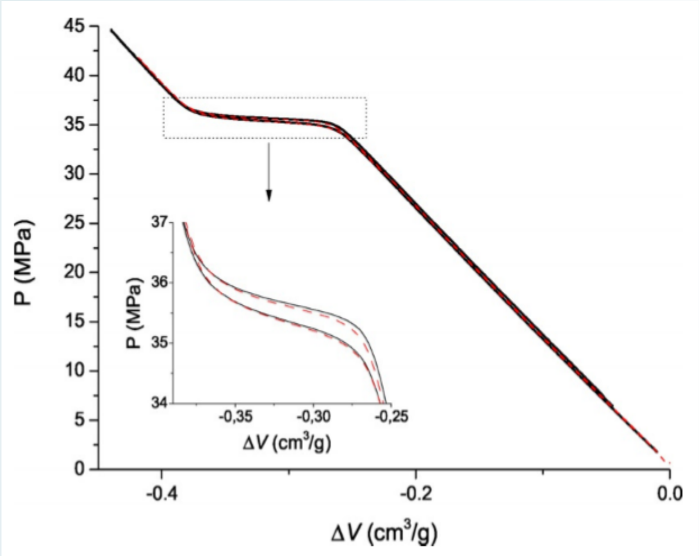
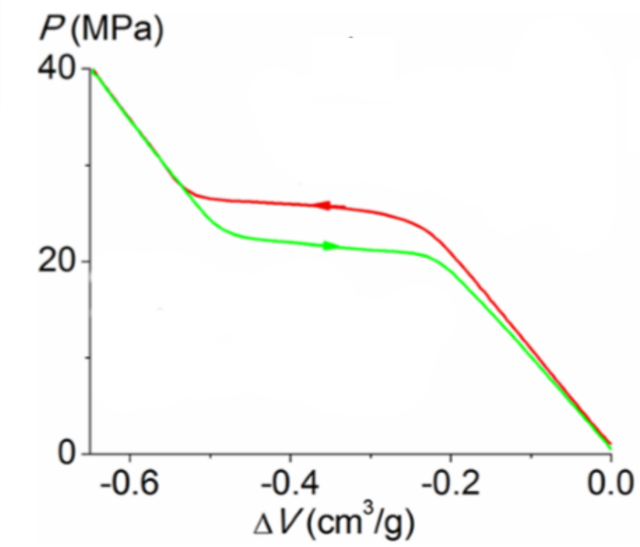
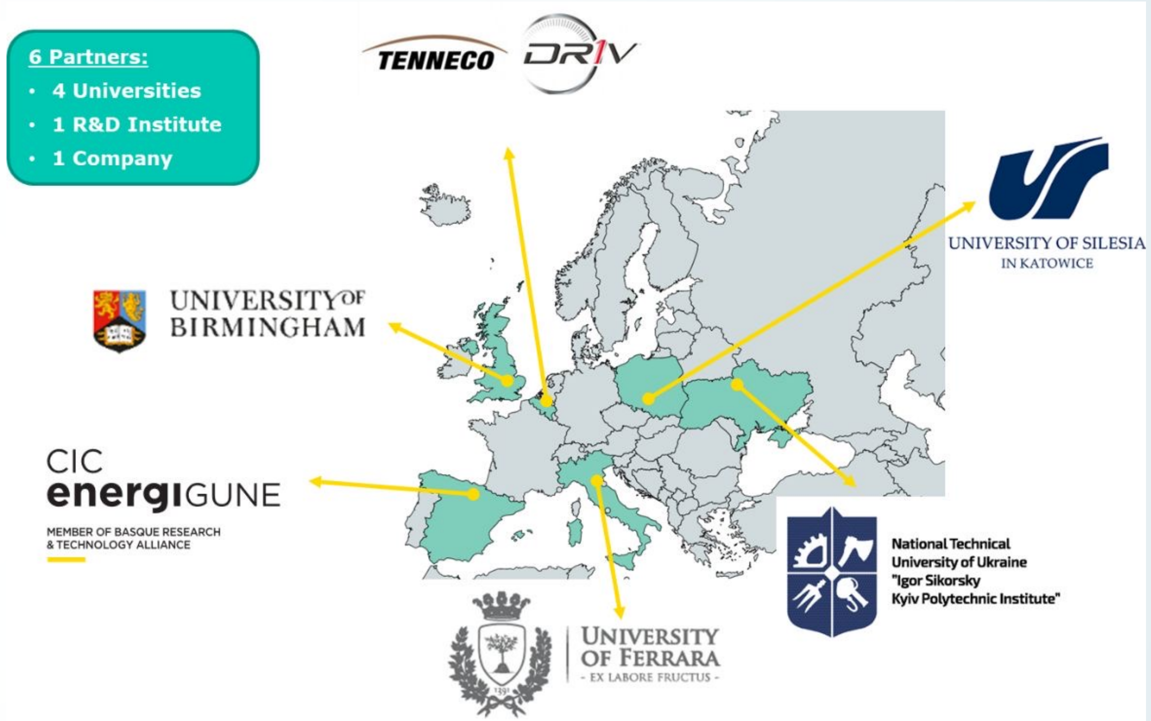
Intrusion mechanism of water in ZIF-8 hydrophobic MOF: capillary condensation or subnanoscopic front advancement?

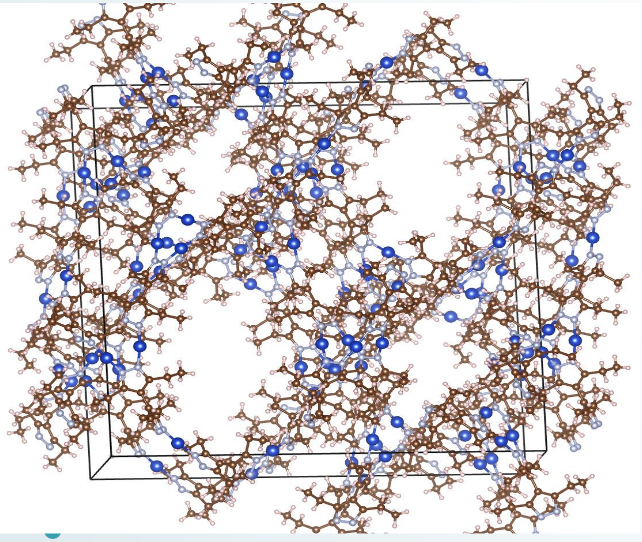
Simone.meloni@unife.it

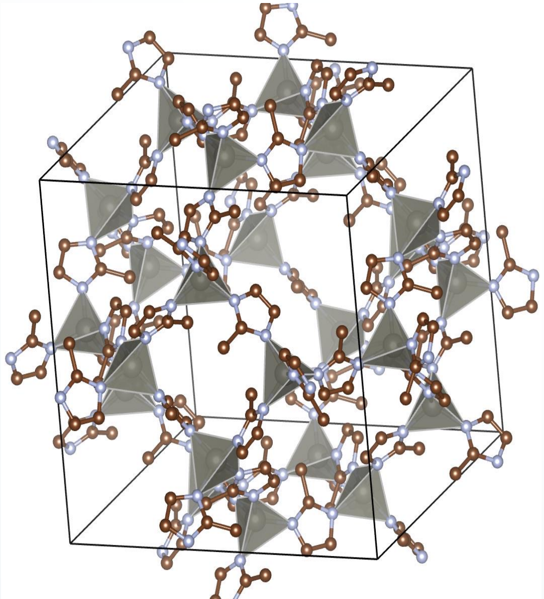
Crystalline porous media: MOFs







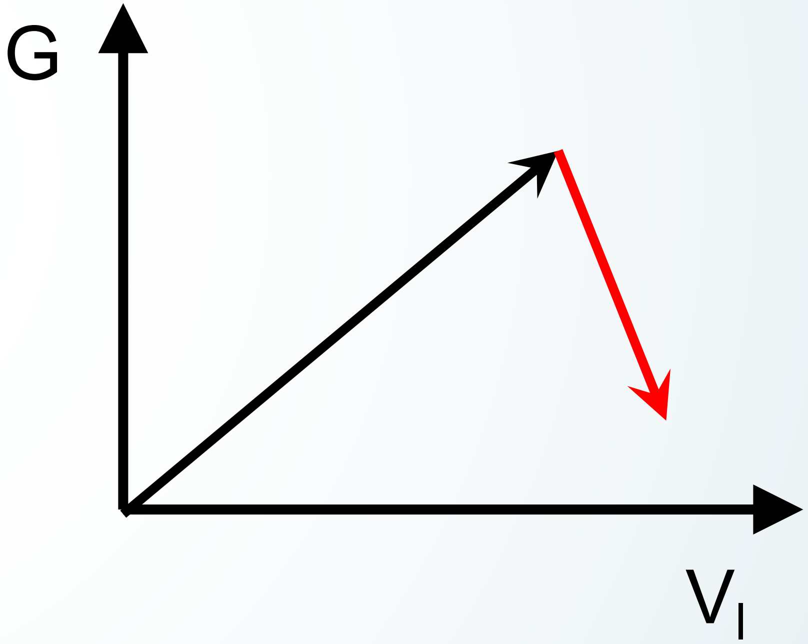




ELECTRO INTRUSION

Intrusion/extrusion in hydrophobic porous materials: a thought experiment

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

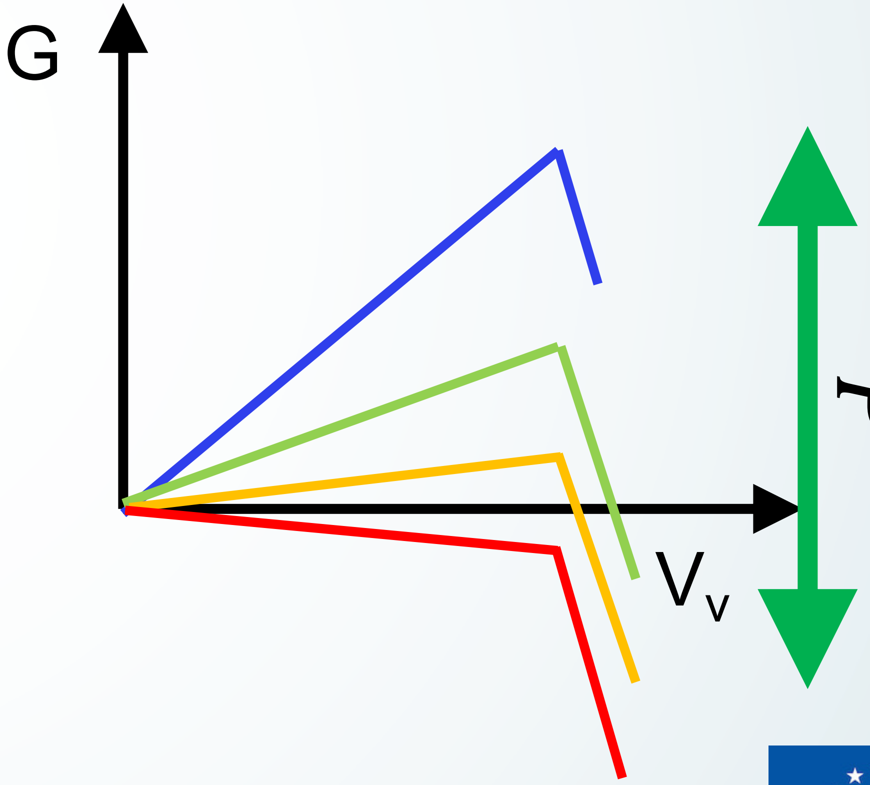


A. Tintii

ELECTRO INTRUSION

Intrusion/extrusion in hydrophobic porous materials: a thought experiment

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



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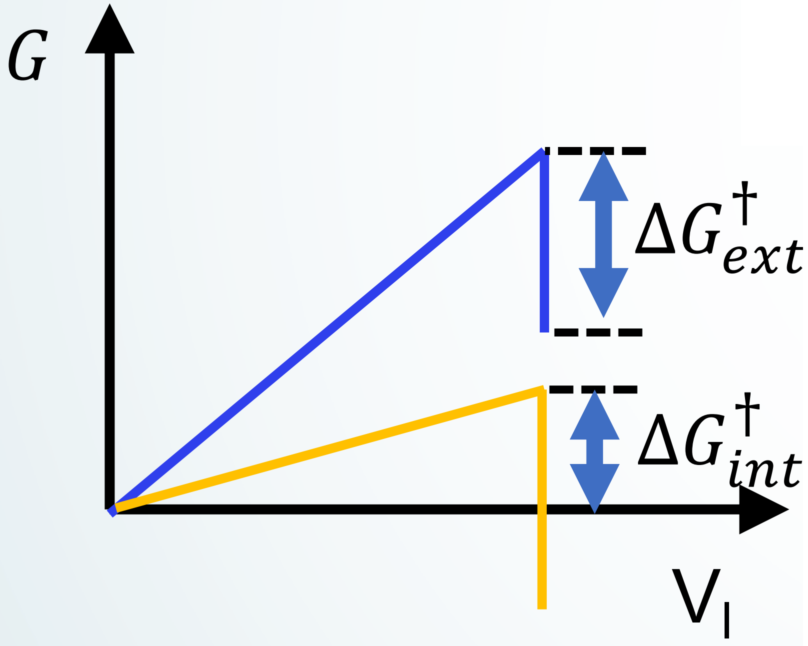
ELECTRO INTRUSION

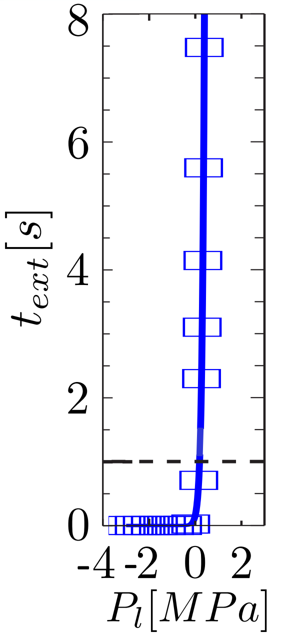
Intrusion and extrusion pressure and hysteresis

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

TST
Kramers theory
…

$$\tau = \tau_0 \exp[\Delta\Omega^\dagger / k_B T]$$



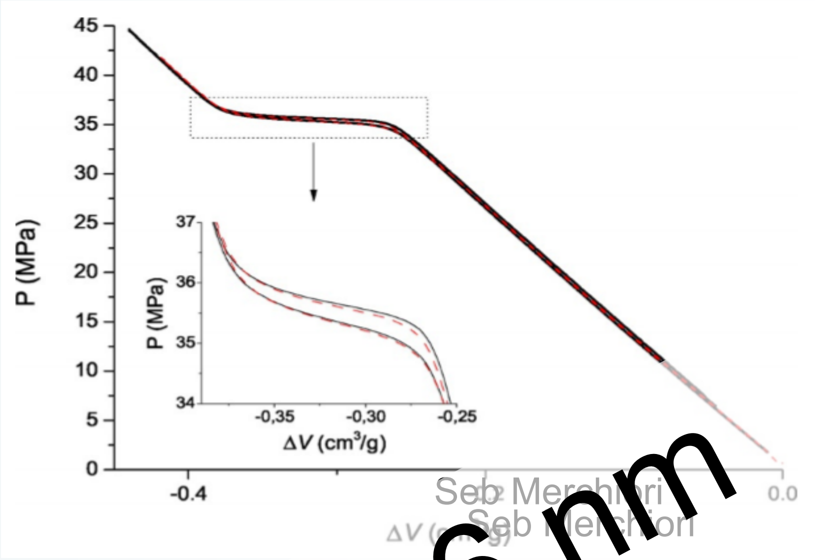


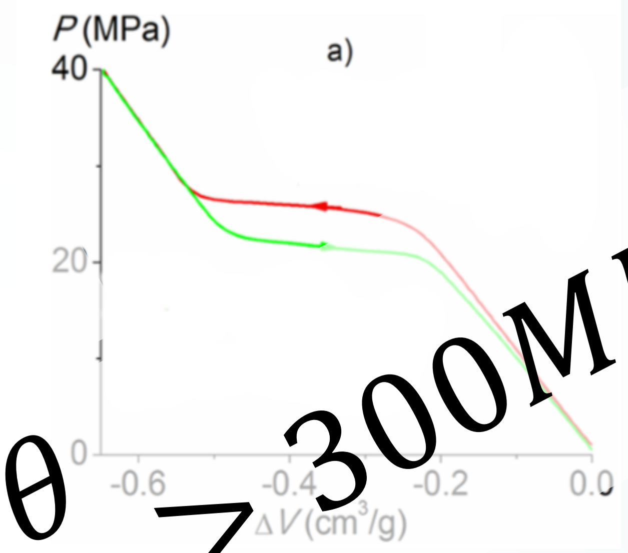
- Hysteresis originates from the over/underpressure you must apply for the barrier to become ~1 $k_B T$

- intrusion extrusion barriers determine/allows to control P_{int}/P_{ext} and hysteresis by tuning the

Confined Classical nucleation Theory
cCNT

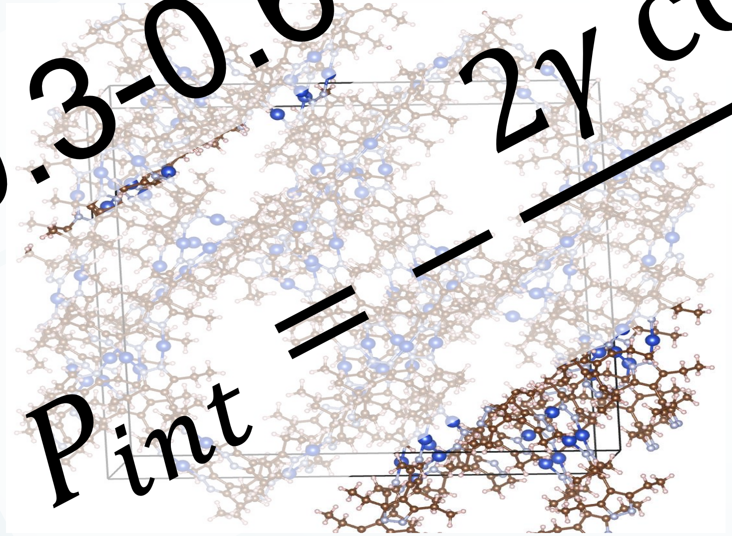
Crystalline porous media: MOFs

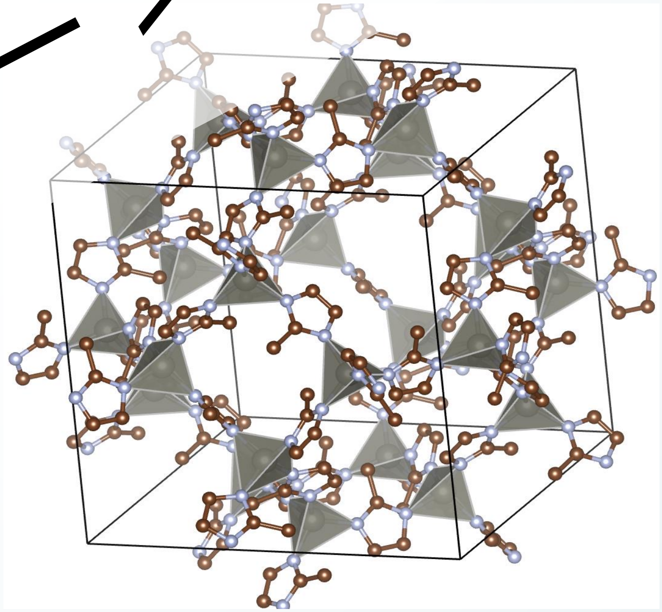




r=0.3-0.6 nm

$$P_{int} = -\frac{2\gamma\cos\theta}{r} > 300\,MPa$$





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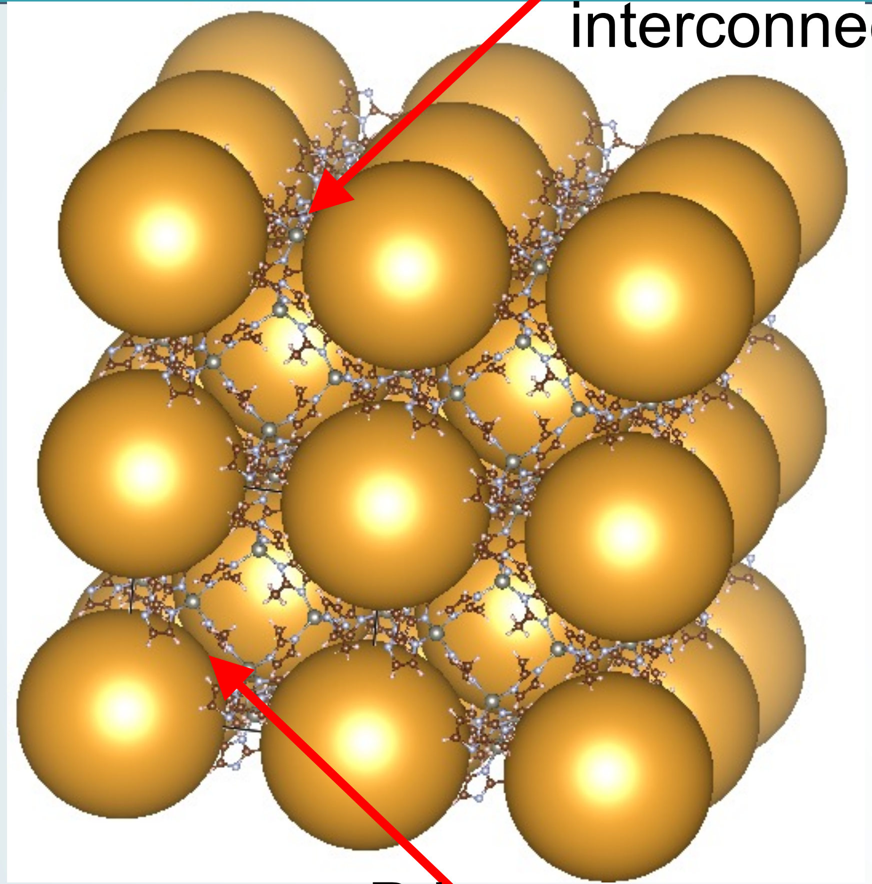
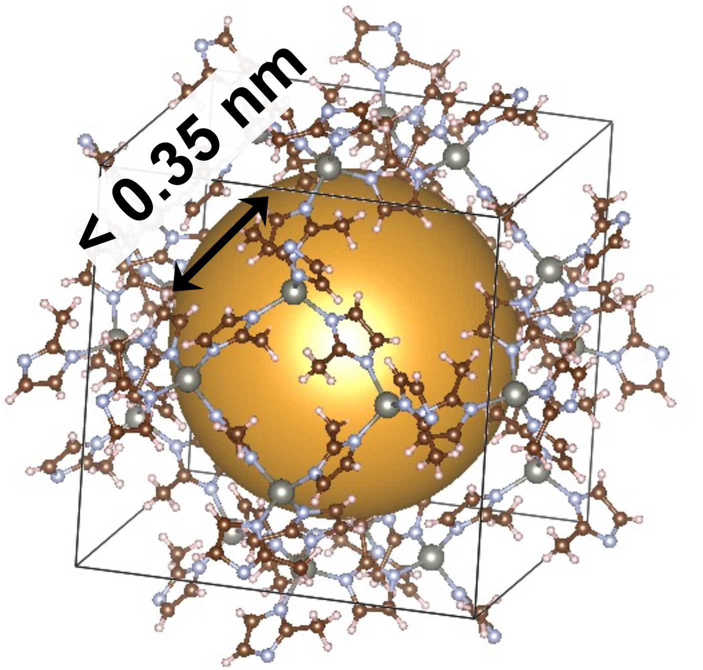
Peculiarities of ZIF-8

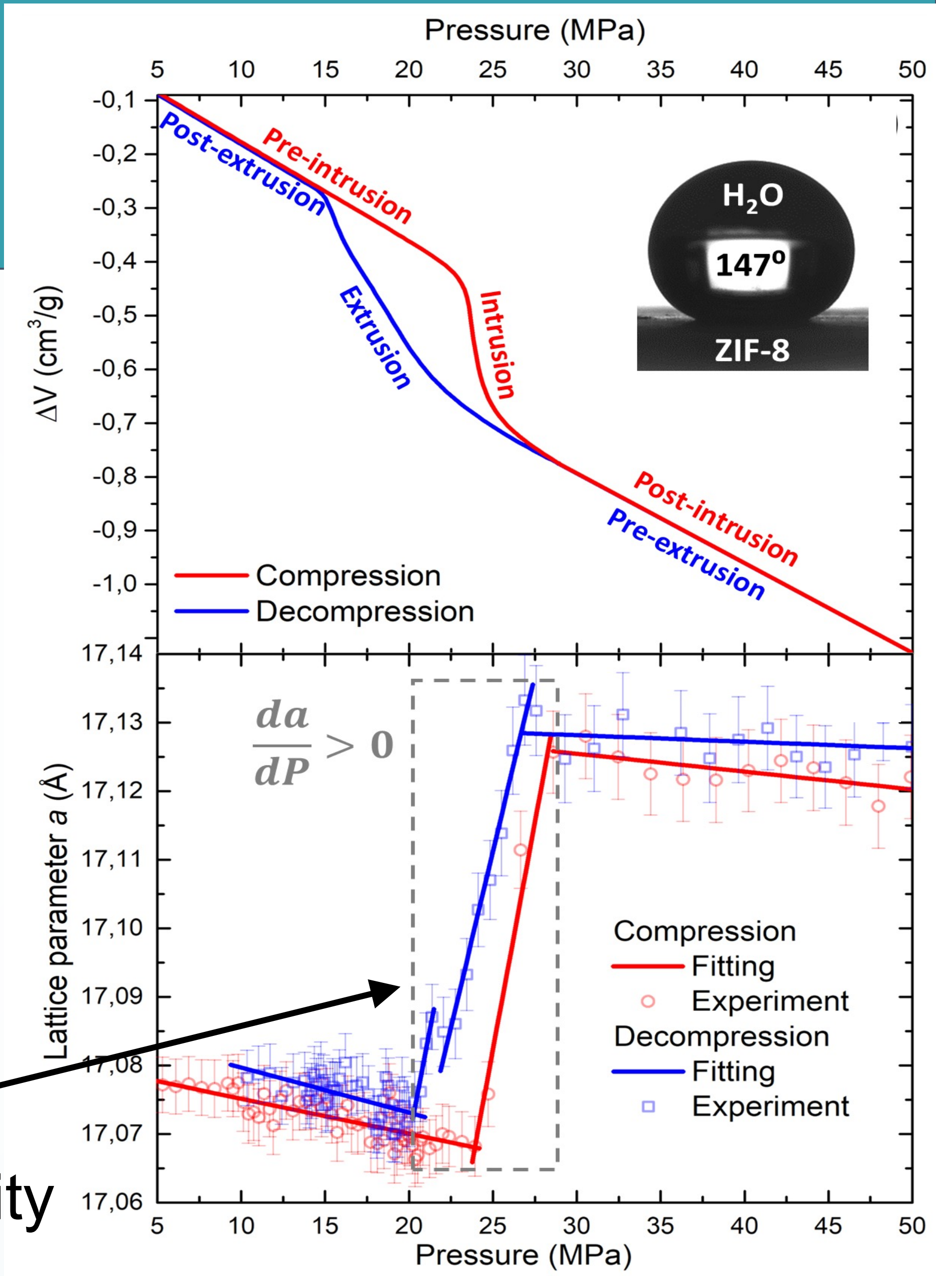
Secondary interconnections



Primary interconnections



Exceptional Negative Compressibility



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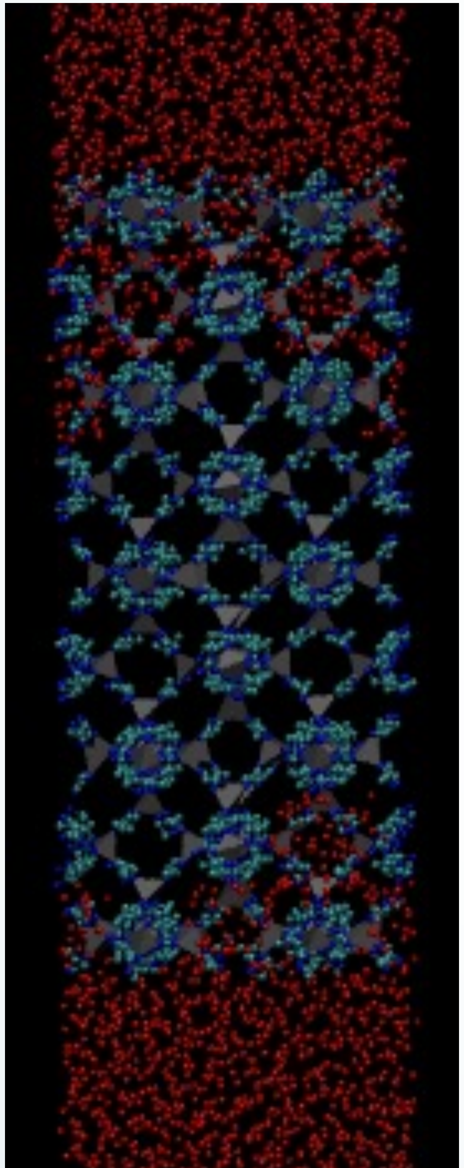
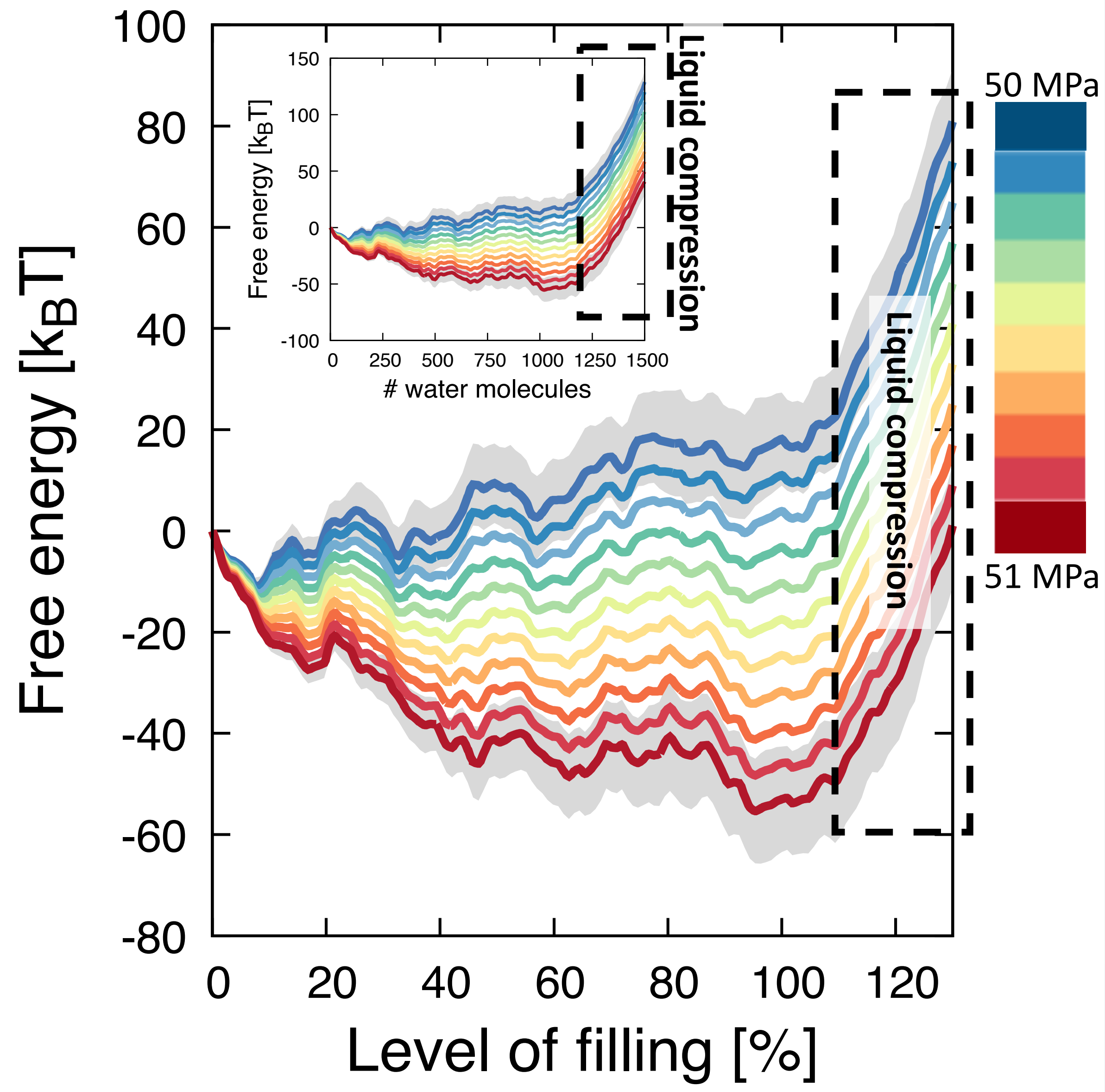
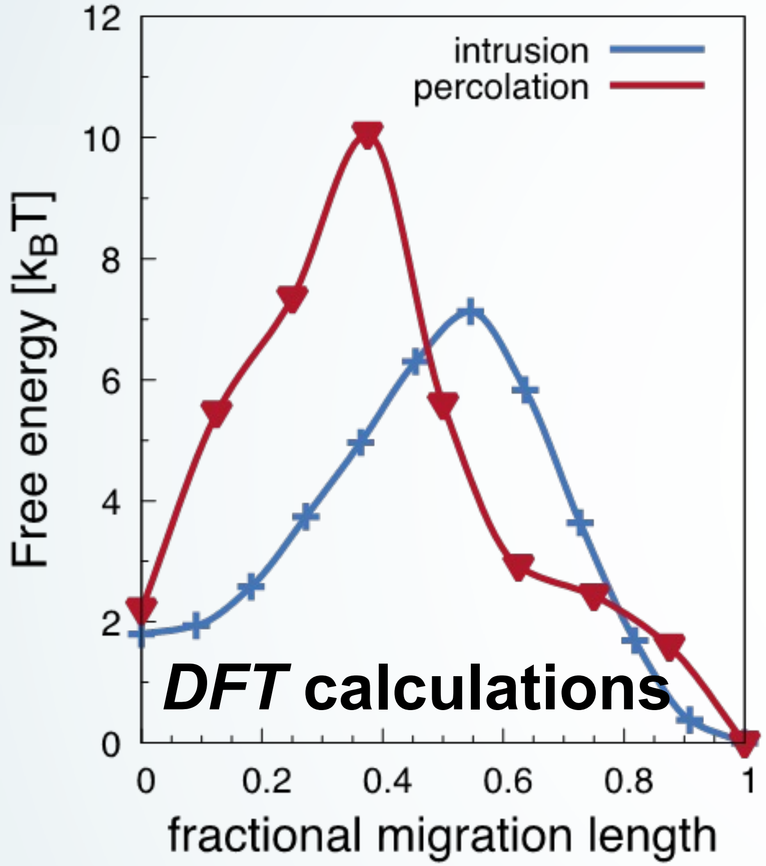
Giant Negative Compressibility by Liquid Intrusion into Superhydrophobic Flexible Nanoporous Framework Tortora et al, Nano Letters 21, 2848-2853

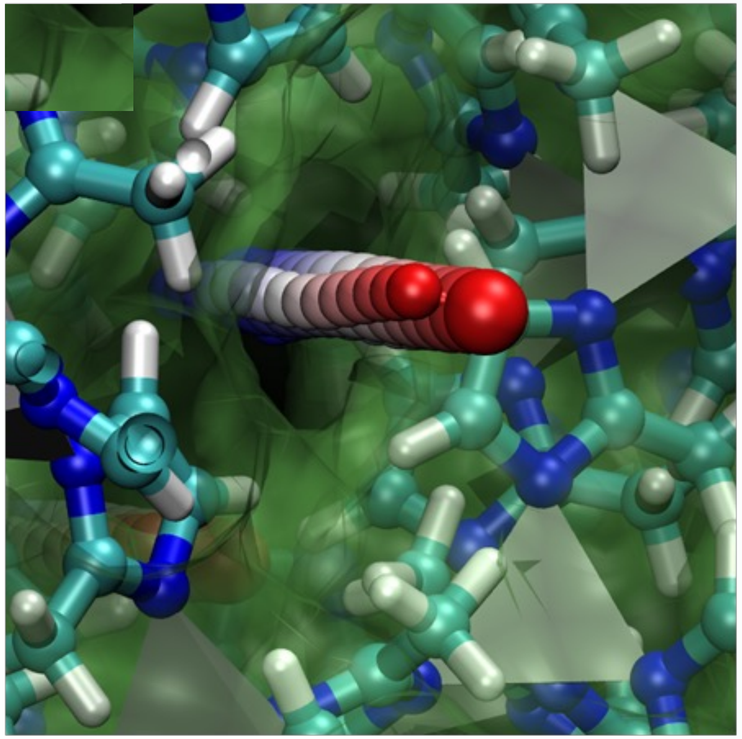
Int/ext free energy profile *vs* pressure



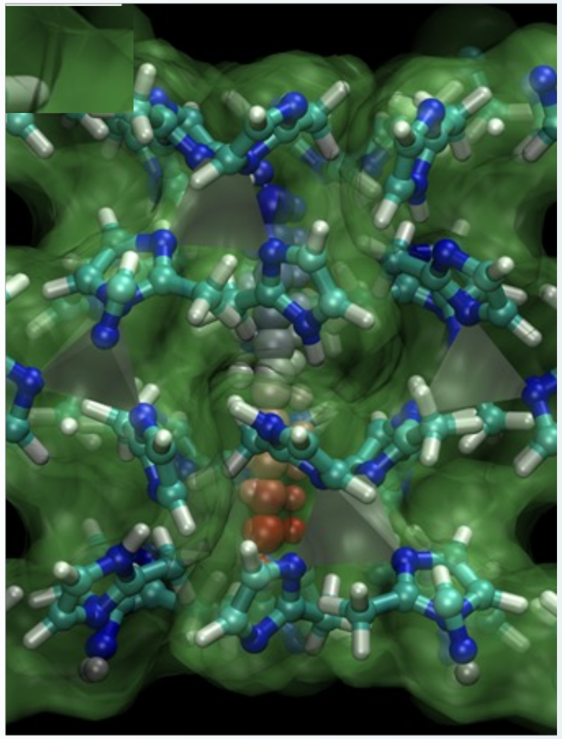


Single water molecules “intrusion”





Intrusion



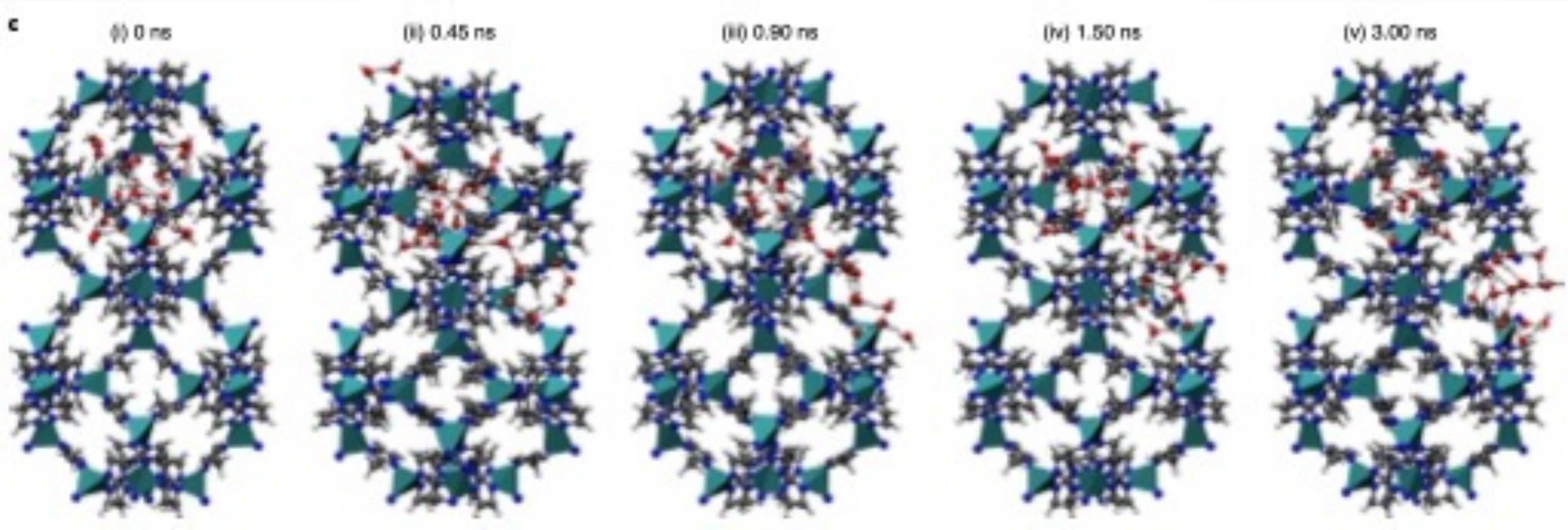
Percolation

Slow intrusion cannot be due to single water molecules crossing 6MR apertures: barrier very low, very low intrusion pressure and no hysteresis

ELECTRO INTRUSION

Turning molecular spring into nano-shock absorber: the effect of macroscopic morphology and crystal size on the dynamic hysteresis of water intrusion-extrusion into-from hydrophobic nanopores, Zajdel et al., ACS Appl. Mater. Interfaces 2022, 14, 26699

Proposed mechanism: capillary condensation



Grand Canonical simulations

Sun *et al.* “High-rate nanofluidic energy absorption in porous zeolitic frameworks”, *Nat. Mater.* **20**, 1015 (2021).

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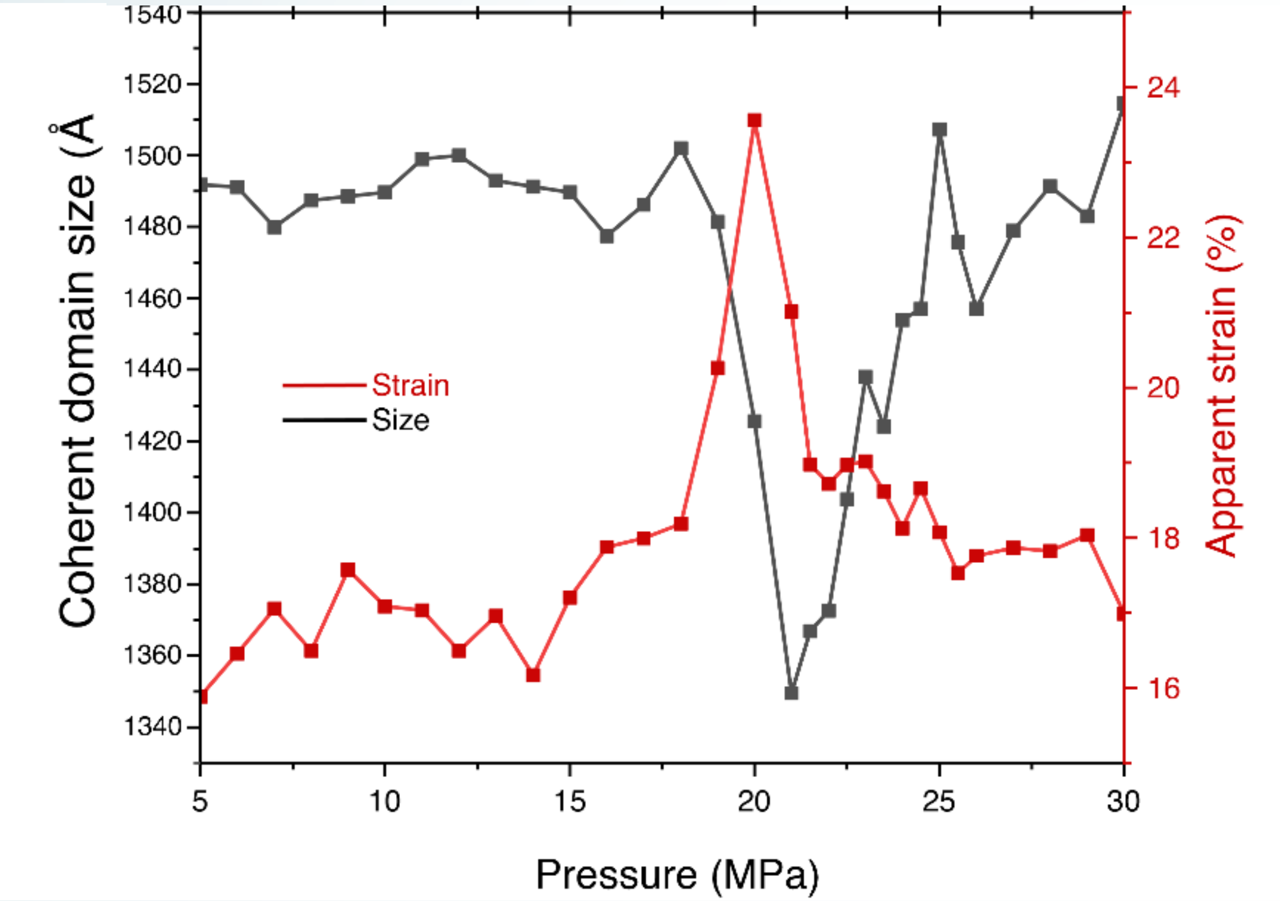
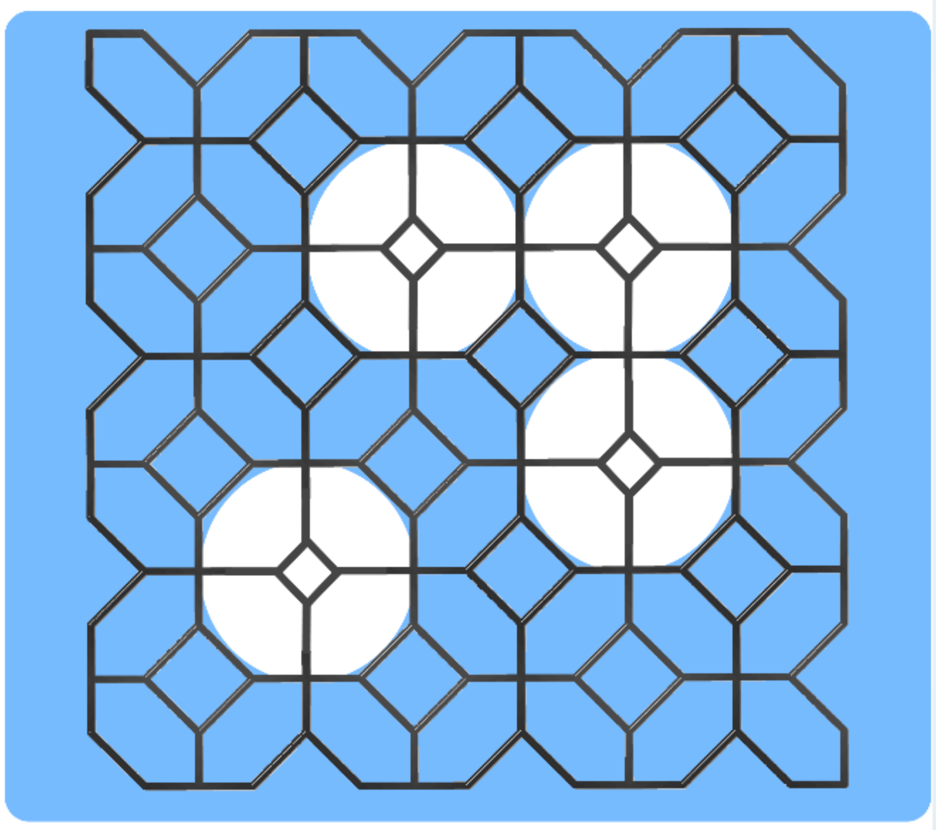
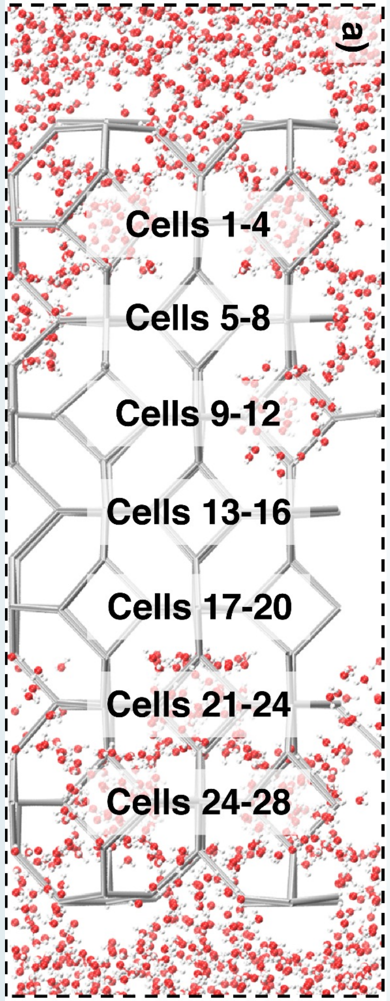
Mismatch with experimental evidence

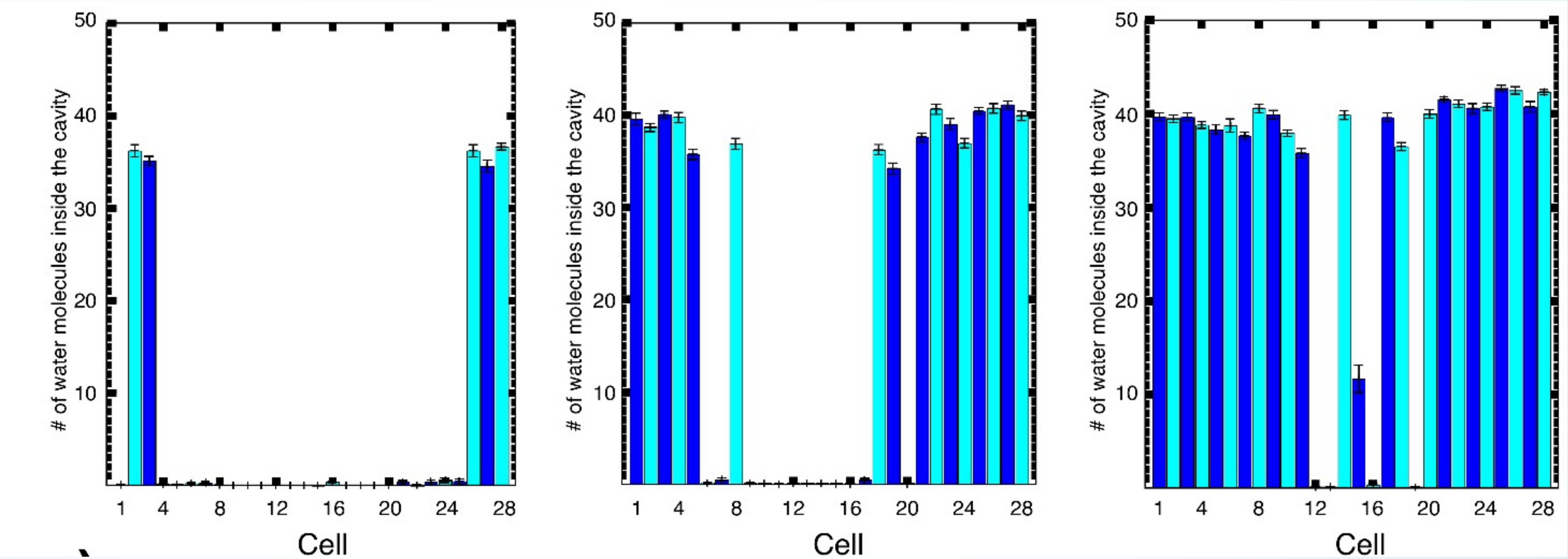




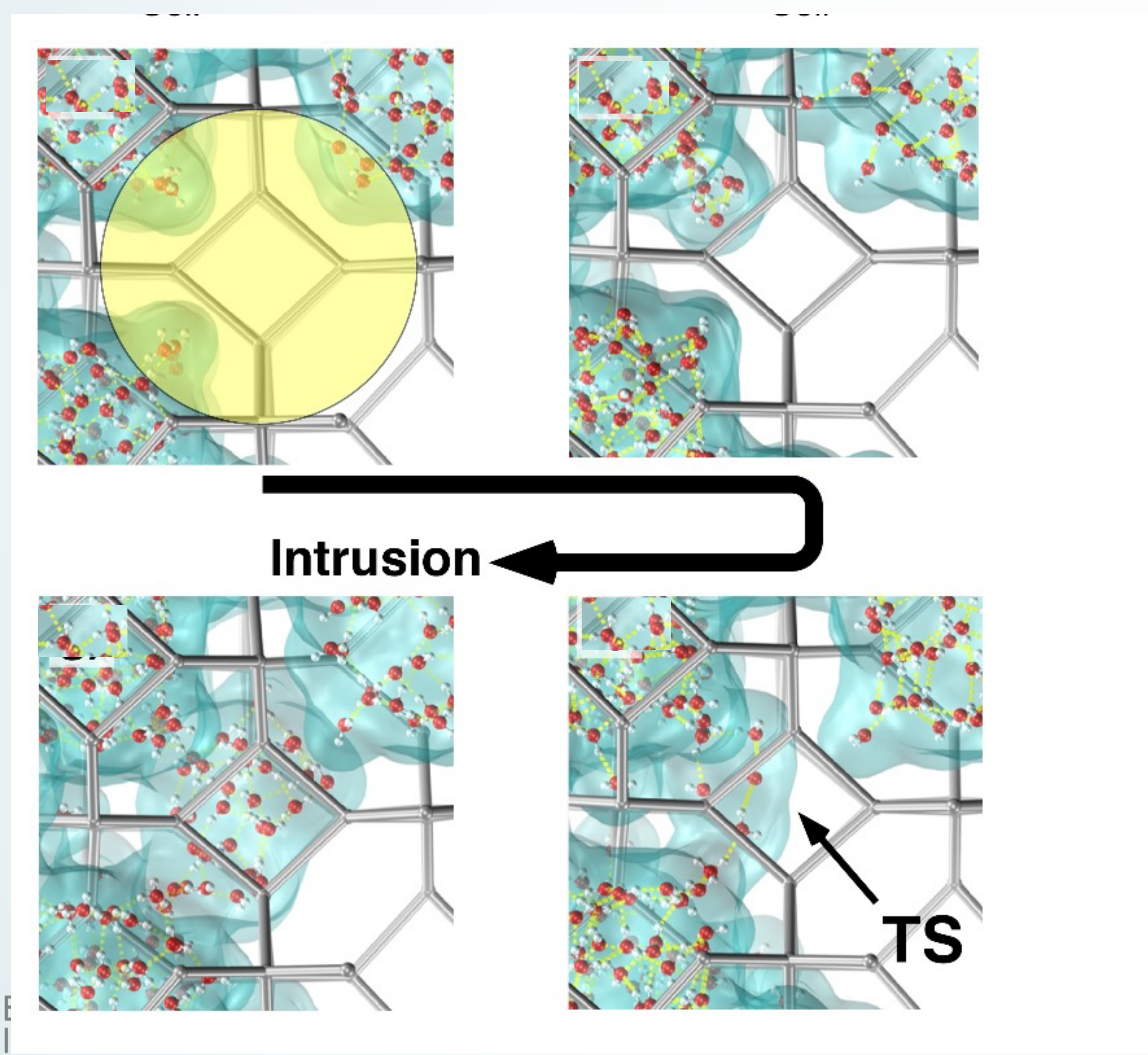
On the mechanism of water intrusion into flexible ZIF-8: liquid is not vapor, Amayuelas et al, https://doi.org/10.1021/acs.nanolett.3c00235

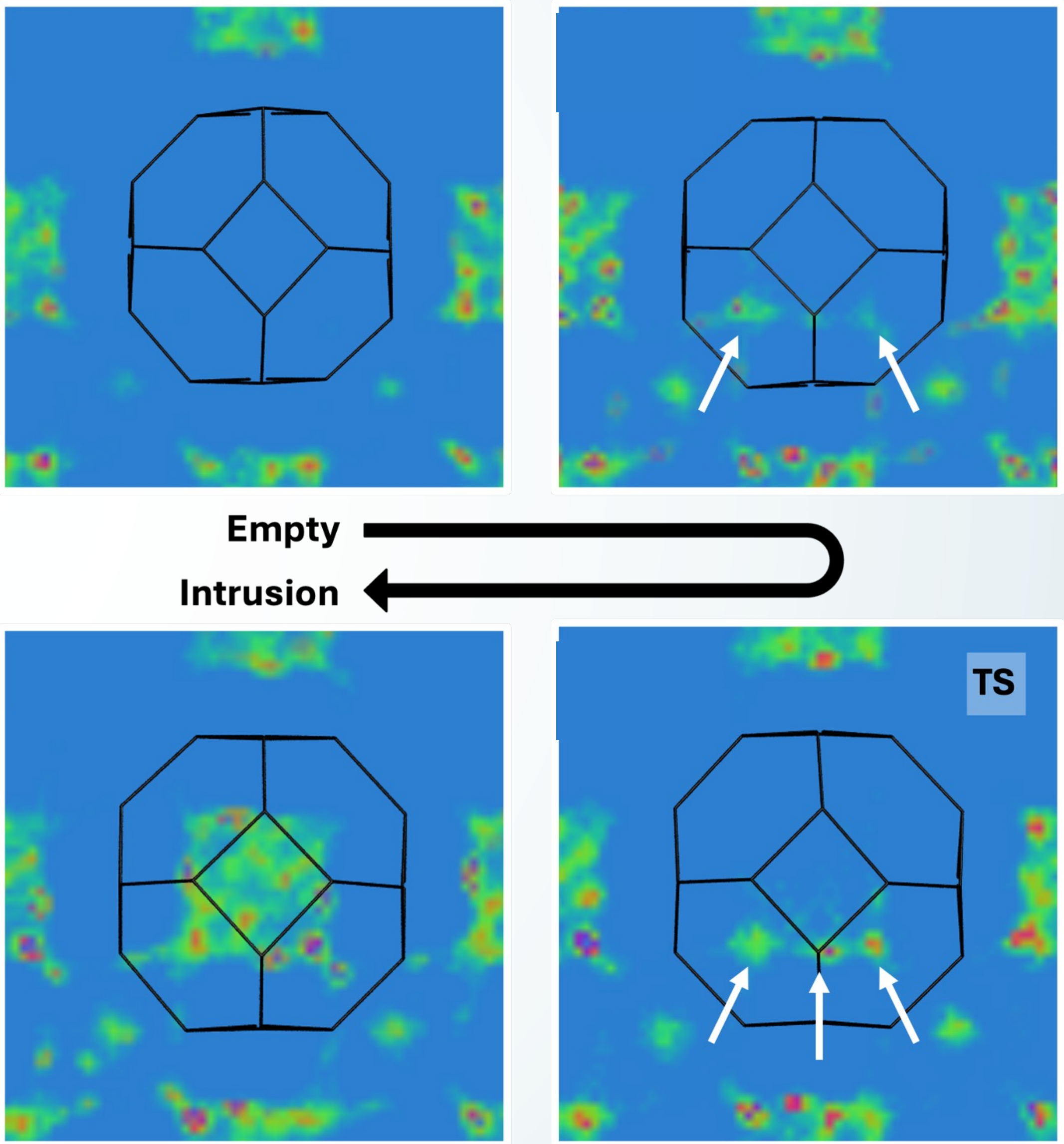
Cage-by-cage intrusion mechanism



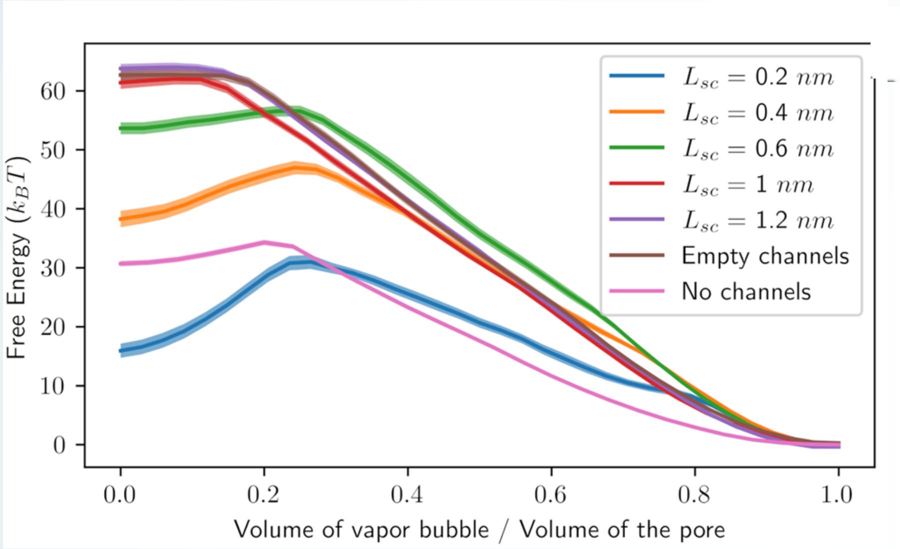


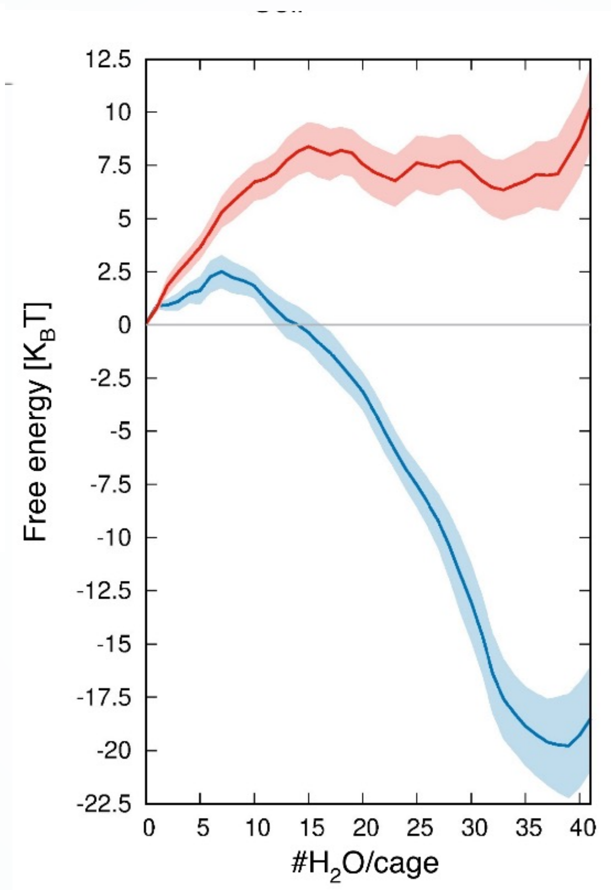
Origin of the intrusion barrier

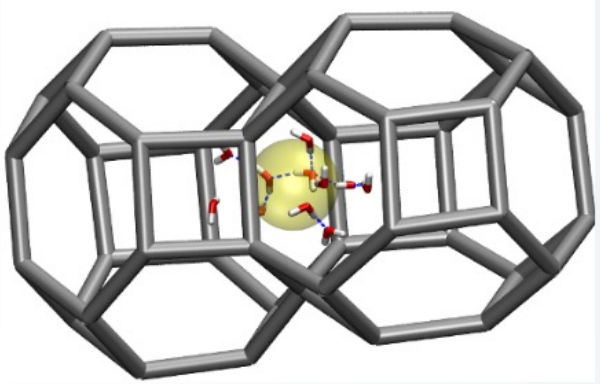


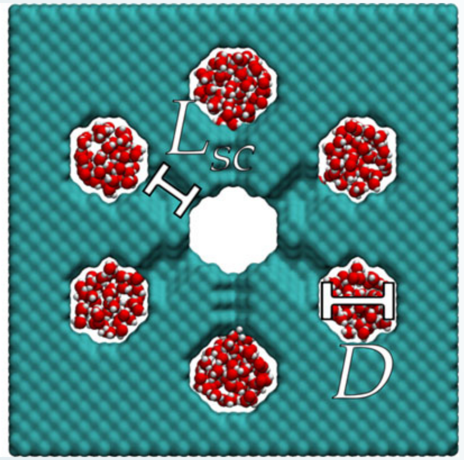


Why cage-by-cage intrusion









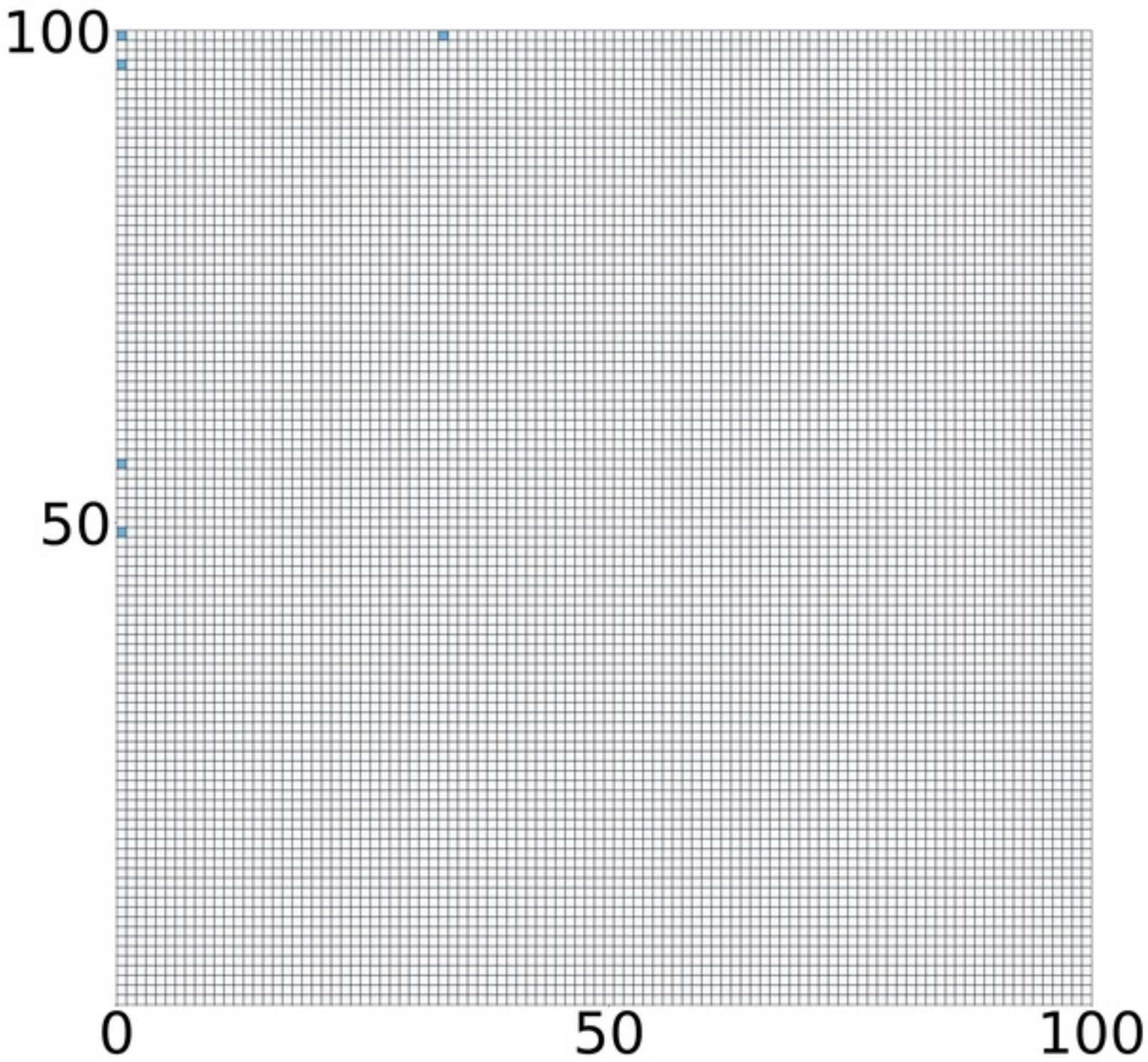
	θ_ι
Std ZIF-8	101°
Clogged pores	114°

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

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

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

Effective surface tension in a (porous) medium



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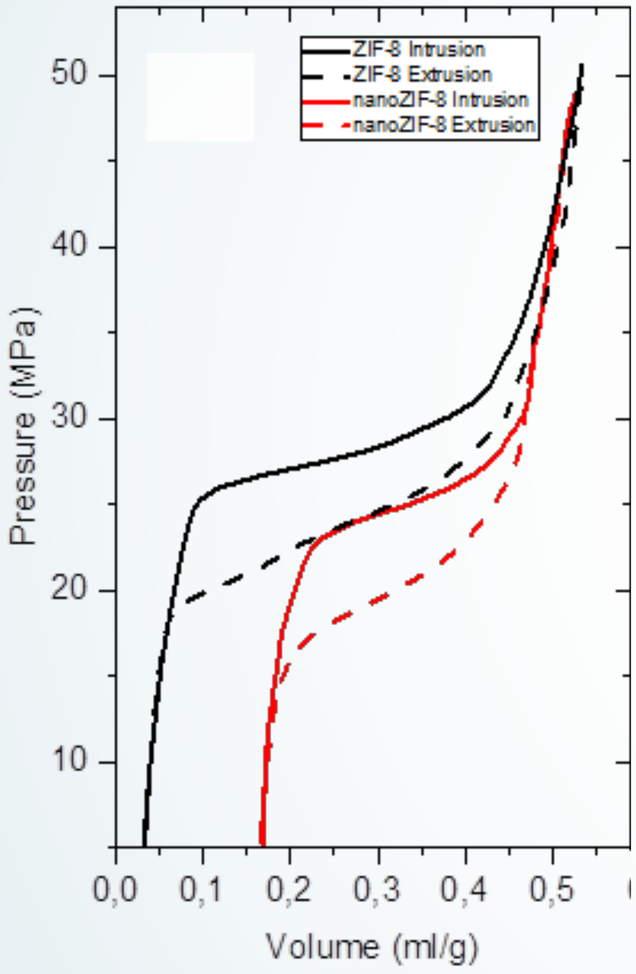
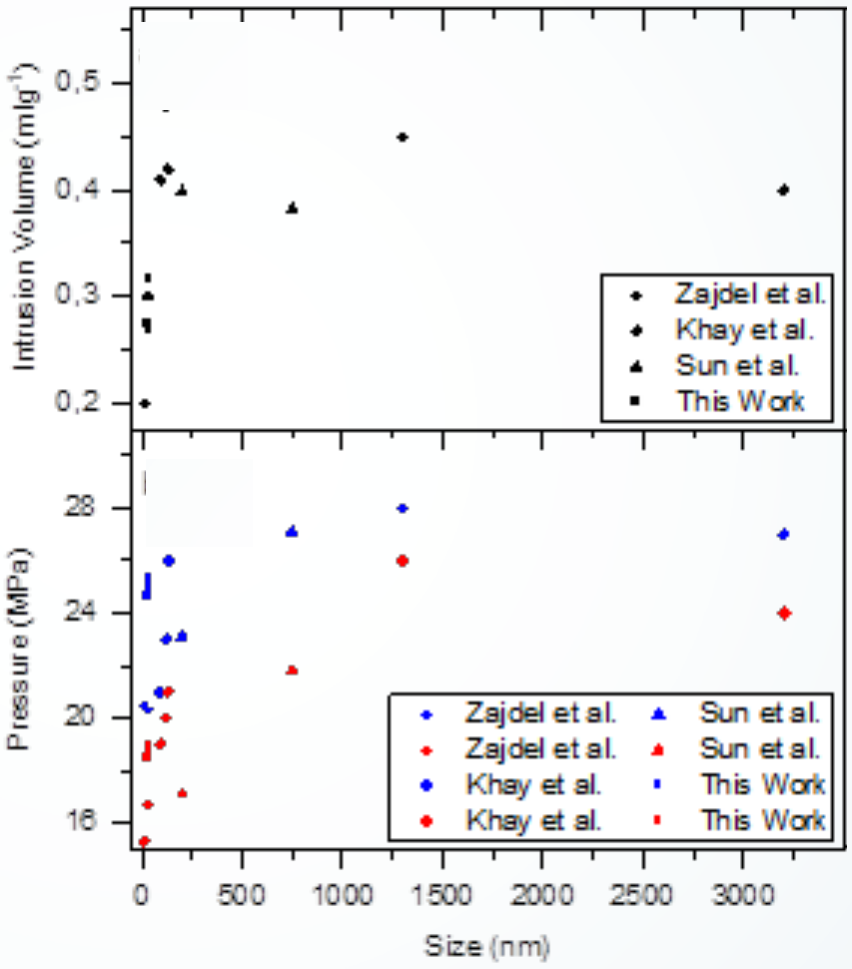
Crystallite size dependency in intrusion





Visit Liam’s poster

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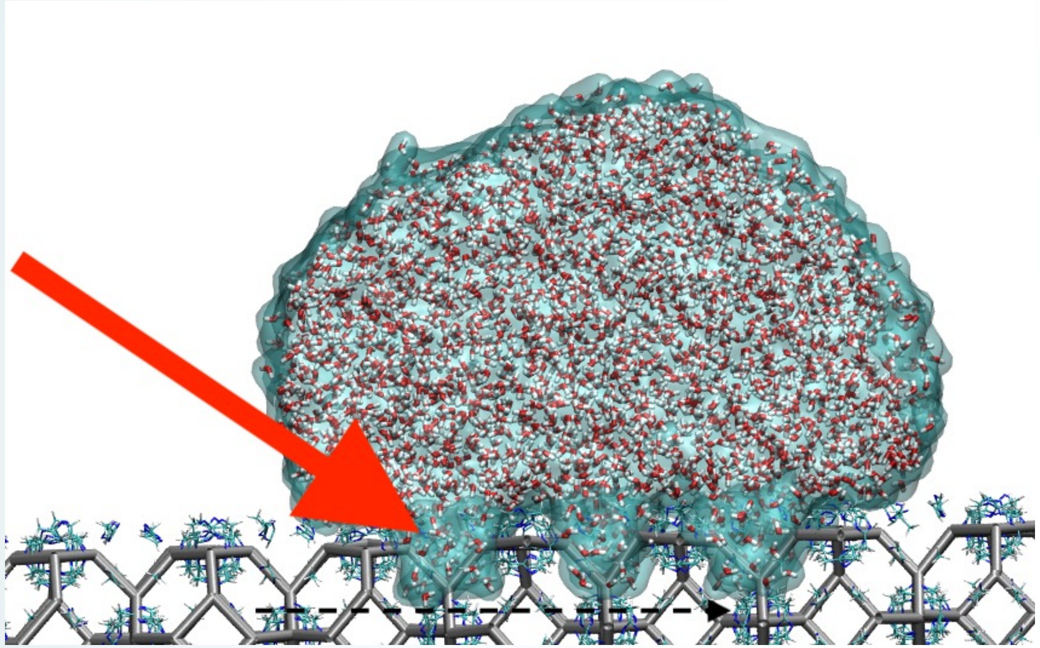
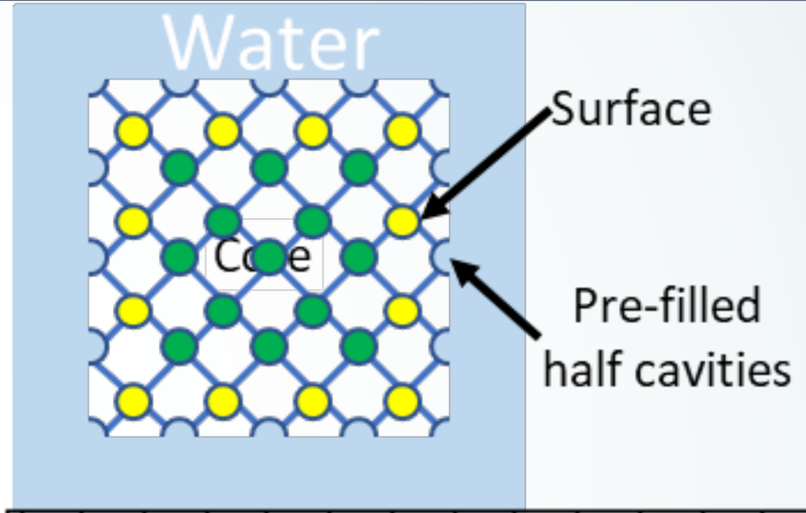
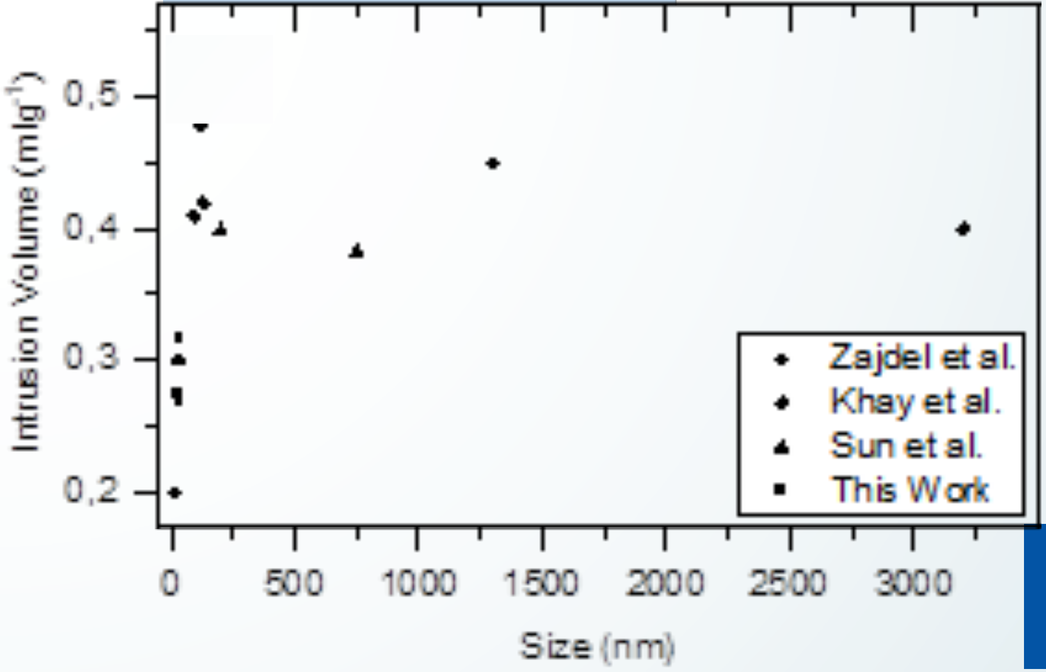
Optimization of the Wetting-Drying Characteristics of Hydrophobic Metal Organic Frameworks via Crystallite Size: The Role of Hydrogen Bonding between Intruded and Bulk Liquid, Johnson et al, J. Colloid Interface Sci. 645, 775 (2023)

Intruded volume shrinking with decreasing size



$$\frac{V}{m} = \left(1 - \frac{3}{2N}\right)\frac{V_\infty}{\mathrm{m}}$$

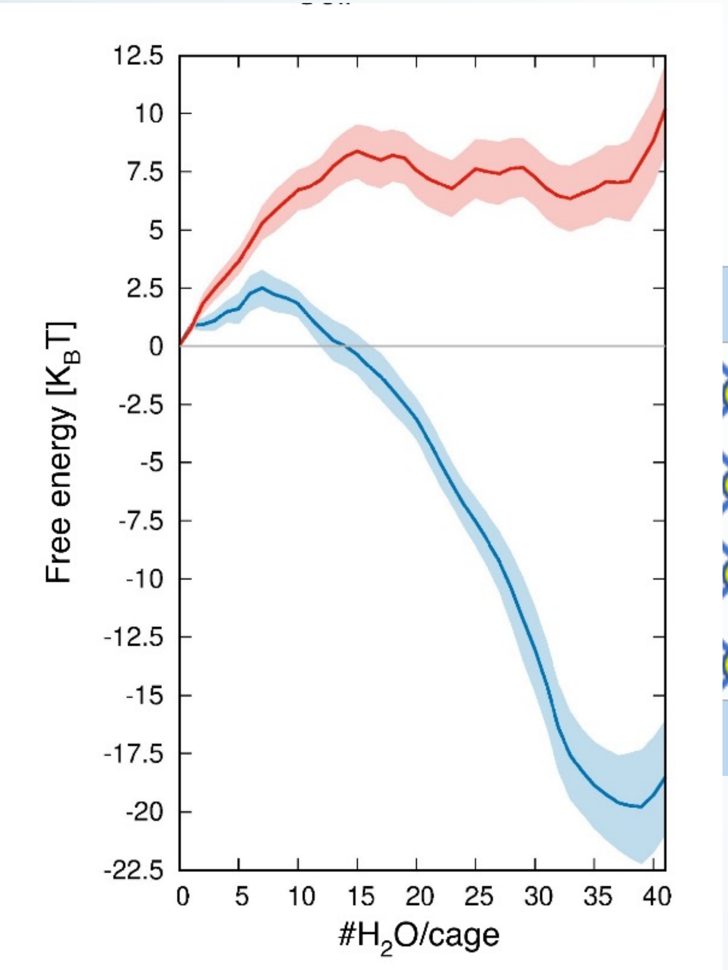


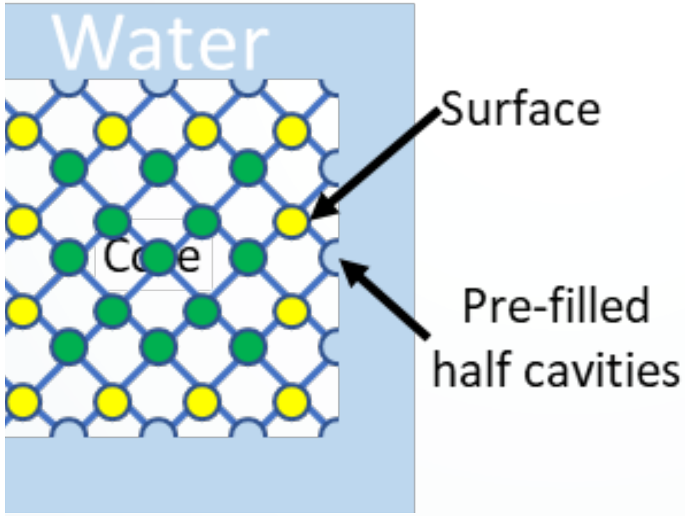


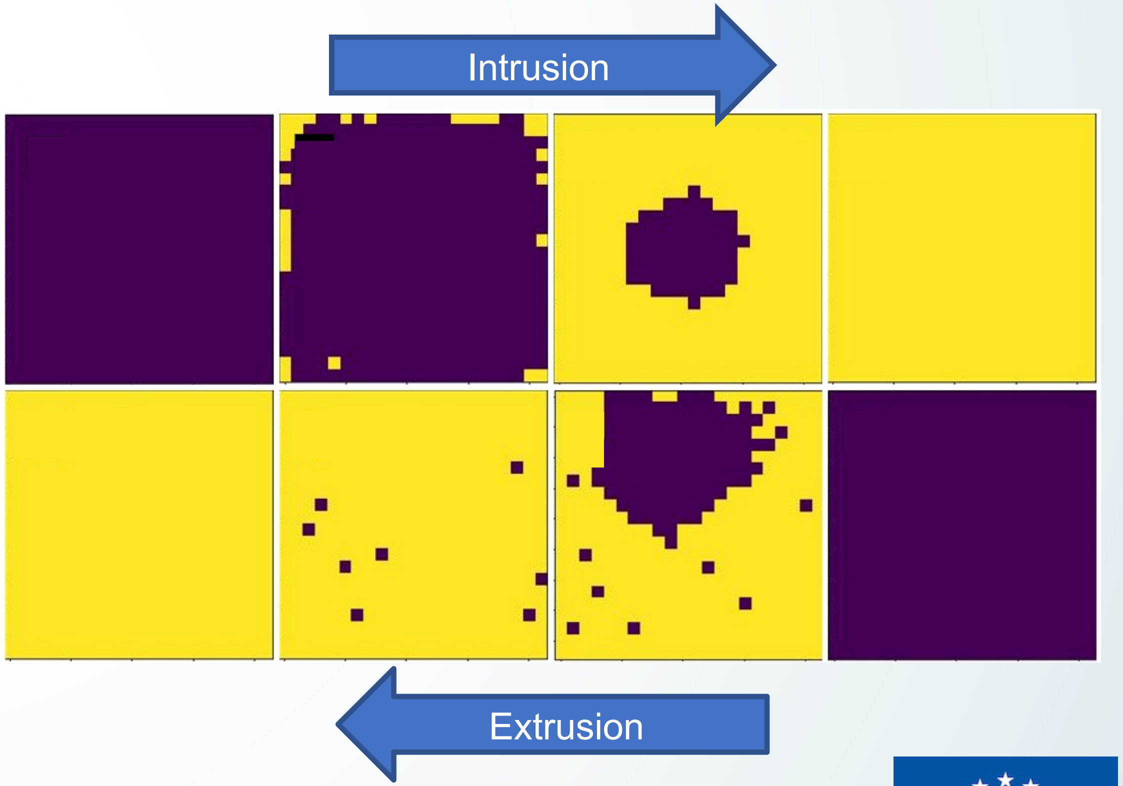
Stochastic model of intrusion in crystallites

$$t_f = t_f^0 e^{\frac{\Omega_f}{k_B T}}$$

$$t_e = t_e^0 e^{\frac{\Omega_e}{k_B T}}$$







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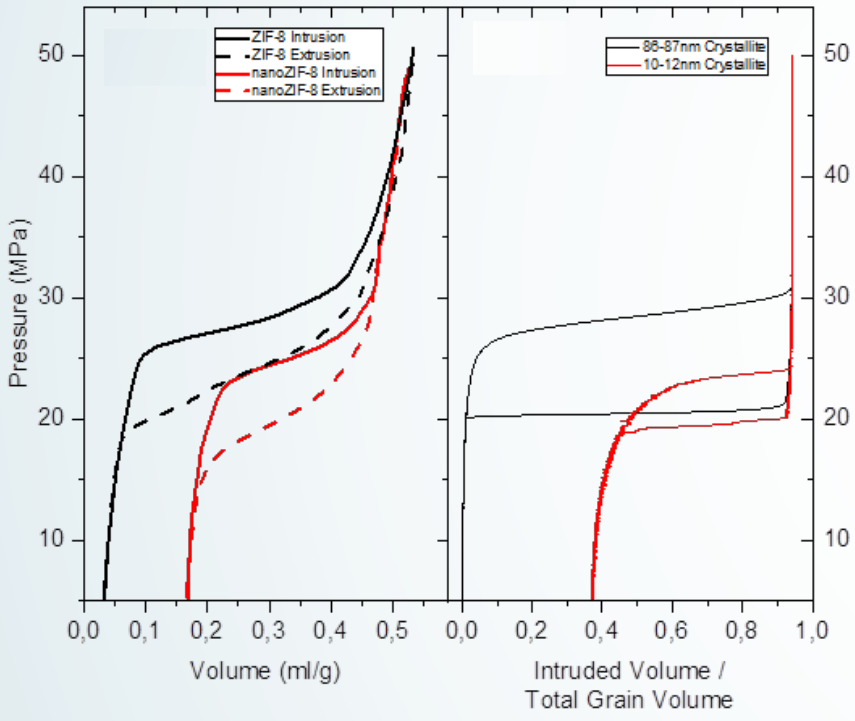
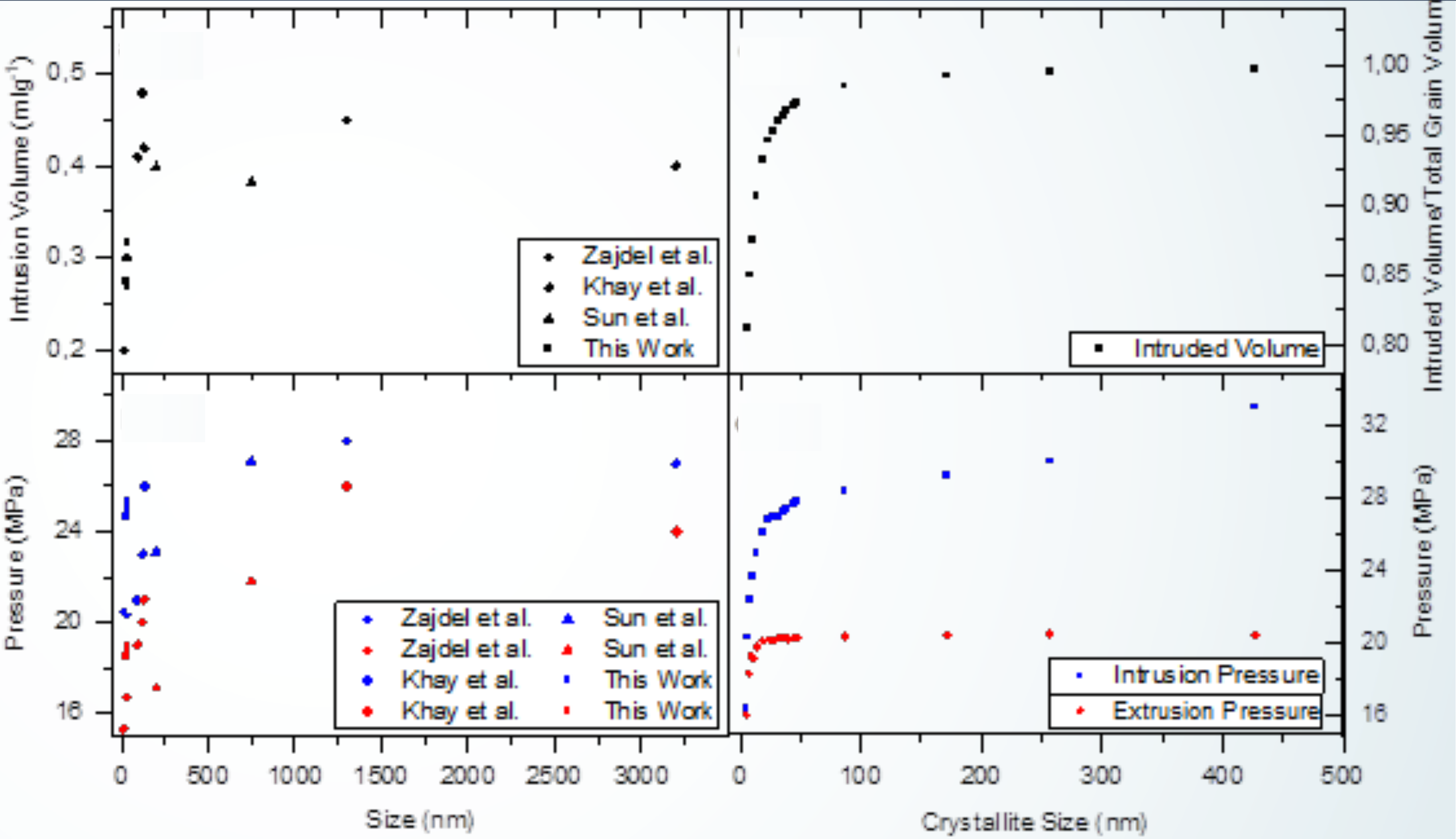




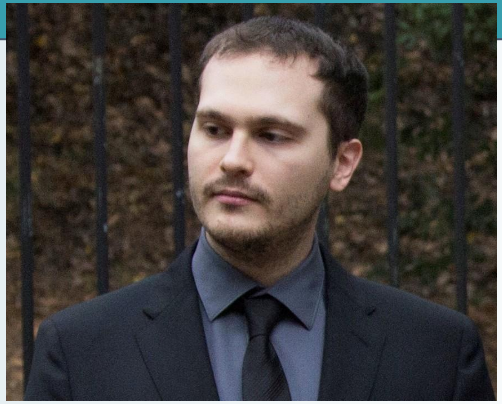
Conclusions

- Kinetics and int/ext pressures in nanometric materials with sub-nanometric apertures violate Young-Laplace, which previously we have shown to work for slightly larger apertures.

- The process is not capillary condensation, it still looks like front advancing, minimizing the pseudo-liquid/pseudo-vapor interface area.

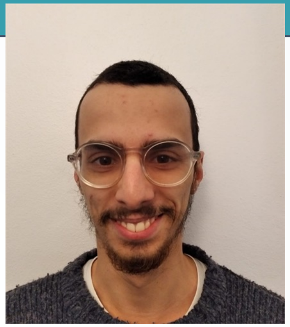
- This mechanism determines the crystallite size dependence of the int/ext pressure, opening novel perspectives for exogenit tuning.

Acknowledgements


Marco Tortora

Seb Merchiori


Alberto Giacomello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Yaroslav Grosu


Carlo Massimo Casciola


Josh Littlefair


Andrea Le Donne


Liam Johnson


Eder Amayuelas

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