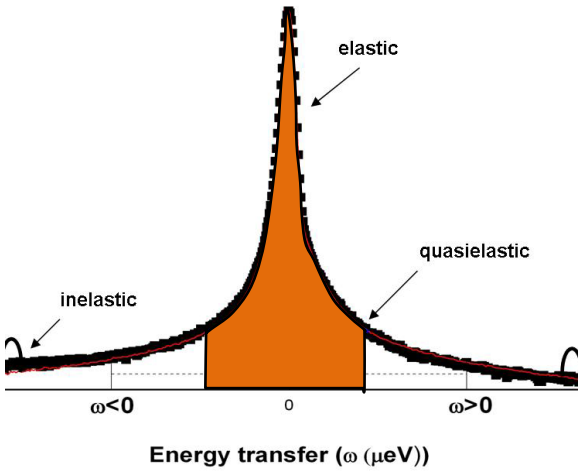
- bacteria found in super-heated deep sea vents
- RdPf – small iron-sulfur protein
  - Electron transfer protein

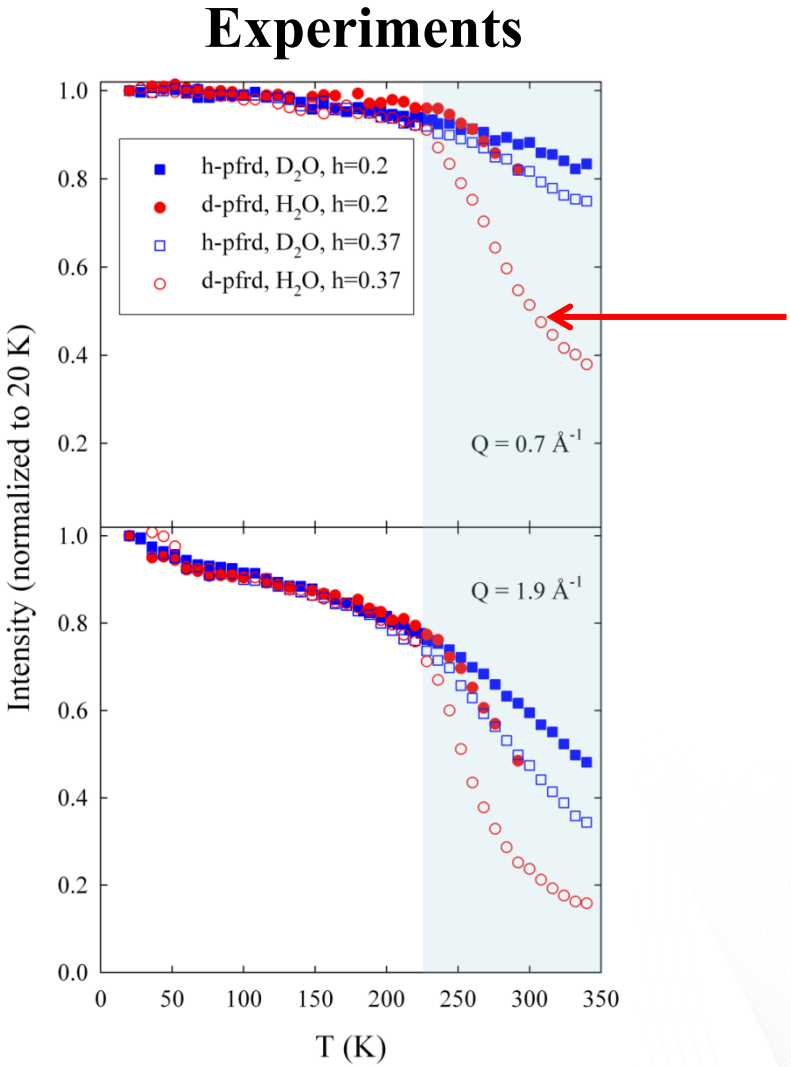






Comparing the area under the Peak



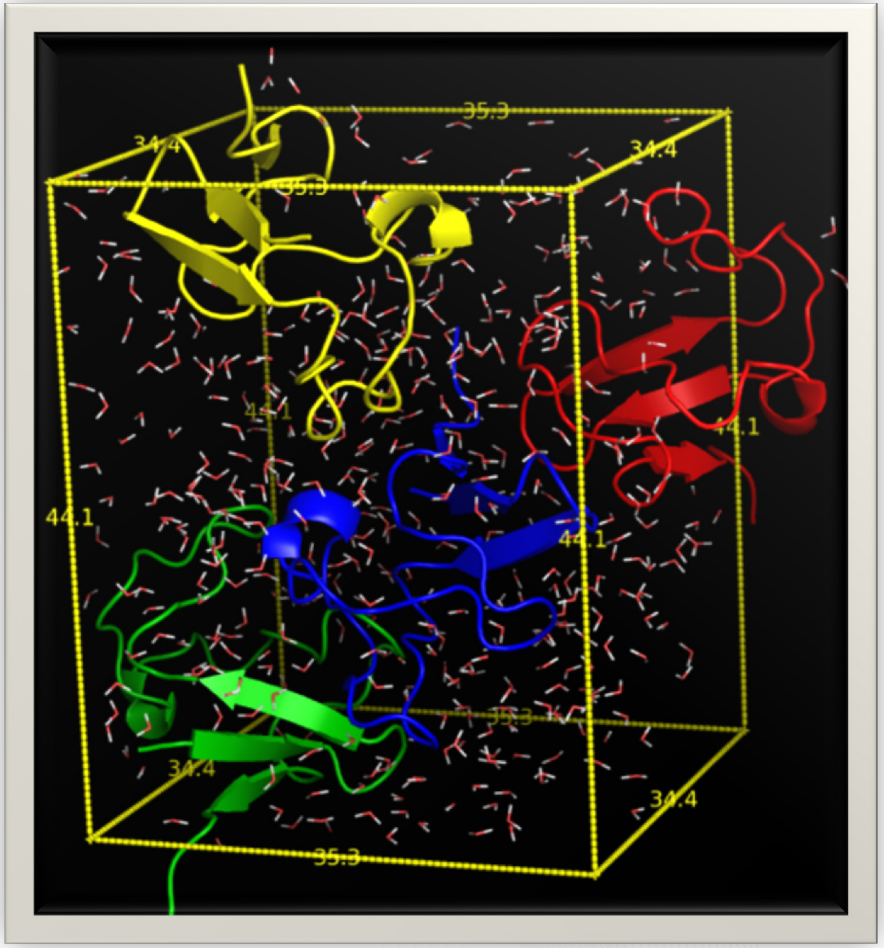


Sudden broadening for T > 220K → Increased mobility related to function?

Constructing the Primitive Cell

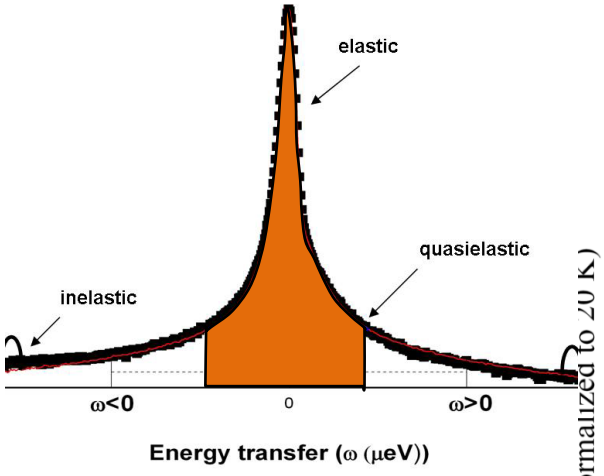
- The sample is a powder composed of micro-crystals

h=0.37 (484 water molecules)

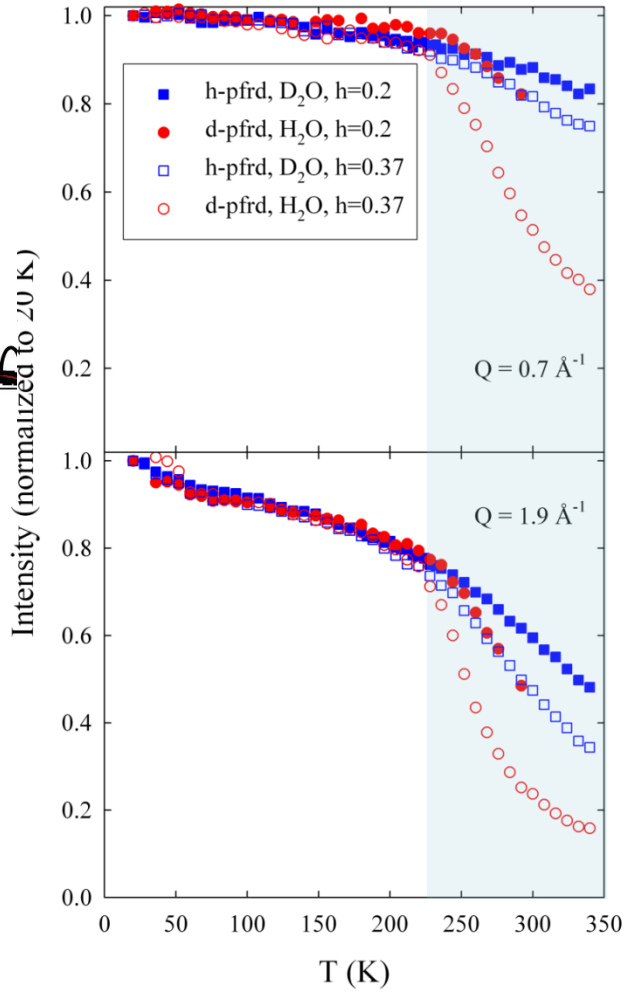


Simulation must mimic the sample and the environment conditions

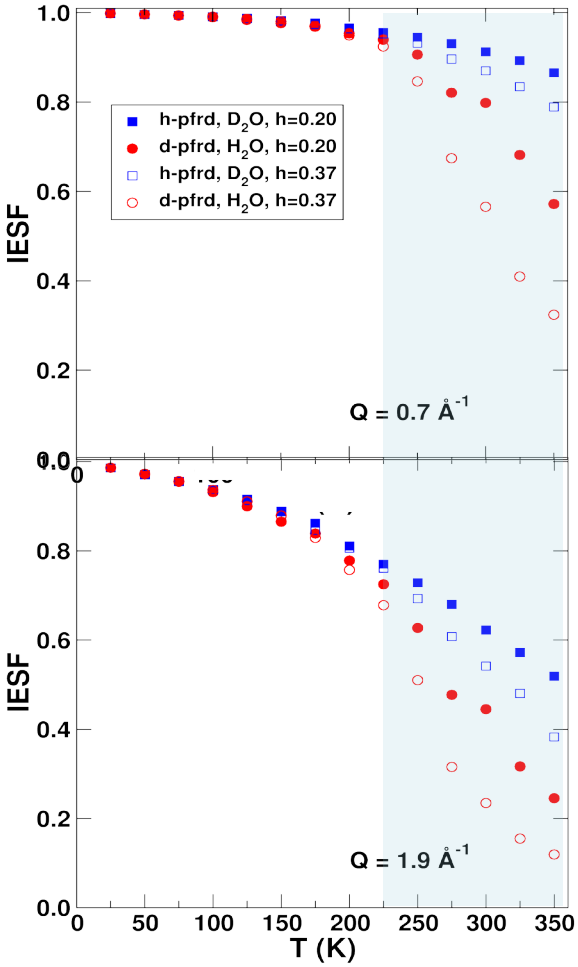
Comparing Experiments and Simulations



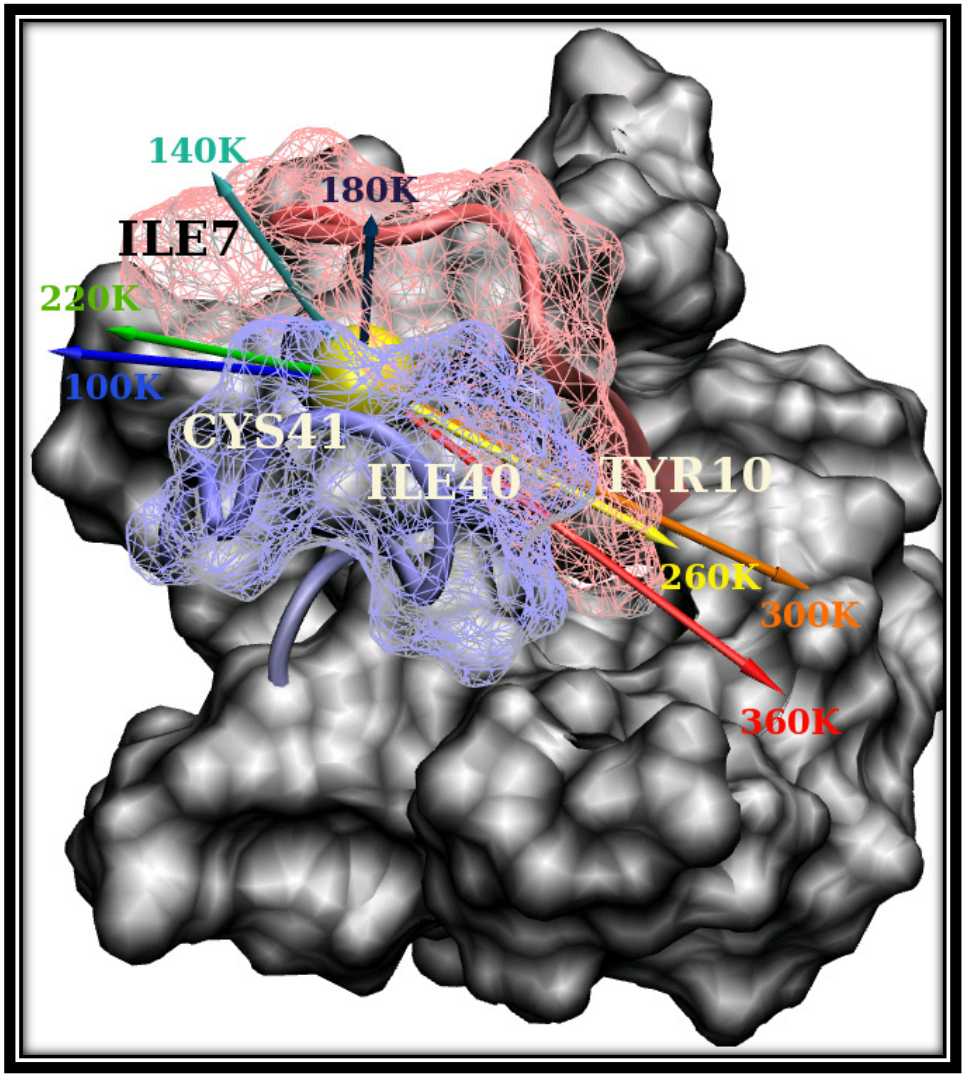
Experiments

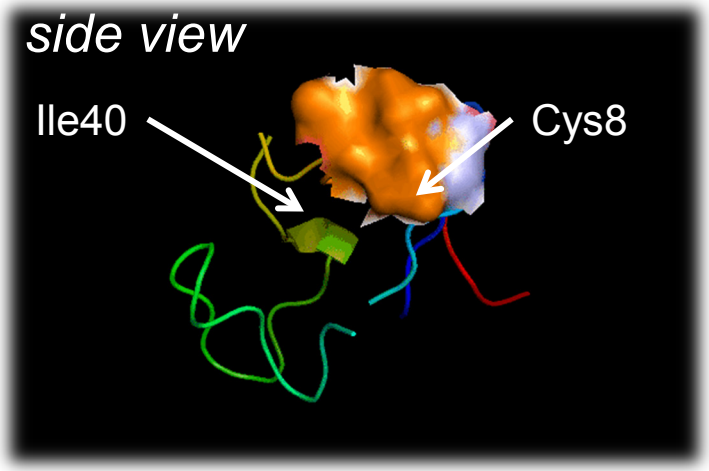


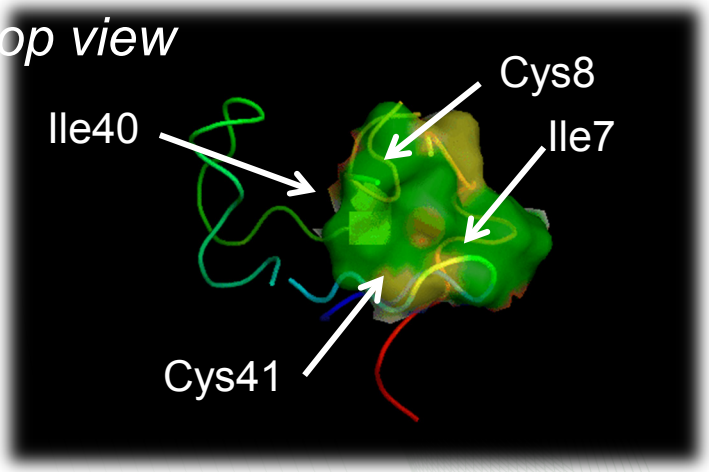
Simulations



Preferential route for Fe oxidation

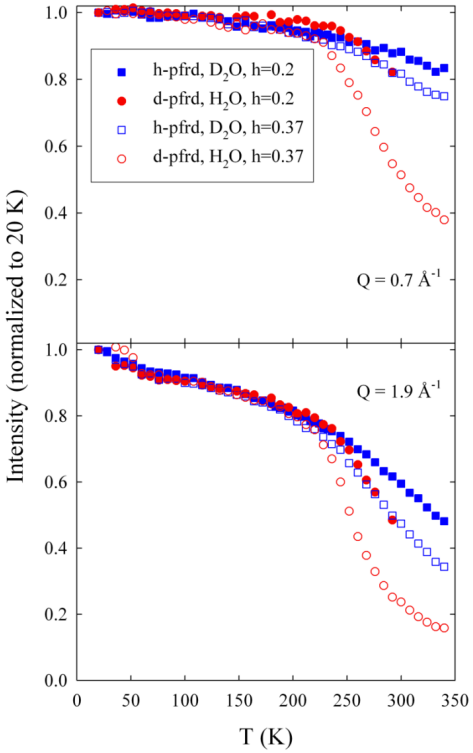


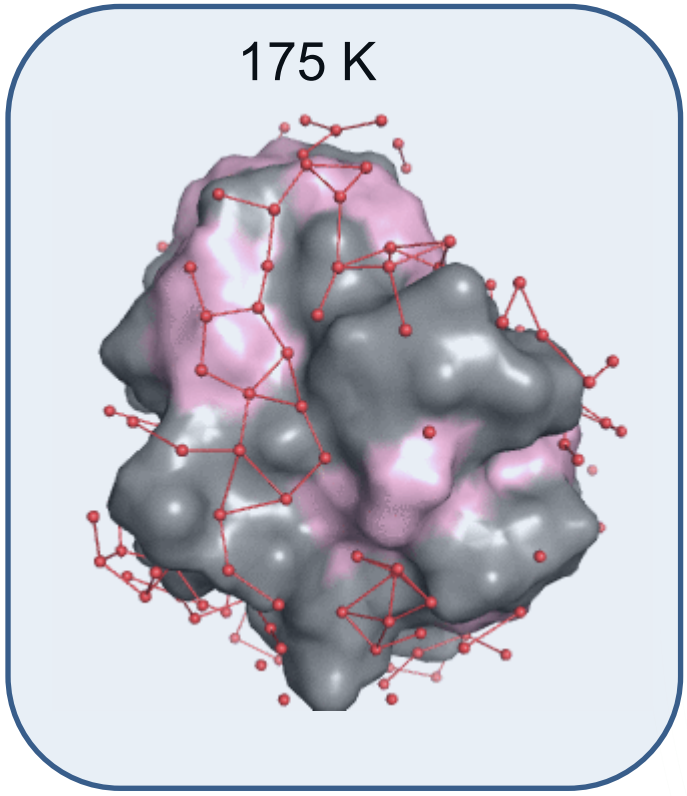


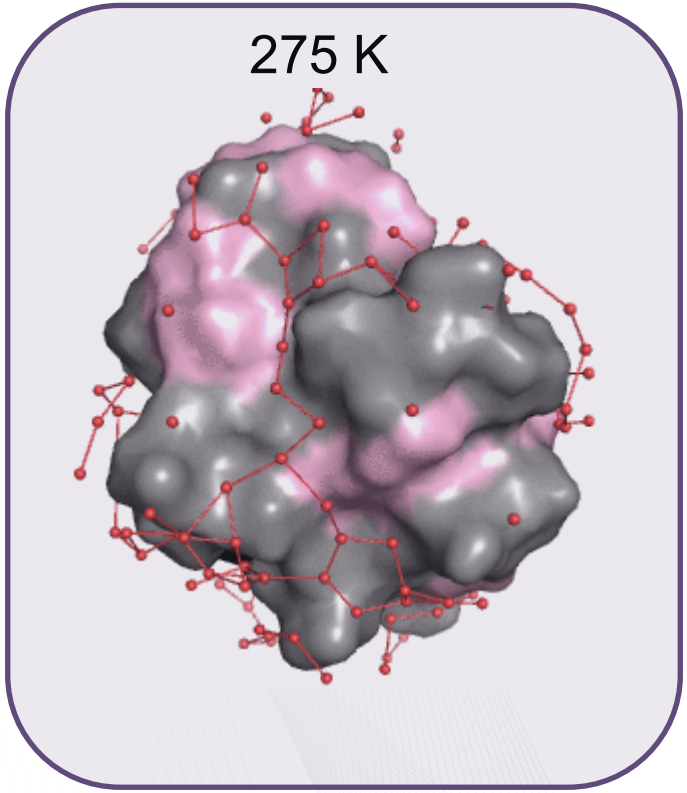


Dynamics of hydrogen bond network

- The rate of formation and breaking of water-water hydrogen bond around the protein is temperature dependent

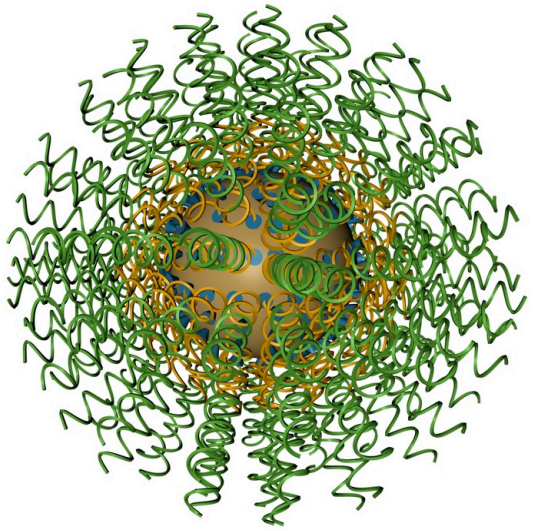






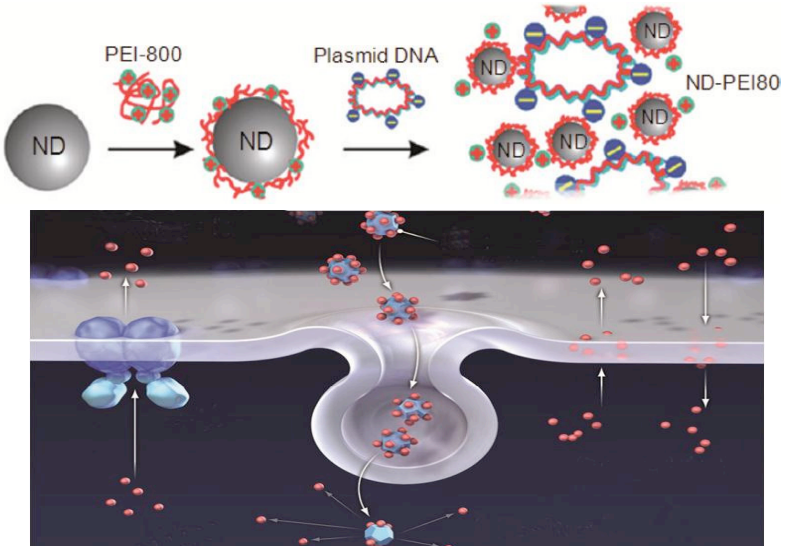
RNA and Nanodiamond Applications

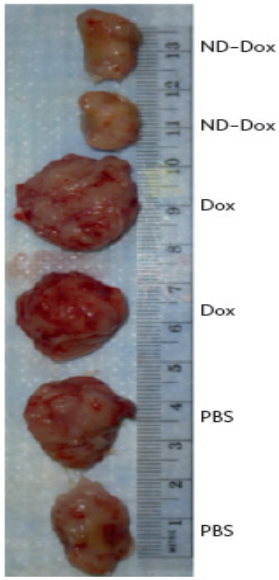
RNA Nanotechnology



[1] S.A. Jensen *et al., Sci. Transl. Med.*, **5**, 209ra152 (2013)
[2] P. Gao, *Nature Nanotech.*, **5**, 833 (2010)

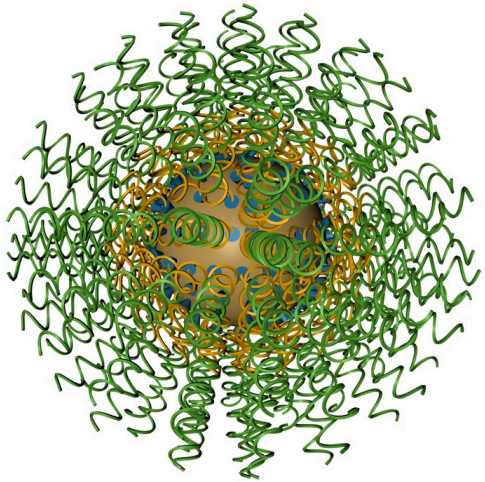
ND Potential Applications





[1] Chow *et al., Sci. Transl. Med.*, **3**, 73ra21 (2011).
[2] Markel *et al., Sci. Transl. Med.*, **3**, 73ps8 (2011).
[3] V. M. Mochalin *et al.*, *Nature Nanotech.*, **7**, 11 (2012)

RNA-ND COMPOSITE CAN GENERATE SIMILAR TECHNOLOGY !!!



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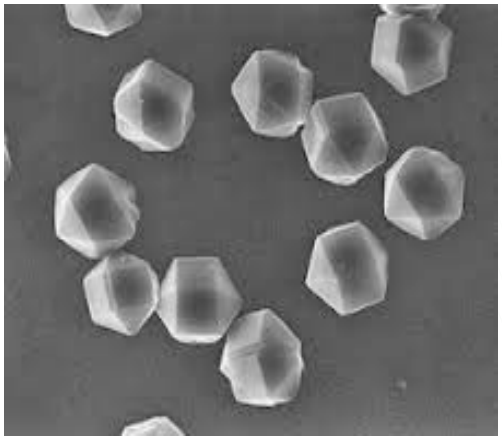
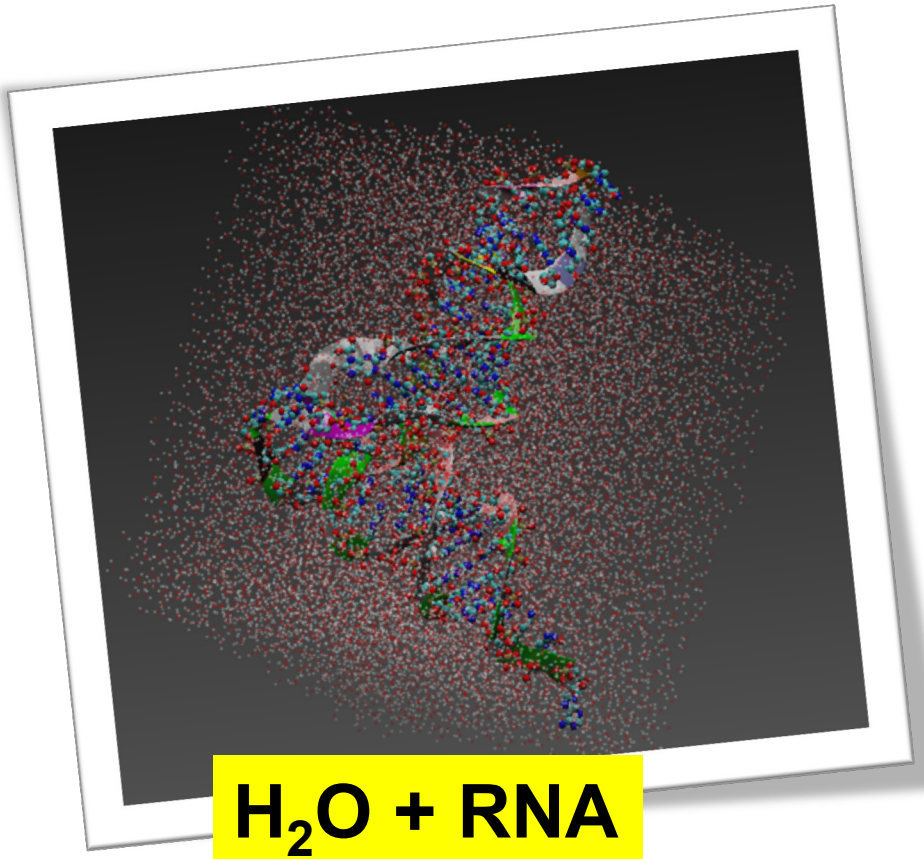
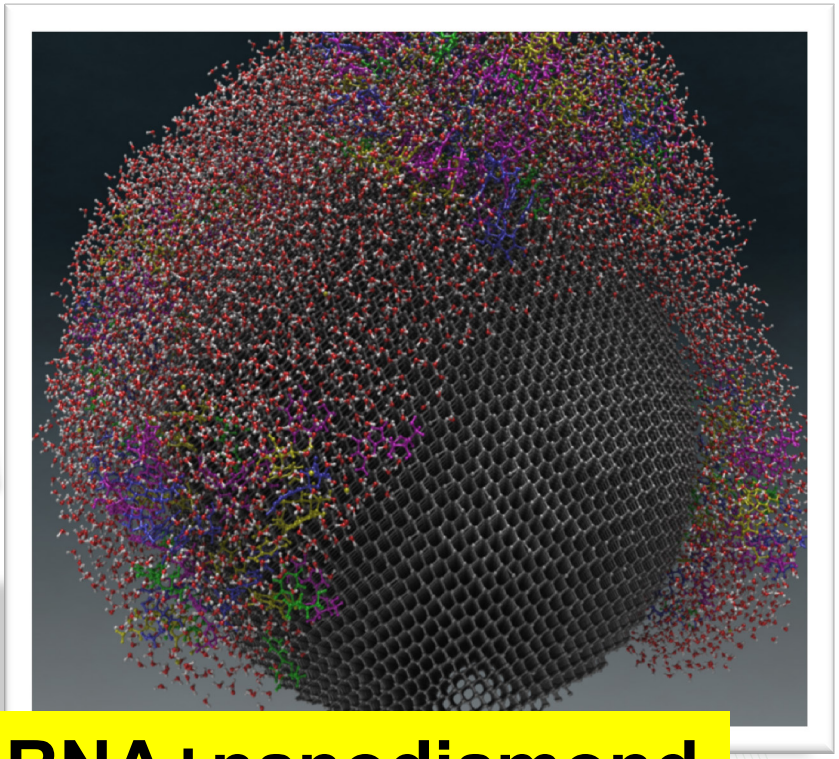


BUT, First we have to understand the fundamental physics ("Dynamics") of RNA+ND composites

Dynamics of RNA adsorbed in Nanodiamond

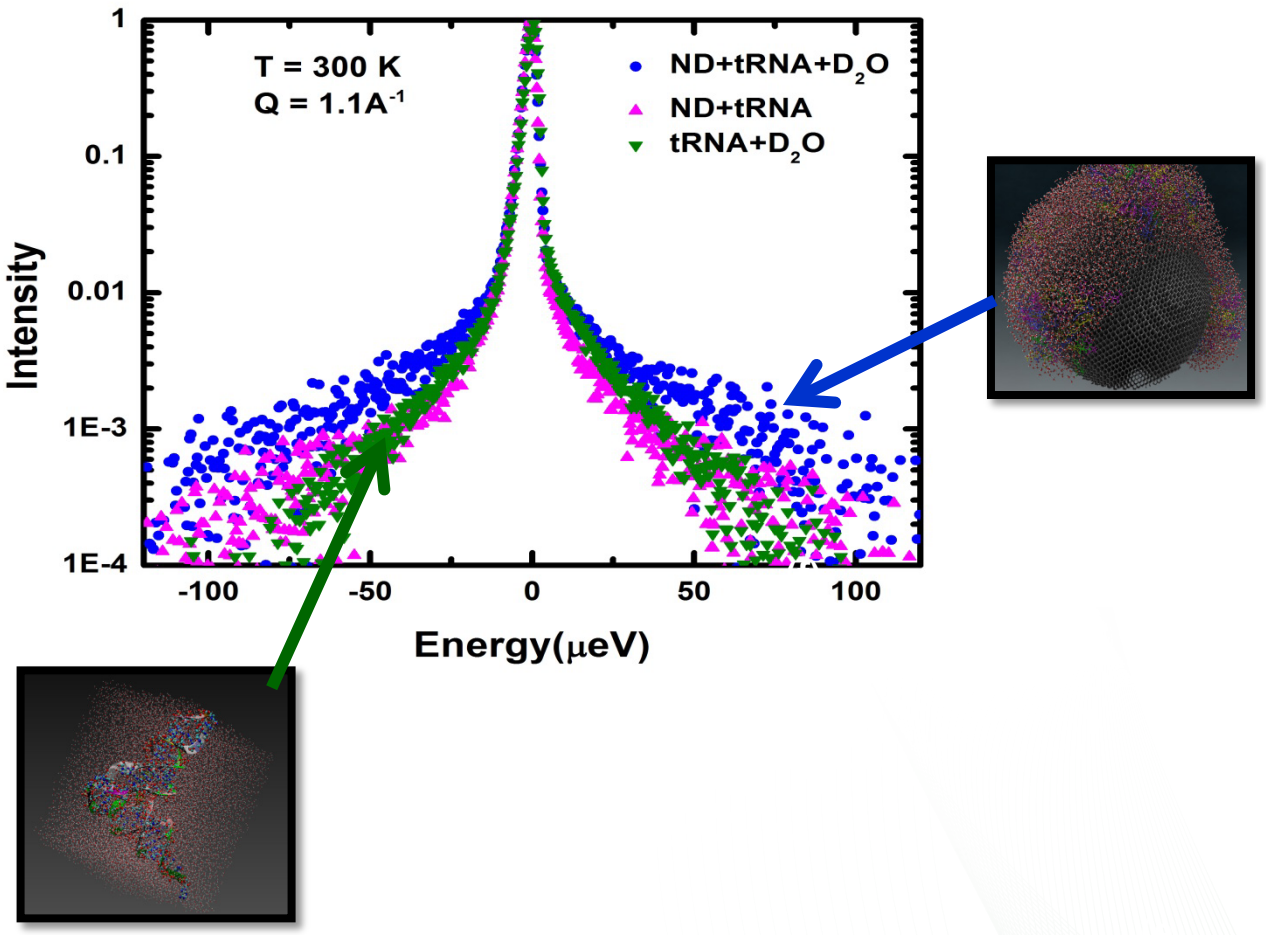


H_2O + RNA



H_2O + RNA+nanodiamond

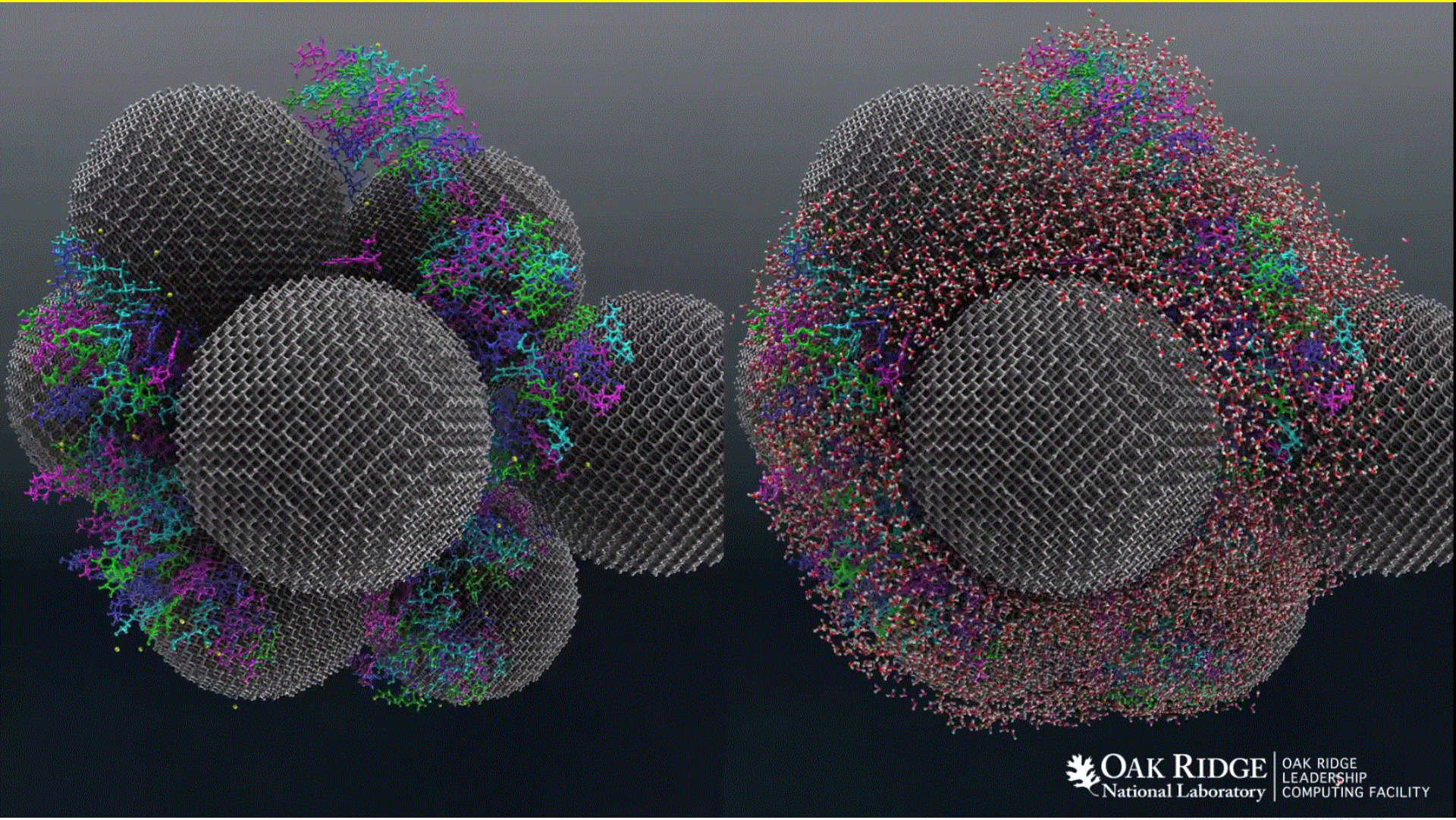
QENS experiments



RNA more mobile in the presence of nanodiamonds…why?

MD Simulations

Simulation must mimic the sample and the environment conditions



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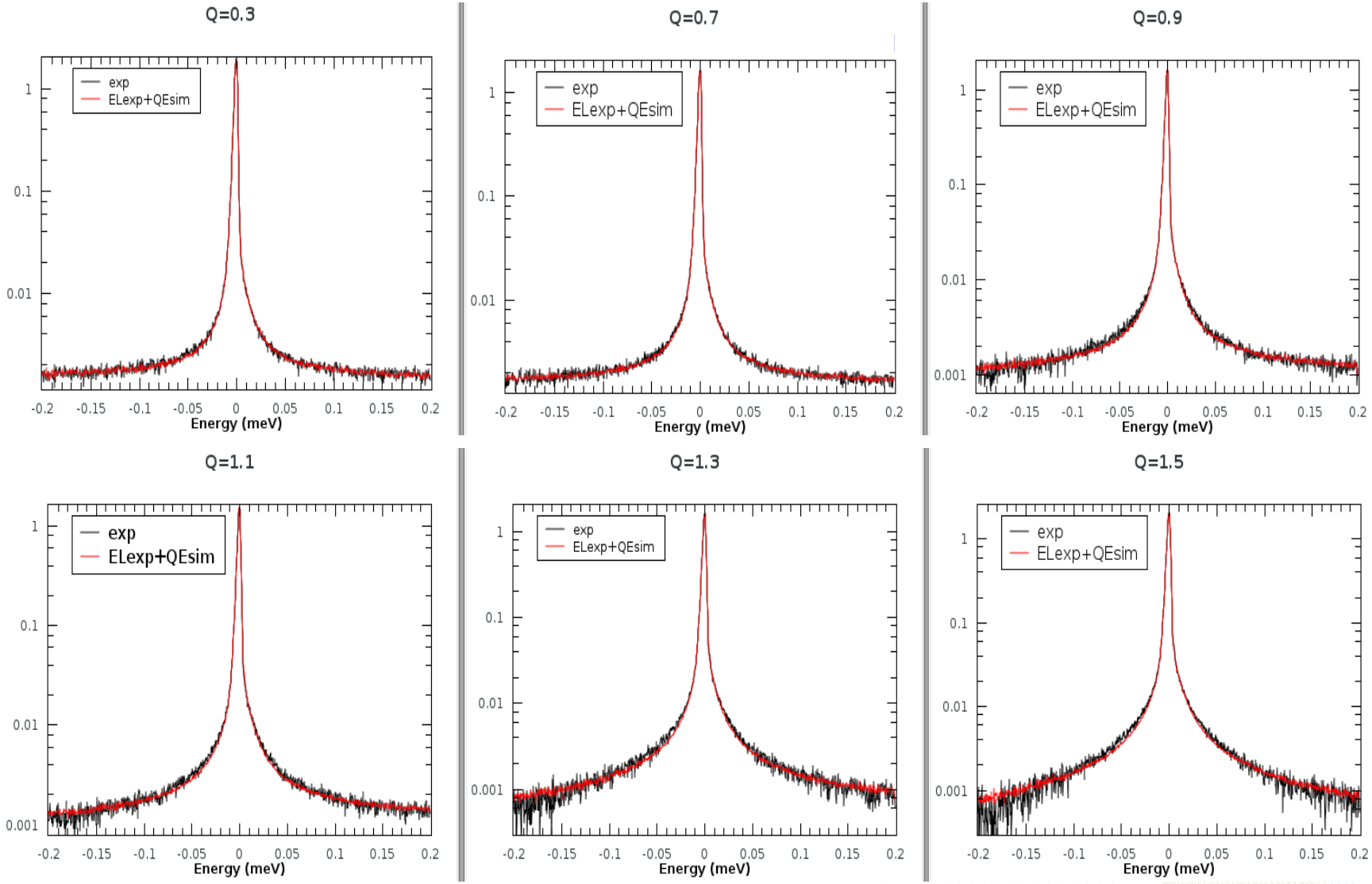
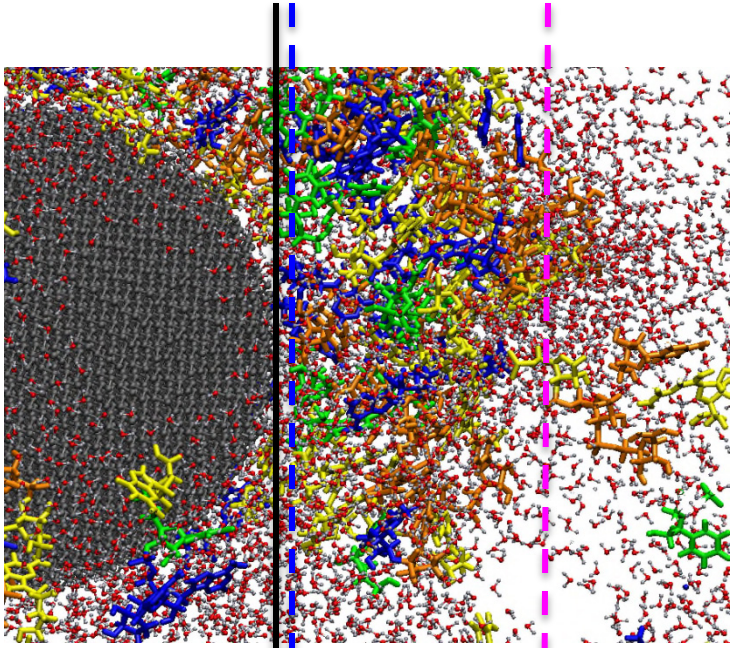
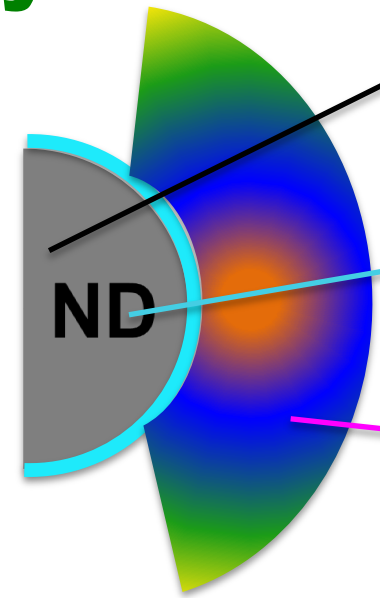


Atomistic Structural Analysis



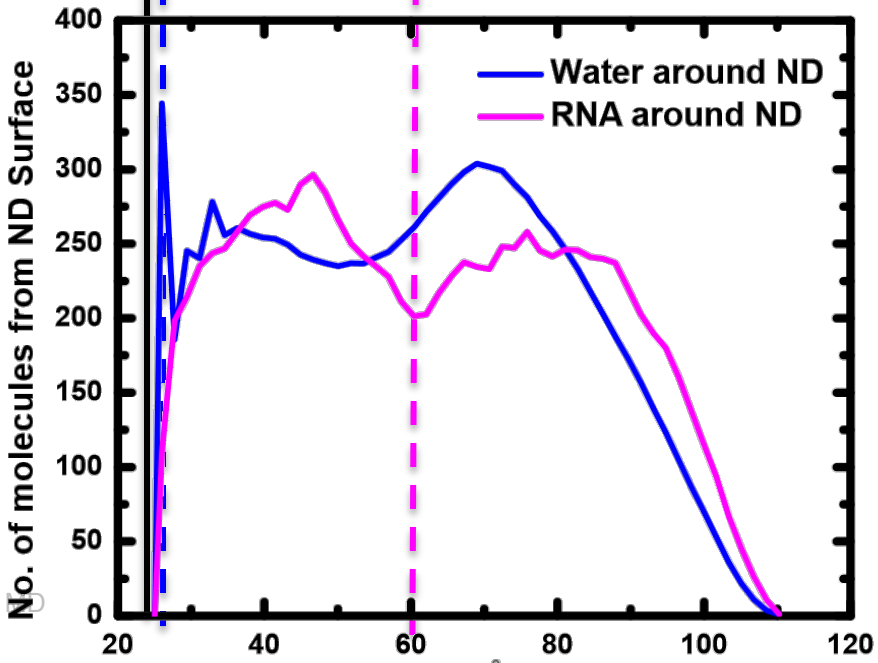
CARTOON



ND
25 Å

Water
1 Å

RNA and
Water 34 Å



Water forms interfacial layer

Enhanced aqueous environment with ND:

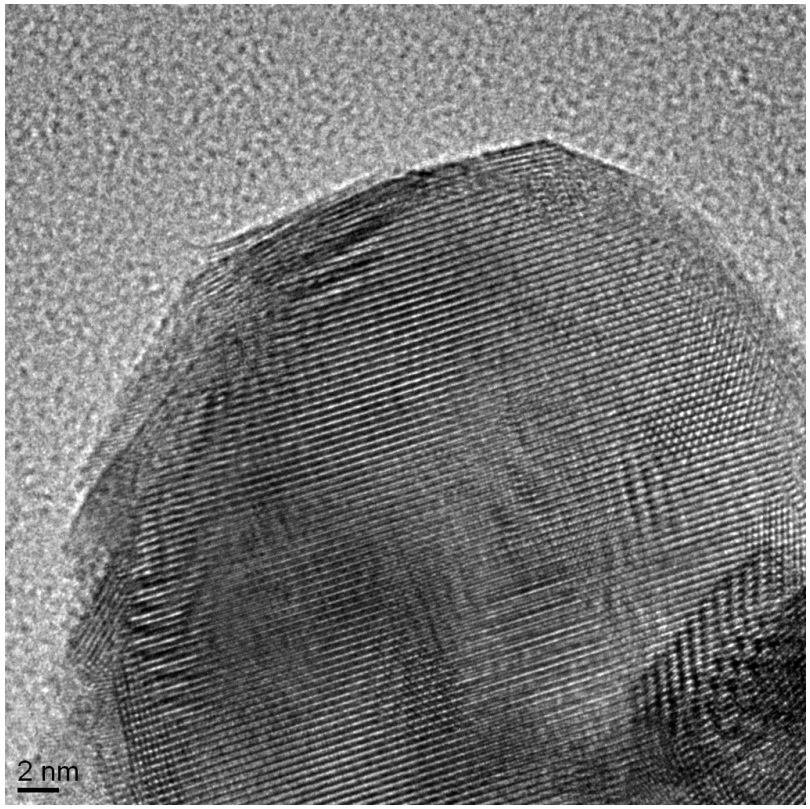
With ND	Without ND
43.56 Å	28.61 Å

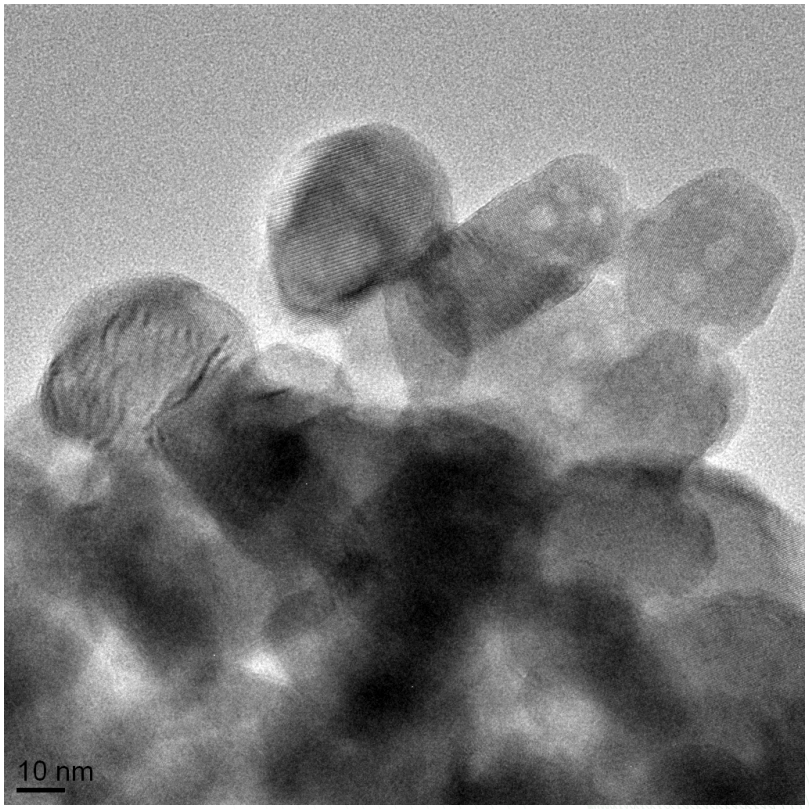
Swollen RNA with ND.

Water Exchange on a Mineral Surface

- Barite ($BaSO_4$) nanoparticles
- Water exchange rates may limit the rate of the mineral surface

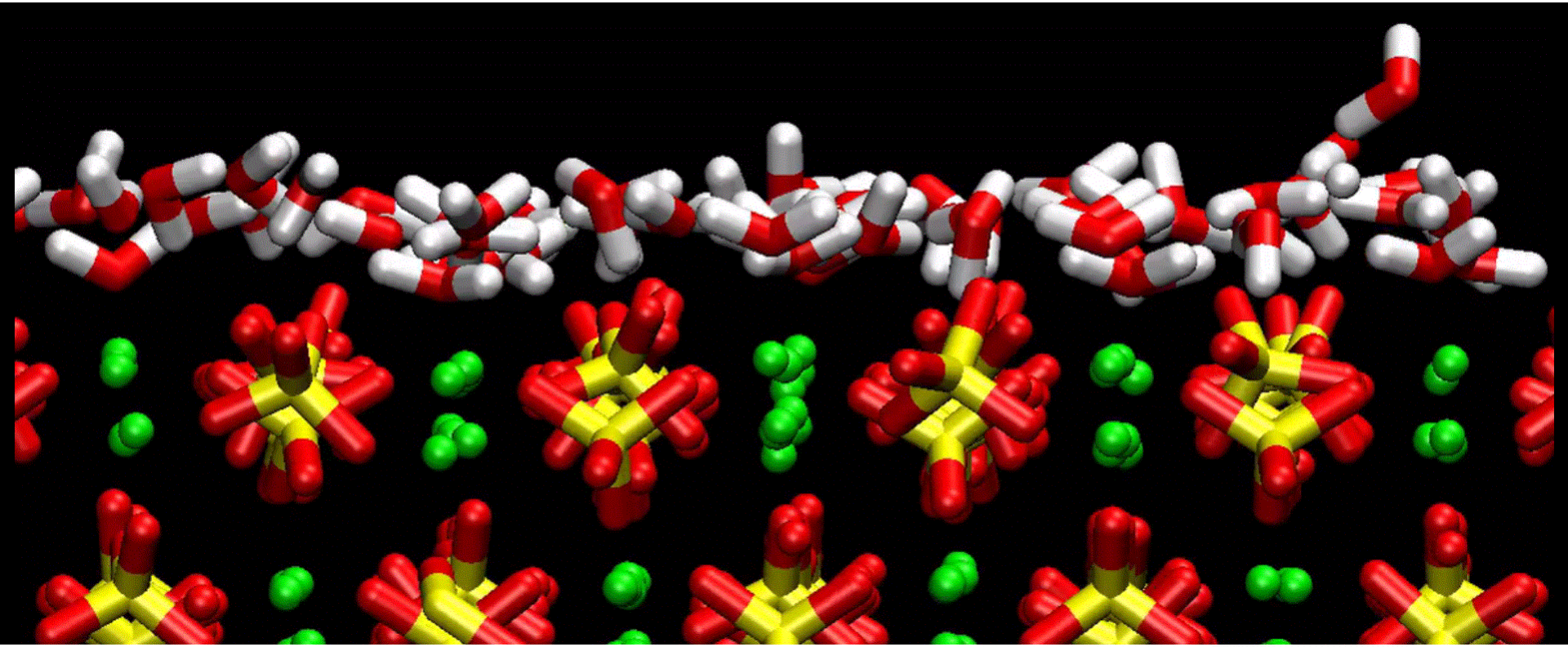
How long does water stay bound to the mineral surface? → Water dynamics



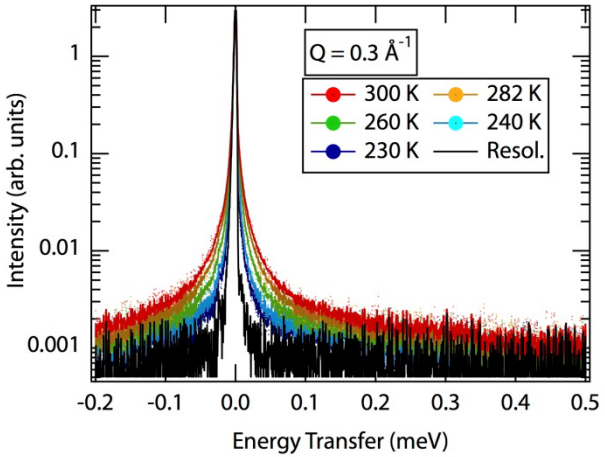


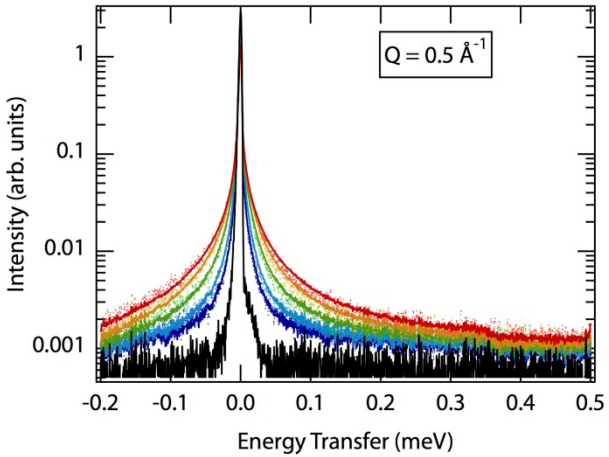
Simulation of water near Barite surface

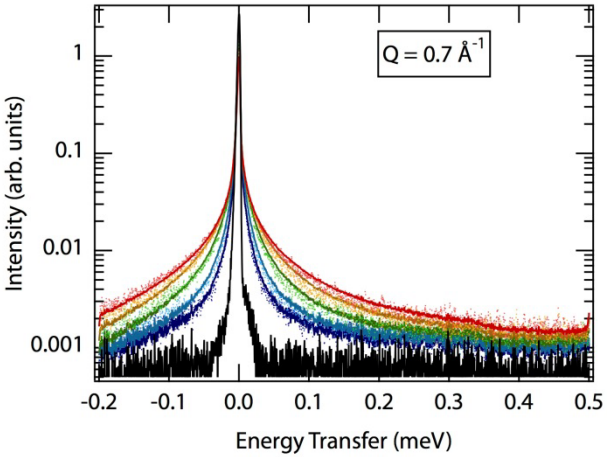
Simulation must mimic the sample and the environment conditions

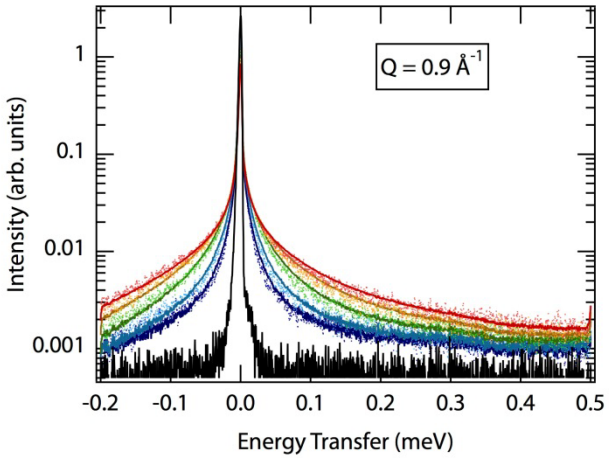


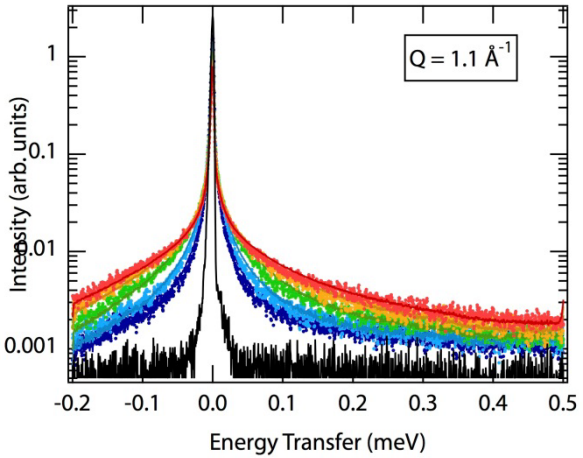
Comparing Experiments and Simulations





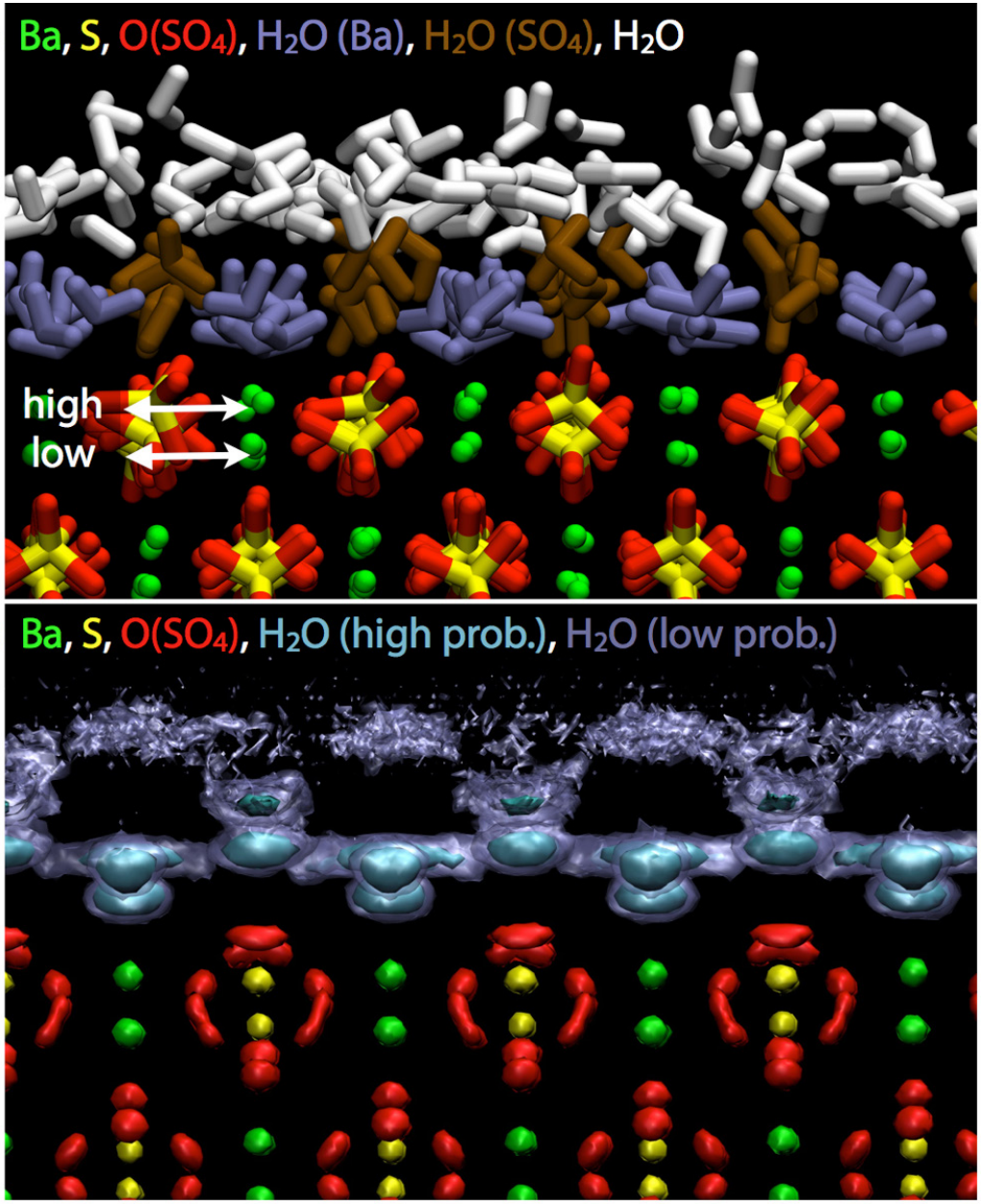




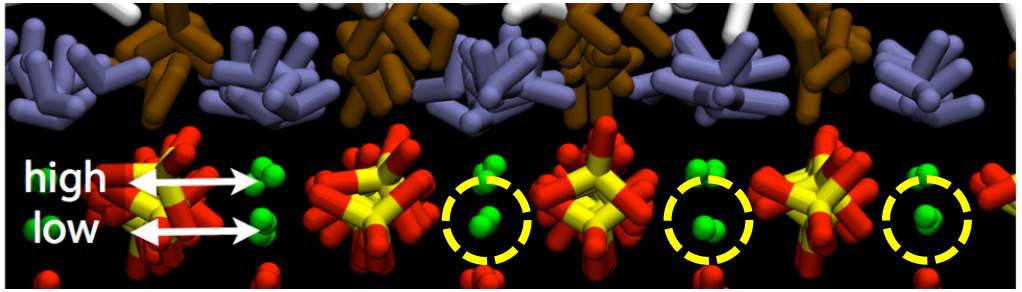


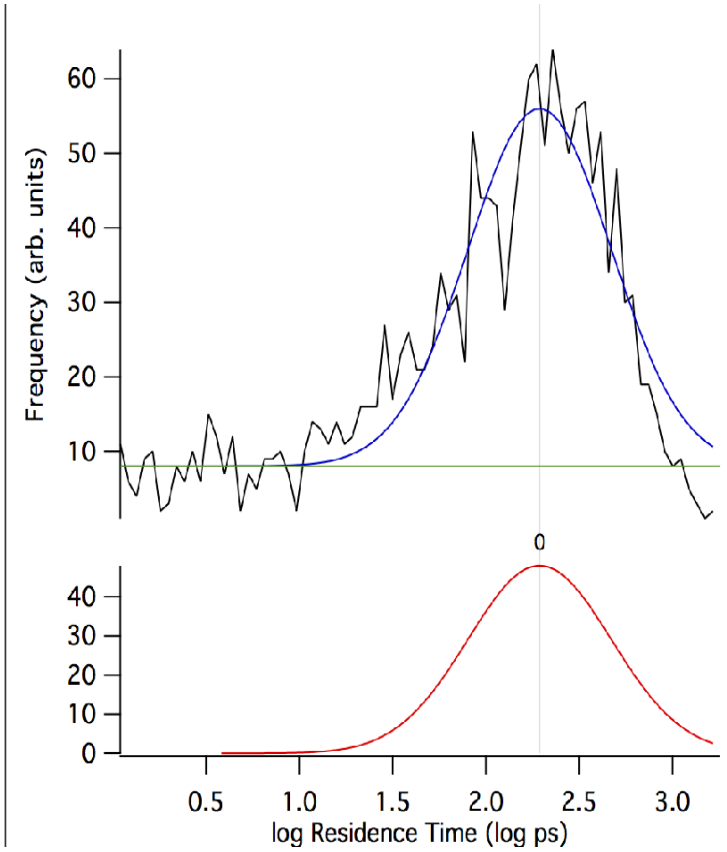
Identification of Binding sites

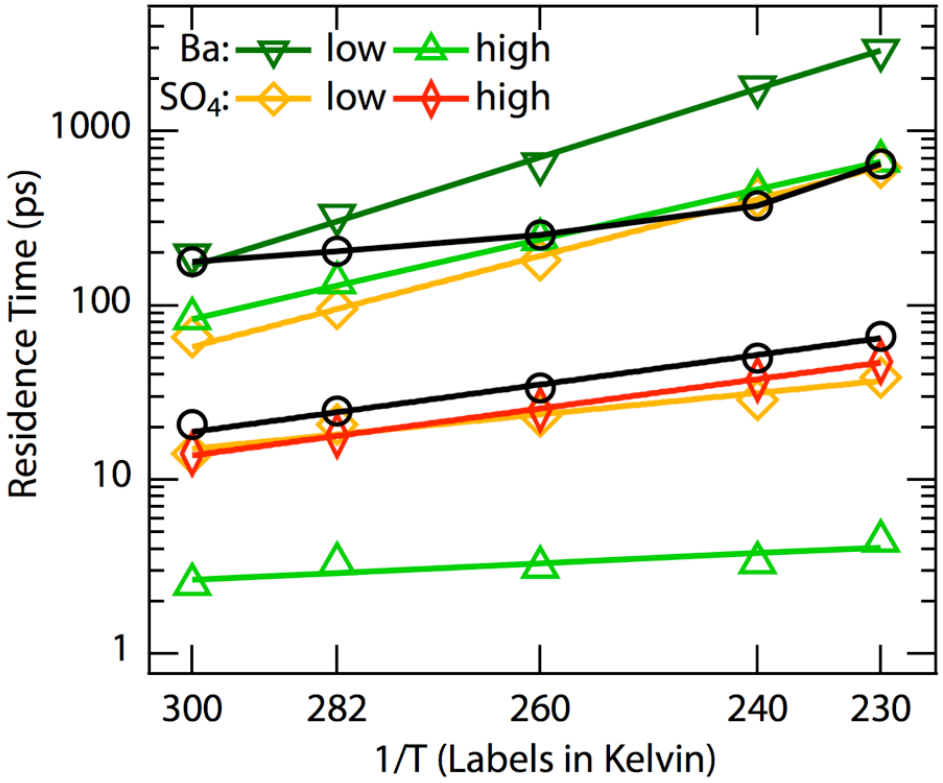
Four distinct sites where water binds the mineral



Following the history of every water





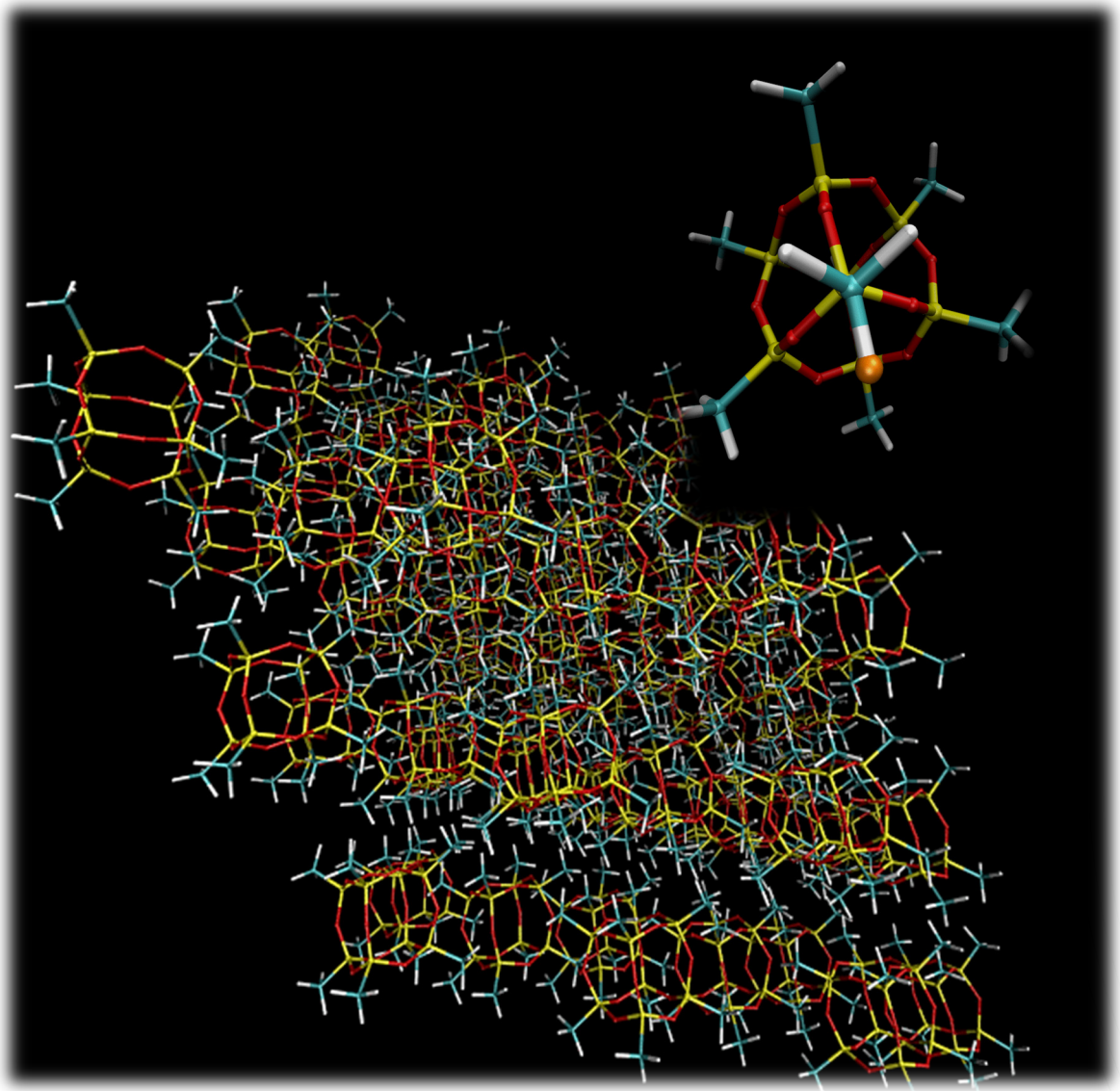


Experiments Validating Simulations

Problem: Often simulations do not reproduce the QENS data

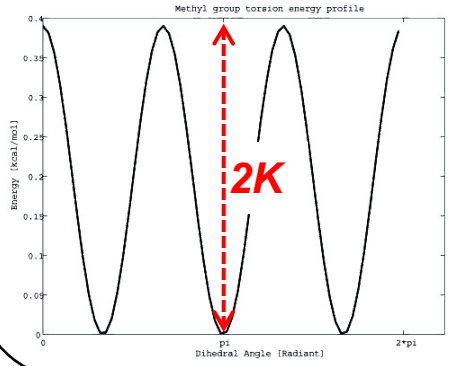
Solution: Modify the forces (potential energy) between atoms until simulations fit the experiment

Refining Torsional Barriers

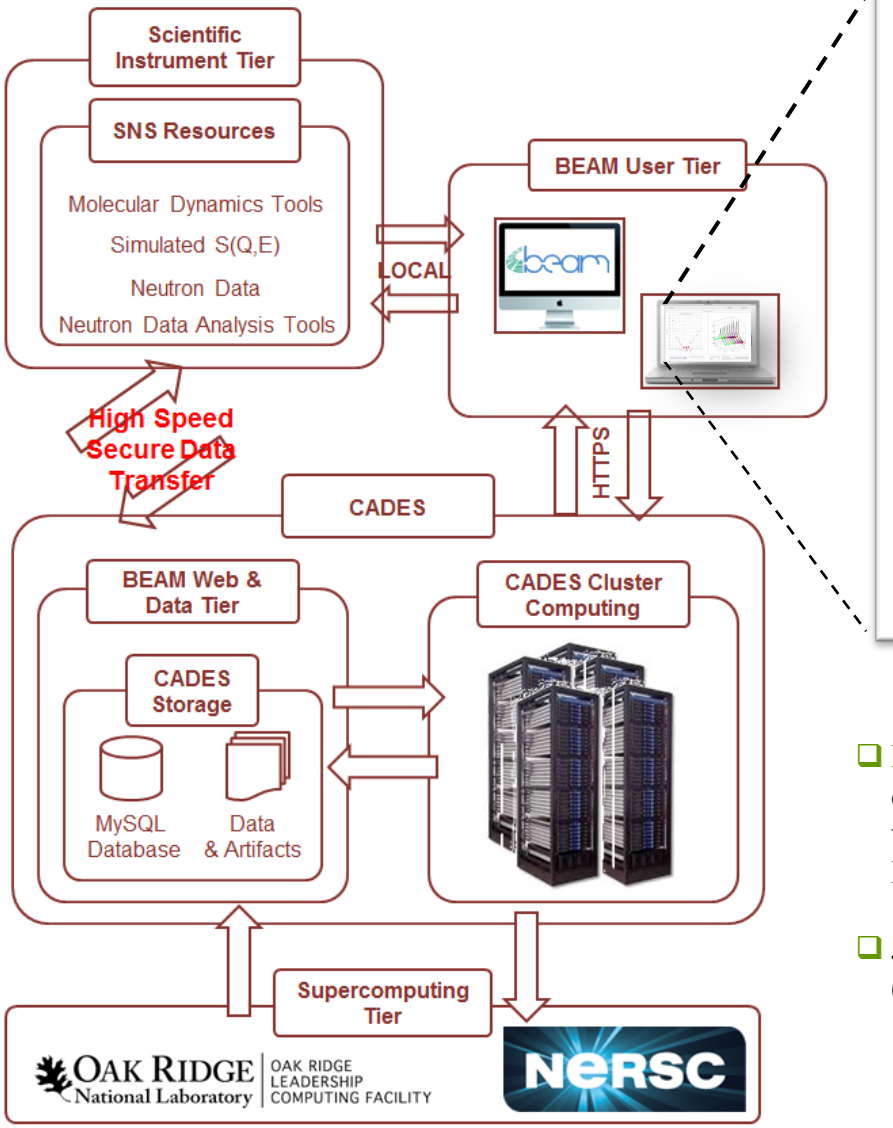


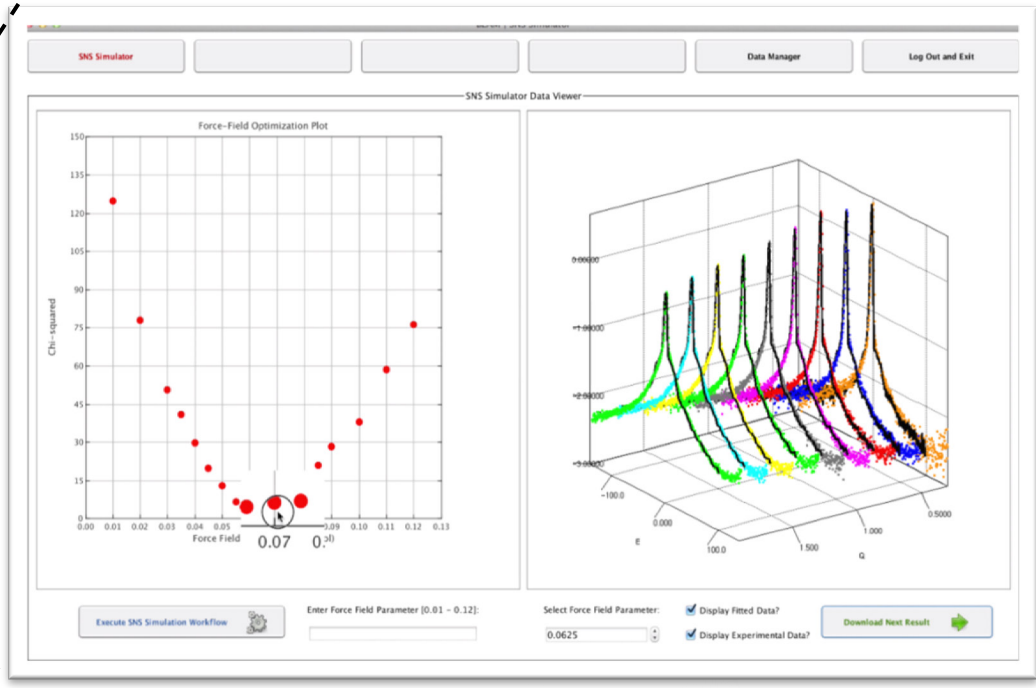
Methyl Rotations

$$V(\phi) = K[1 + cos(3\phi)]$$



An Infrastructure to Refine Interatomic Potentials





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Summary

- A QENS experiment tells us of the average diffusion properties.
- Simulations are rich in detail, but first make sure they are reliable.
- QENS data can help us correct an unreliable simulation

Thanks to

Experiments

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