# Does nanoconfined water looks like bulk water?

Simone.meloni@unife.it

**Computational chemistry across scales and disciplines: celebrating Ursula's birthday**

ELECTRO INTRUSION

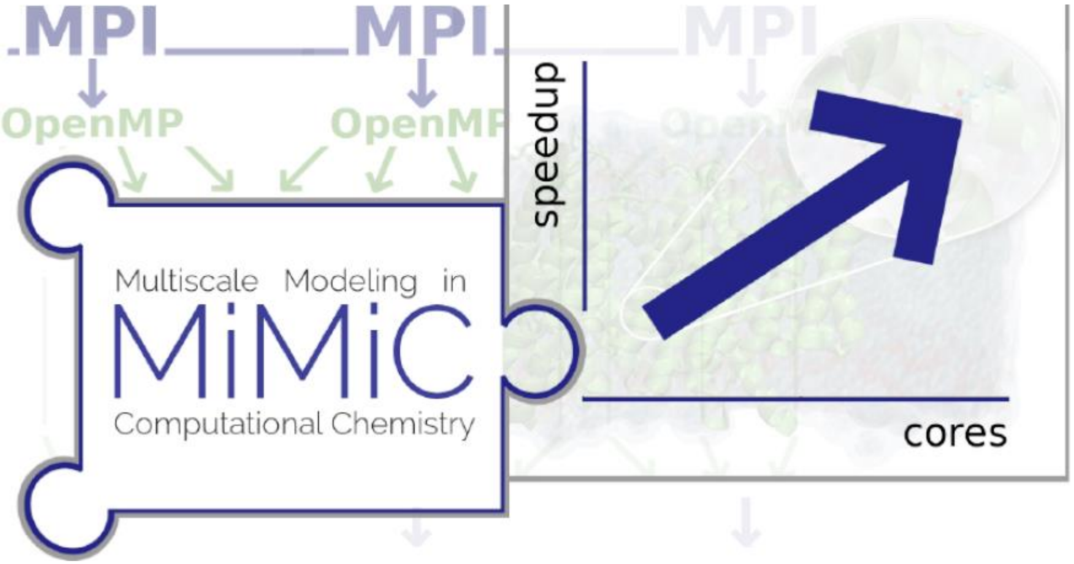
European Innovation Council

Funded by the European Union


ELECTRO INTRUSION

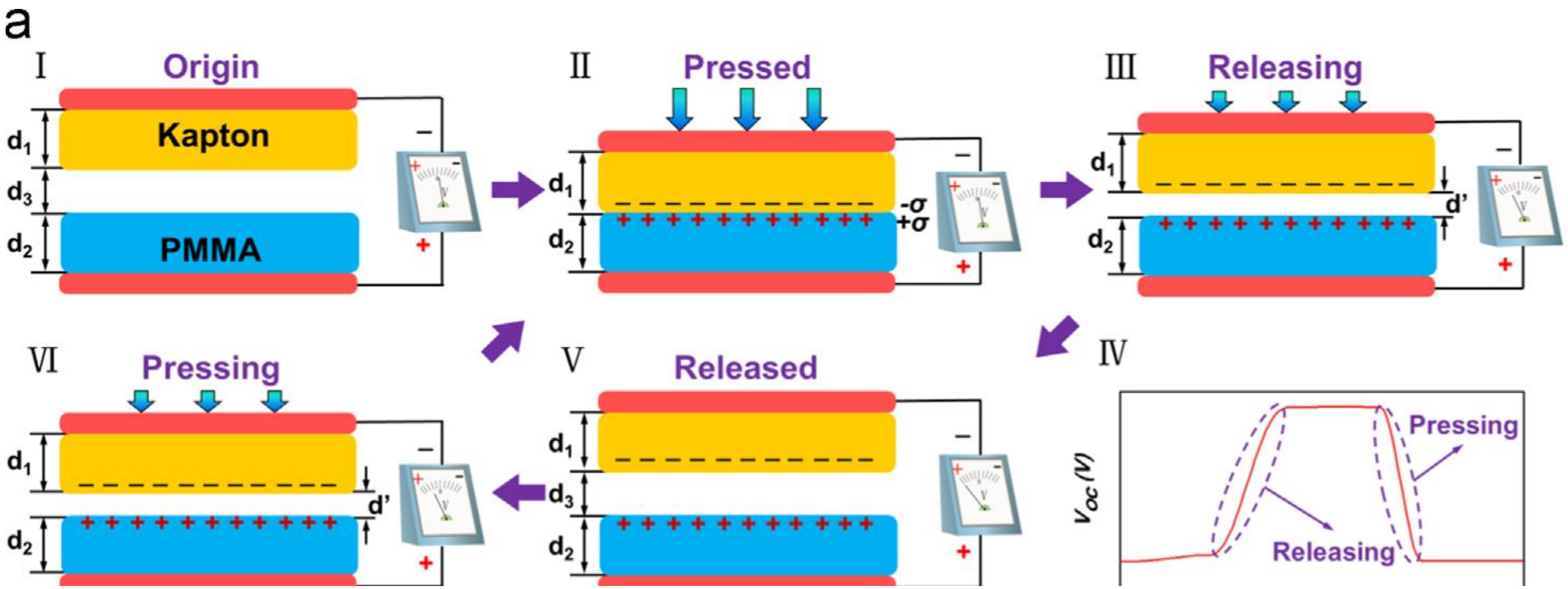
European Innovation Council

Funded by the European Union

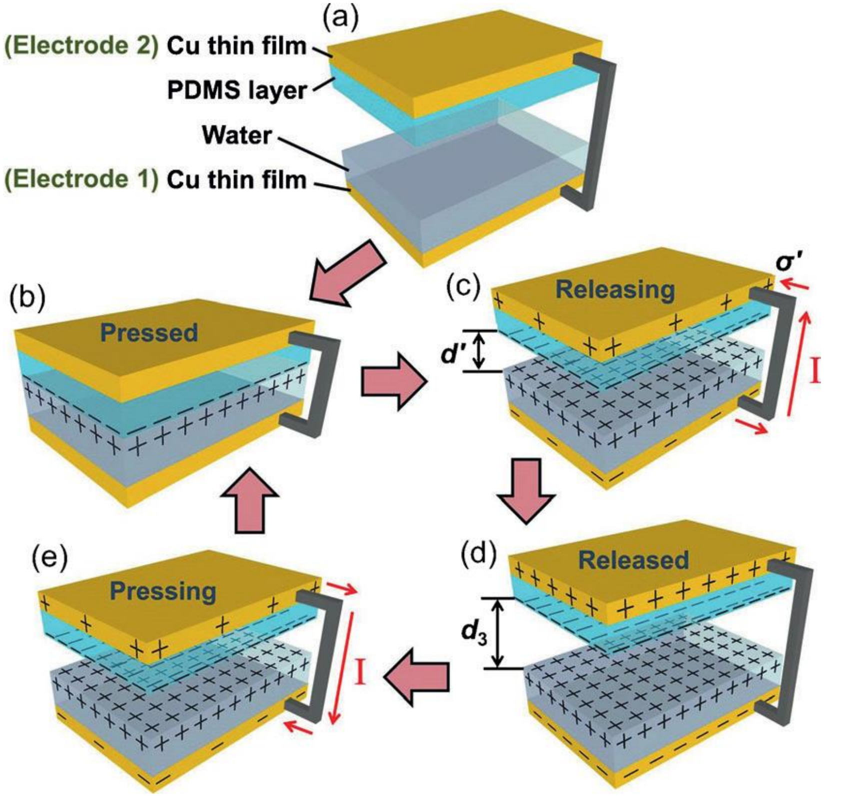

MPI
MPI
MPI
OpenMP
OpenMP
Multiscale Modeling in
MiMiC
Computational Chemistry
speedup
cores

# Technological applications: energy harvesting

Nano Energy 14, 126, 2015




Angew. Chem. Int. Ed. 52, 12545, 2013

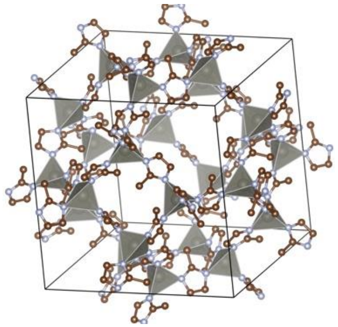



ELECTRO INTRUSION

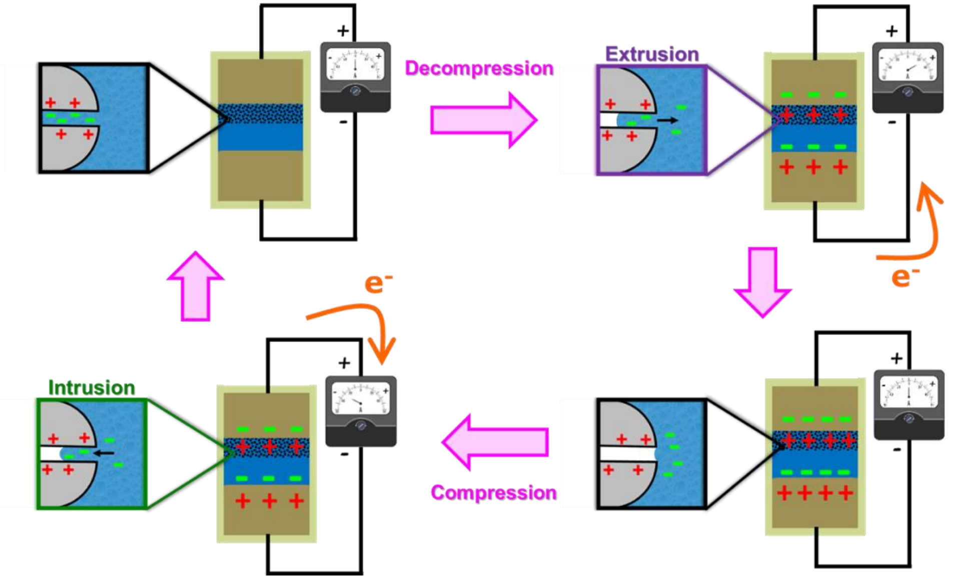
$A_{MOFs}$=10000-2000 $m^2/g$

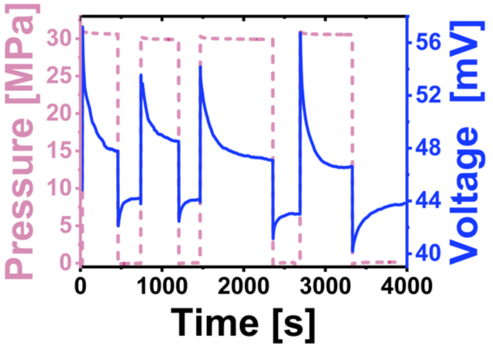
European Innovation Council
Funded by the European Union

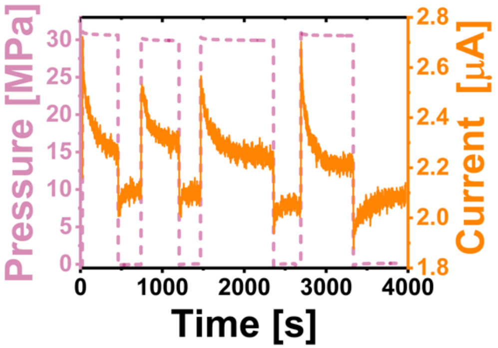
# Electro-Intrusion

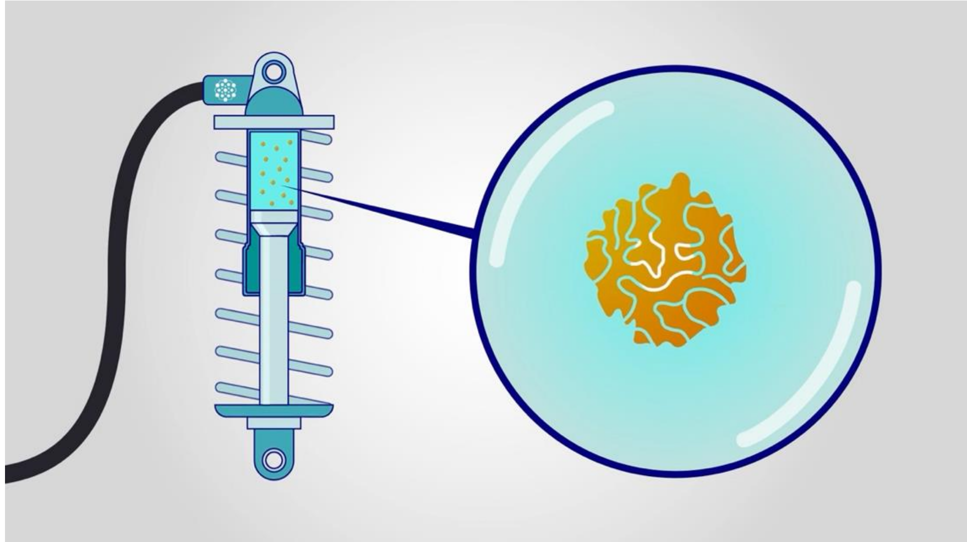


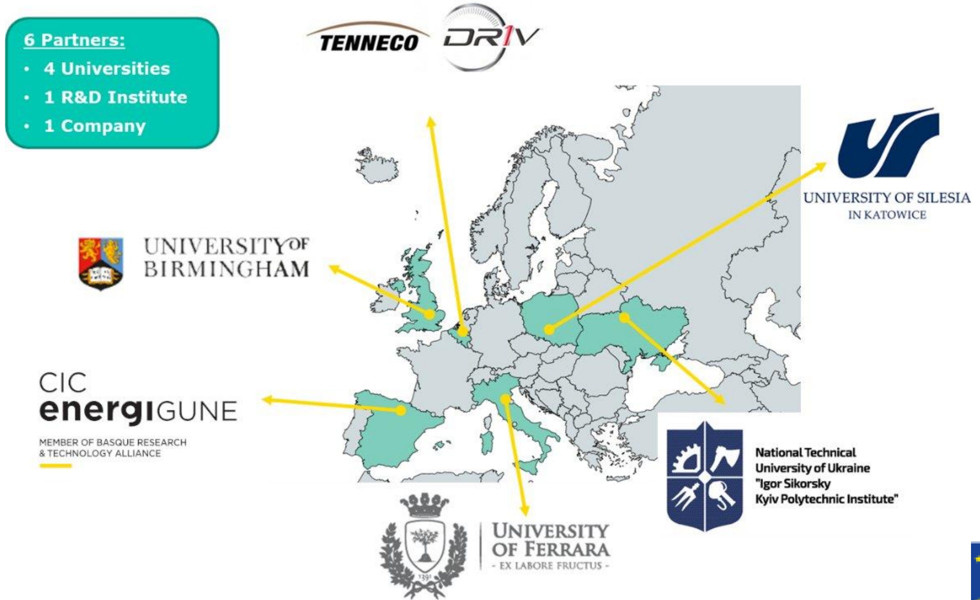
Hydrophobic porous mateials






Funded by the European Union

# Two main ingredients of the process

- Intrusion/extrusion of water in/from the porous hydrophobic medium

- Solid/liquid contact electrification with internal walls of the porous material

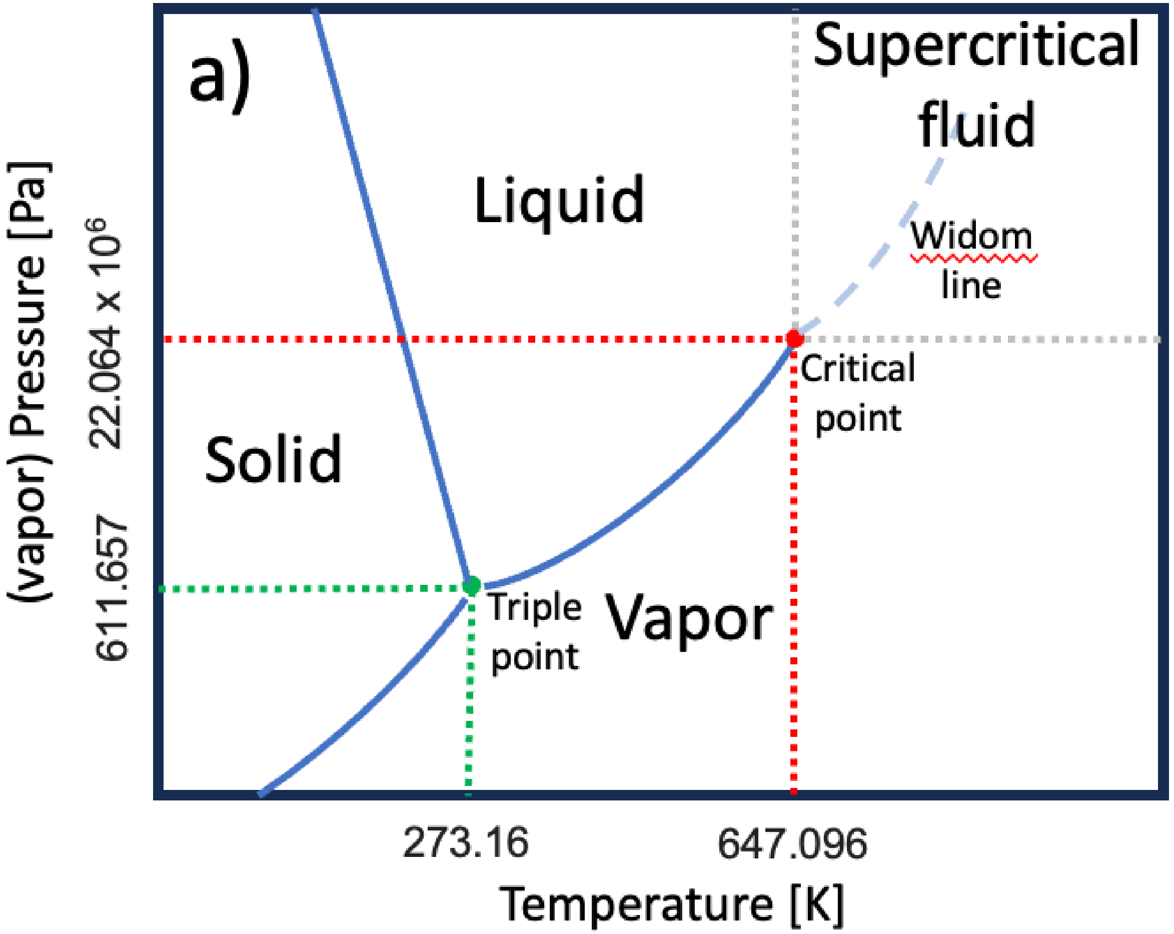
European Innovation Council
Funded by the European Union

# Two main ingredients of the process

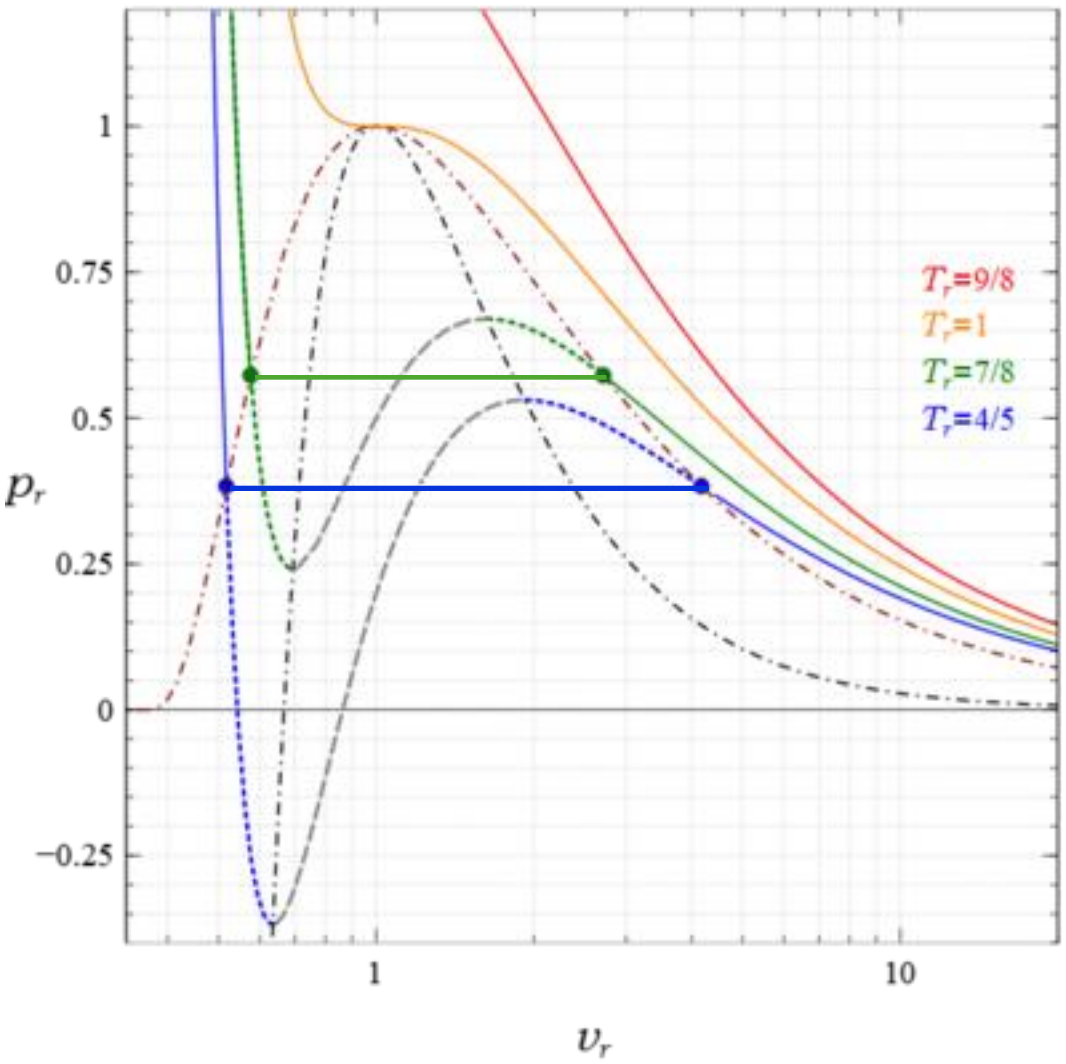
- **Intrusion/extrusion of water in/from the porous hydrophobic medium**

- Solid/liquid contact electrification with internal walls of the porous material

# Phase diagram of bulk water

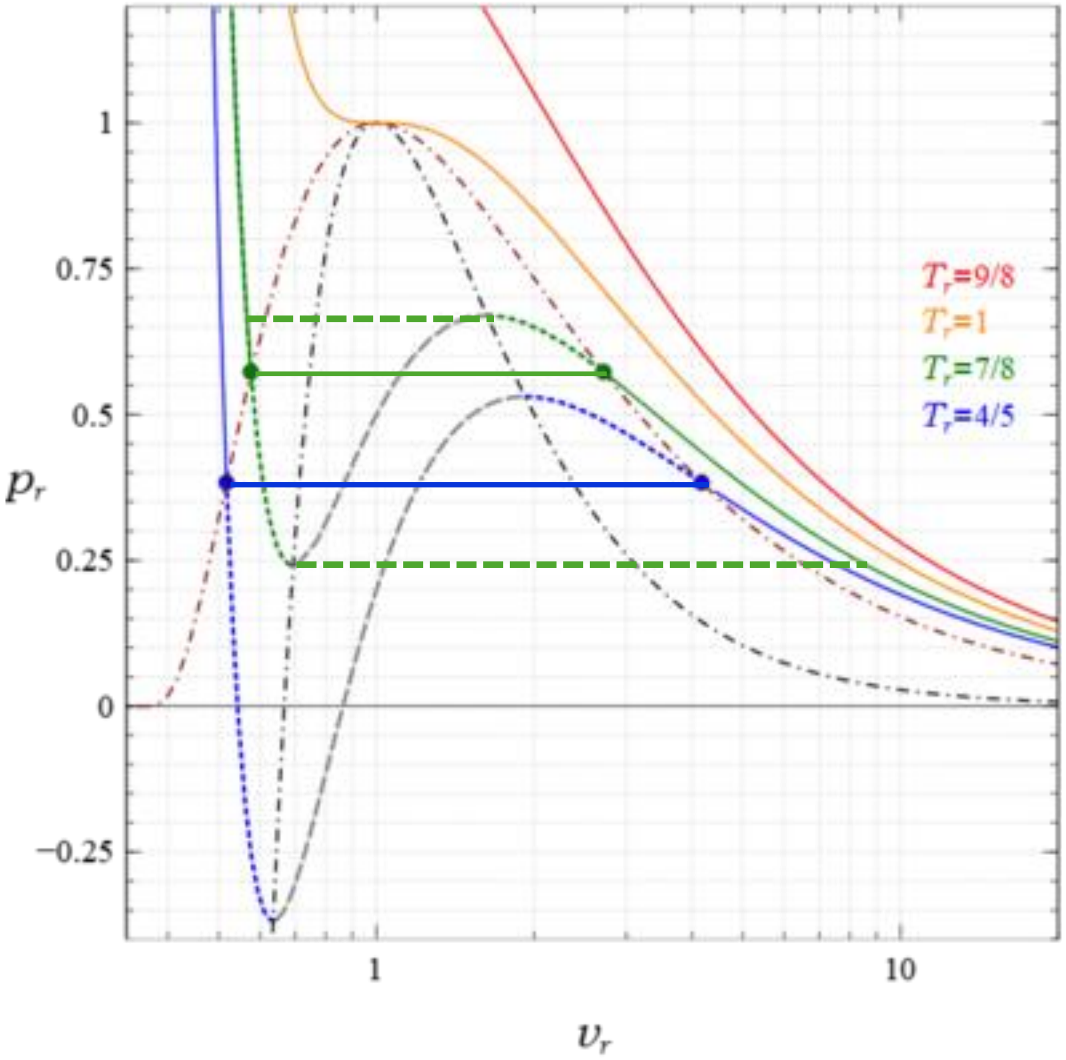



# Liquid/vapor Phase transition



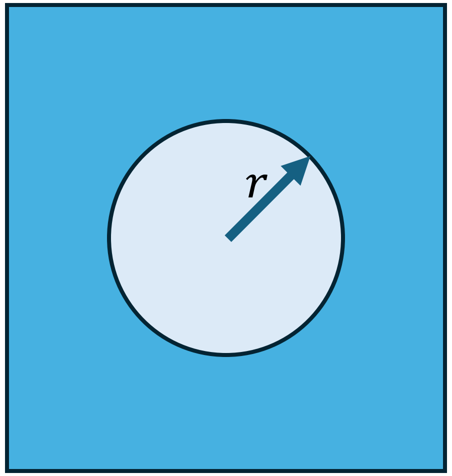

European Innovation Council
Funded by the European Union

# Liquid/vapor Phase transition

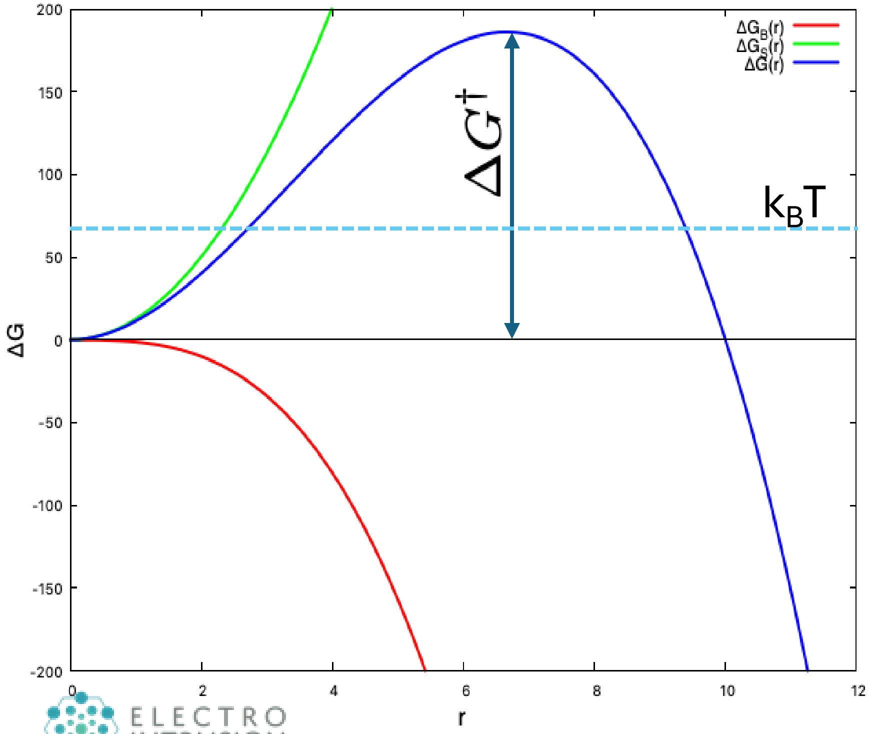


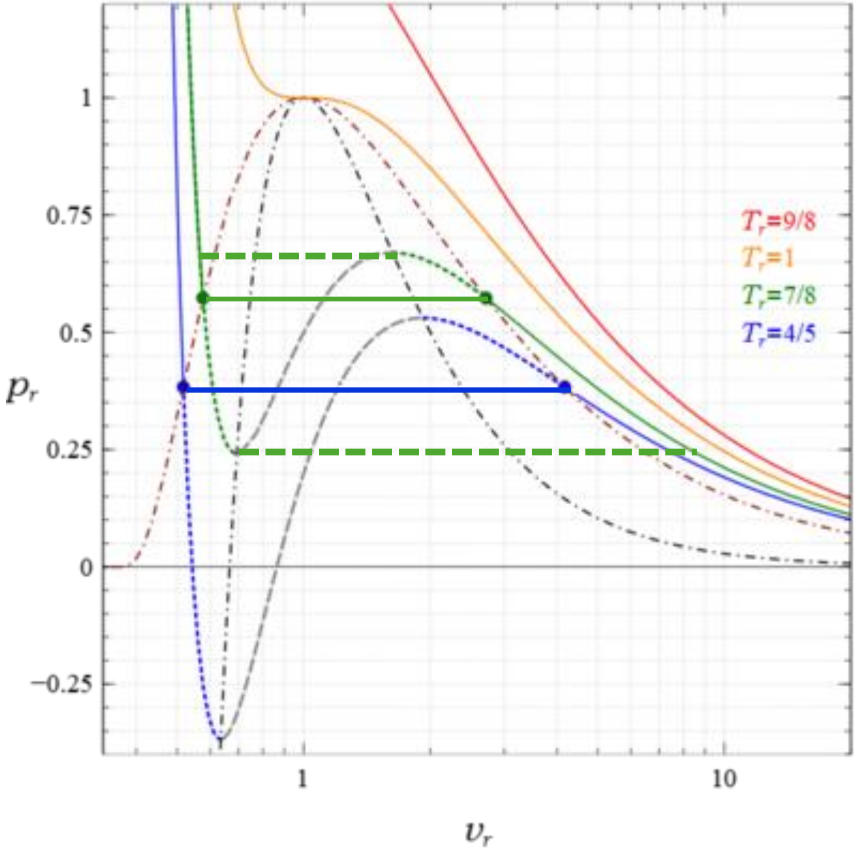

European Innovation Council
Funded by the European Union

# Liquid/vapor Phase transition




$$\Delta G(r) = \frac{4\pi r^3}{3\nu}\,\Delta\mu\ + 4\pi r^2\gamma$$

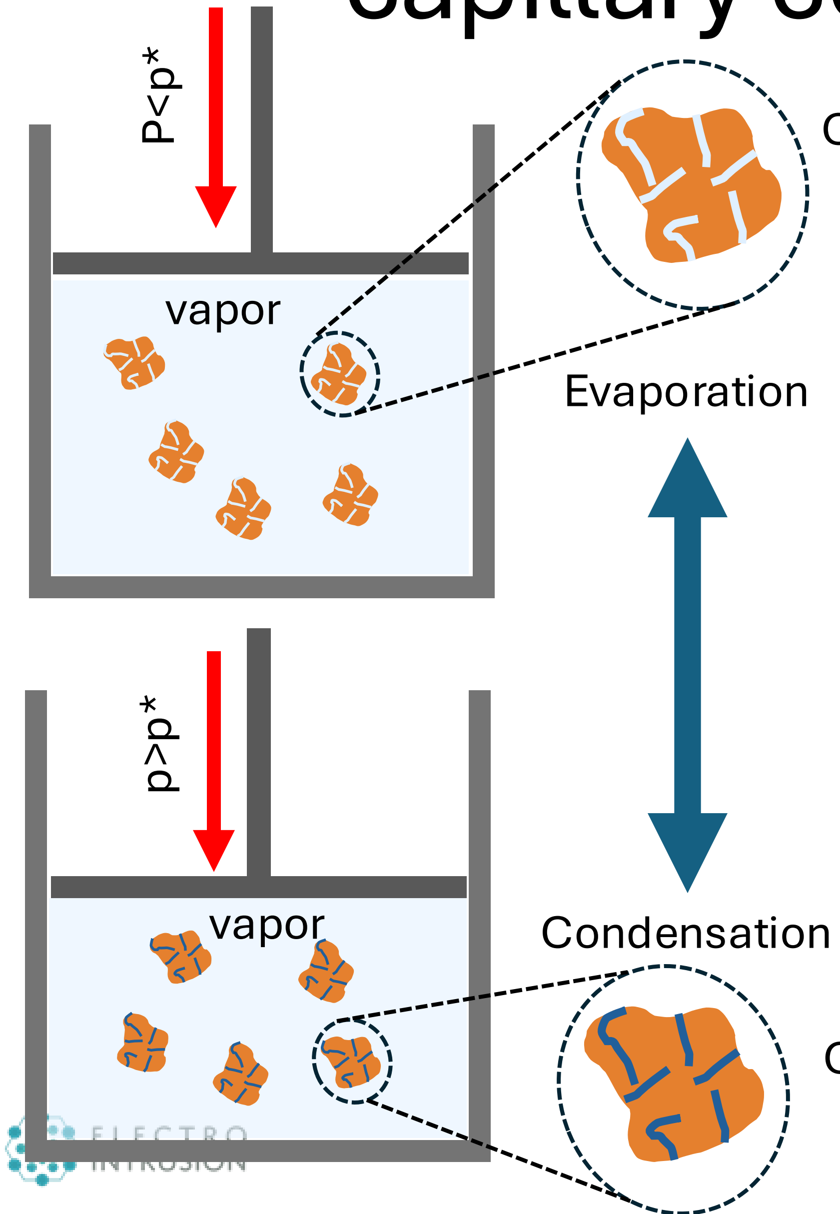


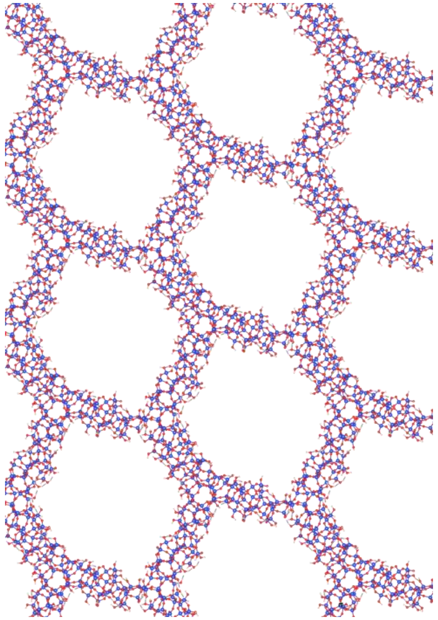



European Innovation Council
Funded by the European Union

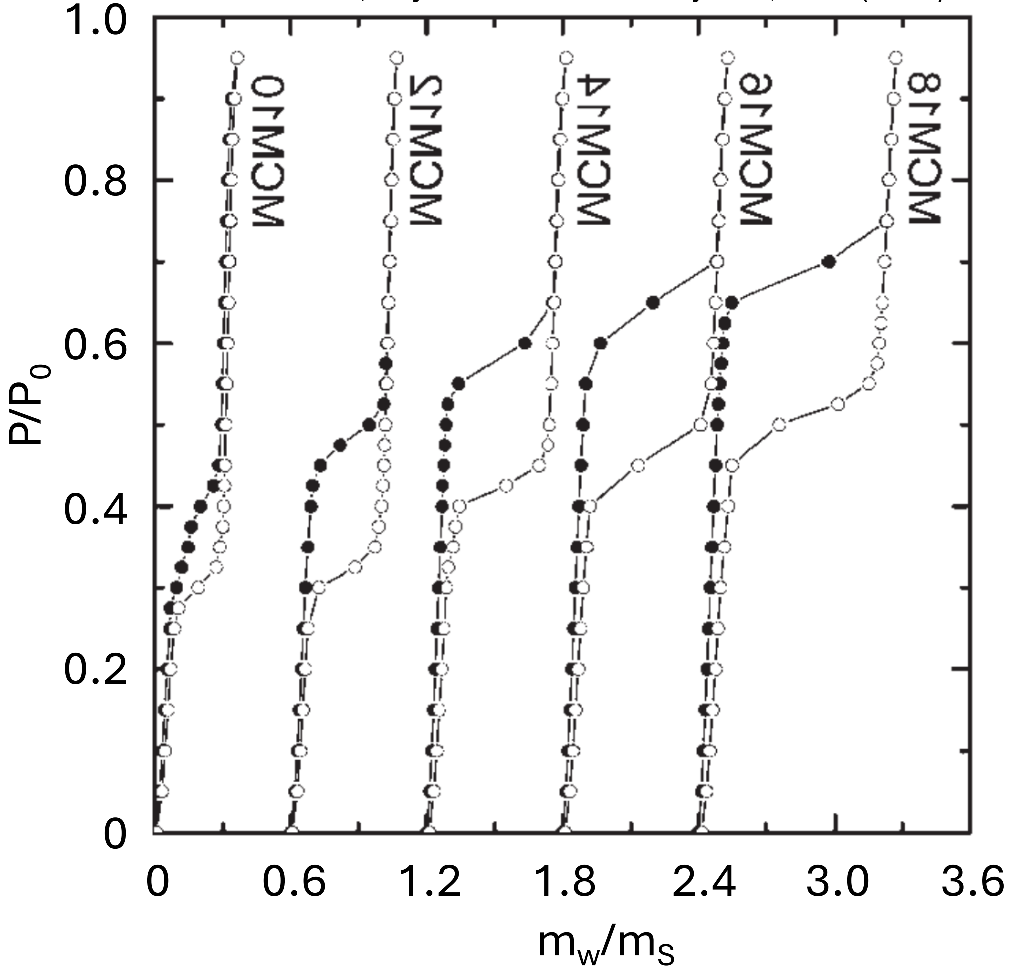
# Confined liquid-vapor phase transition: capillary condensation/evaporation




MCM
$\emptyset \in (2.5nm, 4.5nm)$

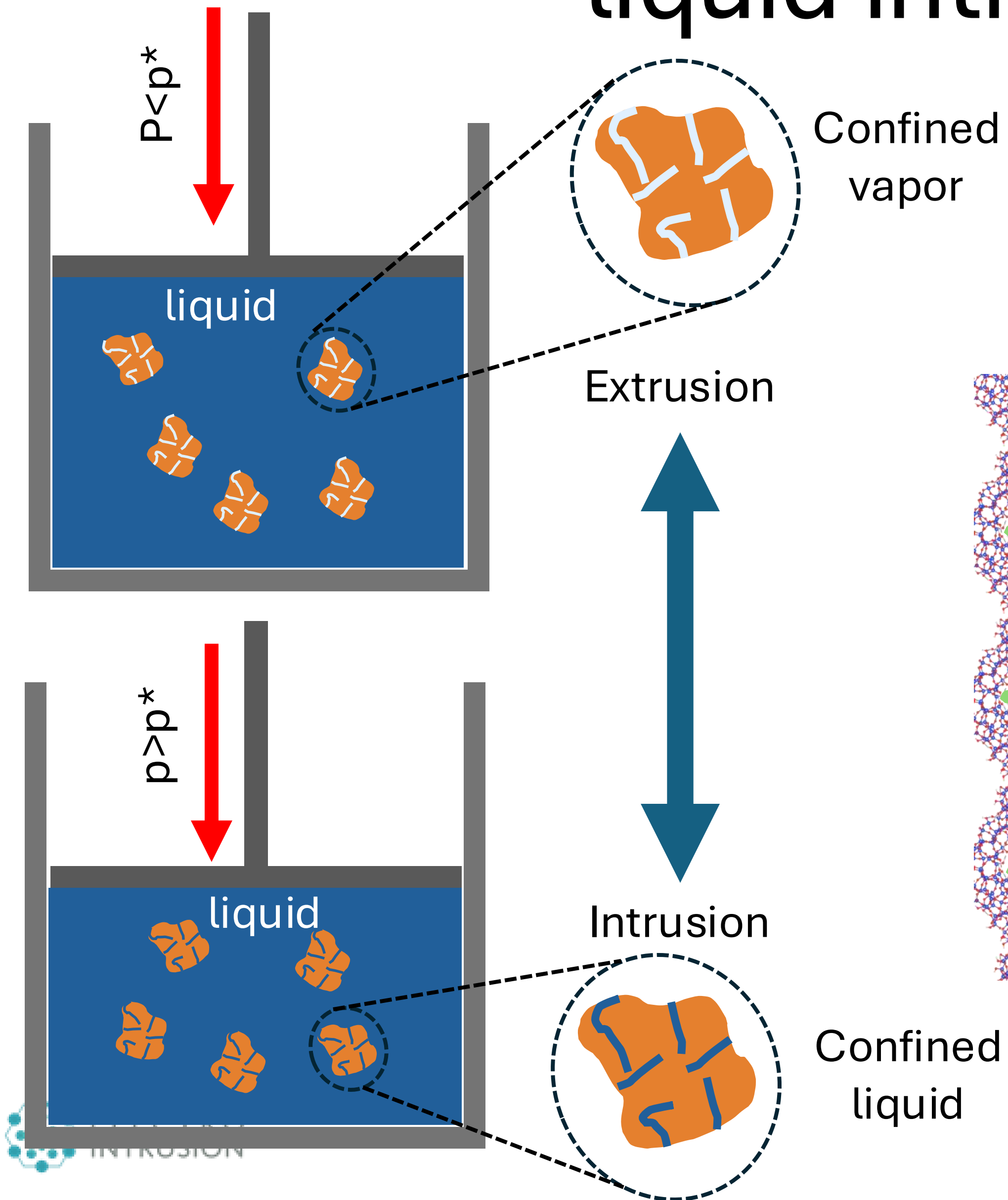


Jähnert et al, Phys. Chem. Chem. Phys. 10, 6039 (2008)

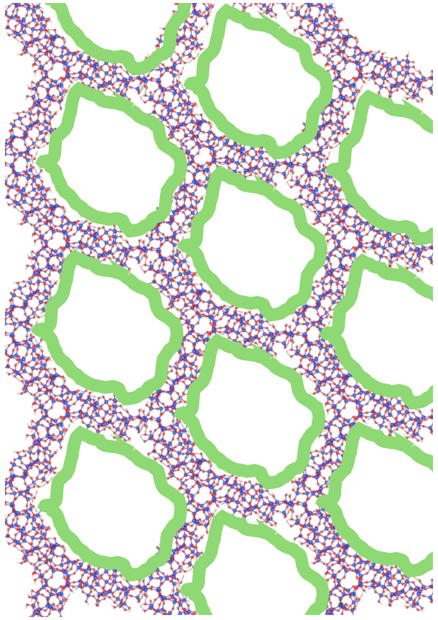



European Innovation Council
Funded by the European Union

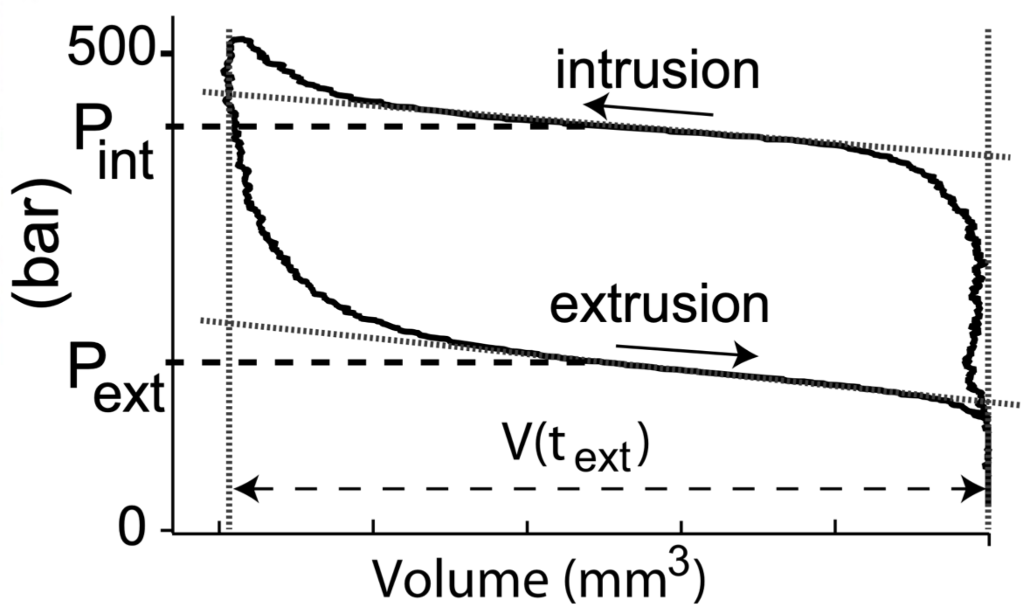
# Confined liquid-vapor phase transition: liquid intrusion/extrusion




Grafted MCM-41 hydrophobic

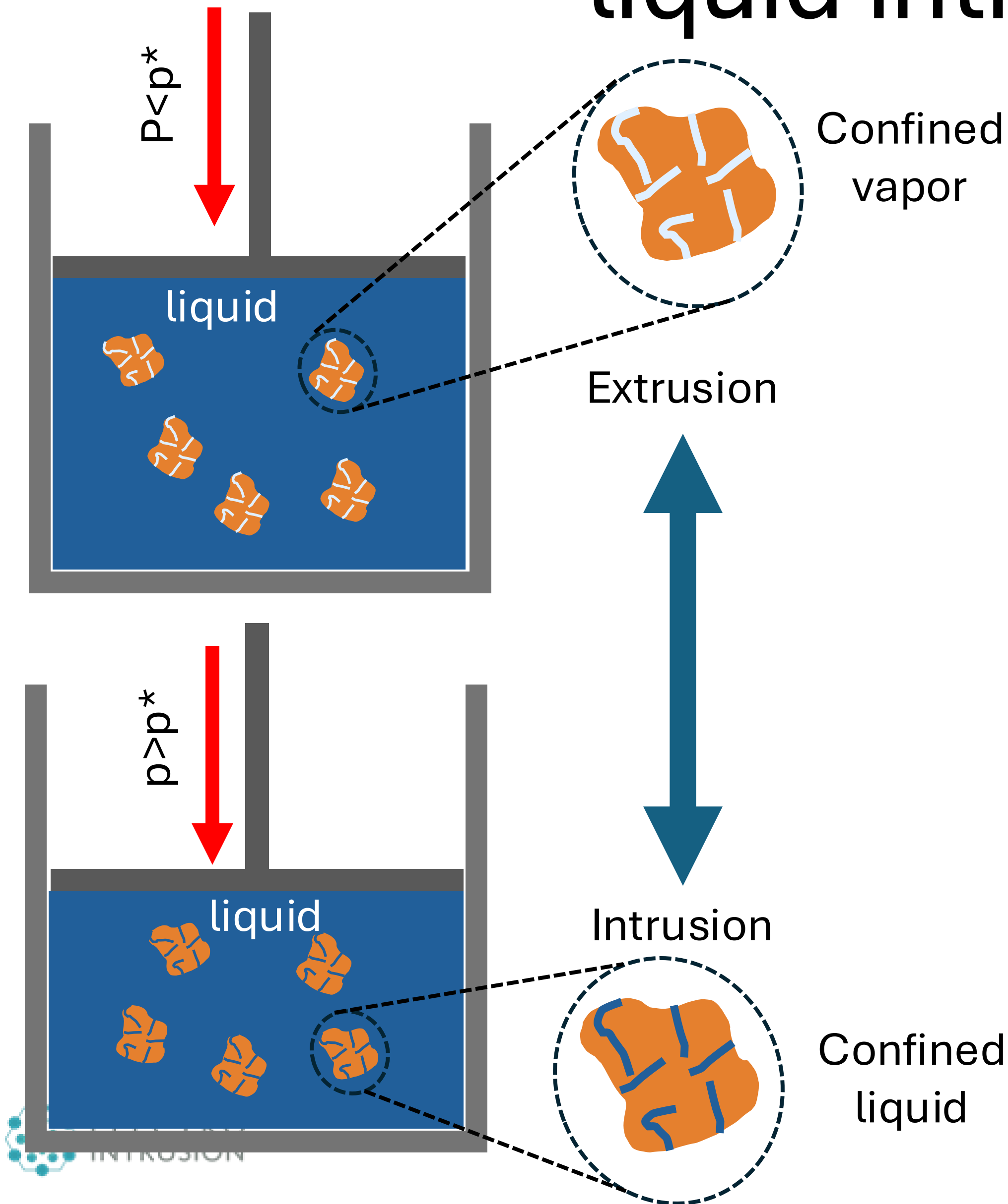


Guillemot et al, PNAS 109,19557 (2012)

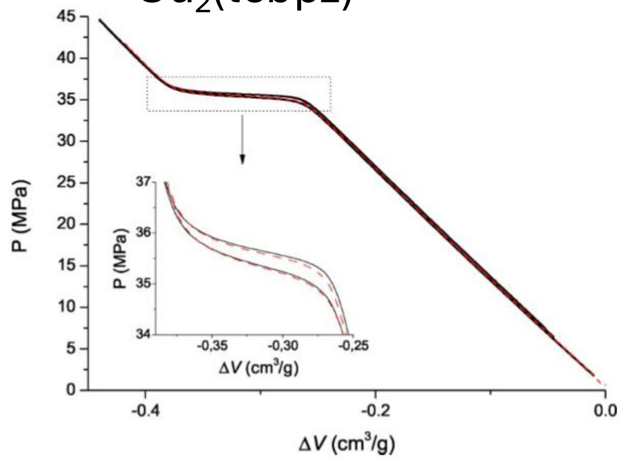



European Innovation Council
Funded by the European Union

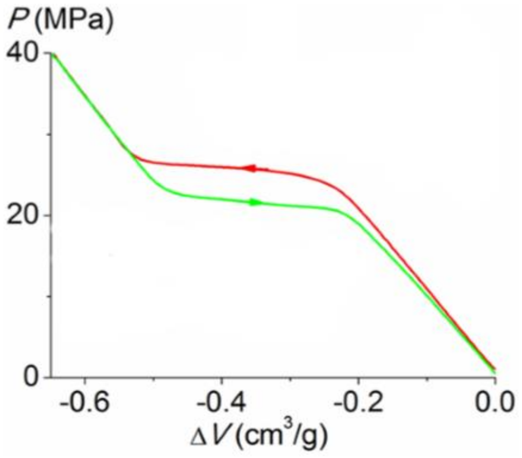
# Confined liquid-vapor phase transition: liquid intrusion/extrusion

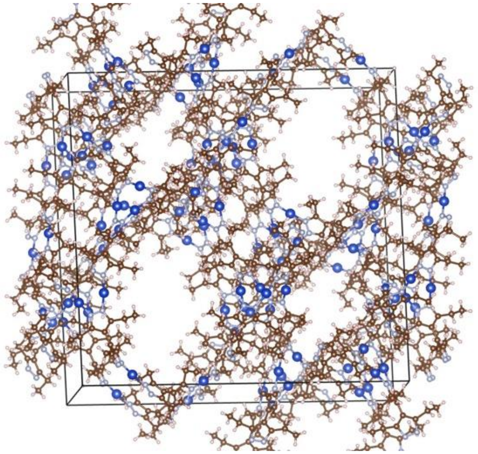


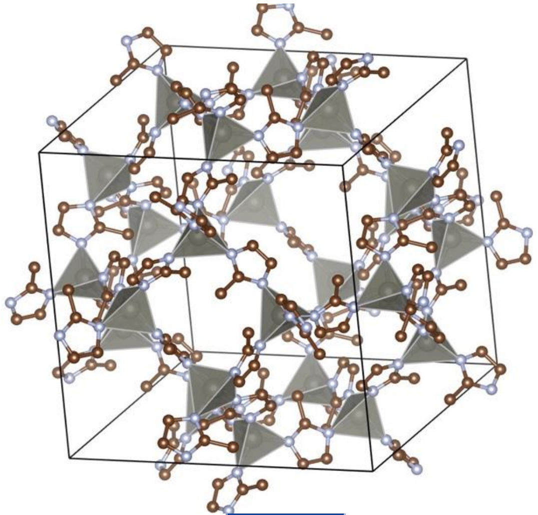

$Cu_2$(tebpz)




ZIF-8



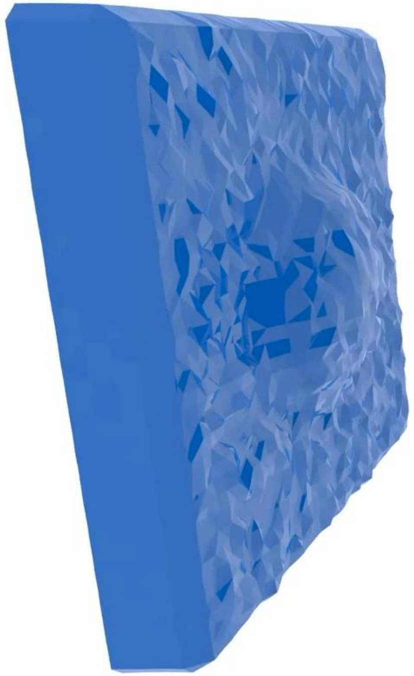



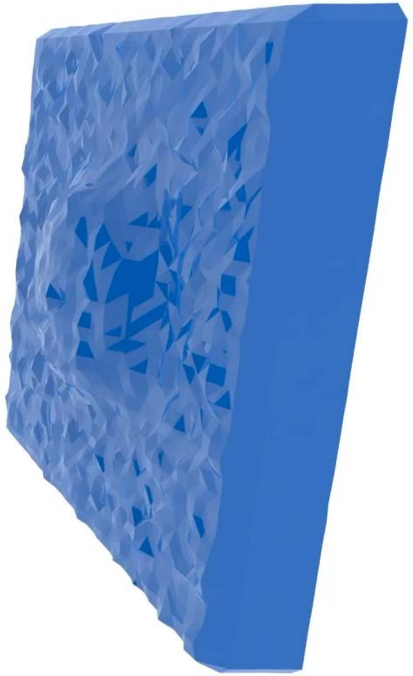


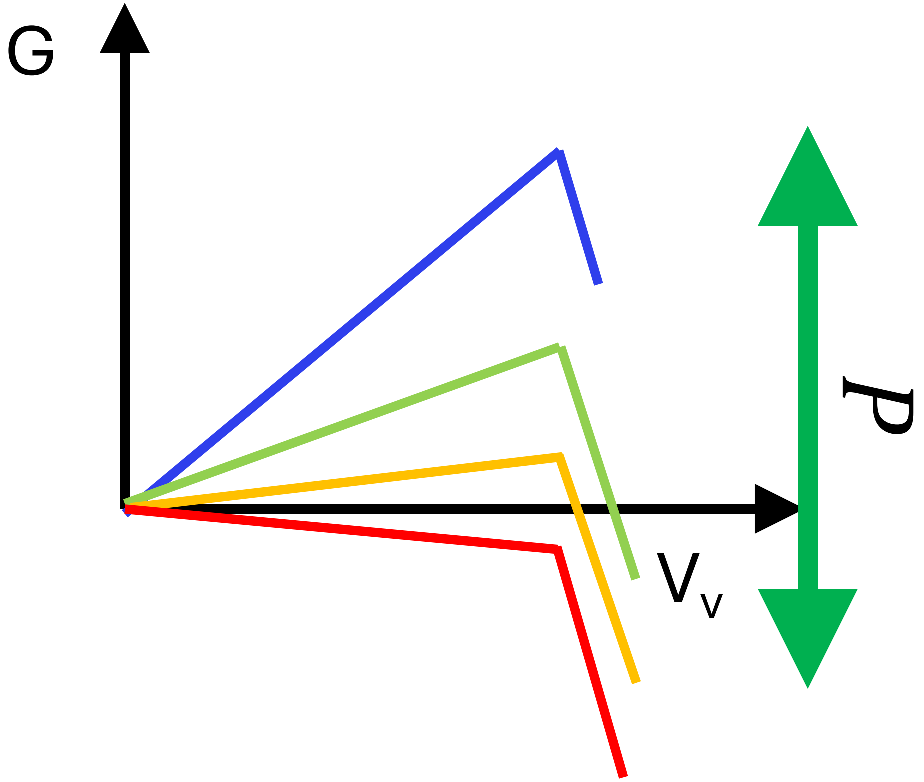
European Innovation Council
Funded by the European Union

# Intrusion/extrusion in hydrophobic porous materials: a thought experiment

$$\Omega = \Delta P V_v + \gamma \left( A_{lv} + \cos(\theta) A_{sv} \right)$$

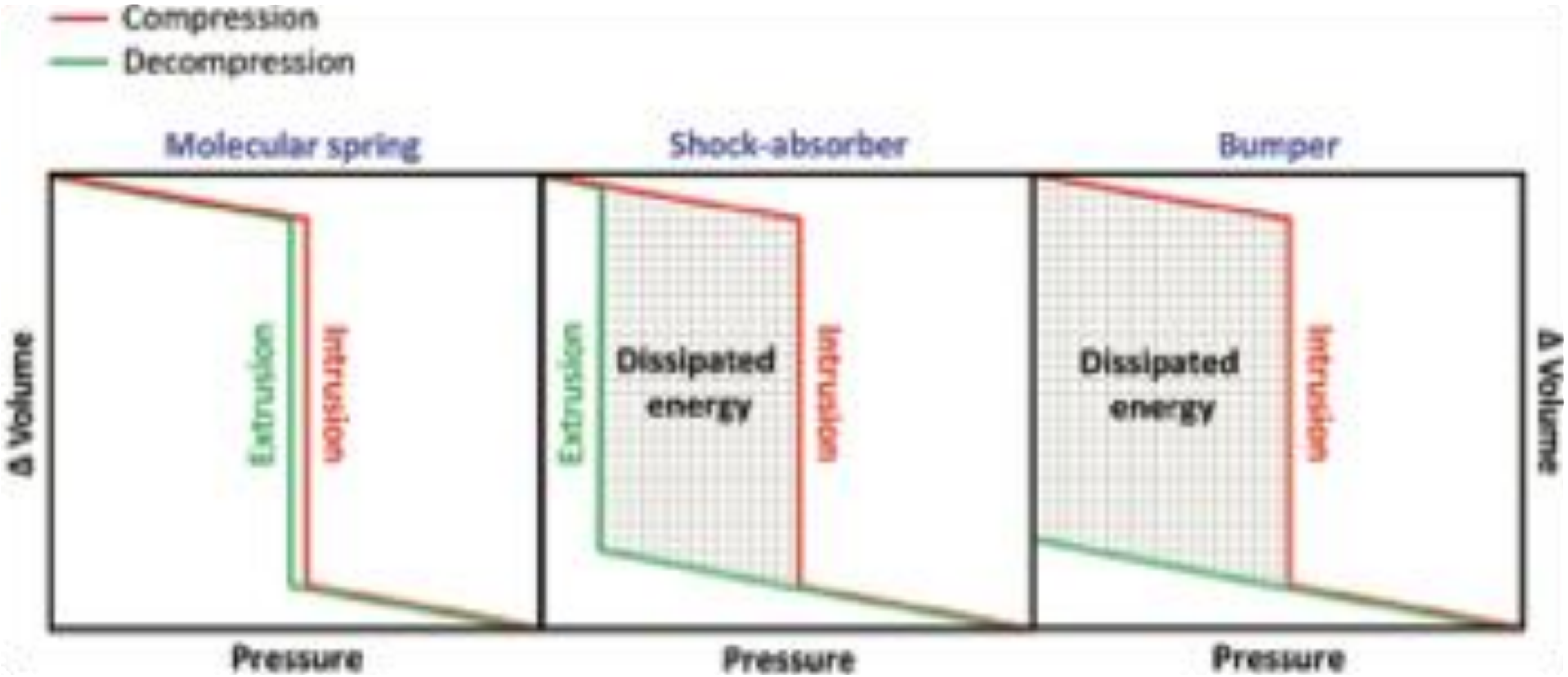






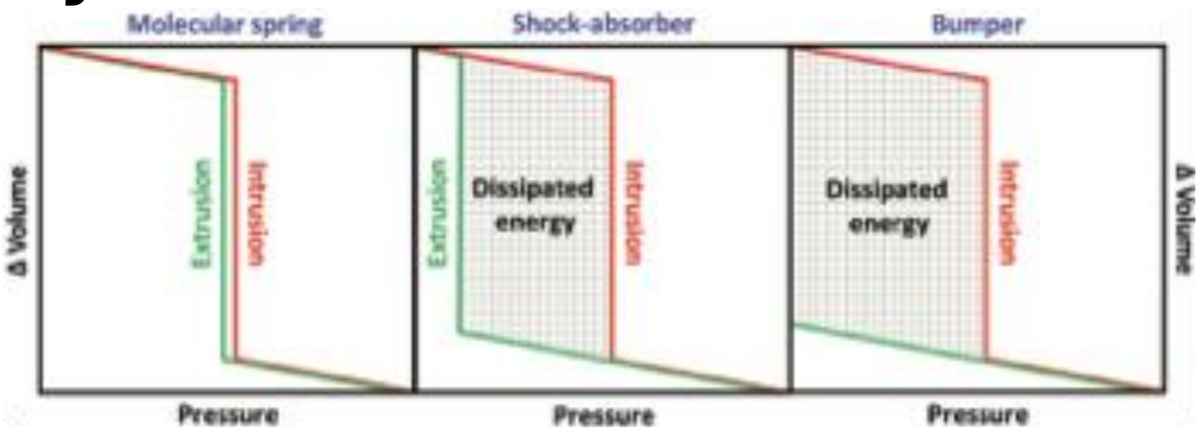

ELECTRO INTRUSION
European Innovation Council
Funded by the European Union

# Technological applications: energy storage and dissipation



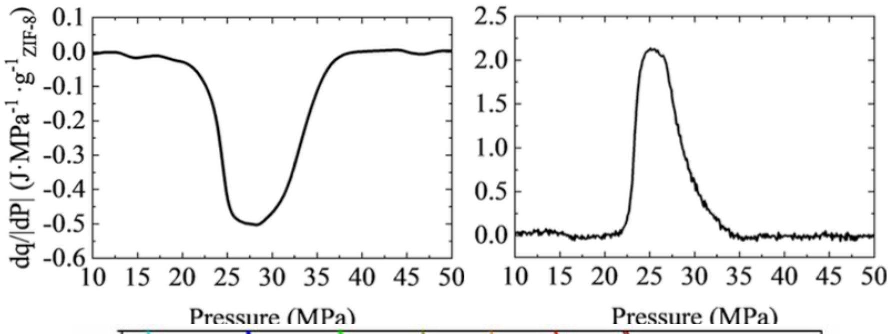

Adv.Phys.: X, 7, 2052353, 2022

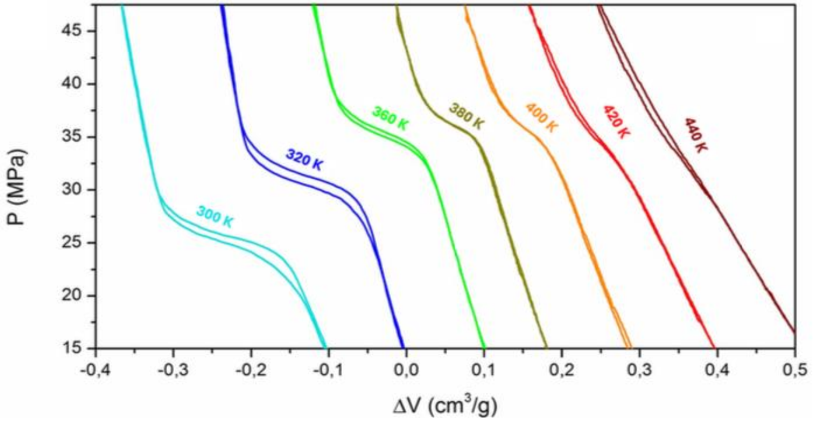
# Key characteristics for technological applications



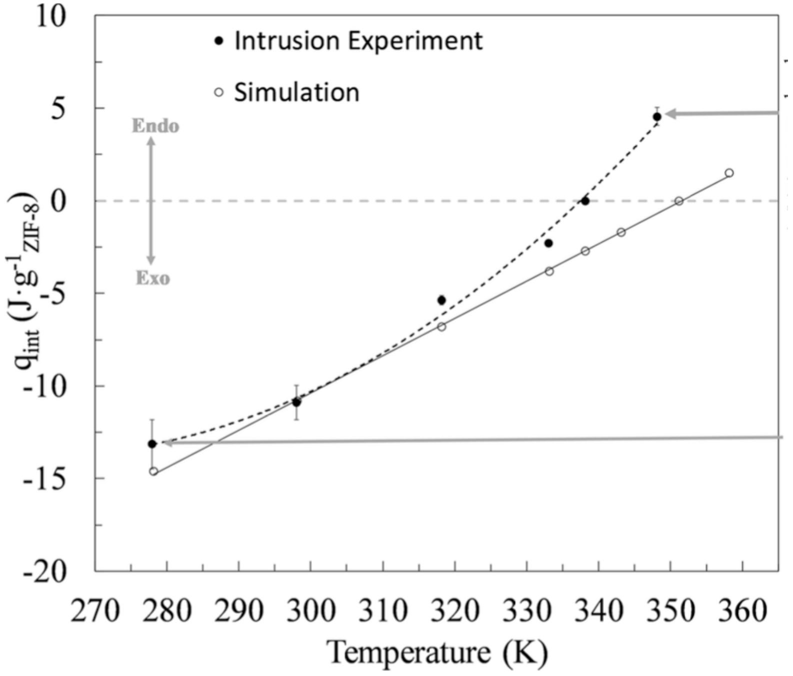

Adv. Phys.: X, 7, 2052353, 2022

Heat of Int/ext



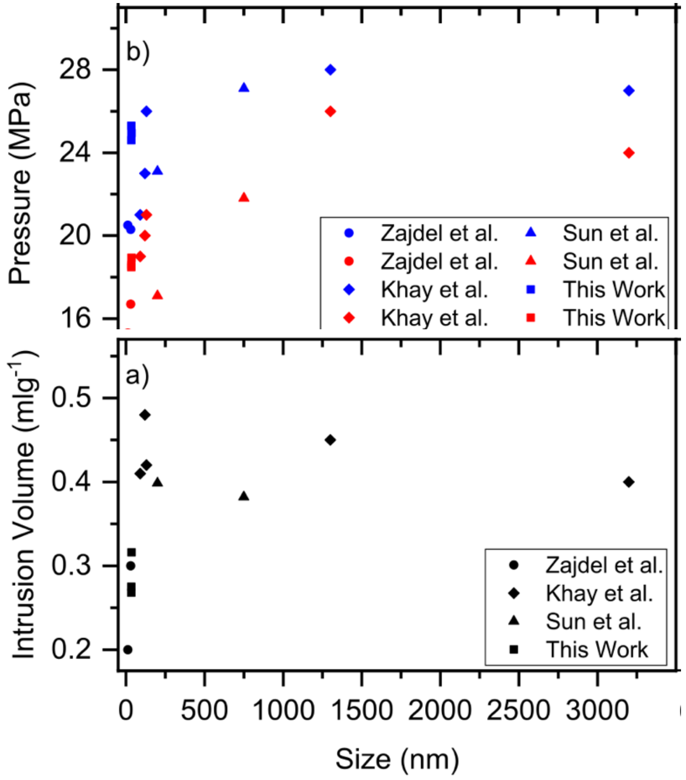




J. Coll. Interf. Sci. 645, 775, 2023




*ACS Appl. Mater. Interfaces* 16, 5286, 2024

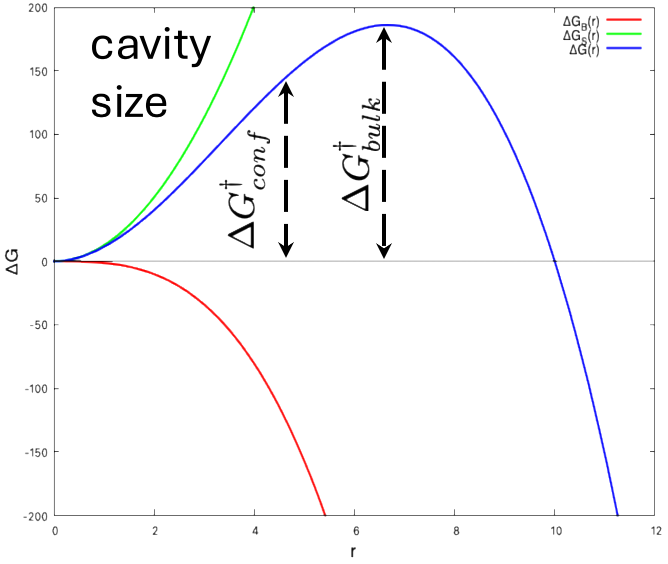
*J. Am. Chem. Soc.* 146, 13236, 2024

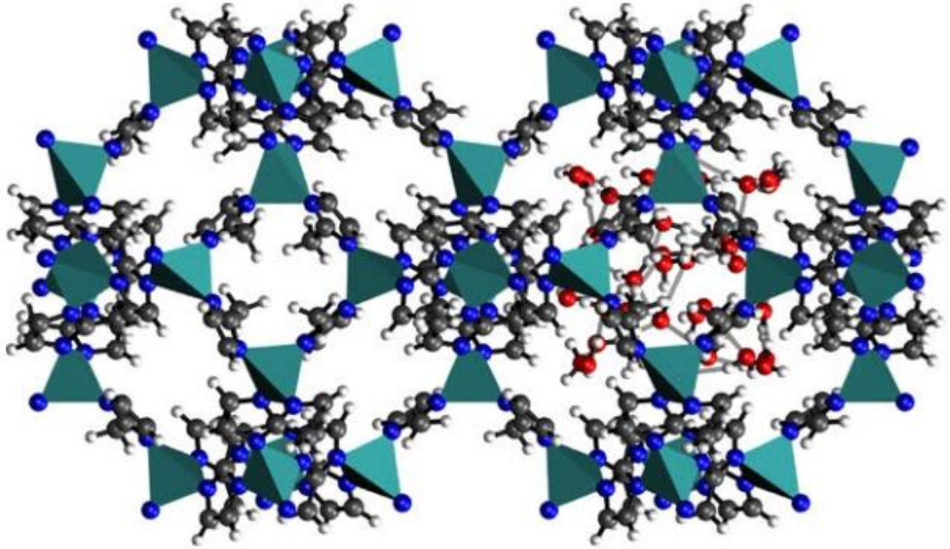


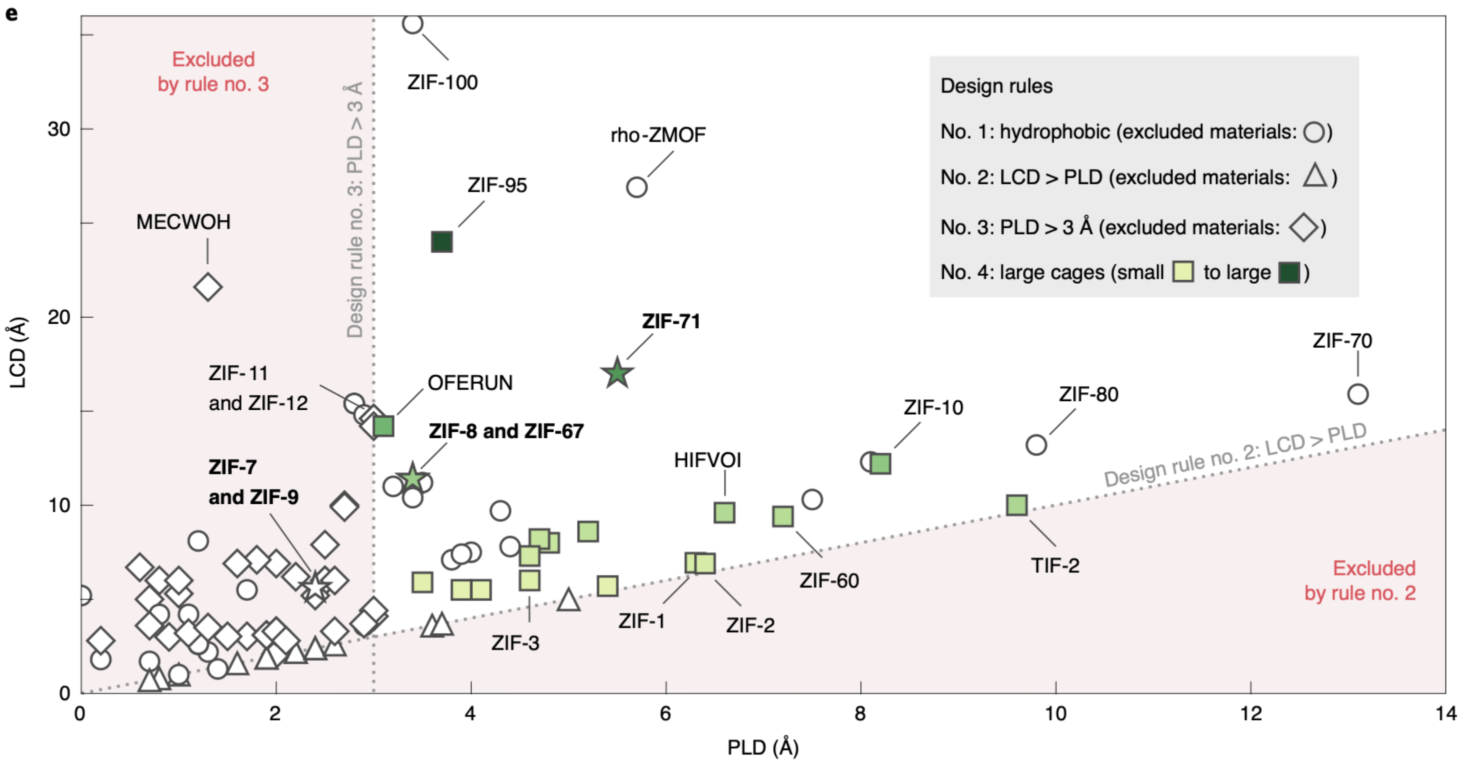

European Innovation Council

Funded by the European Union

# Mechanism of intrusion of water in ZIFs: confined vapor nucleation



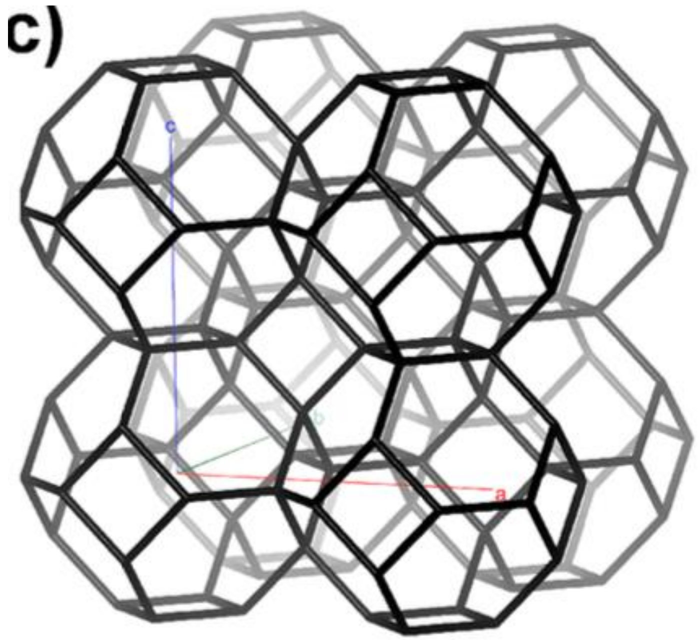



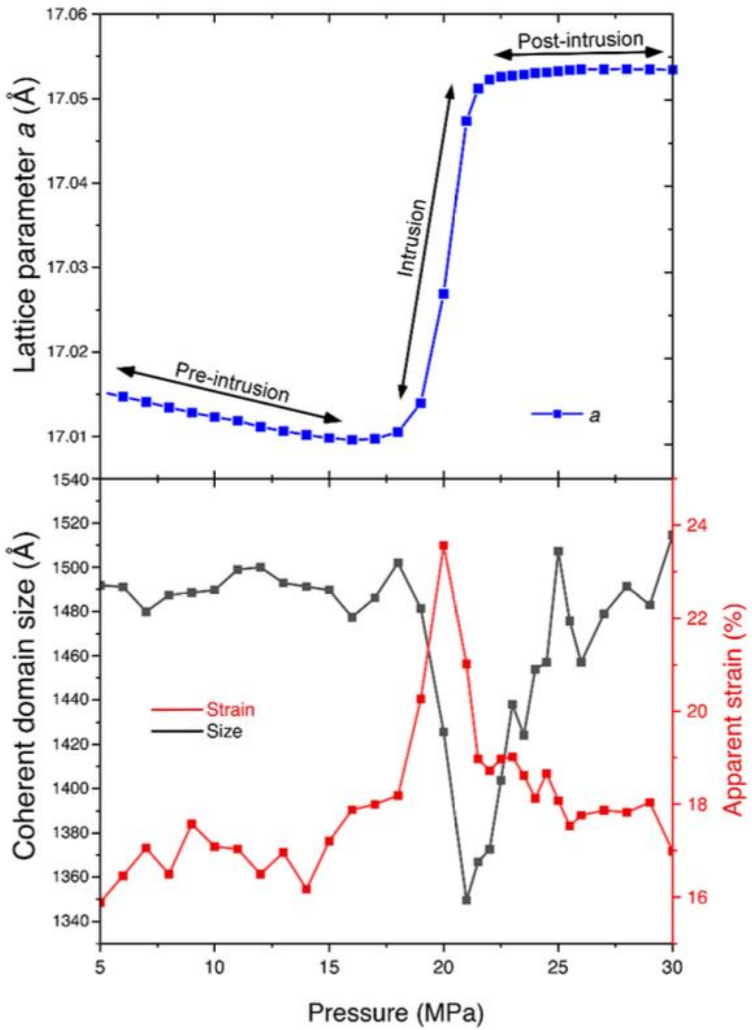


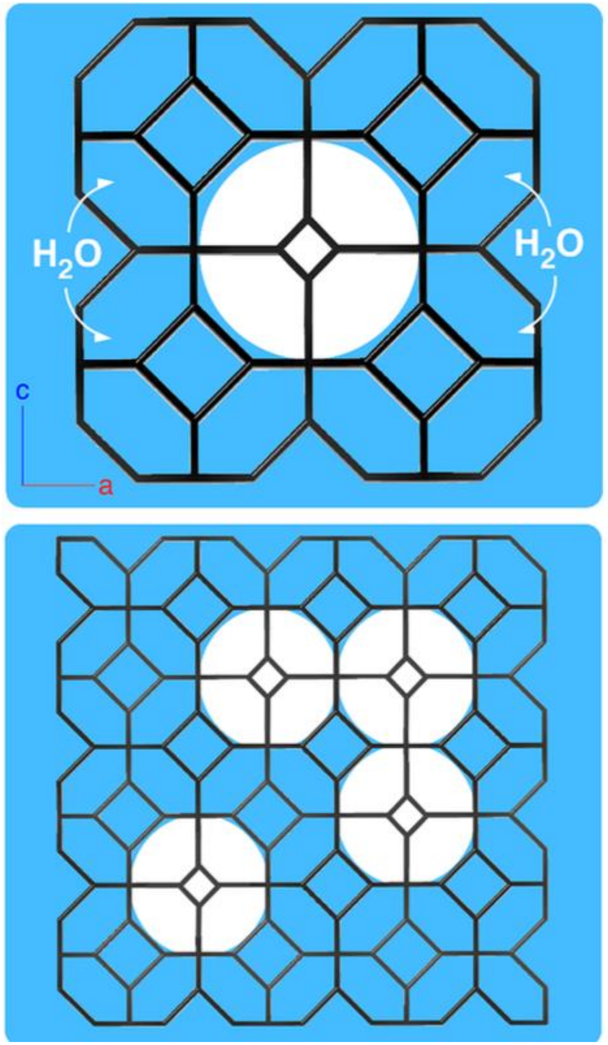

PLD = pore-limiting diameter
LCD = largest cavity diameter

European Innovation Council
Funded by the European Union

# Mechanism of intrusion of water in ZIFs: water-front advancement.

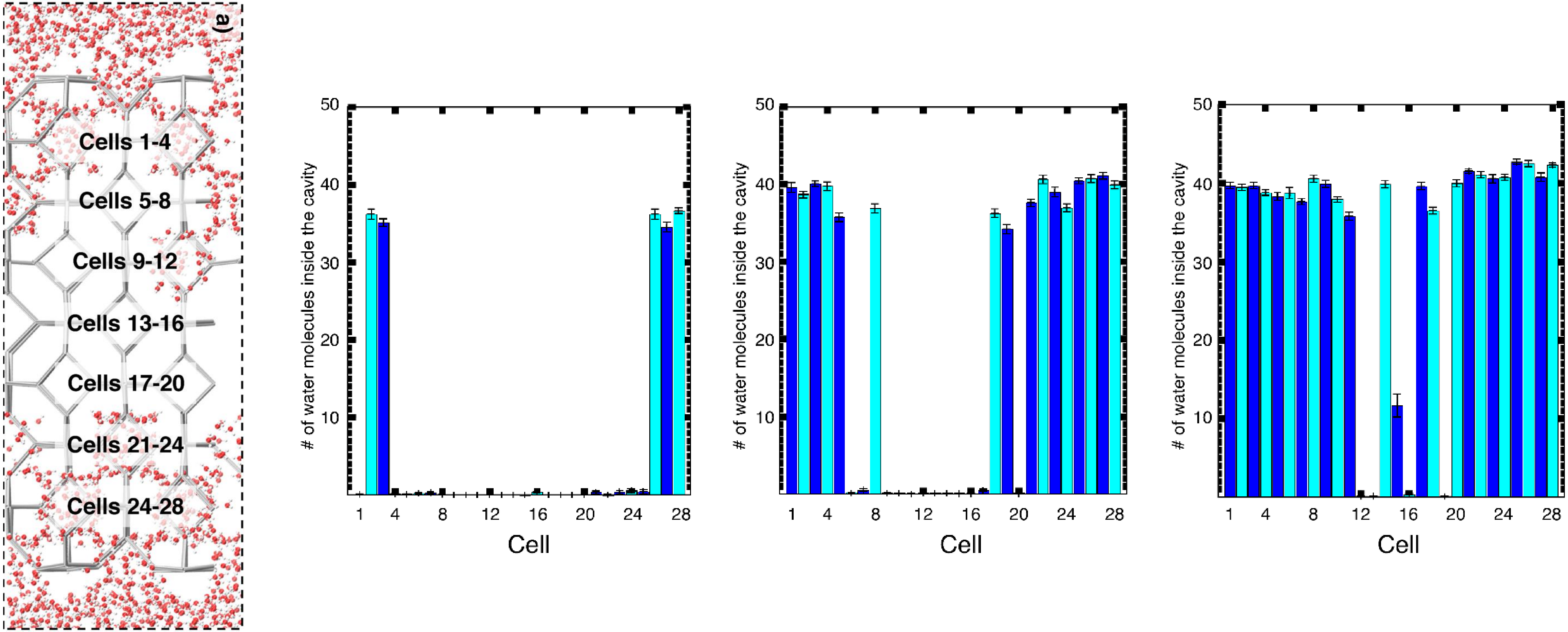



*Nano Lett.* 23, 5430, 2023

# Mechanism of intrusion of water in ZIFs: water-front advancement.



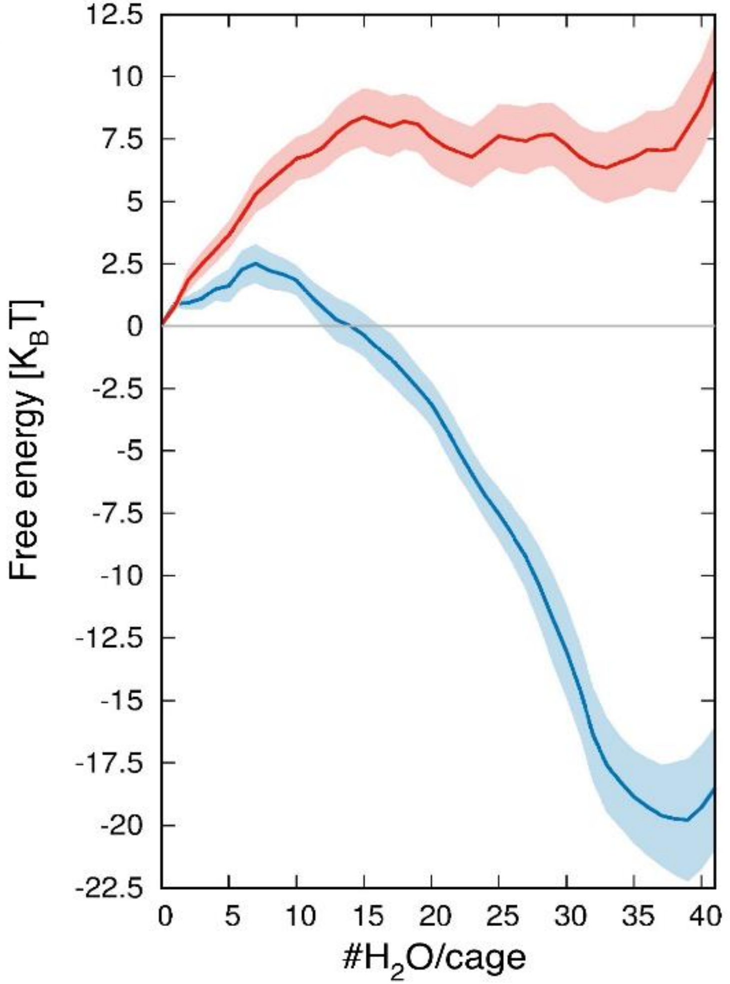

ELECTRO INTRUSION

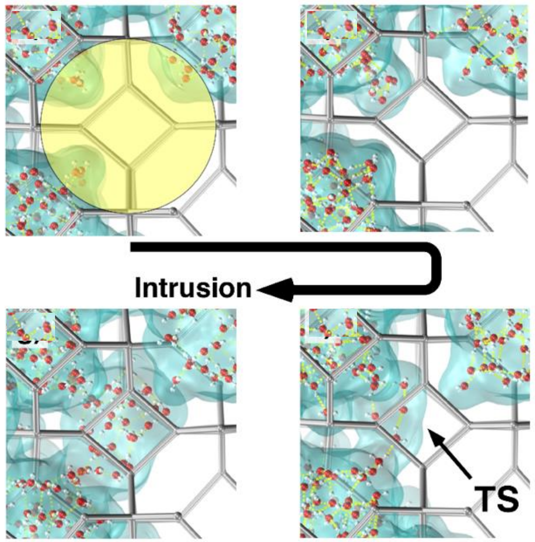
European Innovation Council

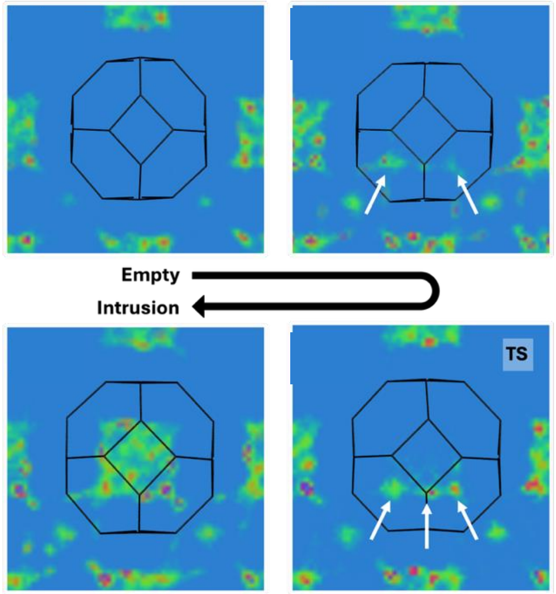
Funded by the European Union

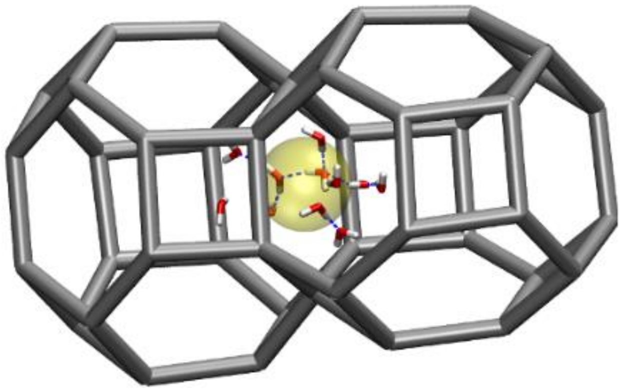
*Nano Lett.* 23, 5430, 2023

# Mechanism of intrusion of water in ZIFs: water-front advancement.



| | $\theta_i$ |
|---|---|
| Std ZIF-8 | 101° |
| Clogged pores | 114° |

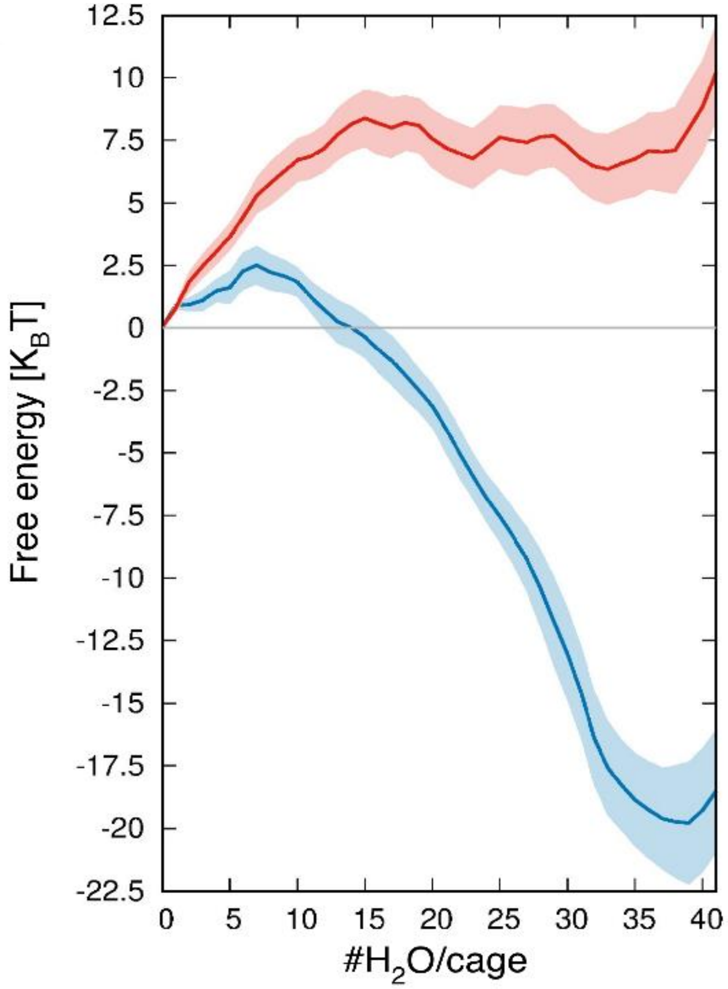
ELECTRO INTRUSION

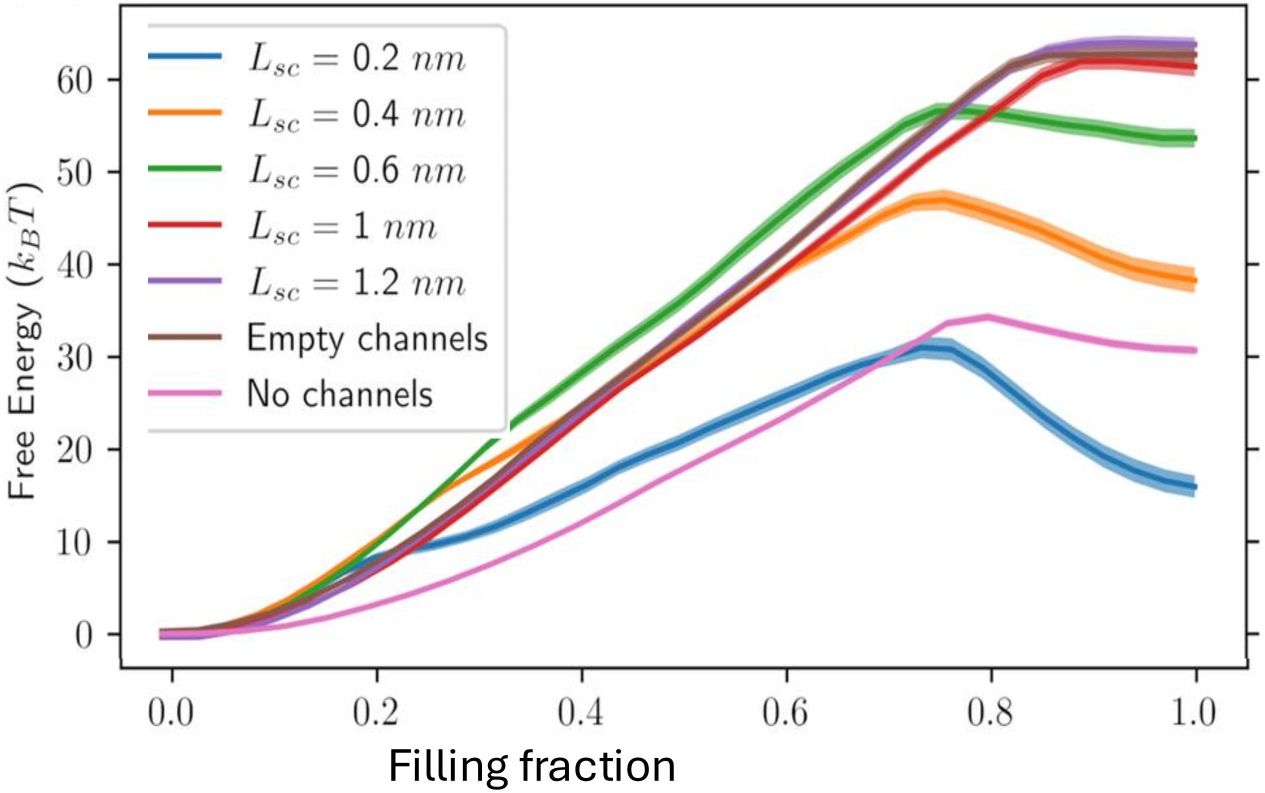

Nano Lett.22, 2164, 2022; ACS Appl. Mater. Interfaces 2022, 14, 30067; Comm. Phys. 6, 21 2023; Nano Lett. 23, 5430, 2023

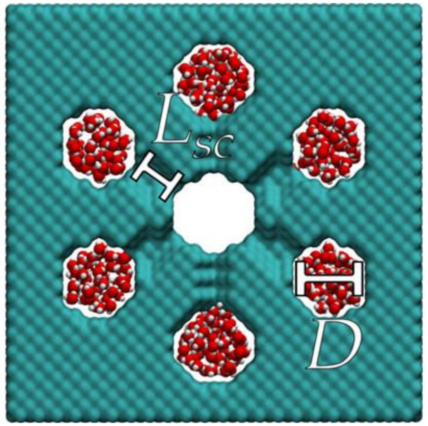


European Innovation Council
Funded by the European Union

# Mechanism of intrusion of water in ZIFs: water-front advancement.




**Model of the ITT zeolite**

Non-classical effect, against the Young-Laplace law:

$P_{int} = -2\gamma \cos(\theta)/d$

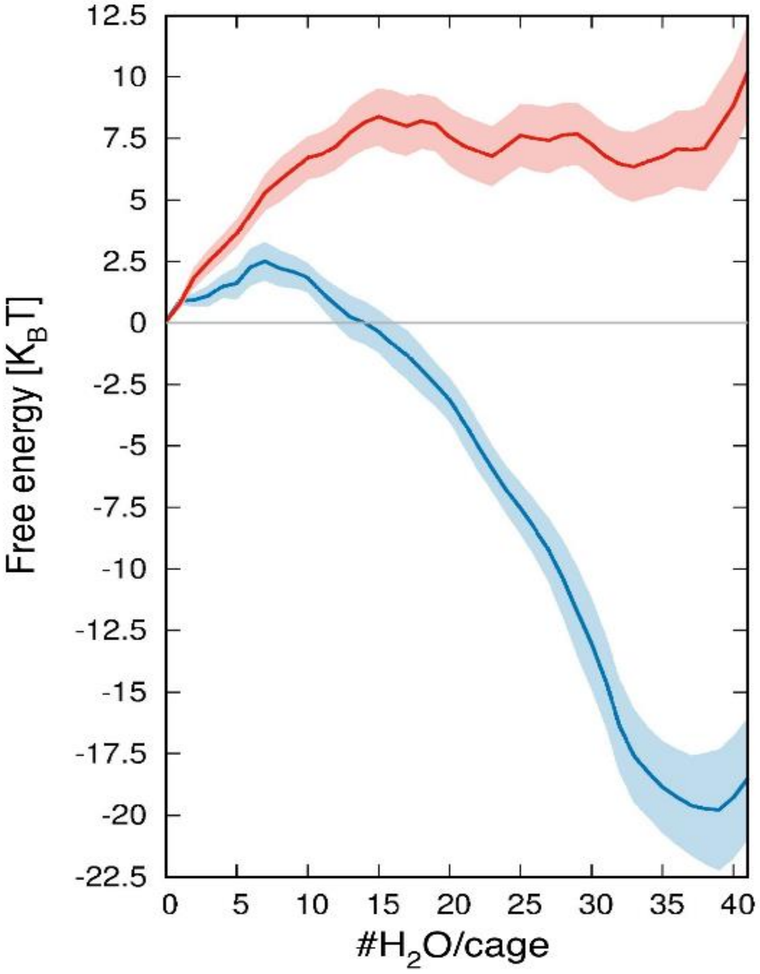
narrower pores fill together with the bigger ones



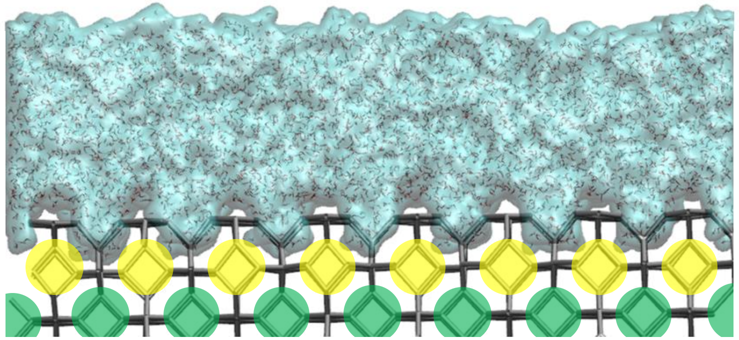
Nano Lett.22, 2164, 2022; ACS Appl. Mater. Interfaces 2022, 14, 30067; Comm. Phys. 6, 21 2023; Nano Lett. 23, 5430, 2023

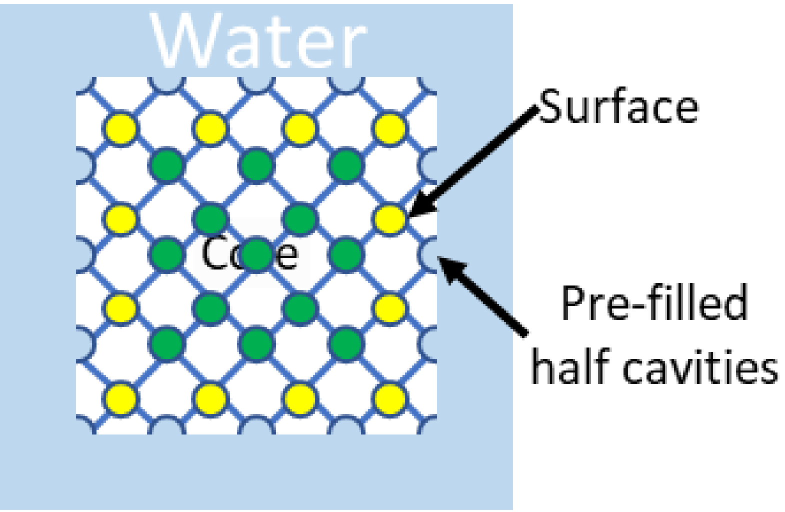
European Innovation Council
Funded by the European Union

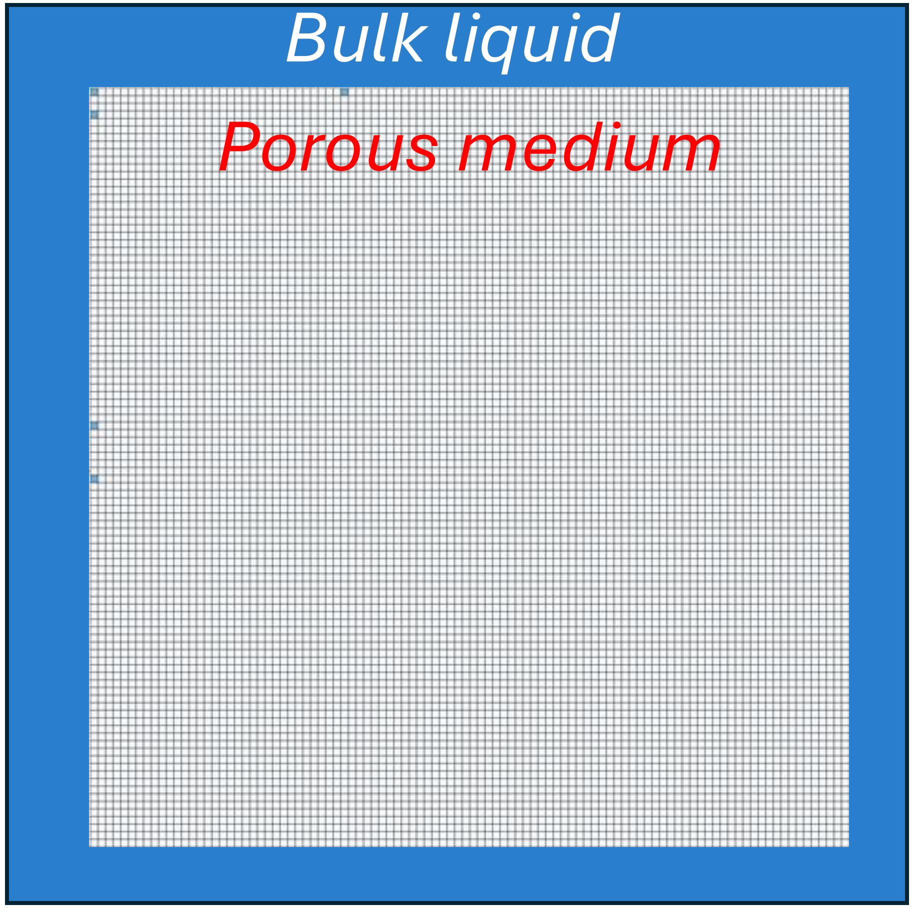
# Mechanism: what did we learn on the thermodynamics of confined water?




$$t_f = t_f^0 e^{\frac{\Omega_f^\dagger}{k_B T}};\ t_e = t_e^0 e^{\frac{\Omega_e^\dagger}{k_B T}}$$






*Effective surface tension in a (porous) medium: meta-liquid*

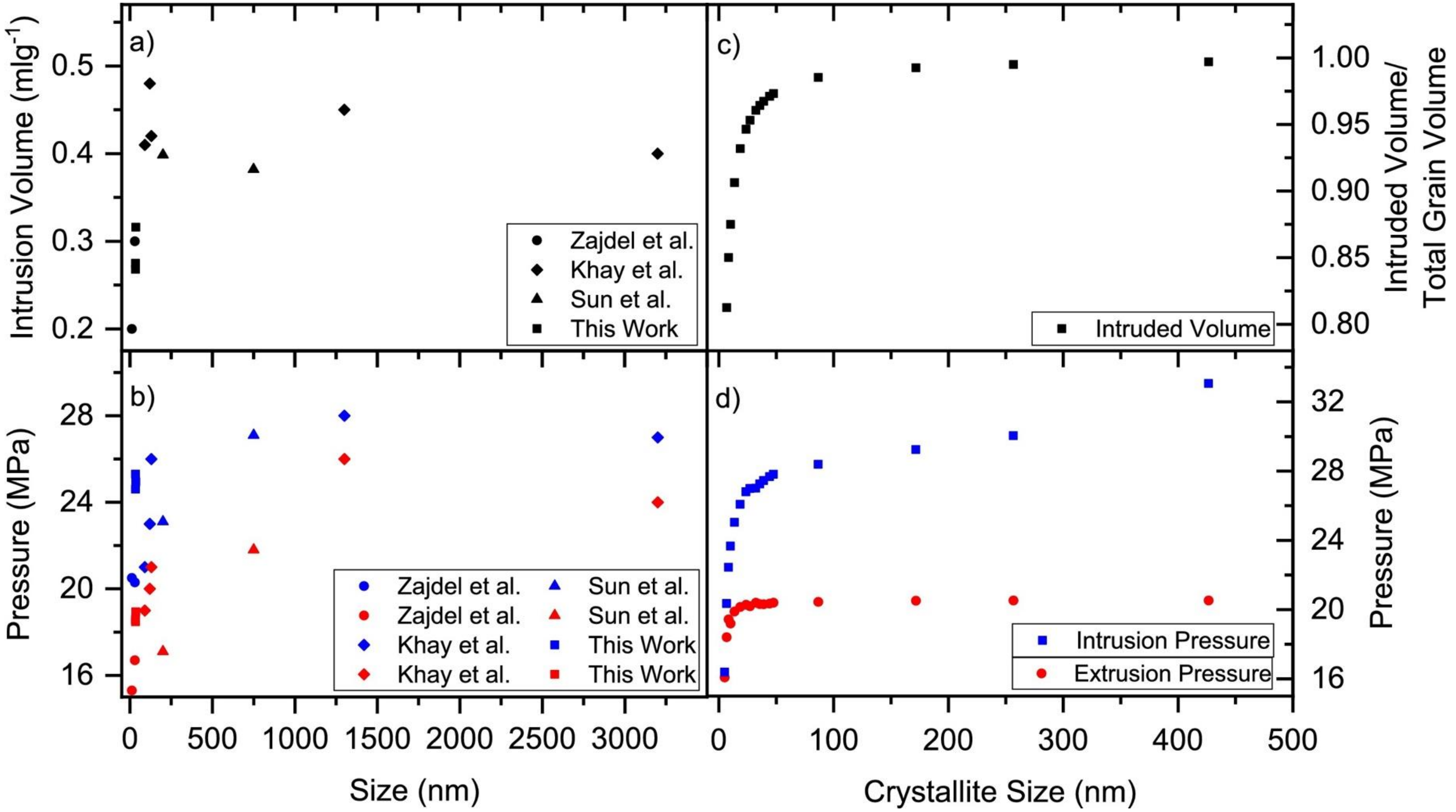

ELECTRO INTRUSION

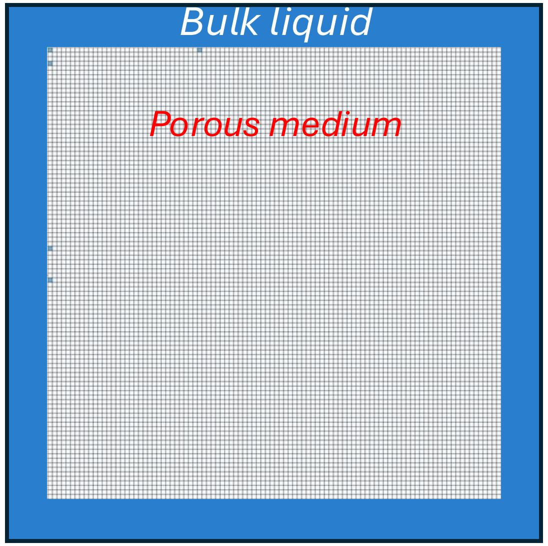
Nano Lett. 23, 5430, 2023; J. Coll. Interf. Sci. 645,775, 2023.

European Innovation Council

Funded by the European Union

# Mechanism: what did we learn on the thermodynamics of confined water?



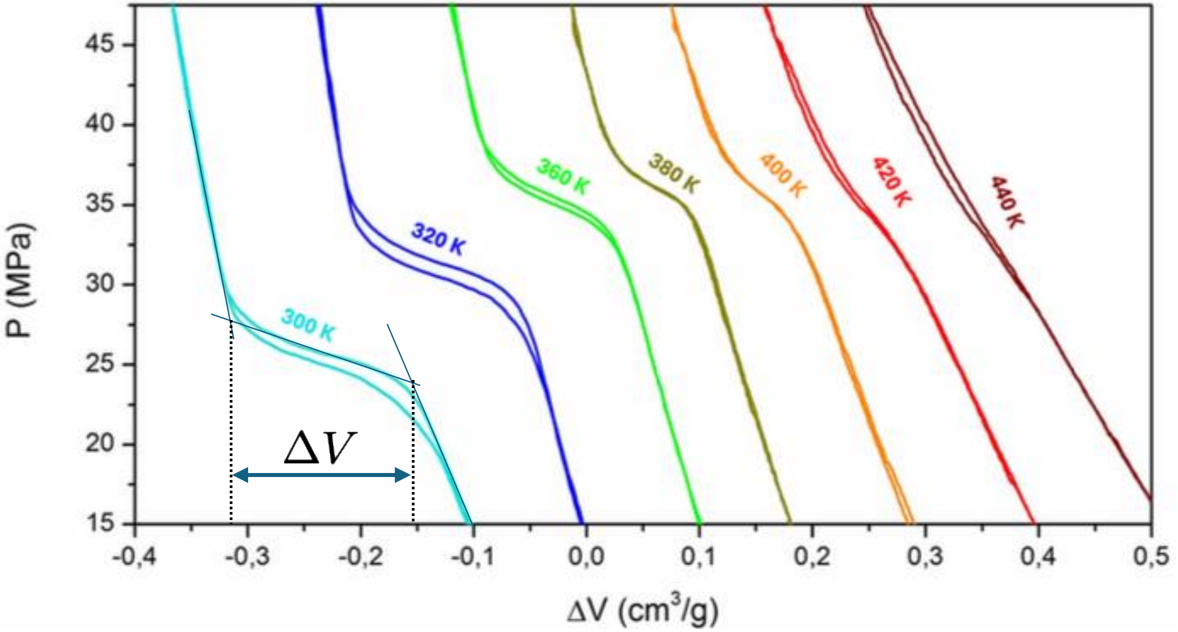

*Crystallite size allows one to tune the thermodynamic characteristics of water confined within monodisperse porous materials*

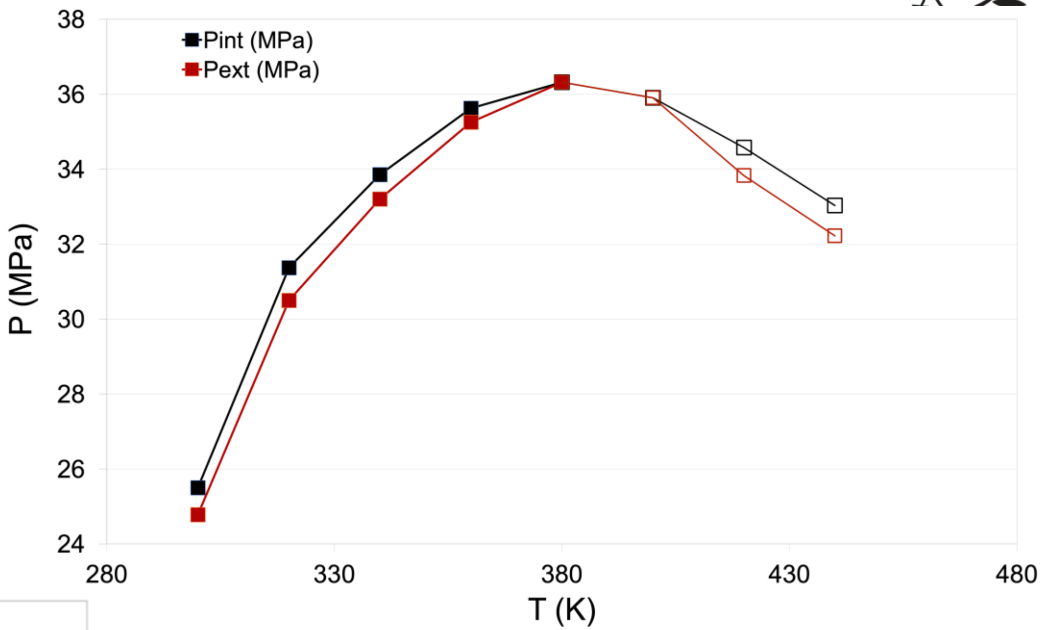
ELECTRO INTRUSION

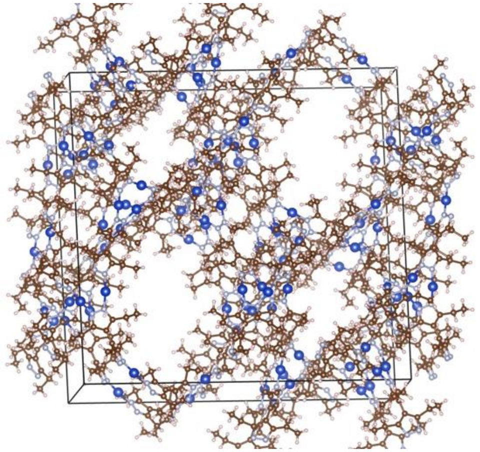
Nano Lett. 23, 5430, 2023; J. Coll. Interf. Sci. 645,775, 2023.

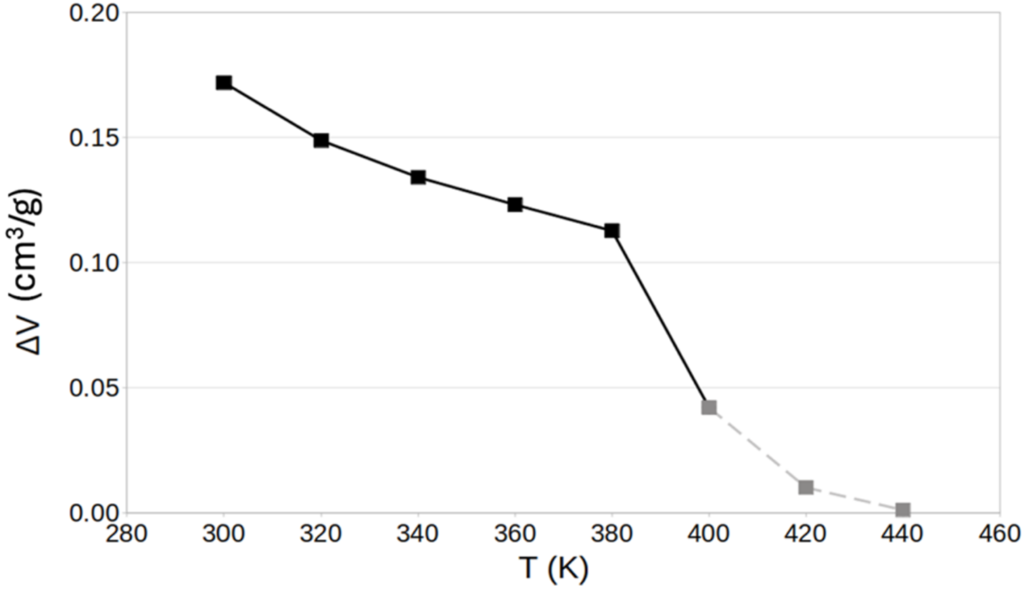

European Innovation Council
Funded by the European Union

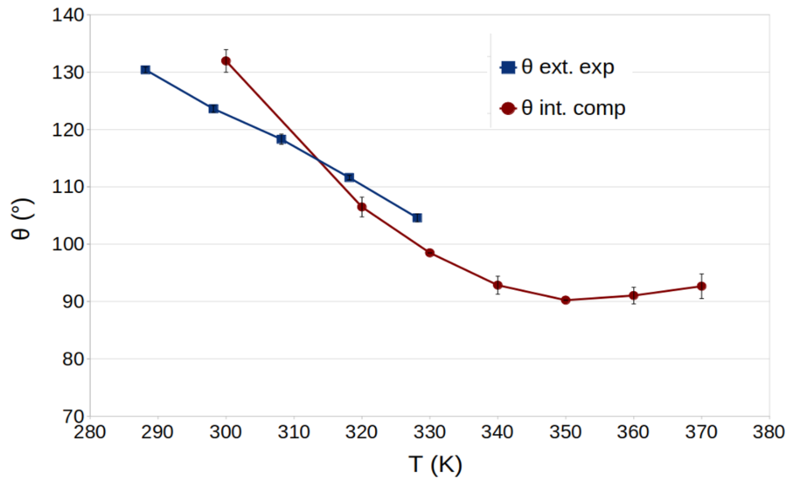
# Effect of the temperature





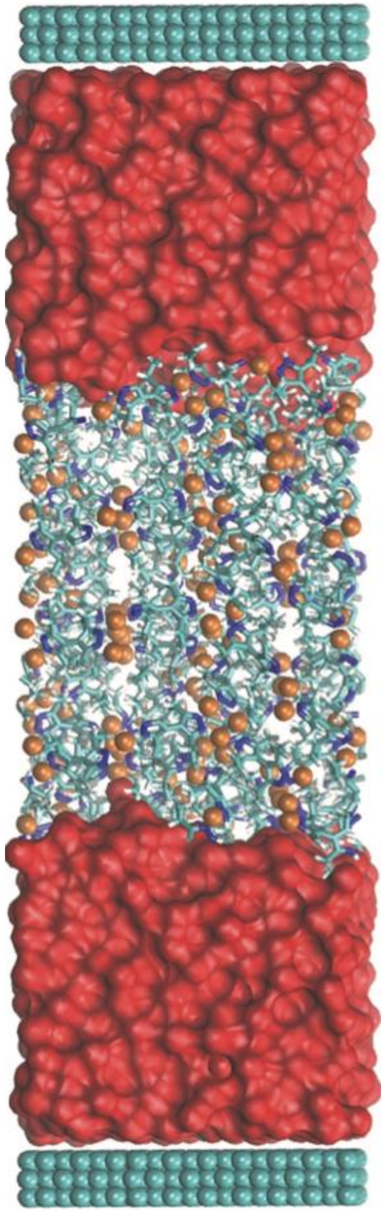



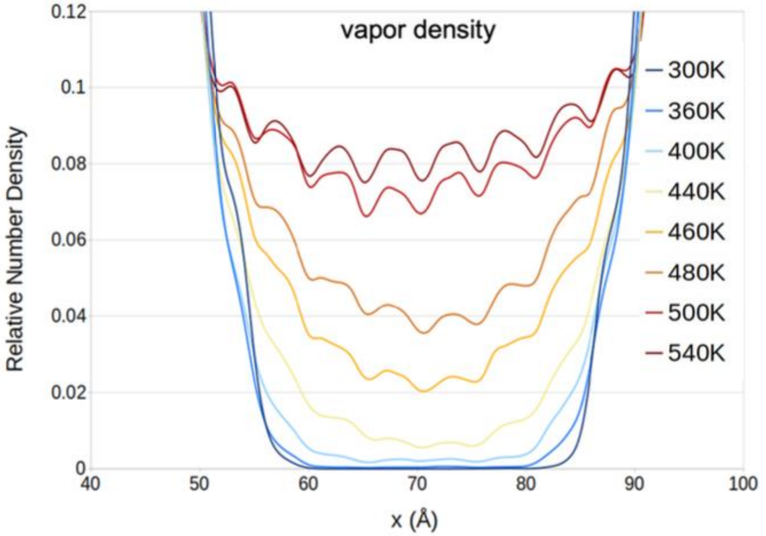

ELECTRO INTRUSION

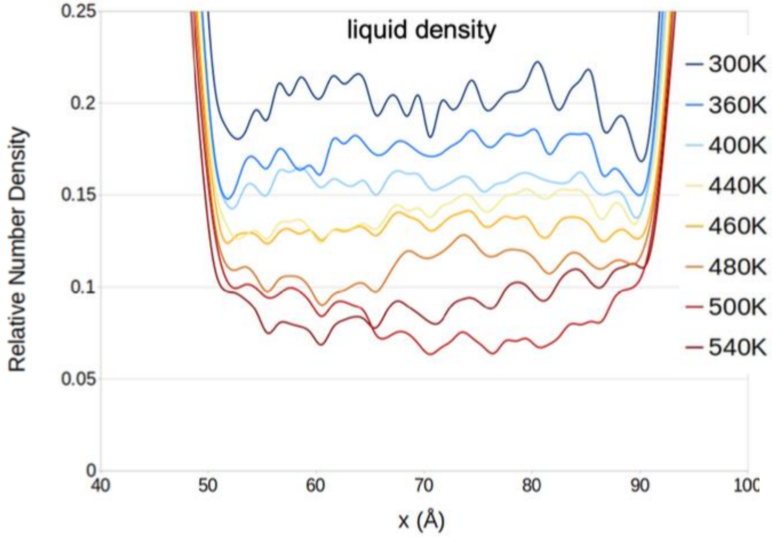
*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

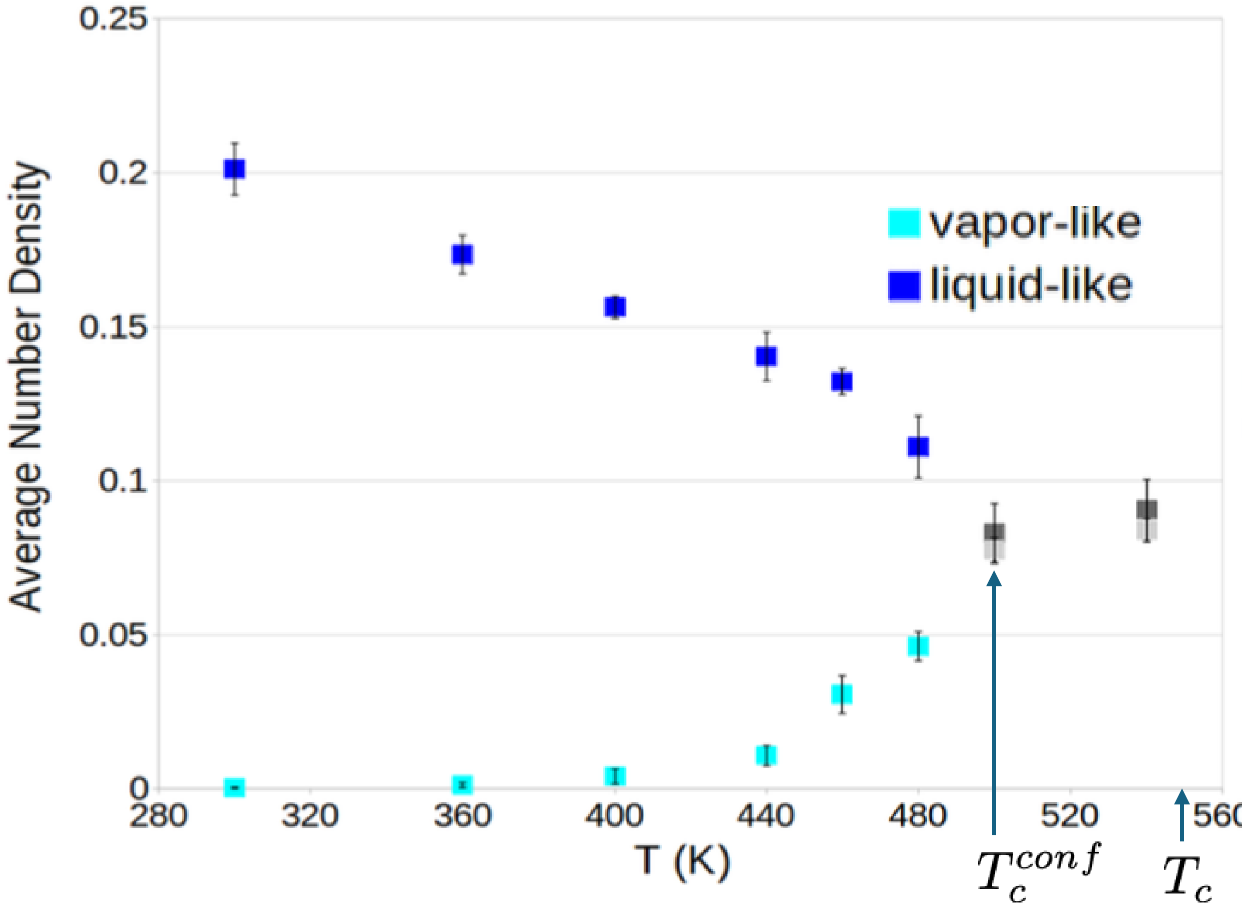
European Innovation Council
Funded by the European Union

# Confined, Low-T, supercritical water





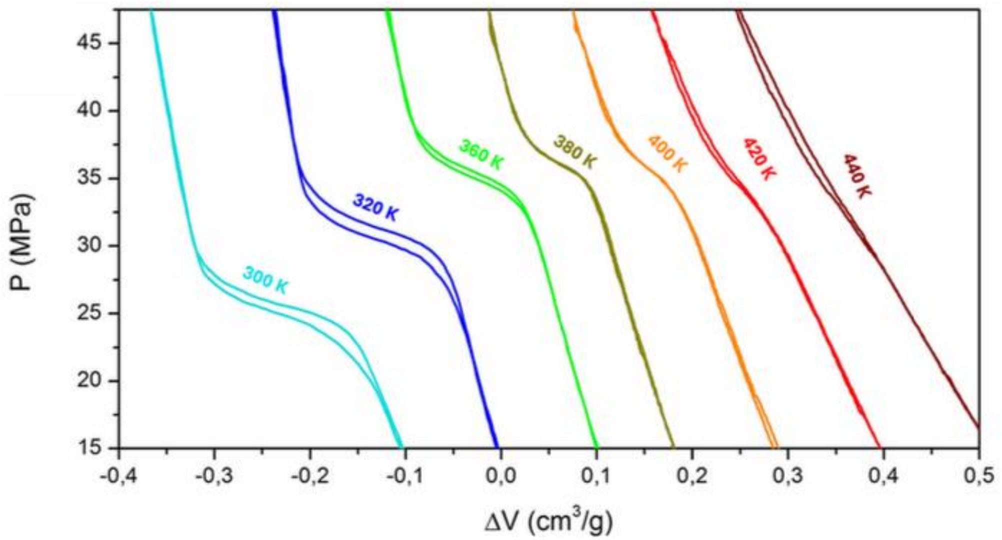

ELECTRO INTRUSION

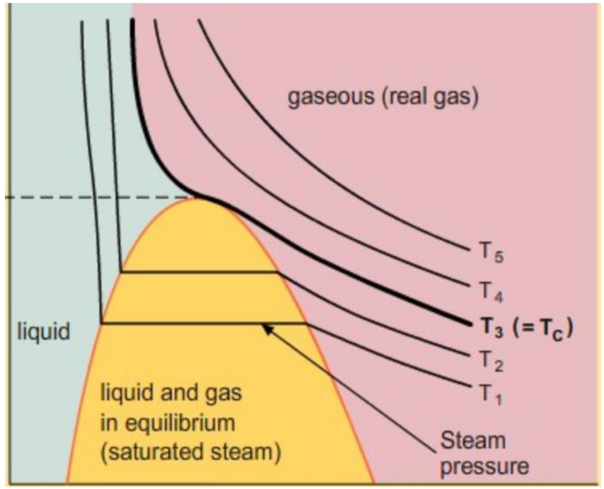
European Innovation Council

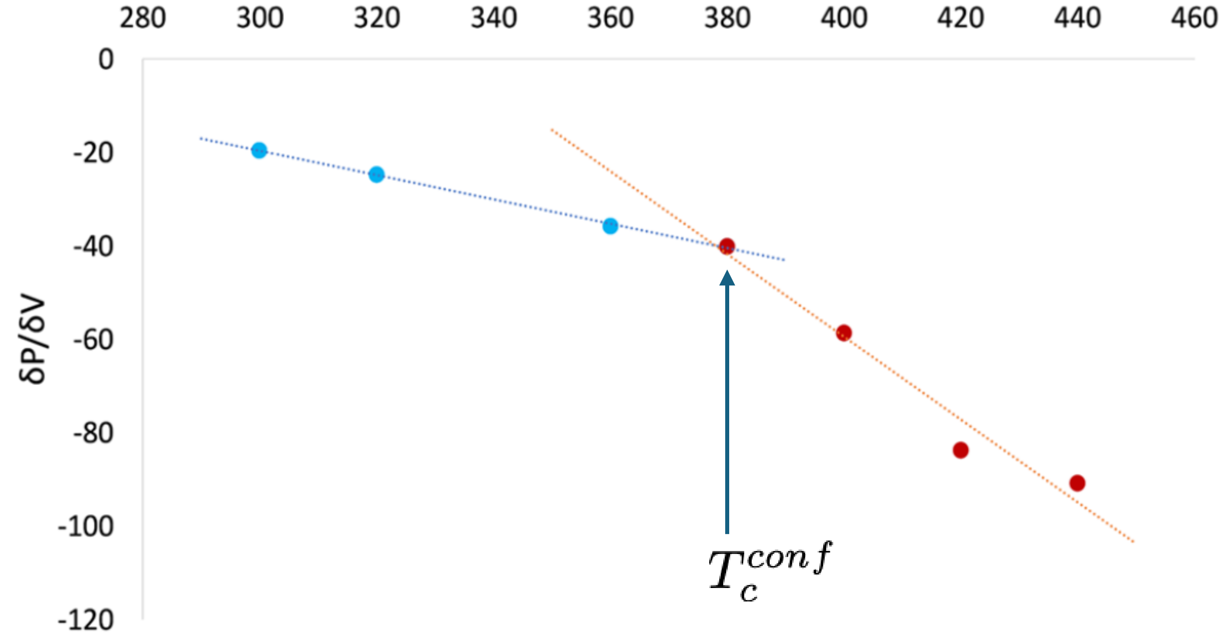
Funded by the European Union

*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

# Confined, Low-T, supercritical water



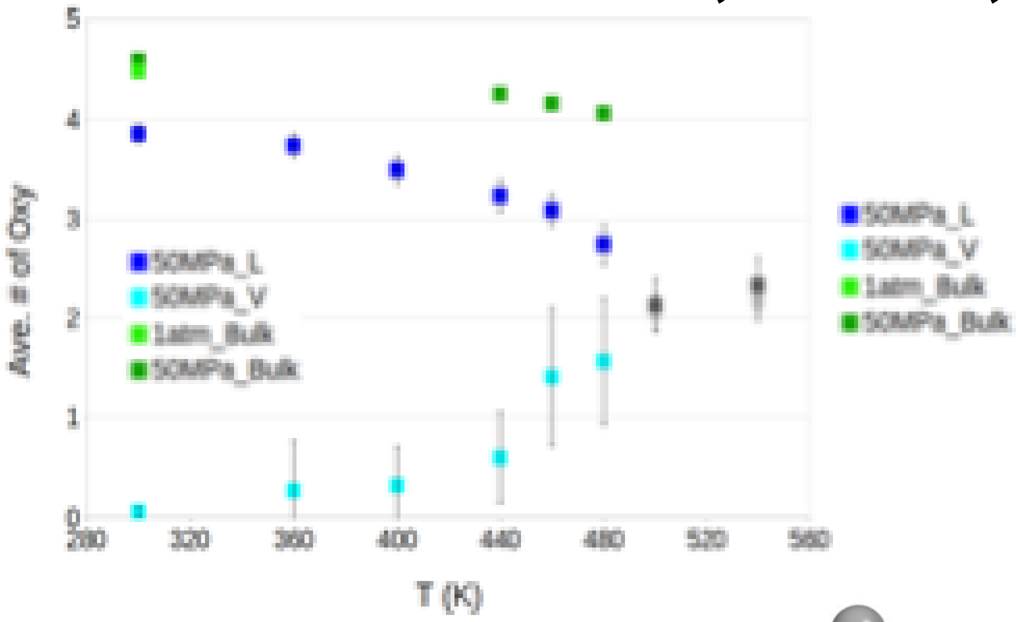

ELECTRO INTRUSION

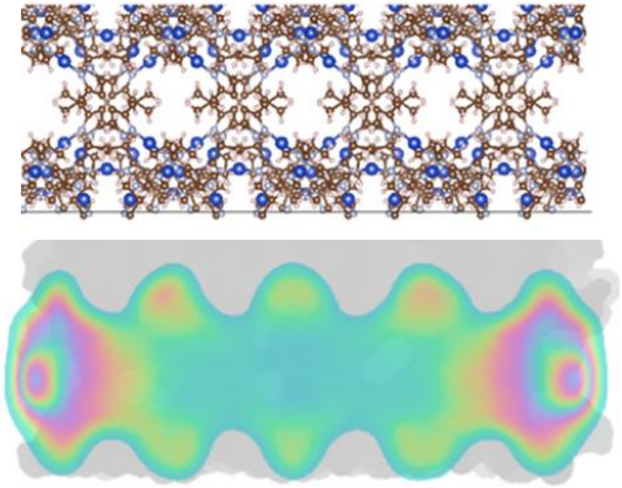
European Innovation Council

Funded by the European Union

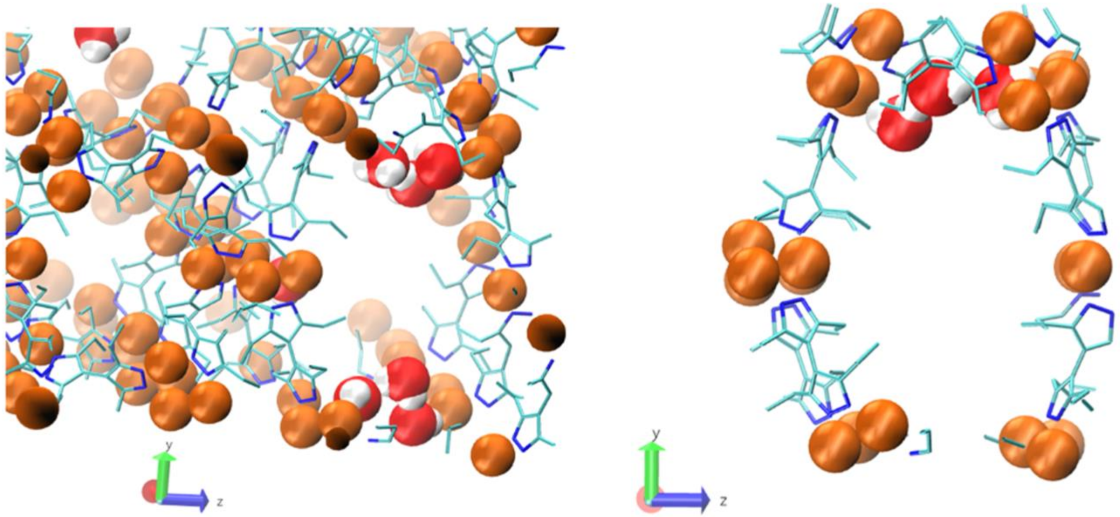
*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

# Confined, Low-T, supercritical water

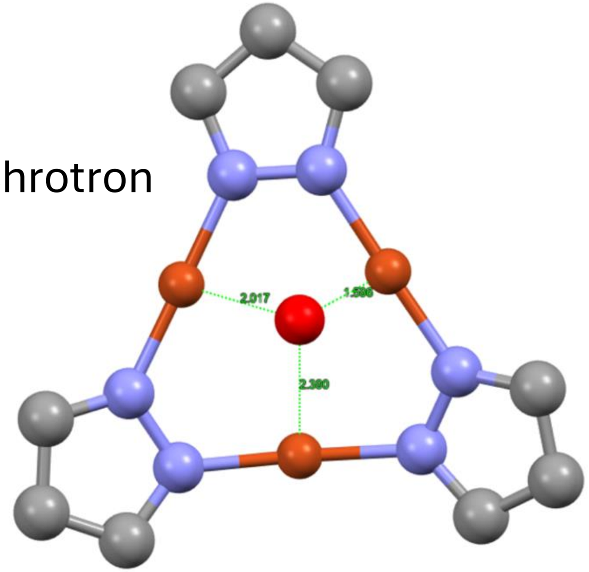


Simulations



Synchrotron

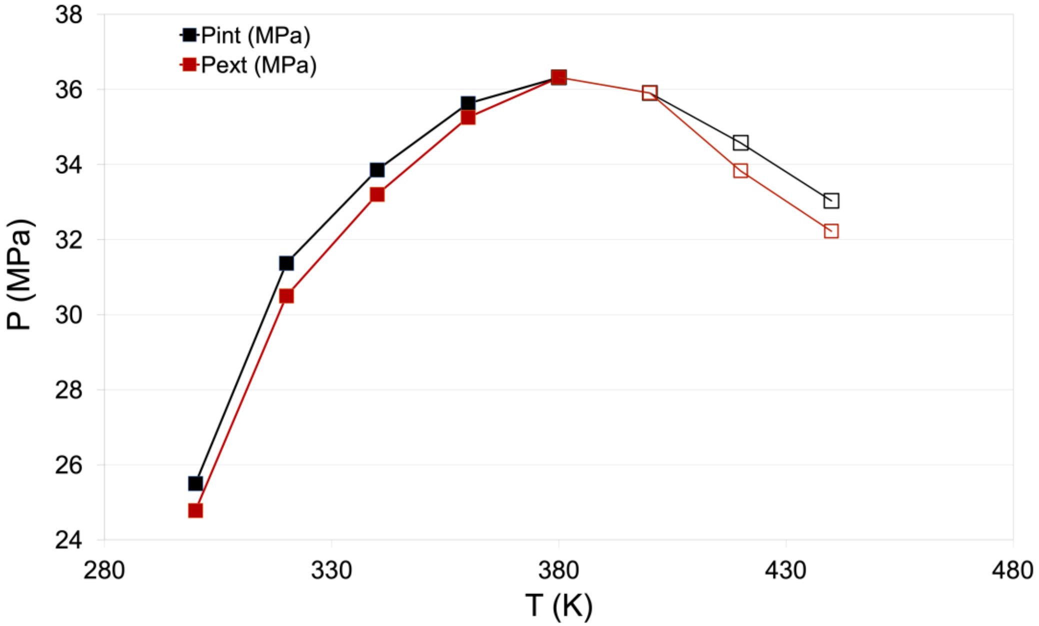


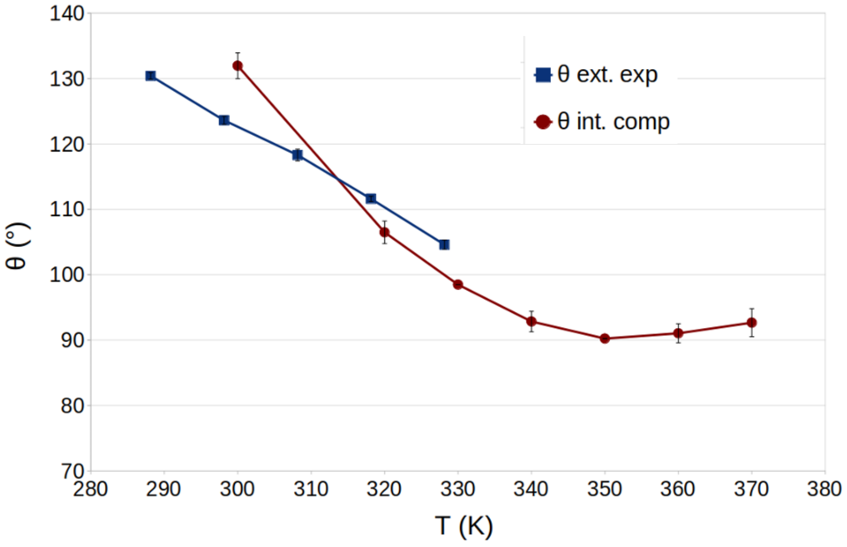
ELECTRO INTRUSION

*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

European Innovation Council
Funded by the European Union

# Effect of the temperature: reprised




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

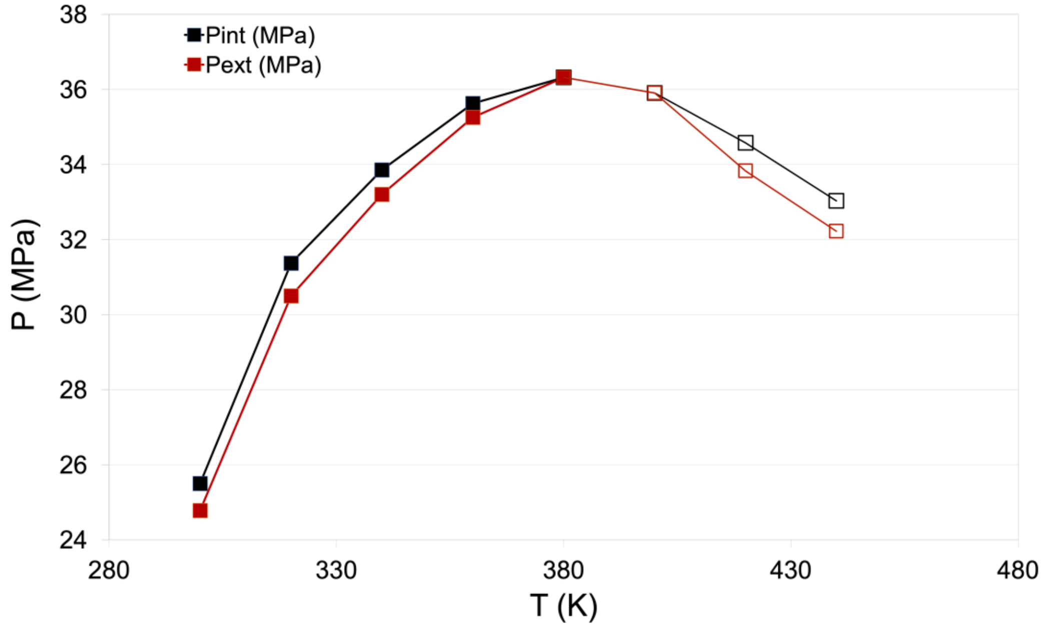
ELECTRO INTRUSION

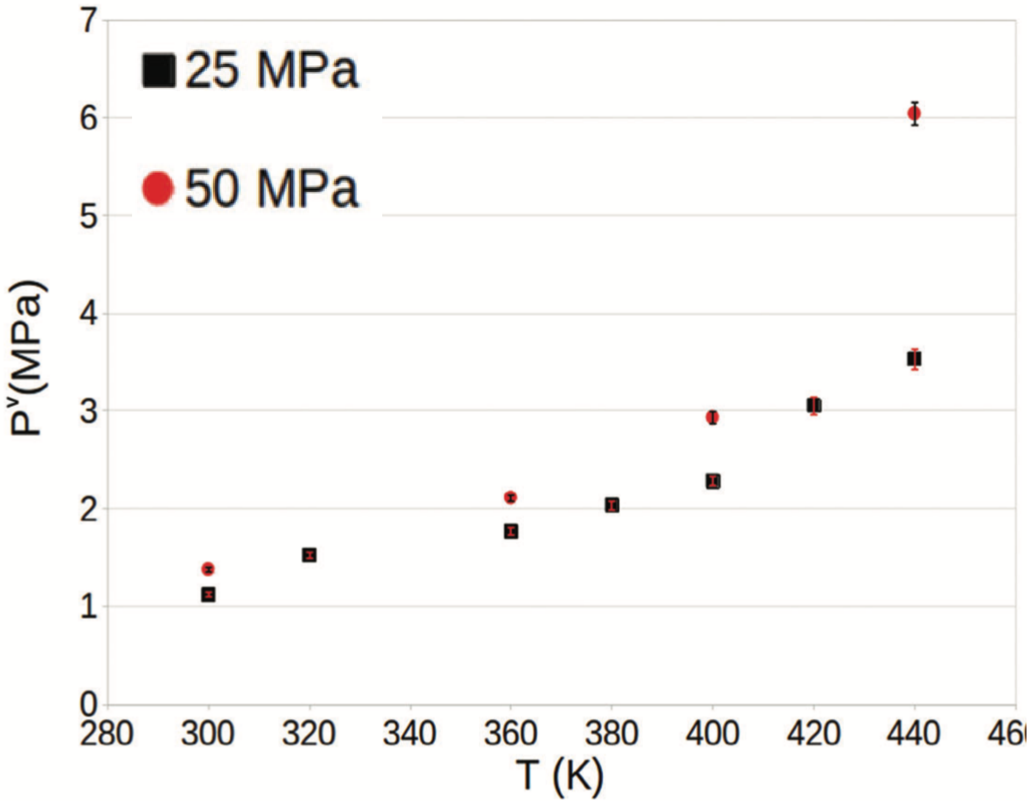
European Innovation Council

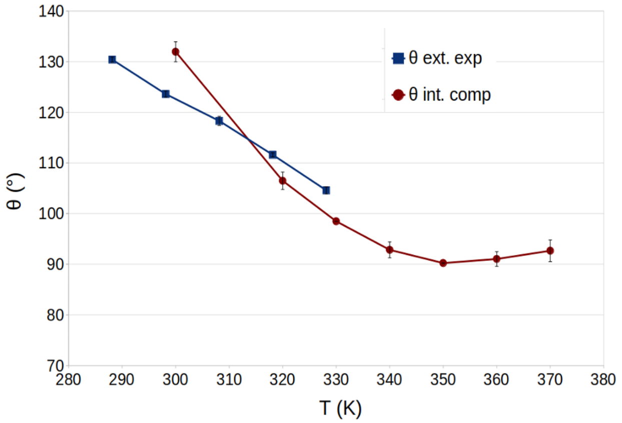
Funded by the European Union

*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

# Effect of the temperature: reprised



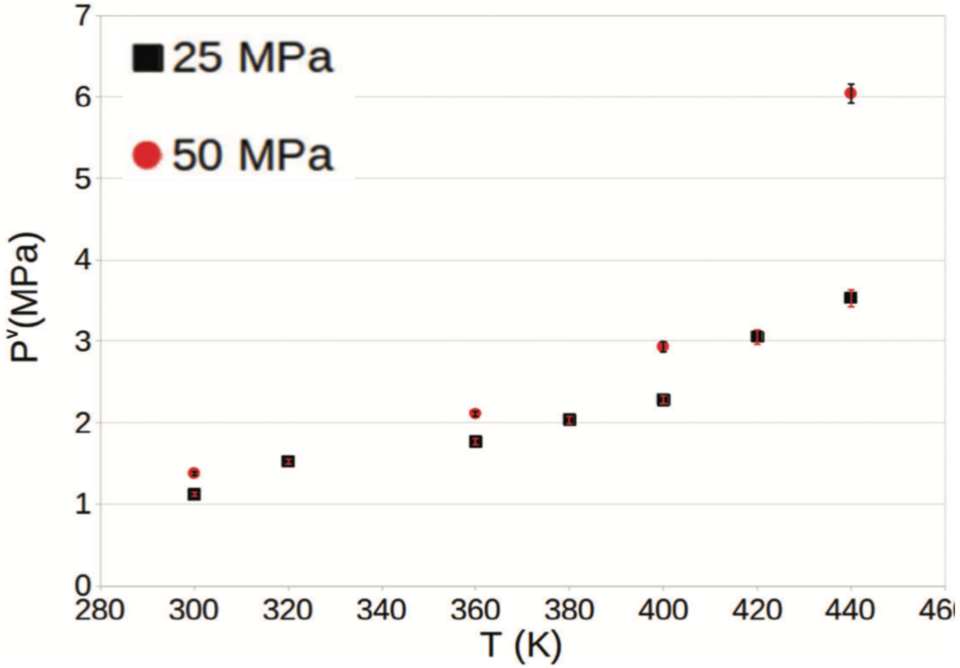

$$P^i = -2\gamma \cos \vartheta / a + P^\nu$$

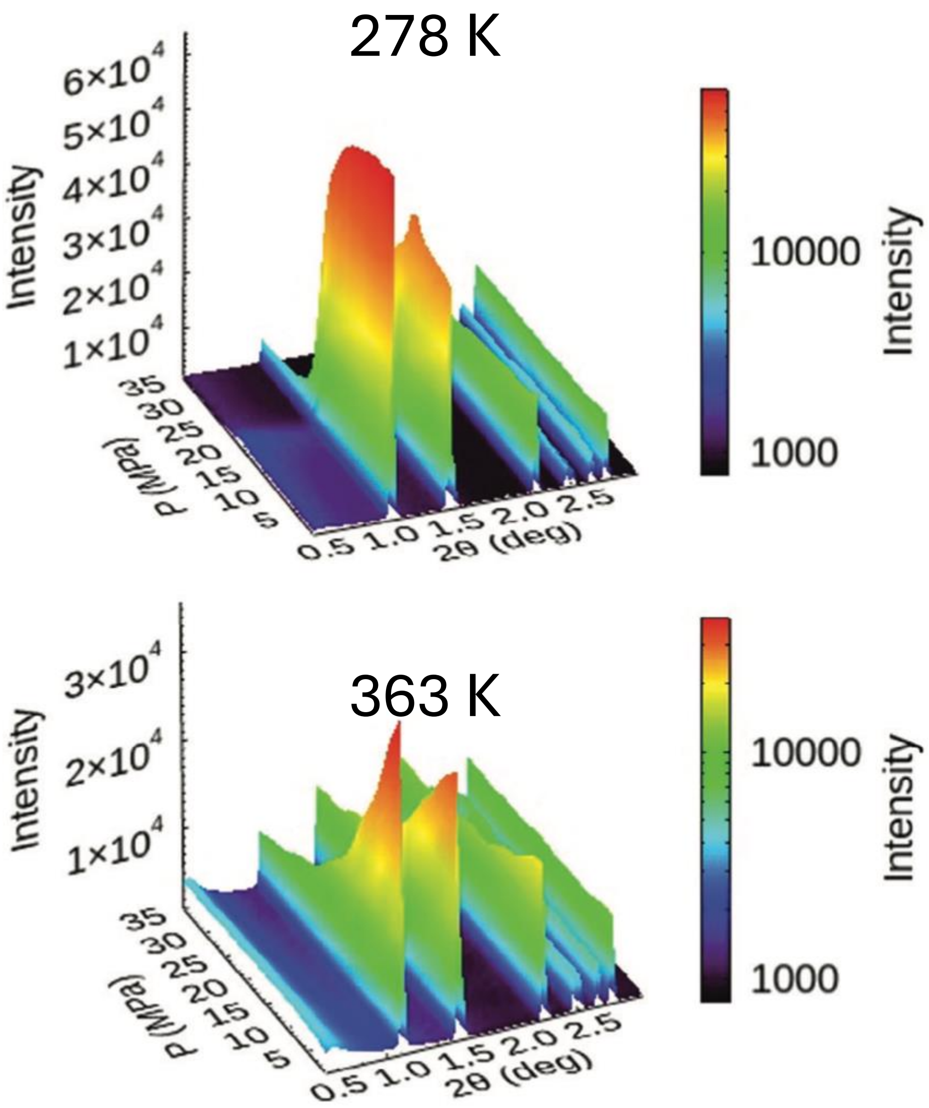


*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

European Innovation Council
Funded by the European Union

# Effect of the temperature: reprised



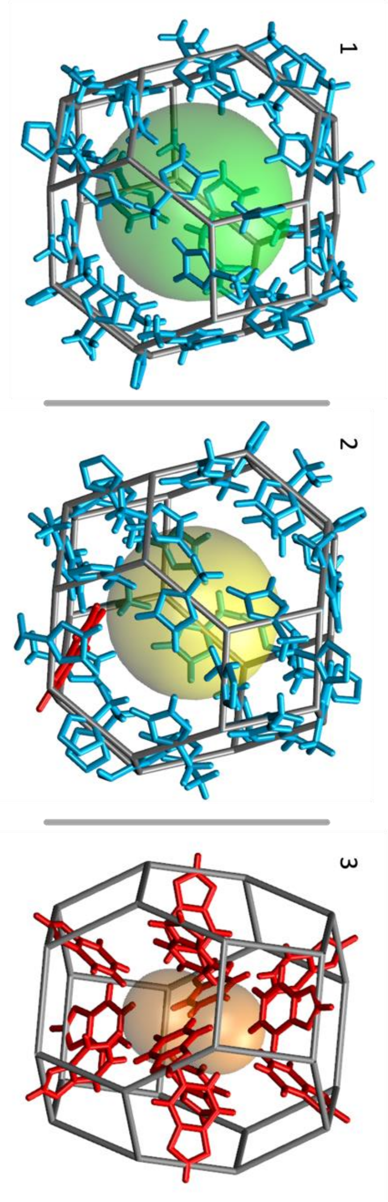



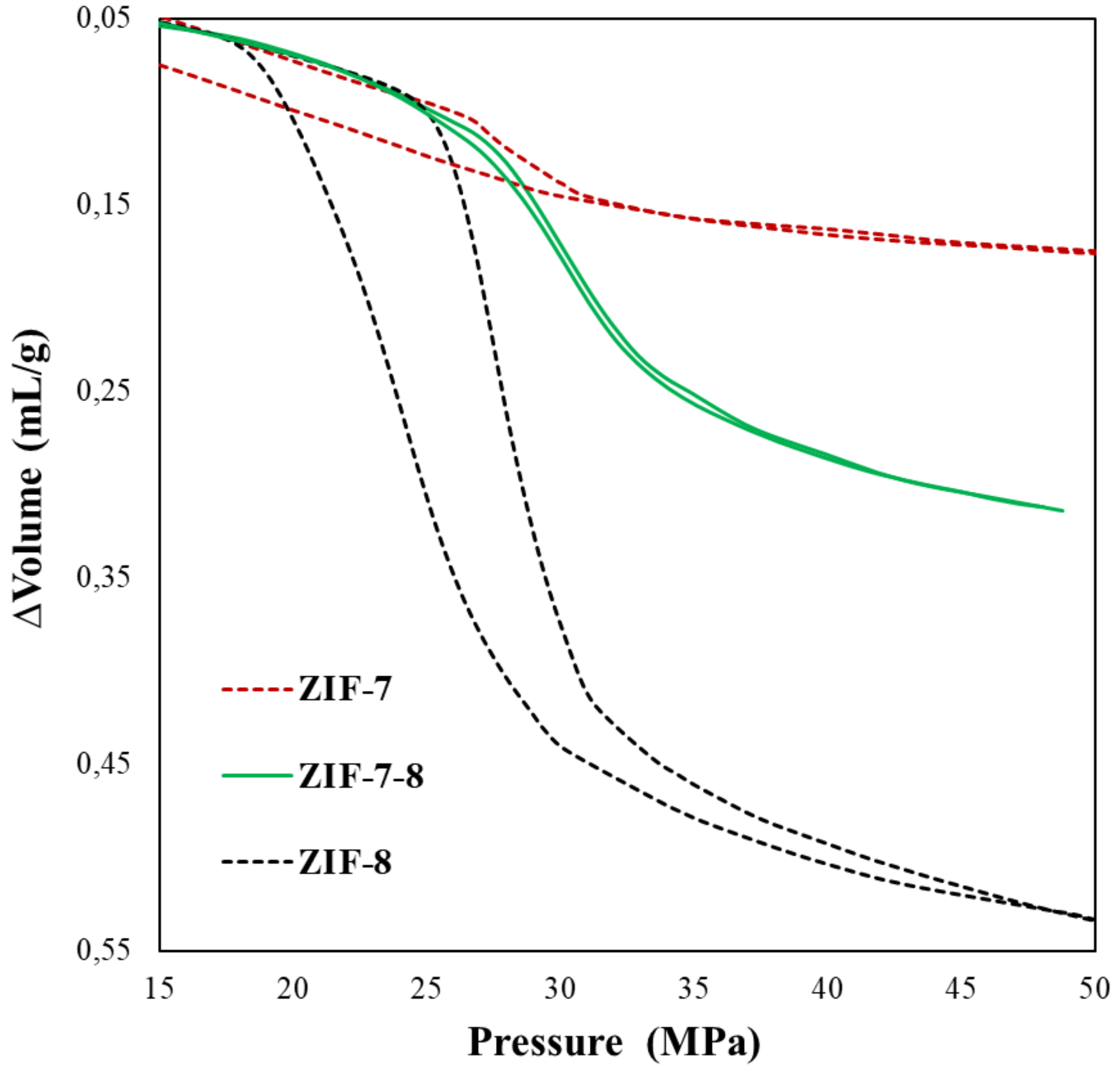



*J. Am. Chem. Soc.* 146, 13236, 2024; Small 2402173, 2024

European Innovation Council
Funded by the European Union

# Mixing linkers

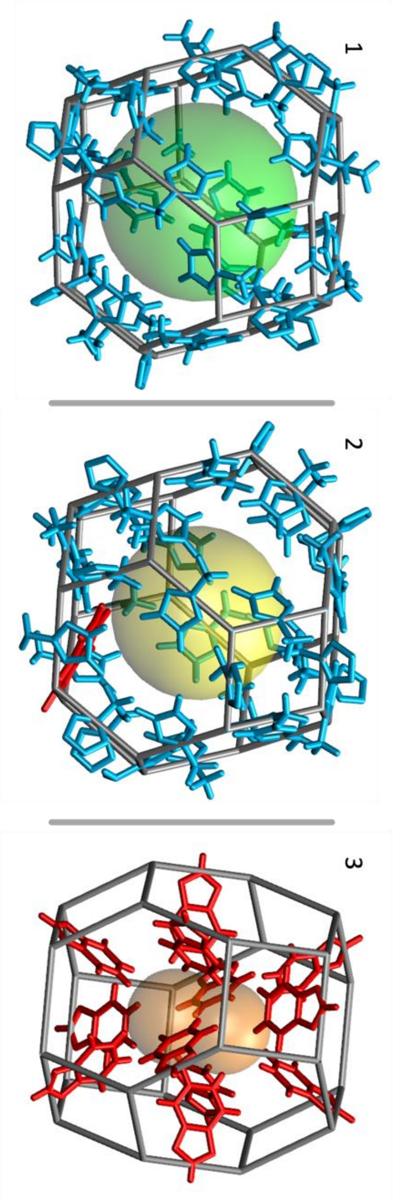


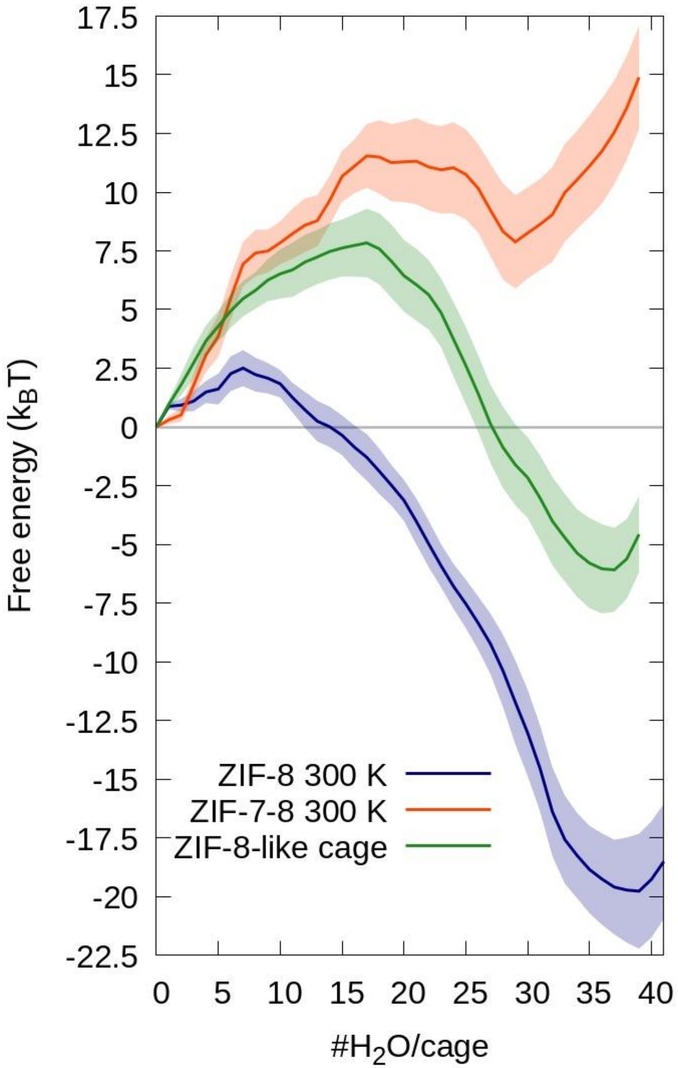



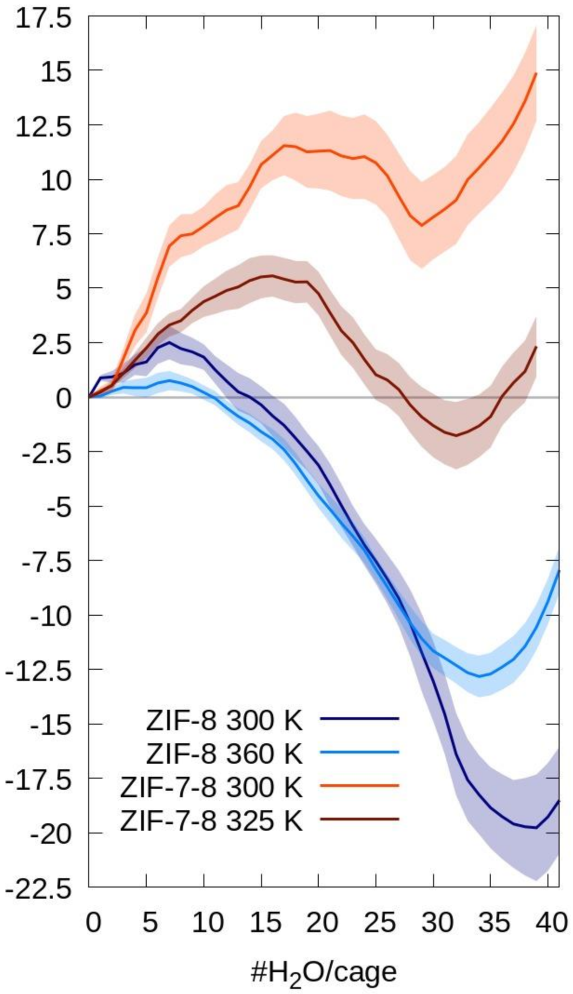

ELECTRO INTRUSION

European Innovation Council
Funded by the European Union

# Mixing linkers




ELECTRO INTRUSION
European Innovation Council
Funded by the European Union

# Conclusions and outlook

- The ordinary fluid phases of water, liquid(-like) and vapor(-like) exist also under extreme confinement, down to 1 nm pore size.
- However, the porous material plays a role beyond the classical physics picture: it is not an inherit confining medium.
- Many questions remain to be addressed, e.g., the relation between hysteresis and confined critical T, how to control int/ext pressure and hysteresis, etc.
- Exploitability for technological applications in energy storage, dissipation, conversion (not discussed, here)…
- …Moreover, low-T hysteresis opens new perspective in sensible thermal energy storage, supercritical solvents for chemistry. Additionally, the existence of (confined) supercritical water and bulk water at the same P/T allows to dream of a all-water fluid/fluid chromatography

ELECTRO INTRUSION
European Innovation Council
Funded by the European Union

# Acknowledgements


S. Merchiori (UNIFE)


A. Le Donne (UNIFE)


M. Tortora (Sapienza)


M. Alvelli (UNIFE)


Y. Grosu (CIC)


L. Johnson (CIC)


L. Bortolomé (CIC)


E. Amayuelas (CIC)


Pawel Zajdel (USK)


PRACE

European Innovation Council

Funded by the European Union

# Happy birthday Ursula!