Neutron scattering and MD simulations applied to geo-inspired nanotubes

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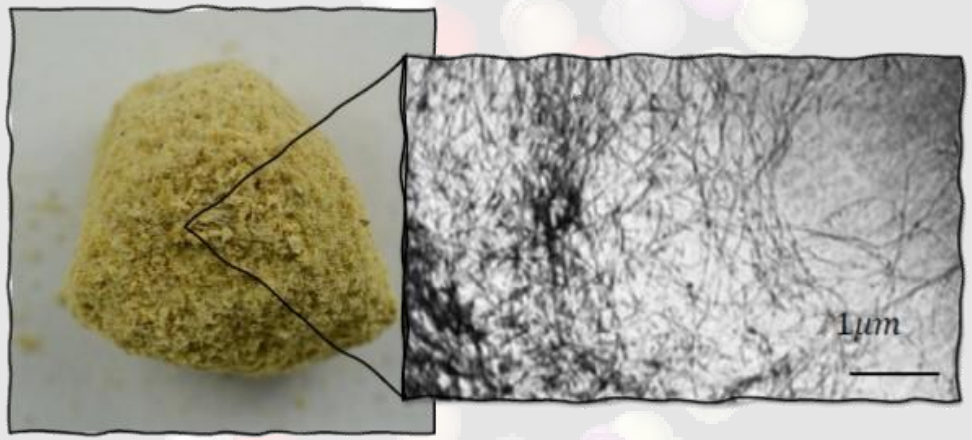
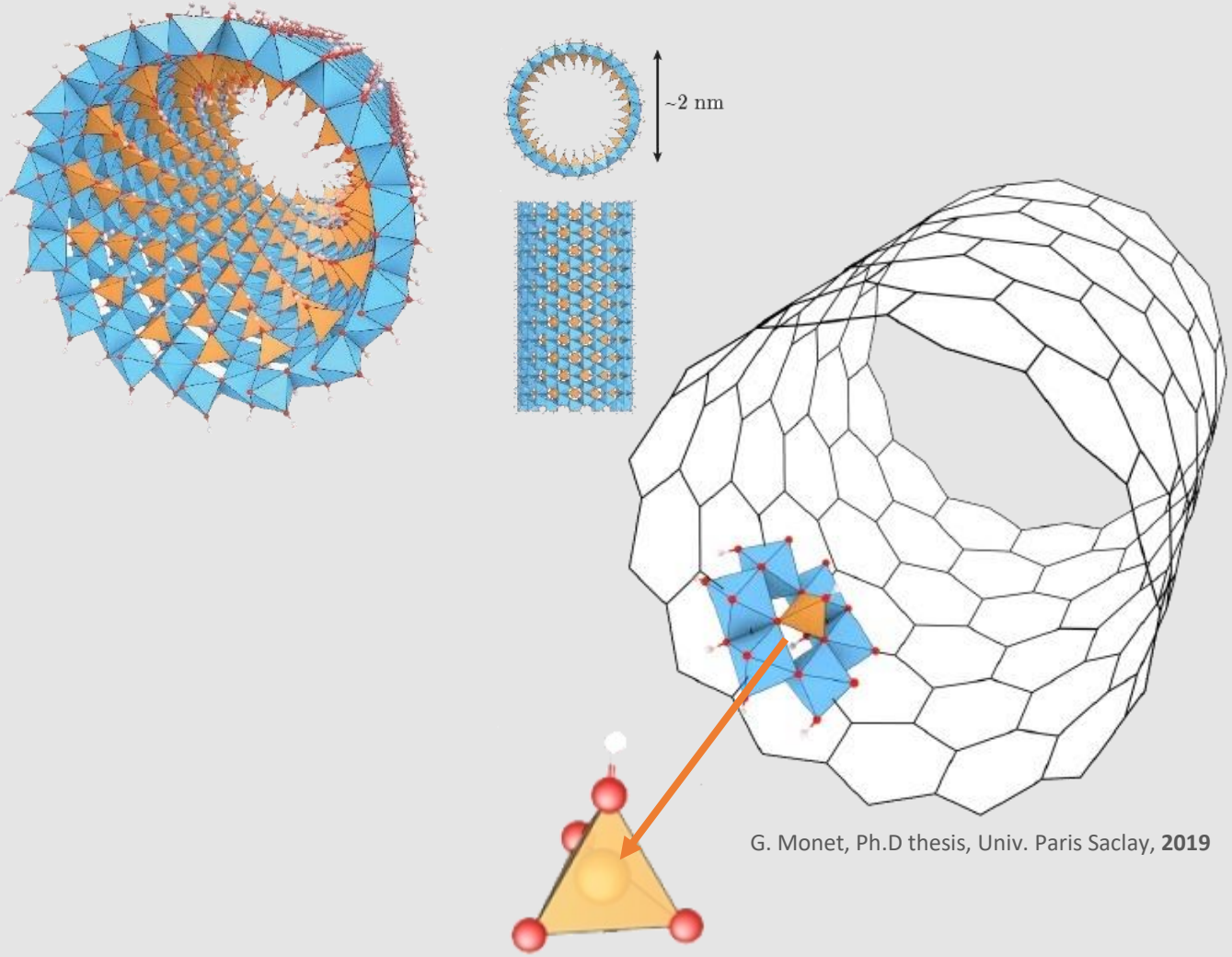
What are imogolites?

Imogolite nanotubes (INT) are natural clay nanotubes with nominal formula $(OH)_3Al_2O_3Si(OH)$



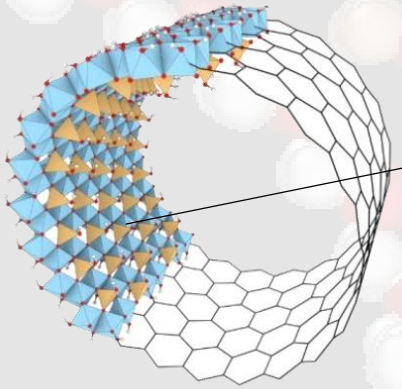
N. Yoshinaga and S. Aomine, (**1962**), SSPN, 8, 22



G. Monet, Ph.D thesis, Univ. Paris Saclay, **2019**

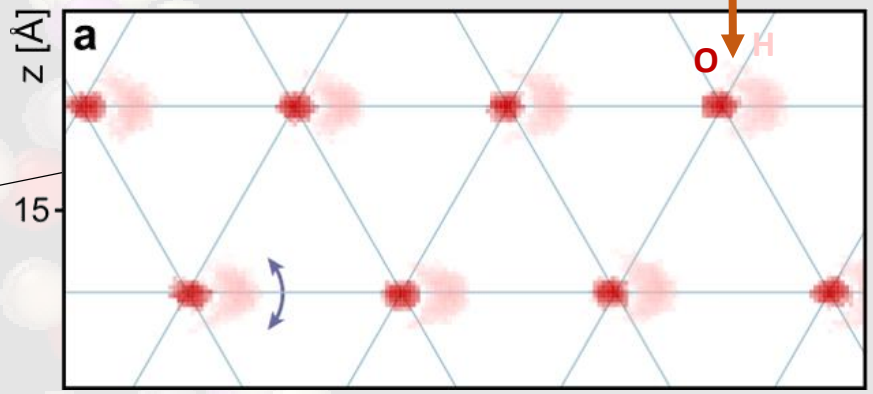
The **Si atom (Si-INT)** can be substituted with a **Ge atom (Ge-INT)**

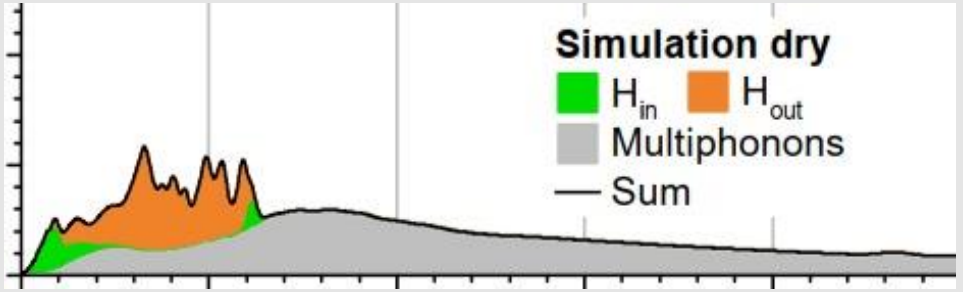
Imogolites and nanoconfinement



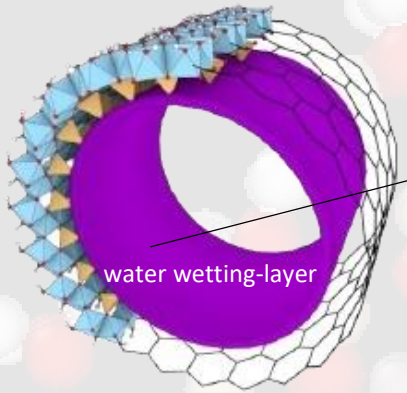
Ge-INT

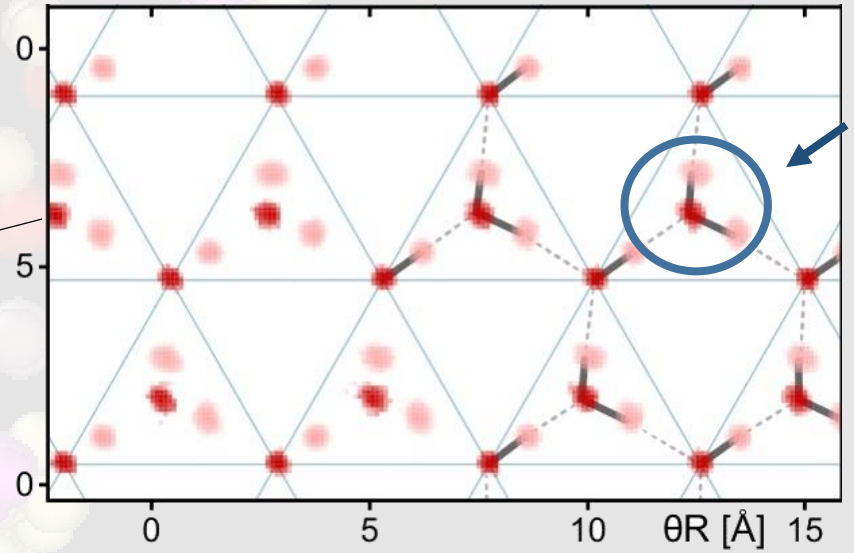
Inner hydroxyl of the nanotube



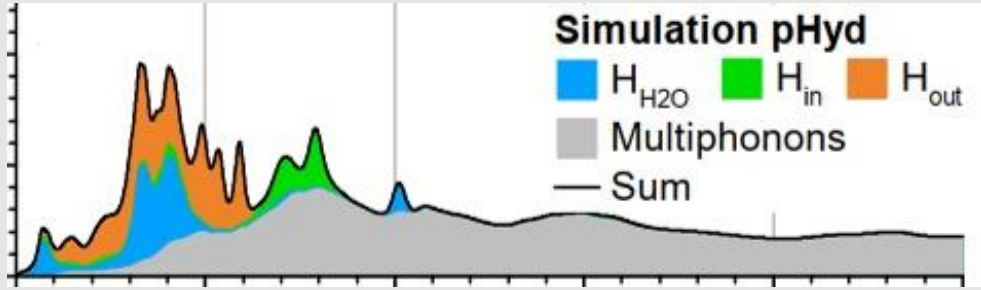


Imogolites can confine water molecules in geometries markedly different from those in the macroscopic scale



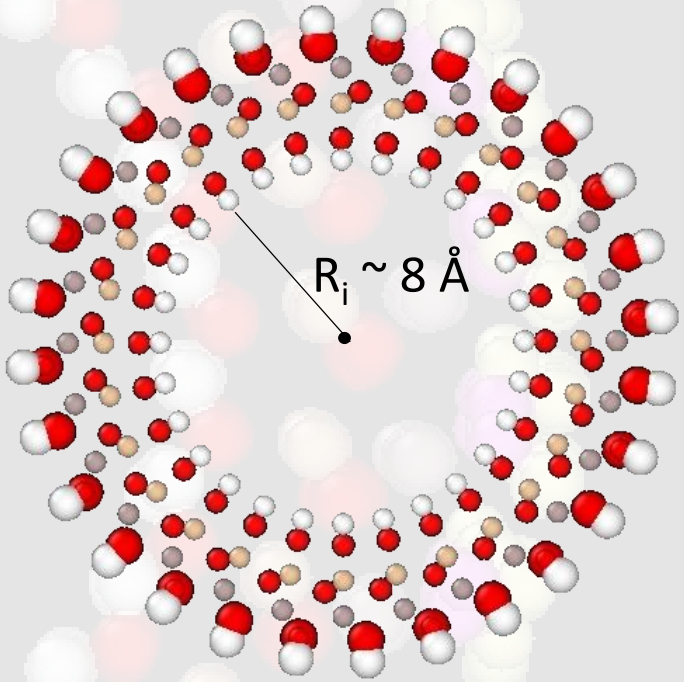


H_2O molecule

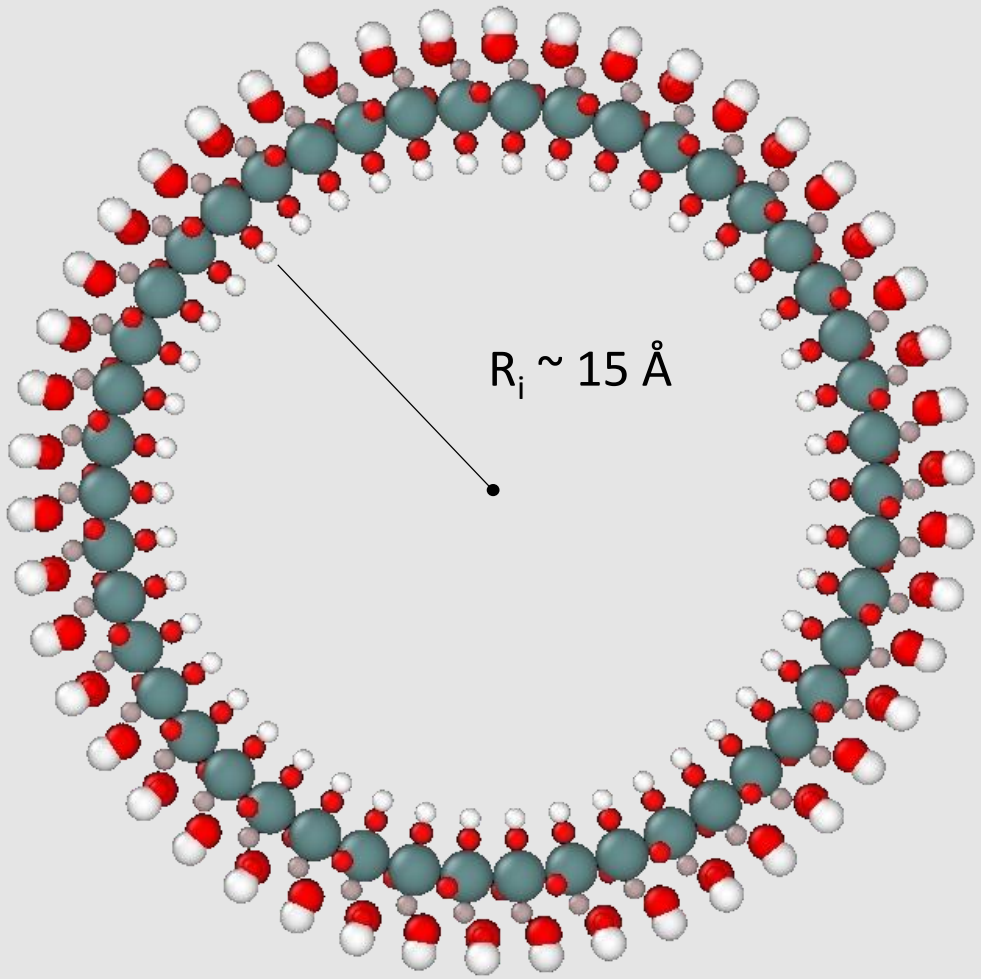


Monet et al., (2020) Nanoscale Adv., 2, 1869

Si-INT

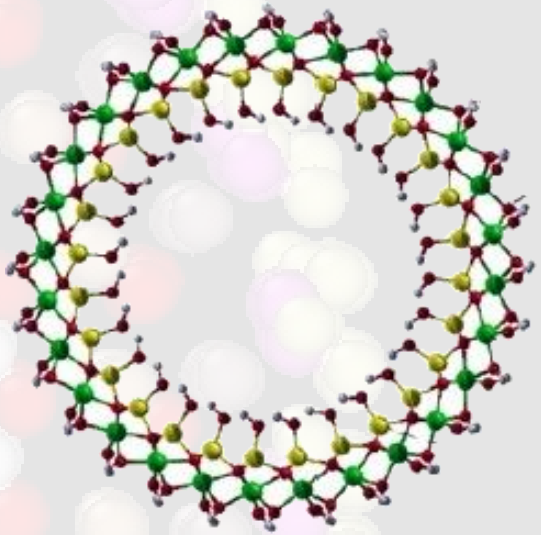


Ge-INT



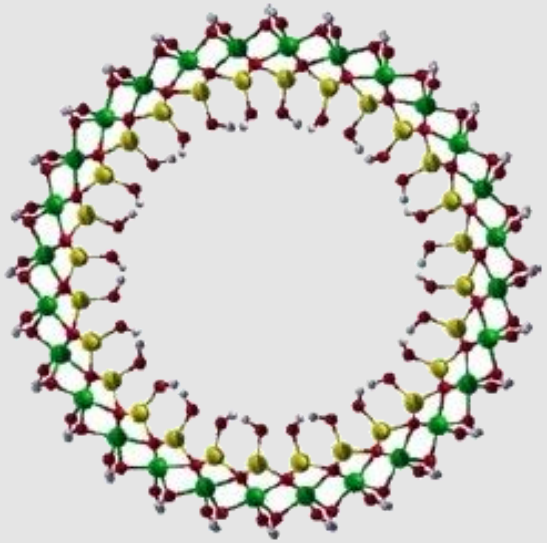
Structure of the dry nanotube

Hydroxyl alignment



Minimum energy state at low T

Opposite angles



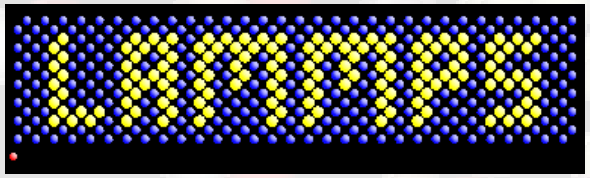
Energetically unfavorable at low T !

Lourenço et al., (**2014**) *J. Phys. Chem. C*, 118, 11, 5945–5953

Although simulations have shown it years ago, this preferential orientation has never been proven experimentally

Molecular Dynamics simulations

- **LAMMPS** (Large-scale Atomic/Molecular Massively Parallel Simulator) code



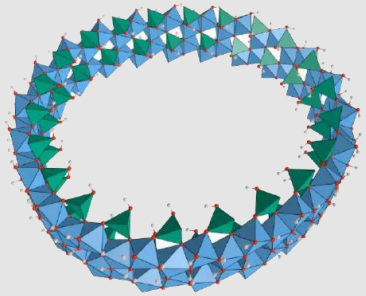
- Interactions modeled by the **CLAYFF force field**

$$U = \frac{e^2}{4\pi\epsilon_0}\sum_{ij}\frac{q_i q_j}{r_{ij}} + \sum_{ij} D_{0,ij}\left(\left(\frac{R_{0,ij}}{r_{ij}}\right)^{12} - \left(\frac{R_{0,ij}}{r_{ij}}\right)^{6}\right) + \sum_{bonds\ ij} K_b(r_{ij} - r_0)^2 + \sum_{angles\ ijk} K_a(\theta_{ijk} - \theta_0)^2$$

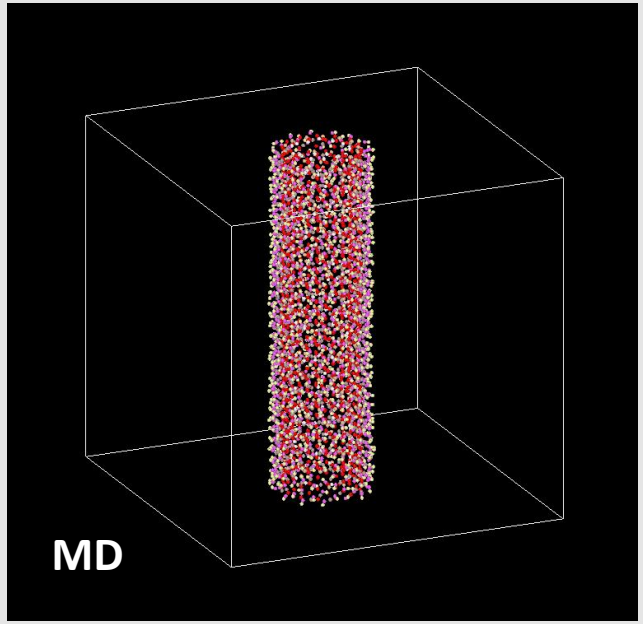
- Neutron observables were calculated with **MDANSE** (Molecular Dynamics Analysis for Neutron Scattering Experiments)

→ Access to long-time simulations and large-scale systems

- Simulation of an isolated Si-nanotube (11 unit cells instead of only one)
- 100 ps long simulations

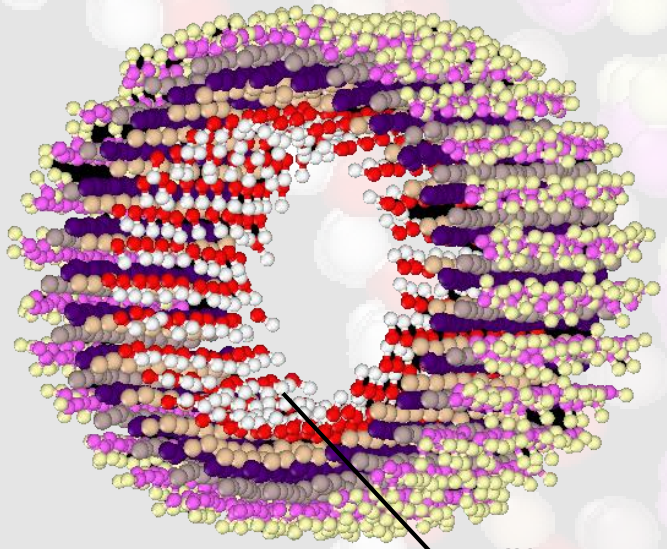


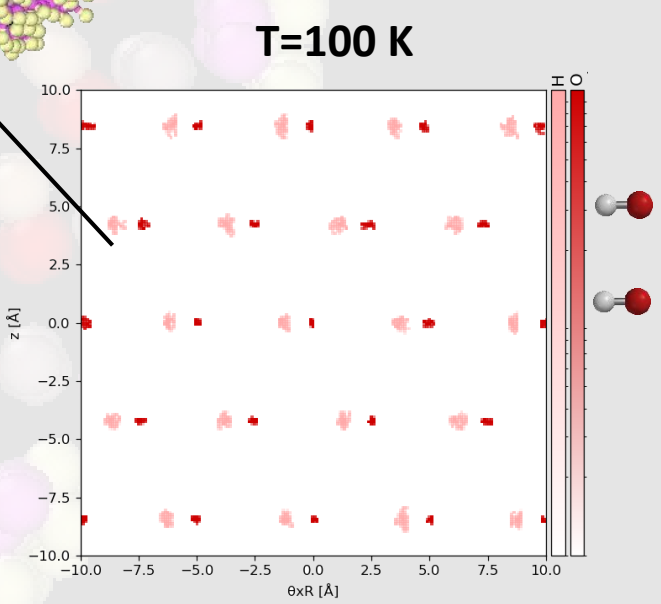
DFT-MD vs

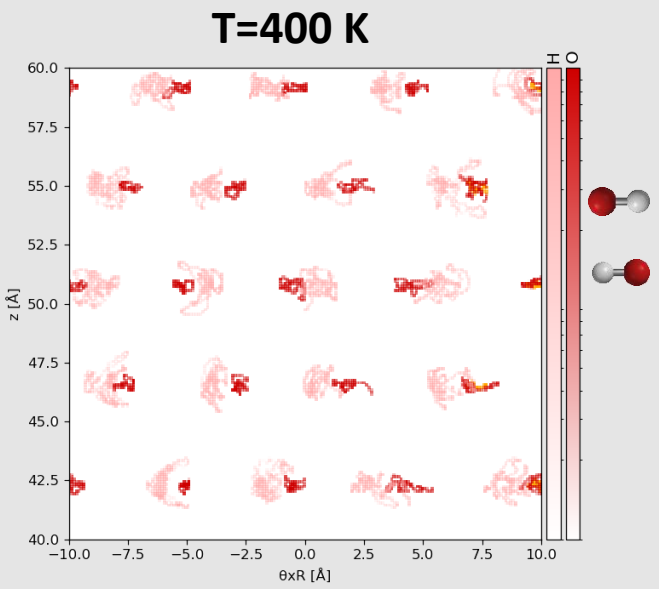


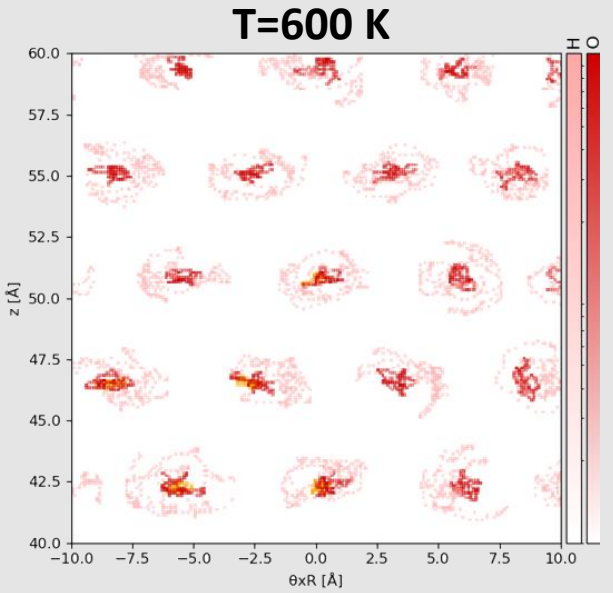
Molecular Dynamics simulations

- A Nose-Hoover thermostat was used to thermalize the nanotube at a certain temperature







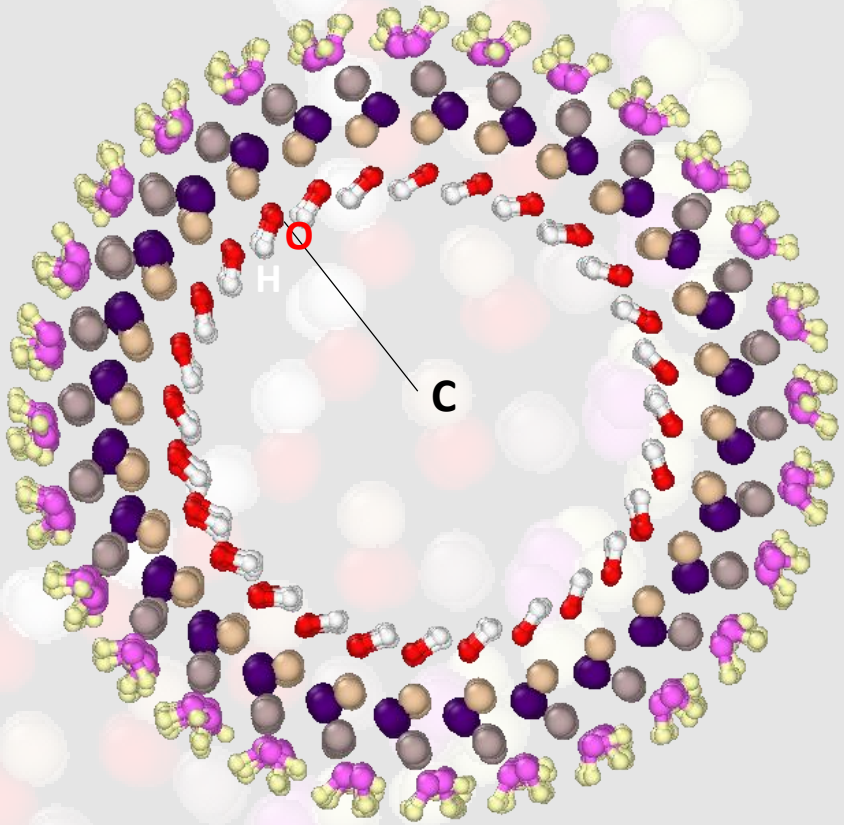


An order-disorder transition happening

To quantify the degree of order in the hydroxyls, an order parameter can be defined:

$$OrderParameter = \frac{1}{N_t}\sum_{i}^{N_t}\frac{1}{N_{OH}}\sum_{i}^{N_{OH}}\frac{(OH \wedge OC)_z}{\|OH \wedge OC\|}$$

= 1 if all the hydroxyls are on the same side with respect to the nanotube radius



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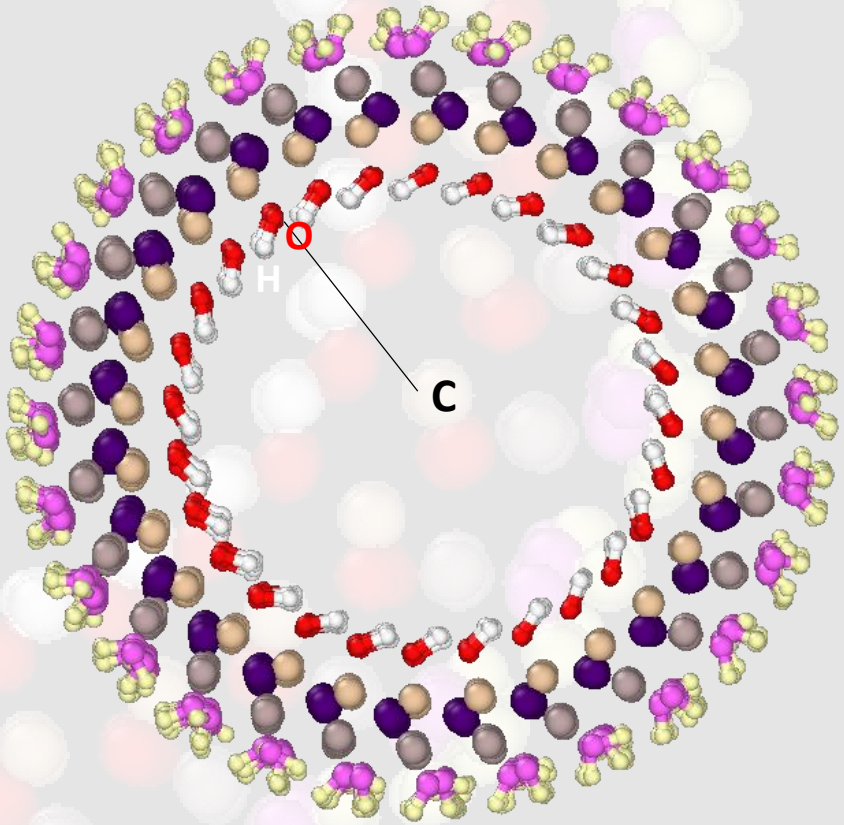
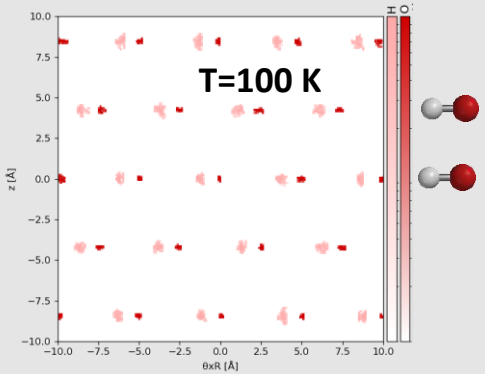
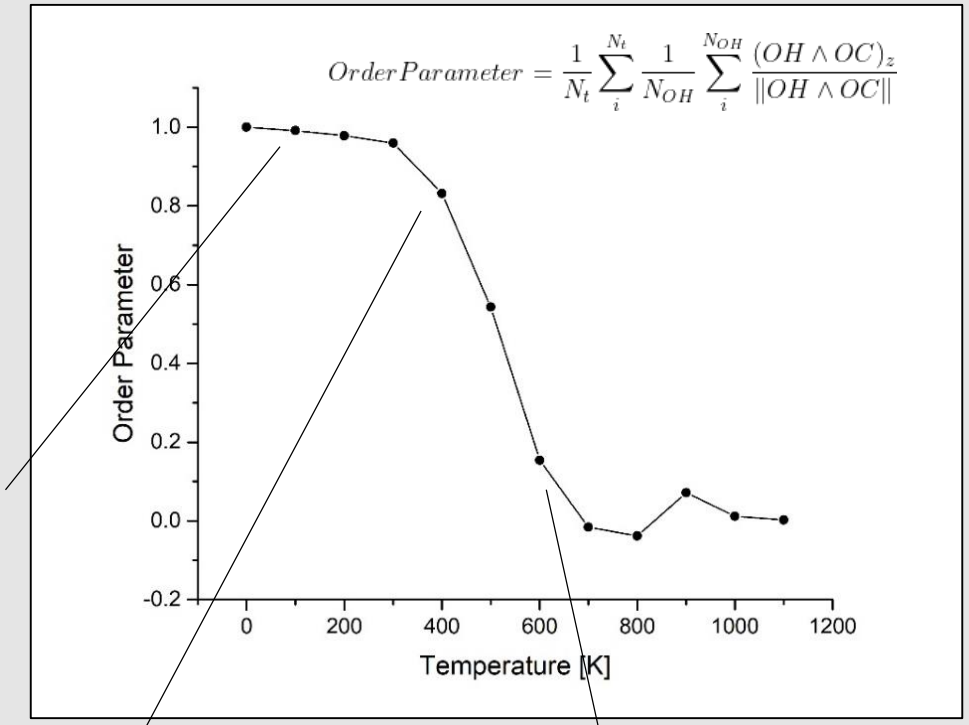
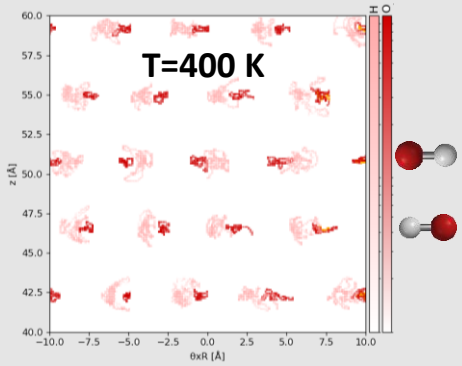
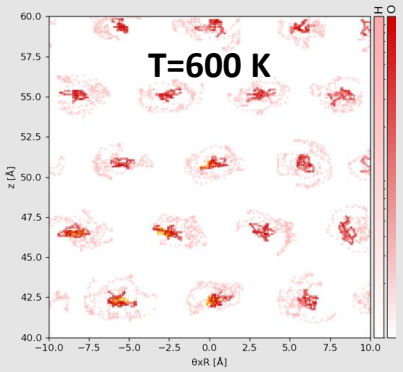






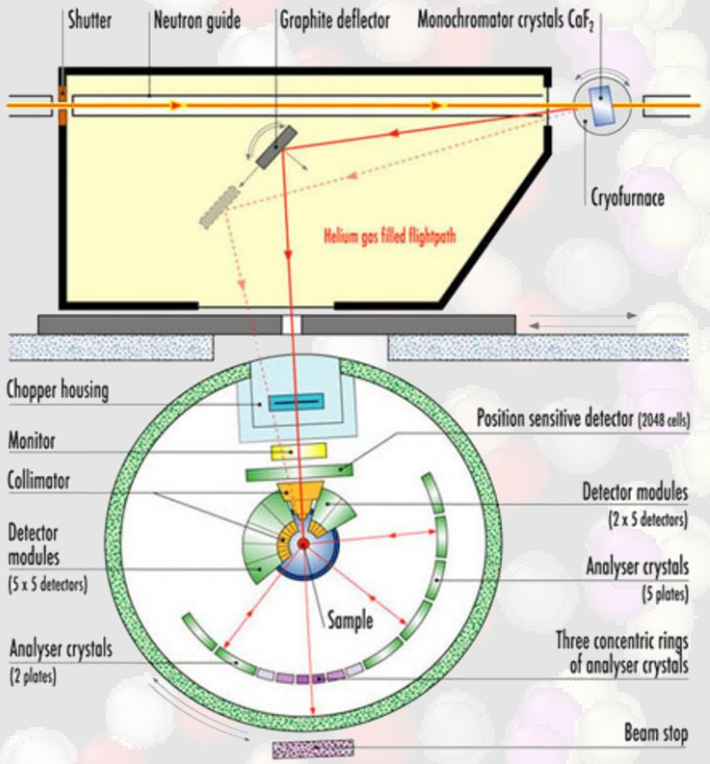




An order-disorder transition happening

Above 300 K, the ordered configuration is not stable anymore and an experimentally observable dynamics is activated

IN13 backscattering spectrometer



$\Delta E = 8\ \mu eV$

→ $\Delta t \sim 100$ ps

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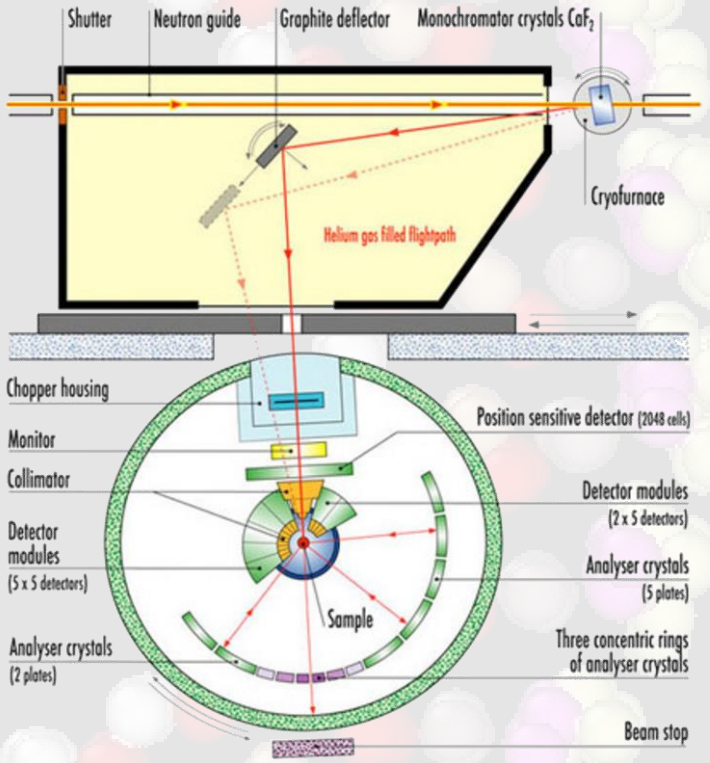
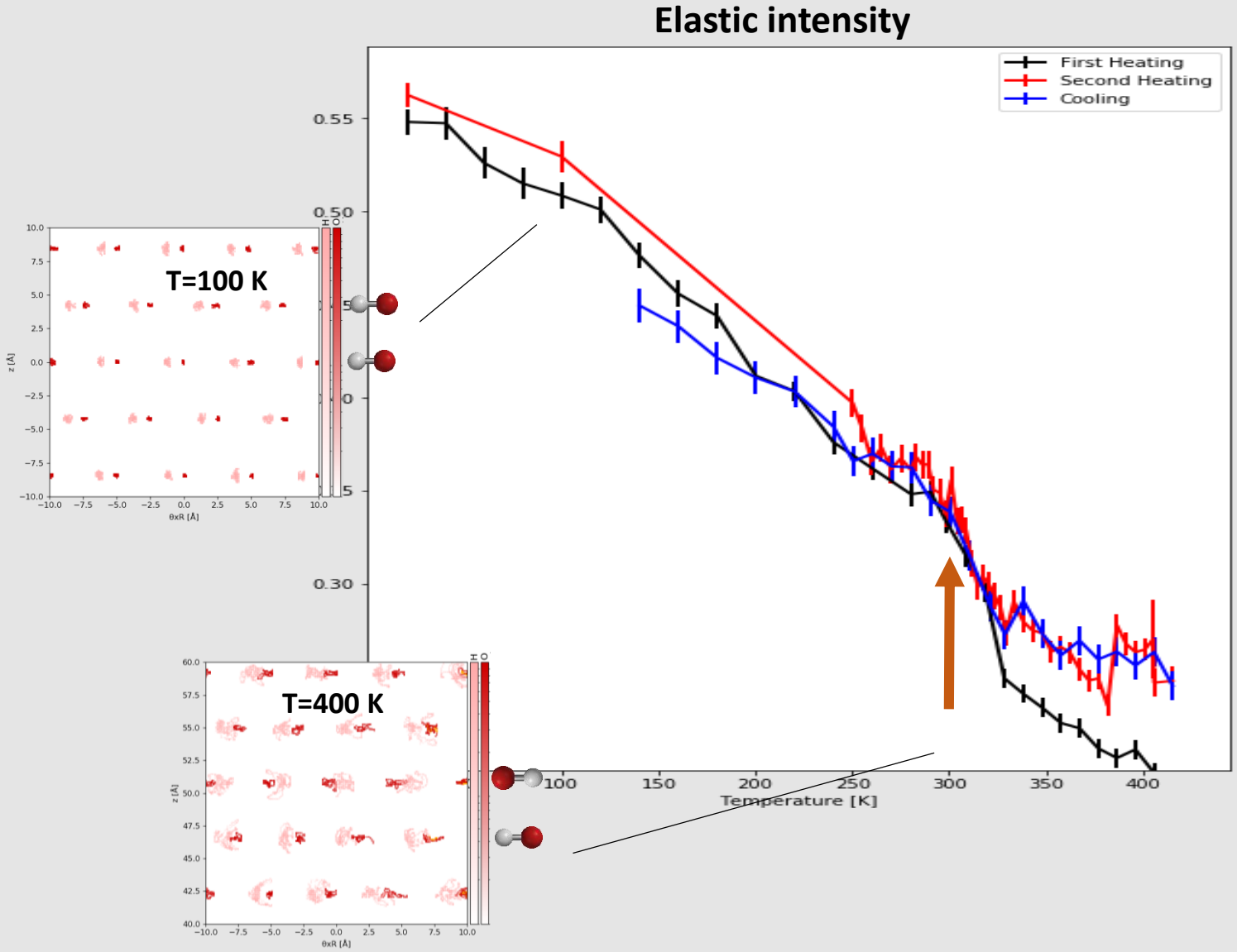


ΔE = 8 μeV

→ Δt ~ 100 ps

Elastic intensity



Thank you for your attention !