PhD in Chemistry
XXXVII cycle Final Dissertation, 01.04.2025

Thermodynamics of water confined within hydrophobic Metal-Organic Frameworks and the dynamics of intrusion/extrusion process

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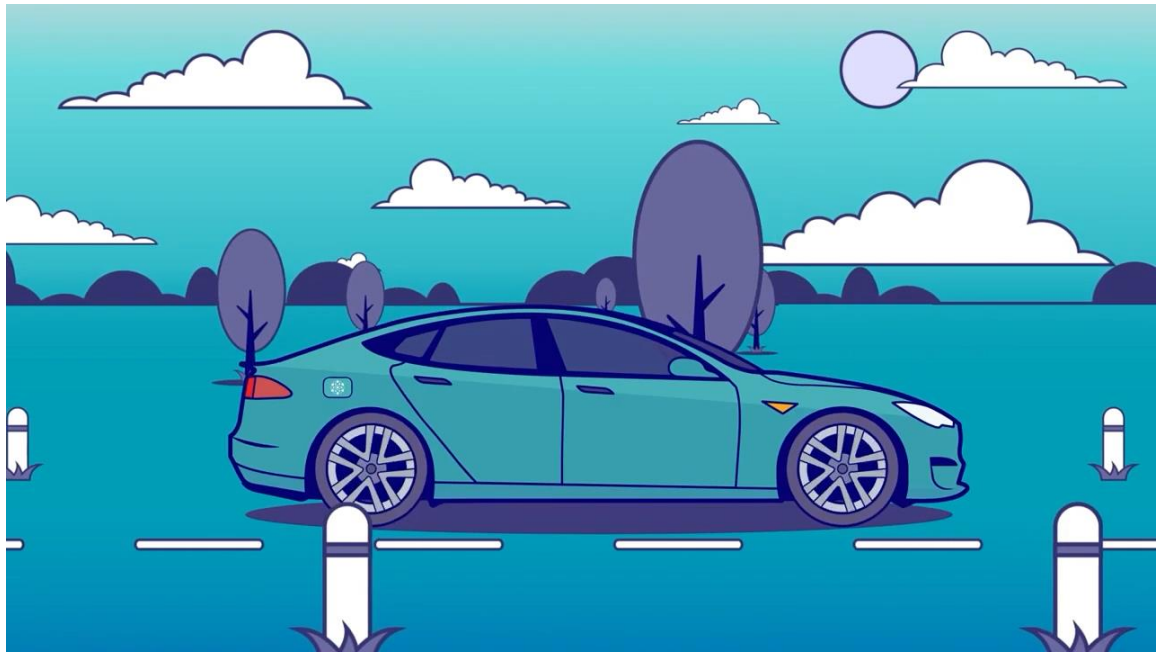
Aim of the Thesis

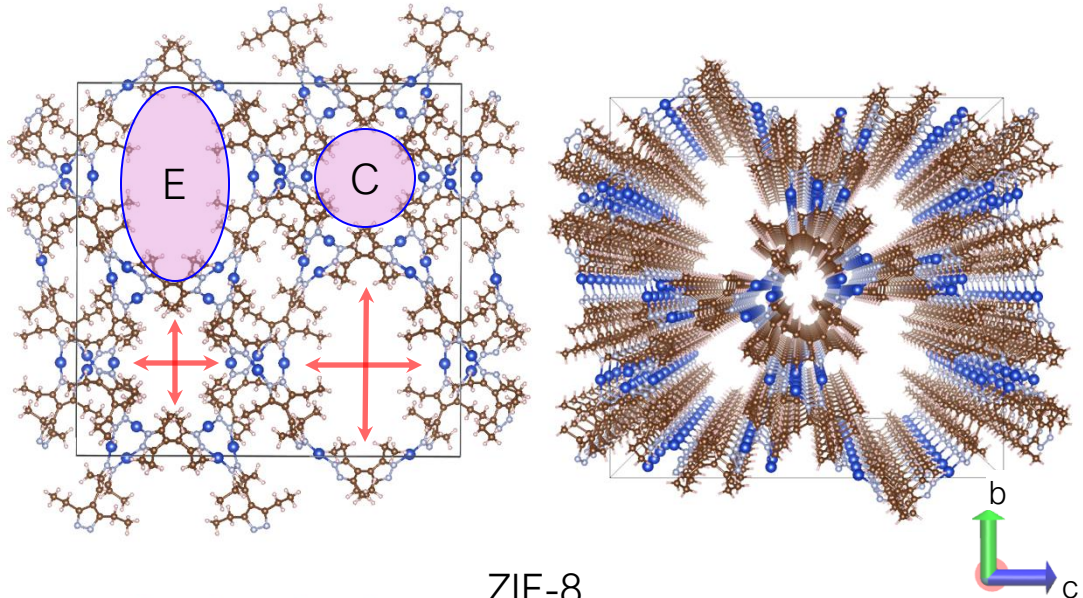


computational study on
hydrophobic {microporous material + water} systems

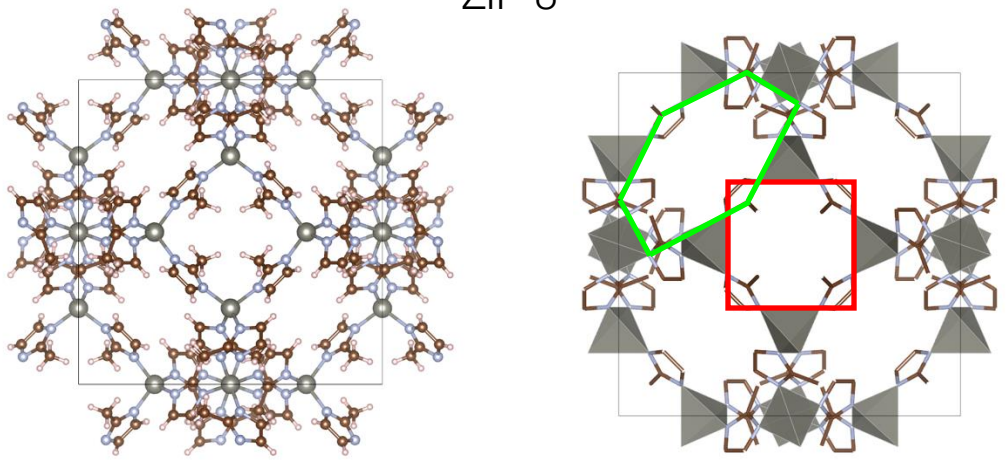
- liquid intrusion/extrusion mechanism and influence of T and P.
- role of morphology/topology.
- role of hydrophobicity.

Cu_2 (tebpz = 3,3'5,5' tetraethyl-4,4'-bipyrazolate) a.k.a. Cu_2L

E: 0.13 x 0.67 nm C: 0.62 x 0.62 nm



ZIF-8



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A glimpse of theory – **Molecular Dynamics**

$$A = \bar{A} = \langle \hat{A} \rangle = \int_{\Omega} \mathrm{d}\boldsymbol{\Gamma} \hat{A}(\boldsymbol{\Gamma}) \rho(\boldsymbol{\Gamma}) = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} \mathrm{dt} \hat{A}(\boldsymbol{\Gamma}(\mathrm{t}))$$

$$\rho_{NPT}(\boldsymbol{\Gamma}, \mathrm{V}) \propto e^{-[H(\boldsymbol{\Gamma}) + PV]}$$

- isothermal isobaric ensemble a.k.a. **NPT**.

  → mimic experimental conditions

- **R**estrained **M**olecular **D**ynamics

  → free energy landscape

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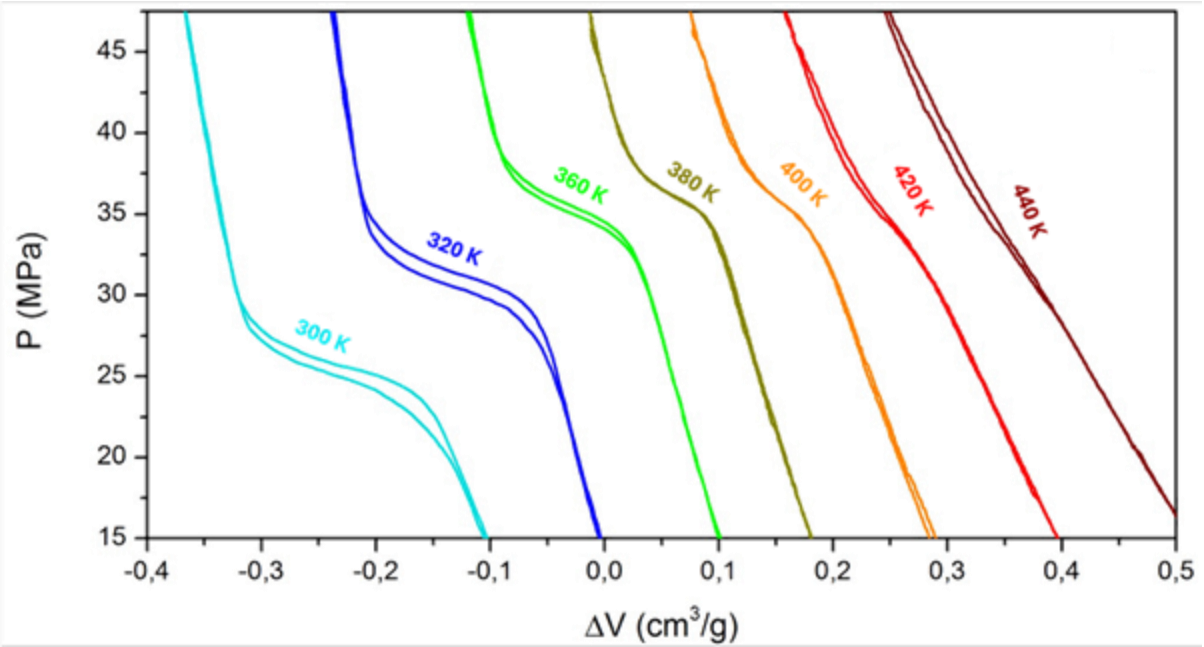
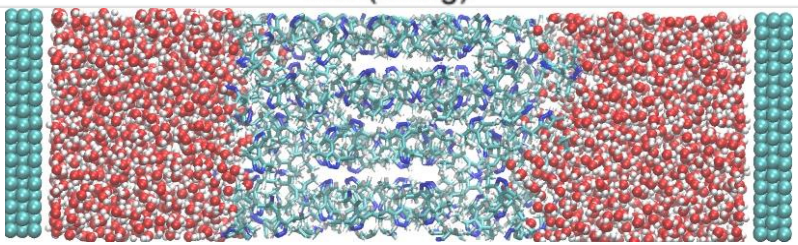
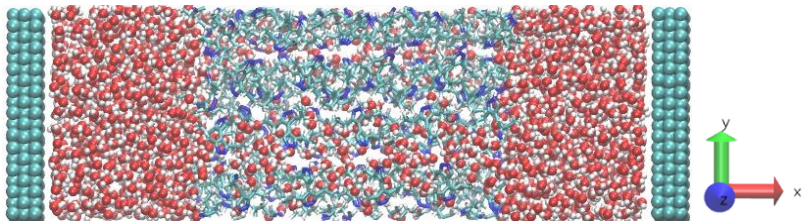
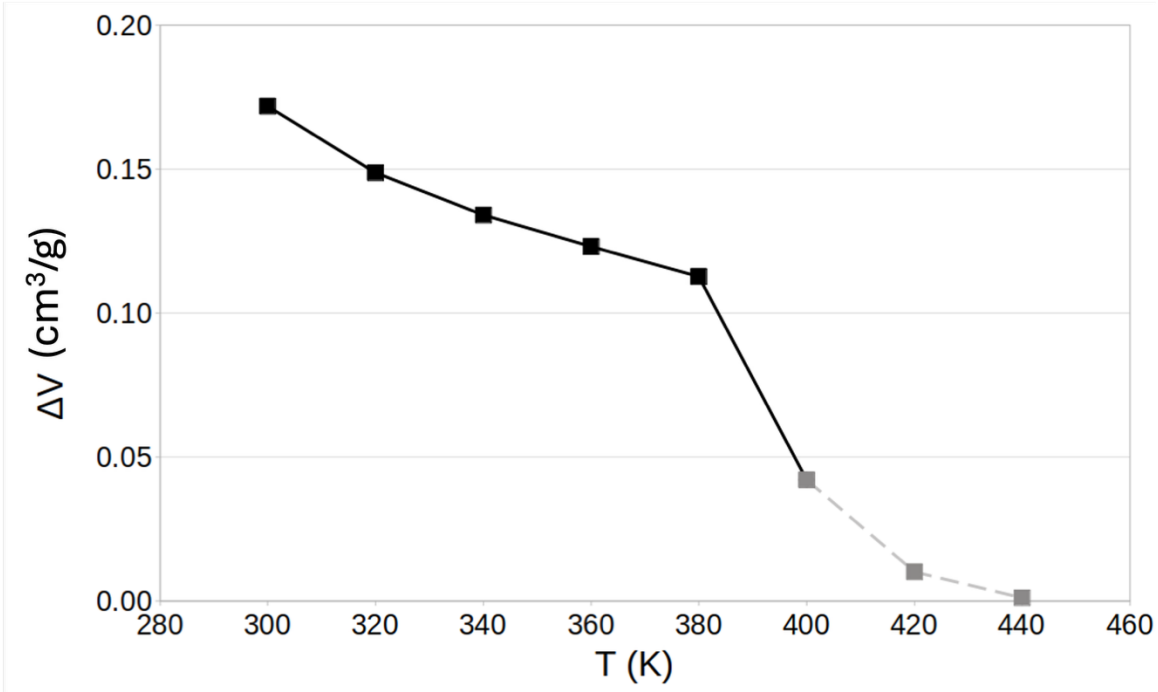
Supercritical water **inside** Cu_2(tebpz) – 1/4









$$\Delta V(T,P) = \frac{V_{pore}\left(\rho_l^C(T,P) - \rho_v^C(T,P)\right)}{\rho_l^B(T,P)}$$

$\rho_l^C(T) = \rho_v^C(T)$ the intruded volume vanishes: the system reached the **confined critical temperature**.

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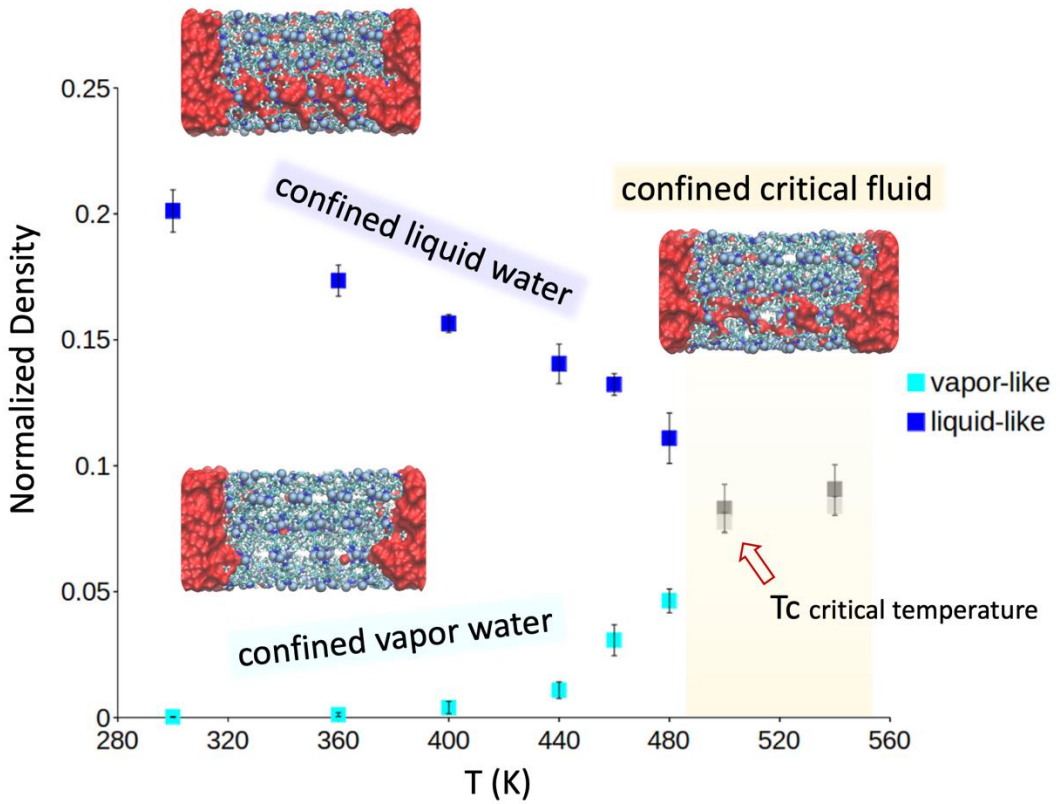
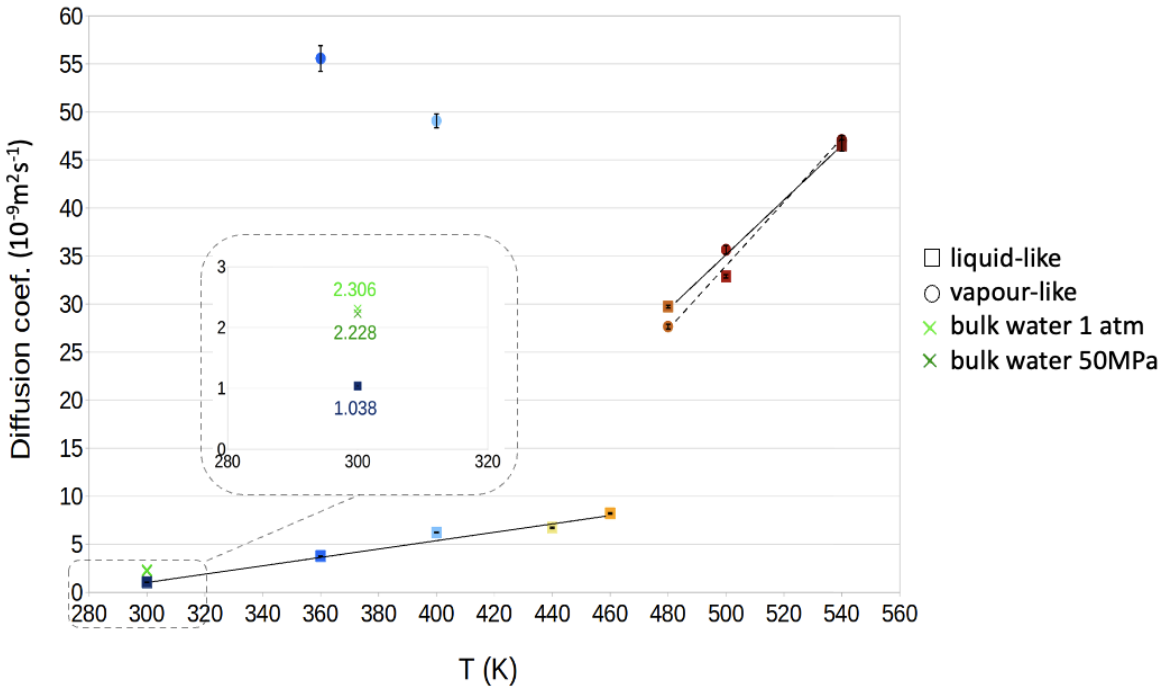
Supercritical water **inside** Cu_2(tebpz) – 2/4



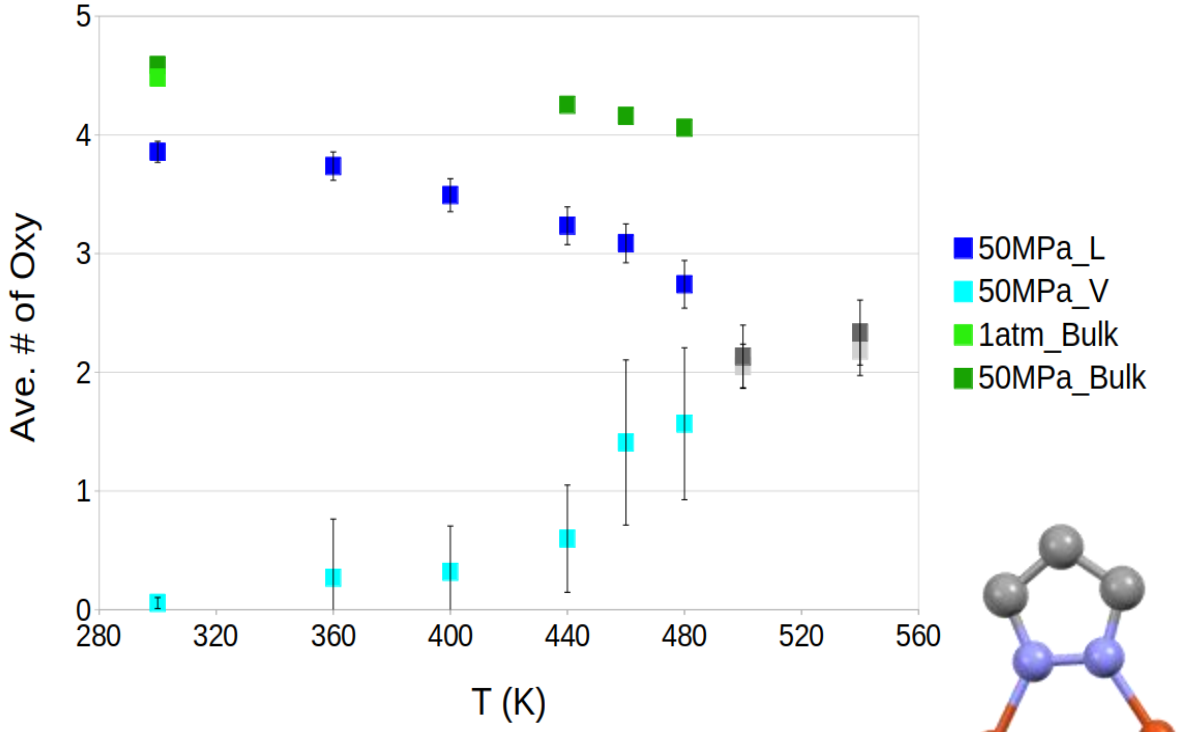


Supercritical phase of confined water at 480-500K 647.5 K bulk value [first evidence of such a major reduction].

Narrow difference between the diffusion coefficients for T = 500-540 K, i.e., confined water is supercritical.

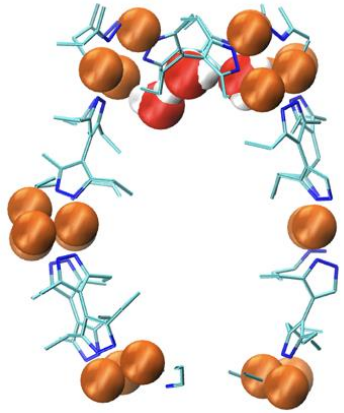
Supercritical water **inside** Cu_2(tebpz) – 3/4

Synchrotron data – localized vapour molecules

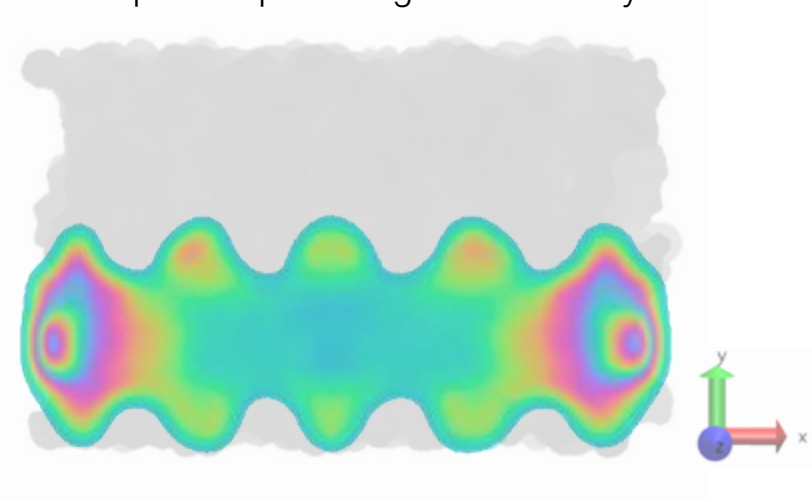


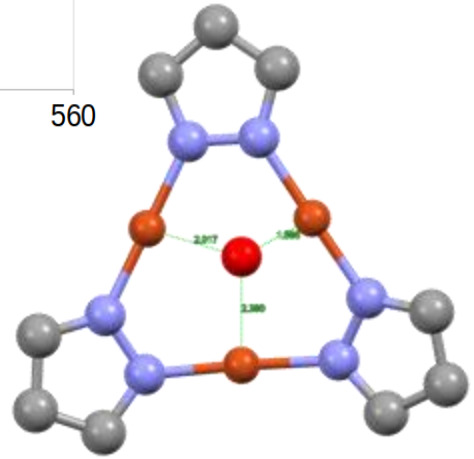
Origin of T_c downshift:

Trimer vapor-like cluster



Vapor-like phase high local density





- Cu **locally attractive sites** for water, despite **global hydrophobicity.**
- Maxima in secondary porosity of elliptical channels.
- Electronic density localized at a short distance from Cu atoms:

  Sync ~ 0.2 nm MD~ 0.28 nm

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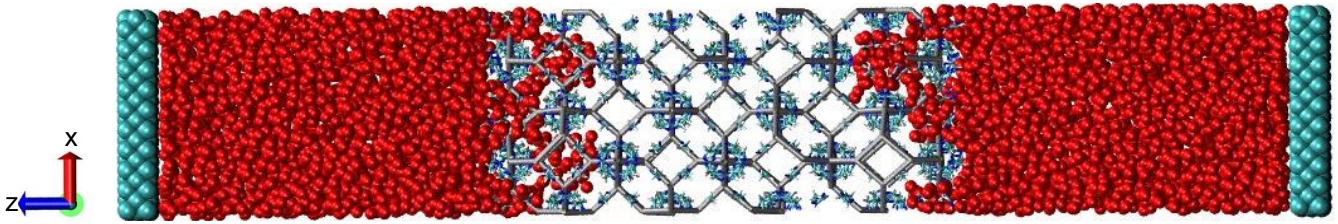
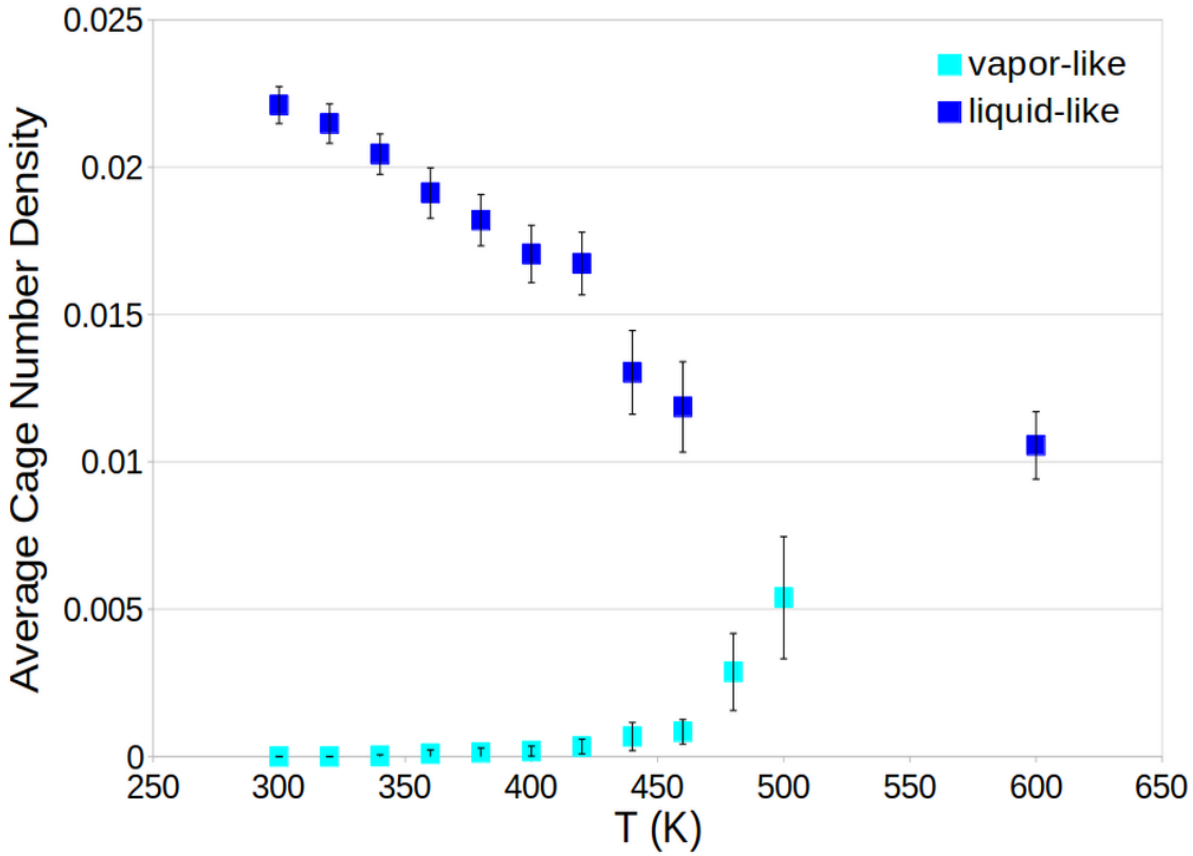
Supercritical water **inside** Cu_2(tebpz) – 4/4

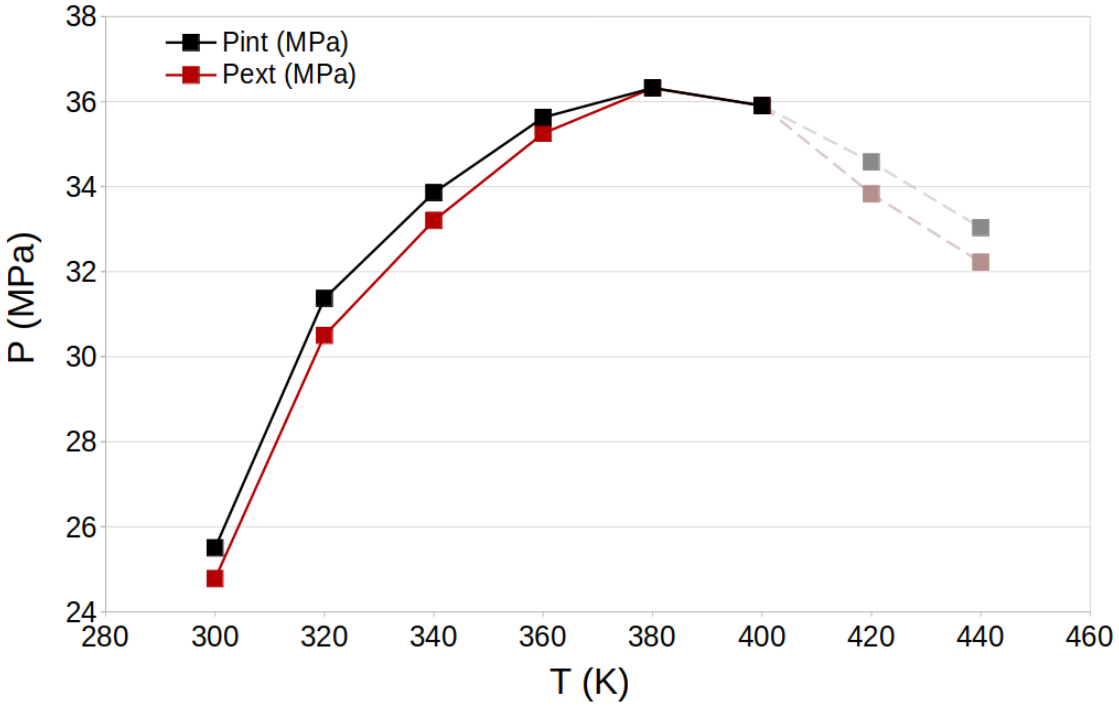
*Supercritical water – the case of **ZIF-8***

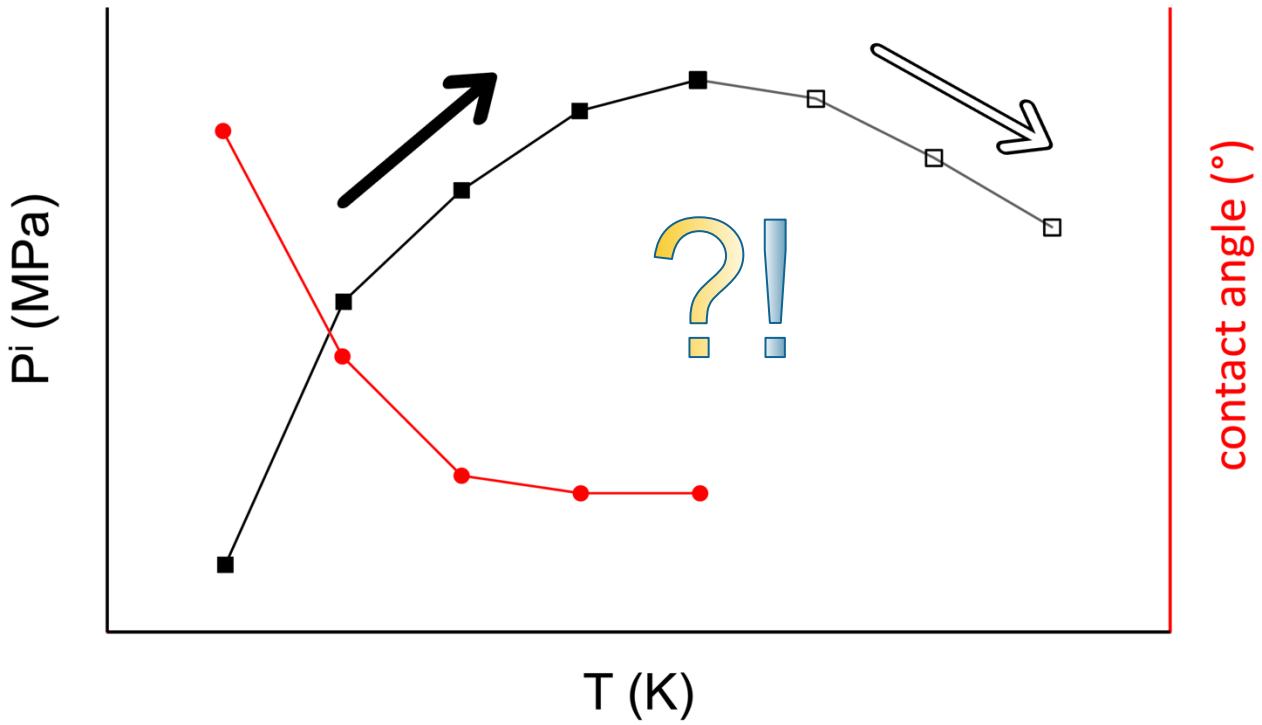




- Vapour density increases with T.
- Computational supercritical transition around 500 K.
- General phenomenology for other hydrophobic microporosu material.

Counterintuitive trend of P^i in Cu_2(tebpz) MOF – 1/3





Young-Laplace law

$$P^i = -2\gamma \cos\vartheta / a + P^v$$

usually neglected

γ = l/g surface tension

a = pore radius

ϑ = contact angle

P^v = vapor pressure

- P^i increases with T, reaches a maximum and then decreases.
- **Against** the **Young-Laplace** law.

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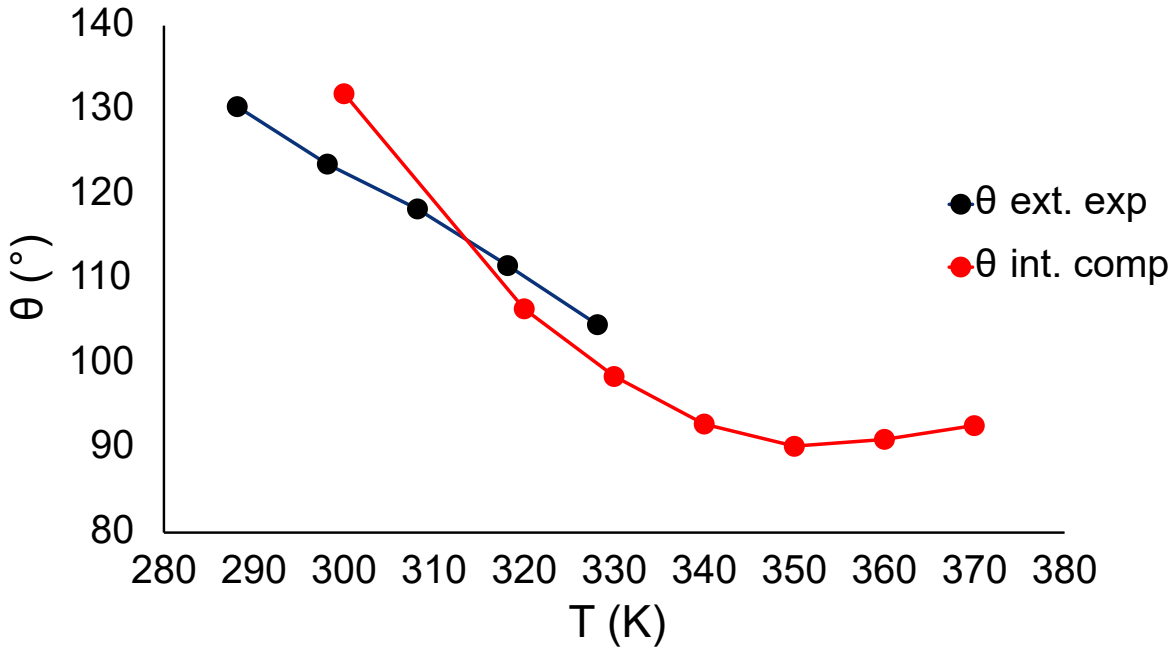
Counterintuitive trend of P^i in Cu_2(tebpz) MOF – 2/3

*CA – **Young-Douprè** equation*



- Young-Douprè equation:

$$\theta_{YD} = \arccos\left(\frac{\gamma_{lg} - \Delta W_{slg}}{\gamma_{lg}}\right)$$

- total energy of the three separate systems: {Cu_2(tebpz) + H2O}, Cu_2(tebpz), H2O:

$$\Delta W_{slg} = E_{\{Cu_2(tebpz)+H_2O\}} - E_{H_2O} - E_{Cu_2(tebpz)}$$

ΔW_{slg} = liquid/solid wetting energy

- and the surface tension?

γ_{lg} : 72 mN/m comp. vs 73.30 mN/m exp.

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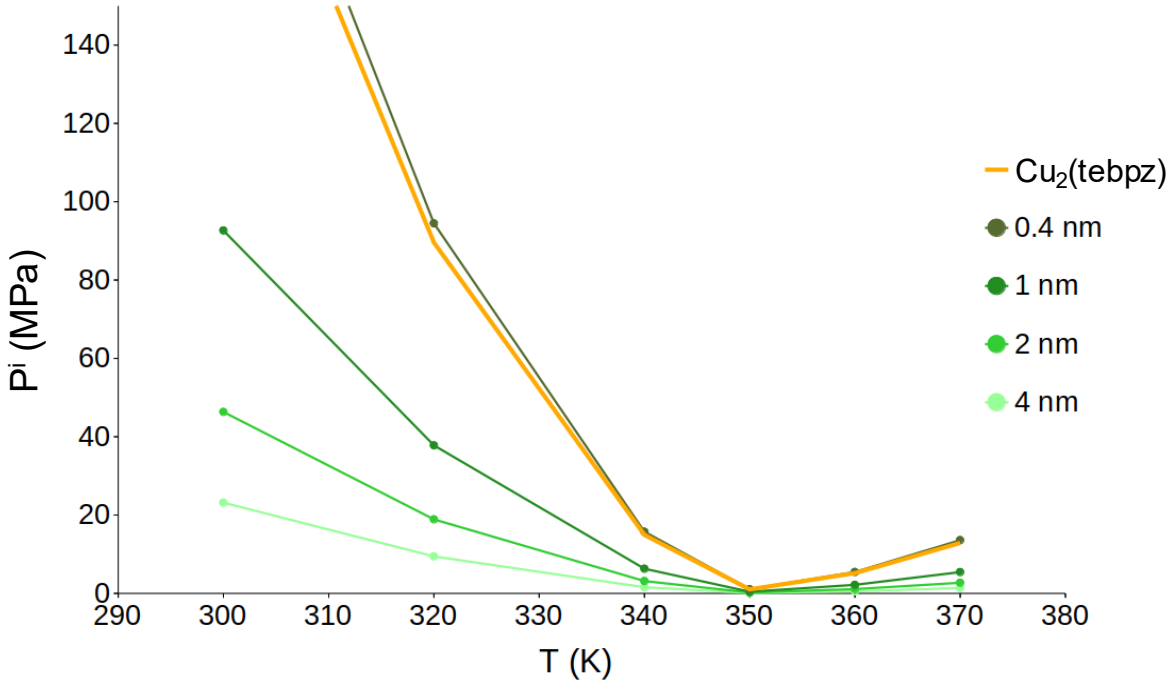
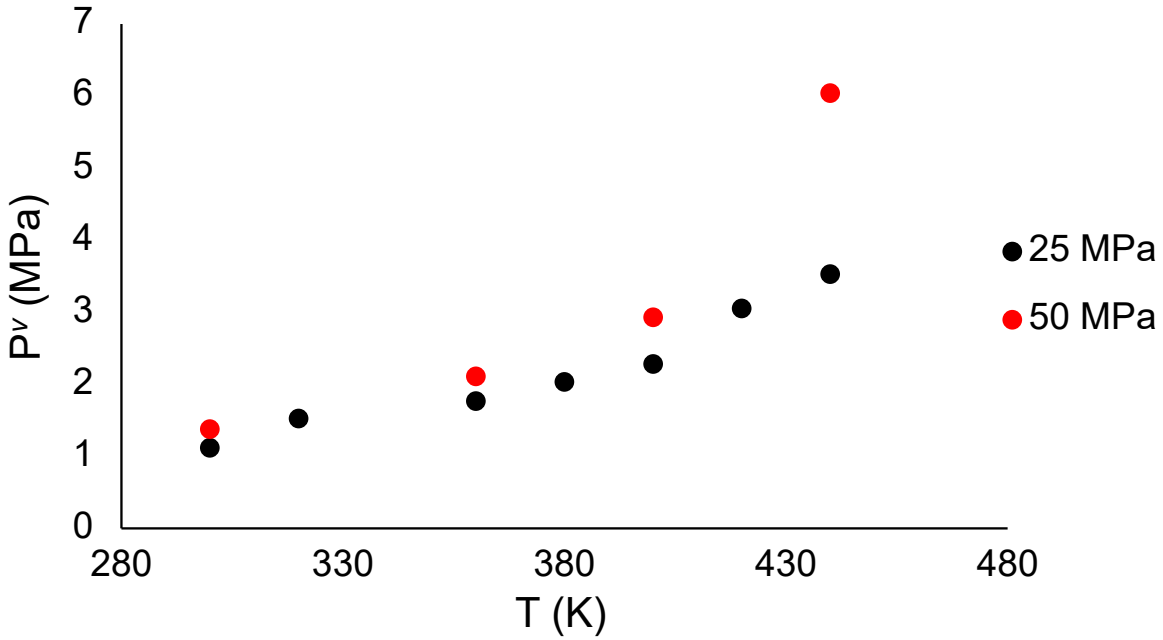
Counterintuitive trend of P^i in Cu_2(tebpz) MOF – 3/3



$$P^i = -2\gamma \cos\vartheta / a + P^v$$

- **increase** of **vapor density** inside the channels corresponds to an **increase** of P^v inside the MOF.



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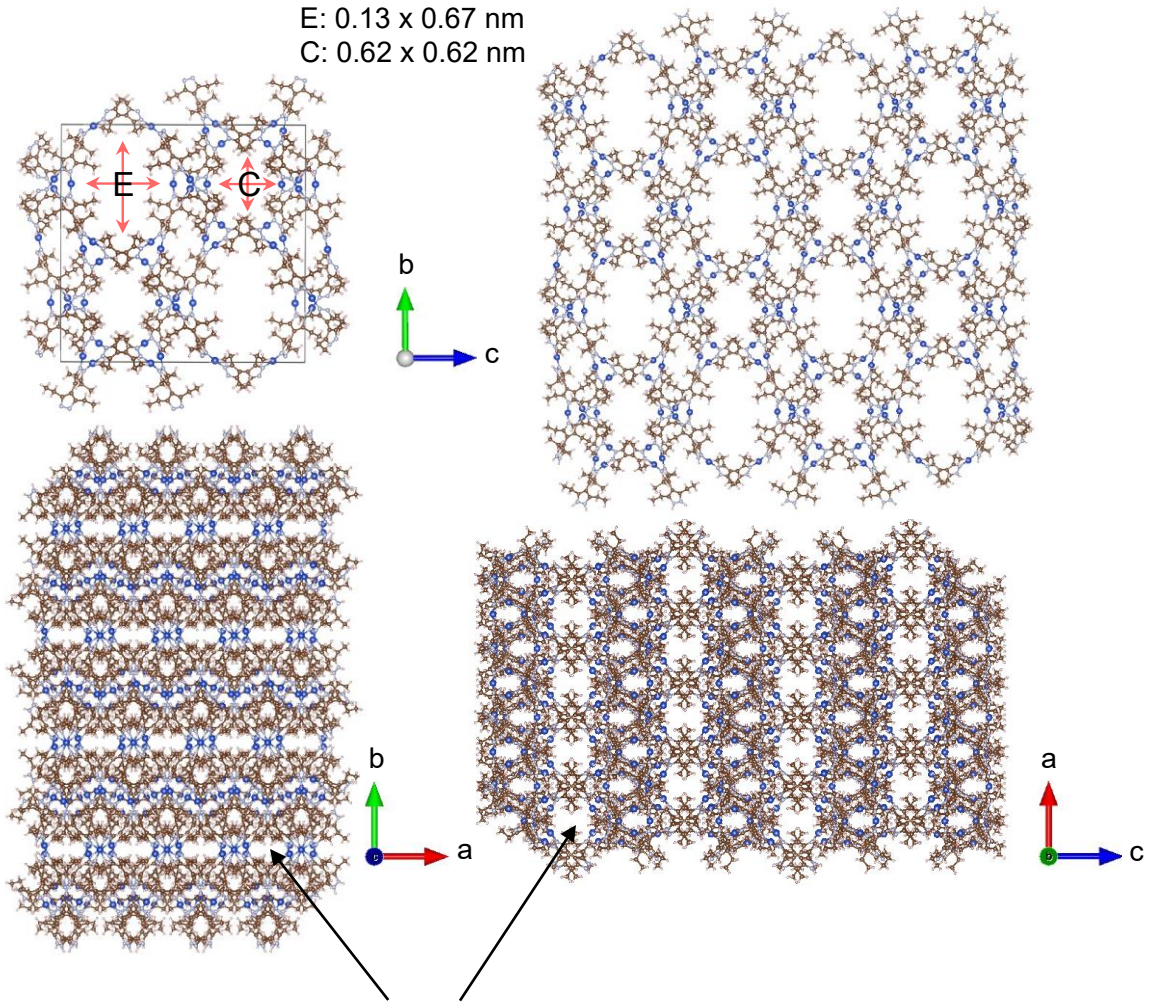
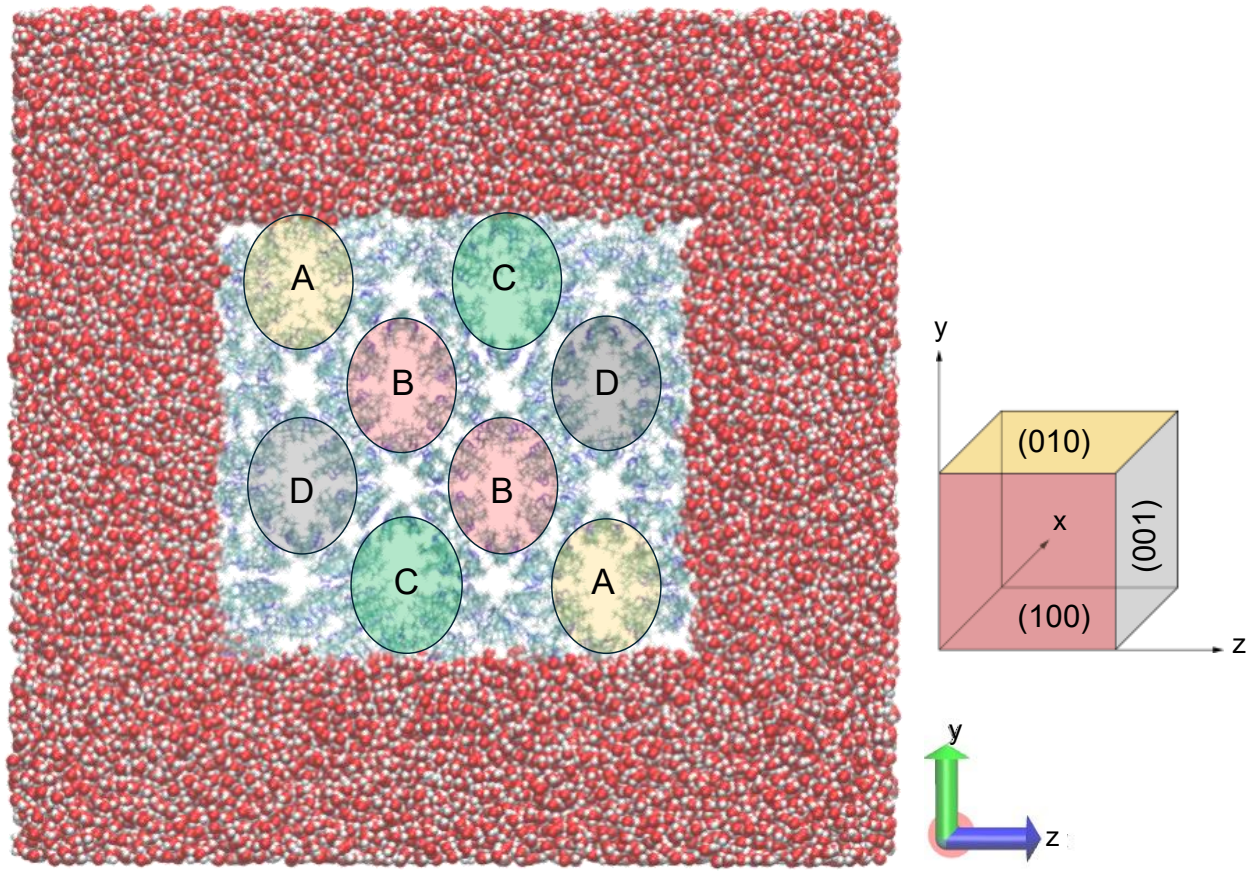
Water **intrusion mechanism** in Cu_2(tebpz) crystallite – the role of **complex** geometry – 1/5

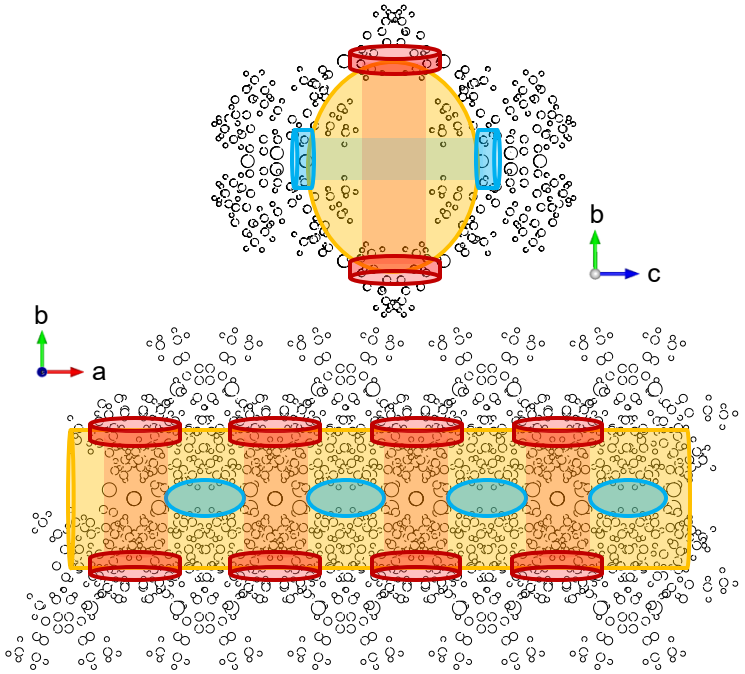


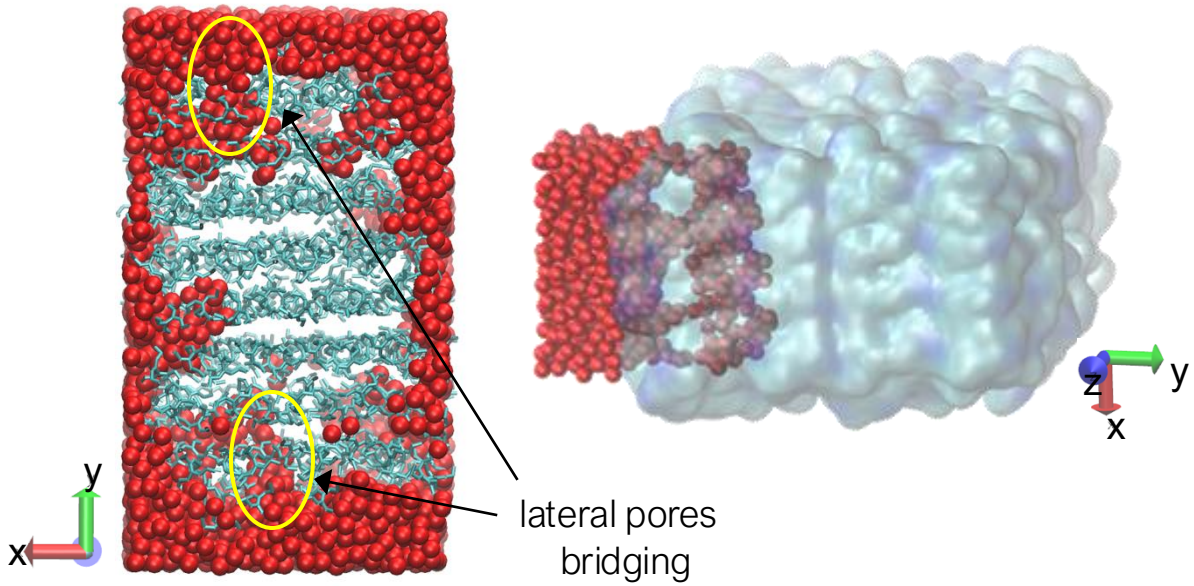


4 kind of elliptical channels: group **A**, **C**, **D** in direct contact with **bulk water** also through the **secondary porosity**. group B in contact with water only with the main openings.

Water **intrusion mechanism** in Cu_2(tebpz) crystallite – the role of **complex** geometry – 2/5

*Hydrogen bond **bridging***





- Bridging **accelerates** the **intrusion** process through the reduction of the intrusion energy barrier.
- Intrusion in **step**: first A and C channels then B and D.

- The reduction of the barrier may be interpretated as a **local reduction** in the **hydrophobicity**.
- Again against Youn-Laplace law…

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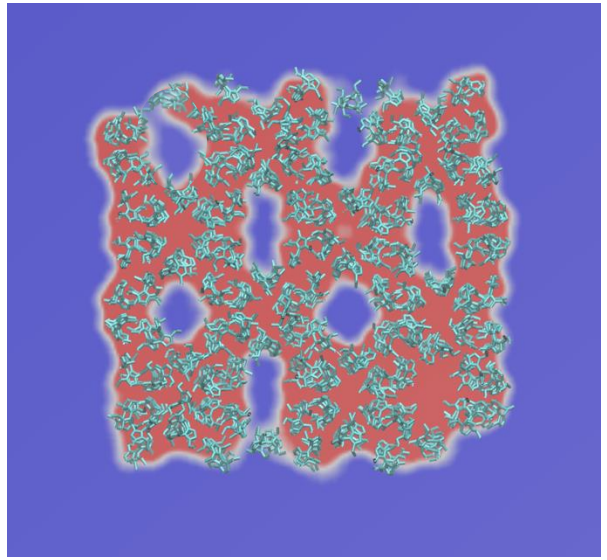
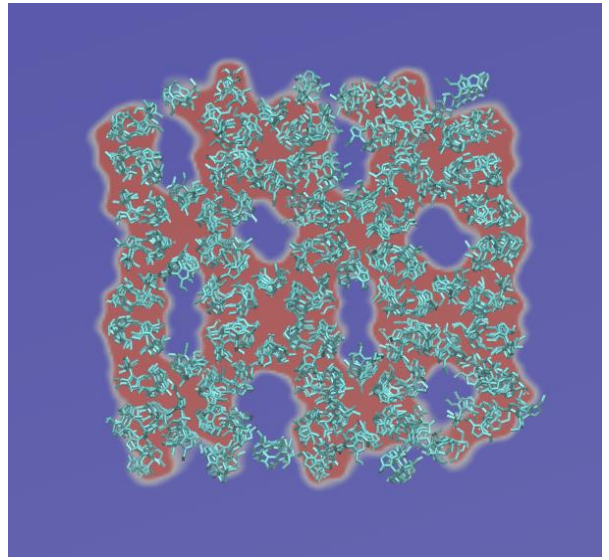
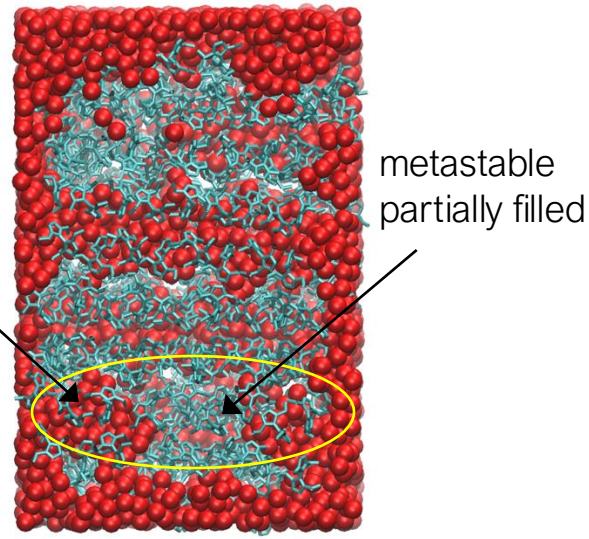
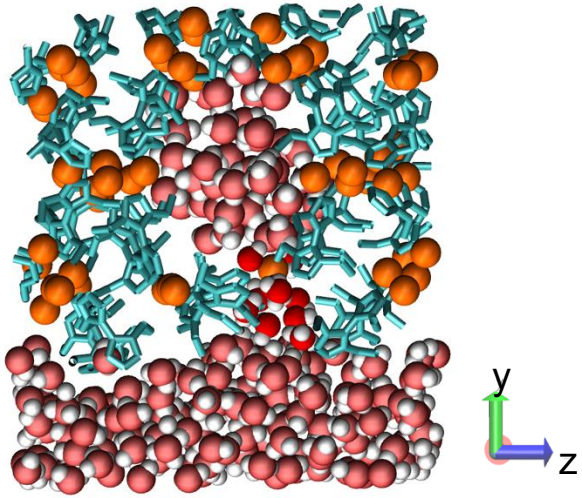
Water **intrusion mechanism** in Cu_2(tebpz) crystallite – the role of **complex** geometry – 3/5

I. 3D density Map





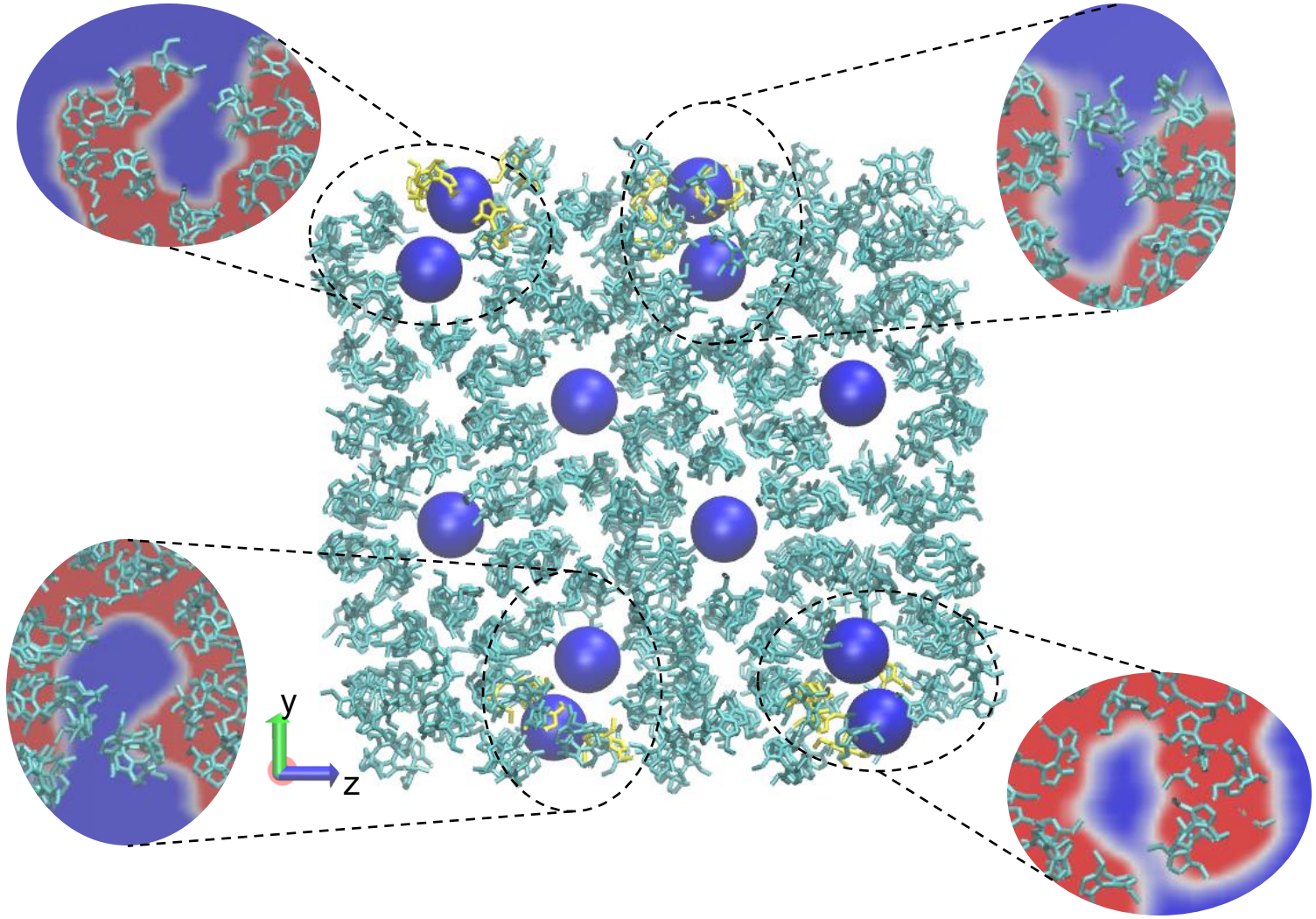




Water **intrusion mechanism** in Cu_2(tebpz) crystallite – the role of **complex** geometry – 4/5

I. 3D density Map

II. Water denisty maxima



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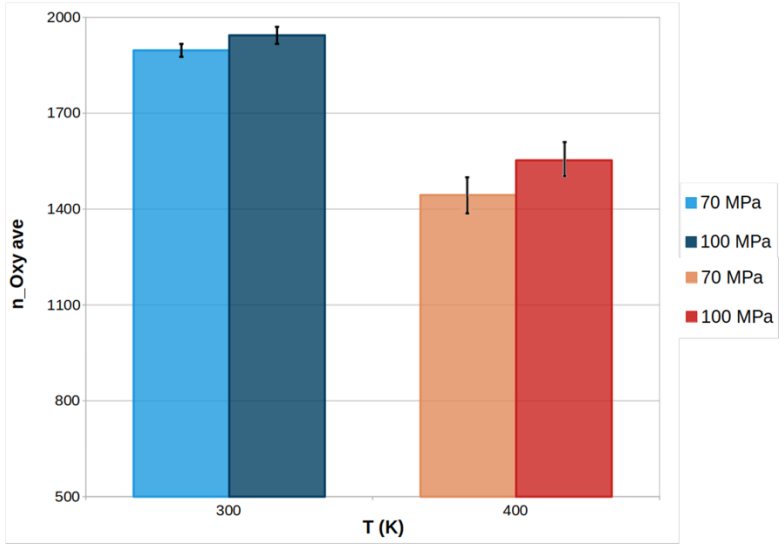
Water **intrusion mechanism** in Cu_2(tebpz) crystallite – the role of **complex** geometry – 5/5

I. 3D density Map

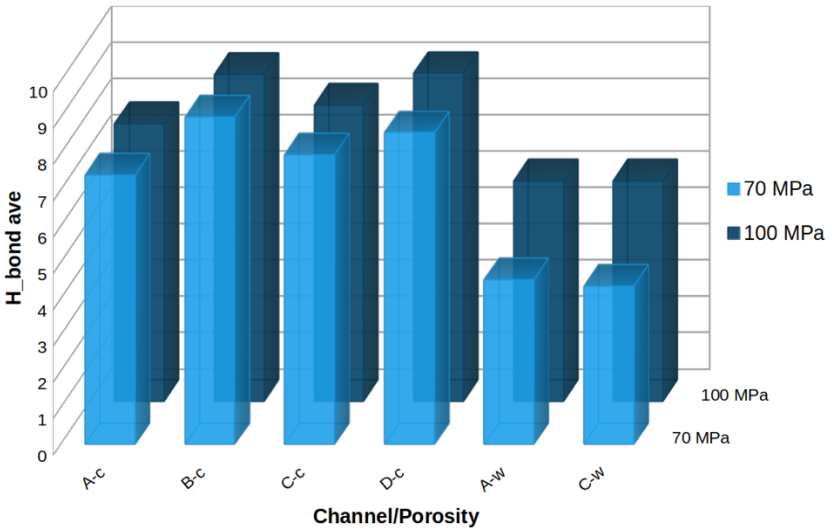
II. Bader analysis

III. Hydrogen bonds analysis

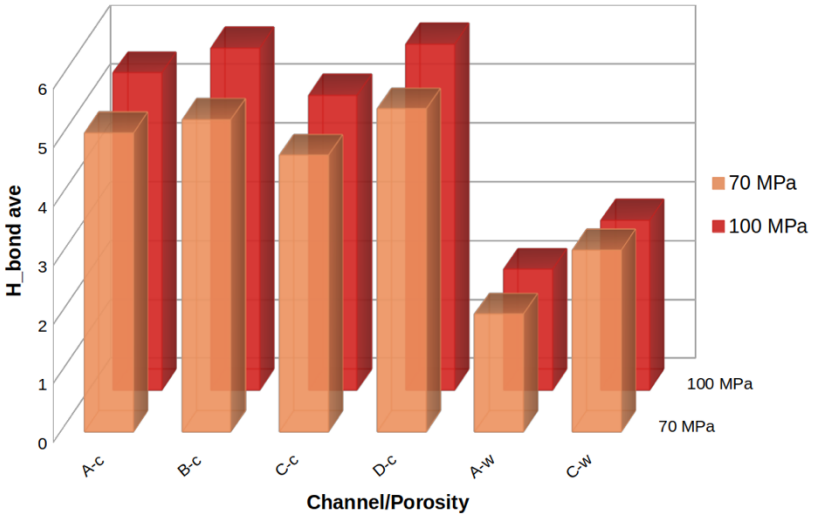


- **Same** intrusion **mechanism** for both temperatures
- The average number of **hydrogen bonds decreases** with increasing **temperature**
- The **density** of intruded water molecules **decreases** with **temperature**

300 K



440 K



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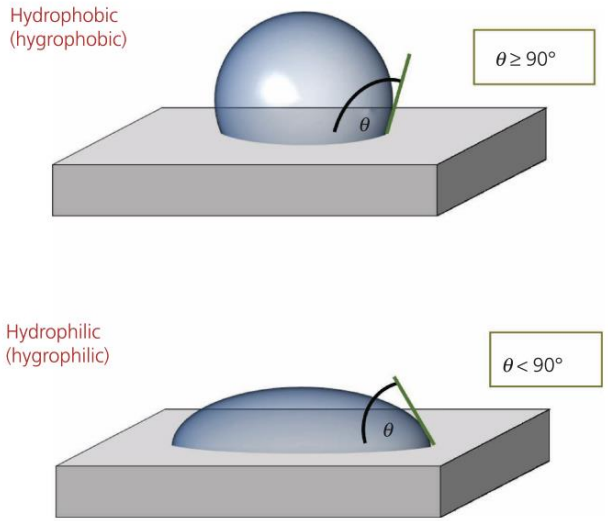
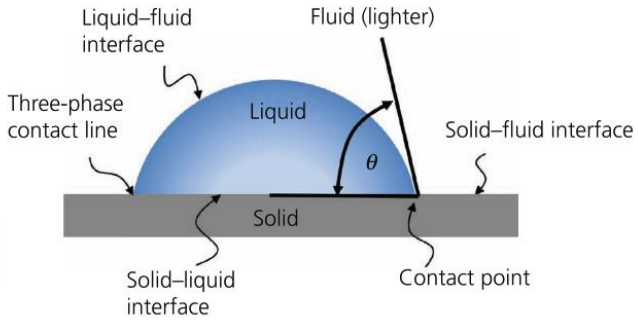
Hydrophobicity – the **role** of the ZIF-8 **surface texture** – 1/3



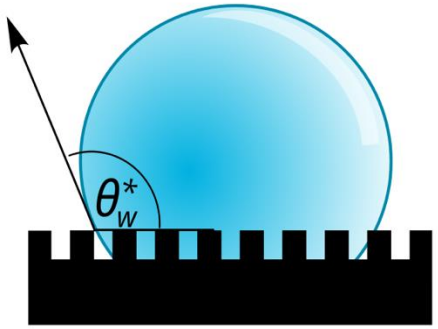


Young

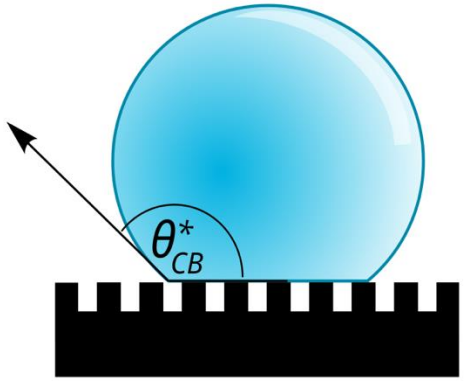
Liquid on a corrugated surface can achieve two stationary states:

I. wet state (**Wenzel**)

II. suspended state (**Cassie-Baxter**), reducing the L/S contact area.



Wenzel



Cassie-Baxter

- ZIF-8 **surface chemistry** affects hydrophobicity

$$\cos(\theta_W) = r\cos(\theta_Y) \quad \cos(\theta_{CB}) = f\,[\cos(\theta_Y)+1]-1$$

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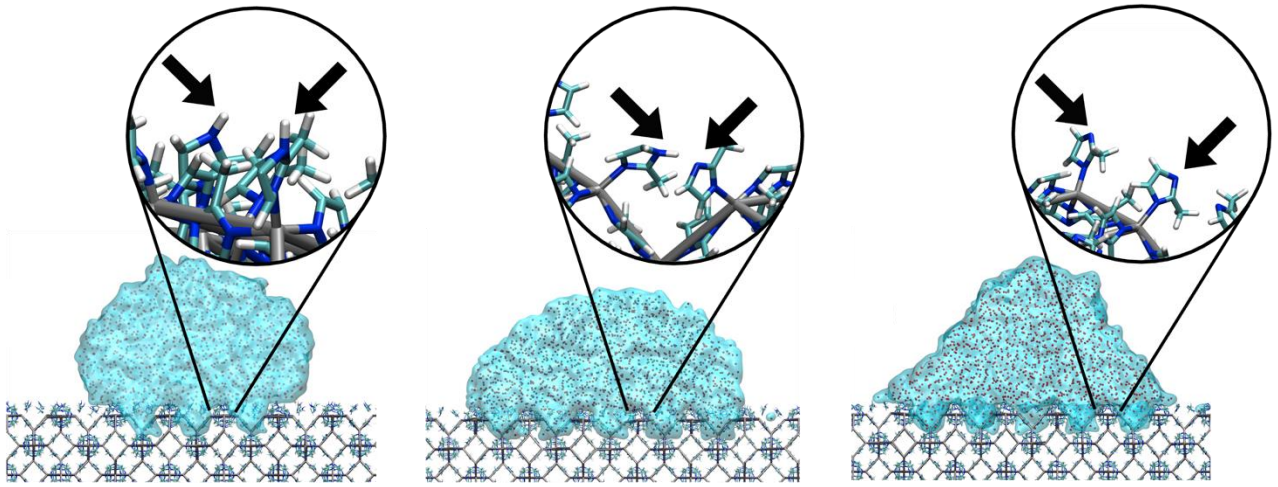
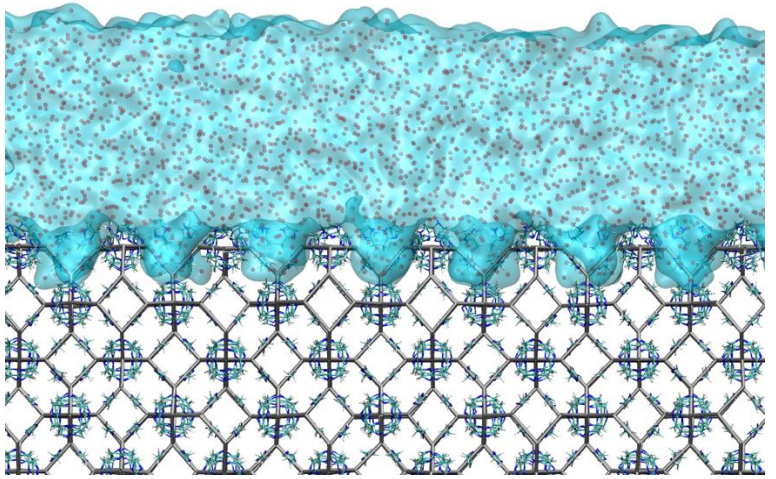
Hydrophobicity – the **role** of the ZIF-8 **surface texture** – 2/3

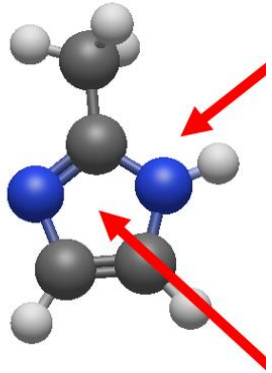


100% sp3 | 50% sp2-sp3 | 100% sp2

hydrophobicity



water is in nanoW-like states



- Contact Angle increases as surface sp3 N exposure increases, while surface-water contact reduces.

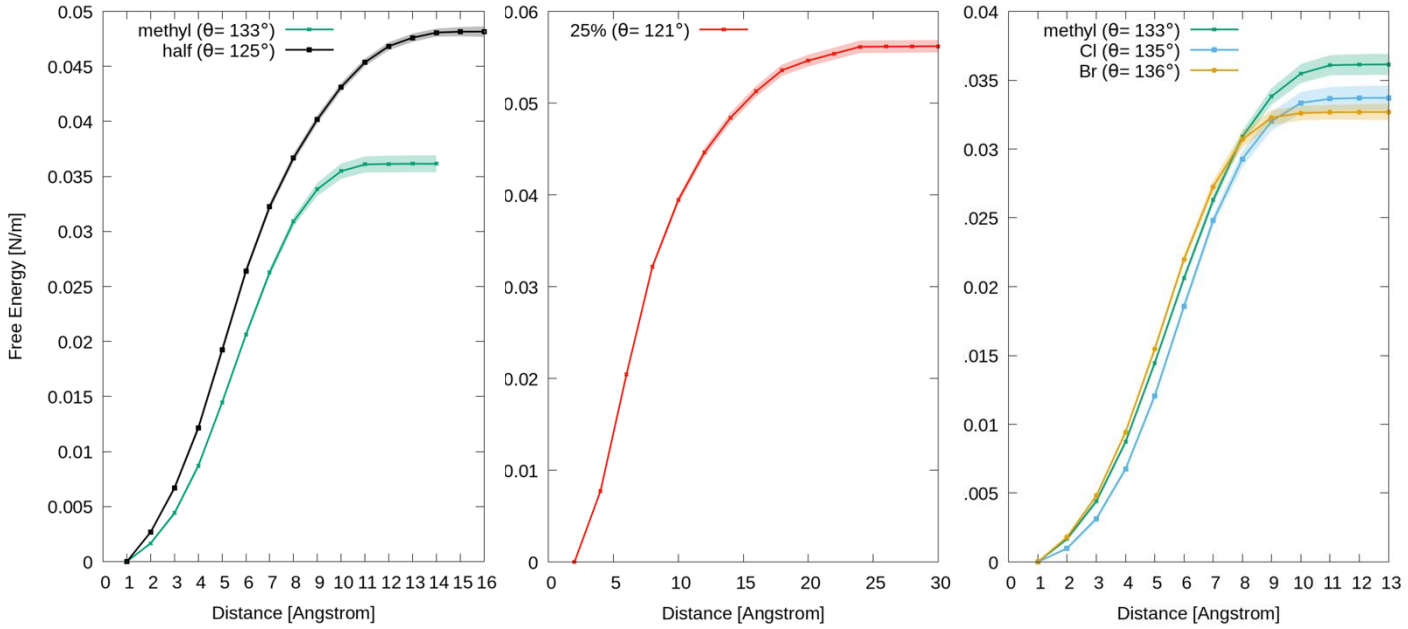
Hydrophobicity – the **role** of the ZIF-8 **surface texture** – 3/3

*CA – **energetic** approach, free energy calculation*

Young-Douprè:

$$\cos(\theta_Y) = \frac{W_{slg}}{\gamma_{lg}} - 1 \qquad W_{slg} = \int_{R_{min}}^{R_{max}} \frac{dG_{\text{ZIF-8+H}_2\text{O}}(r^*)}{dr^*} dr^*$$

free energy as a function of the distance between the water and the solid surface with **RMD**



Surface Termination exposed to H_2O	θ°_{YD}
100% sp^3 N	134 (1)
50% sp^3 N/50% sp^2 N	125 (1)
25% sp^3 N/75% sp^2 N	121 (1)
100% sp^2 N	0* (0)
100% Zn^{2+}	0* (0)

hydrophobicity

- close to exp CA ~140°

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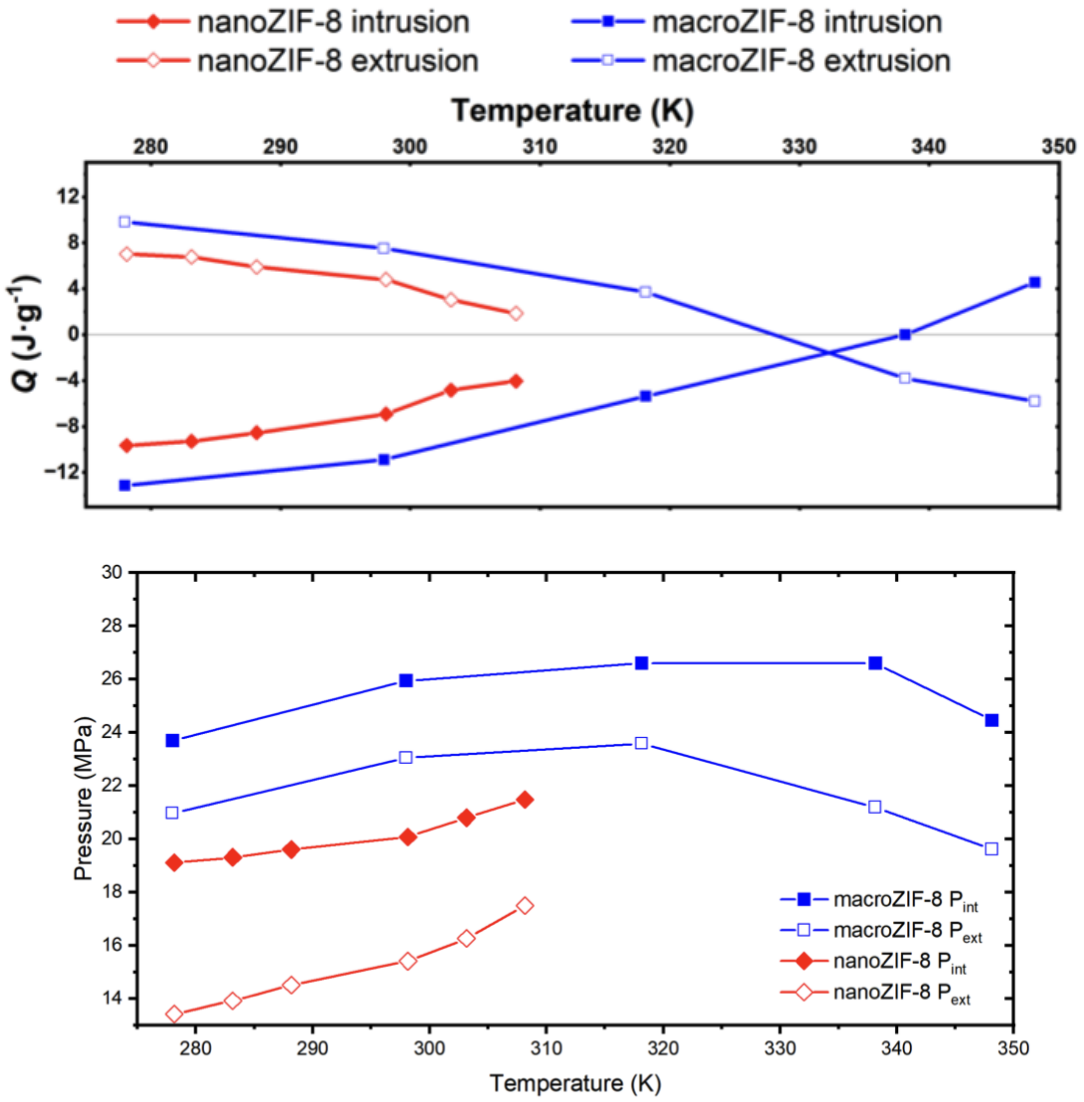
Crystallite **size effects** on the **Heat** of water **intrusion/extrusion** in ZIF-8 – 1/2



P^i nano- vs macro- ZIF-8 ≠ ~ 5 MPa

↓

- larger (external) SA/V ratio corresponds to a larger fraction of ZIF-8 external wetted cages.
- Hydrogen bonds with bulk water, which eases the intrusion of these cages.

Crystallite **size effects** on the **Heat** of water **intrusion/extrusion** in ZIF-8 – 2/2

- Effect of the crystallite size on the heat of intrusion via P_{int} :

I. **direct**: pressure affecting Δ(PV)

II. **indirect**: ↑ P_{int} = ↑ confined water density, affecting ΔU_{int}

$$\begin{aligned}\Delta Q &= Q_{int}(25\ \text{MPa}) - Q_{int}(20\ \text{MPa}) = \\ &= \Delta U_{\text{int}}(25\,\text{MPa}) + P(25\,\text{MPa})\Delta V(25\,\text{MPa}) \\ &\quad - (\Delta U_{\text{int}}(20\,\text{MPa}) + P(20\,\text{MPa})\Delta V(20\,\text{MPa})) \\ &= \Delta\Delta U_{\text{int}}(25\,\text{MPa}, 20\,\text{MPa}) \\ &\quad + (P(25\,\text{MPa})\Delta V(25\,\text{MPa}) - P(20\,\text{MPa})\Delta V(20\,\text{MPa}))\end{aligned}$$

- Reduction from macro- vs nano- ZIF-8:

  from MD ~ 33%

  from Exp ~ 36 %

so what is the **origin**?...

mechanical contribution

~13% is due to PΔV

~ **87%** from $\Delta\Delta U_{int}$(25MPa, 20MPa)

internal energy contribution

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Conclusions

- **Unexpected** properties of water intruded into microporous hydrophobic MOFs: Cu_2(tebpz) and ZIF-8
  - simulations and experiments shows an **unprecedented** water Tc **reduction** of 200 K
  - large reduction of Tc **promoted by** the **geometry** and **chemistry** of Cu_2(tebpz): global hydrophobicity with hydrophilic sites
- **Counterintuitive** trend of intrusion pressure, **against** the classical Young-Laplace law
- The role of complex morphology/topology in the intrusion/extrusion process
  - hydrogen bond **bridging** through the secondary porosity of Cu_2(tebpz)
  - bridging reduces local hydrophobicity, lowering the intrusion barrier and **promoting** water intrusion
- The importance of **hydrophobicity** in the ZIF-8 intrusion/extrusion mechanism
  - surface texture critically **determines** its hydrophobic characteristics
  - **alternative** approach based on the Young-Douprè equation for the CA calculation
- Crystallite **size effect** on the heat of intrusion/extrusion of ZIF-8
  - decreasing the size **reduces** the magnitude of **heat**
  - reduction of the ZIF-8 degree of filling, mostly affecting the **variation** of internal energy

Further research directions

- Confined water's non-bulk and porous material properties **influence** on intrusion/extrusion: **key** to understanding liquid behavior in microporous systems and developing a **general** theory.
- Developing/fabricating thermally stable MOFs and **porous systems** is crucial for new **technological** applications like **Thermal Energy Storage** using **supercritical water** under moderate conditions.

Scientific output

Publications in Peer-Reviewed Journals:

1. L. J. W. Johnson, A. R. Lowe, A. Le Donne, E. Arkan, S. **Merchiori**, L. Bartolomè, E. Amayuelas, D. Mirani, G. A. Lopez, G. Grancini, M. Chorazewski, S. Meloni and Y. Grosu, The Journal of Physical Chemistry Letters, 16(6), 2086-2096, 2025. **Q1 IF = 4.9**
2. S. **Merchiori***, D. Ballardini, A. Le Donne, R. Bhatia, N. Verziaggi, C. Gourmand, Y. Grosu, S. Meloni, The Journal of Chemical Physics, 162(6), 064502, 2025. **Q1 IF = 3.1**
3. S. **Merchiori**, A. Le Donne, R. Bhatia, M. Alvelli, A. R. Lowe, J-J. Yu, XD. Wu, M. Li, D. Li, M. Geppert-Rybczynska, L. Scheller, B. A. Trump, A. Yakovenko, P. Zajdel, M. Chorazewski, Y. Grosu, S. Meloni, Small, 20(42), 2402173, 2024. **Q1 IF = 13**
4. S. **Merchiori**, A. Le Donne, J. D. Littlefair, A. R. Lowe, J-J. Yu, X-D. Wu, M. Li, D. Li, M. Geppert-Rybczynska, L. Scheller, B. A. Trump, A. Yakovenko, P. Zajdel, M. Chorazewski, Y. Grosu and S. Meloni, Journal of the American Chemical Society, 146(19), 13236-13246, 2024. **Q1 IF = 14.5**
5. A. Le Donne, J. D. Littlefair, M. Tortora, S. **Merchiori**, L. Bartolomè, Y. Grosu, S. Meloni, The Journal of Chemical Physics, 159, 184709, 2023. **Q1 IF = 3.1**

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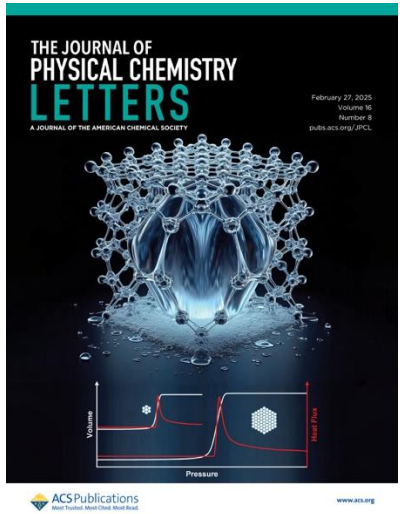
6. F. Zanotto, A. Sirico, A. Balbo, P. Bernardi, S. **Merchiori**, V. Grassi, B. Belletti, A. Malcevschi, C. Monticelli, Construction and Buildings Materials, 420, 135509, 2024. **Q1 IF = 7.4**
7. S. Barbi, F. Barbieri, S. Marinelli, B. Rimini, S. **Merchiori**, M. Bottarelli, M. Montorsi, Polymers, 14(3), 135509, 2022. **Q1 IF = 4.7**

Scientific Awards:

1. **Principal Investigator** of **ISCRAb Project** (Italian Supercomputing Resource Allocation) "HERMOSA-Hydrophobic MOF + water system as a mechanical battery: intrusion/extrusion mechanism by advanced molecular simulations", Funded by CINECA, Italy. Amount: 2.000.000 core hours on **HPC LEONARDO** cluster **(corresponding to ~200.000€/year)**. August 2023-October 2024.
2. **Cultore della Materia-Chimica**. (Cultor of Matter-Chemistry), ai sensi art. 42 del Regio Decreto 4 giugno 1948, n. 1269. 16/12/2024.

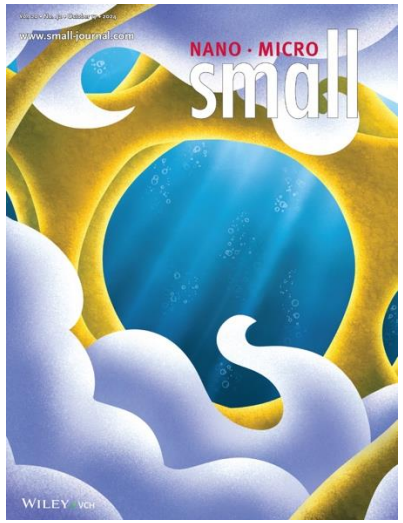
International Conferences:

1. **EMRS2022** Fall Meeting–**Talk** "Thermomechanical and structural properties of Cu_2(tebpz) MOF + water molecular spring in a wide temperature range". Warsaw, Poland. 20/09/2022



IF = 4.9

IF = 13



Others:

1. **1st PhD Symposium of Chemical Sciences**, University of Ferrara "Counterintuitive trend of intrusion pressure with temperature in the hydrophobic Cu_2(tebpz) MOF". **Poster**. 12/06/2024.
2. **1st PhD Symposium of Chemical Sciences**, University of Ferrara "Mild-temperature supercritical water confined in hydrophobic metal-organic frameworks". **Talk**. 12/06/2024.
3. **La chimica per un futuro sostenibile**-Workshop in memoria della Dr.ssa Doriana Scittarelli "Electro-Intrusion: Materials for energy storage via contact electrification processes. **Talk**. 09/09/2022.
4. ElectroIntrusion **website management**.

Thanks for your attention

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