

ELECTRO
INTRUSION



Effect of alcohol-water mixture on intrusion-extrusion process in nanoporous materials

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EMRS – Breakthrough zero-emissions energy storage and
conversion technologies for carbon-neutrality

19/09/2022

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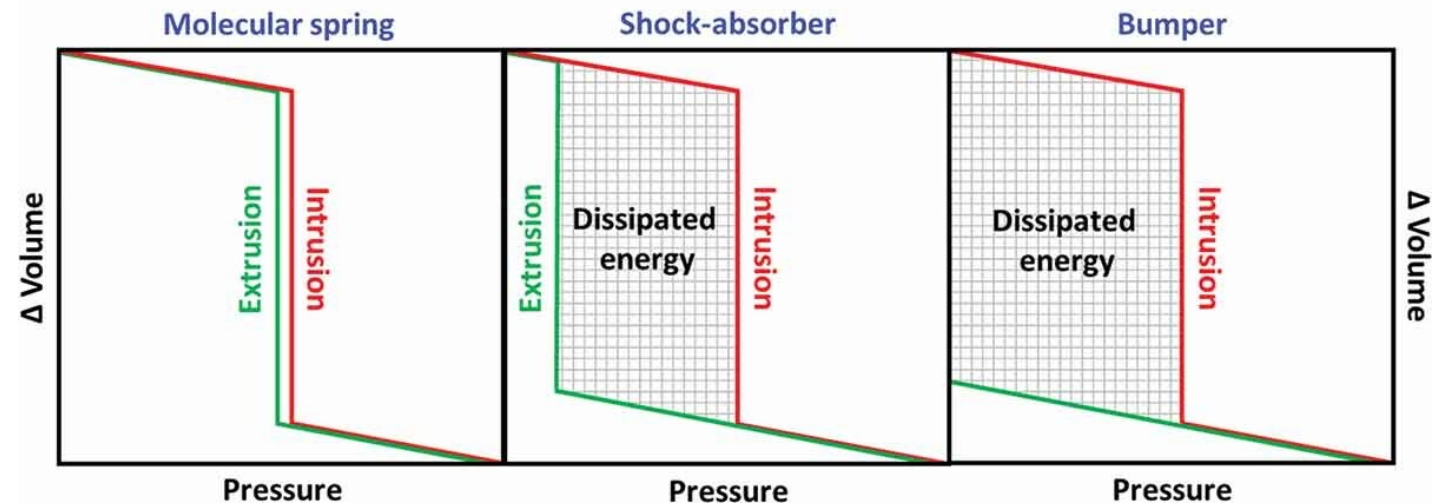




Introduction

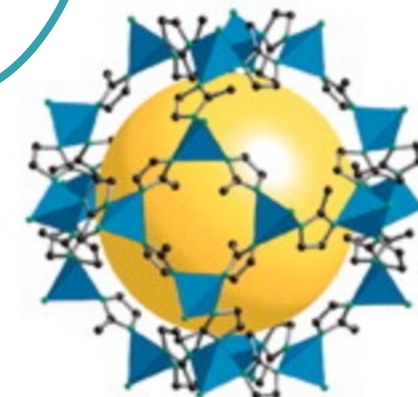
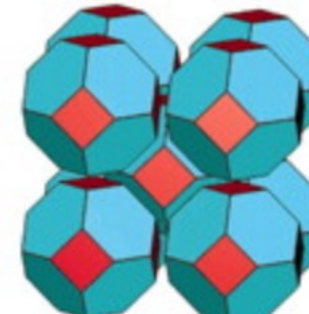
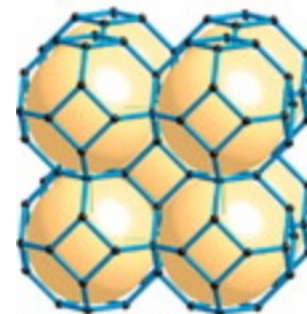


— Compression
— Decompression

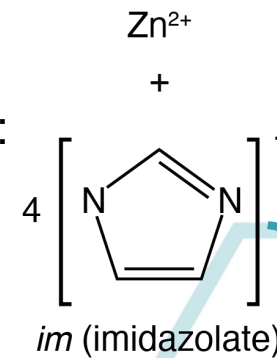


Adv. Phys. X, **2022**, 7, 2052353.
DOI: 10.1080/23746149.2022.2052353

3D structure of ZIF-8:

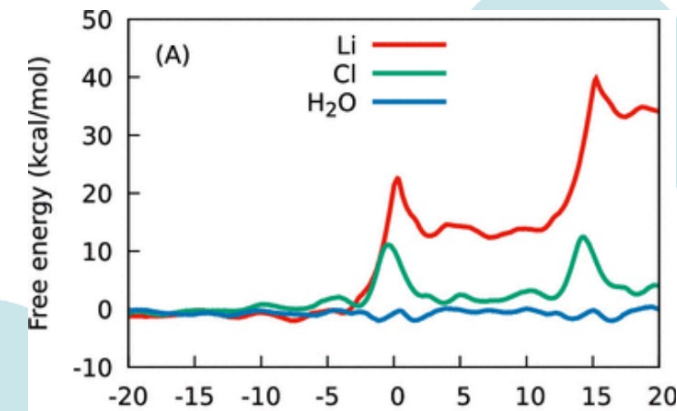
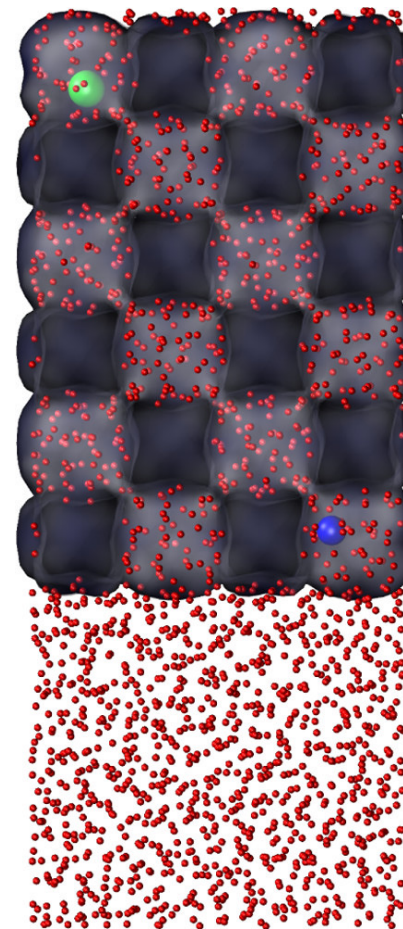
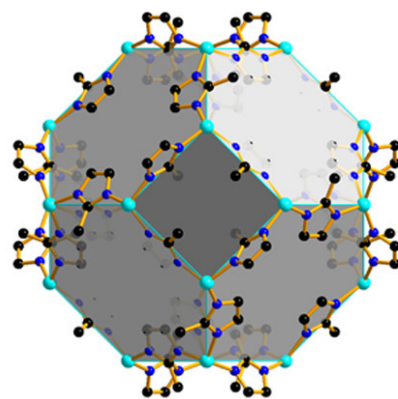
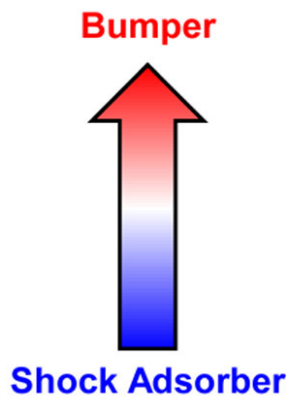
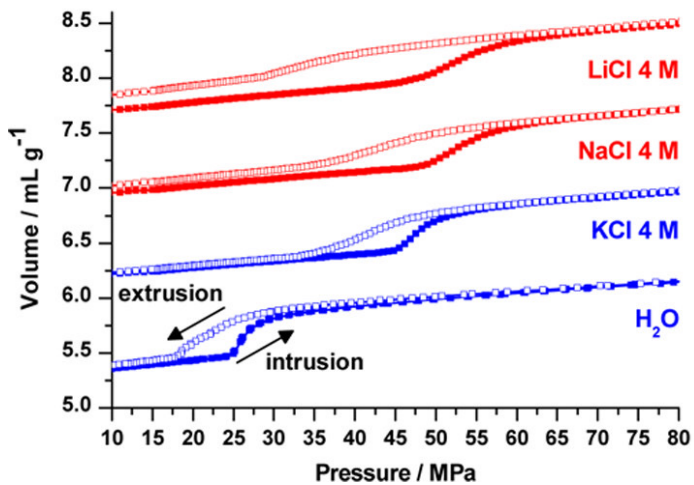
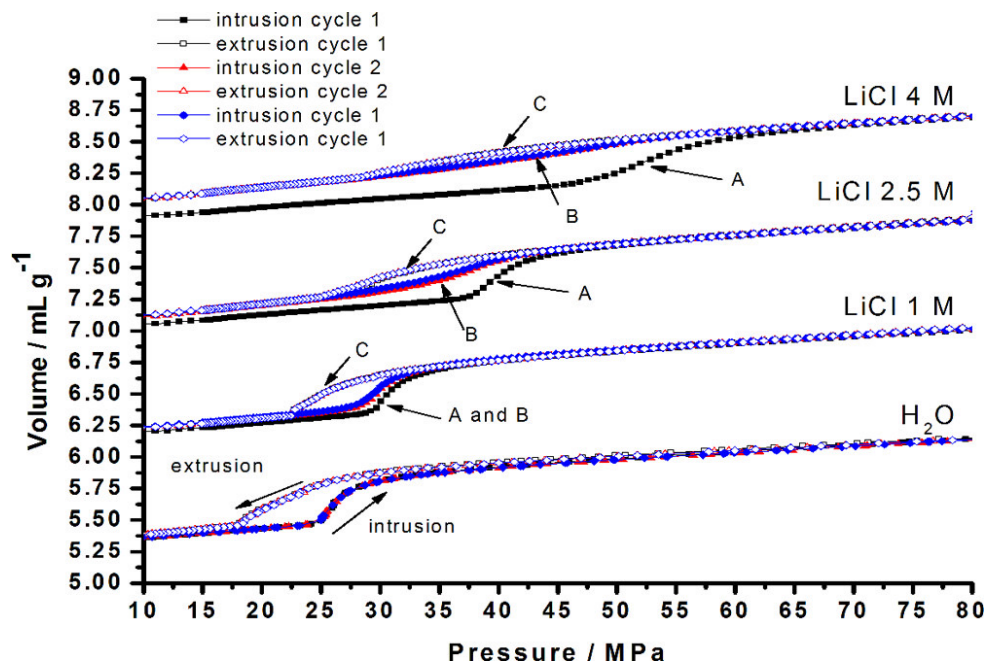


ZIF-8
Precursors:



P. Natl. Acad. Sci. U.S.A., **2006**, 103: p 10186-10191.
DOI: 10.1073/pnas.060243910

Example of solution with salts

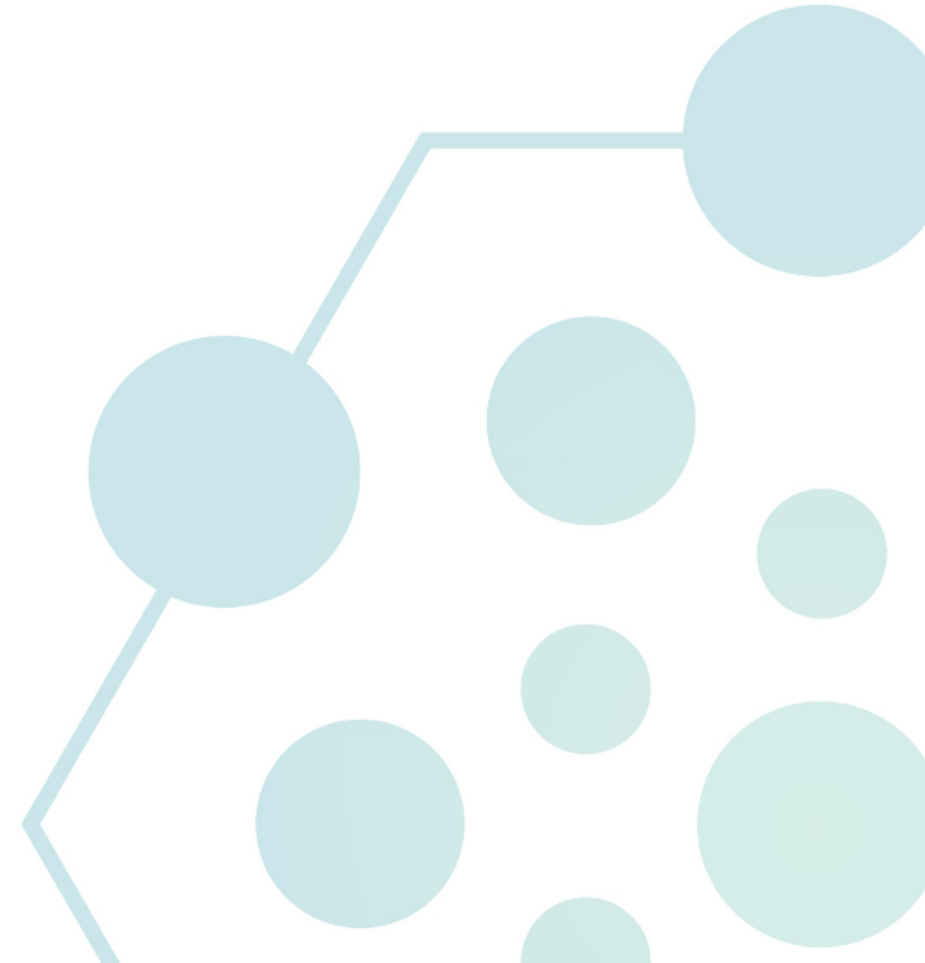


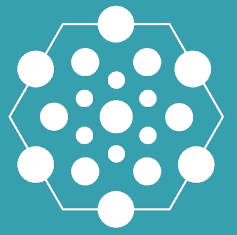


Why chose alcohol solution

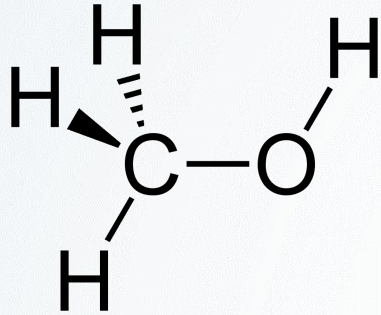


- More friendly with MOFs;
- Alcohol are soluble;
- they are bigger than typical ions used (they don't enter inside the materials);
- Identify those with a suitable size (and degree of polar groups).

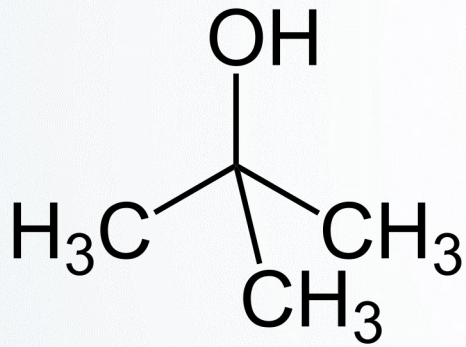




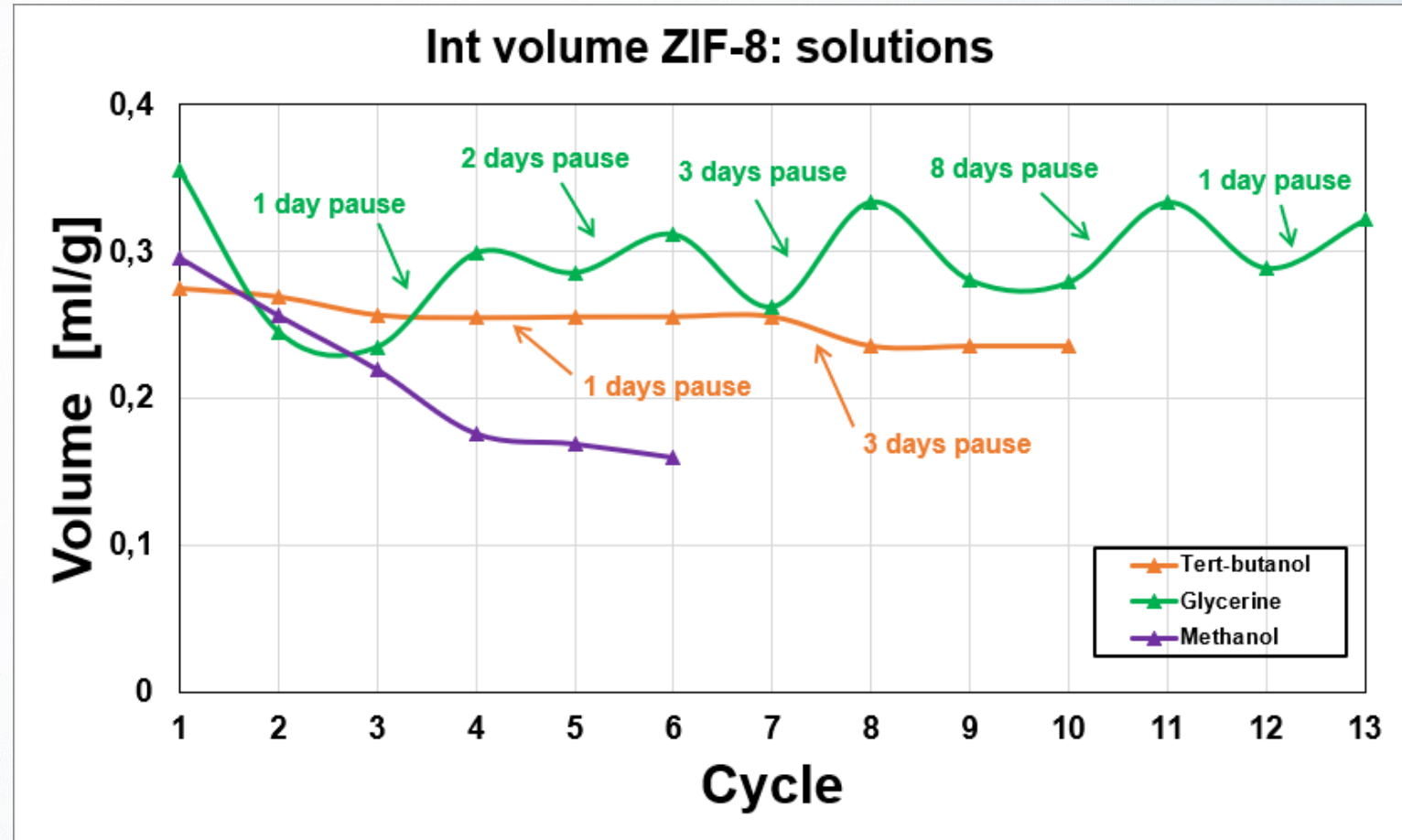
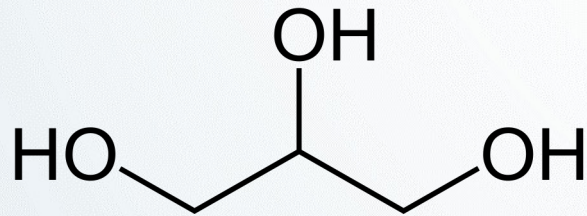
Methanol

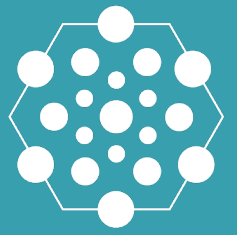


Tert-butanol



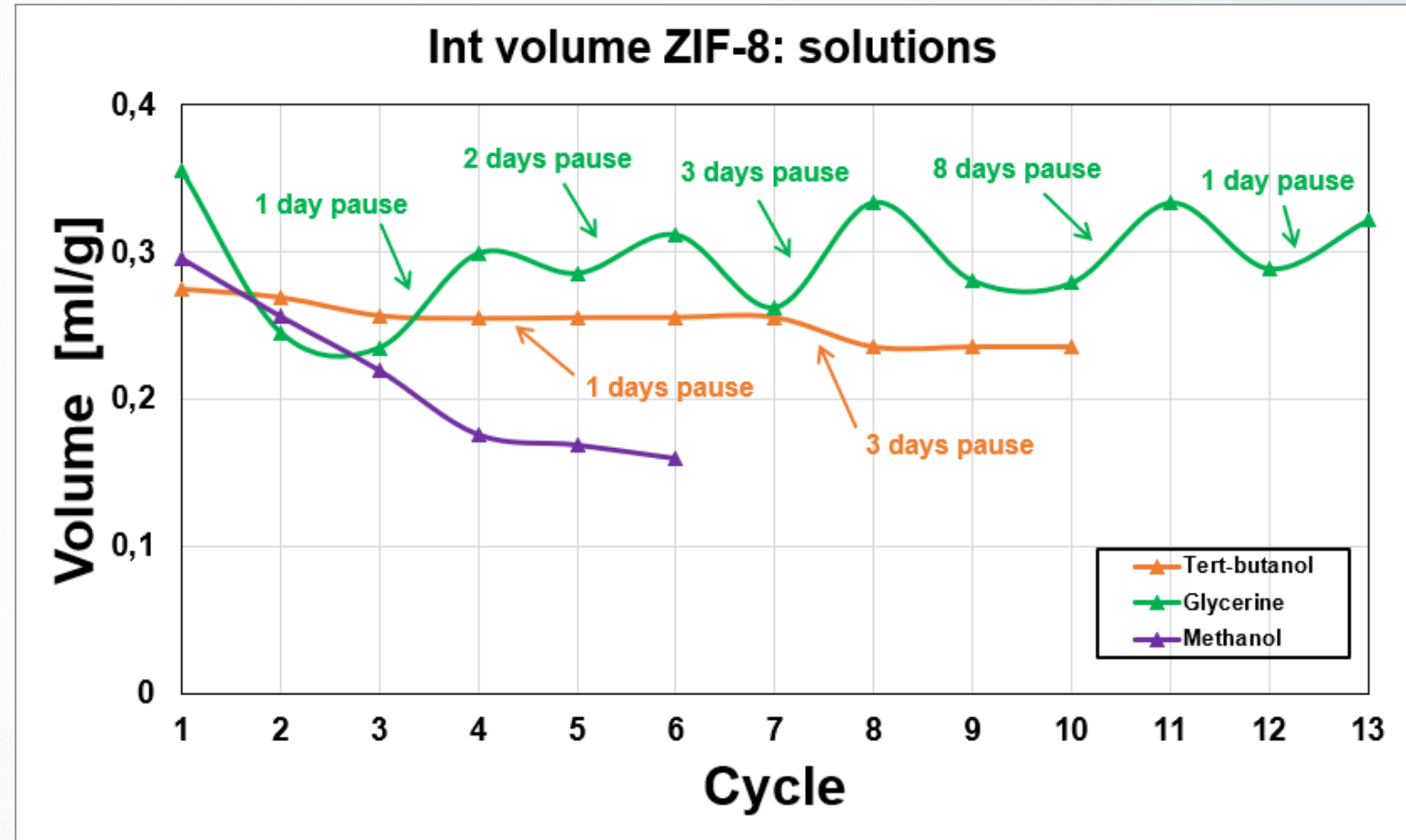
Glycerol



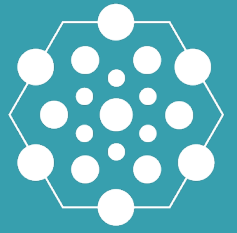


Working hypotheses:

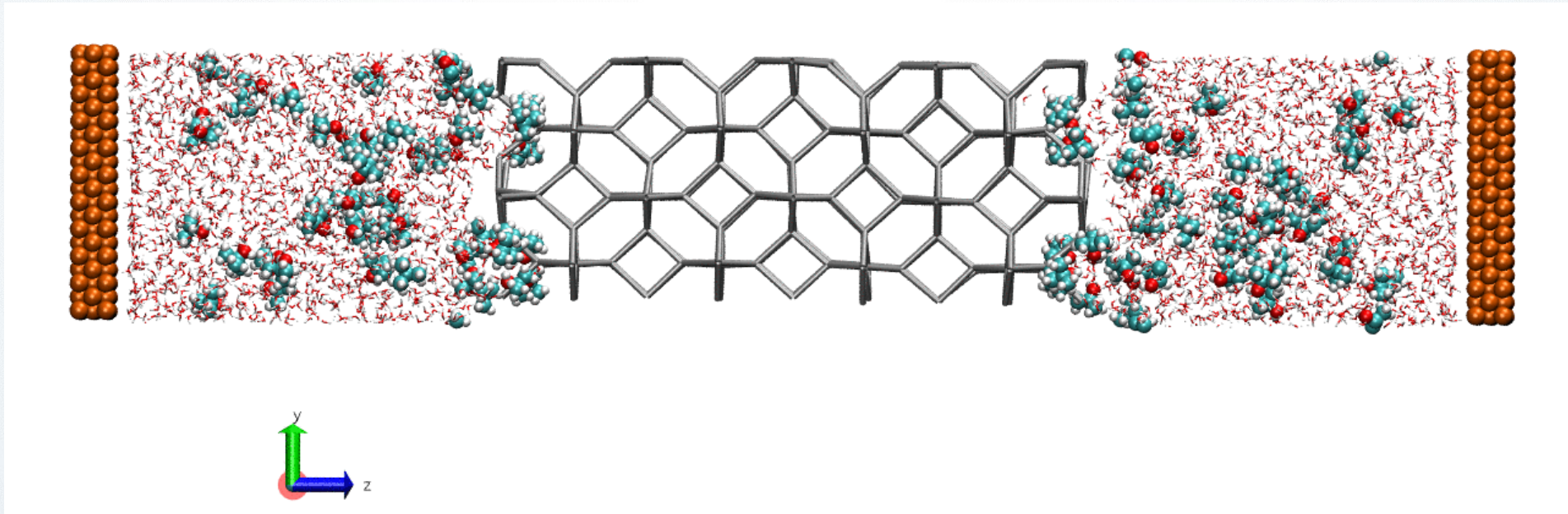
- Possible intrusion of alcohol inside ZIF8
- Formation of “structures” that prevent the intrusion of water molecules

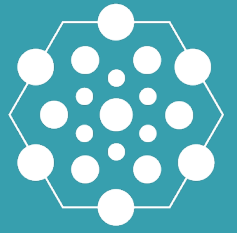


Computational techniques: Classical Molecular Dynamics



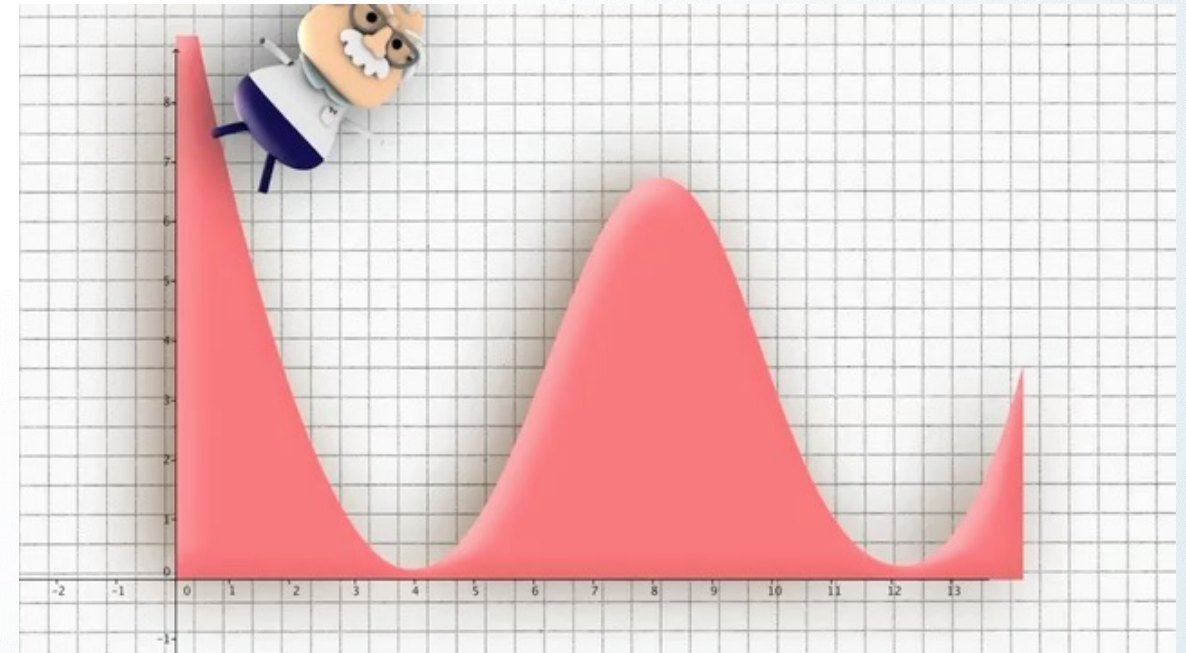
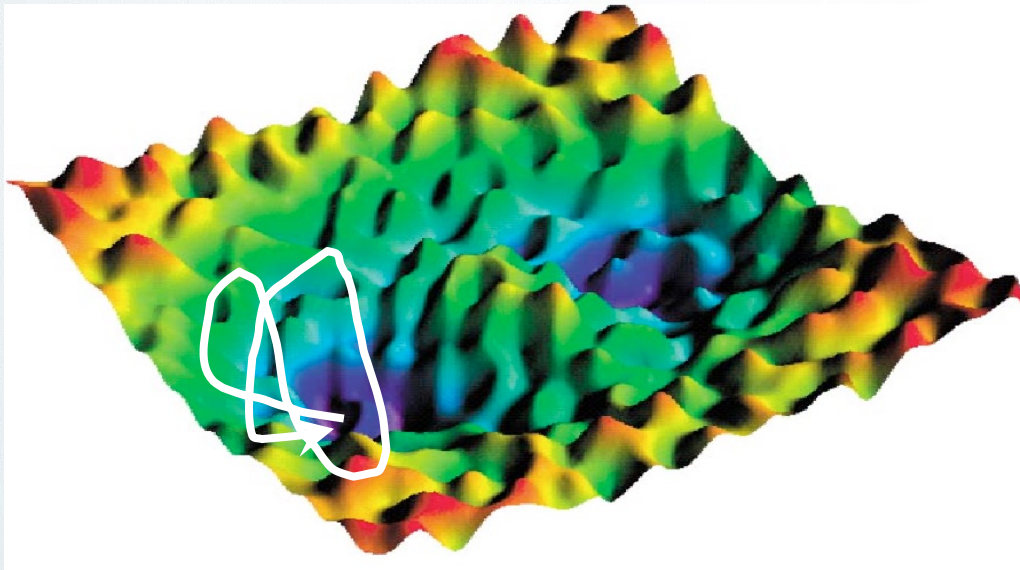
- Brute force simulations: standard molecular dynamics of empty ZIF-8 in contact with alcohol solutions of 11.5% wt, 300 K and two pressure. Each simulation is 20 ns long.

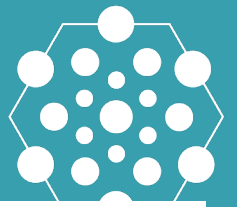




Many problems (chemical reactions, diffusion in solids, nucleation, folding and unfolding of proteins) occur on timescale inaccessible by simulations

Rare events



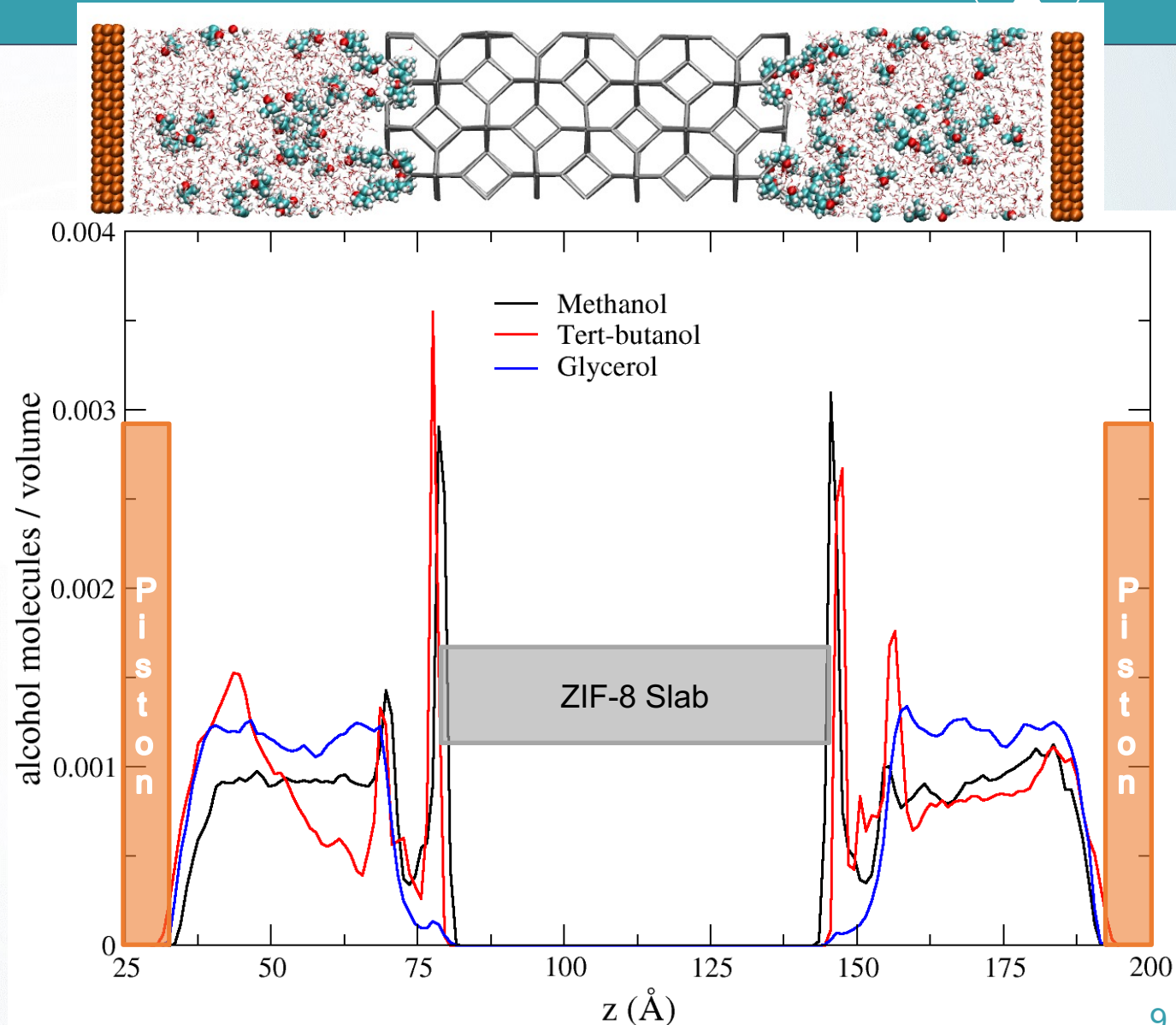


Brute force simulations:

Number density profile along z-axis:

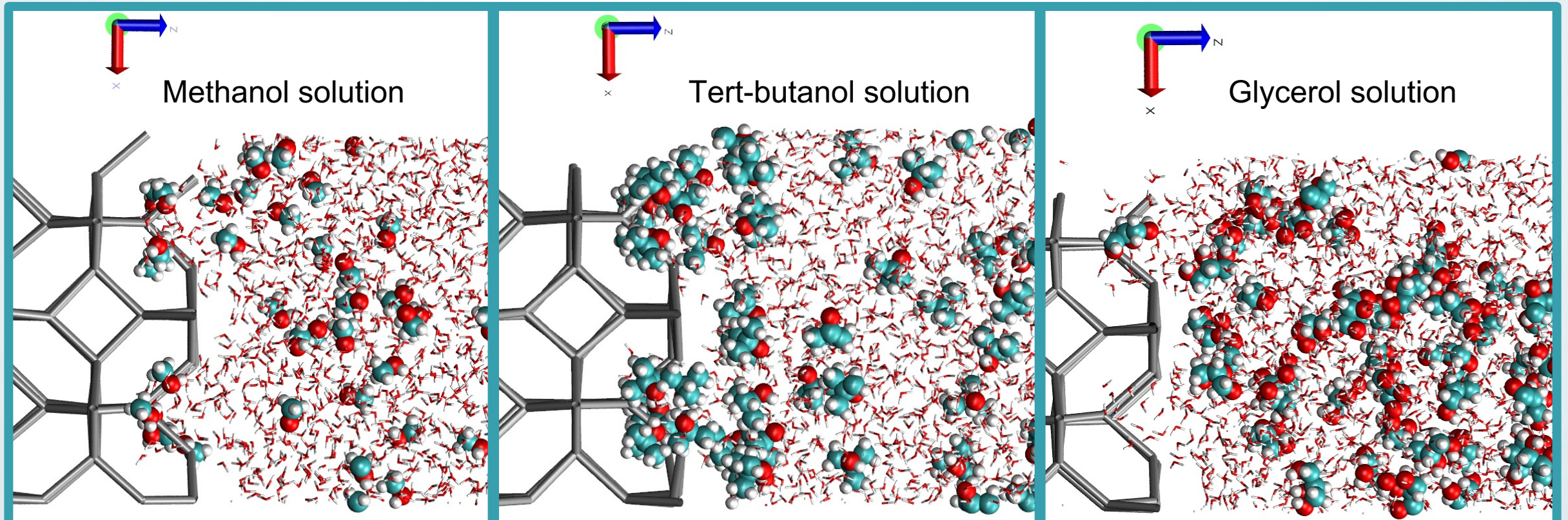
Number of alcohol molecules/volume.

Different behaviour between glycerine and methanol (tert-butanol) solutions

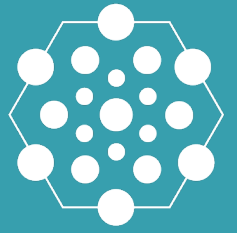


Affinity between ZIF-8 and solutions

A zoom to highlight the surface-alcohol interactions; it also show the tert-butanol (and methanol) trend to stay close to hexagonal window and to occupy the center of those windows.

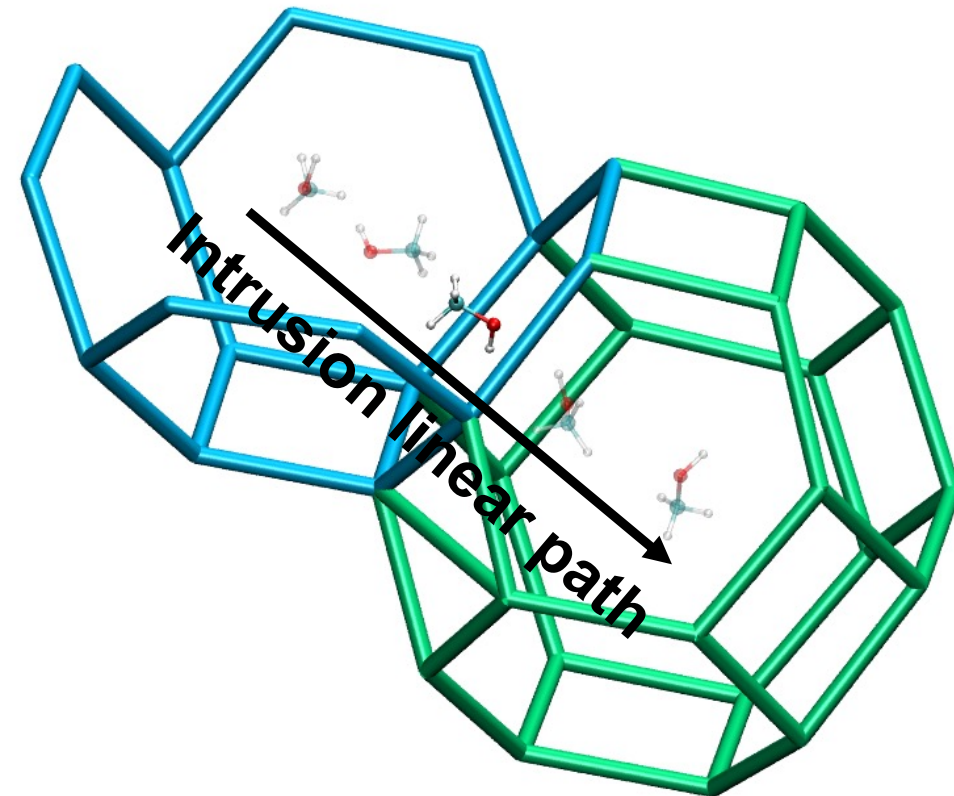
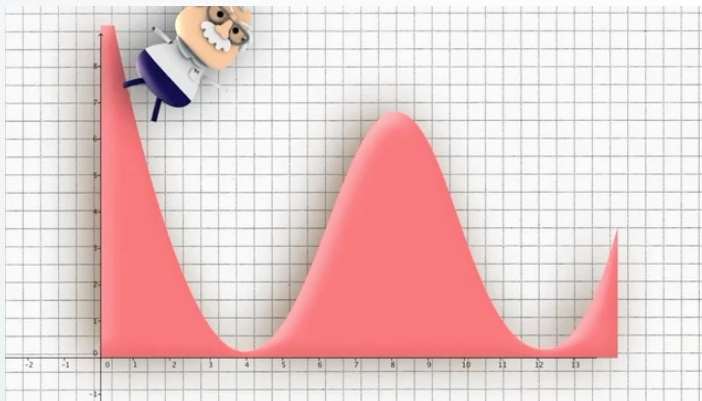


Advance sampling Techniques: combining RMD and Parallel Tempering simulations

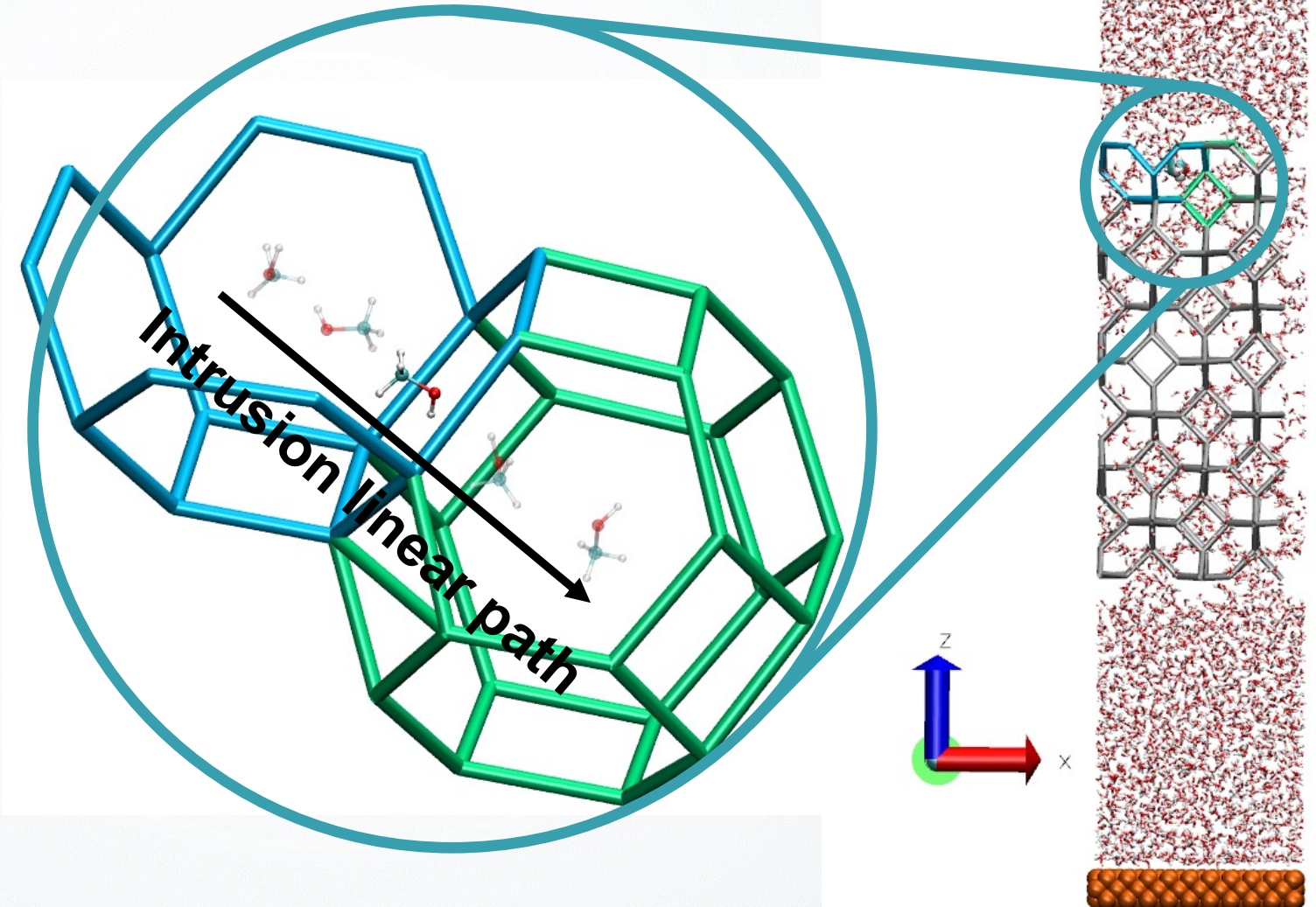


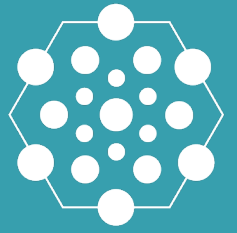
- Advanced sampling techniques: Restrained Molecular Dynamics (RMD) along a linear path of intrusion coupled with Parallel Tempering techniques (T= 300-350 K). Every single simulation is 1 ns long.

Eq of integration of force

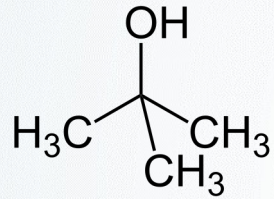


Advance sampling Techniques: combining RMD and Parallel Tempering simulations

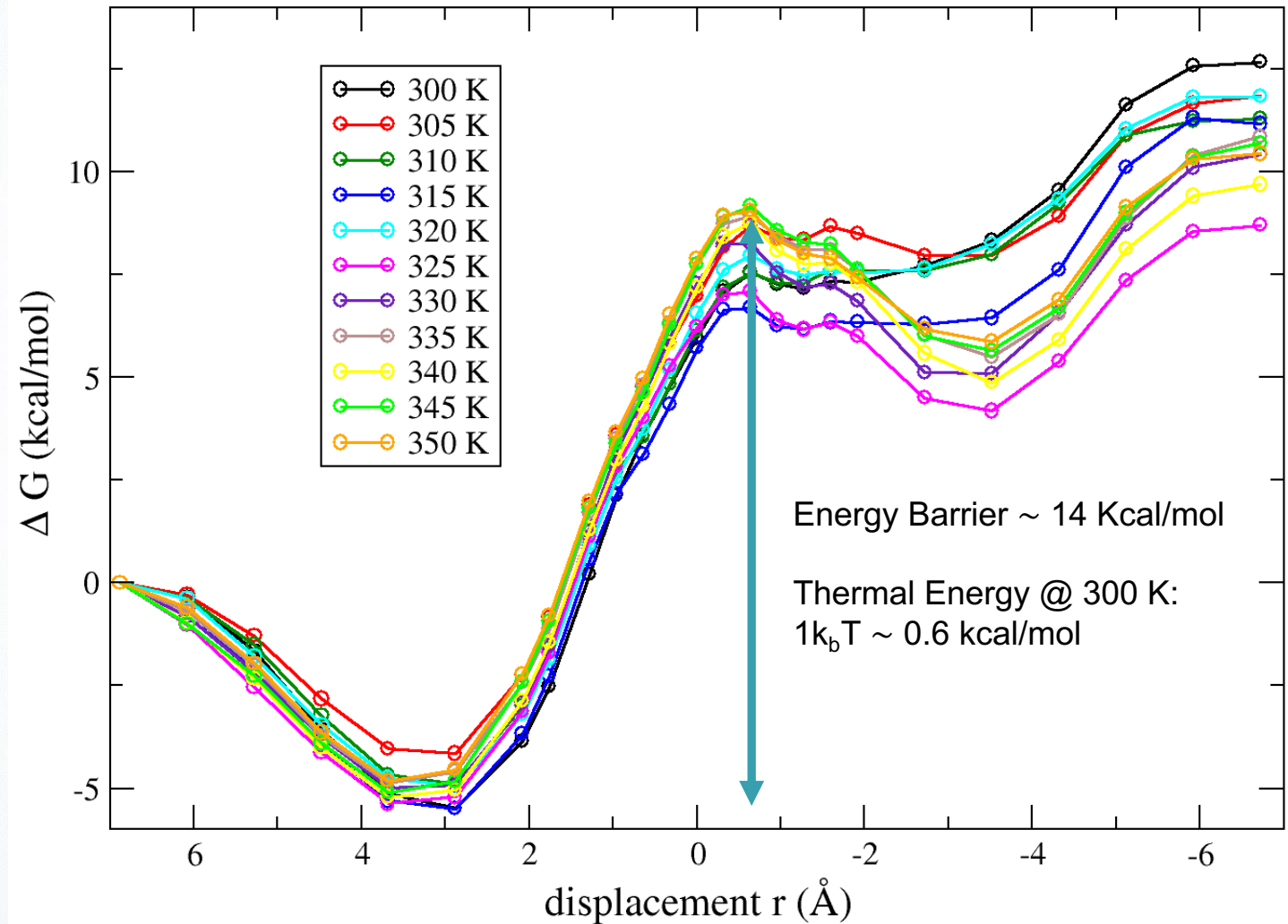


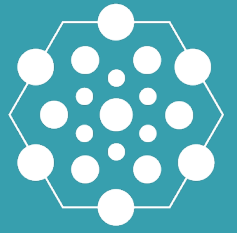


Tert-butanol

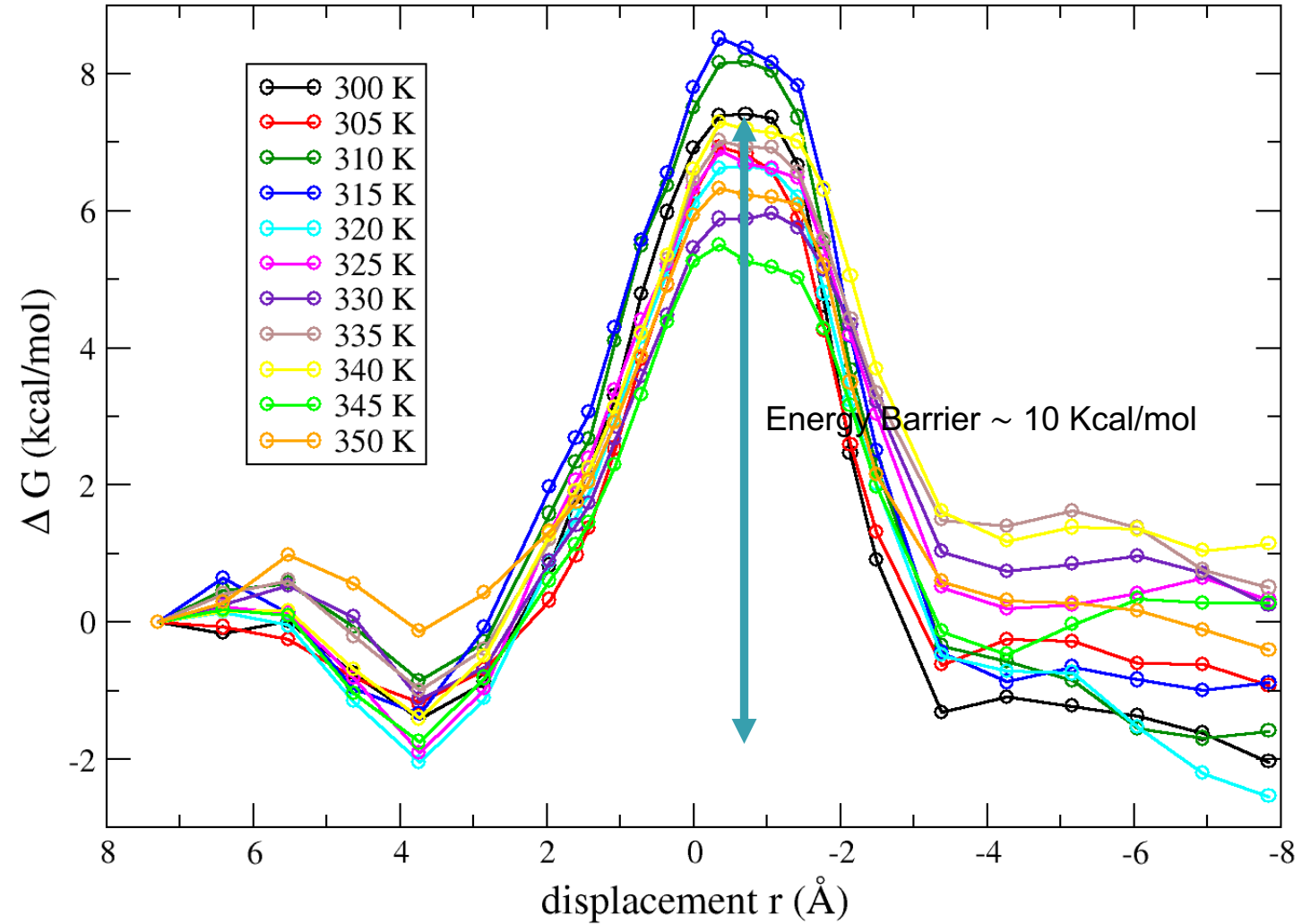
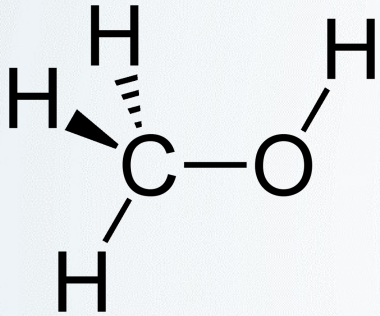


$$p_i \propto e^{-\frac{\epsilon_i}{k_B T}}$$





Glycerine





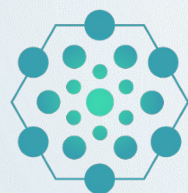
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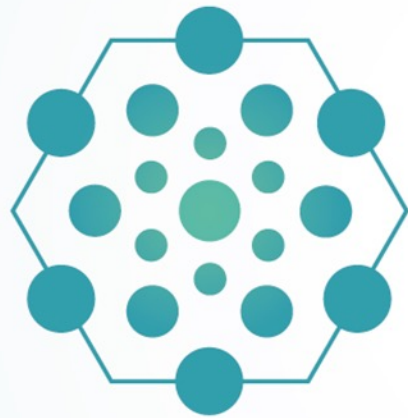
Thanks for your attention!



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