Probing nanoscale functional dynamics by neutron time-of-flight spectroscopy

Margarita Russina
WHAT HAPPENS DURING THE EXPERIMENT

Particle

\[ E_{\text{kin}} = \frac{mV^2}{2} \]

Wave

\[ p = k\hbar \]

Scattering process

\[ \hbar\omega = E_{\text{out}} - E_{\text{inc}} = \frac{m}{2} (V_{\text{out}}^2 - V_{\text{inc}}^2) \]

\[ Q = k_{\text{out}} - k_{\text{inc}} \]

Information about the atomic motion or energy of quantum states

Information about structure
Differential cross-section

\[ \frac{d^2 \sigma}{d\Omega dE} = \frac{\sigma_s}{4\pi N} \frac{k_{\text{inc}}}{k_{\text{out}}} S(Q, \omega) \]

number of neutrons scattered per second into solid angle \(d\Omega\) and \(dE\)
Nuclear Neutron Scattering from a single fixed atom

- A neutron beam incident on a single atom. The incident neutron can be described as a complex plane wave.

\[
\psi_{\text{incident}} = \frac{1}{\sqrt{Y}} \exp(i k_i \cdot r) \quad \Phi_0 = |\psi_i|^2 \quad v_i = \psi_{\text{incident}} \psi_{\text{incident}}^* \quad v_i = \frac{1}{Y} \frac{\hbar k_i}{m_n}
\]

Where Y is the normalisation constant.

- Assuming just nuclear forces, which are very short range, the neutron sees the scattering centre as a point and as a result the scattering will be isotropic. The scattered wavefunction is

\[
\psi_f(r) = \psi_i(r_j) \left( \frac{-b_j}{r} \right) \exp(i k_f \cdot r)
\]

The quantity \(b_j\) is known as the scattering length.
What we see in the detector is the sum of all spherical waves, which in its turn reflect the position of scattering centers $R_i$

- These positions can be time dependent – we see the dynamics $R_i(t)$

$$S(Q, \omega) = \frac{1}{h} \frac{k_f}{k_i} \sum_{i,j} b_i b_j \int_{-\infty}^{\infty} \{\exp(-QR_i(0)) \exp(-Q(R_j(t)))\} \exp(-i\omega t)$$

Where $Q = k_f - k_i$
Neutrons and applications

$1 \text{ meV} \approx 8 \text{ cm}^{-1} \approx 240 \text{ GHz} \approx 12 \text{ K} \approx 0.1 \text{ kJ/mol} \approx \text{ ps}$

length $d = \frac{2\pi}{Q} \text{ [Å]}$
**WHAT HAPPENS DURING THE EXPERIMENT**

### Particle
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- Information about the atomic motion or energy of quantum states
- Information about structure
Neutron TOF spectroscopy delivers information about molecular excitations/motion and how these excitations/motion propagate in space.
EXAMPLES OF TOF SPECTROSCOPY APPLICATIONS

Novel materials for AI and quantum computing

Kagome spin ice state in non-artificial compounds
Science 2020

Exotic excitations in quantum spin liquid in Kitaev systems
Nat Communication 2021

Energy materials

Nanoreactions in hydrated NT
Nanoscale advances 2020

Reversible adsorption induced graphitization of porous carbon
CARBON 2021

Materials for health and medical imaging applications

Novel mechanism of hydrogen isotope separation
Advanced Materials 2021

Cooperative low dimensional transport of water
WHAT TO CONSIDER FOR AND DURING THE EXPERIMENT

\[ S(Q, \omega) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} \langle \exp\{-iQR_j(0)\} \exp\{iQR_j(t)\} \rangle \exp(-i\omega t) dt \]

What do you want to study?

- Phonons
- Quantum excitations
- Molecular diffusion
- .......

What are your ranges/ domains?

- Frequency (min, max)
- Time (min, max)
- Momentum transfer (min, max)
- Temperature (min, max)
**WHAT TO CONSIDER FOR AND DURING THE EXPERIMENT**

Q range?

\[ Q = k_i - k_f \]

\[ |Q|^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta \]

\[ |Q_{elastic}| = \frac{4\pi \sin \theta}{\lambda} \]

\( Q_{\text{min}} \) and \( Q_{\text{max}} \) is determined by the maximum and minimum scattering angle \( \Theta \) and incoming neutron wavelength \( \lambda \)
**INELASTIC SCATTERING - SCATTERING TRIANGLES**

- Conservation of energy and momentum

\[
E_i - E_f = \frac{1}{2} m v_i^2 - \frac{1}{2} m v_f^2 = \frac{1}{2m} \hbar^2 (k_i^2 - k_f^2) = \hbar \omega
\]

\[Q = k_i - k_f\]

- Inelastic Scattering triangles

Neutron loses energy

An excitation is created

Neutron gains energy

An excitation is destroyed

Maximum energy range observed depends on energy of incoming neutrons

Maximum energy range observed depends on energy of existing excitations in scattered system
Energy [meV]

OBSERVED SPECTRUM

Sample: confined H$_2$O
E_{\text{min}} \sim 1/t \text{ depends on the instrumental resolution}

Elastic resolution of instrument defines us the slowest motion what we can observe in the experiment

1\mu\text{eV} \times 1\text{ns} = 0.658
$E_{\text{max}}$ on neutron energy gain site depends on the energy of existing excitations, i.e. on the temperature due to Bose-Einstein occupation statistics. At some certain $T$ energy range up to $3k_B T$ is populated: $k_B T = 297K \sim 25$ meV.

$E_{\text{max}}$ on neutron energy loss site depends on the energy of incoming neutrons. It is usually used for investigation of phenomena at low temperatures, i.e. quantum rotational transitions of hydrogen.
Sample: H$_2$O in MCM-41

Small energy changes
Slow motion, diffusion
$10^{-11} - 10^{-12}$s

Fast motion, vibration, $10^{-13}$s

ΔE = 0

$E_k = E_i$

Elastic resolution of instrument defines us the slowest motion what we can observe in the experiment
WHAT TO CONSIDER FOR AND DURING THE EXPERIMENT

Data treatment steps

\[ I(\Theta,t)_{\text{meas}} = (I(\Theta,t)_{\text{background}} + I(\Theta,t)_{\text{sample}}) \times k_{\text{det efficiency}} \]

\[ S(\Theta,E) = I(\Theta,t)_{\text{meas}} \times k(t)_{\text{energy conversion}} \]

\[ S(Q,E) = \text{interpolation based array of } S_i(\Theta,E) \]
> Determine what you want to measure: energy range, q range, temperature
> Based on that choose experimental configuration: incoming neutron wavelength and resolution in angle and energy
> Measure signal of the sample + background
> Measure background
> Measure standard scatter to establish energy resolution and response of each individual detector to correct for detector efficiency
> Treat the data: correct for detector efficiency, convert to energy $(\Theta, \omega)$ space, subtract background, convert to $(Q, \omega)$ space

What you get is $S(Q,E)$ – enjoy further analysis!
**Diffusion** – motion of particles when time average position within certain time window is not constant

**Types of diffusion:**

- Long range translation diffusion - related to mass transfer
- Diffusion in confinement – no mass transfer
- Rotational diffusion – reorientation of molecules
Stationary part

- Particles immobile within time window defined by instrumental resolution
- Preferential positions of motion if they stay the same over long period of time

Mobile part

\[
S(Q, \omega) \sim e^{-Q/3\langle u^2 \rangle} A_0^0(Qr_0) \delta(Q, \omega) + \sum_{l=1}^{n-1} A_l(Qr_n)L(\omega, \Gamma(Q))
\]
Long range translational diffusion:

Fickian diffusion:

\[ G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt} \]

\[ S(Q, \omega) \sim \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2} \]

\[ \Gamma(Q) \sim DQ^2 \quad D = \frac{1}{6t} \langle r^2 \rangle \]

- Continuous flow usually due to a gradient of concentration
- \( A_0 = 0 \) since all particles are moving
- No interaction between the particles
Long range translational diffusion:

\[ S(Q, \omega) \sim \frac{1}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2} \]

Random jump diffusion:

\[ \Gamma(Q) = \frac{DQ^2}{1 + DQ^2/E_0} \quad \tau = \frac{\hbar}{E_0} \quad \text{and} \quad l = \sqrt{6D\tau} \]

Chudley Elliott – jump diffusion in crystals

\[ \Gamma = \frac{\hbar}{\tau} \left( 1 - \frac{\sin(QL)}{QL} \right) \]

Gaussian distribution

\[ \Gamma = \frac{\hbar}{\tau} \left( 1 - \exp\left(-\frac{Q^2l^2}{6}\right) \right) \]

- Stronger interactions between the particles
- Particles are caged in between the neighbors
- Particles resides time \( \tau \) and undergo jumps with the length \( l \)
Properties of bulk hydrogen

**Melting point**: 14.01K at ambient pressure

**Boiling point**: 20.28K at ambient pressure

**Critical point**: 32.9K

**Triple point**: 13.8033 at 7.042kPa
Bulk Hydrogen at $T=15K$

Long range translational diffusion:

- Linewidth is a function of $Q^2$
  - $D \sim Q^2$ and is $0.43 \pm 0.01 \text{ Å}^2 / \text{ps}$ at 15K
  - $E_0 = 3.38 \pm 0.27 \text{ meV}$

No stationary part – not confined

F. Fernandez-Alonso et al, PRL 1998
H$_2$ confined into ice based clathrates

Guest-host interactions are “switch off”

Rigid structure

Large cage: $R=4.75 \text{ Å}$
$P_{\text{synth}} = 2000 \text{ bar}$

Small cage: $R=3.95 \text{ Å}$
$P_{\text{synth}} = 200 \text{ bar}$

Pentagon window: $E_A = 26 \text{ kcal/mol}$
Hexagon window: $E_A = 6 \text{ kcal/mol}$

Reason in such differences is in-cage potential landscape reflected in in-cage H$_2$ behavior
Confined H₂:

- **Small cage:** H₂ motion is “frozen” up to 50 K (14 K) at experimental time scale
- **Large cage:** Enhanced mobility in the large cage already at T=10K
CONFINED DIFFUSION – \( \text{H}_2 \) IN POROUS ICE

Small cage – rotation within a small sphere in the cage center

Large cage - jumps between four well defined and tetrahedrally shaped positions

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Radius [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.08±0.12</td>
</tr>
<tr>
<td>50</td>
<td>0.19±0.07</td>
</tr>
<tr>
<td>90</td>
<td>0.47±0.06</td>
</tr>
<tr>
<td>150</td>
<td>0.63±0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Jump length [Å]</th>
<th>Occupation time ( \tau_s ) [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.4±0.6</td>
<td>6.0±0.13</td>
</tr>
<tr>
<td>20</td>
<td>2.4±0.2</td>
<td>6.1±0.19</td>
</tr>
<tr>
<td>30</td>
<td>3.22±0.2</td>
<td>6.3±0.16</td>
</tr>
<tr>
<td>50</td>
<td>3.6±0.3</td>
<td>4.4±0.13</td>
</tr>
</tbody>
</table>

IMPACT OF $H_2$ NANOSCALE DYNAMICS ON FUNCTIONAL PROPERTIES

Small cage $\varnothing$ 7.9Å:
- Nanoscale: Strong localization within a sphere with radius $R=0.08\pm0.12$ Å@10K and $0.63\pm0.04$ Å@150K
- Macroscopic effect: About 200 bar are required to get $H_2$ in small cage

Large cage $\varnothing$ 9.5Å:
- Nanoscale: Superfluid behavior, jump diffusion between tetrahedrally shaped equilibrium sites in large cage; no activation barrier confirm flat potential
- Macroscopic effect: About 2000 bar is required to get $H_2$ inside large cage

- Confinement can have an effect similar to pressure!
- The confinement of $\sim$ 6-7 Å works best!

Superionic conductors $\text{Cu}_2-x\text{Se}$ with high ionic conductivity $\sigma \geq 1 \ \Omega/\text{cm} \Rightarrow$ ion diffusion $\sim 10^{-5} \ \text{cm}^2/\text{s}$

Self diffusion of $\text{H}_2\text{O} @ 300 \text{K} \quad D_s = 2.27 \times 10^{-5} \ \text{cm}^2/\text{s}$ K. Tanaka. J. Chem. Soc., Faraday Trans. 1, 1978, 74, 1879-1881

$\alpha$- $\text{Cu}_2\text{Se}$: high temperature phase with cubic anti-fluorite structure and fcc arrangements of Se ions

$\beta$- $\text{Cu}_2\text{Se}$: low temperature phase with monoclinic structure

EXAMPLE 2: ION DIFFUSION IN SUPERIONIC CRYSTALS

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EXAMPLE 2: ION DIFFUSION IN SUPERIONIC CRYSTALS

- Propagation along the route
  \(8c \langle 111\rangle \rightarrow 32f \langle 100\rangle \rightarrow 32f \langle 111\rangle \rightarrow 8c\)

- Slowdown of the Cu ion diffusion with the decrease of stoichiometry due to the increase of the residence time caused by interactions between Cu and Se

Chudley–Elliott model for ion jump diffusion in crystal lattice:

\[
\Gamma_{\text{trans}}(Q) = \frac{\hbar}{\tau} \left(1 - \frac{\sin(Ql)}{Ql}\right)
\]

<table>
<thead>
<tr>
<th>Composition</th>
<th>(D_{\text{self}} \times 10^{-5} (\text{cm}^2/\text{s}))</th>
<th>(\tau (\text{ps}))</th>
<th>(l (\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_{1.75}\text{Se})</td>
<td>3.4 ± 0.2</td>
<td>3.7 ± 0.3</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>(\text{Cu}_{1.90}\text{Se})</td>
<td>5.2 ± 0.2</td>
<td>1.7 ± 0.1</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>(\text{Cu}_{1.98}\text{Se})</td>
<td>6.1 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>Distance between nearest 8c sites</td>
<td>2.9 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance between next nearest 8c sites</td>
<td></td>
<td></td>
<td>4.1 Å</td>
</tr>
</tbody>
</table>
EXAMPLE 3: PROPAGATION OF WATER IN POROUS MATERIALS

- Water (obviously) is part of many electrolytes systems
- Water has a number of anomalous thermodynamic and structural properties differing it from other liquids which impact water macroscopic behavior

Question: WATER TRANSPORT IN PORES?
SUPERFAST

Simulations: Superfast diffusion of confined water

A. Striolo Nano Lett., Vol. 6, No. 4, 2006

Permeability measurements of water flow through stacked carbon nanotubes: Fast mass transport exceeding the values in the bulk water

OR IMMOBILE / FROZEN?

MD simulations: observation of ice-like water at elevated temperatures


Observation of square ice in carbon at room temperature

EXAMPLE 3: PROPAGATION OF WATER IN POROUS MATERIALS

POROUS ALUMINOPHOSPHATE ALPO₄-5

<table>
<thead>
<tr>
<th>ICSD collection code</th>
<th>radiation type</th>
<th>sample type</th>
<th>temperature</th>
<th>pressure</th>
<th>R-value</th>
<th>12-ring diameter (O1-O1)</th>
<th>12-ring diameter (O3-O3)</th>
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<tbody>
<tr>
<td>91672</td>
<td>X-ray</td>
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<td>atmospheric</td>
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<td>room temperature</td>
<td>atmospheric</td>
<td>0.069</td>
<td>9.946</td>
<td>9.98</td>
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<tr>
<td>91674</td>
<td>X-ray</td>
<td>singlecrystal</td>
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<td>0.069</td>
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<td>10.221</td>
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<tr>
<td>91671</td>
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<td>singlecrystal</td>
<td>room temperature</td>
<td>atmospheric</td>
<td>0.081</td>
<td>9.931</td>
<td>9.98</td>
</tr>
<tr>
<td>93953</td>
<td></td>
<td>theoretically calculated</td>
<td></td>
<td></td>
<td>9.969</td>
<td>10.029</td>
<td></td>
</tr>
</tbody>
</table>

12-membered rings of alternating, corner-sharing AlO₄ and PO₄ tetrahedra connected by oxygen bridges into sheets in the (a, b) plane. The sheets are connected by oxygen bridges along the c crystal axis AND FORM ONE-DIMENSIONAL CHANNELS of which the largest has accessible diameter of about 0.8 nm.

About two H₂O molecules fits in

ALPO₄-5 was proposed for novel heat storage systems

Ultramicroporous, hydrophobic system
EXPERIMENTAL APPROACH

- Multidisciplinary approach, combining GRAVIMETRIC WATER SORPTION, NEUTRON AND X-RAY DIFFRACTION AND NEUTRON SPECTROSCOPY

- Systematic investigation of the evolution of intermolecular interactions during the sorption process by gradual change of the amount of confined particles

MACROSCOPIC CHARACTERIZATION OF WATER INTAKE

- Very low intake up to $P/P_0 = 0.22$ confirming hydrophobicity of the initial zeolite structure

- Switch from hydrophobic to steep rise in the intake around $P/P_0$ indicating COOPERATIVE WATER-WATER INTERACTIONS

M. Schlegel, V. Grzimek et al, Microporous and Mesoporous Materials 2018
https://doi.org/10.1016/j.micromeso.2018.11.025
STAGES OF INTAKE

Water in hydrophobic 1D channels

- **Stage I**: filling of the position close to walls
- **Stage II**: water fills the interior of main channel, water molecules keep distance of about 3.4-4 Å between each other
- Strong intake increase as a result of cooperative effects and water chain formation
CONFINED WATER DYNAMICS

\[ S(Q, \omega) \sim e^{-Q^2/2u^2} A_0(Qr_0) \delta(Q, \omega) + \sum_{l=1}^{n-1} A_l(Qr_l) L(\omega, \Gamma(Q)) \]

Water become more mobile when it enters the center area of the pore!

M. Schlegel, V. Grzimek et al, Microporous and Mesoporous Materials 2018
https://doi.org/10.1016/j.micromeso.2018.11.025
Data show a number of relaxation processes

- Fastest corresponds to rotational motion observed at $E < 5$ meV ($\sim 1$ ps)
- Increasing the time scale to 220 ps two more processes can be detected for RH=32% only.

$$S(Q, E) = \{ A_{\Delta \text{elta}} \delta(E) + A_{L1} L(\Gamma_1, E) + A_{L2} L(\Gamma_2, E) \} \otimes R(Q, E) + BG$$
Confinement lead to highly cooperative transport consisting from several diffusion steps:

- Cooperative exchange of positions between two water molecules placed at about $3.14 \times 10^{-4}$ Å from each other
- Self diffusion related to mass transport along the pore with $D_s \approx (2.4 \pm 0.2) \times 10^{-11}$ m$^2$/s, slower than bulk water

H$_2$O in ALPO$_4$-5 $\varnothing$ 0.8 nm

- **Novel state of water**: highly ordered, crystal like fluid
- Position of the water are well defined forming a spiral like chain along the pore channel in c direction
- Molecules vibrates (cooperatively?) before diffusing
- Cooperative mass transport slower than the bulk water

Quasielastic neutron scattering is a very efficient tool which allow us to zoom to nanoscale and follow motion of ions / molecules.

It provides wealth of details and important information which helps to understand nanoscale transport mechanism in energy related materials:
- diffusion coefficients, residence time, jump length, activation energy
- interactions with neighbors and / or external field
- geometry of motion (cannot be provided by any other techniques)

It is particular successful if combined with other complimentary description:
- macroscopic techniques of functional properties (impedance spectroscopy, gravimetric and volumetric adsorption, MD simulations and etc.)