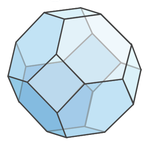
Understanding and modeling aequous liquid-ZIF intrusion to design reusable and high-impact shock absorbers

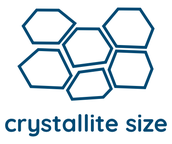
Jelto Neirynck, Sven M.J. Rogge
Center for Molecular Modeling, Ghent University, Technologiepark-Zwijnaarde 46, 9052 Zwijnaarde, Belgium

Liquid-ZIF intrusion...

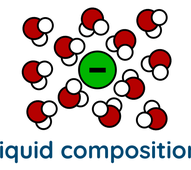
Zeolitic imidazolate frameworks (ZIFs) adsorb aequous liquid under high mechanical pressure, depending on various external and internal factors.

pore geometry

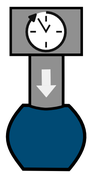




crystallite size



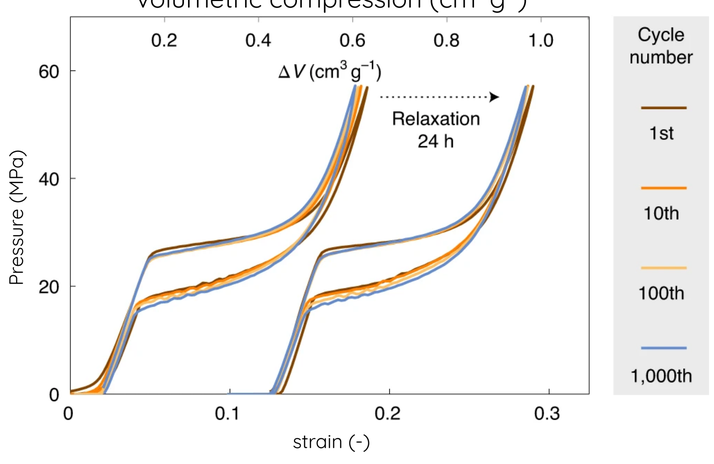
liquid composition



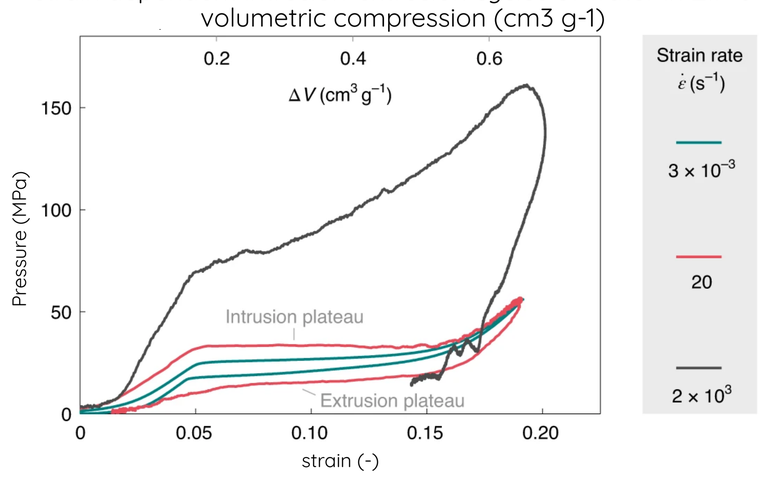
strain rate

The amount of energy stored or dissipated during the intrusion/extrusion process is determined by the **hysteresis** between intrusion and extrusion pV curves.

repeated intrusion-extrusion cycle of water in ZIF-8[1]



strain dependent intrusion-extrusion cycles of water in ZIF-8[1]



...to create the ideal shock absorber?

Depending on the choice of ZIF, electrolyte and crystallite size, different macroscopic behaviours can be realised ranging from **springs, shock adsorbers and bumpers.**

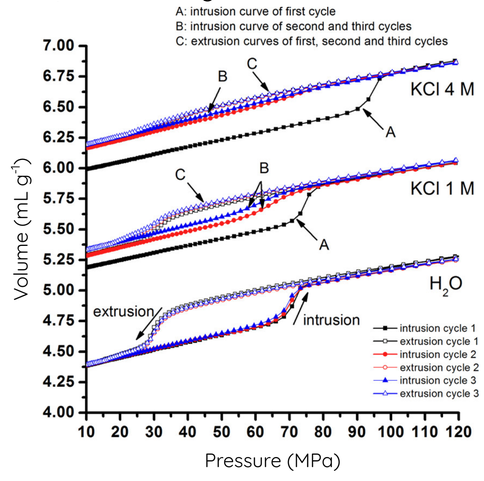
By screening many ZIFs and aequous solutions, understanding and examining their behaviour under different strain rates and finding the best crytallite size **the best shock absorber can be engineered in silico.**

...how does intrusion work on the nanoscale?

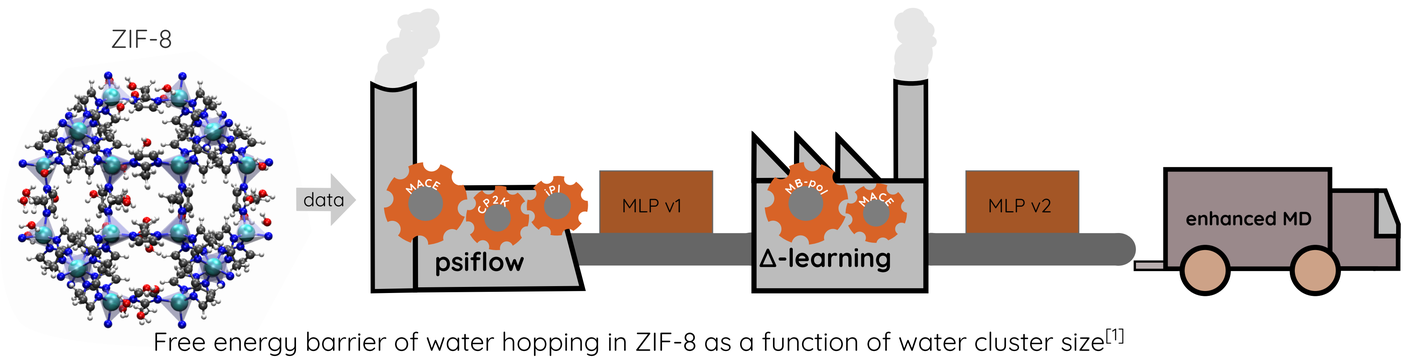
...how to couple water hopping (ns timescale) to intrusion/extrusion (ms timescale)

...how to model the strain rate?

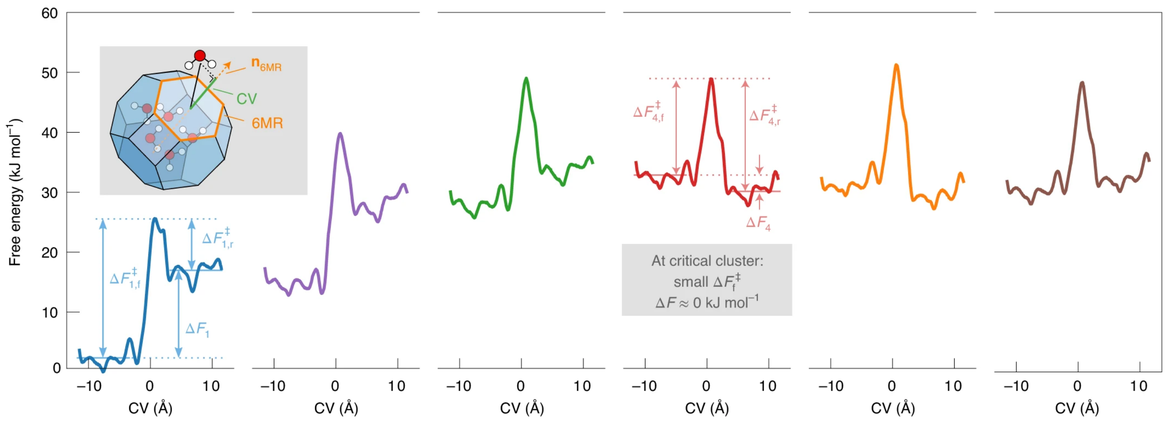
intrusion/extrusion cycles of KCl solution in ZIF-8[2]



Machine learning potential (MLP) to model intrusion on the nanoscale



Free energy barrier of water hopping in ZIF-8 as a function of water cluster size[1]



1st transition	4th transition
No of water molecules	No of water molecules
cage 1 6 → 5	cage 1 6 → 5
cage 2 0 → 1	cage 2 3 → 4
2nd transition	**5th transition**
No of water molecules	No of water molecules
cage 1 6 → 5	cage 1 6 → 5
cage 2 1 → 2	cage 2 4 → 5
3rd transition	**6th transition**
No of water molecules	No of water molecules
cage 1 6 → 5	cage 1 6 → 5
cage 2 2 → 3	cage 2 5 → 6

Why MLP enhanced with MB-pol?

low computational cost combined with ab initio accuracy for the ZIF framework (improvement on FF results)

accurate modeling of water-water interactions due to MB-pol

ability to expand to other ZIFs and aequous solutions

Current results using force fields[1]

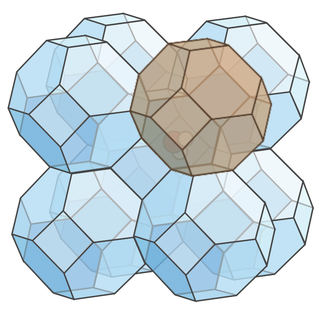
water molecule hopping timescales

free energy barriers explain hydrophobicity

concept of a critical cluster which enhances or limits water hopping

A kinetic Monte Carlo model as a multiscale method to model water intrusion/extrusion

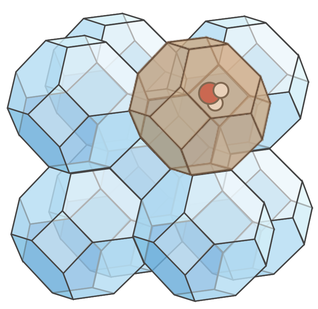
crystallite



event table

event	free energy barrier	probability
cage 1 -> cage 2	dF_1	p_1
cage 1 -> cage 3	dF_2	p_2
cage 1 -> cage 4	dF_3	p_3
...		

randomly chosen event



\+ **pressure modification**

Ability of this model

faster than any MD

predict intrusion/extrusion pressure

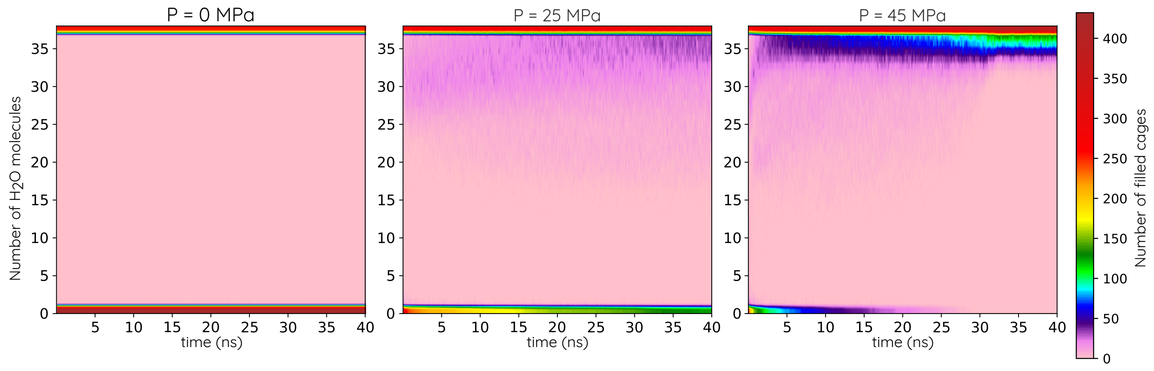
captures full intrusion/extrusion timescales

explains crystallite size effects

can be expanded to other topologies and liquids

example:
intrusion in a
7x7x7 unit cell

edges are being filled
FF derived energy barriers



But...

how to model pressure?

how to model strain rate?

impact of the surface boundary?

what about defects?

What's next?

improve **energy barriers** with the MLP to understand and model the physics of water intrusion

improve the **pressure model & implement strain** to correspond with experiments

expand the MLP and KMC workflow toward **different ZIF-liquid systems**, e.g., ZIF-71, MAF-6... combined with ions or alcohols, which will lead to the choice of most optimal shock absorber

combining all of the above **to model and understand intrusion**

Conclusions

The ab-initio trained MLP should be **enhanced to model water-water interactions** more accurately to improve on the result of the force field method. **MB-pol** looks promising for this goal, but still has to be verified.

The kMC model can describe the **multiscale** intrusion properties. The accuracy is mainly determined by the **energy barriers** and the **hopping frequency**.

The major challenges with the kMC-model is the **implementation of pressure and strain.**

STRAINSWITCH (ERC-StG-2023)
strain engineering to design functional 4D polymorphism in nanostructured materials

[1]Nat. Mater. **20**: 1015, **2021**
[2]J. Phys. Chem. C **118**: 21316, **2014**

Jelto.Neirynck@UGent.be
Sven.Rogge@UGent.be
molmod.ugent.be