Intrusion of water in hydrophobic crystalline porous materials

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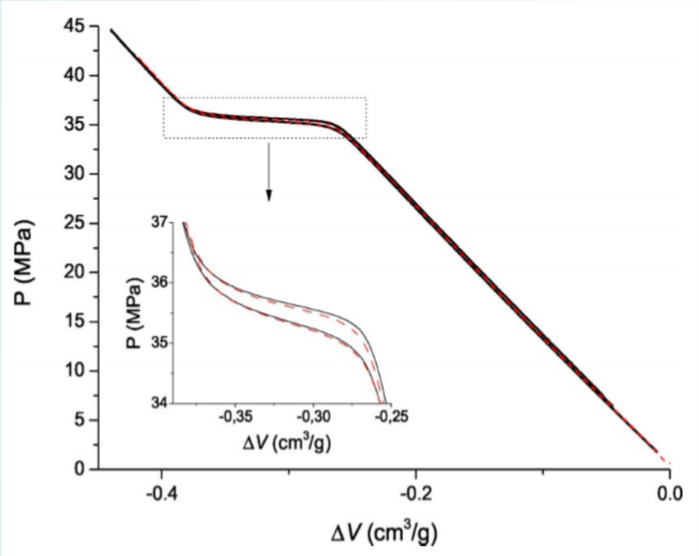
Metastability and multiscale effects in interfacial phenomena

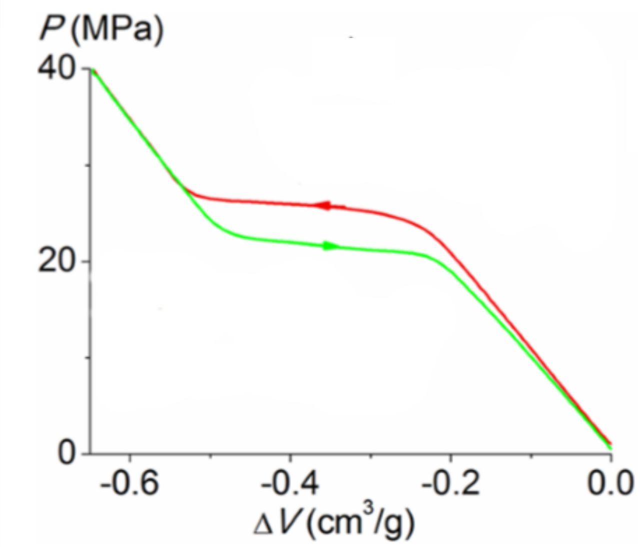
Lausanne, 13-15 March 2023

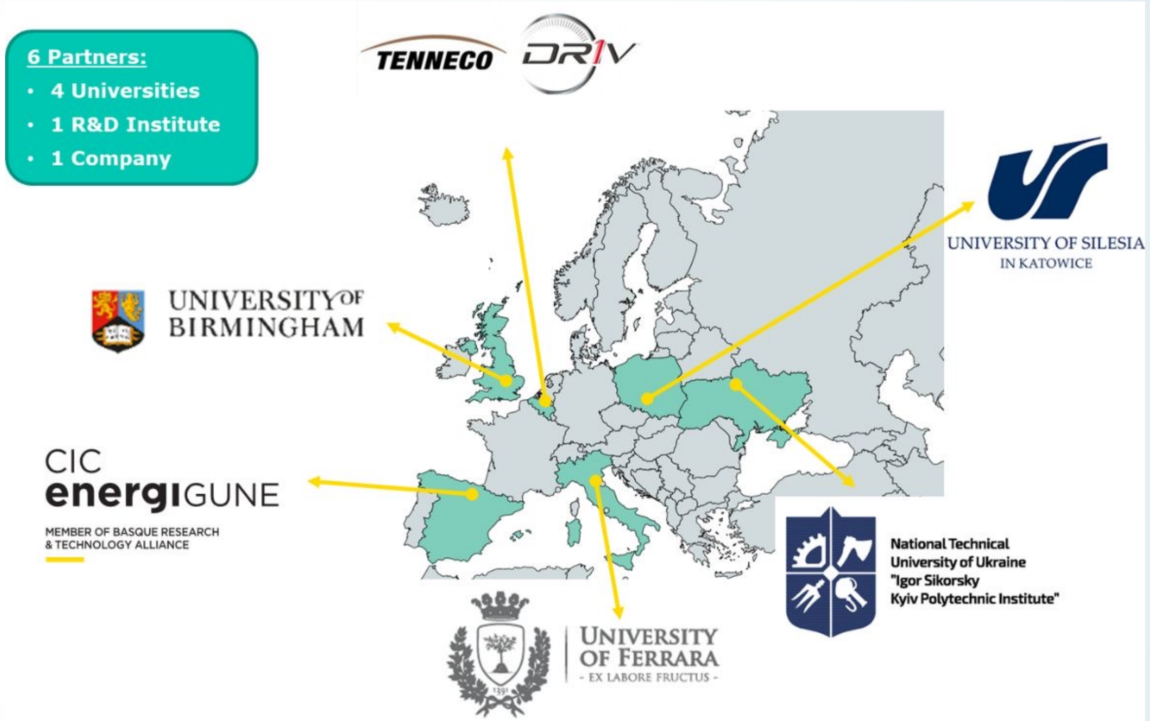
FERRARIAE UNIVERSITAS · 13 91 · EX LABORE FRUCTUS

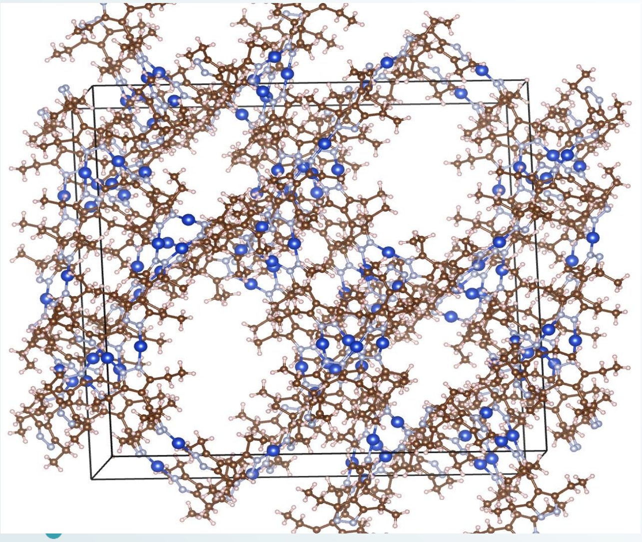
ELECTRO INTRUSION

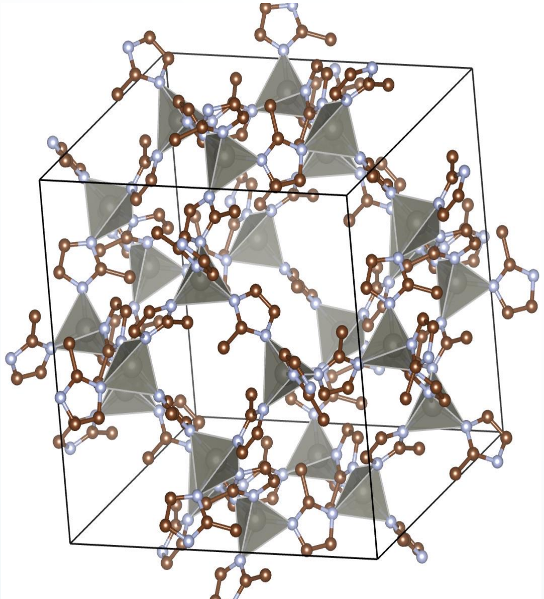
Crystalline porous media: MOFs











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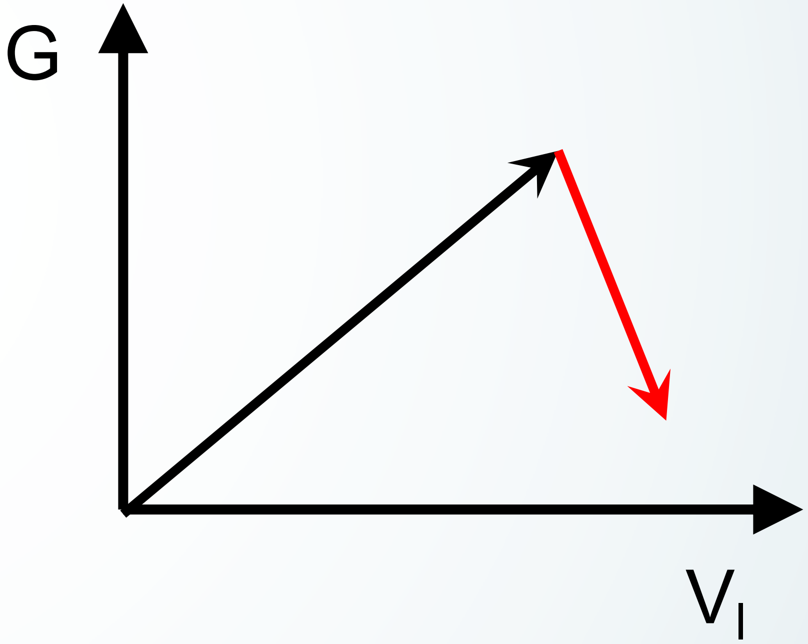
Intrusion/extrusion in hydrophobic porous materials: a thought experiment

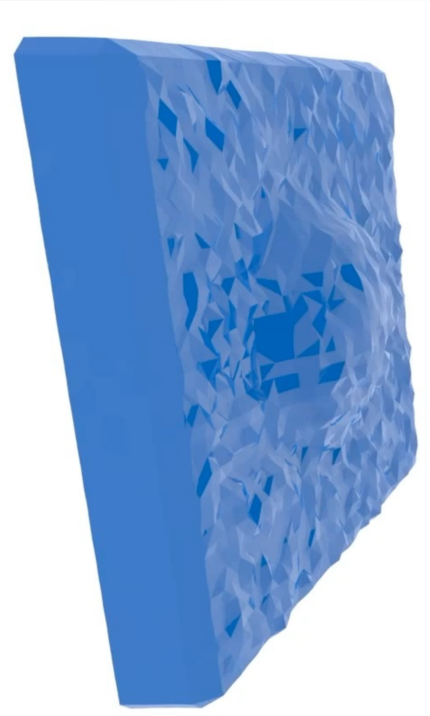
$$\Omega = \cancel{\Delta P} V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

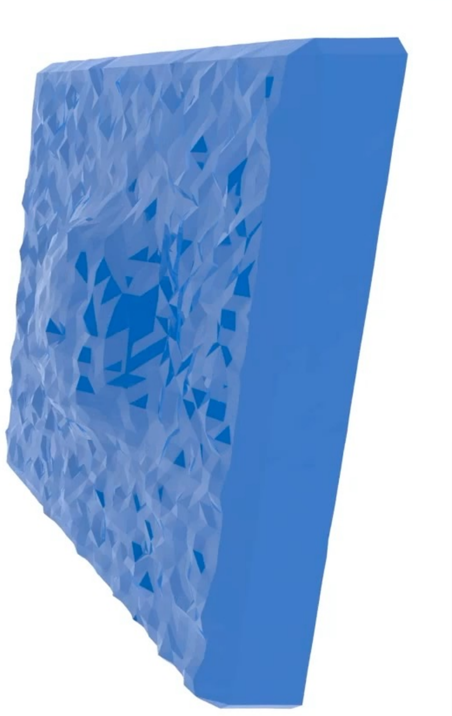


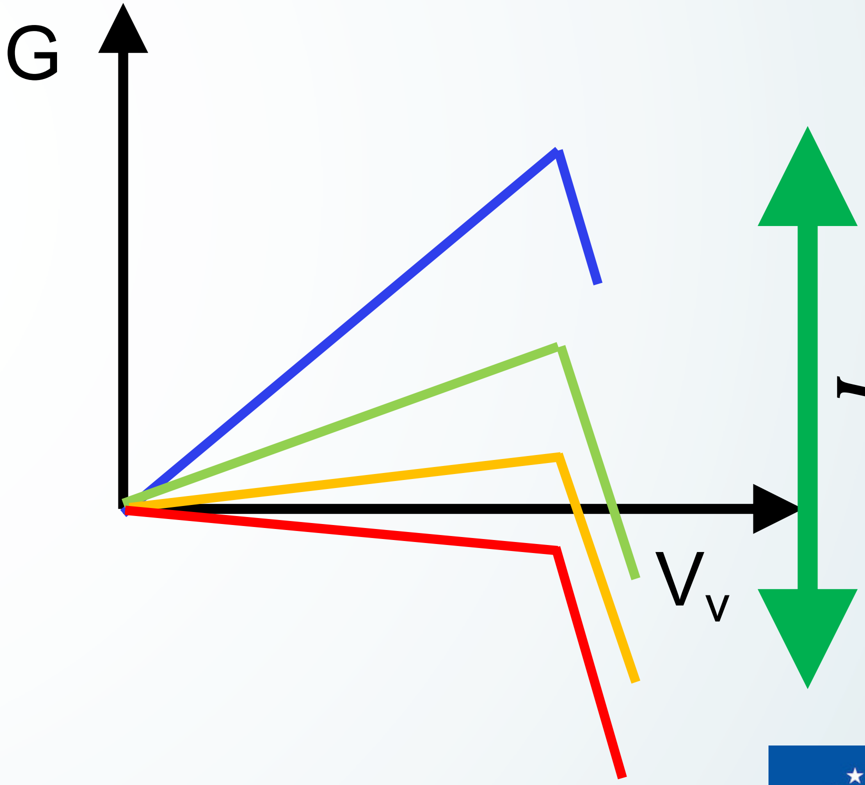

A. Tintii

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

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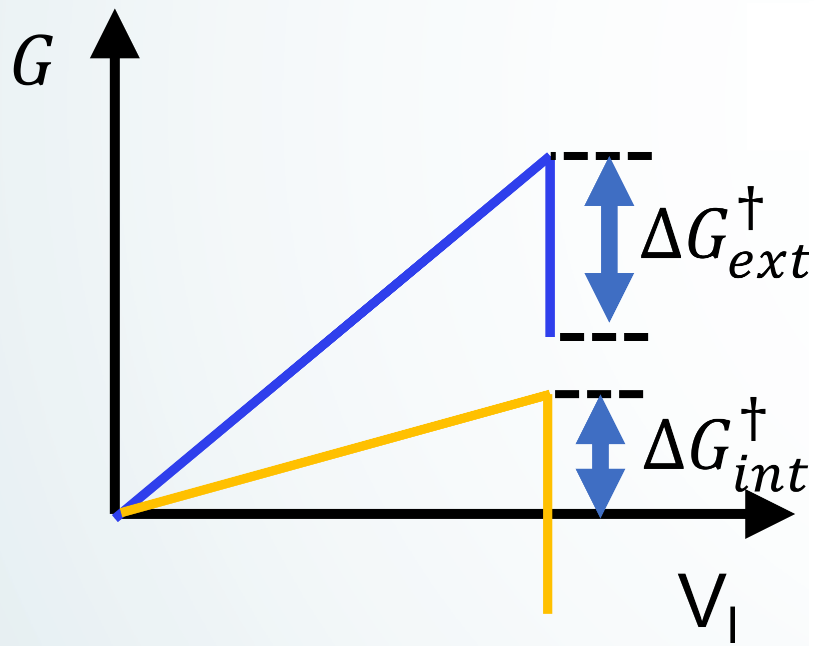
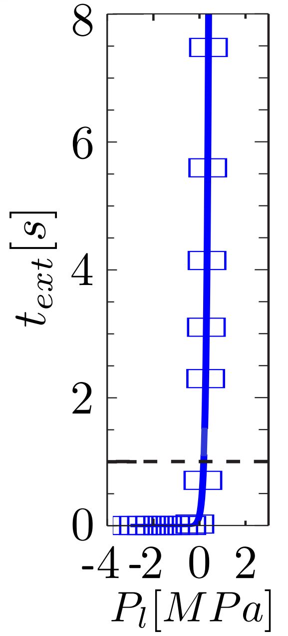
Intrusion and extrusion pressure and hysteresis

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

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

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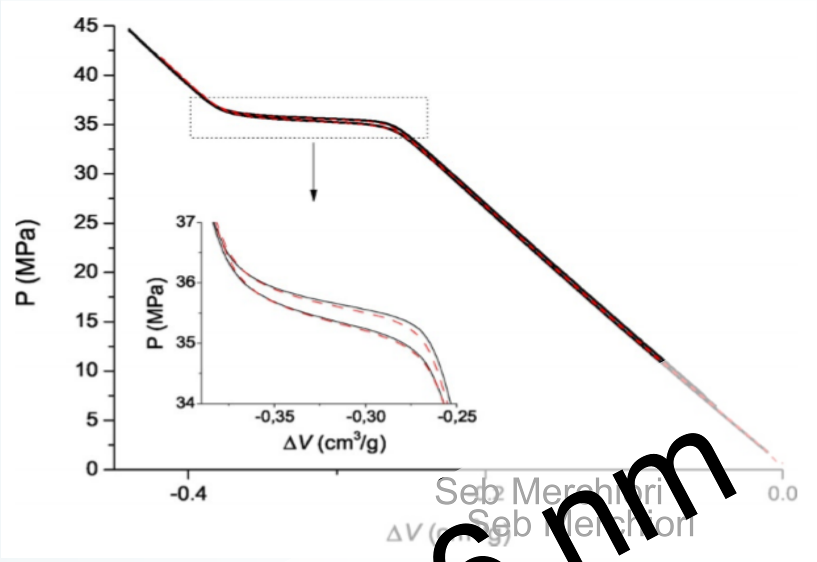
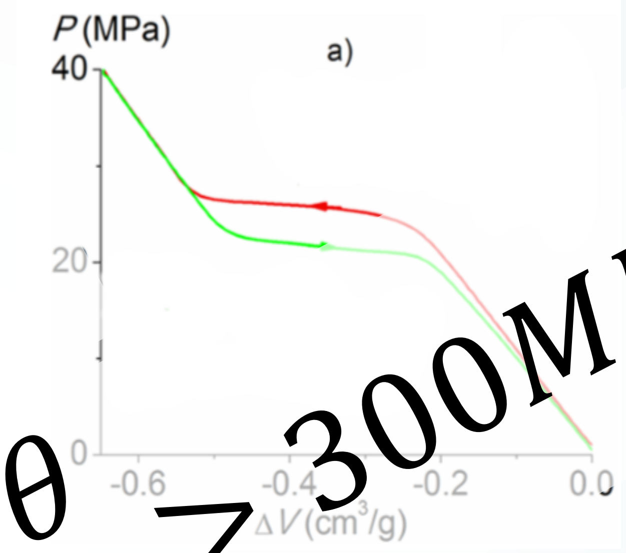
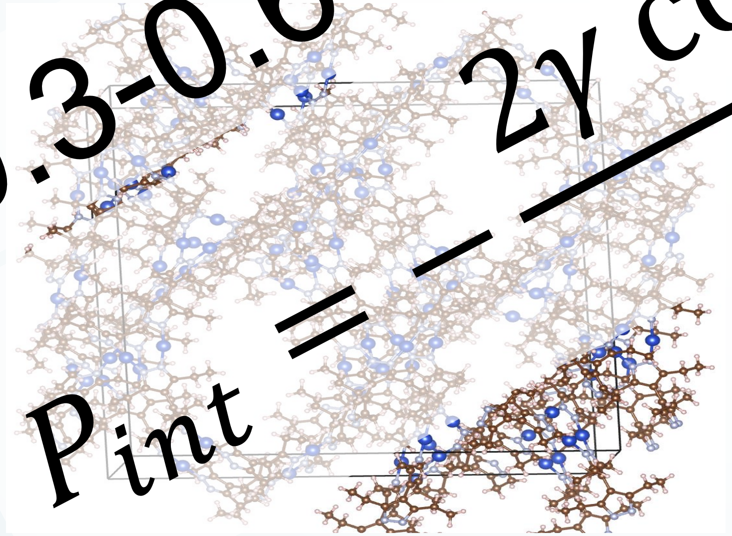
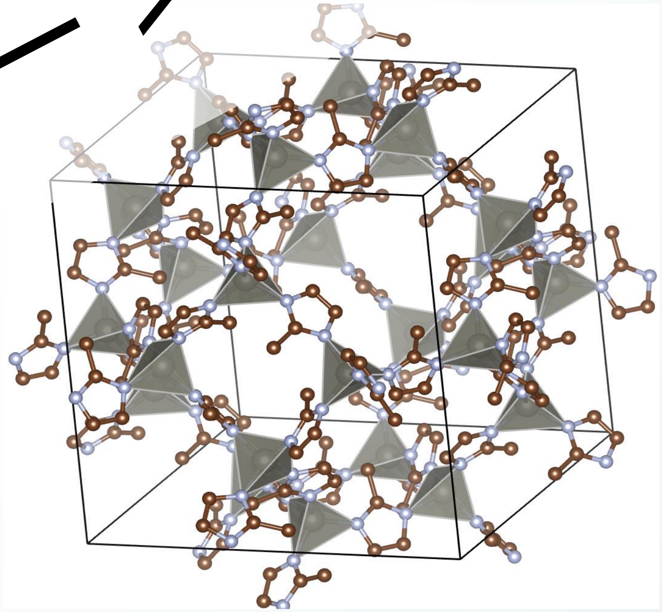




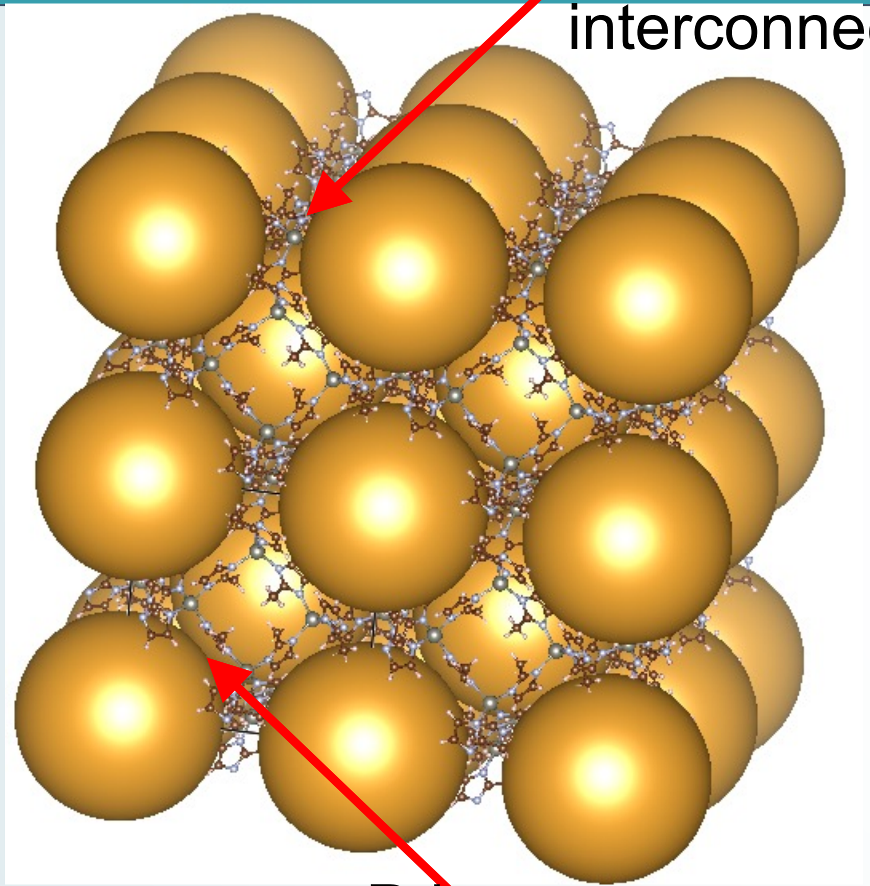
r=0.3-0.6 nm

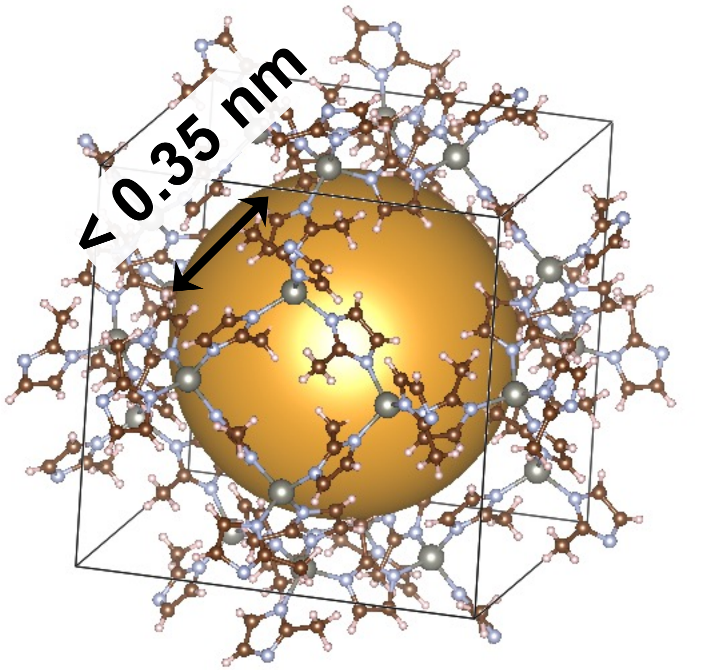
$$P_{int} = -\frac{2\gamma\cos\theta}{r} > 300\,MPa$$



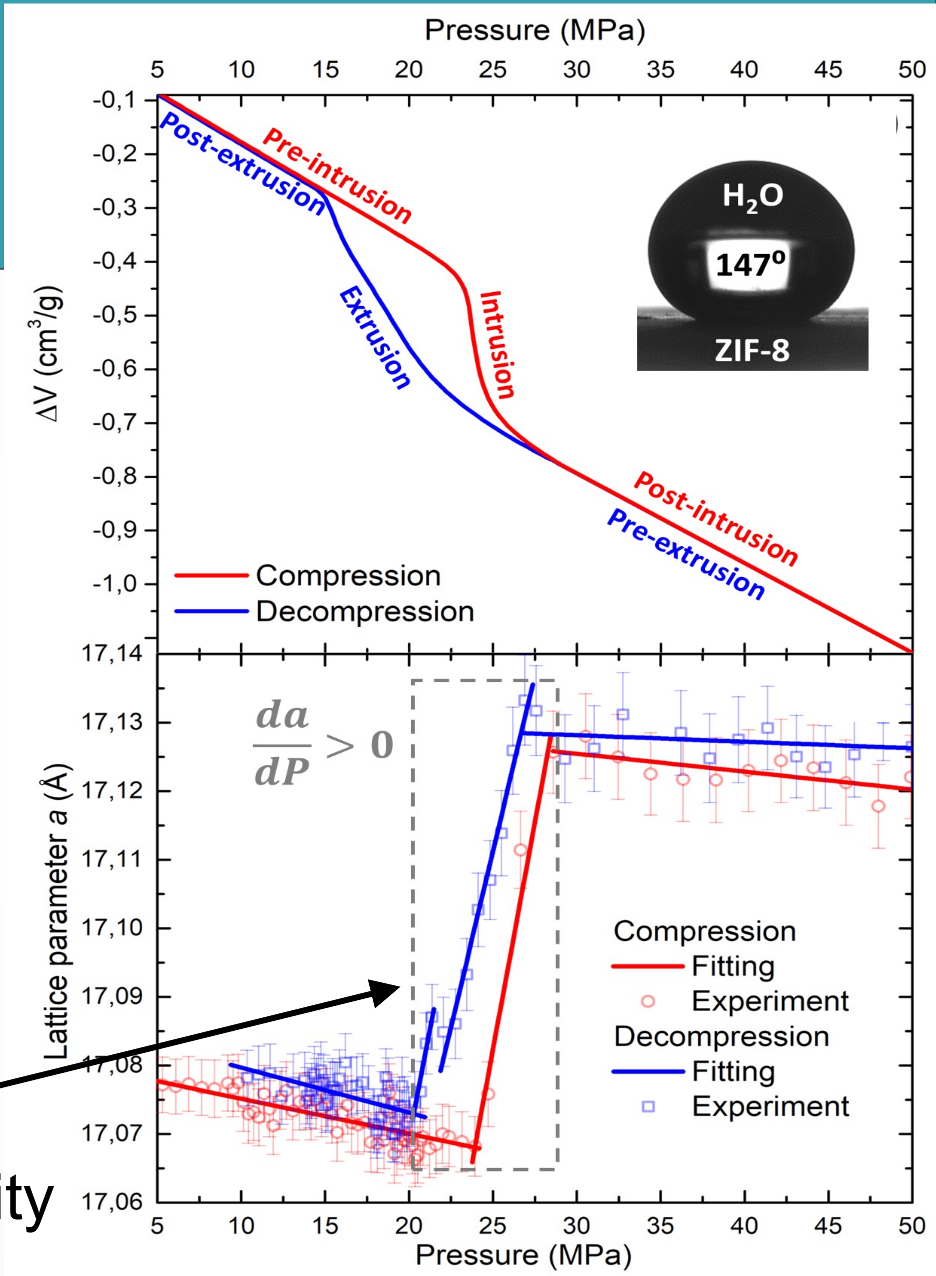


Peculiarities of ZIF-8





Exceptional Negative Compressibility



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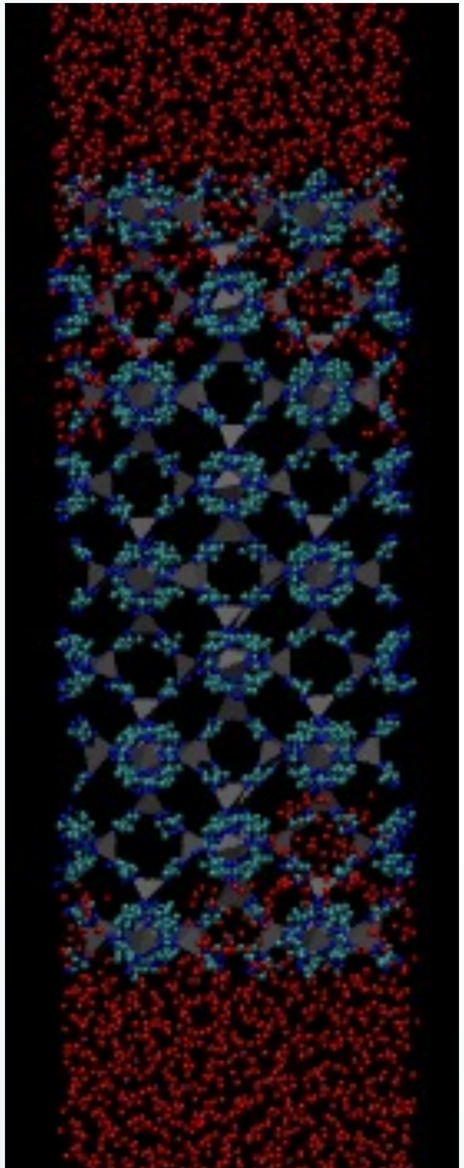
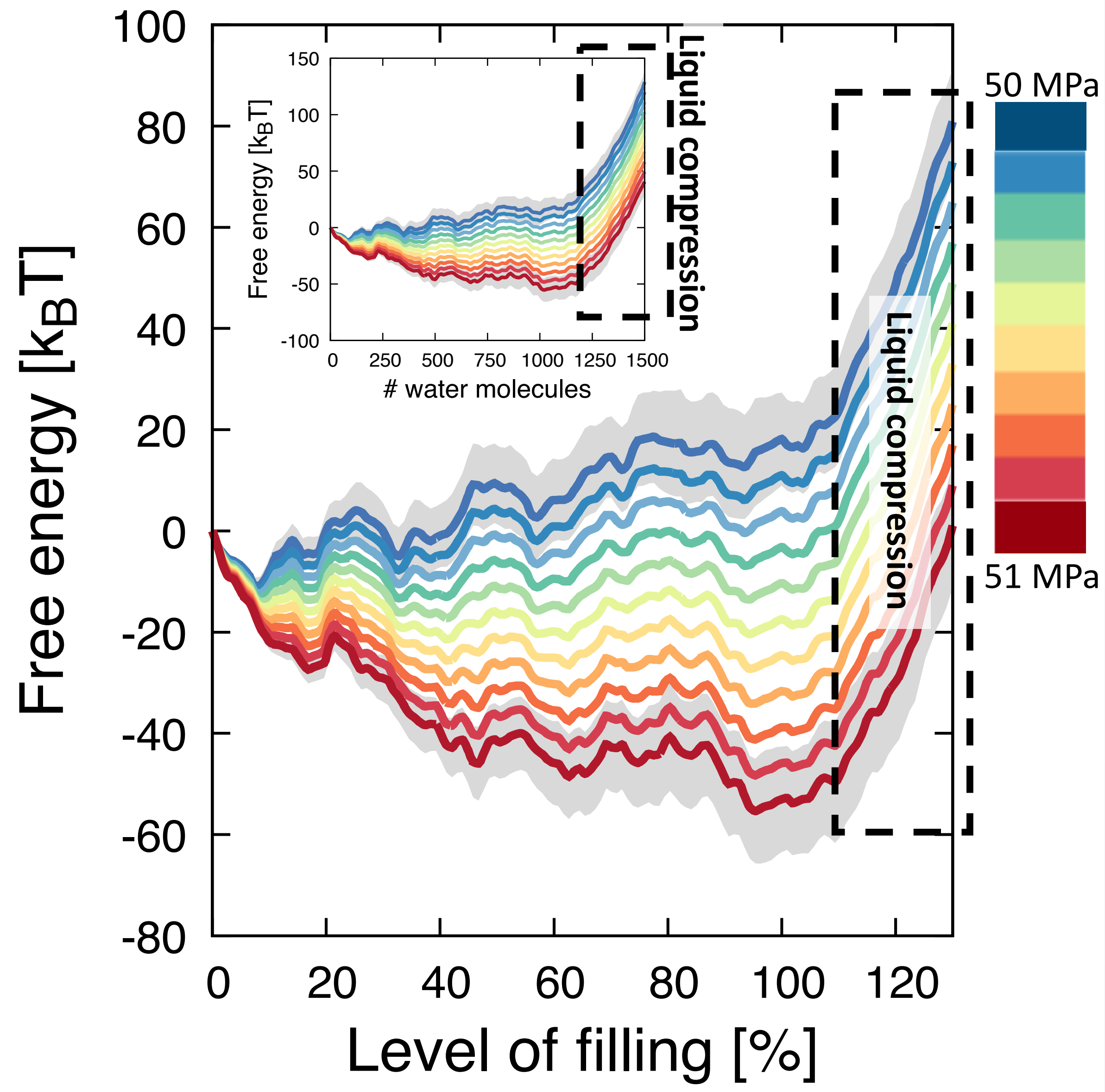
Giant Negative Compressibility by Liquid Intrusion into Superhydrophobic Flexible Nanoporous Framework Tortora et al, Nano Letters 21, 2848-2853

Int/ext free energy profile *vs* pressure





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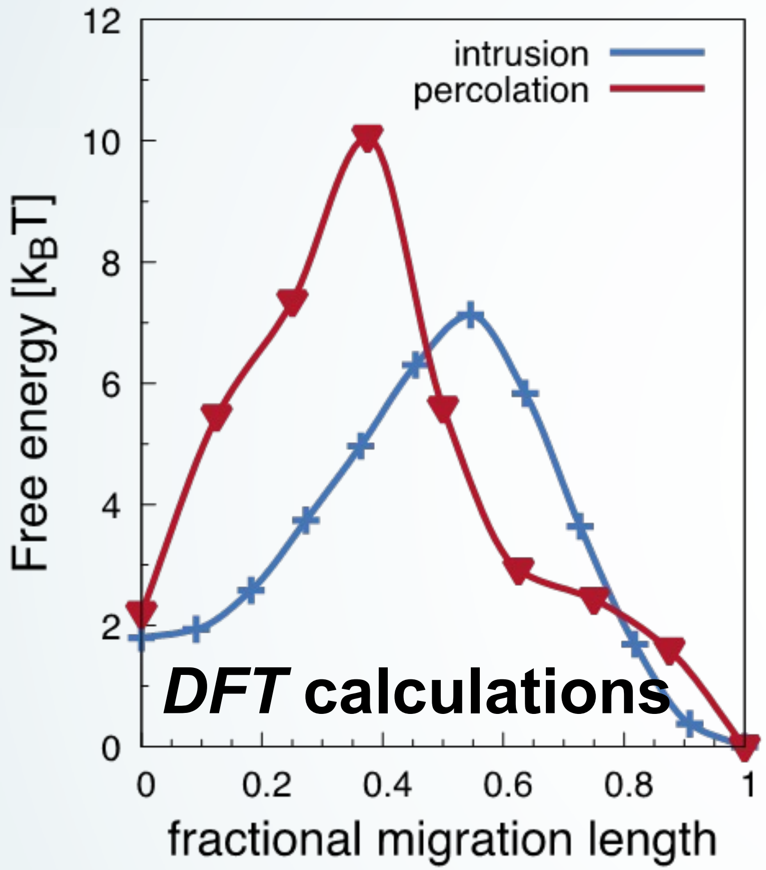
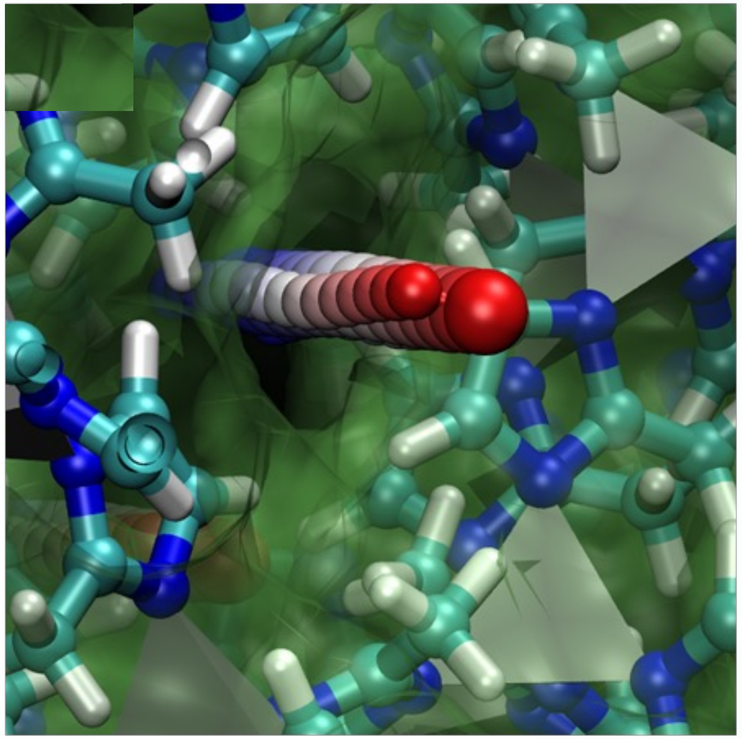
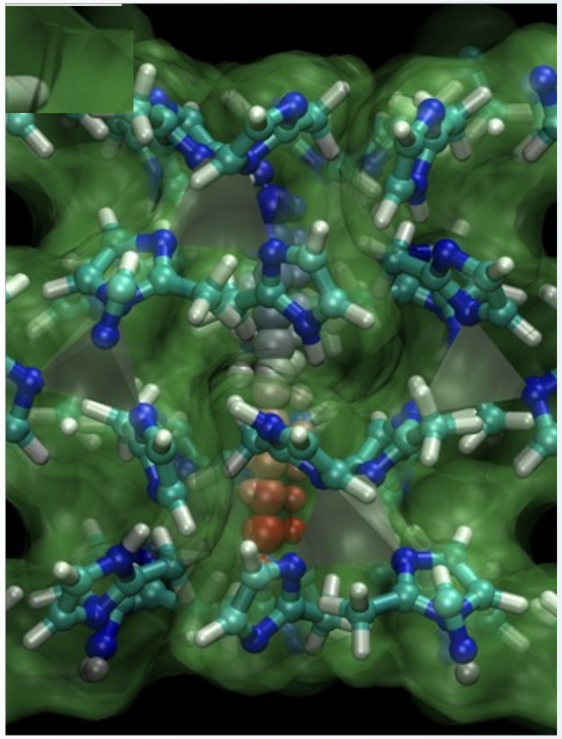
Single water molecules “intrusion”





Intrusion



Percolation

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

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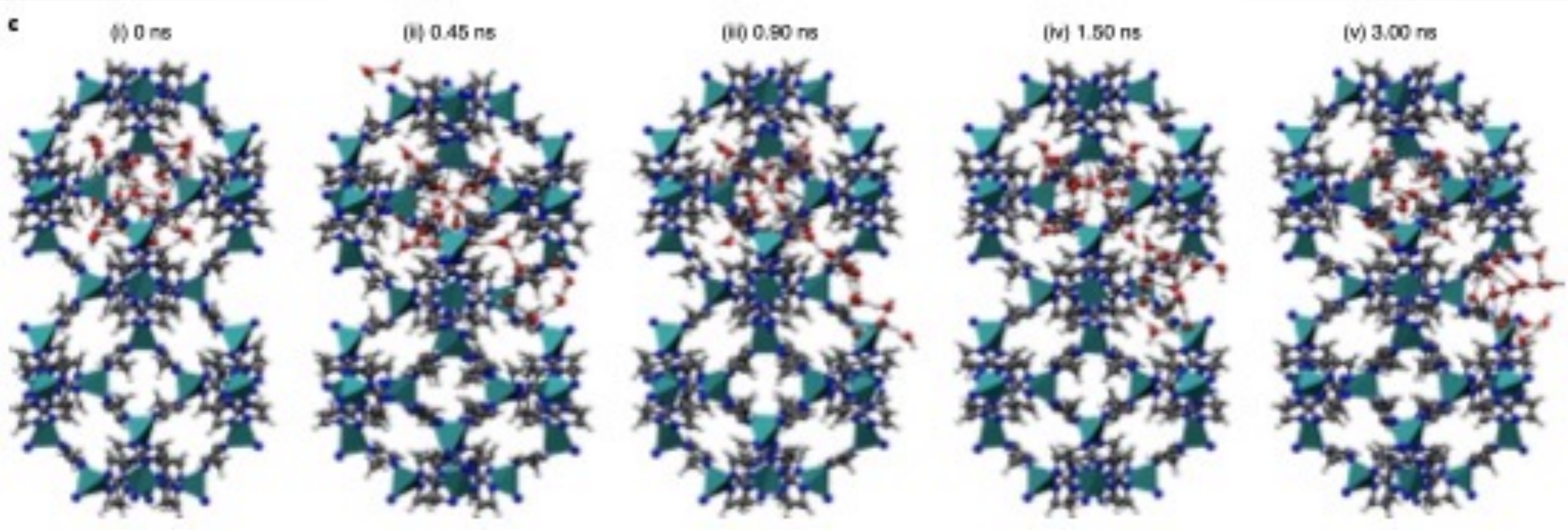
Turning molecular spring into nano-shock absorber: the effect of macroscopic morphology and crystal size on the dynamic hysteresis of water intrusion-extrusion into-from hydrophobic nanopores, Zajdel et al., ACS Appl. Mater. Interfaces 2022, 14, 26699

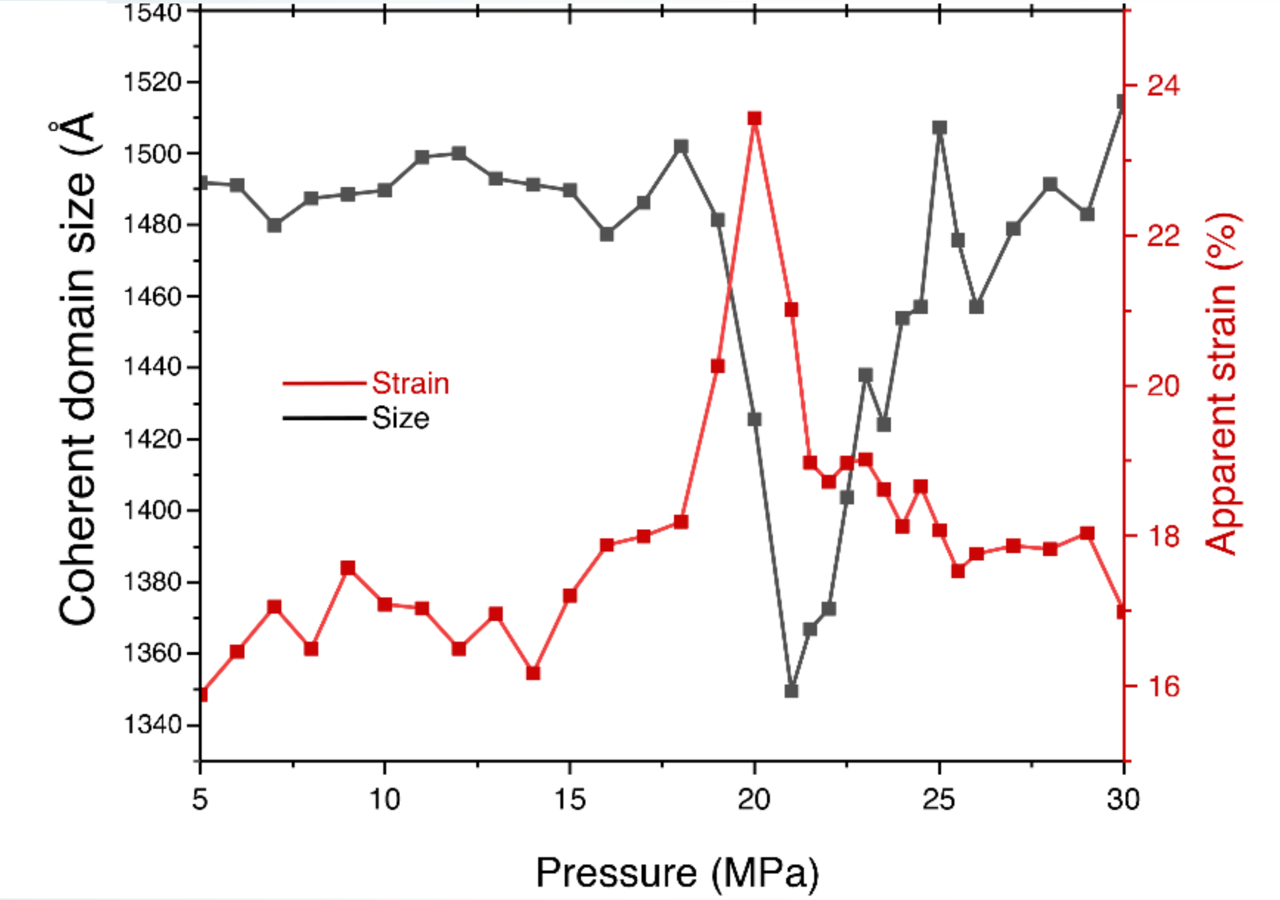
Proposed mechanism: capillary condensation

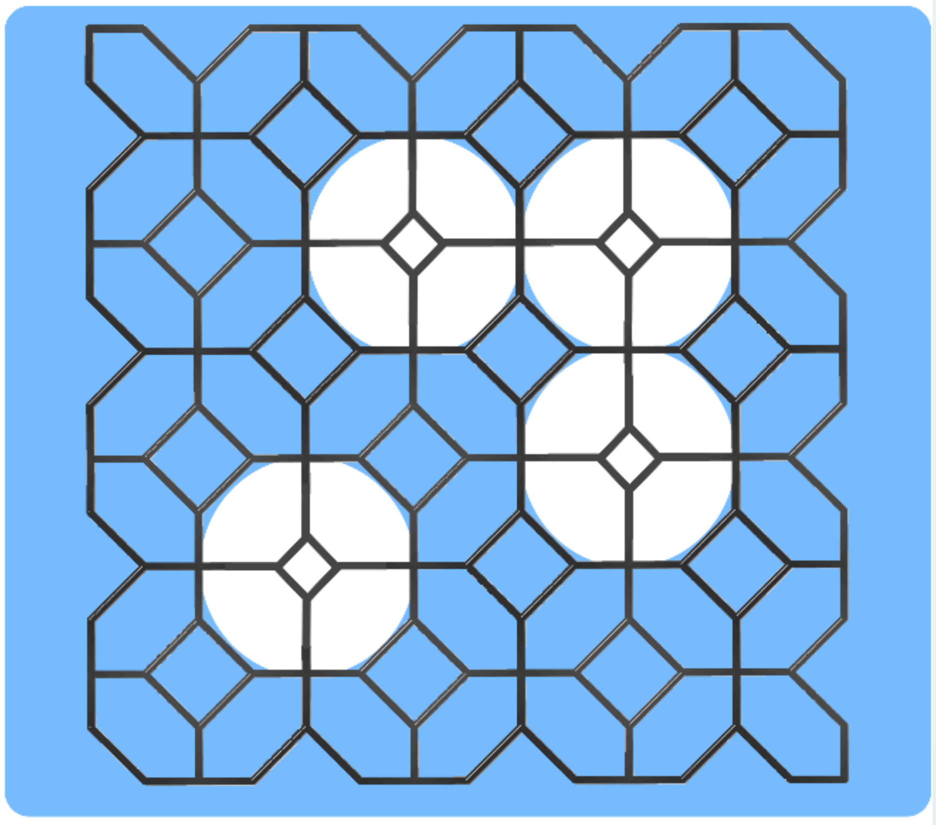


Grand Canonical simulations

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

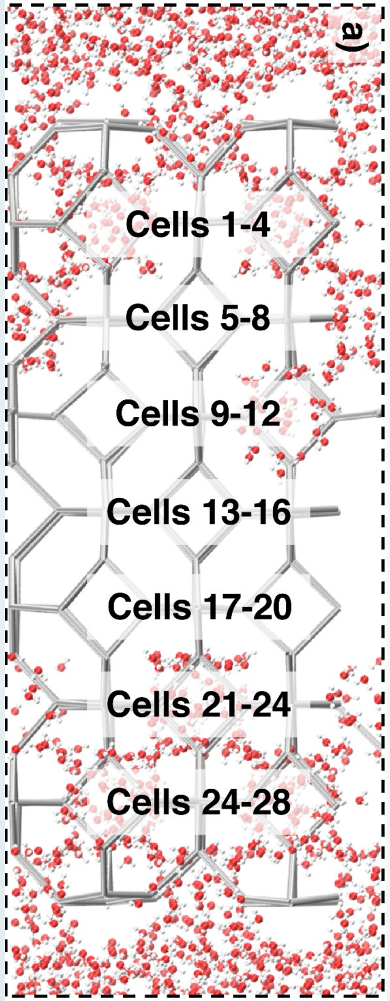
Mismatch with experimental evidence

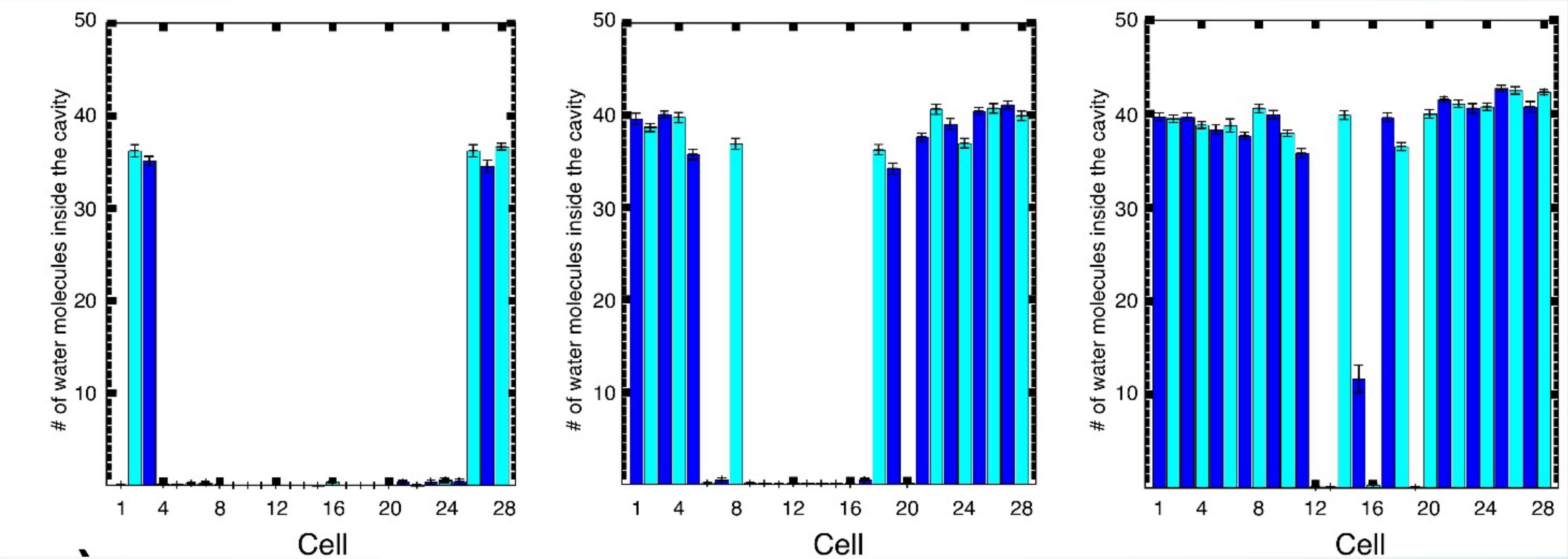




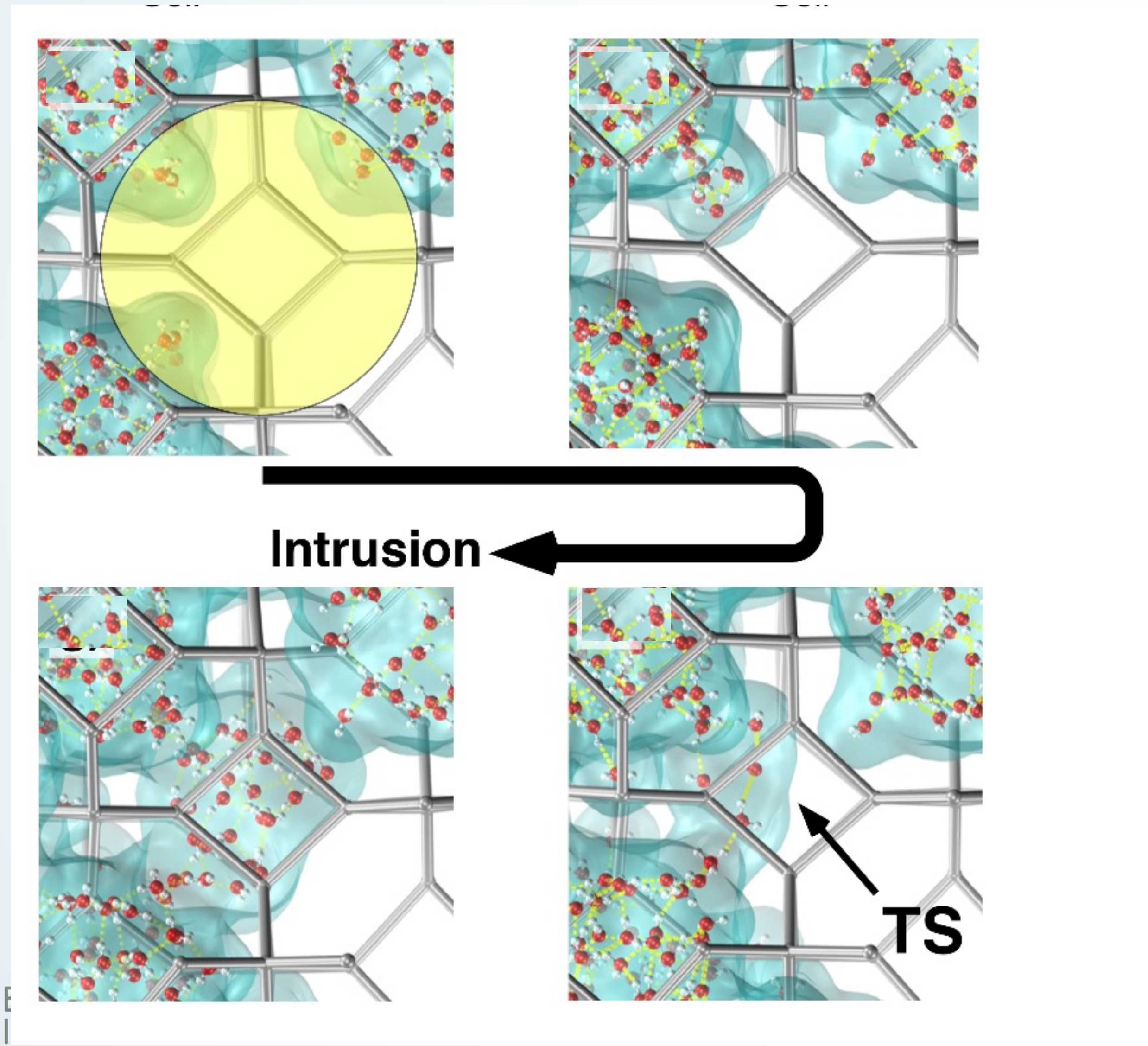
On the mechanism of water intrusion into flexible ZIF-8: liquid is not vapor,
Amayuelas et al, submitted [

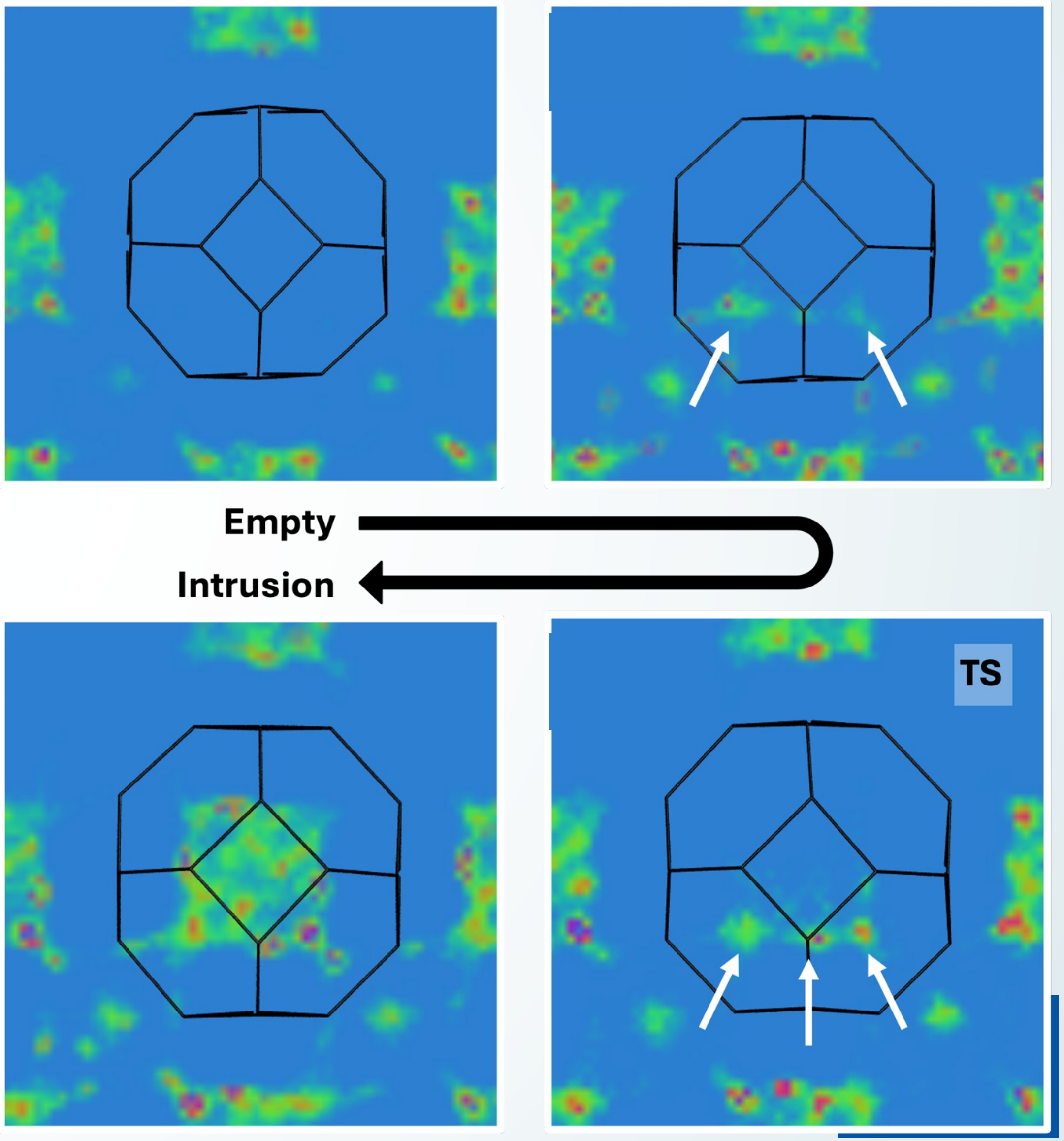
Cage-by-cage intrusion mechanism



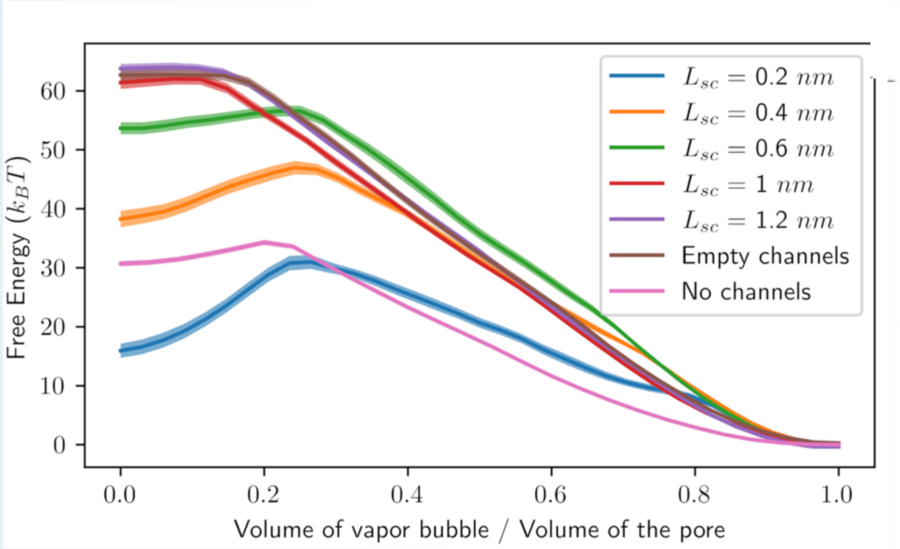


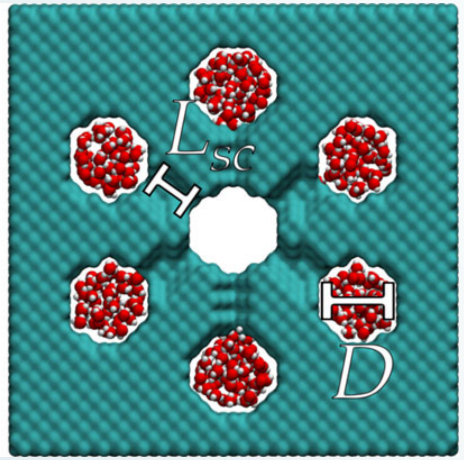
Origin of the intrusion barrier

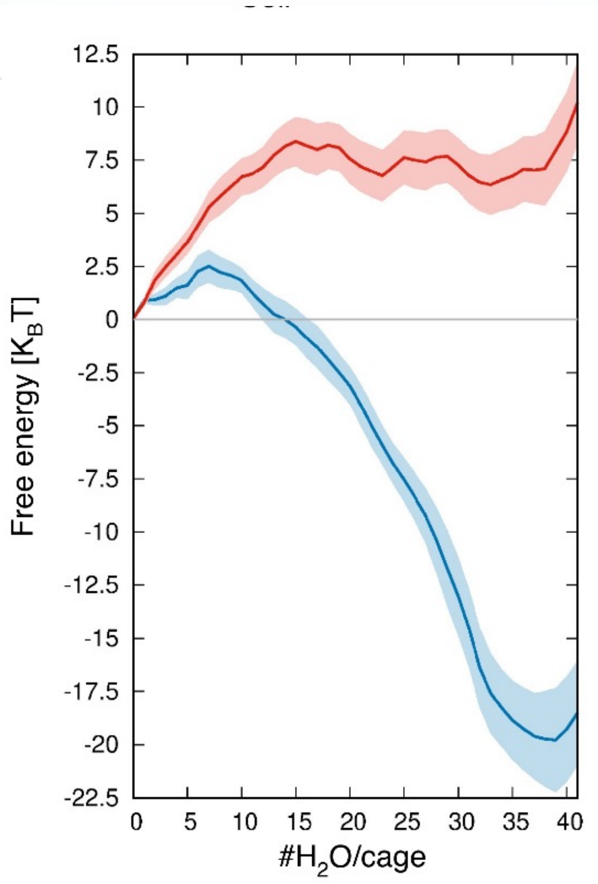


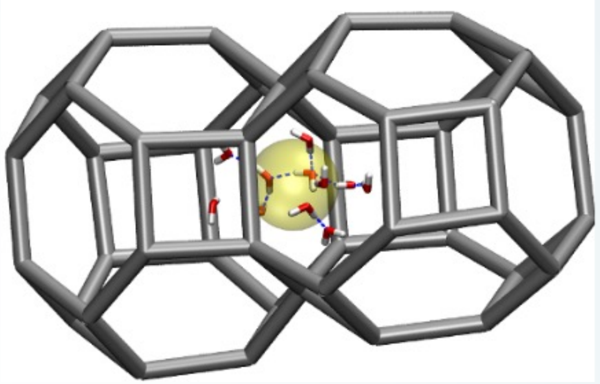


Why cage-by-cage intrusion









	θ_l
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

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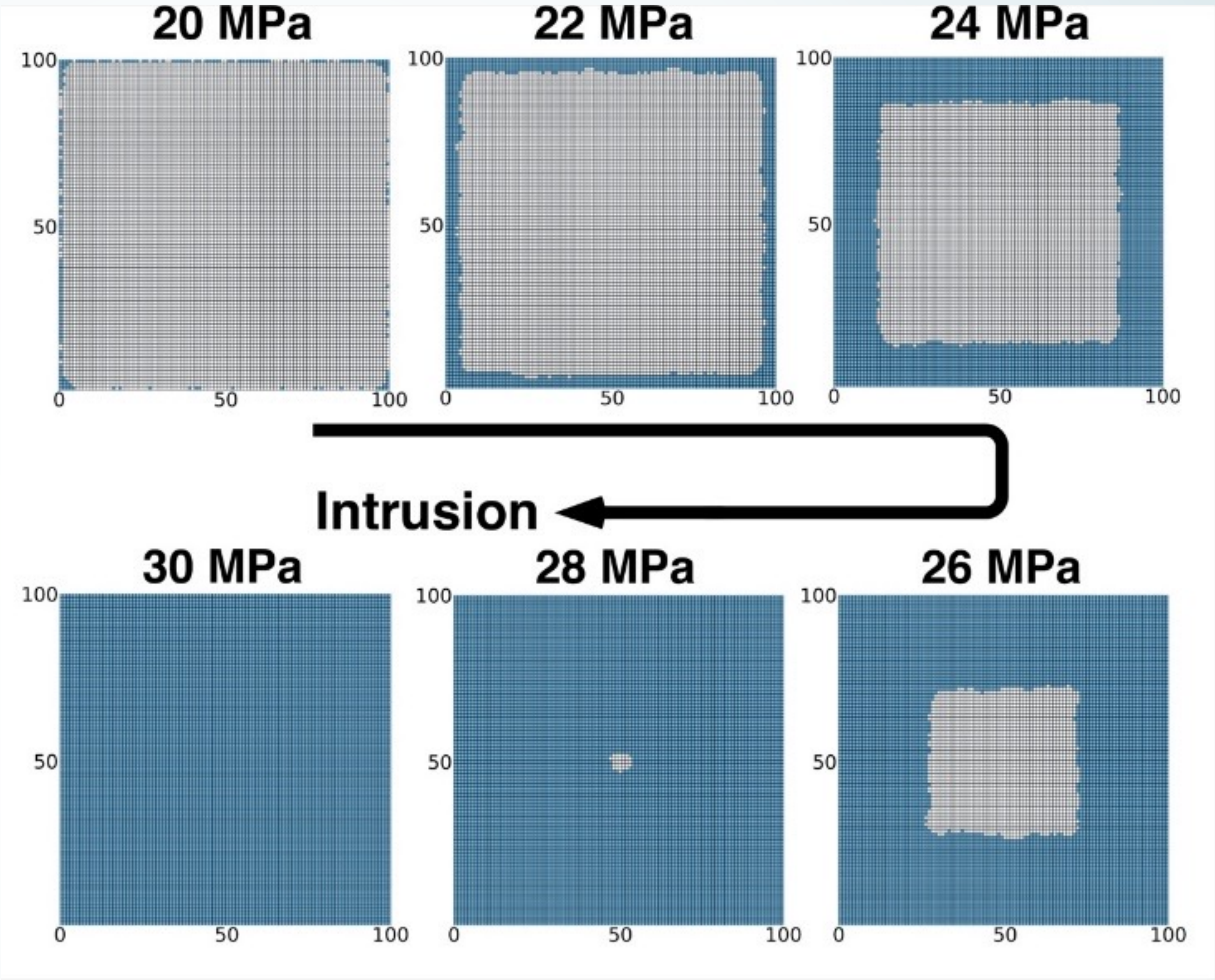
$$t_f = t_f^0 e^{\frac{\Omega_f^\dagger}{k_B T}}$$

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

Effective surface tension in a (porous) medium



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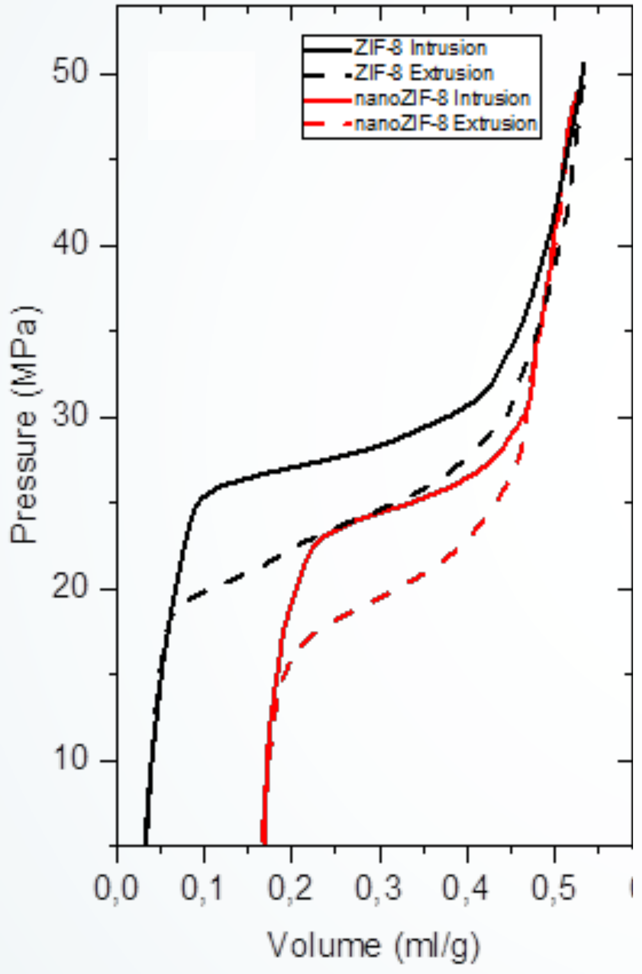
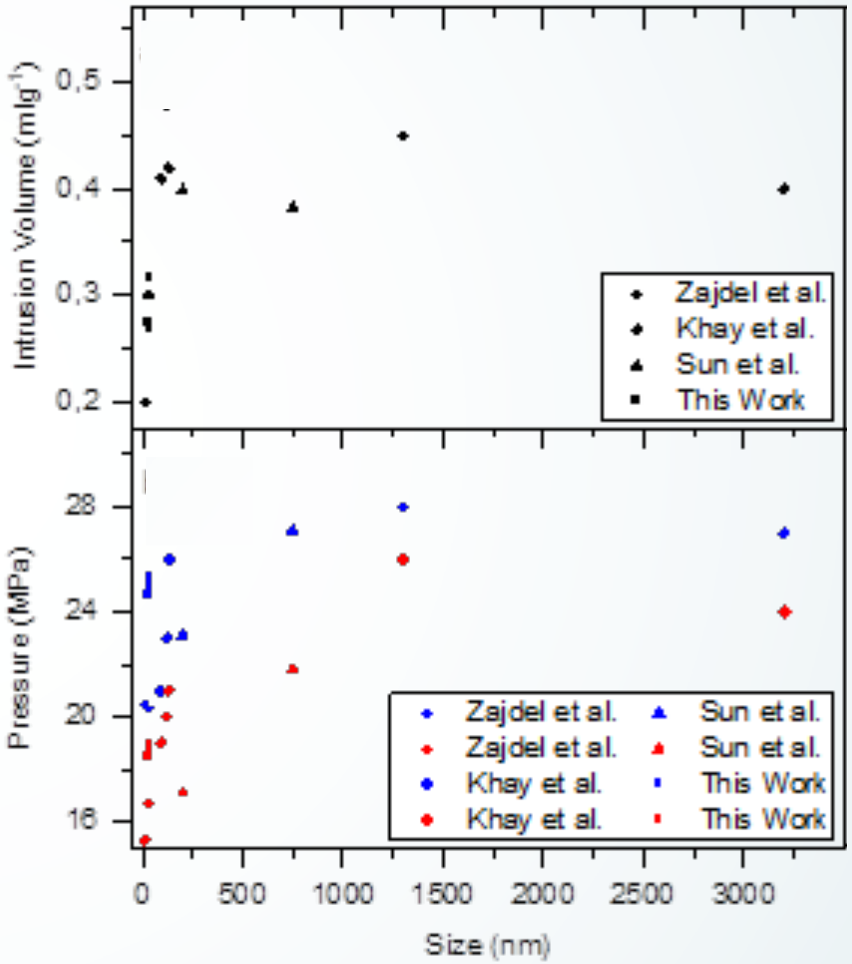
Crystallite size dependency in intrusion





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, submitted

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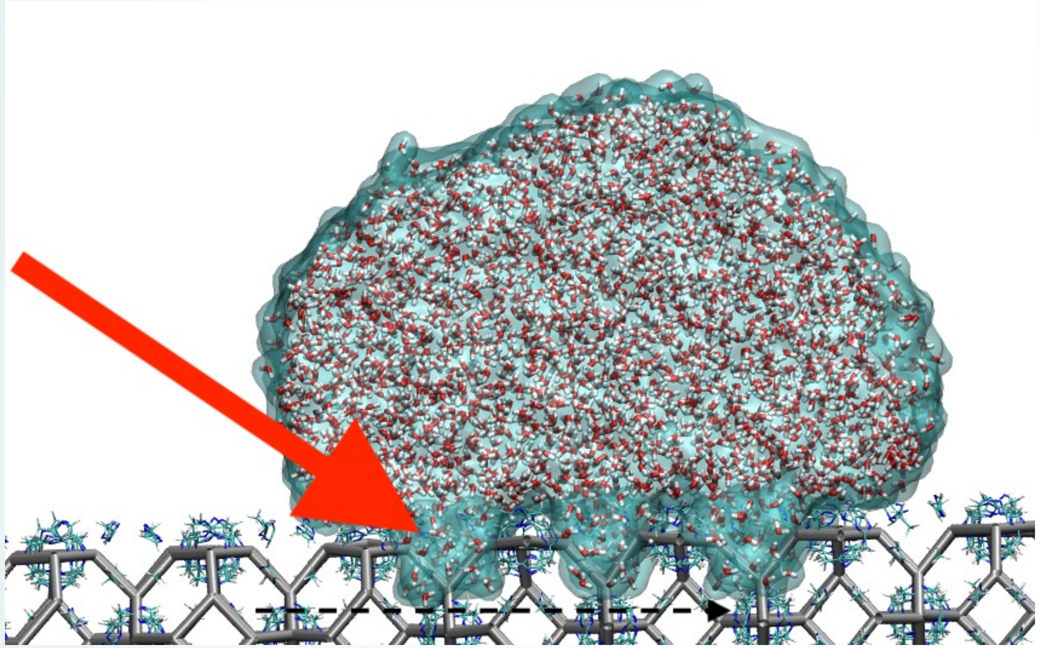
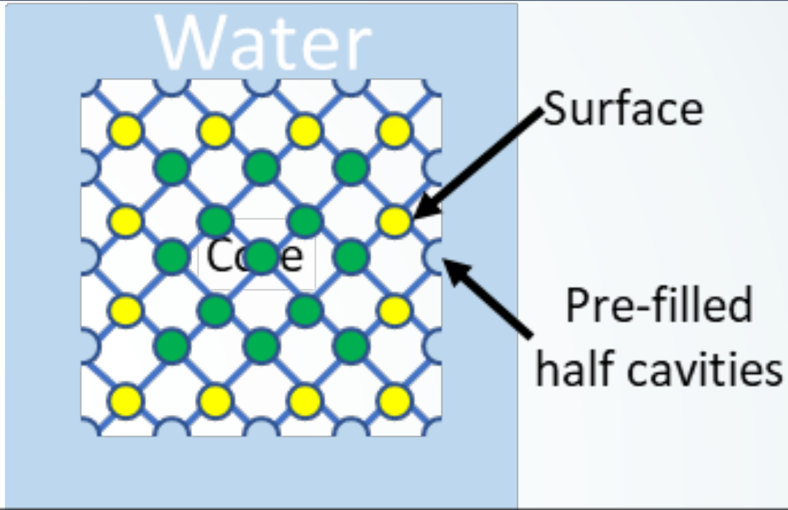
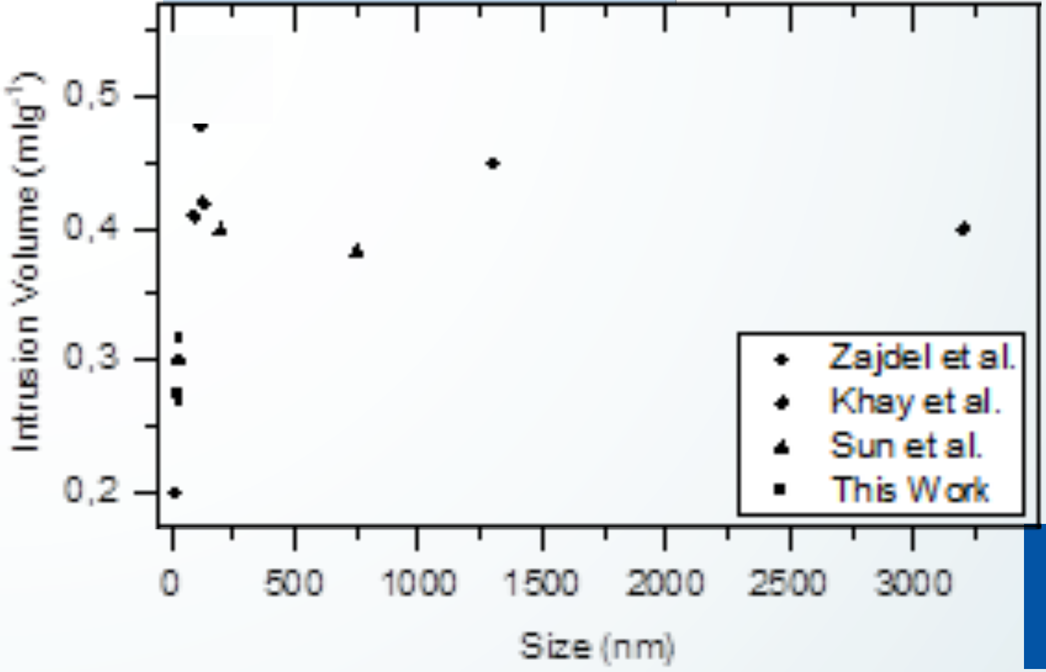
Intruded volume shrinking with decreasing size





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



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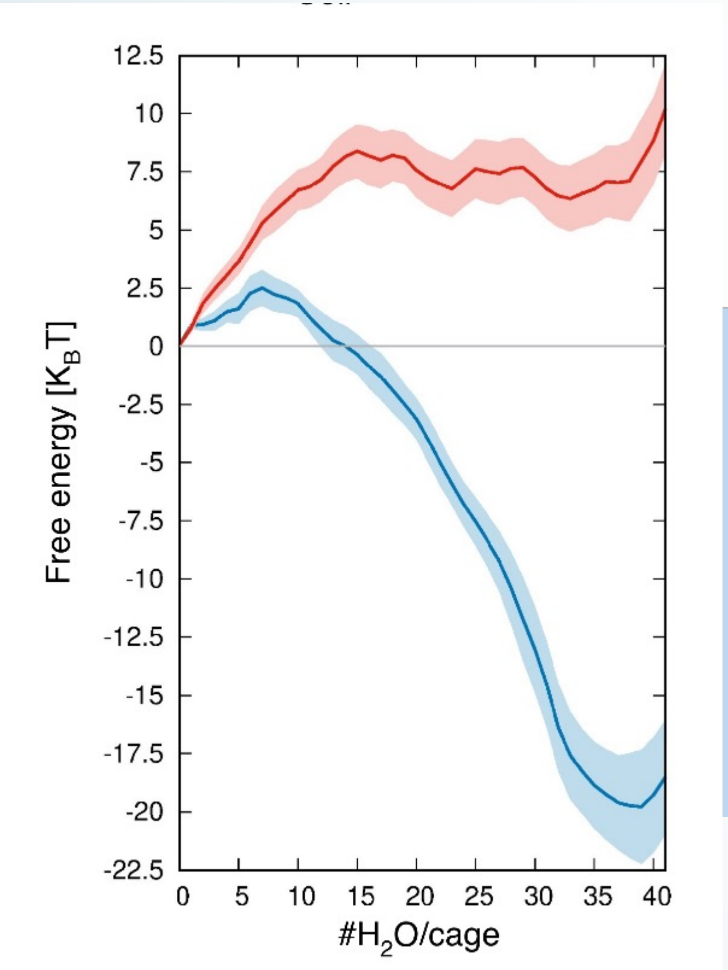
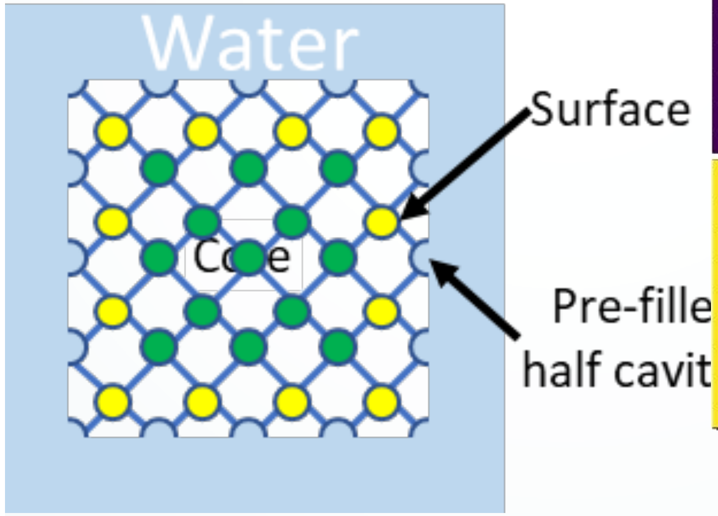
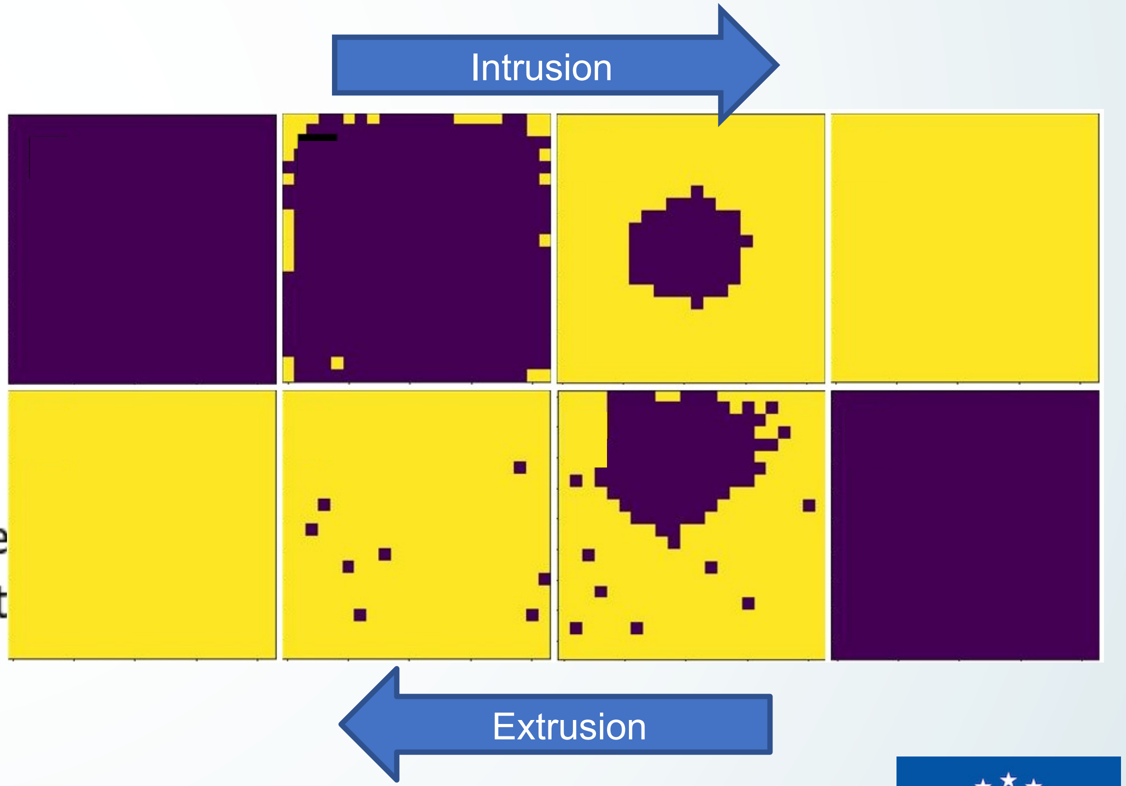
Stochastic model of intrusion in crystallites

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

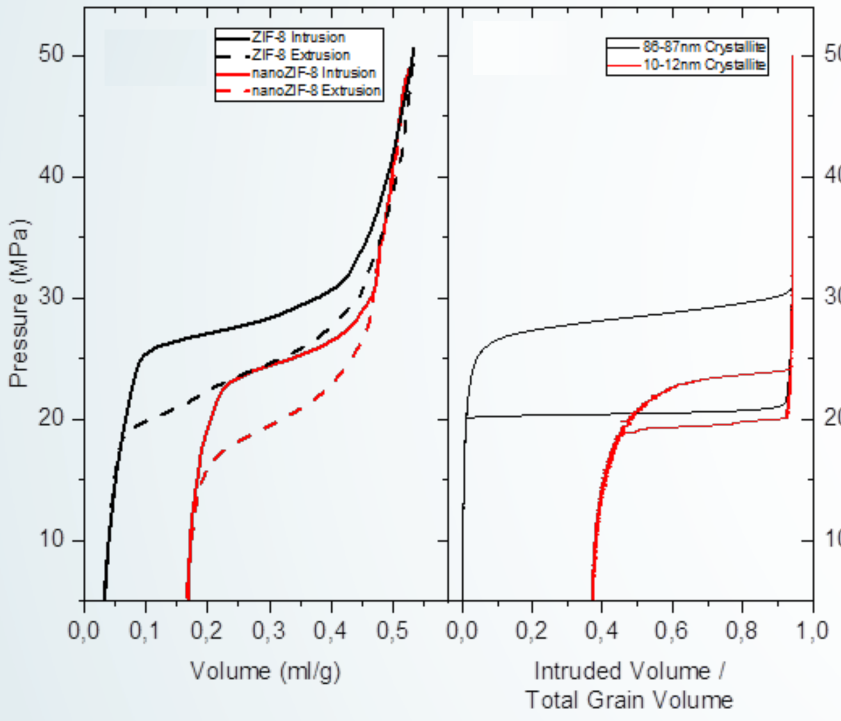
$$t_e = t_e^0 e^{\frac{\Omega_e}{k_B T}}$$

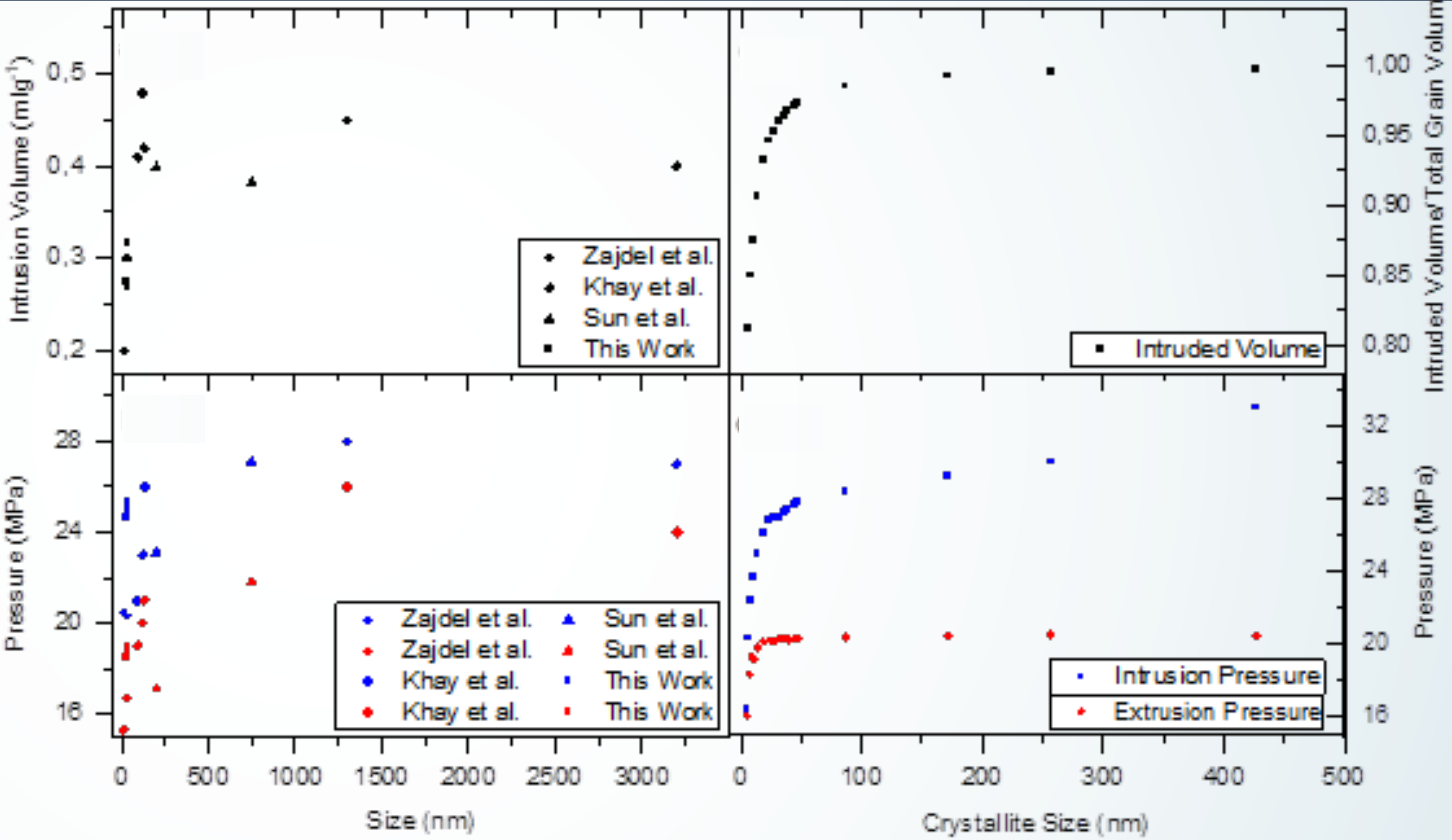






Stochastic model of intrusion in crystallites





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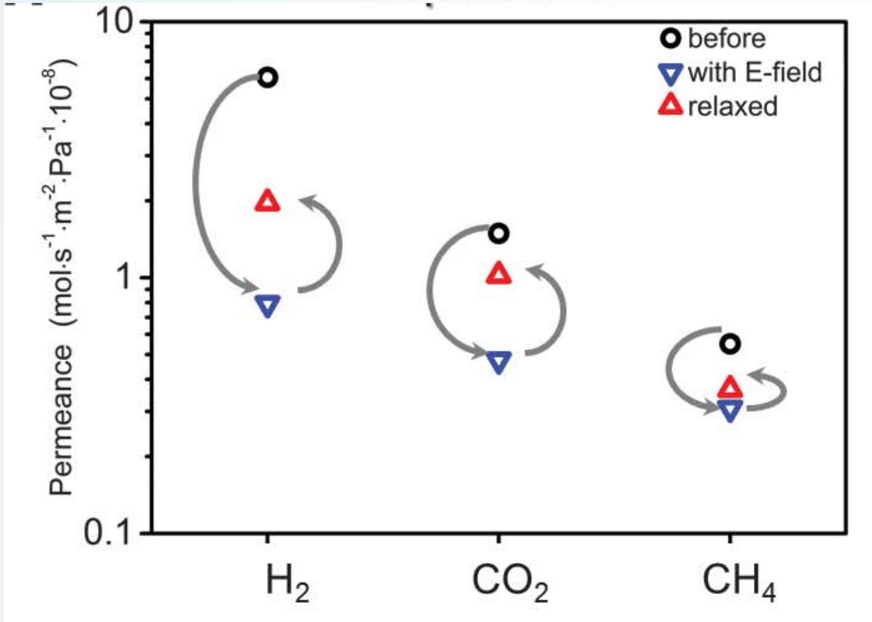
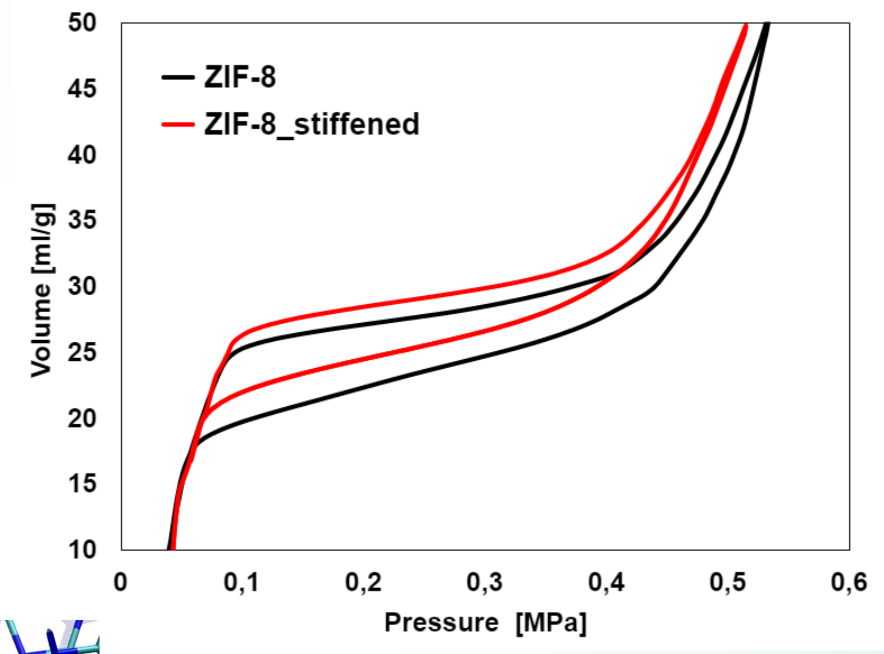
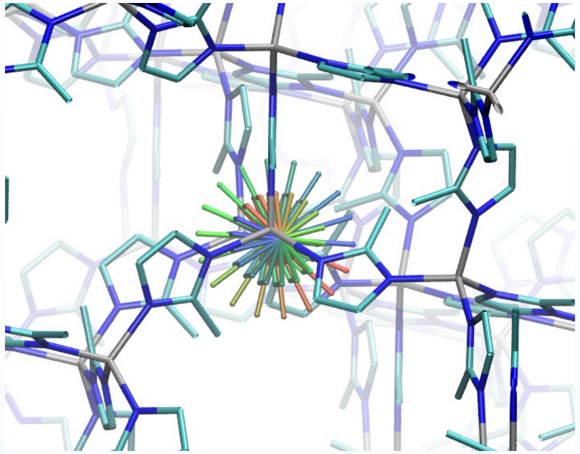
“Stiffened” ZIF-8



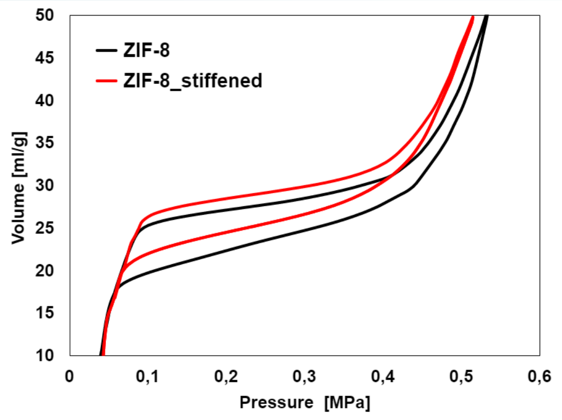


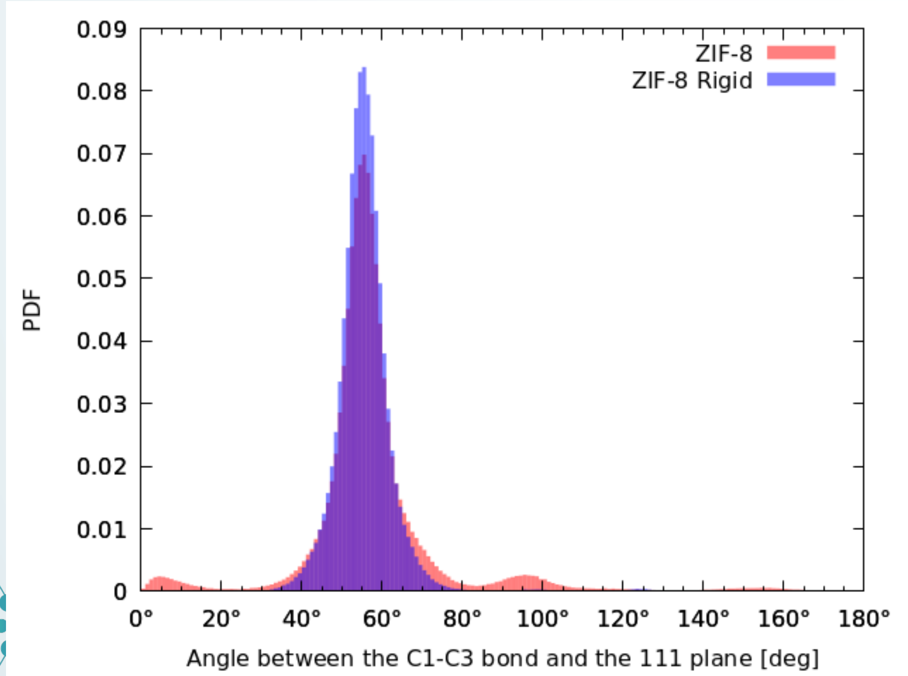


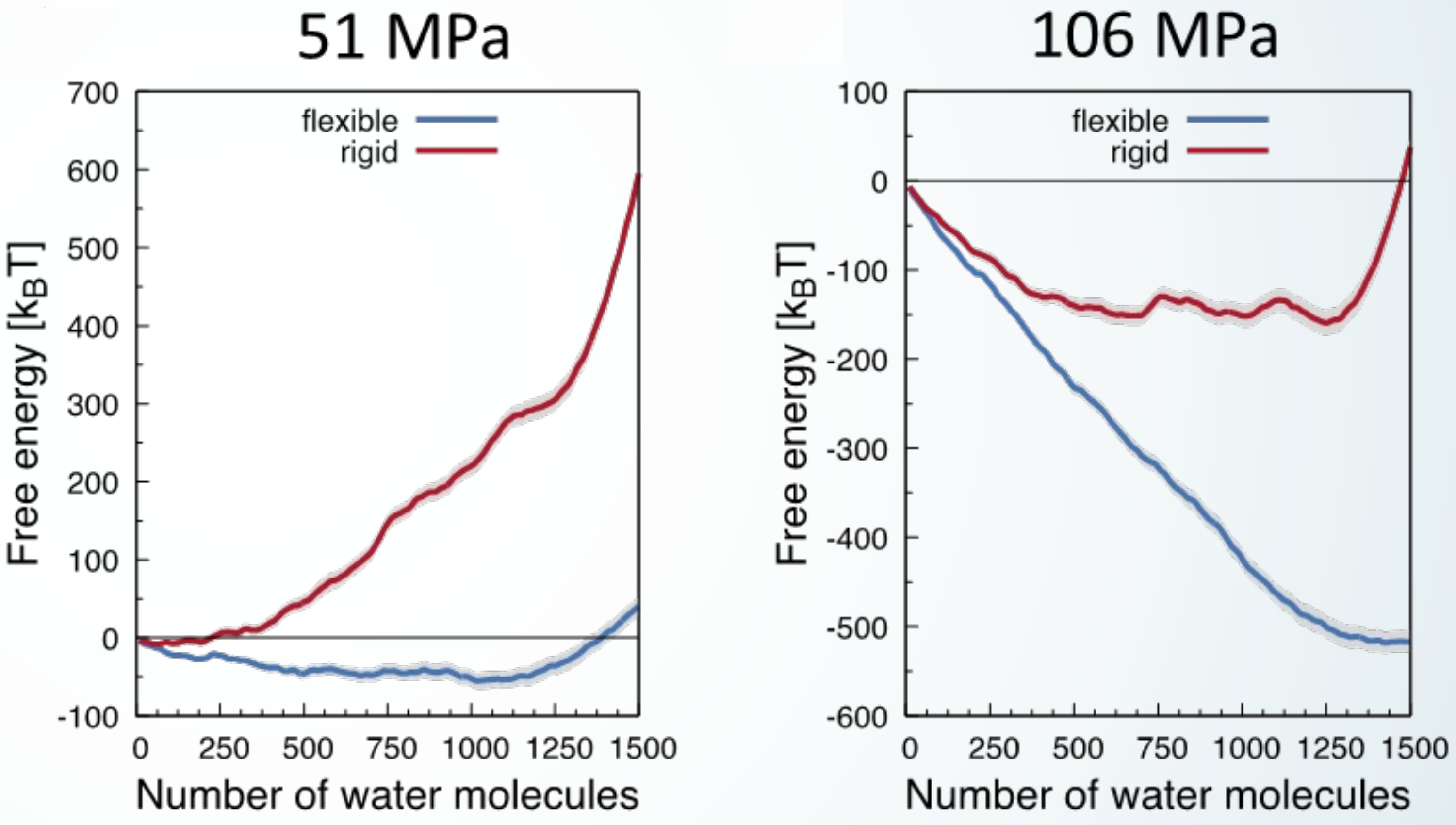
ELECTRO INTRUSION

Knebel et al., “Defibrillation of soft porous metal-organic frameworks with electric fields”, Science 358, 347 (2017)

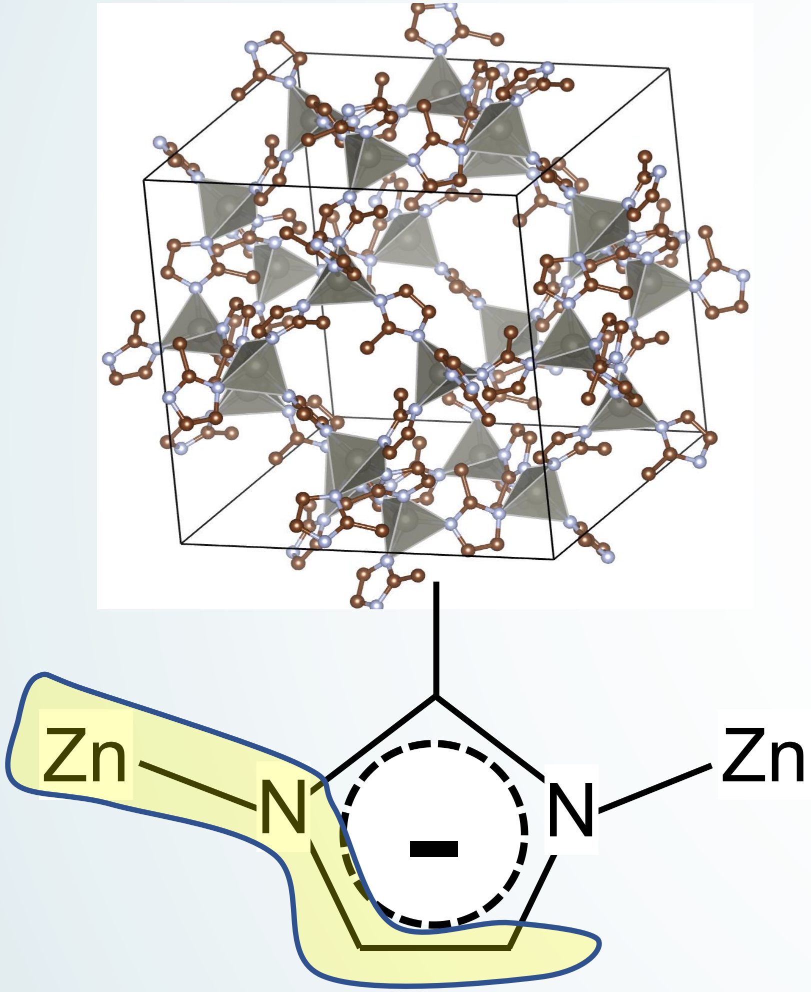
Intrusion in a in-plane rigid slab



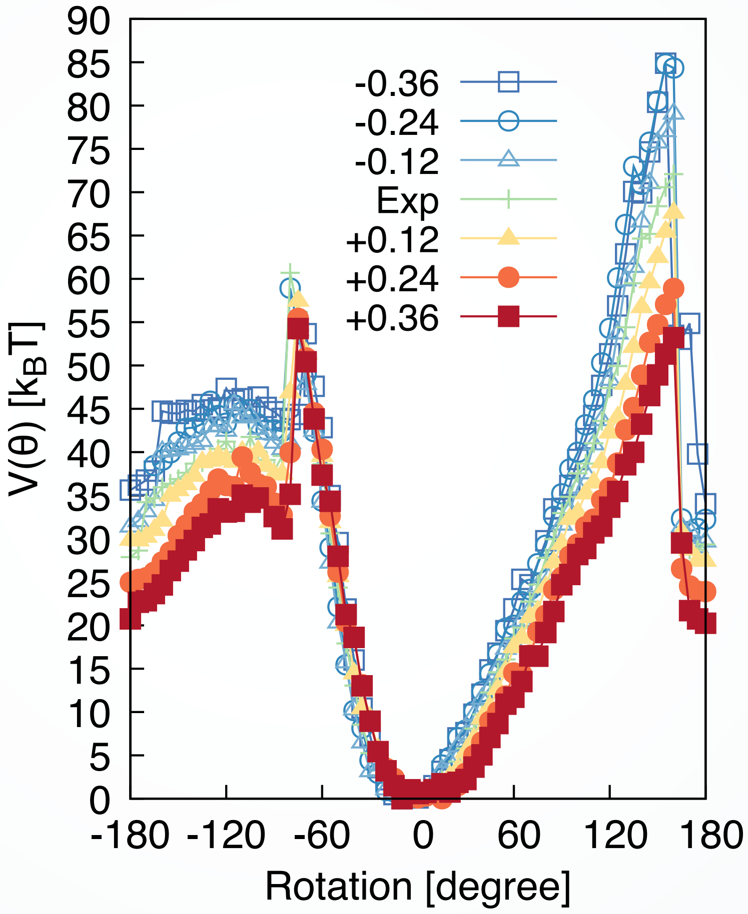


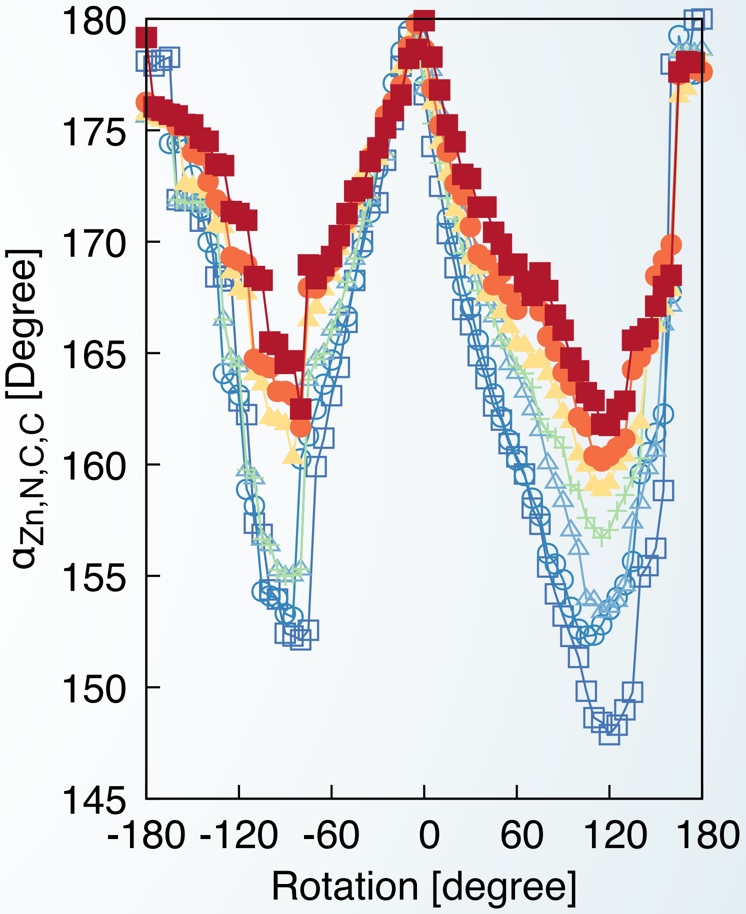


Interplay between physics of intrusion and chemistry of imidazolate



Zn-N-C-C dihedral angle

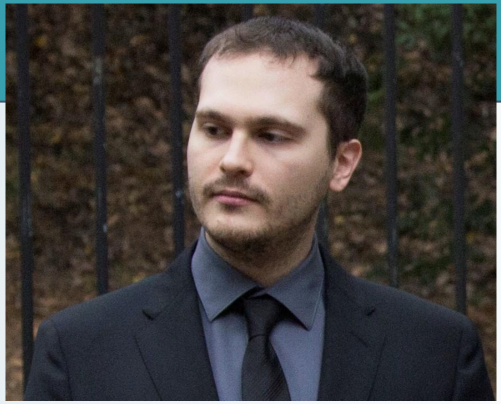




Conclusions

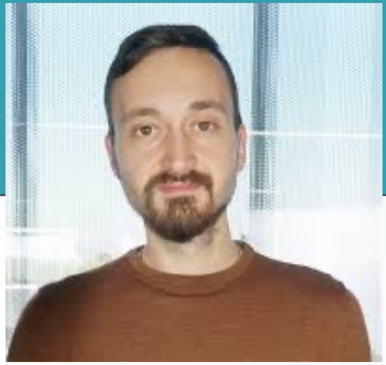
- Kinetics and int/ext pressures in nanometric materials with sub-nanometric apertures violate Young-Laplace, which previously we have shown to work for slightly larger apertures
- The process is not capillary condensation, it still looks like front advancing-like, minimizing the pseudo-liquid/pseudo-vapor interface area
- This mechanism determines the crystallite size dependence of the int/ext pressure
- Stiffened material shows that there is an unknown connection between the physics of intrusion and the chemistry of imidazolate linker

Acknowledgements



Marco Tortora

Seb Merchiori



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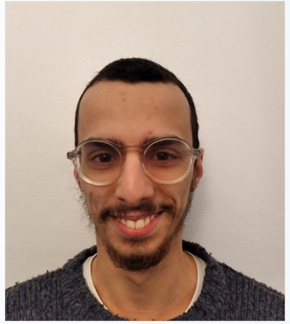
Alberto Giacomello

Carlo Massimo Casciola

Josh Littlefair

Andrea Le Donne



Alberto Giacomello

H2020-FET Electro-Intrusion

PRACE

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