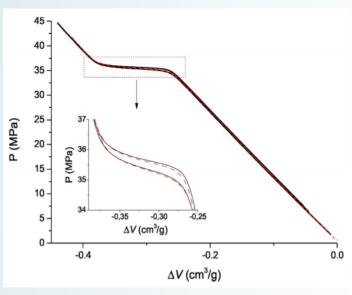
Intrusion mechanism of water in ZIF-8 hydrophobic MOF: capillary condensation or subnanoscopic front advancement?

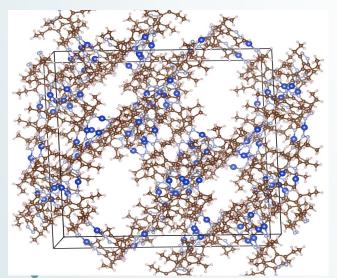


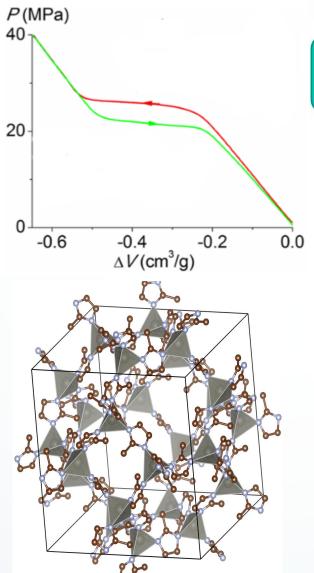


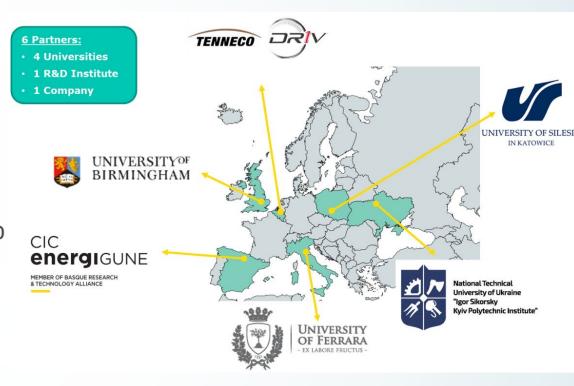
Crystalline porous media: MOFs













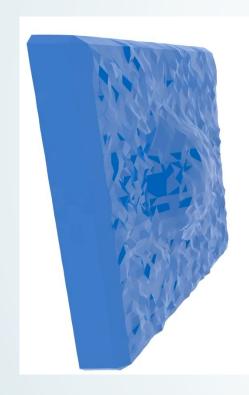


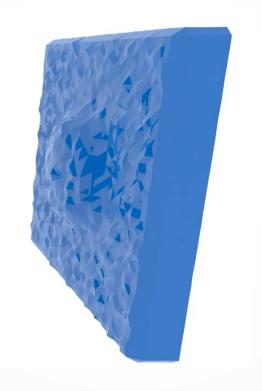


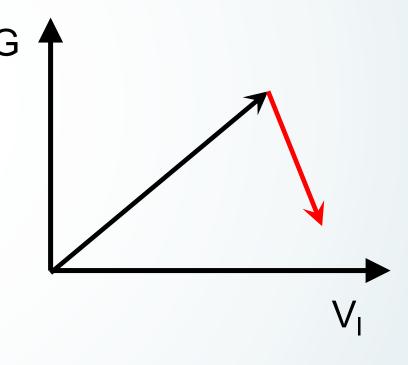
Intrusion/extrusion in hydrophobic porous materials: a thought experiment



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











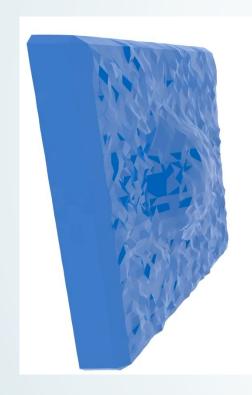




Intrusion/extrusion in hydrophobic porous materials: a thought experiment

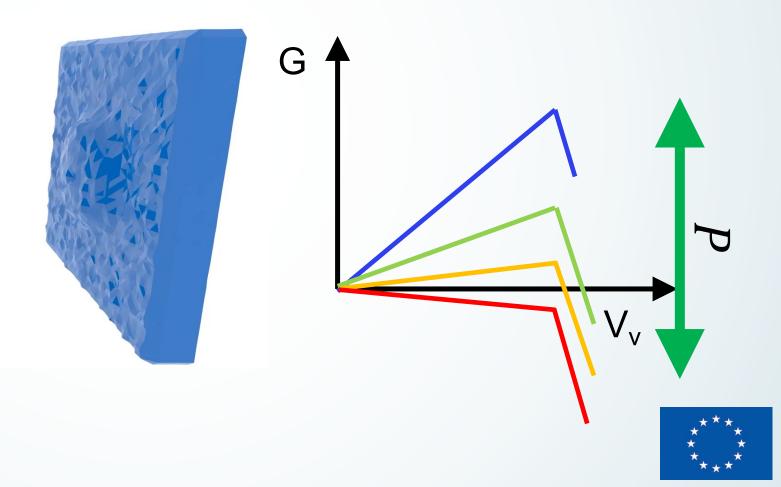


$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$









one is that of minimal $\Omega_{\rm eq}(Z)$ plotted in Fig. 2 [10]. onstant Ewe also $\Omega_{\rm eq}(Z)$ is defined on three contiguous intervals: tions in the areas cos are not inde- $[Z_{\min}, Z^*]$ (continuous line), $[Z^*, Z^{**}]$ (dashed line), and Z^{**}, Z_{max} (dotted-dashed line) each corresponding to a nt to express the family of Σ_{ln} interfaces of different shape (see the right $I = \underbrace{}_{\partial \Sigma_{sl}} S x_{tl} dl$ panel of Fig. 1). When the groove is almost empty, the triple line along contact line is pinned to its sharp edges. Here, Σ_{lv} is the $\delta x_n = \cos\theta \, \delta x_{tl},$

her all the varia-

 $\delta x_{tl} dl = 0, \quad (2)$

Thus, the con-

the liquid-vapor with prescribed

) the constraint

 $_{V}$ dS

extrusion pressure and hysteresis



family of arcs having curvature $1/R = -2\cos\beta/l$, as sketched in Fig. 1 with a continuous line. For this particular family, condition (ii) is substituted by Gibbs' criterion [13], which is the equivalent of Young equation of a sharp edge, 7) prescribing $\theta_Y + \phi - \pi \le \beta \le \theta_Y$, where ϕ is the angle formed by the edge and β is defined as in Fig. 1. Ω_{eq} joins smoothly from the first to the sec**bol** domain at $V_1 = Z^*$, where $\beta = \theta_Y$ (dashed line in Fig. 1 and posting triple) line Rdepinted the meniscus advances with contain curvature along the groove, and Ω_{ea} scales linearly with Z.

$$\tau = \tau_0 \exp \left[\frac{\Lambda \Omega_{\rm ing}^{\dagger} / k_B T}{30 \, \rm NOVEMBER} \right]$$

 $+\gamma (A_{lv} + \cos(\theta)A_{sv})$

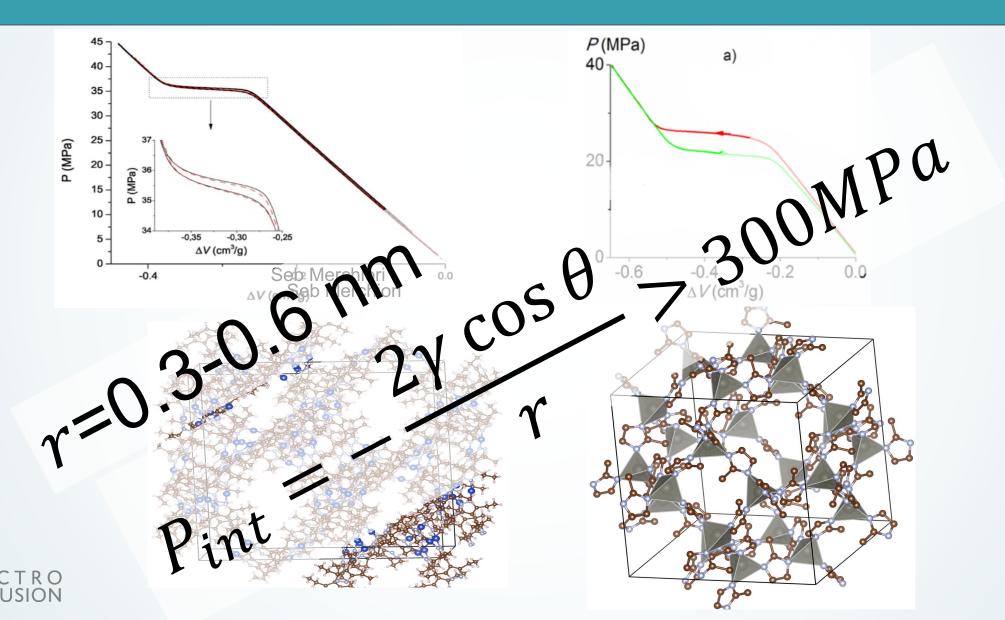
responding to a surface Hysteresis originates from the (1) to a geometr $(\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \equiv$ aplace equation ing one rectangular ____ve as in Fig. 1, by reconcined and erpressure you must apply it of metastable ndependent: i e different thermodynamic conditions at changing the barrier to become ~1 kgT ermined by the given V, T, and system geometry. This is tantamount to elow, important n. The pressure changing $p_v = p_v$ [1]]. Although for more complicated extrusion barriers ce $p - p_v$ is a μ , and T. It is geometries numerical schemes need to be developed start-ing from the general theory, in this 2D geometry it is as an additional e liquid volume. ated on solutions -0.25possible 25 to derive an analytical expression for and hysteresis by tuning the $\partial I_{\rm eq}/\partial Z$. Since t by (thermodyarly, the equilibtace equations by Fiof2 (color potential as a function of the Miration volume filling the compute P_{ig} function of the correlative volume of light inside then that at given Z a plethora of veen CB and V_{ig} is to be θ_{ij} in and the coefficient angle Z is the groove Z and Z is the first of the groove Z is the gr retric adjashed 1. The grand notential is shifted so that the West that a grand value of the west that the west the west that the west that the west that the west the





Crystalline porous media: MOFs

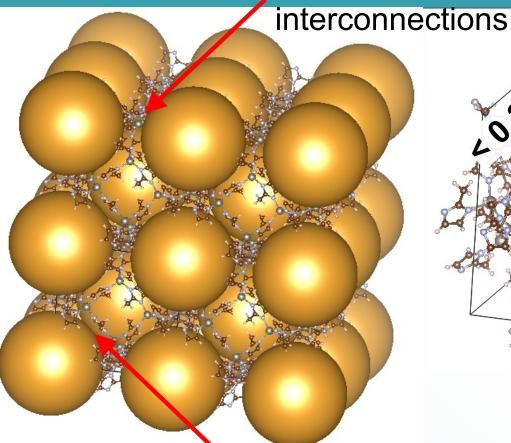




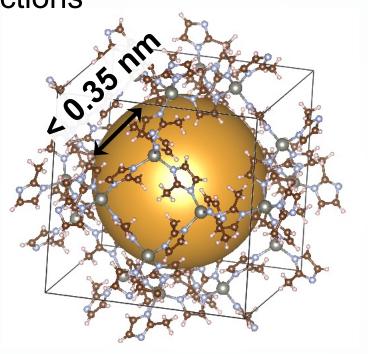


Peculiarities of ZIF-8

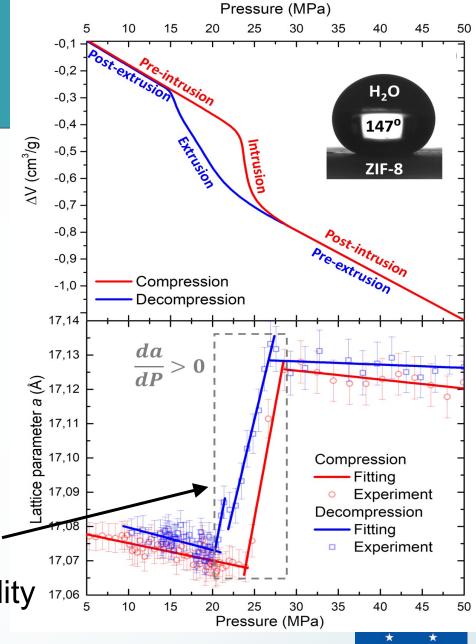
Secondary







Exceptional Negative
Compressibility



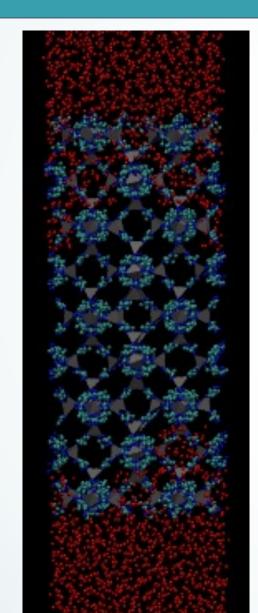


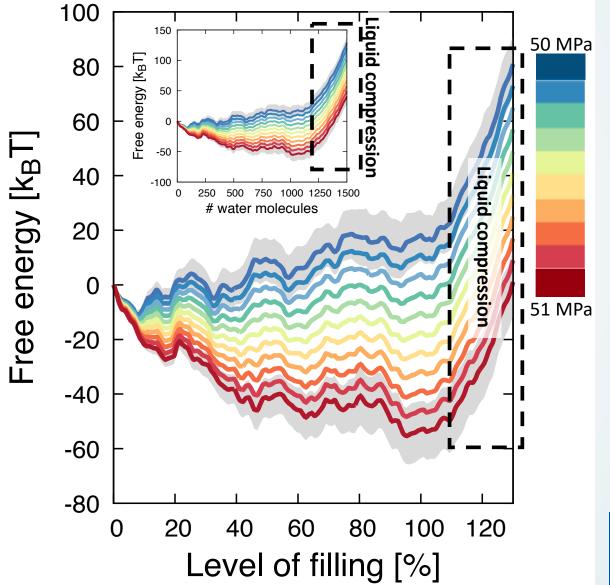




Int/ext free energy profile vs pressure







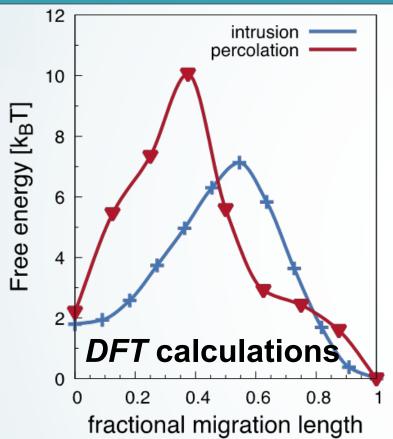


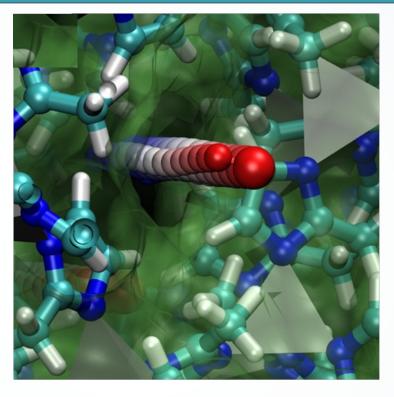


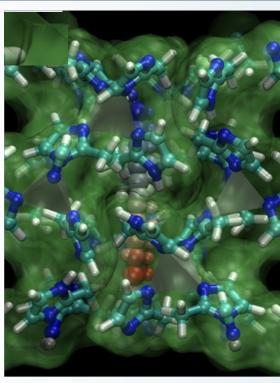


Single water molecules "intrusion"









actional migration length Intrusion Percolation

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



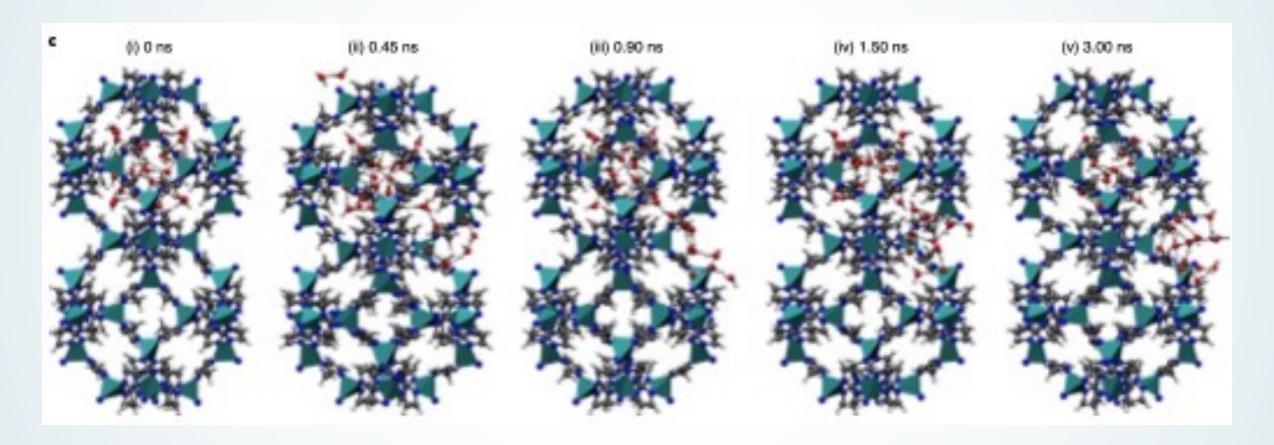
Turning molecular spring into nano-shock absorber: the effect of macroscopic morphology and crystal size on the dynamic hysteresis of water intrusion-extrusion into-from hydrophobic nanopores, Zajdel et al., ACS Appl. Mater. Interfaces 2022, 14, 26699





Proposed mechanism: capillary condensation





Grand Canonical simulations

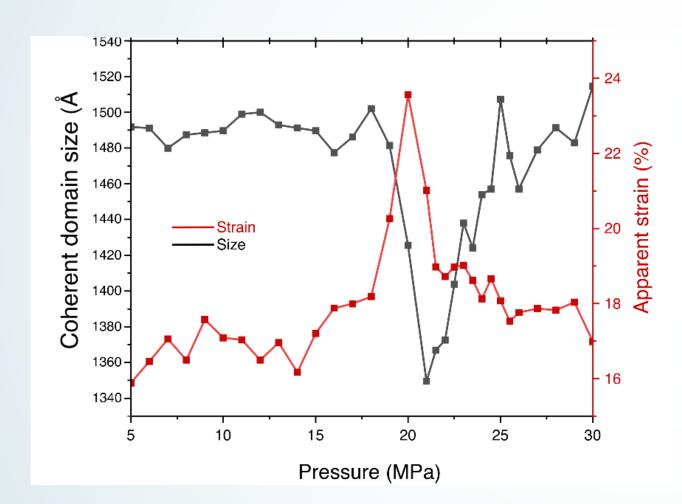


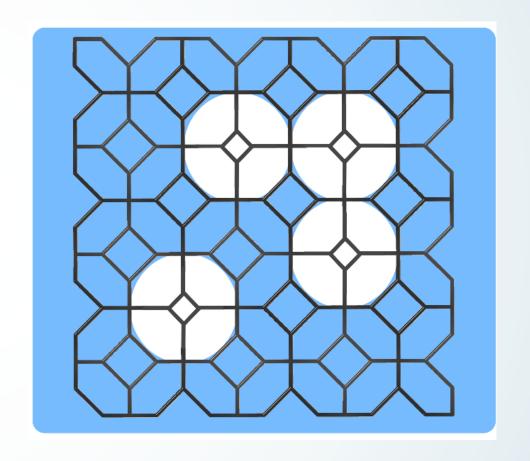




Mismatch with experimental evidence







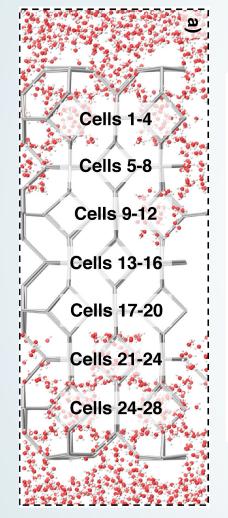


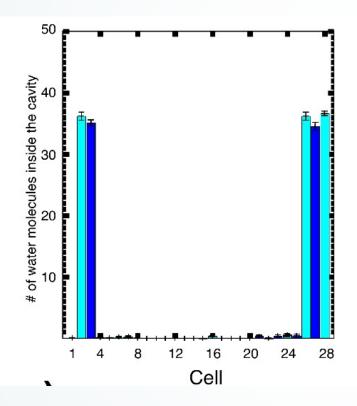


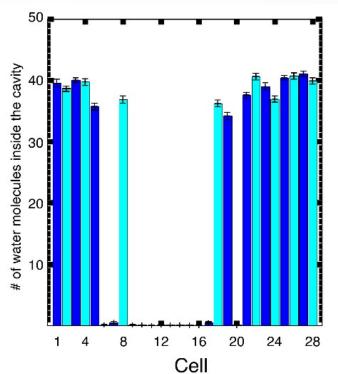


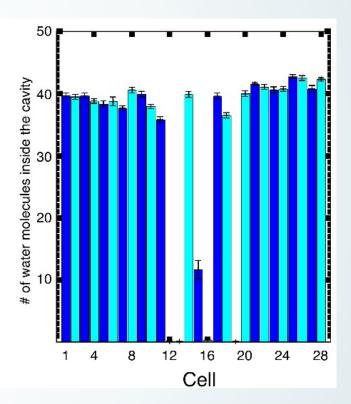
Cage-by-cage intrusion mechanism











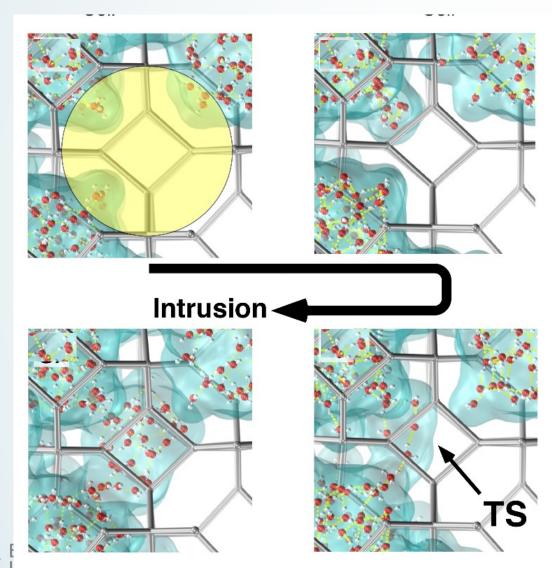


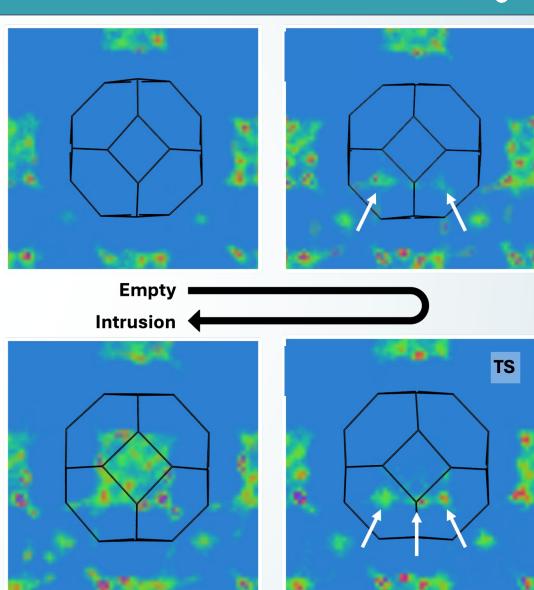




Origin of the intrusion barrier











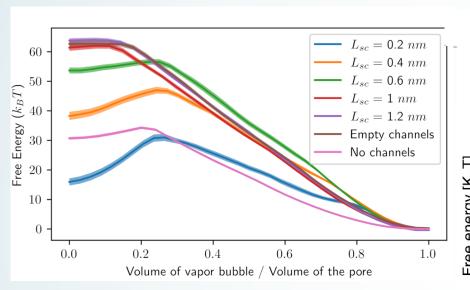
Why cage-by-cage intrusion

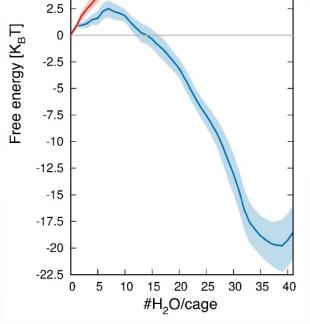
12.5

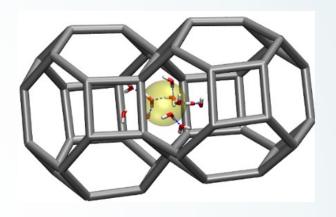
10

7.5









	$ heta_{\iota}$
Std ZIF-8	101°
Clogged	114°
pores	

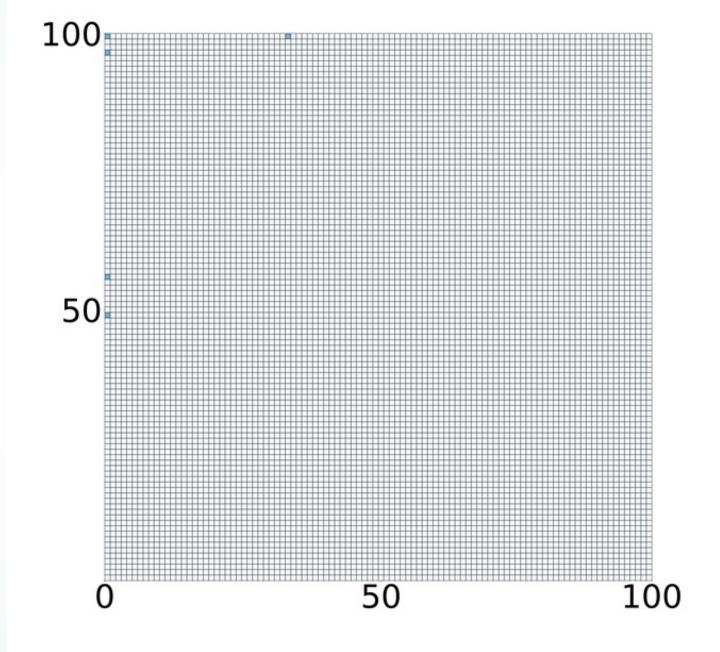
Bushuev et al., Nano Lett. 2022, 22, 2164; Bushuev et al ACS Appl. Mater. Interfaces 2022, 14, 30067 Paulo et al, Comm. Phys. 6, 21 2023



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

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

Effective surface tension in a (porous) medium



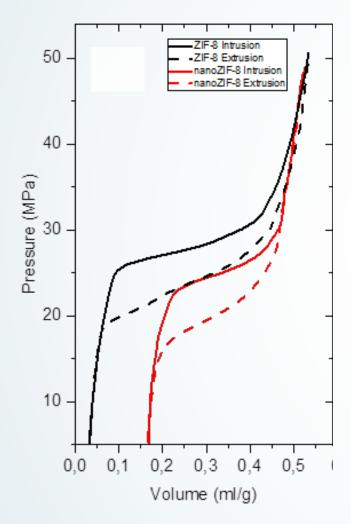


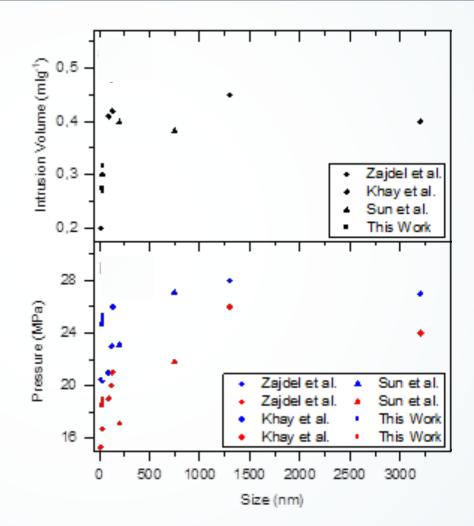




Crystallite size dependency in intrusion









Visit Liam's poster



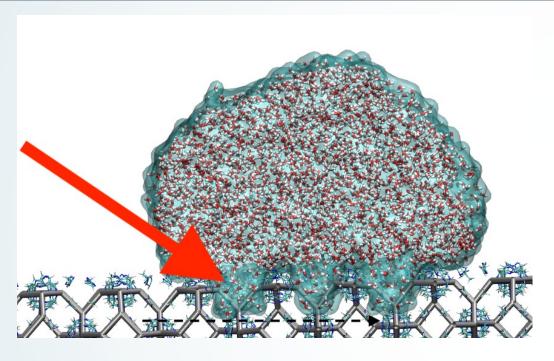
Optimization of the Wetting-Drying Characteristics of Hydrophobic Metal Organic Frameworks via Crystallite Size: The Role of Hydrogen Bonding between Intruded and Bulk Liquid, Johnson et al, J. Colloid Interface Sci. 645, 775 (2023)





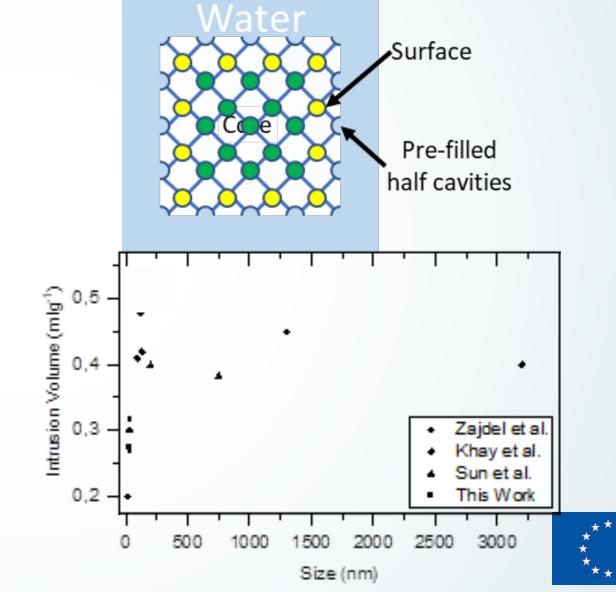
Intruded volume shrinking with decreasing size





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

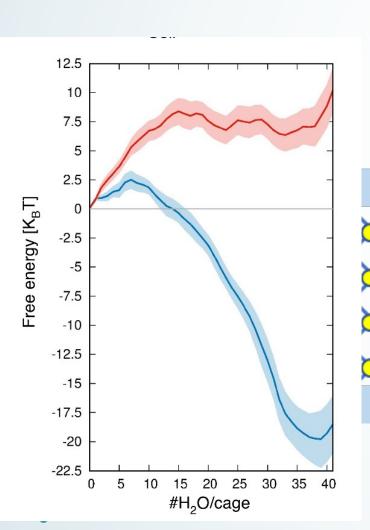


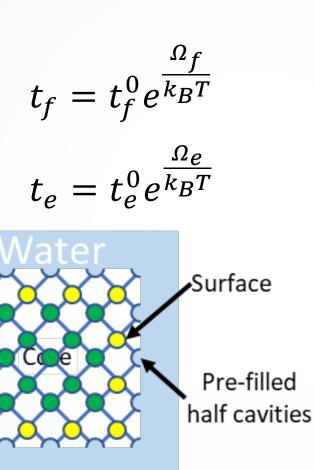


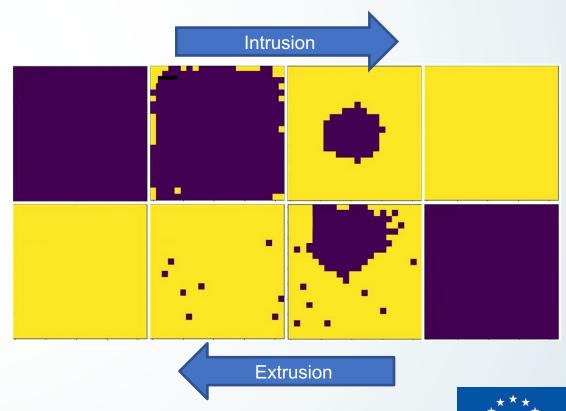


Stochastic model of intrusion in crystallites





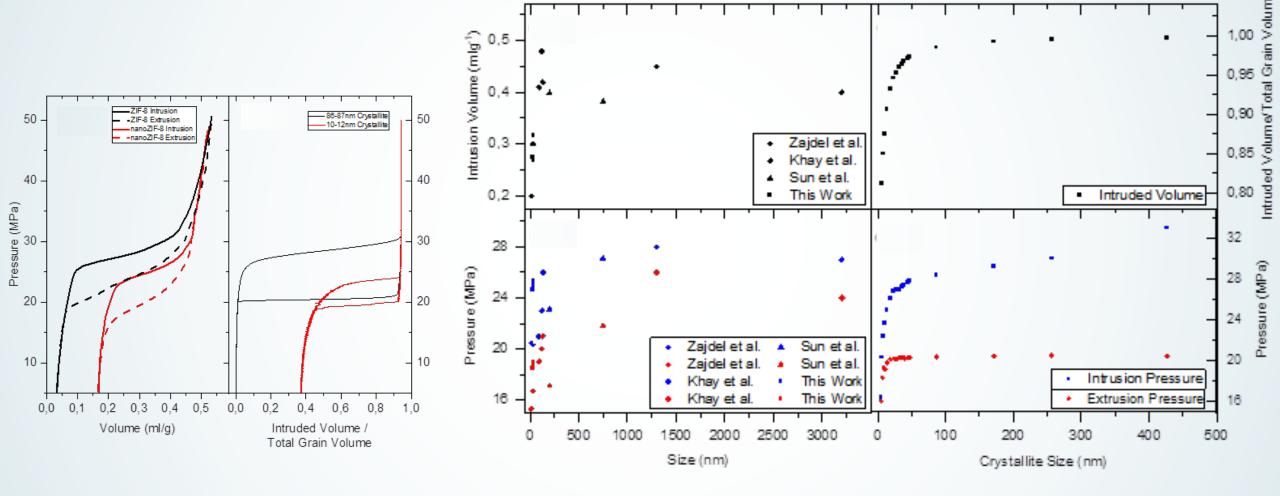






Stochastic model of intrusion in crystallites











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



Carlo Massimo Casciola



Josh Littlefair



Seb Merchiori



Andrea Le Donne





Goncalo Paulo



Yaroslav Grosu



Liam Johnson



Eder Amayuelas









