The Curious Case of… Water in Nanobottles

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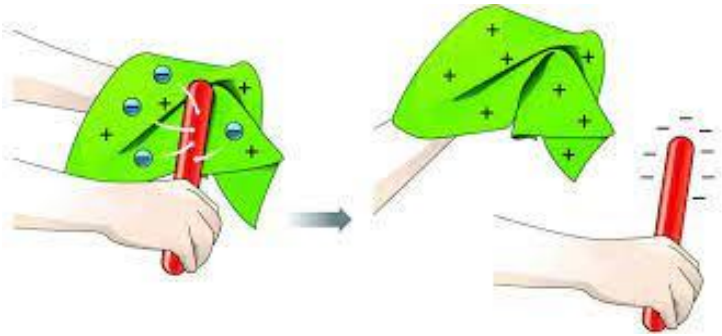
ELECTRO INTRUSION

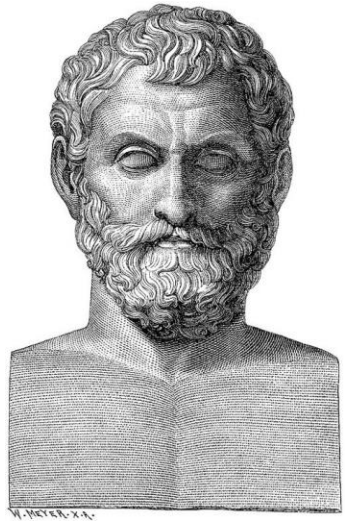
Back to the future: Molecular simulation 40 years after Varenna

European Innovation Council

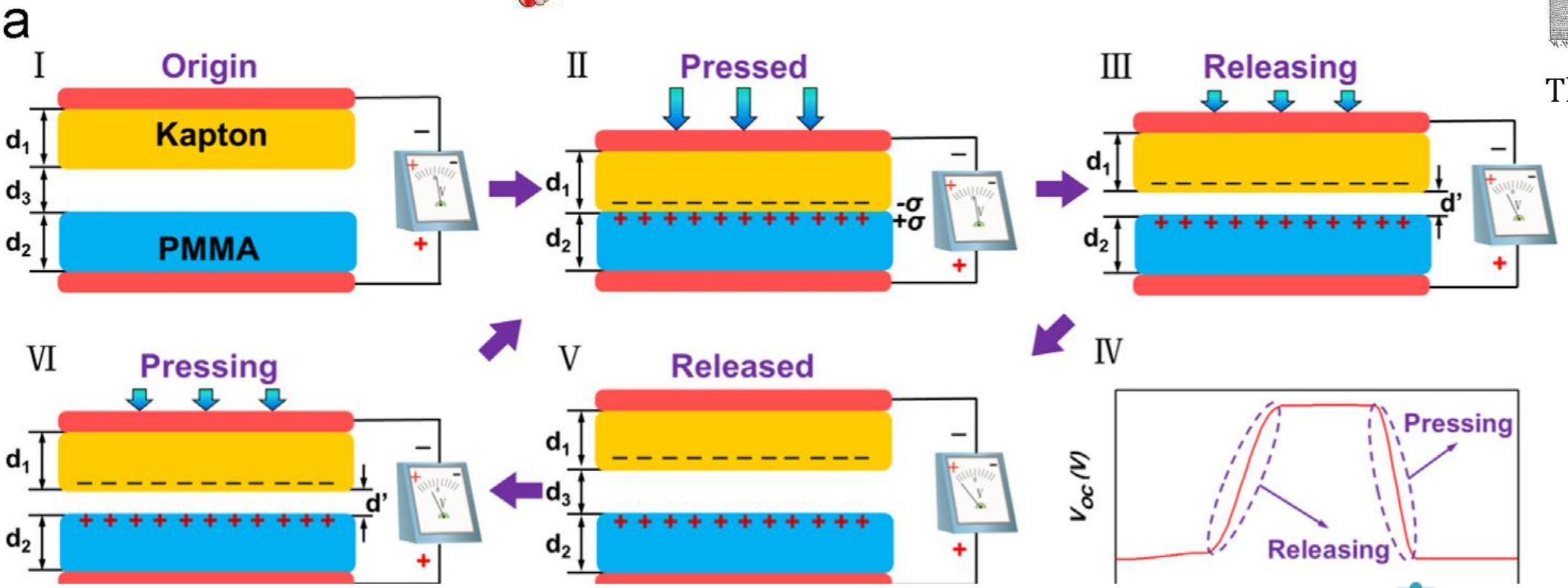
Funded by the European Union

Recovering dissipated mechanical energy





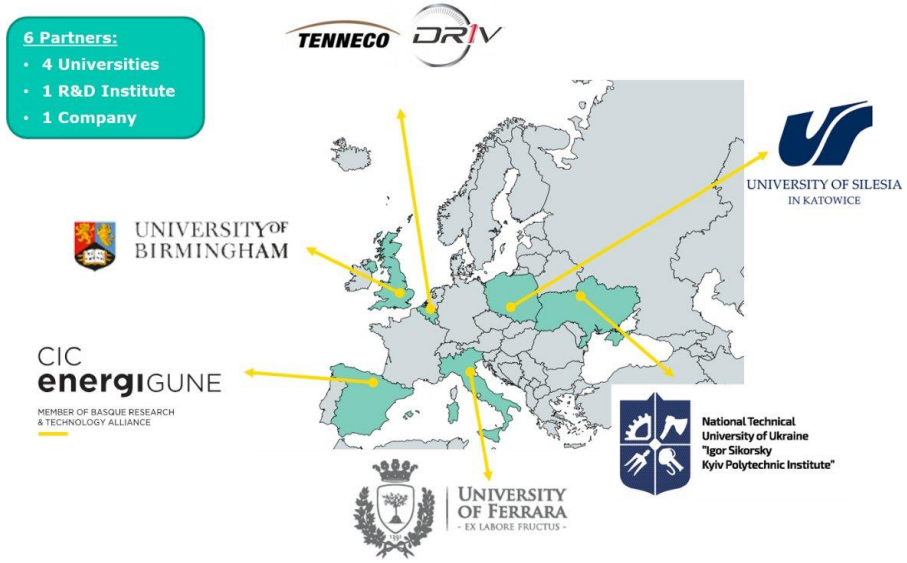
Thales of Miletus



G. Zhu et al, Nano Energy 14, 126, 2015

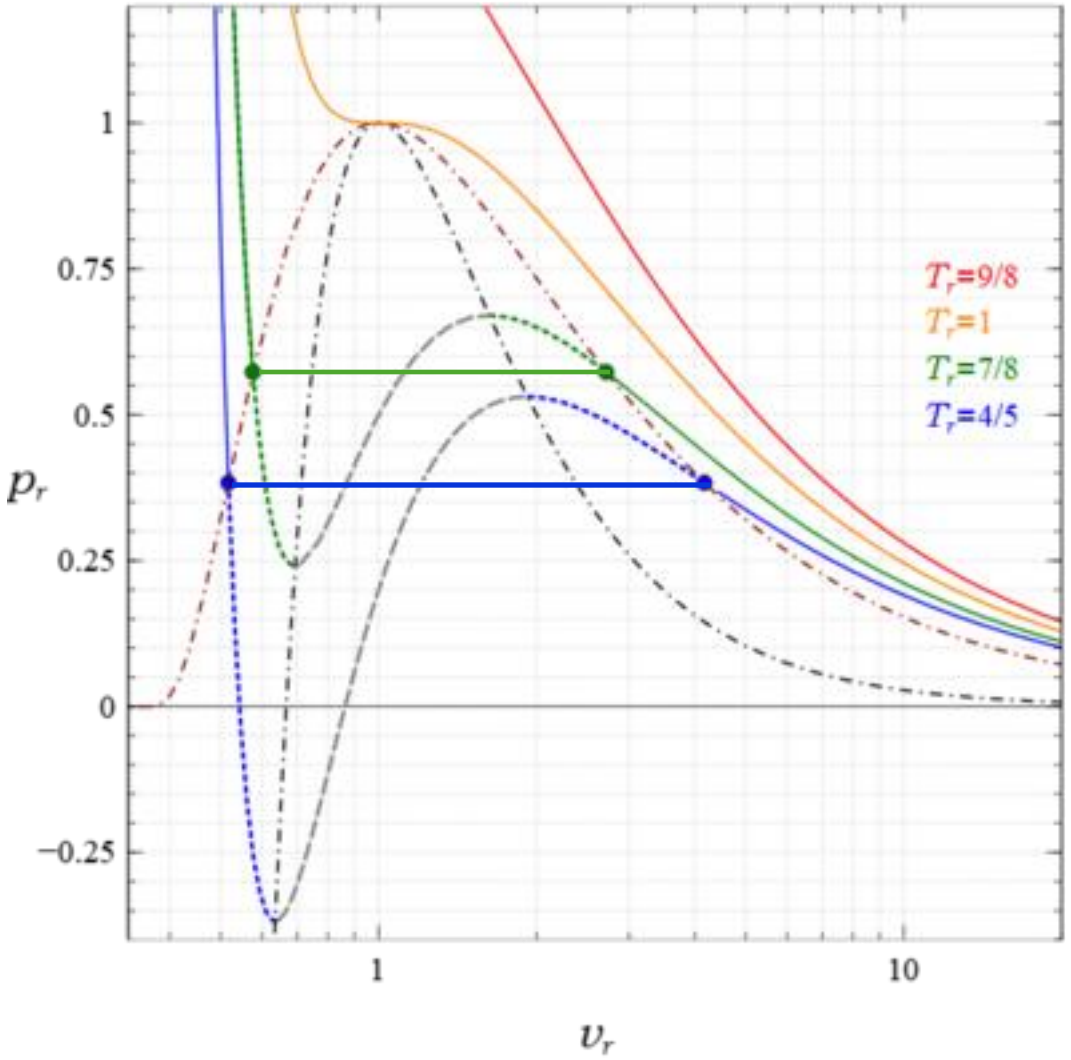
ELECTRO INTRUSION

Confined liquid to develop new energy scavenging technology

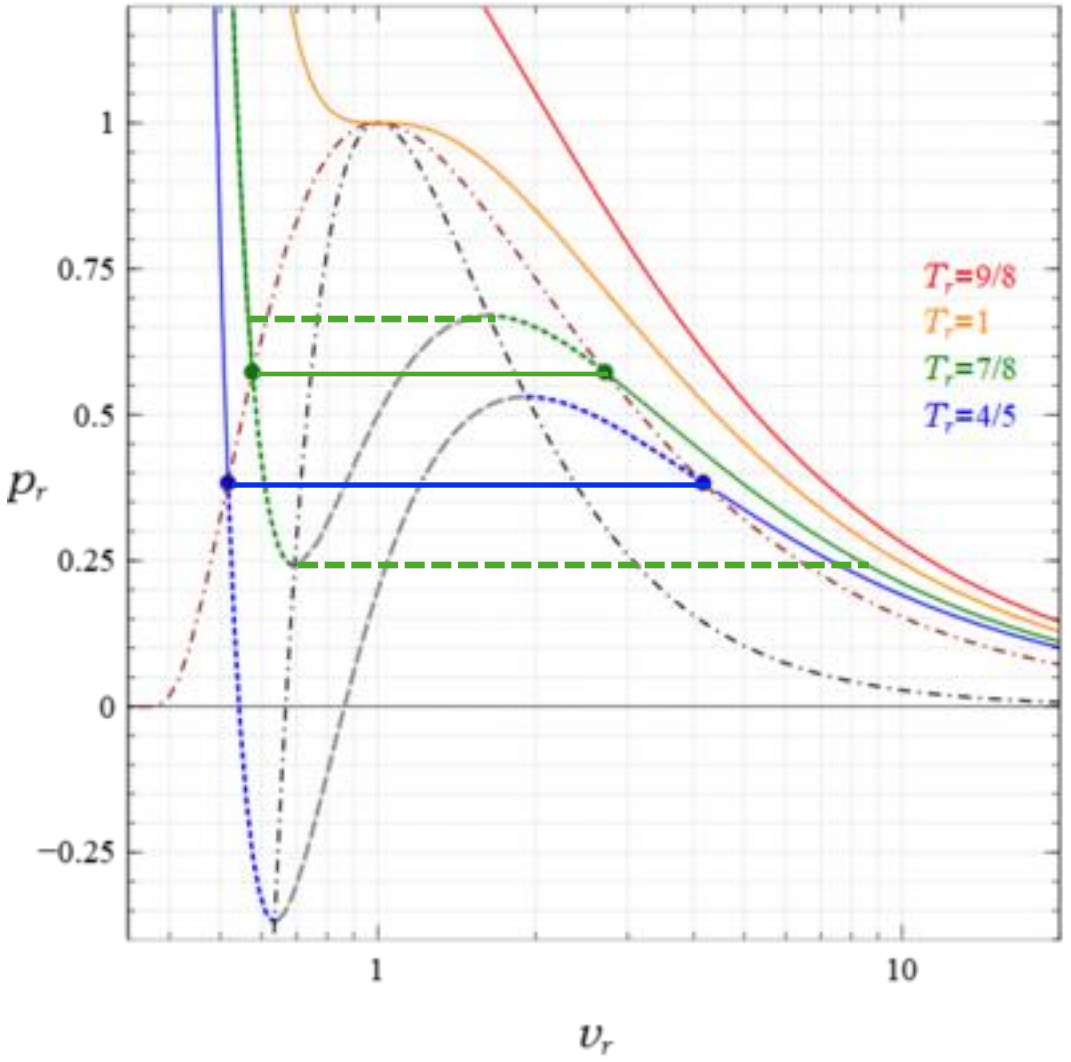


ELECTRO INTRUSION

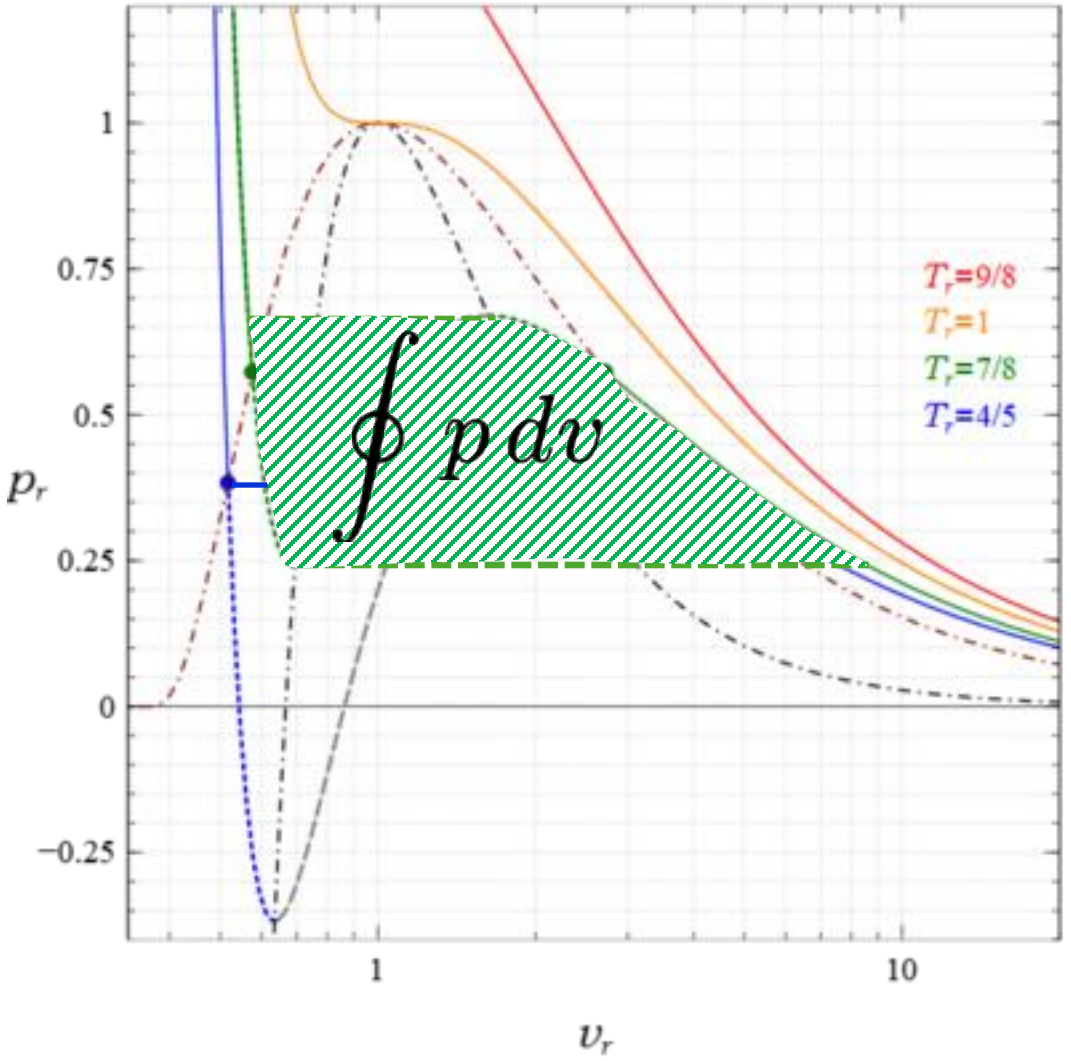
Liquid/vapor Phase transition



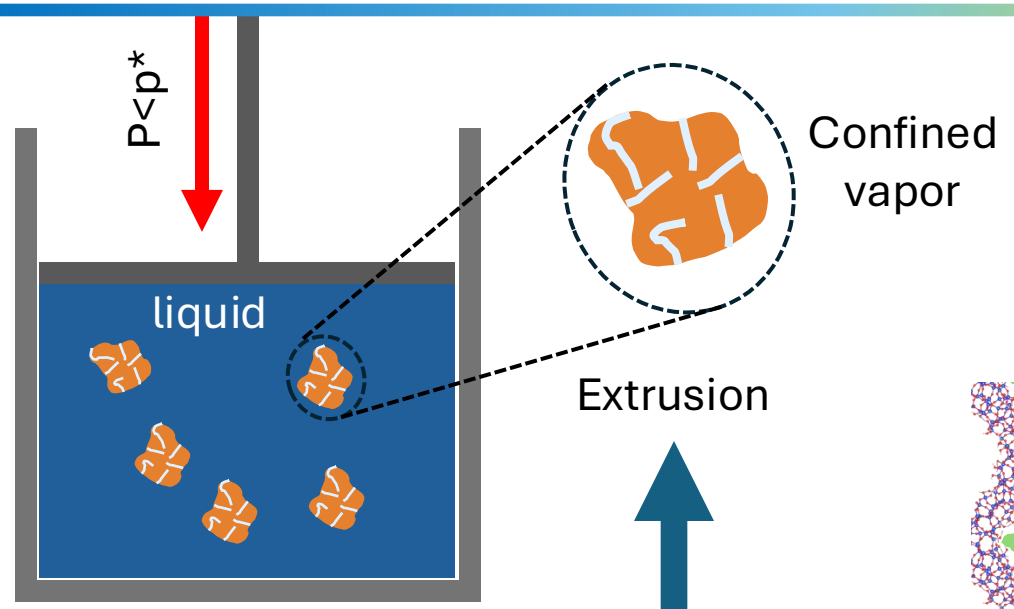
Liquid/vapor Phase transition



Liquid/vapor Phase transition



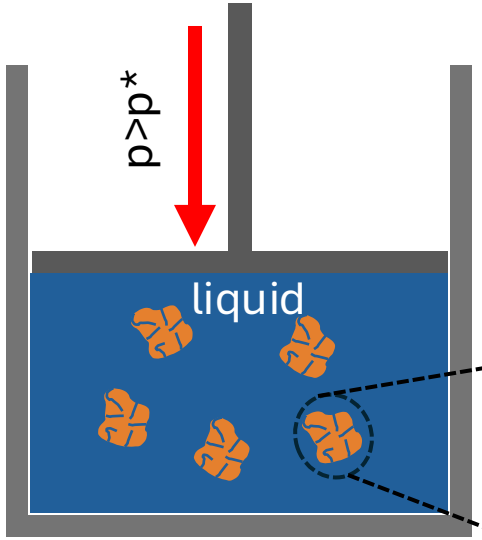
Confined liquid-vapor phase transition: capillary condensation/evaporation



Confined vapor

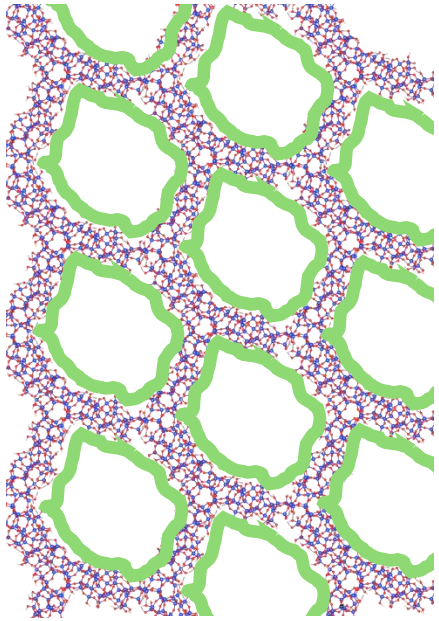
Extrusion

Intrusion

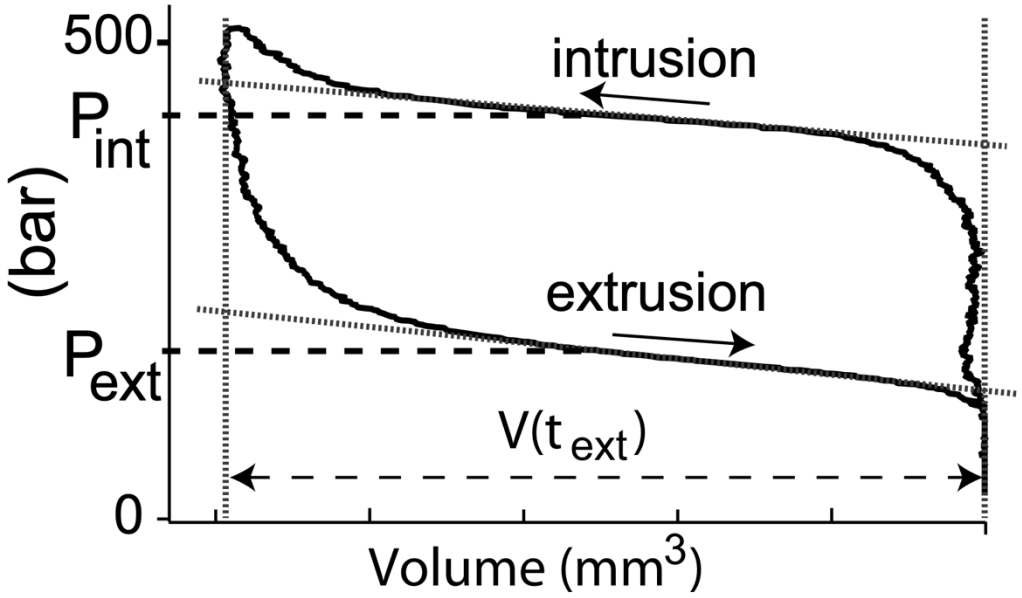


Confined liquid

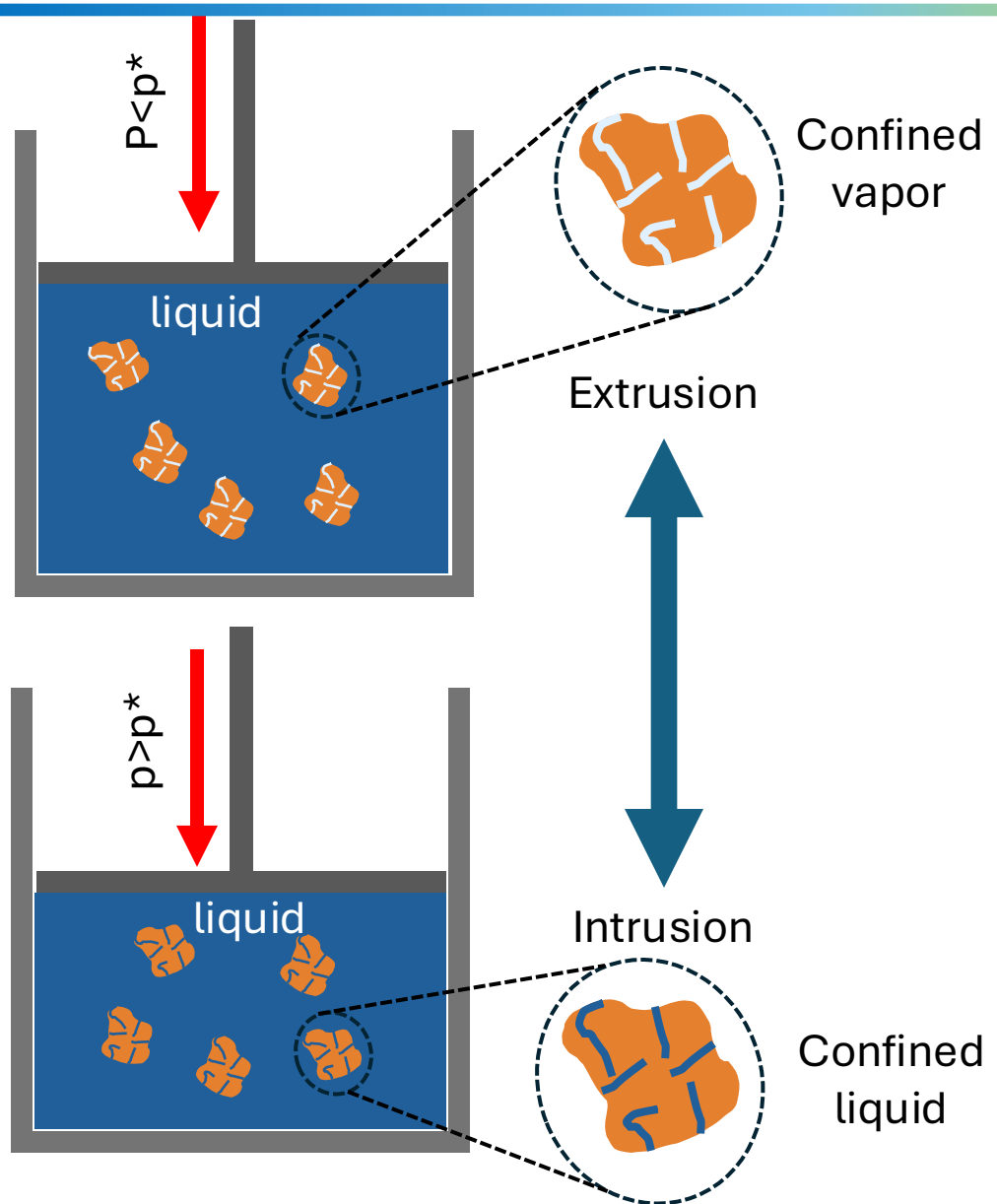
Grafted MCM-41 hydrophobic



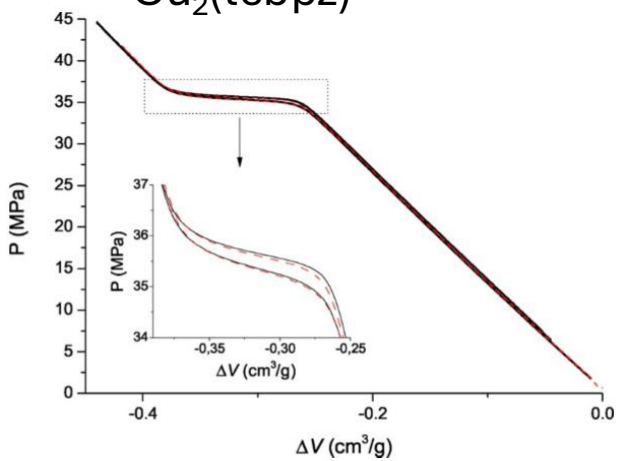
Guillemot et al, PNAS 109,19557 (2012)

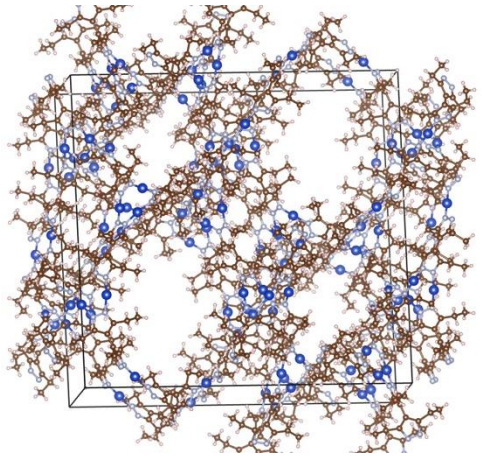


Confined liquid-vapor phase transition: capillary condensation/evaporation

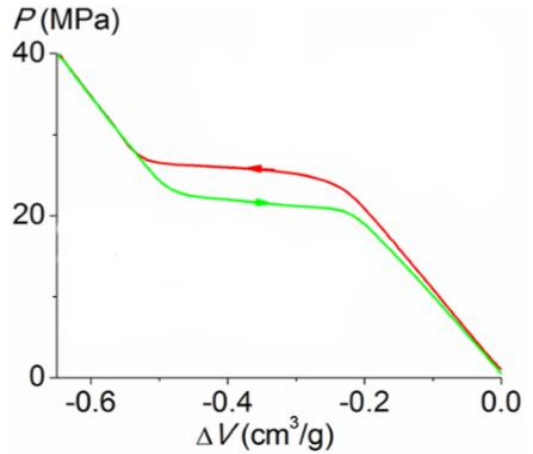


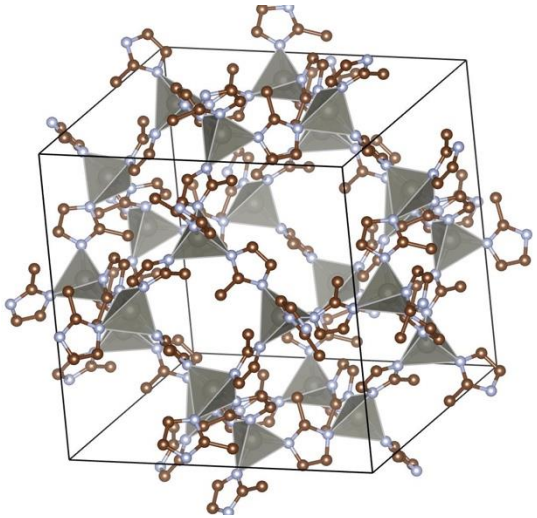
$Cu_2(tebpz)$



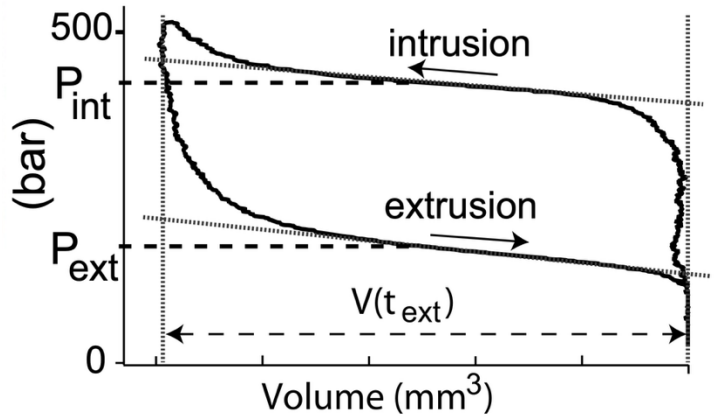


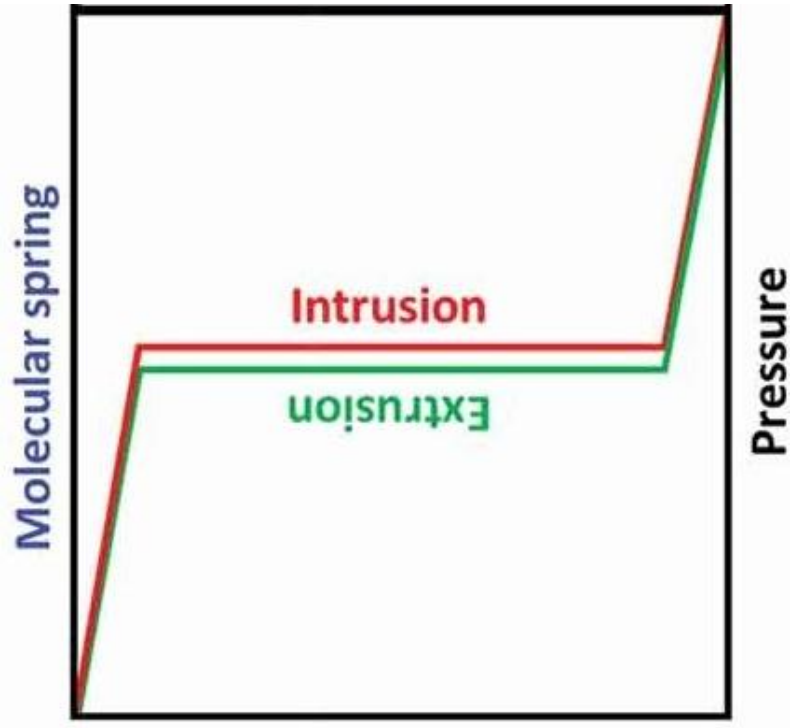
ZIF-8



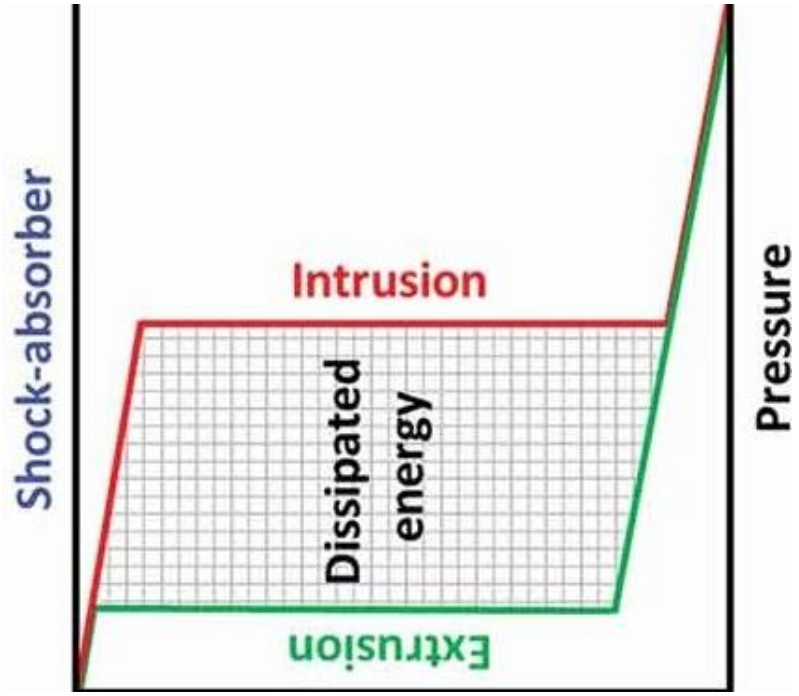


Intrusion/extrusion taxonomy

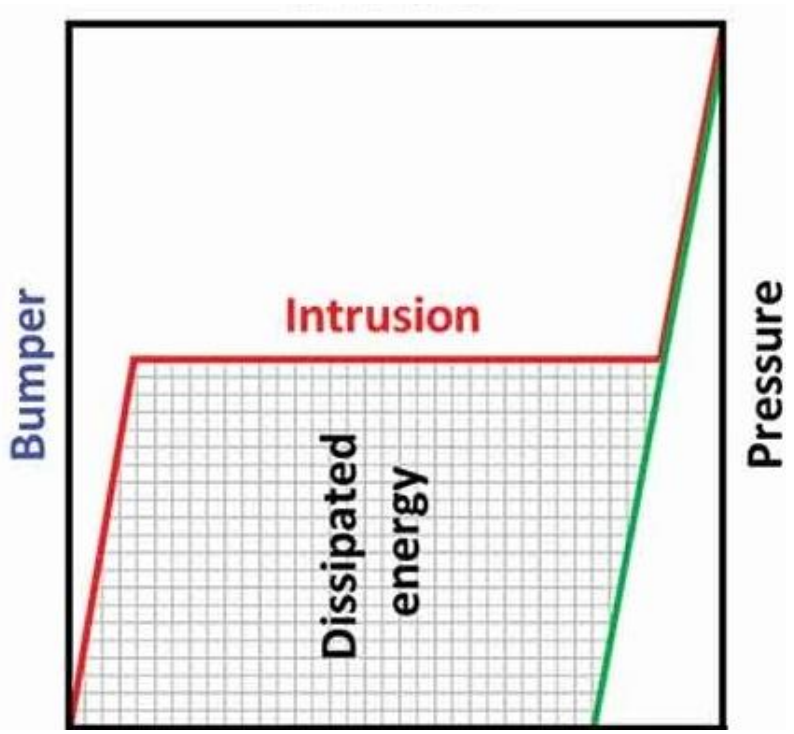




ΔV

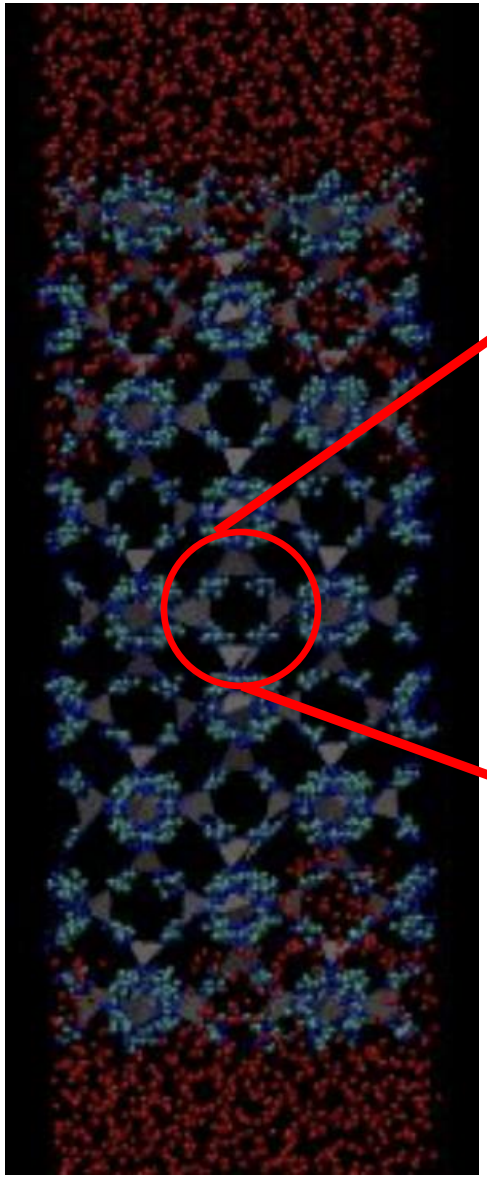


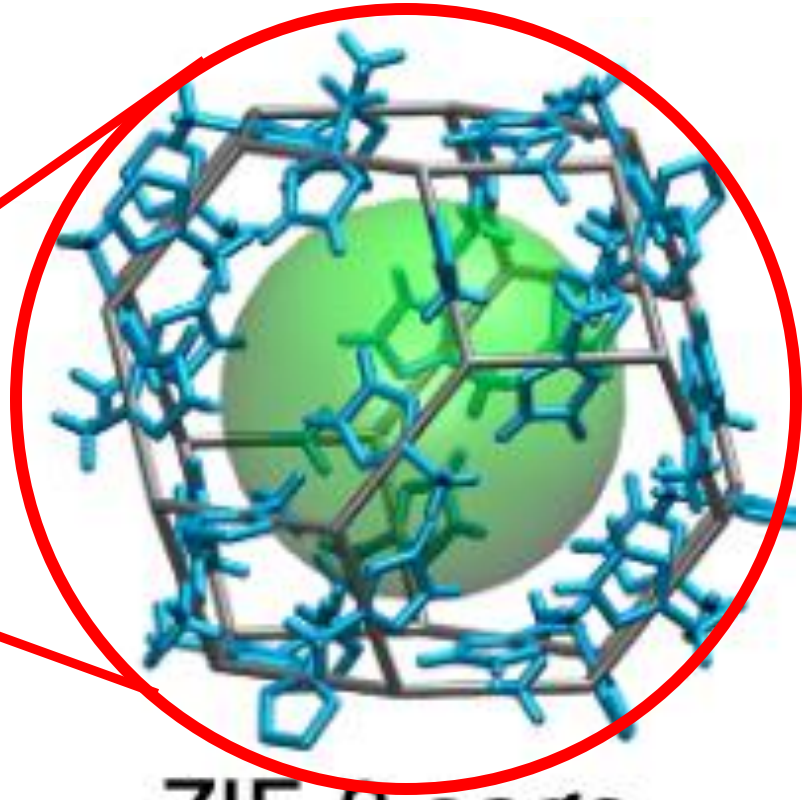
ΔV



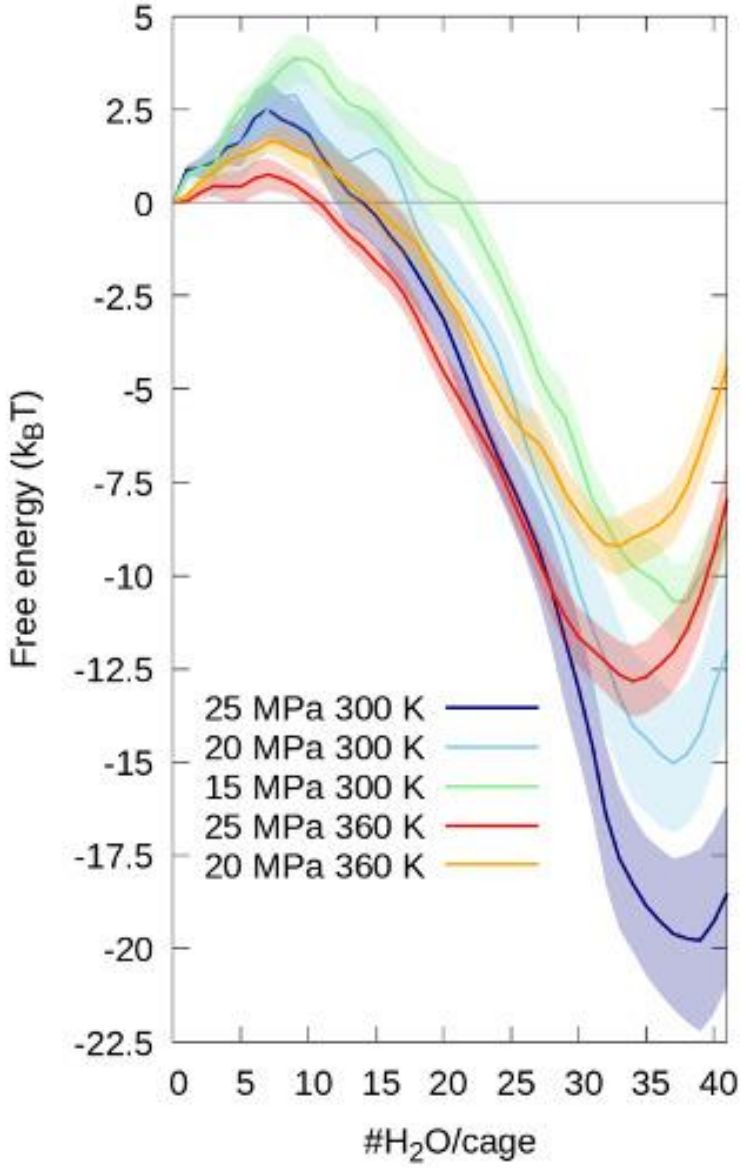
ΔV

Water under extreme confinement





ZIF-8 cage



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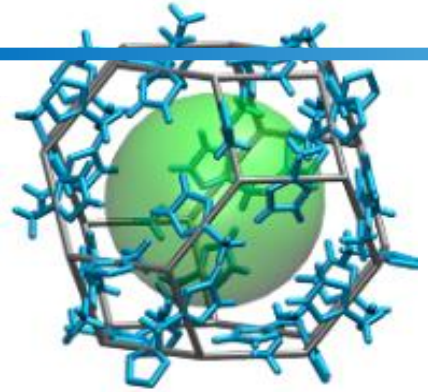

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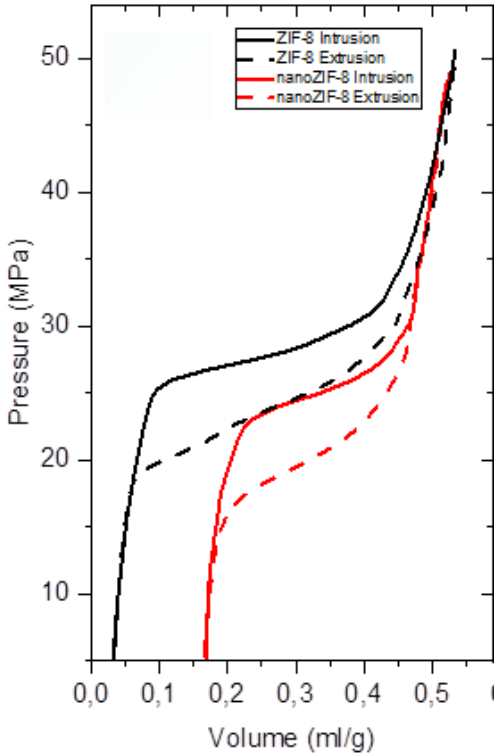

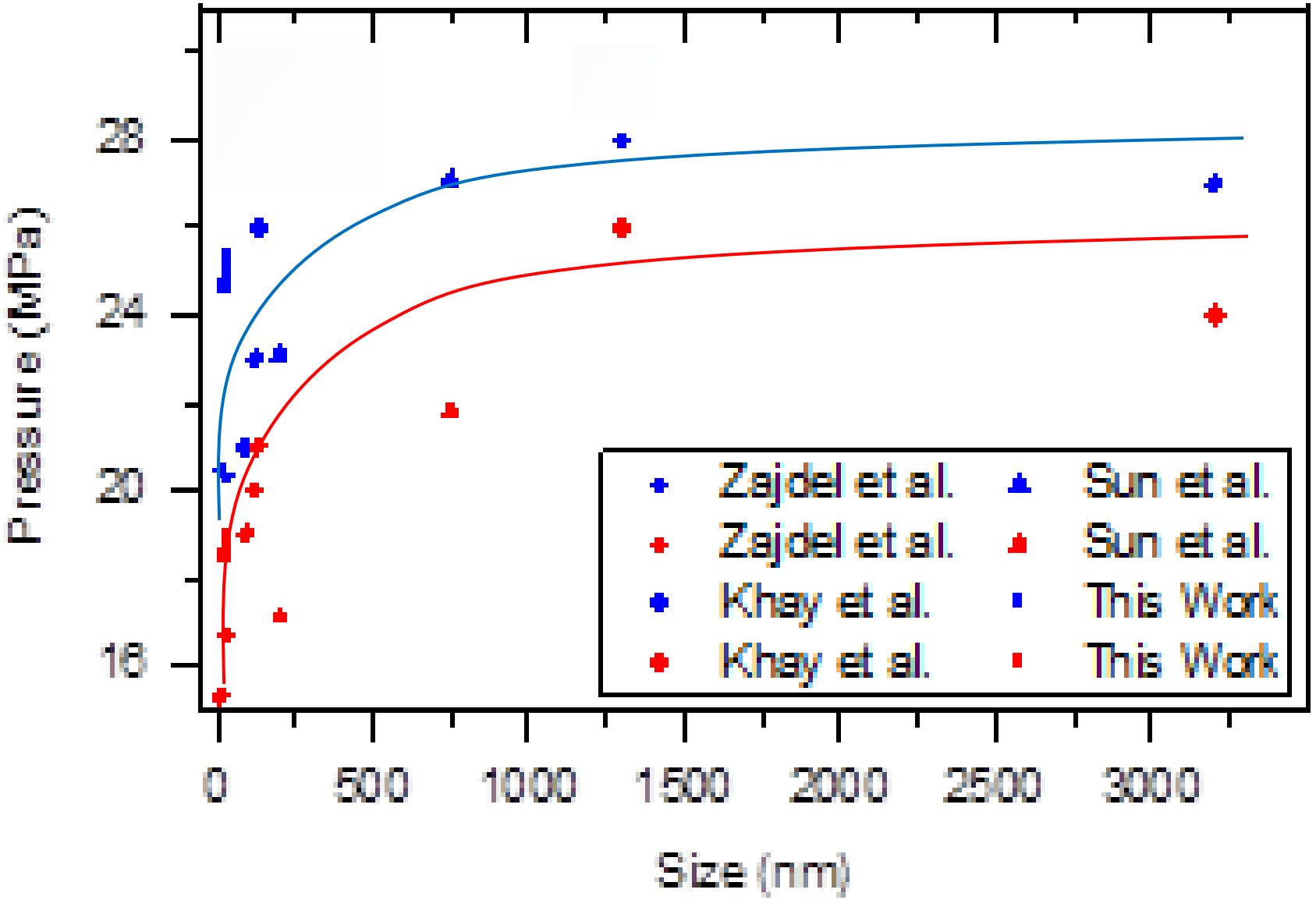

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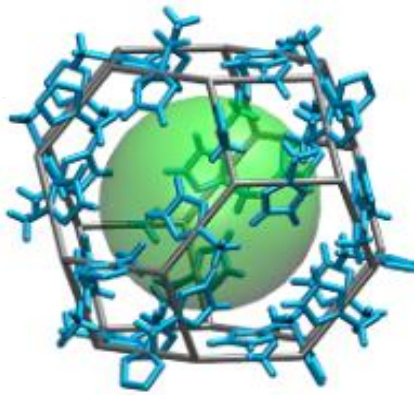

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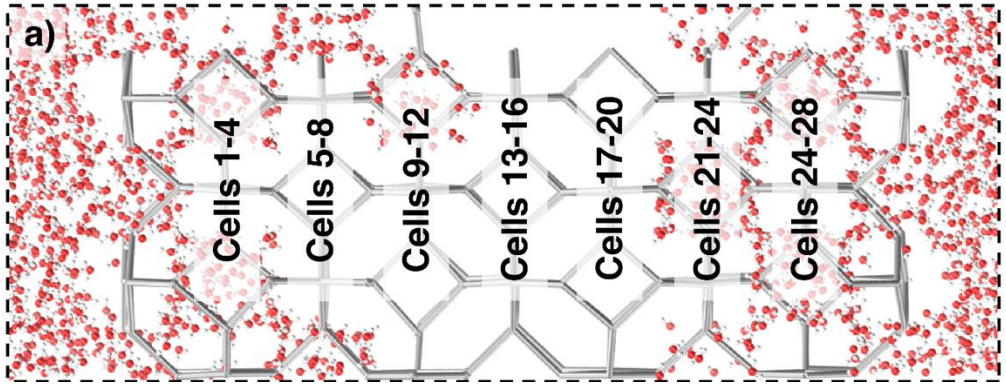

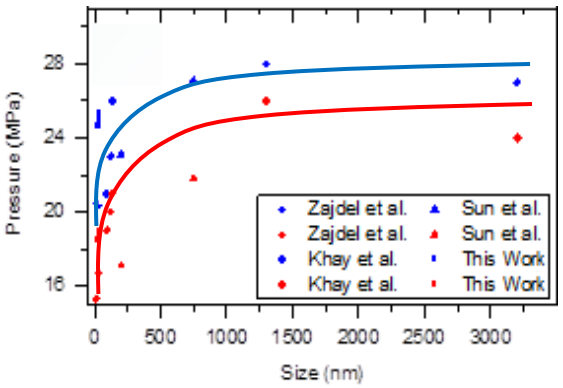

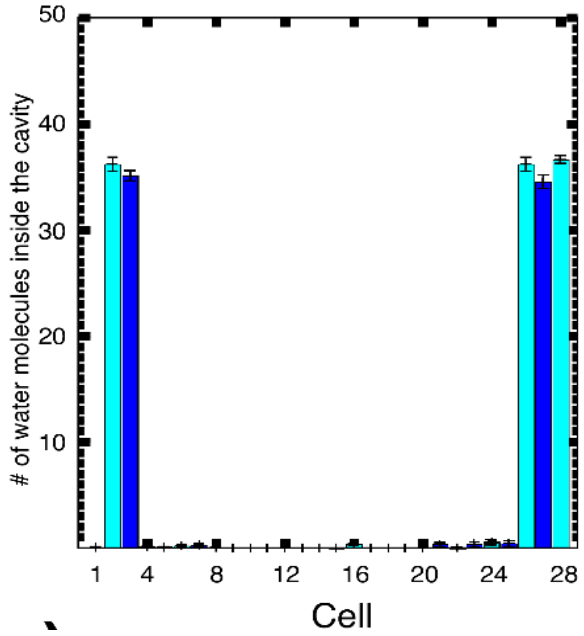

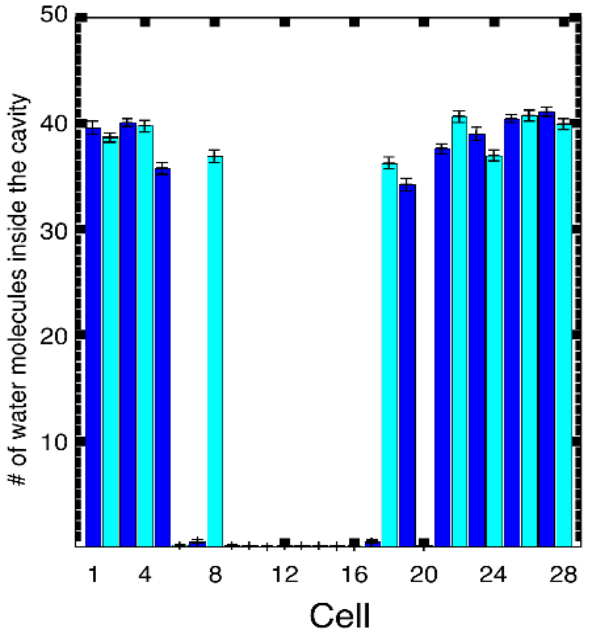

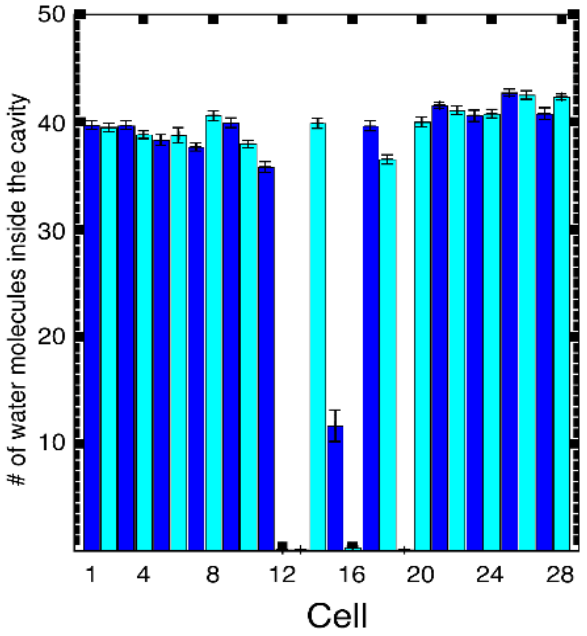

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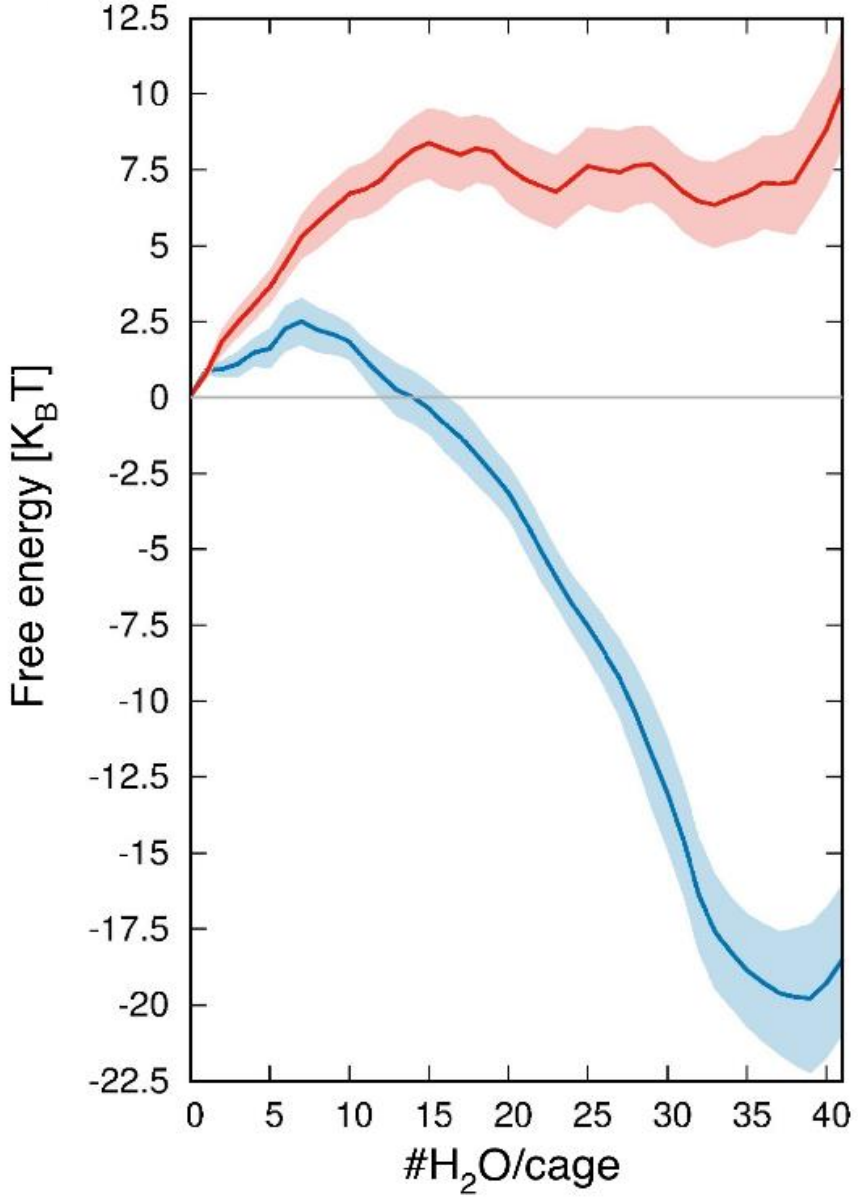
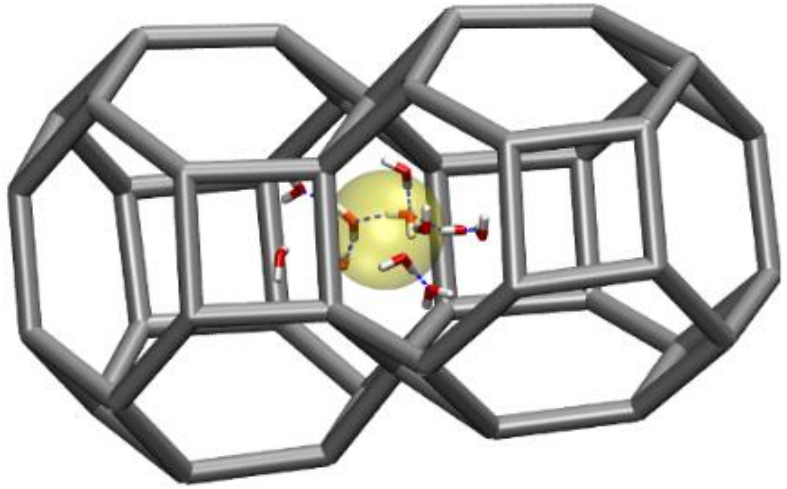
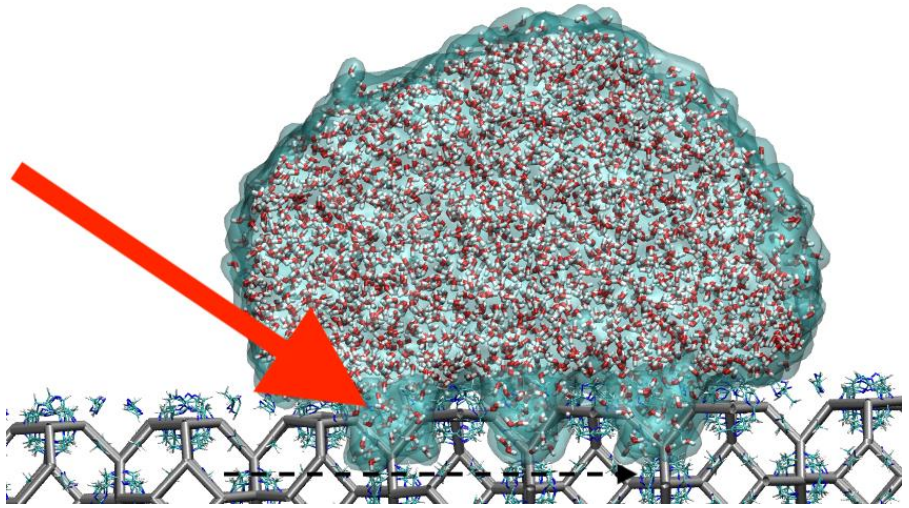




6MR	θ_i
Std ZIF-8	101°
Clogged pores	114°

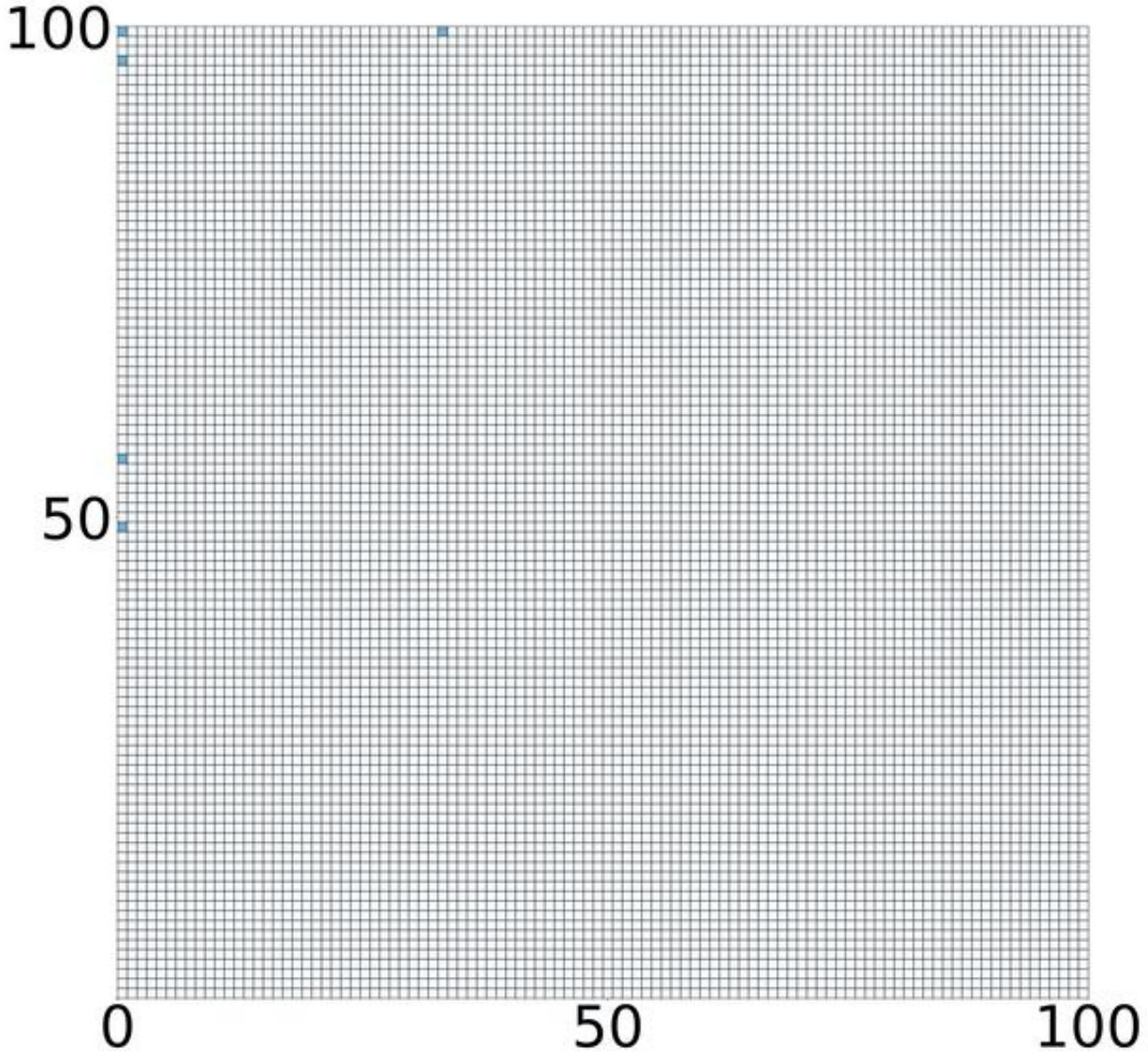


Anti-Wenzel behavior

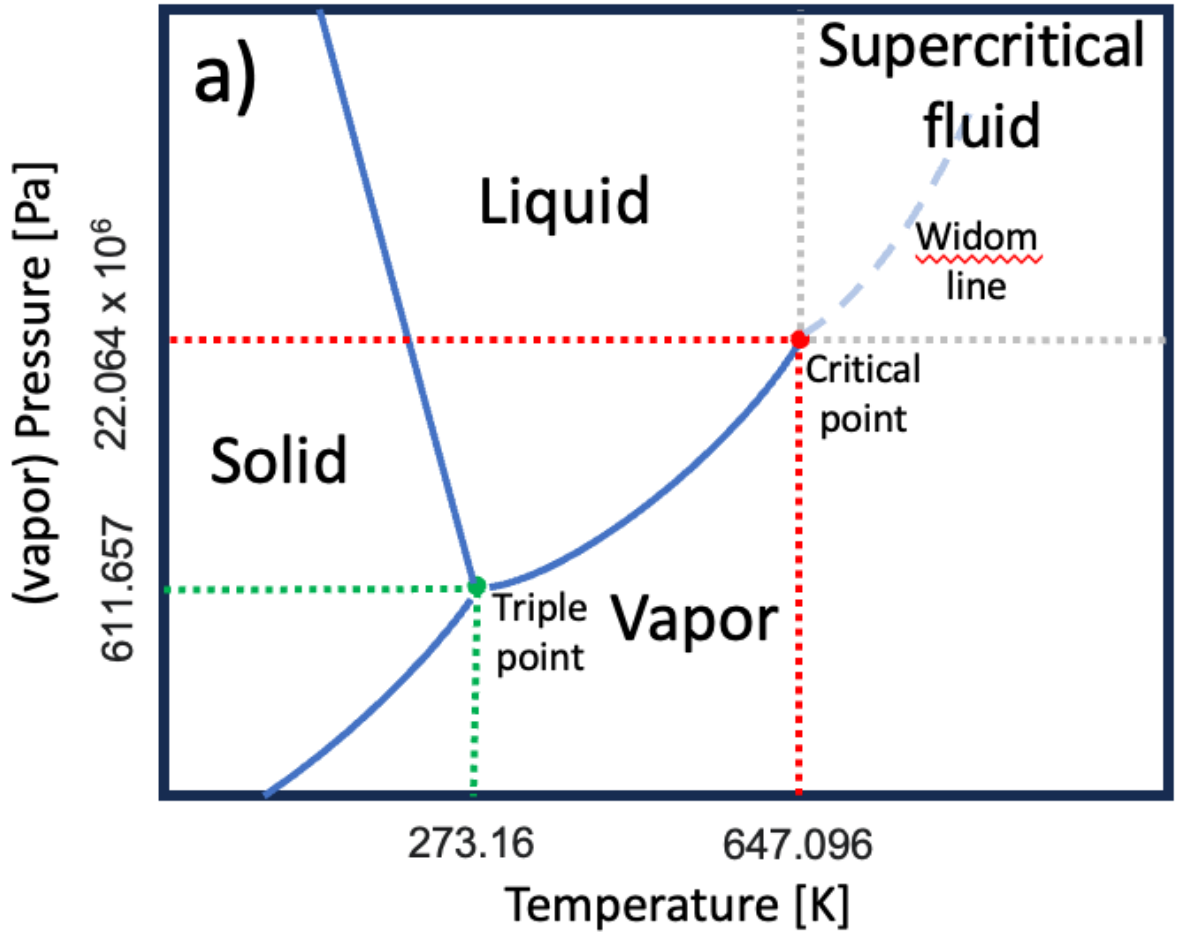
Bushuev et al., Nano Lett. 2022, 22, 2164; Bushuev et al ACS Appl. Mater. Interfaces 2022, 14, 30067; Paulo et al, Comm. Phys. 6, 21 2023

Stochastic model of the crystallite size effect

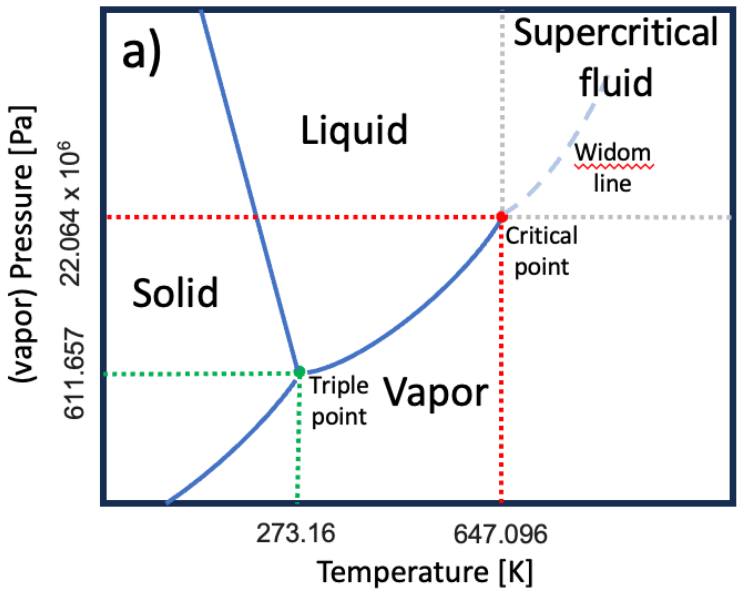
Parameters from atomistic simulations

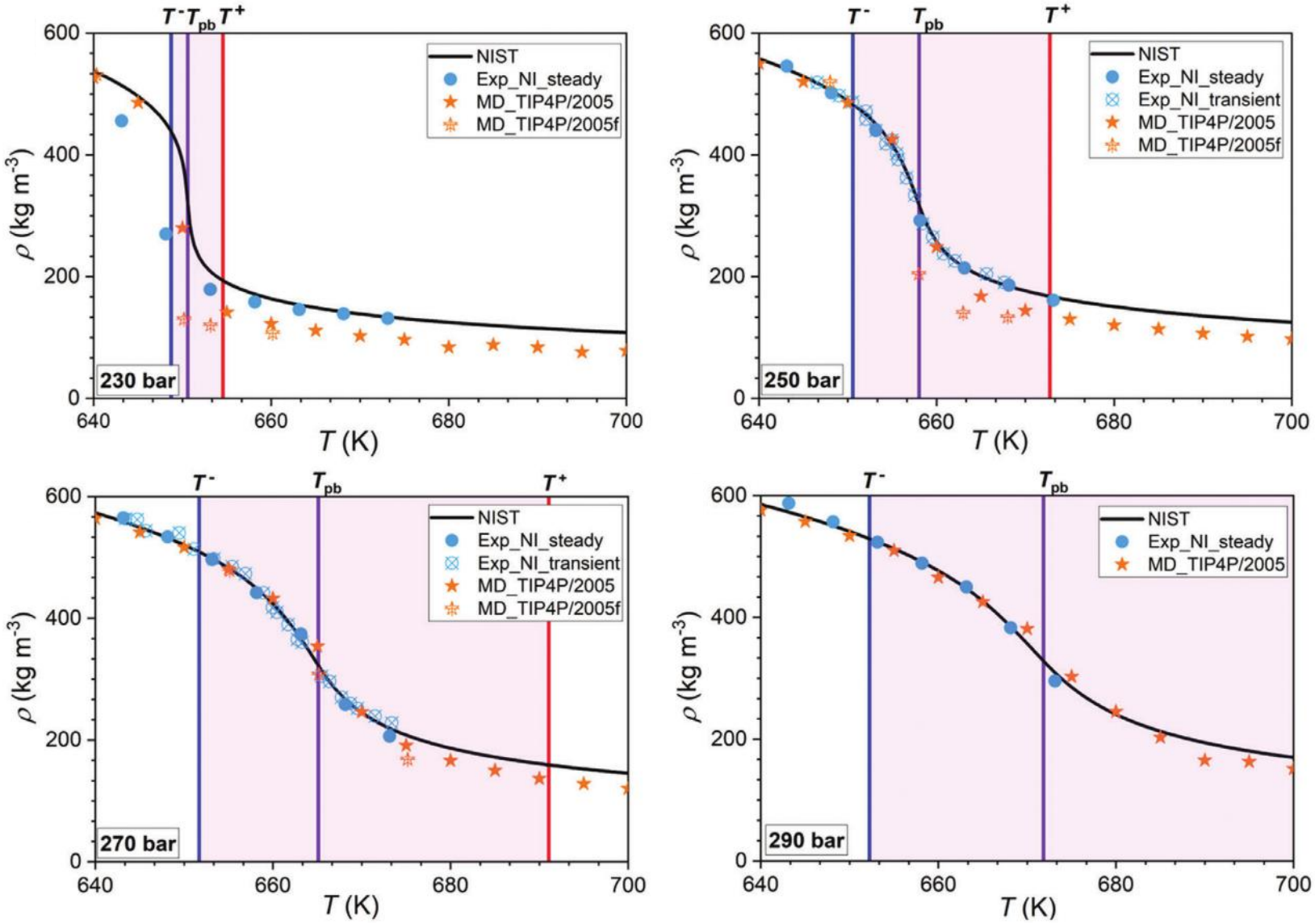


Criticality point (only for your eyes, Giovanni!)



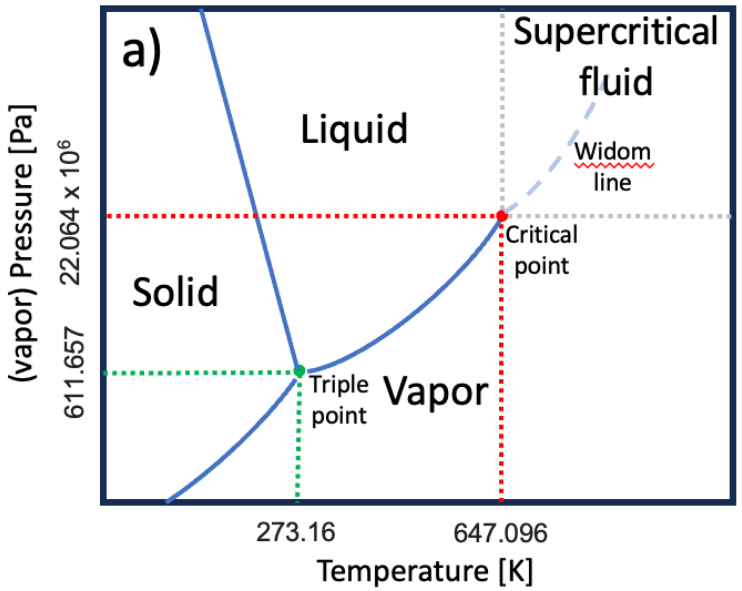
Supercritical water and its kink/boundary lines

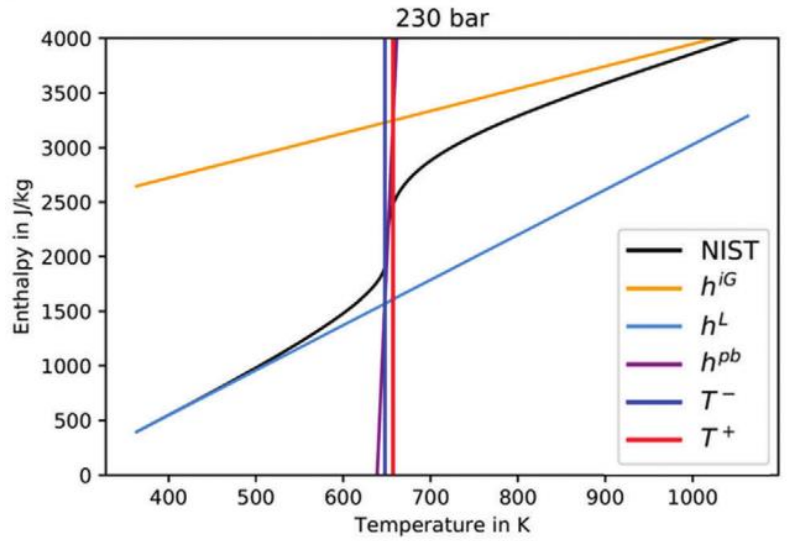


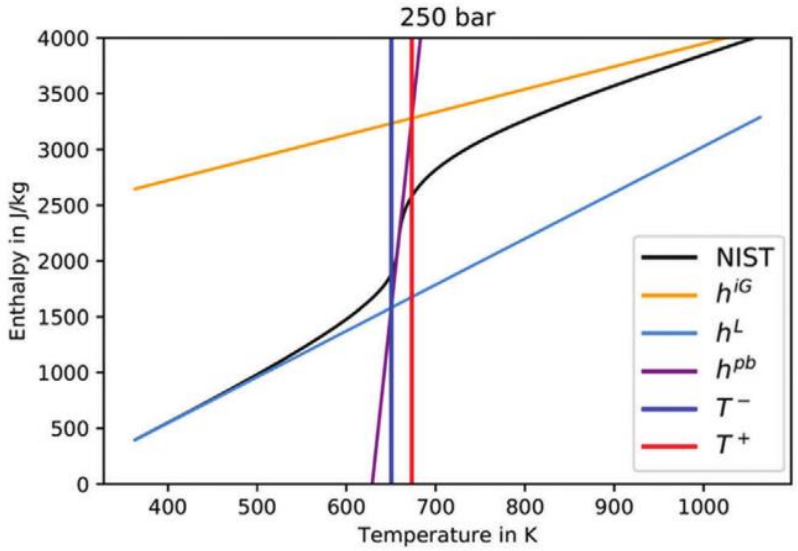


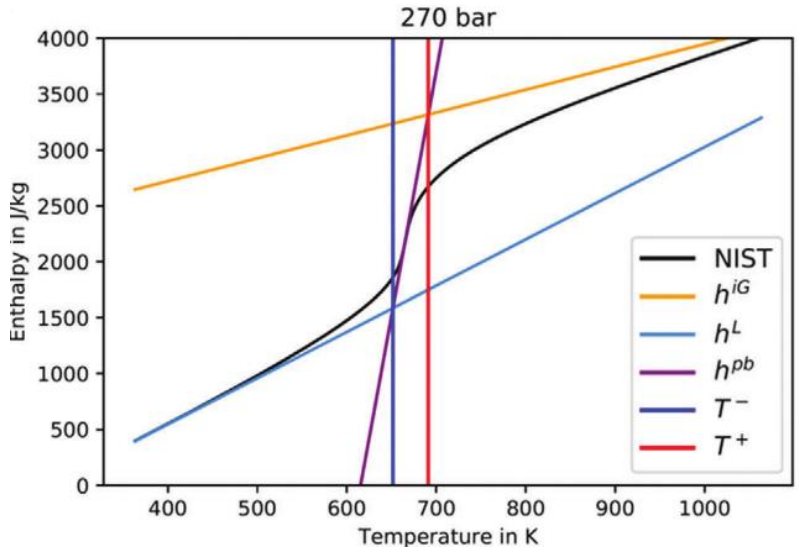
Adv. Sci. 2021, 8, 2002312

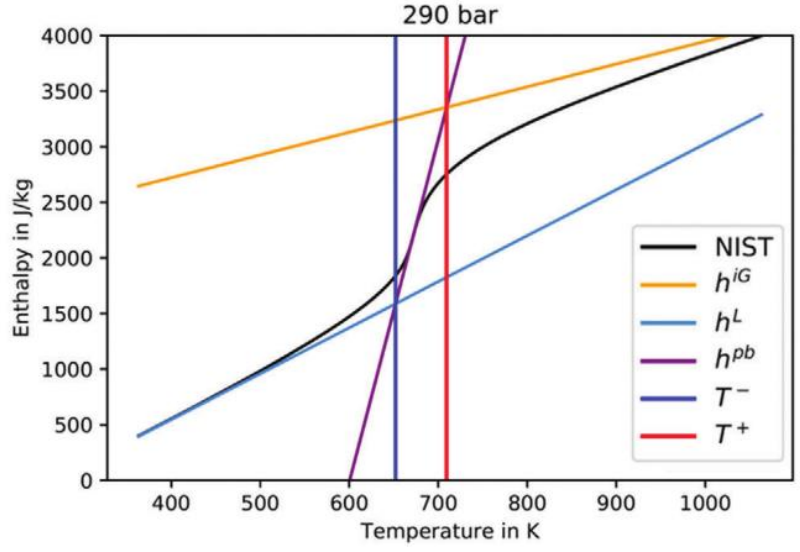
Supercritical water and its kink/boundary lines





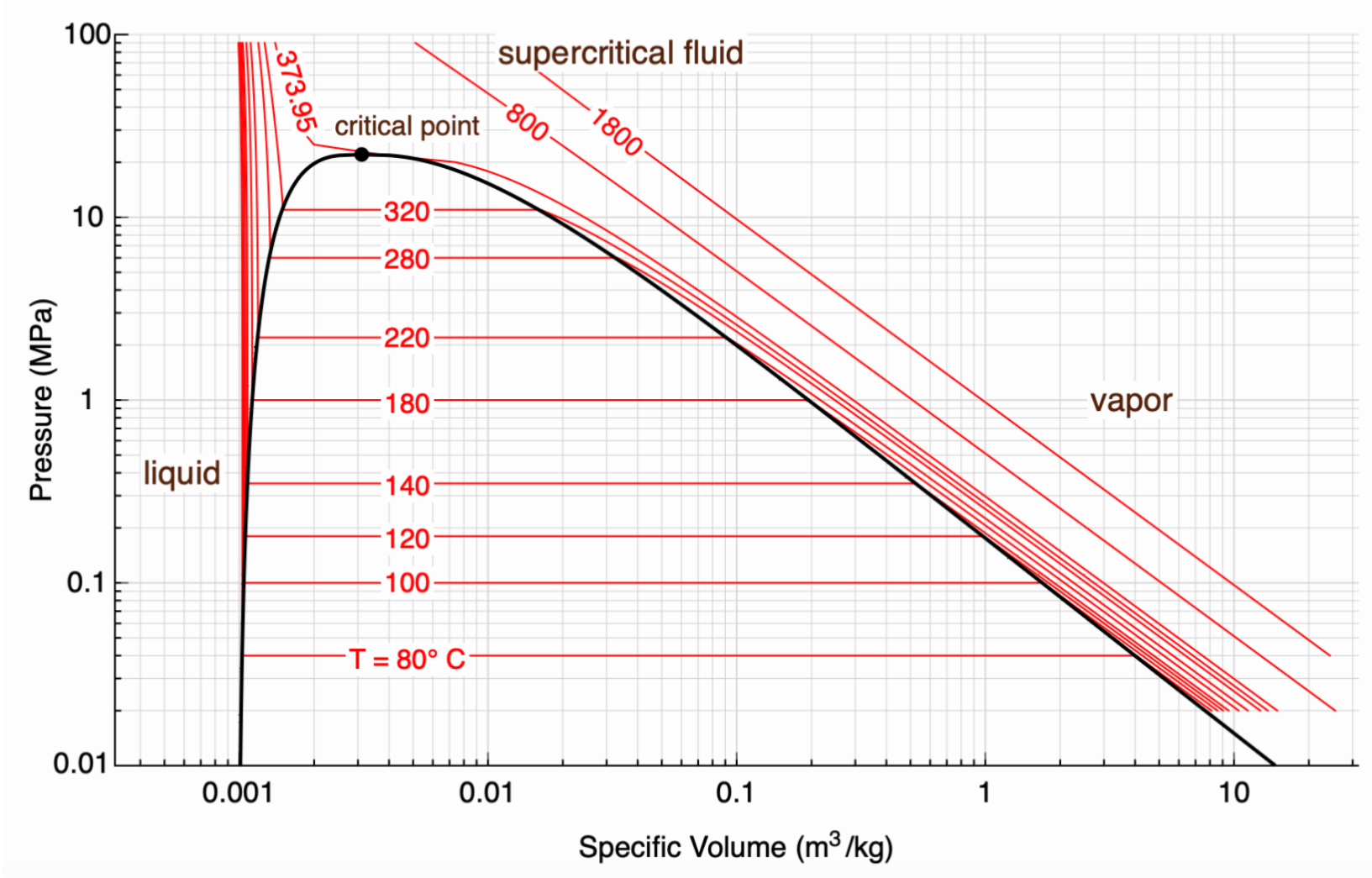


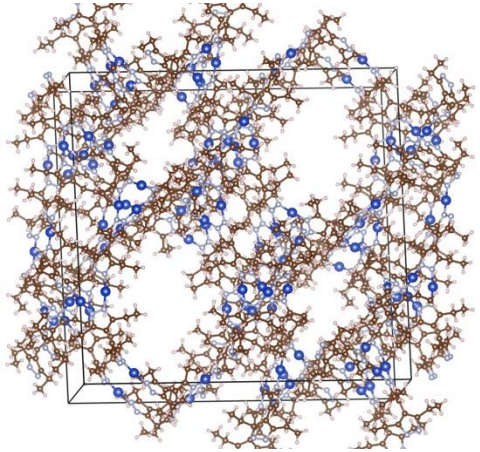




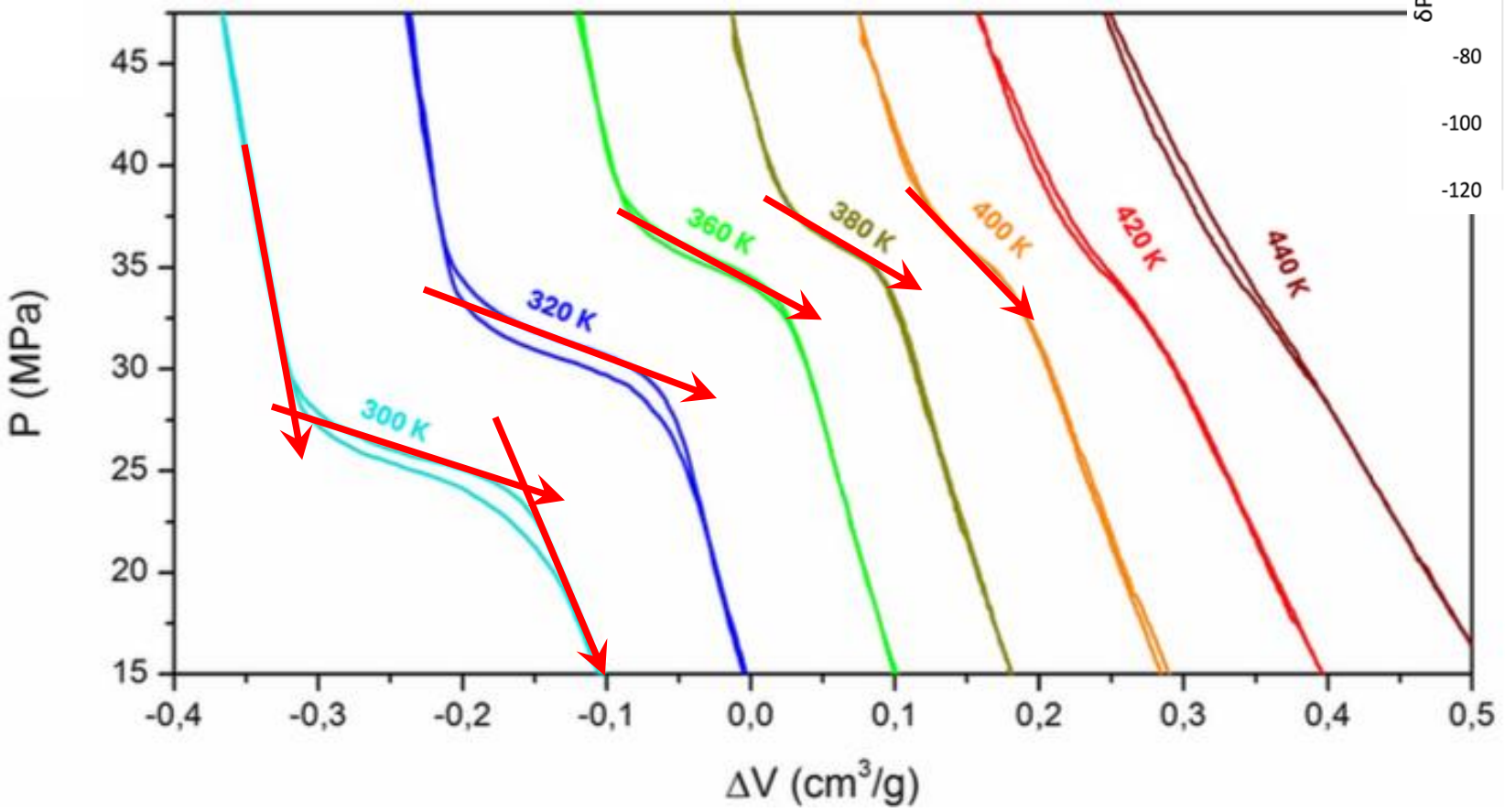
Adv. Sci. 2021, 8, 2002312

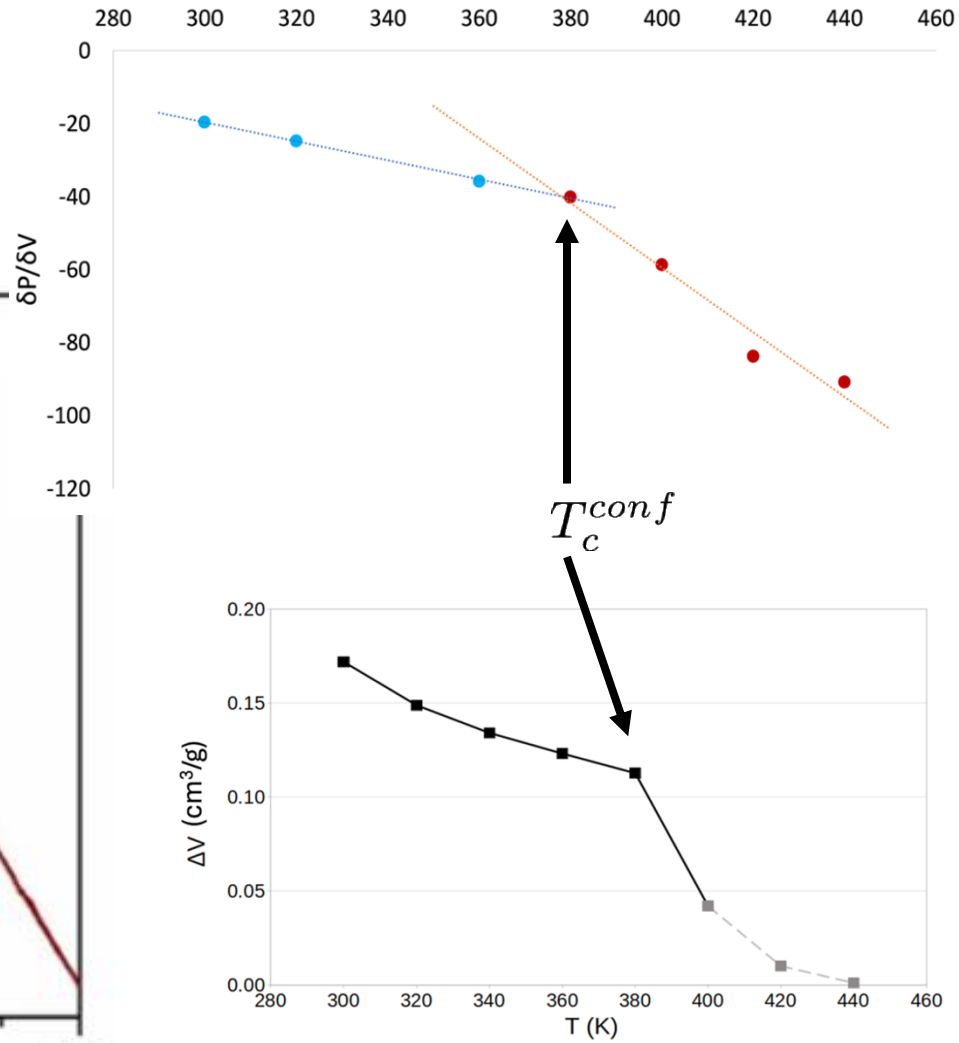
Phase diagram of bulk water…including criticality





Phase diagram of confined water

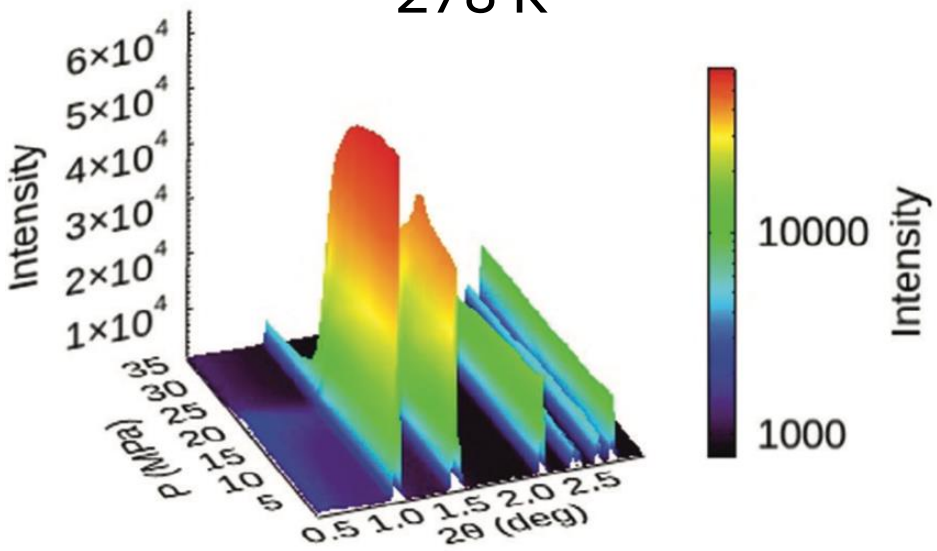




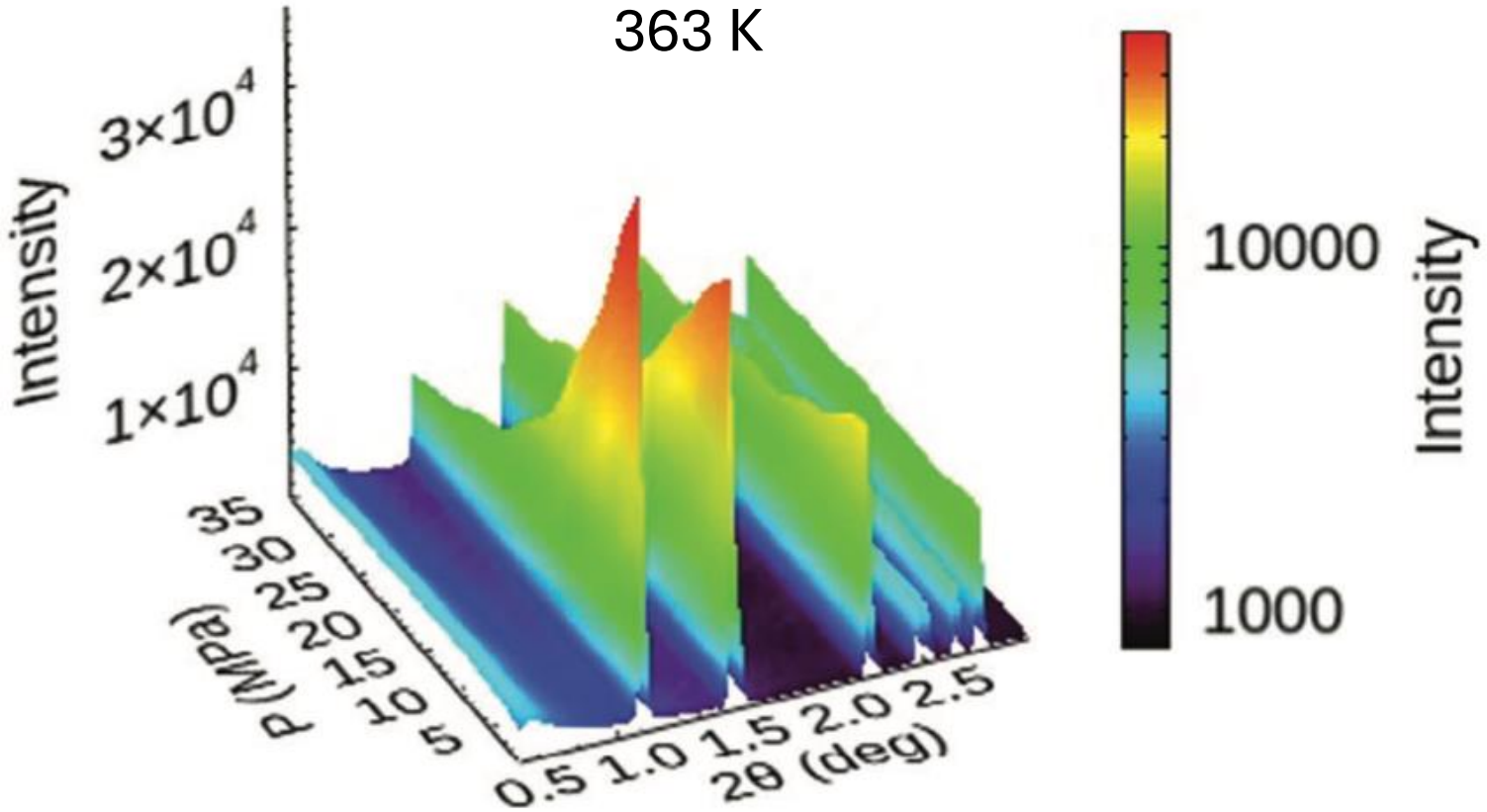
J. Am. Chem. Soc. 146, 13236, 2024; Small 2402173, 2024

High vapor pressure

278 K

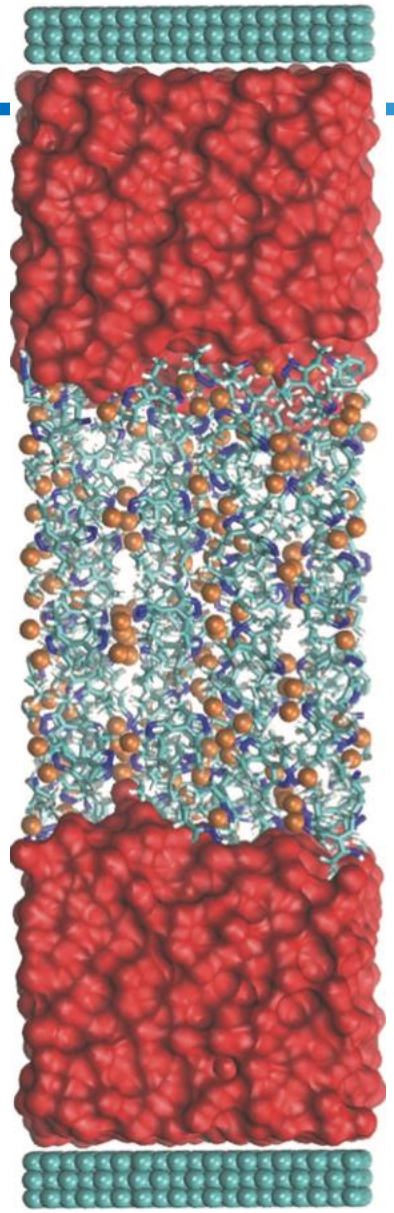


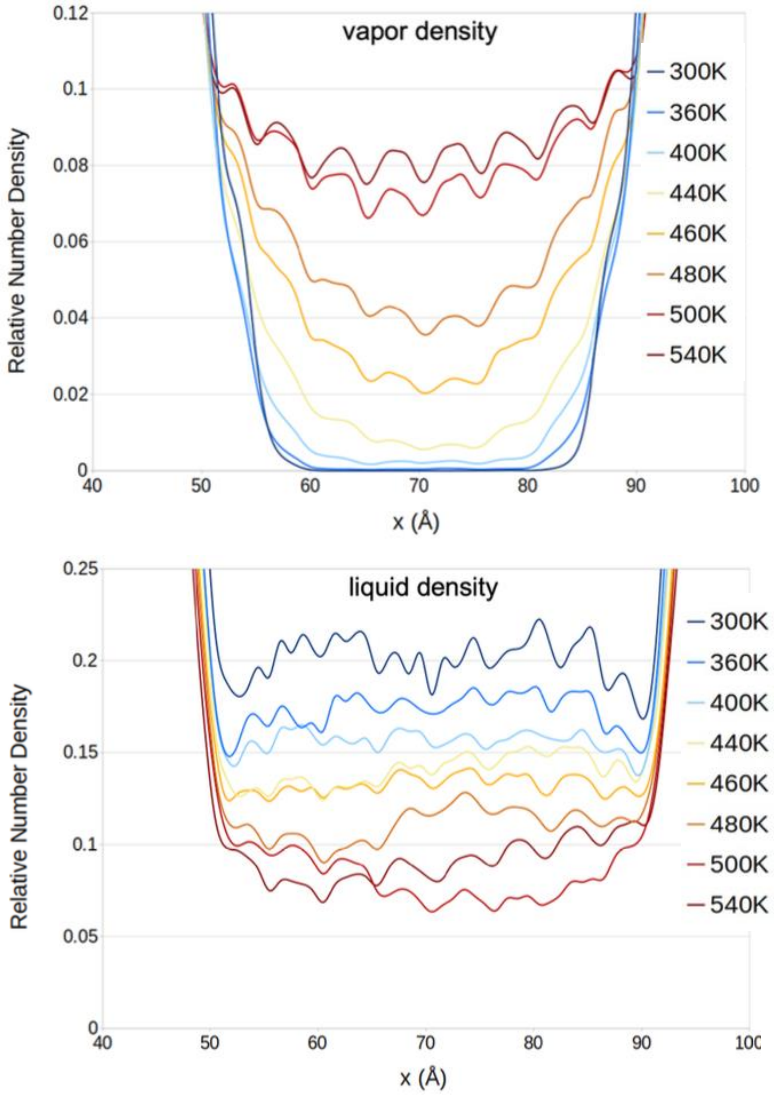
363 K

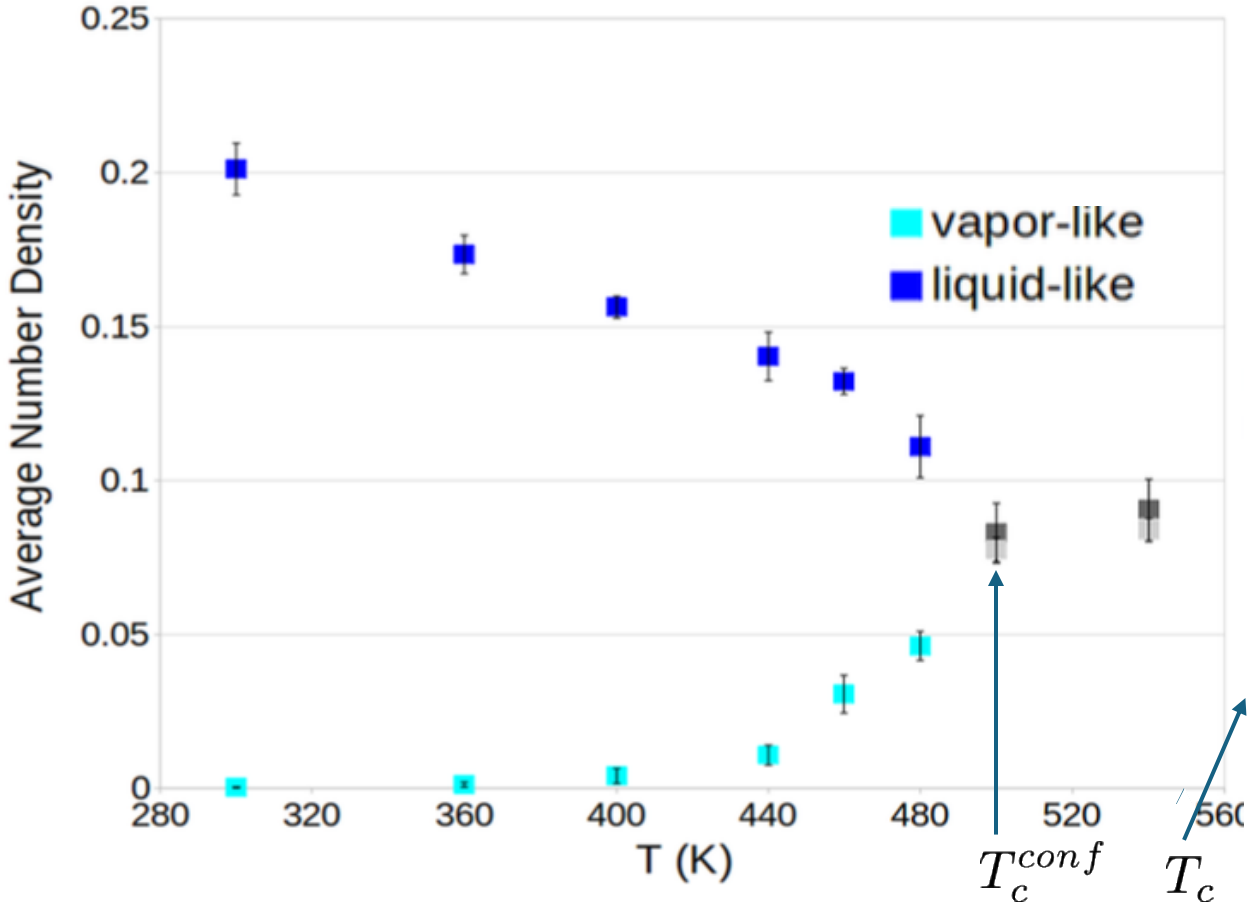


J. Am. Chem. Soc. 146 (2024) 13236,; Small (2024) 2402173

Mild, confined supercritical water

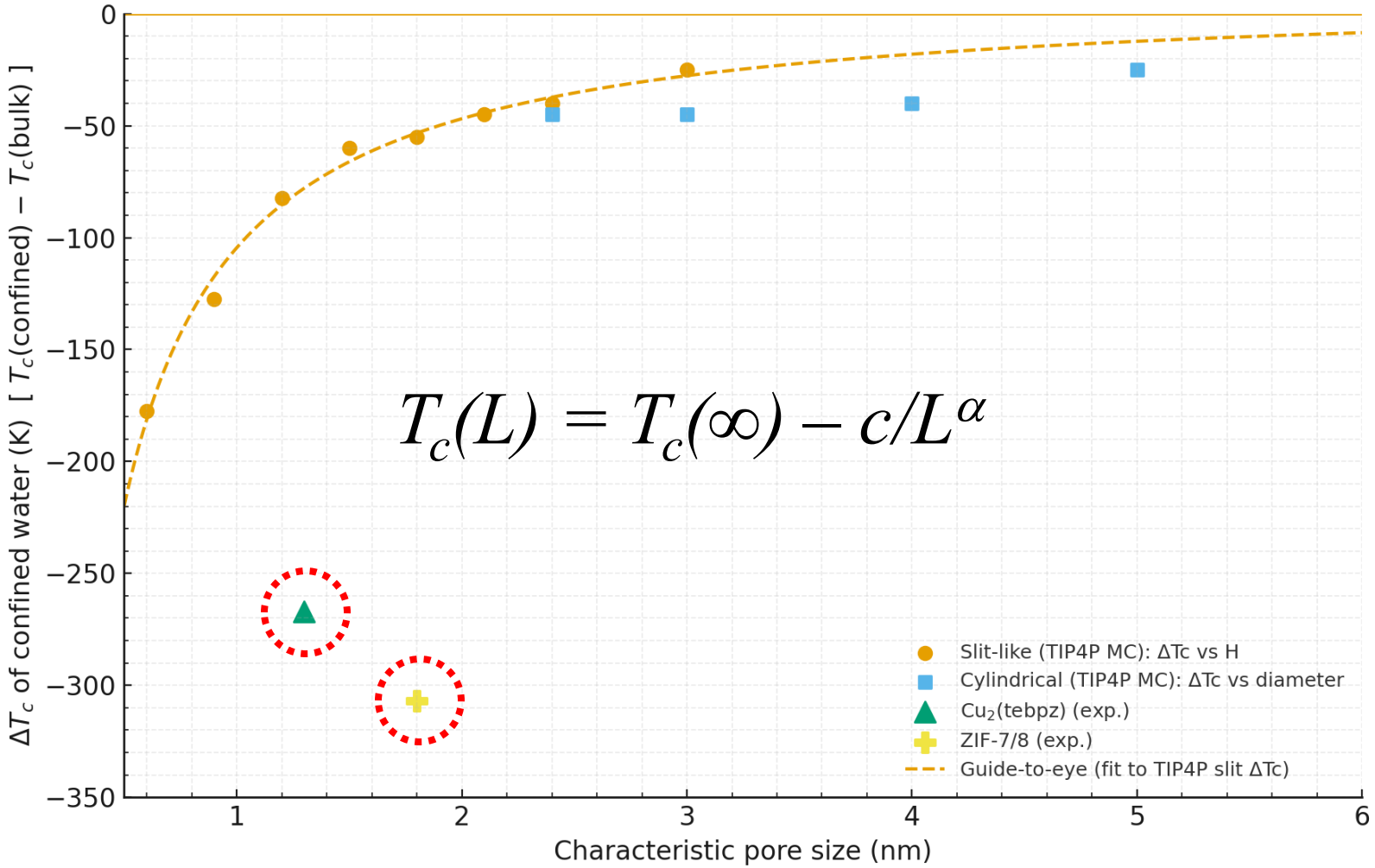






J. Am. Chem. Soc. 146, 13236, 2024; Small 2402173, 2024

Effect of confinement on T_c

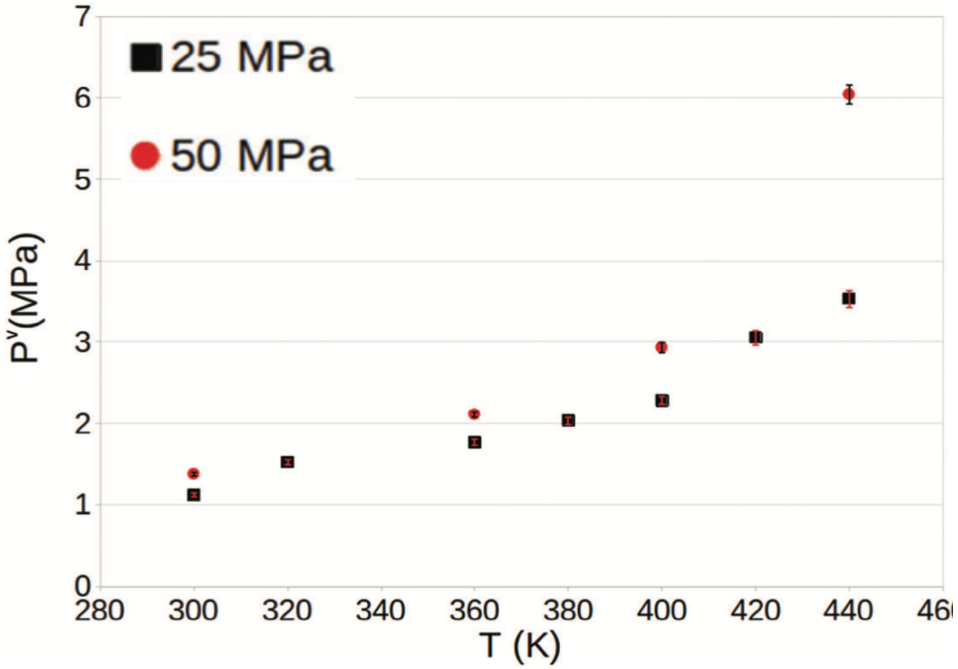


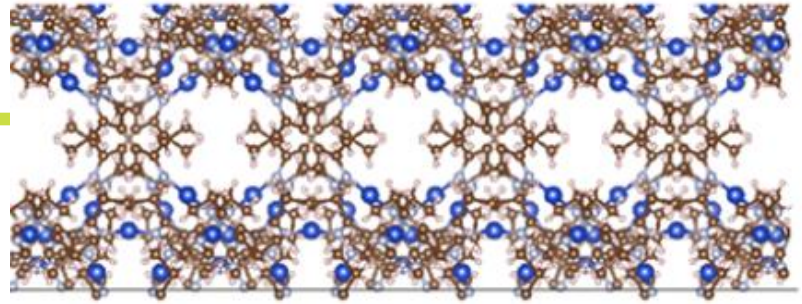
J. Phys.: Condens. Matter 16 (2004) S5345

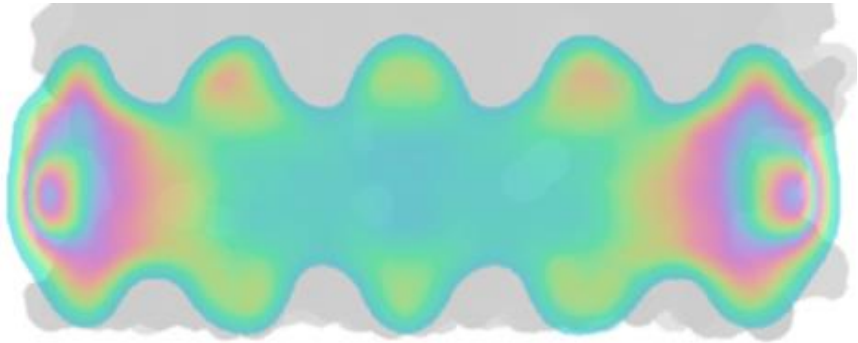
J. Chem. Phys. 120 (2004) 1958

J. Am. Chem. Soc. 146 (2024) 13236

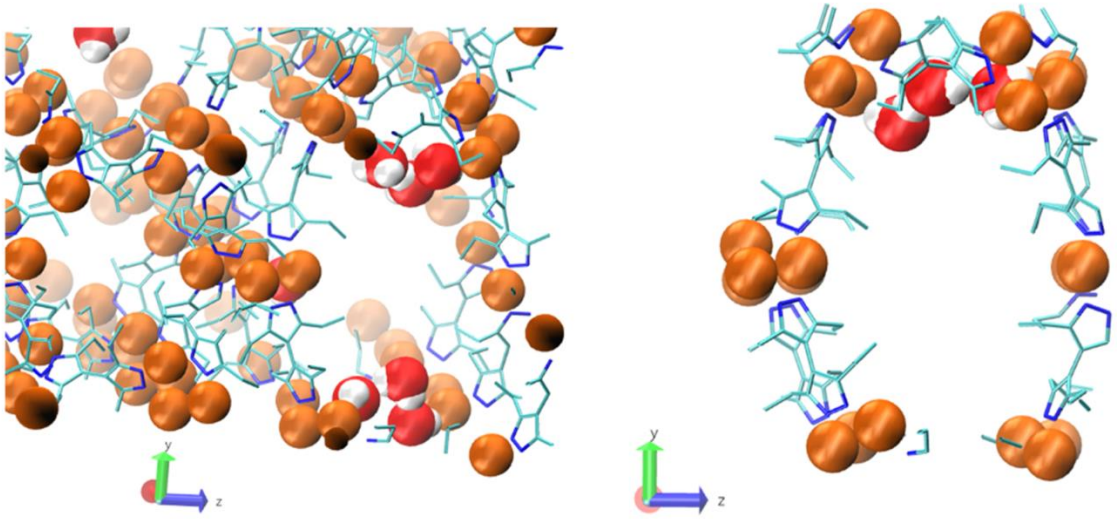
High vapor pressure







Simulations



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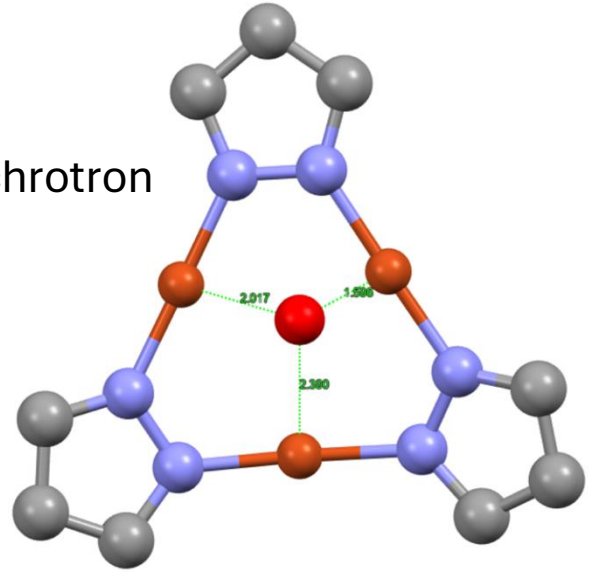

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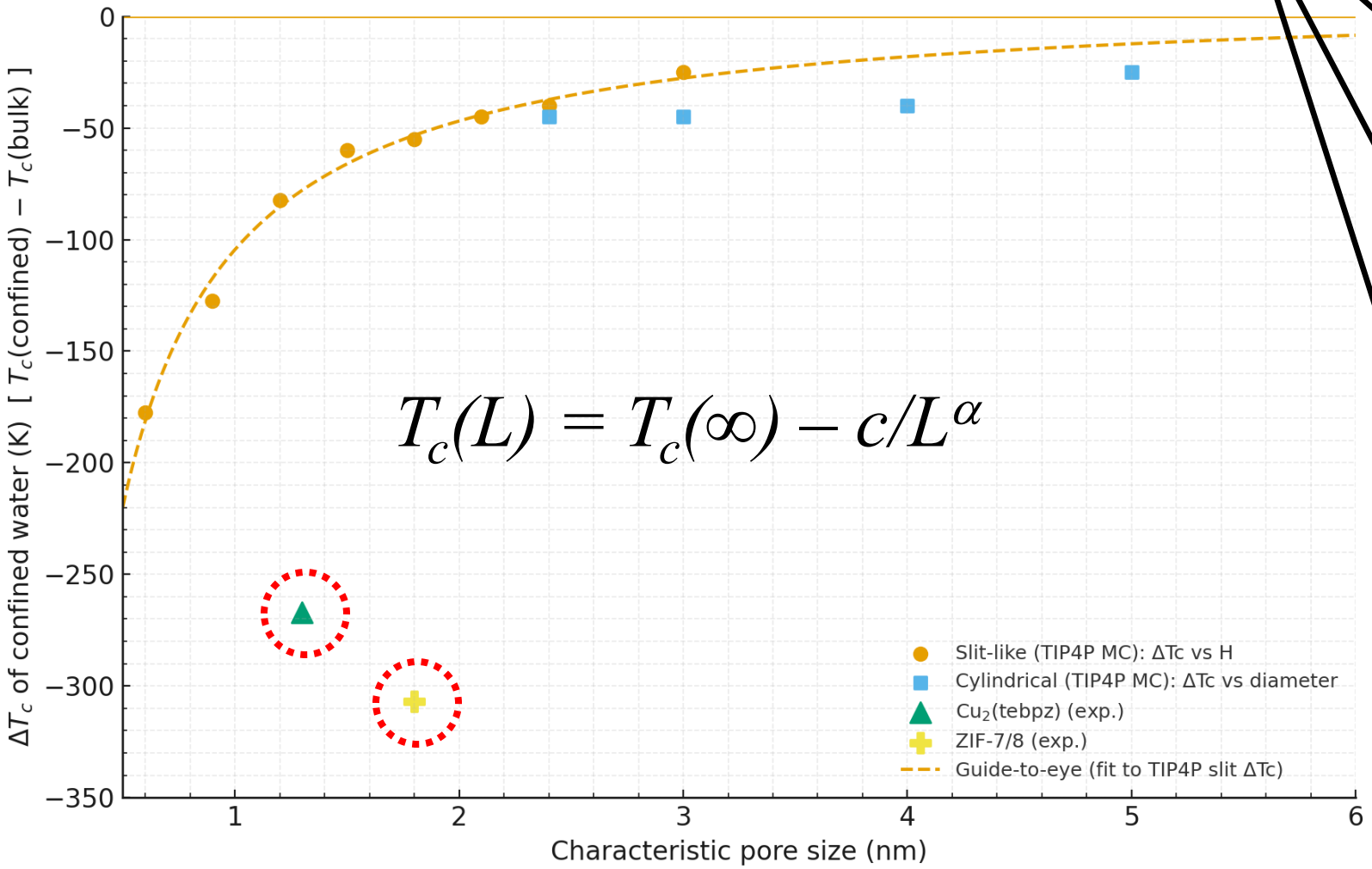
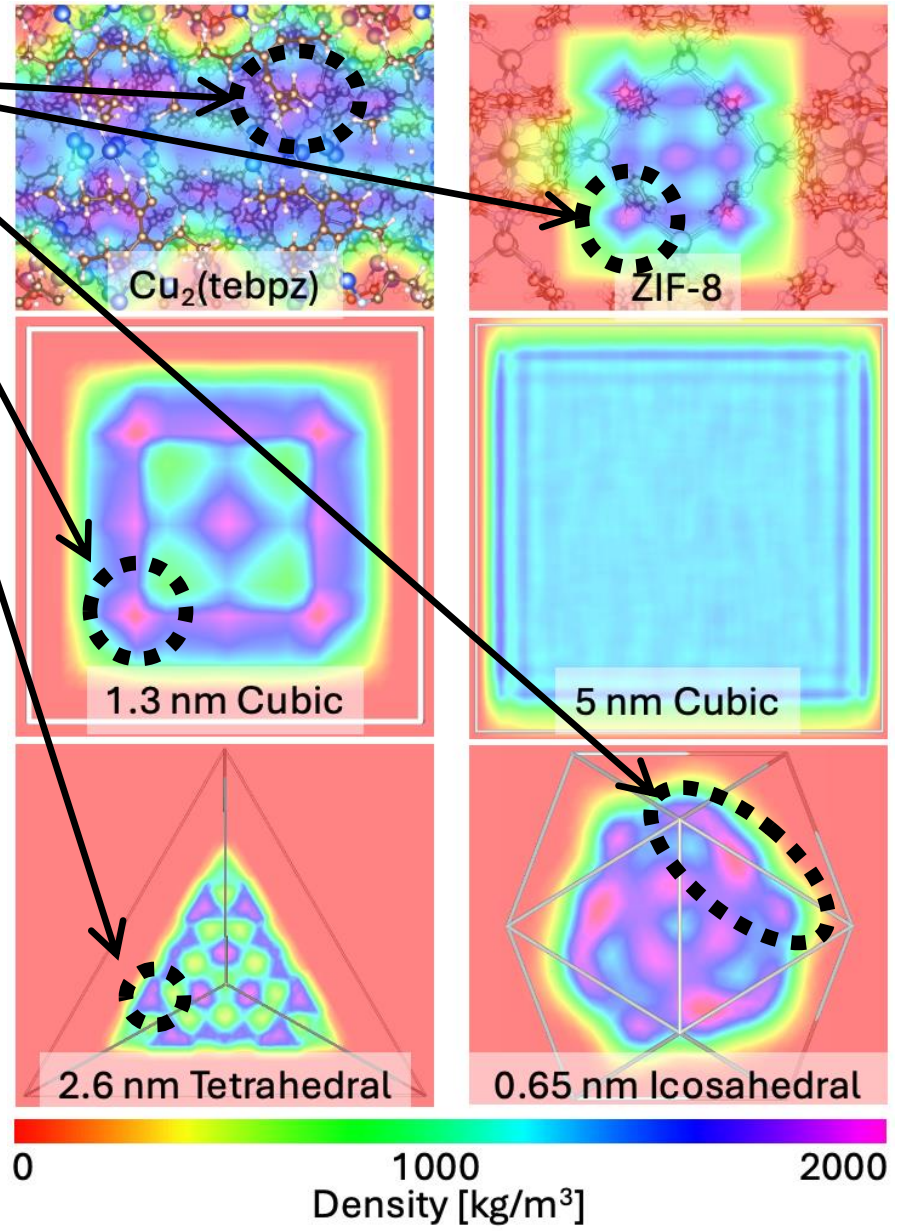
Effect of confinement on T_c

Smeller than the confining cavities





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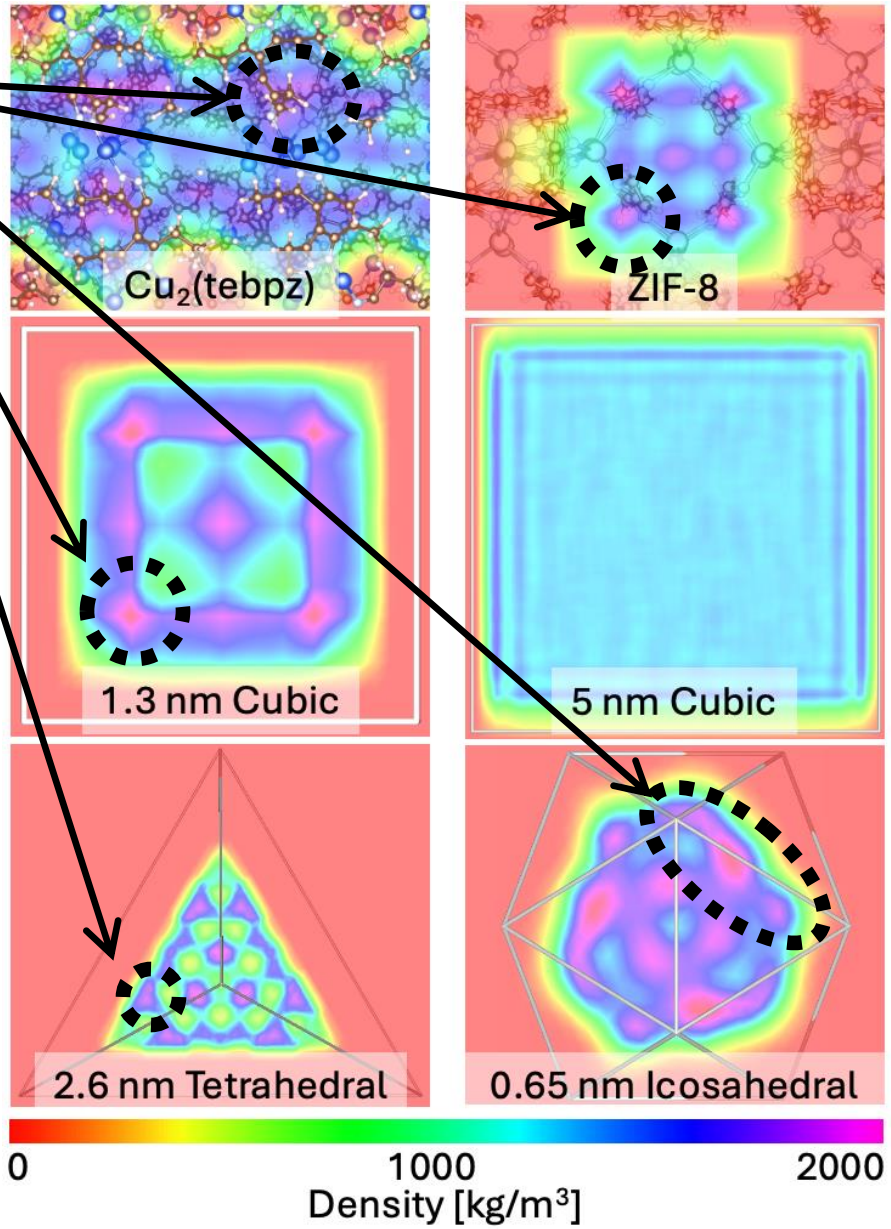

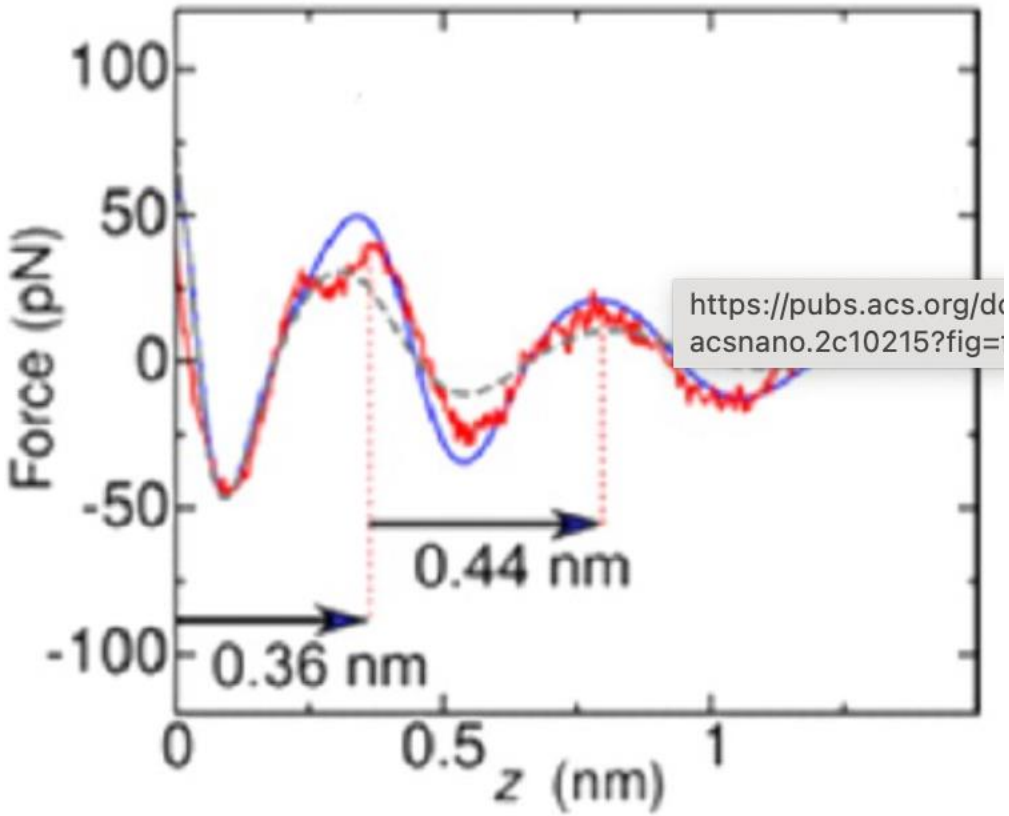

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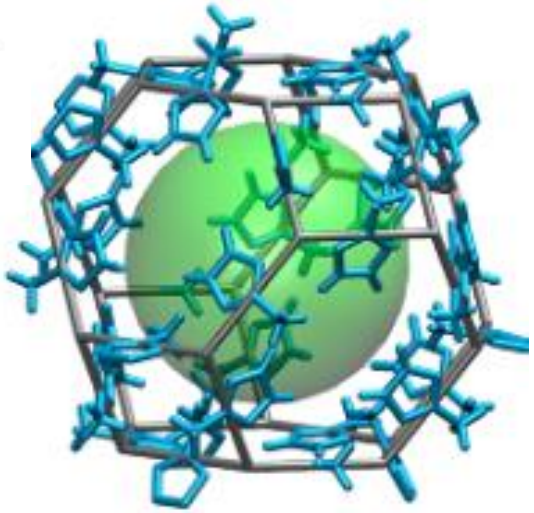
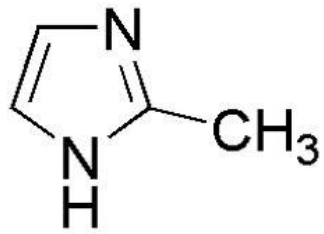
Confinement within mixed linkers MOFs



ZIF-8 cage



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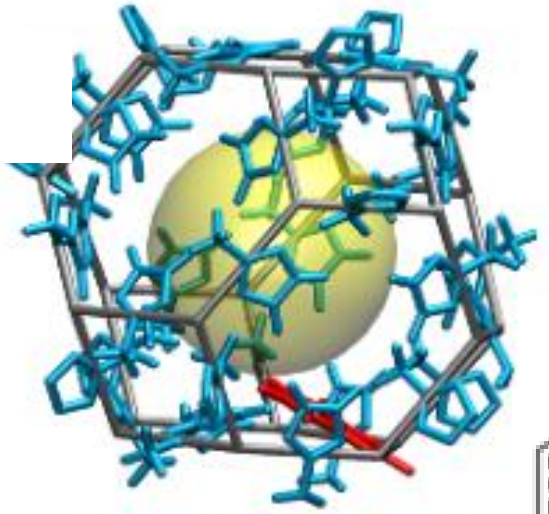

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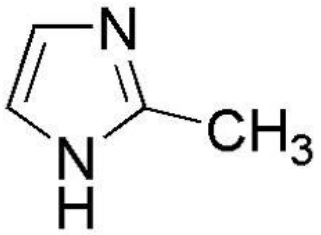

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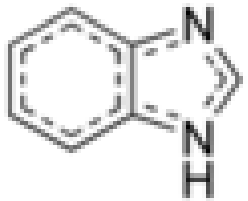
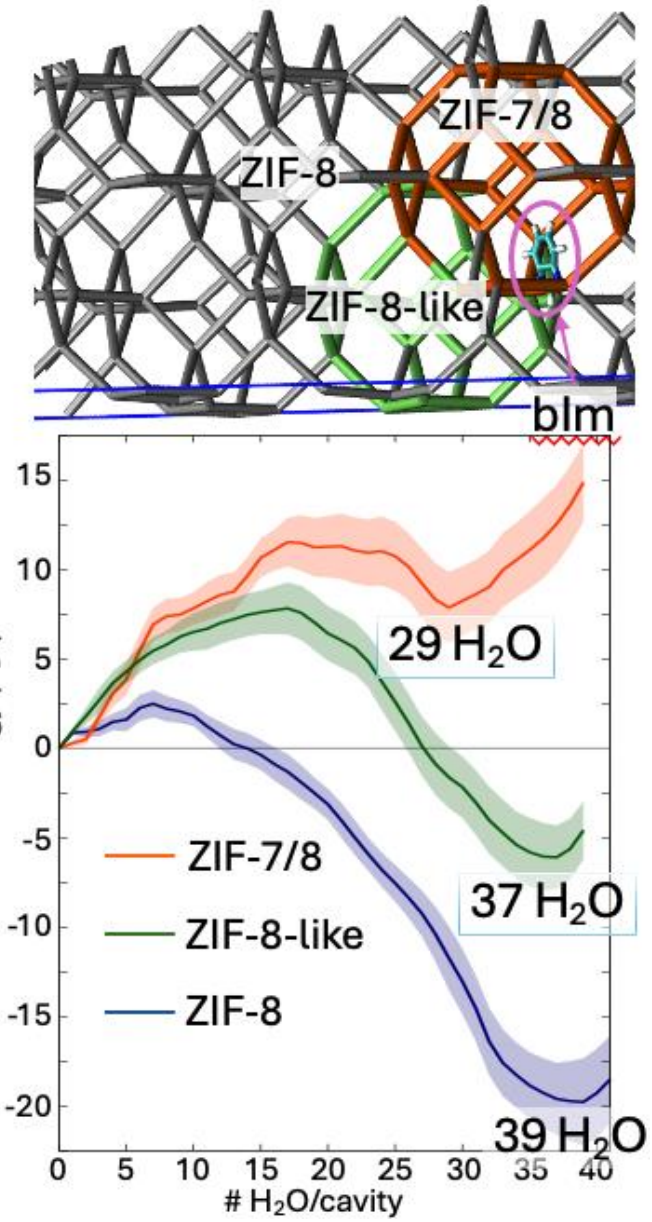
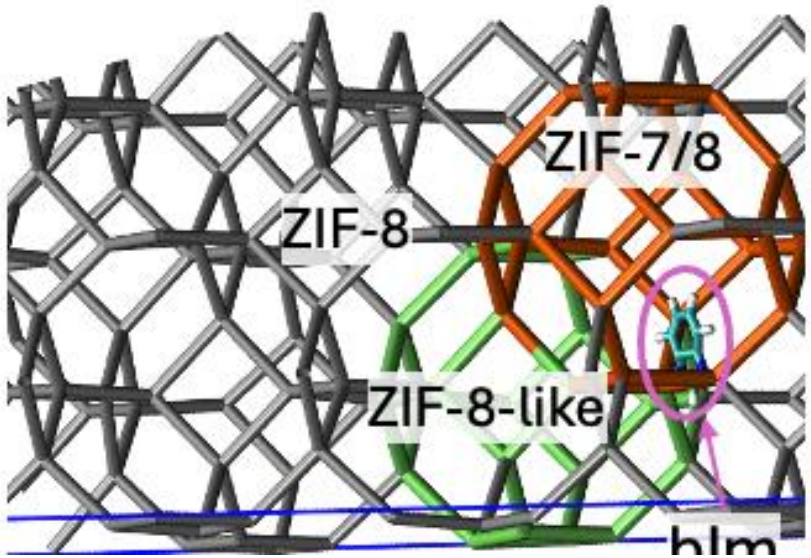
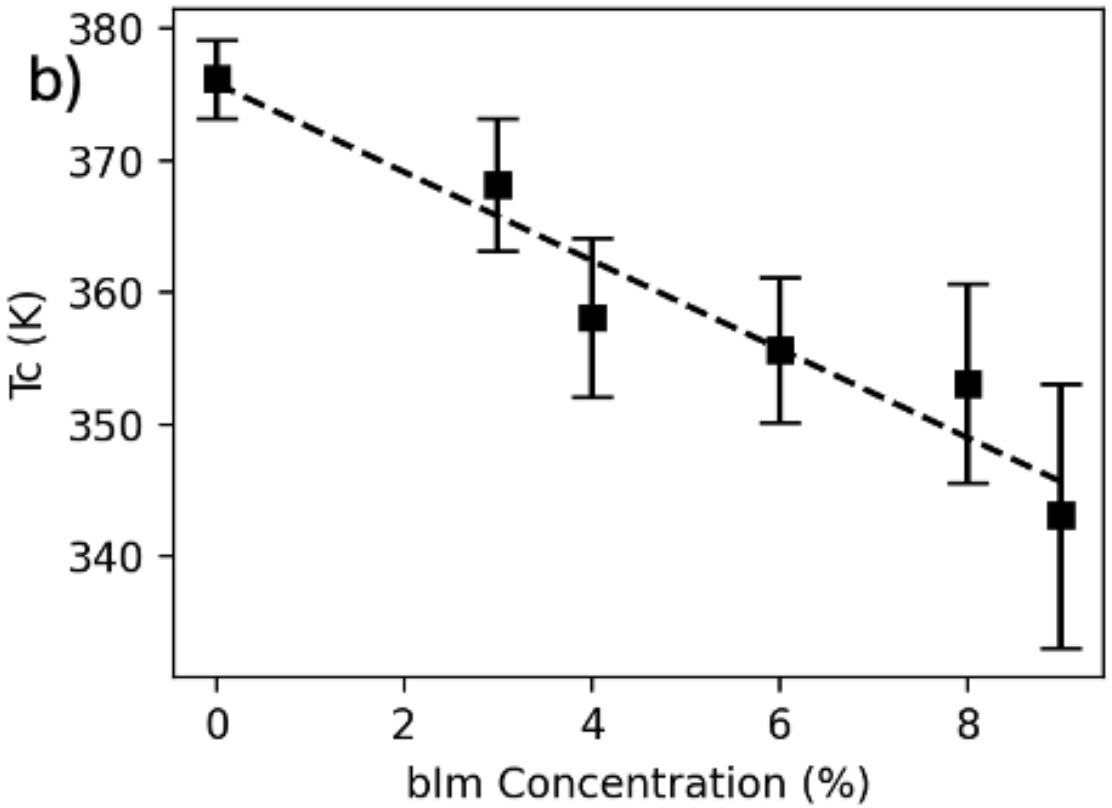
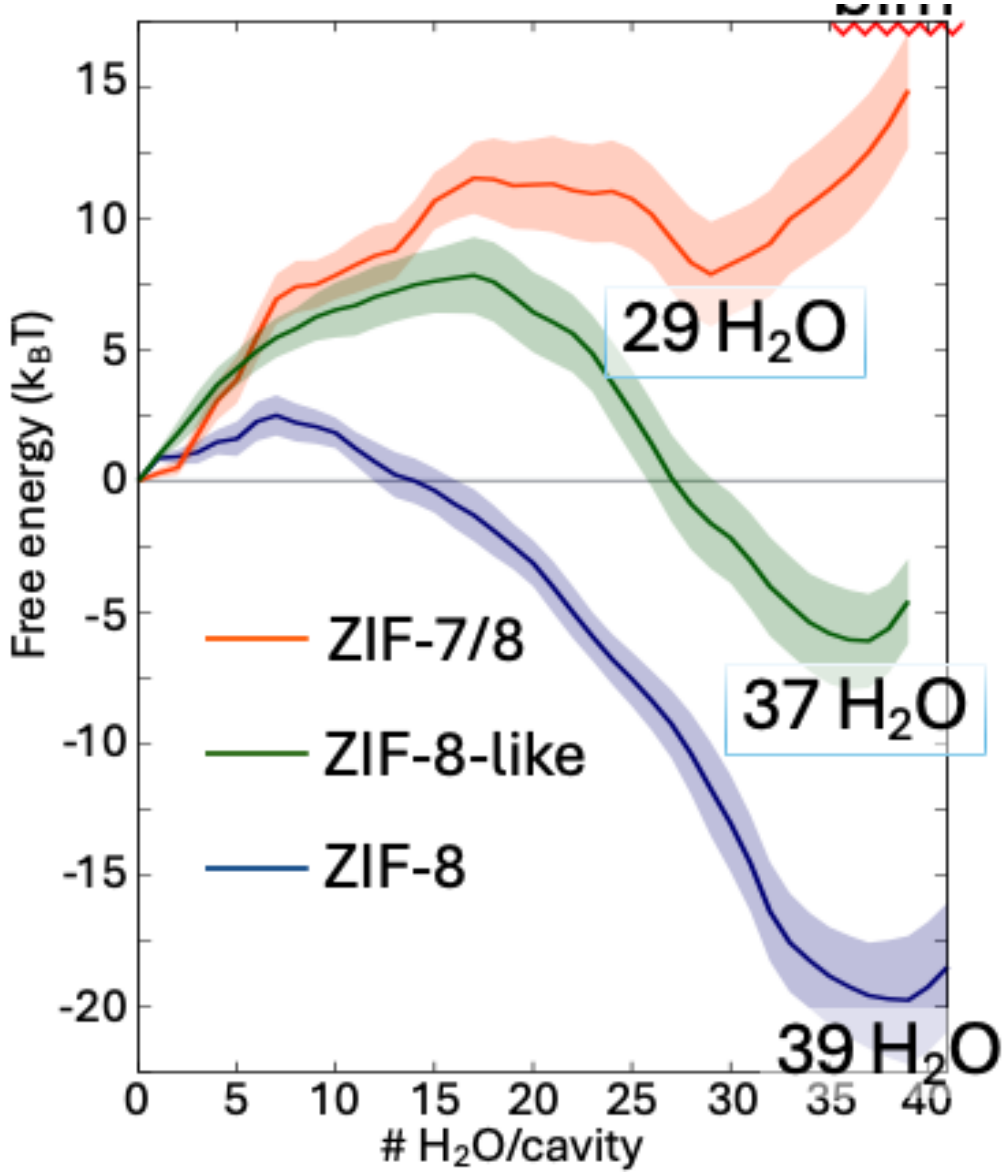




T_{cp} vs MOF's composition







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 inert confining medium.
- Many questions remain to be addressed, e.g., the relation between confined critical T and geometry of the pores, how to control int/ext pressure and hysteresis, etc.
- Exploitability for technological applications in energy storage, dissipation, conversion (not discussed in detail, here)…
- …Moreover, low-T hysteresis opens new perspective in sensible thermal energy storage, supercritical solvents for chemistry. Additionally, the existence of (possibly multiple) confined supercritical water and bulk water at the same P/T allows to dream separation techniques like all-water fluid/fluid chromatography…let aside the “surface tension”-related phenomena between sub/supercritical fluids of the same substance

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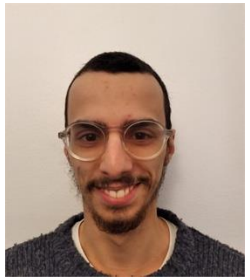

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