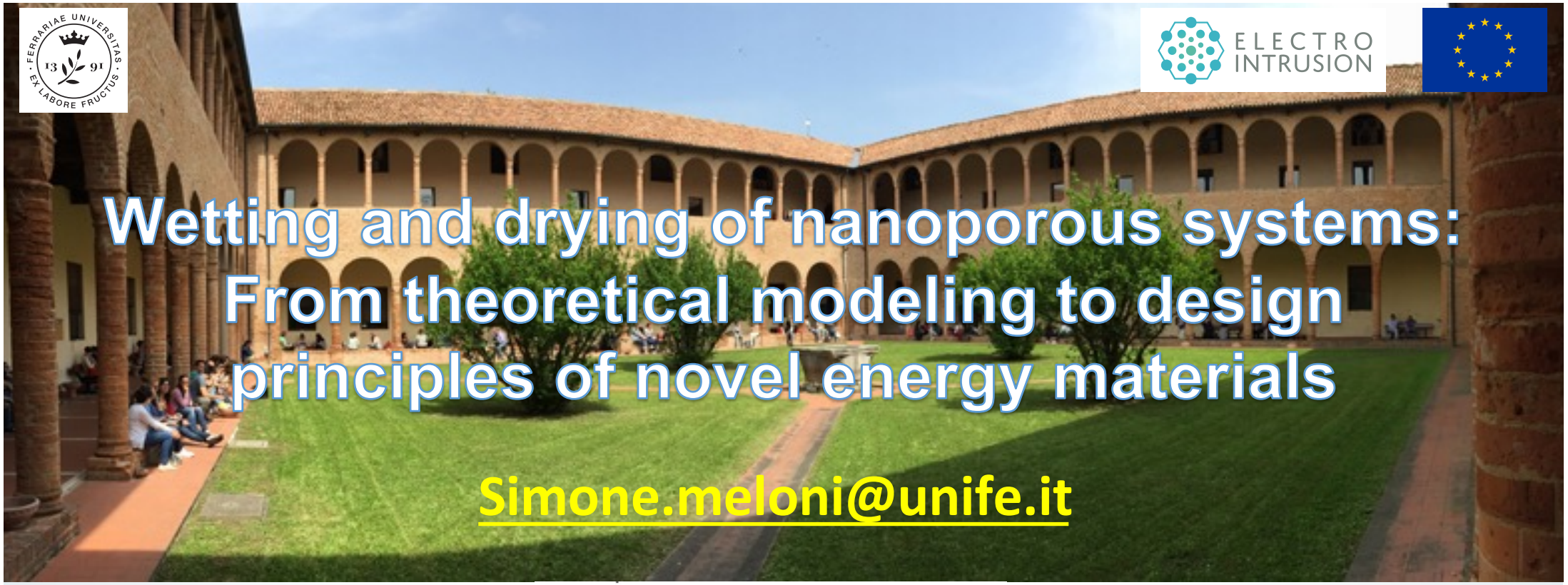
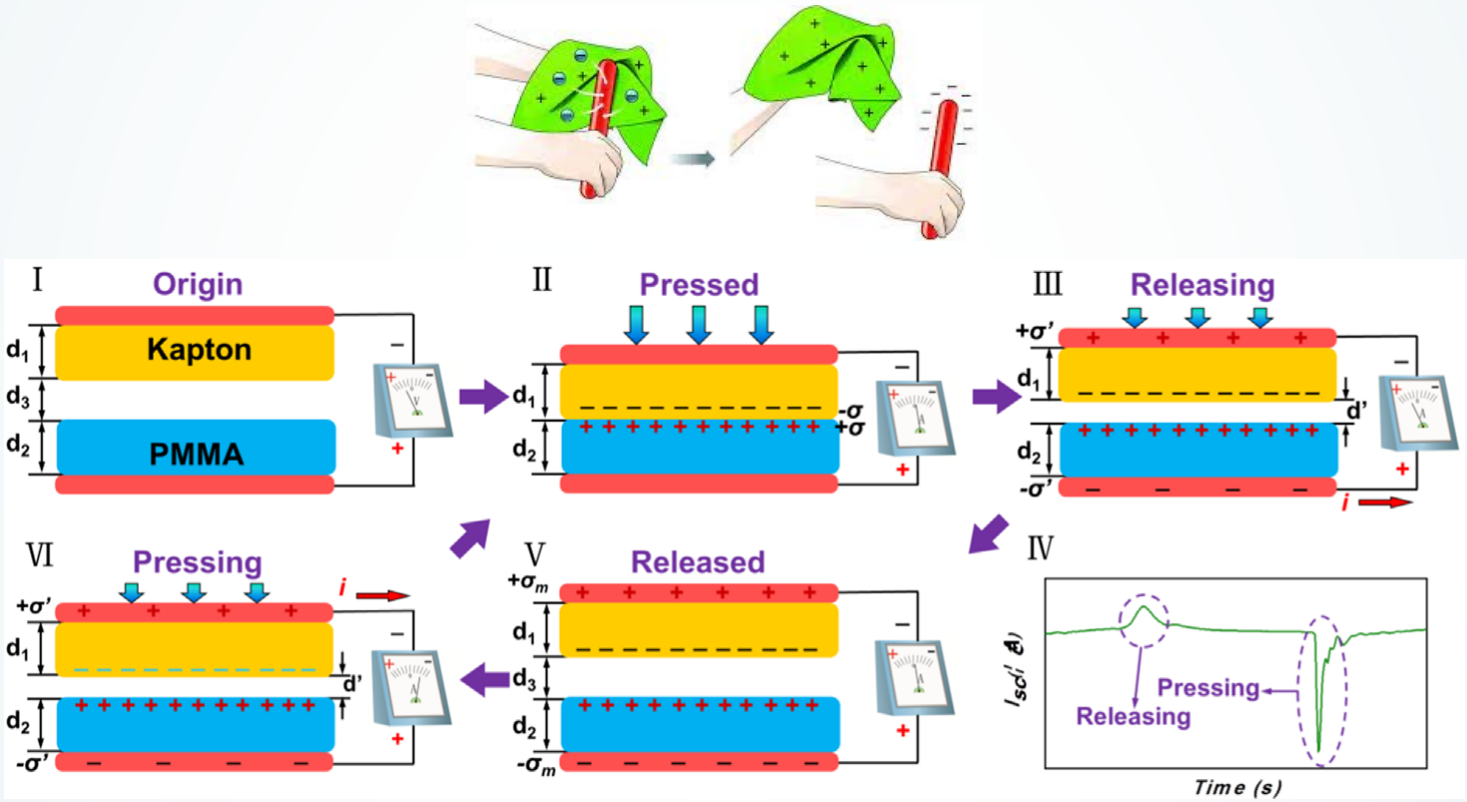


Wetting and drying of nanoporous systems: From theoretical modeling to design principles of novel energy materials

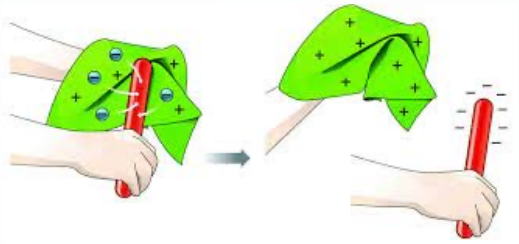
Simone.meloni@unife.it

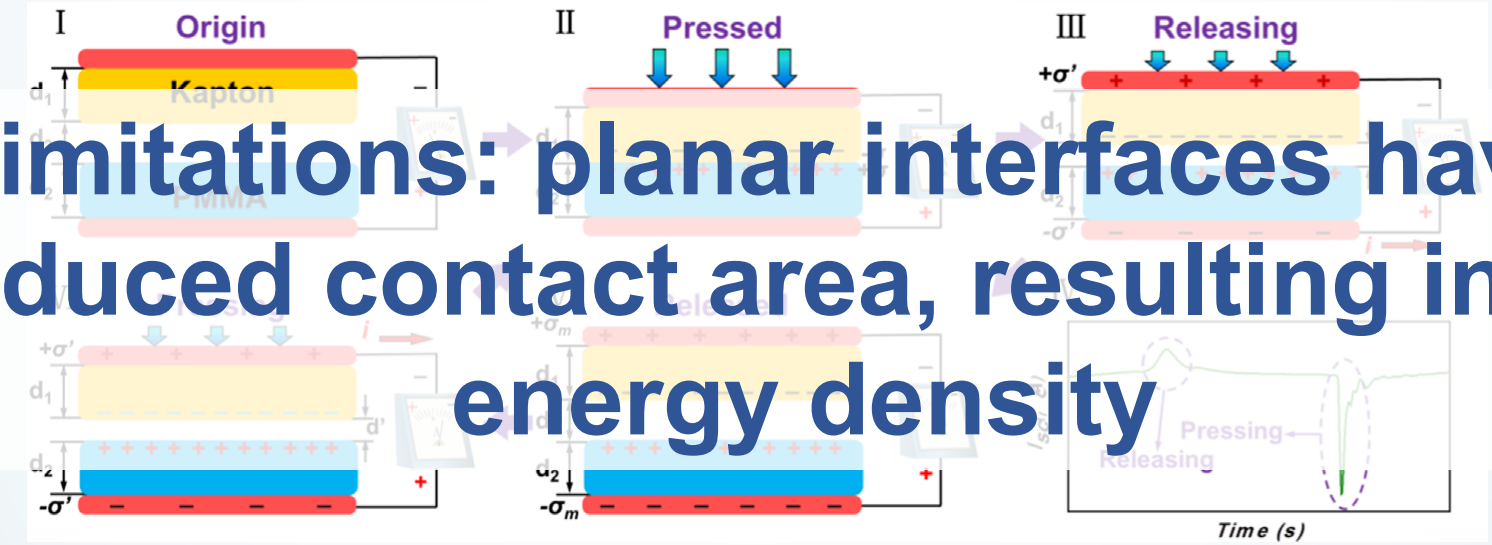
Triboelectric nanogenerators - TENGs



Nano Energy 14, 126, 2015

Triboelectric nanogenerators - TENGs

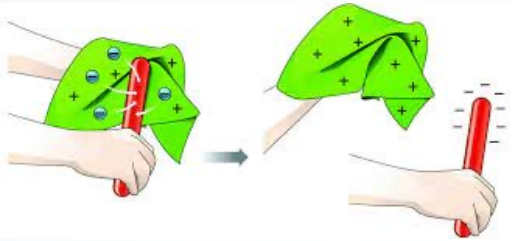


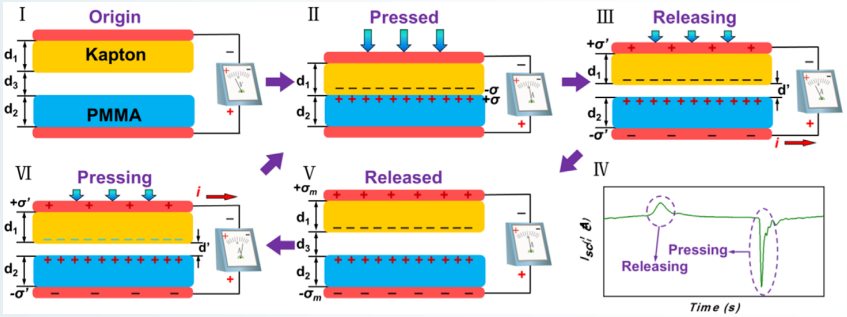


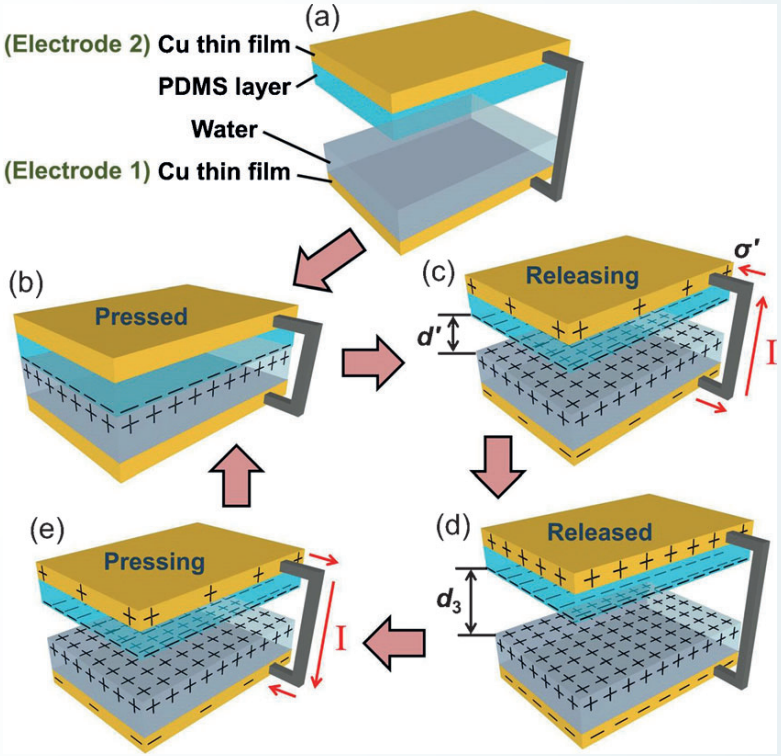
Limitations: planar interfaces have a reduced contact area, resulting in low energy density

Nano Energy 14, 126, 2015

Triboelectric nanogenerators - TENGs

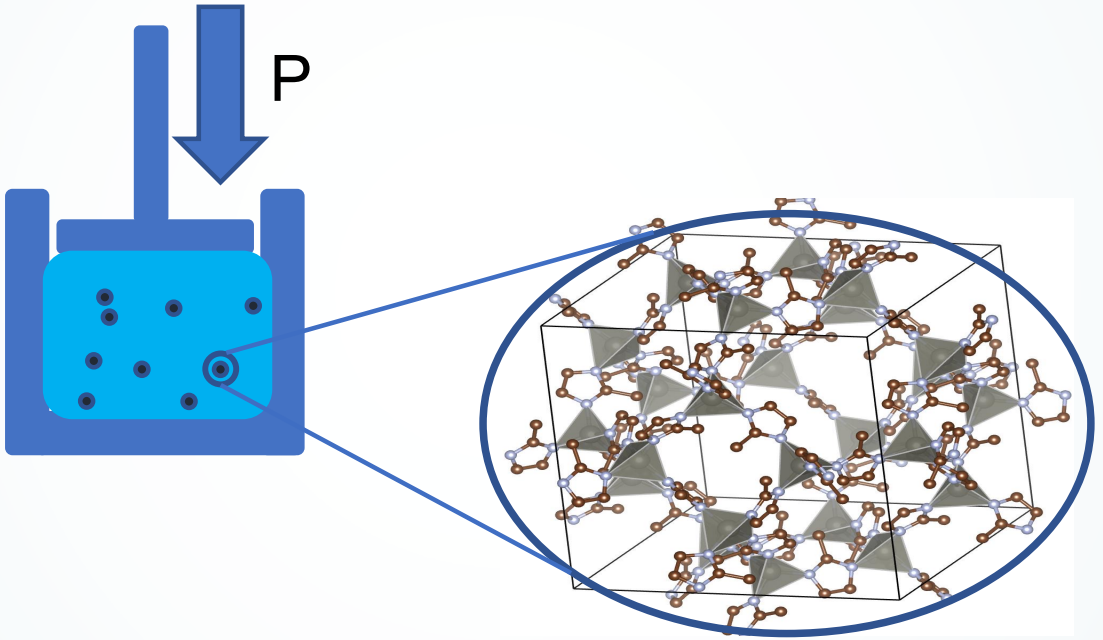






Nano Energy 14, 126, 2015
Angew. Chem. Int. Ed. 52, 12545, 2013

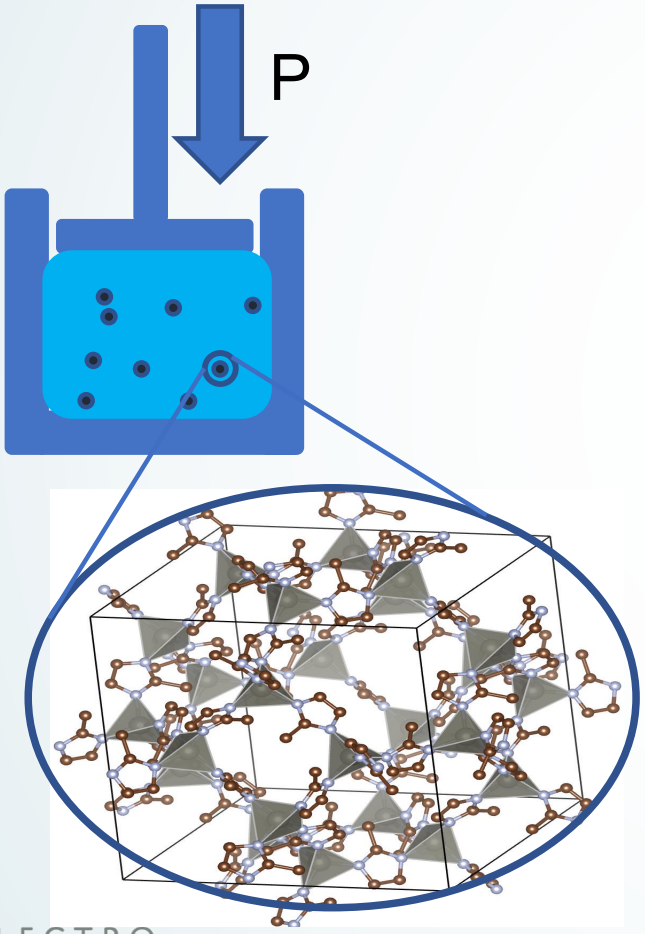
Hydrophobic Nanoporous-based triboelectric nanogenerators: Electro-Intrusion

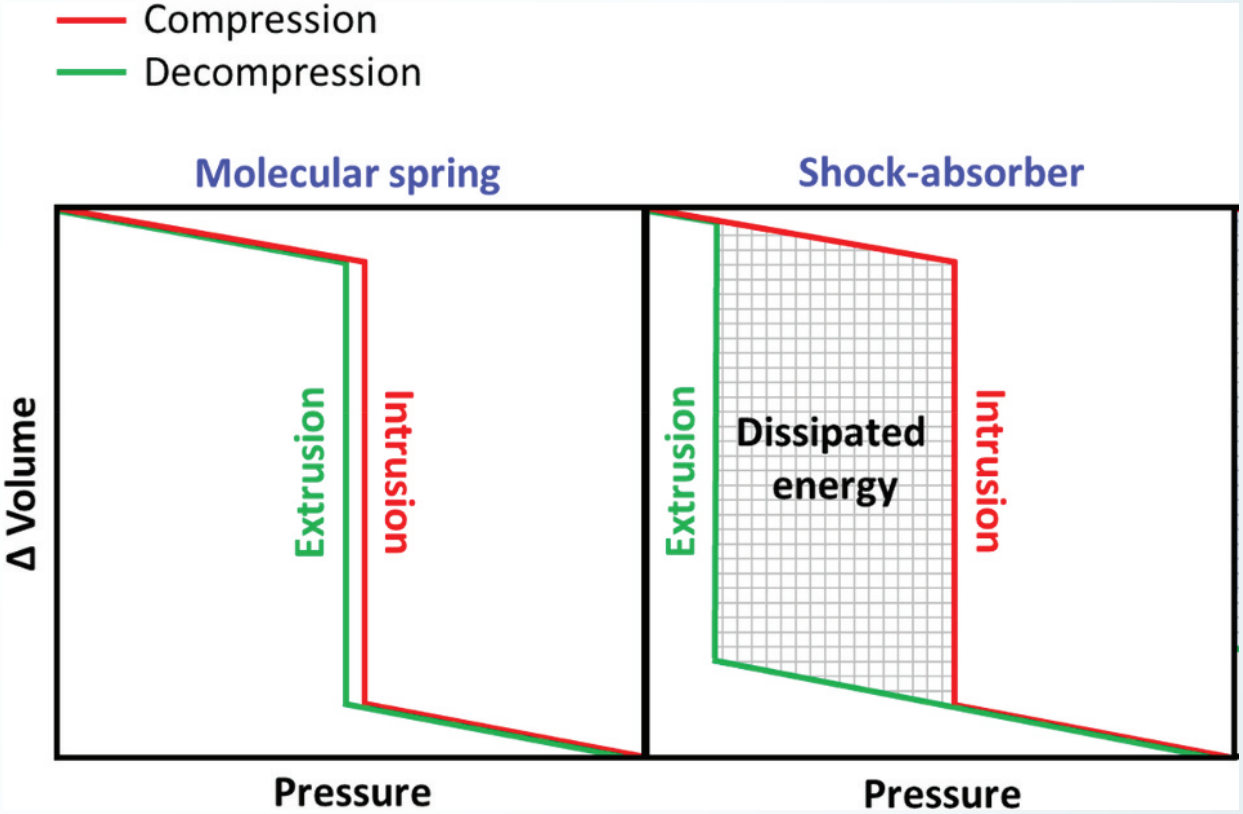


ELECTRO INTRUSION

ACS Applied Materials & Interfaces 11, 40842, 2019
Advances in Physics: X, 7, 2052353, 2022

Hydrophobic Nanoporous-based triboelectric nanogenerators: Electro-Intrusion

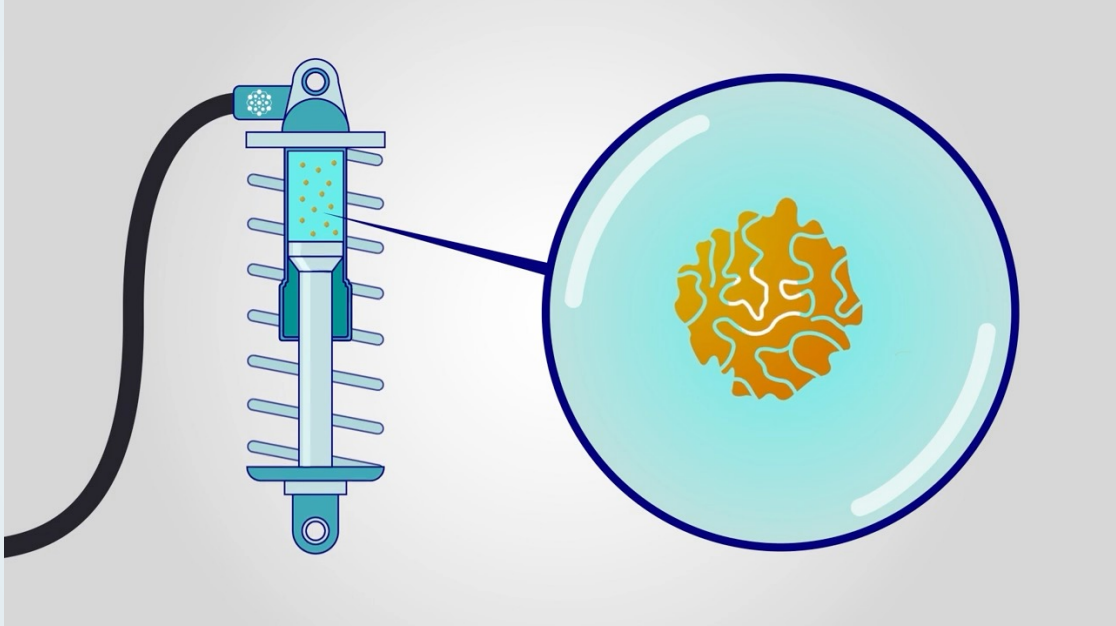


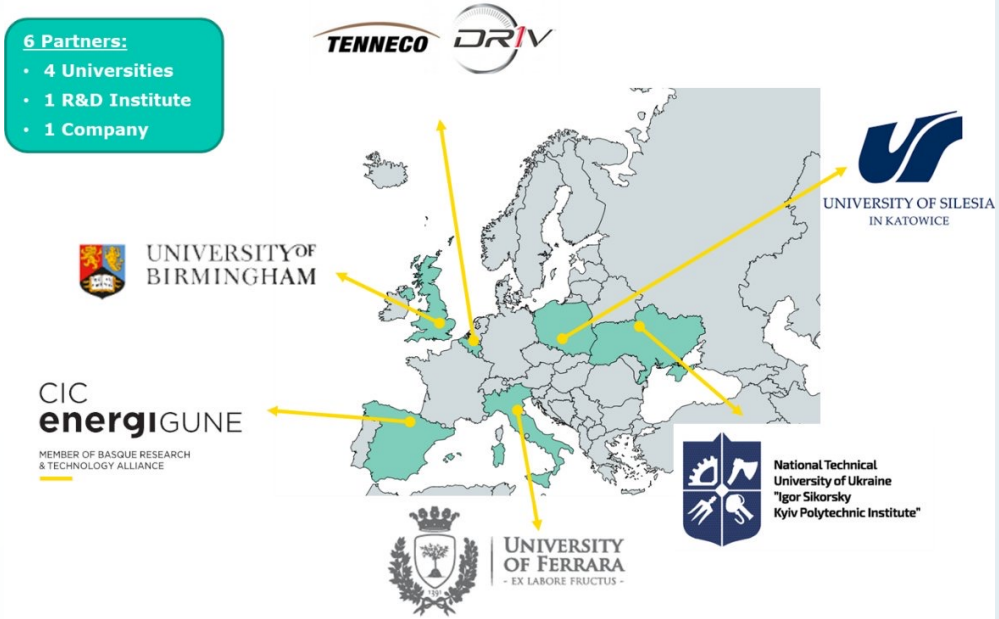


ACS Applied Materials & Interfaces 11, 40842, 2019
Advances in Physics: X, 7, 2052353, 2022

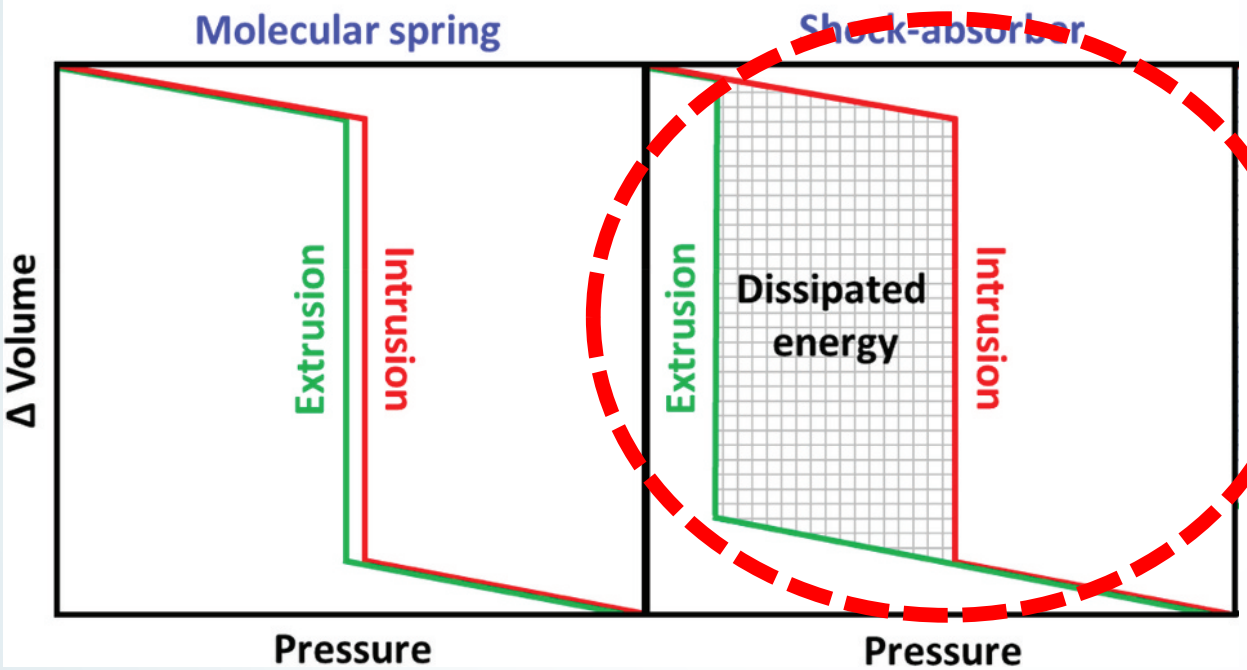
ELECTRO INTRUSION

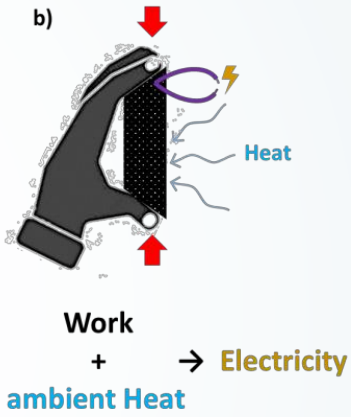
Our final goal





Electro-Intrusion





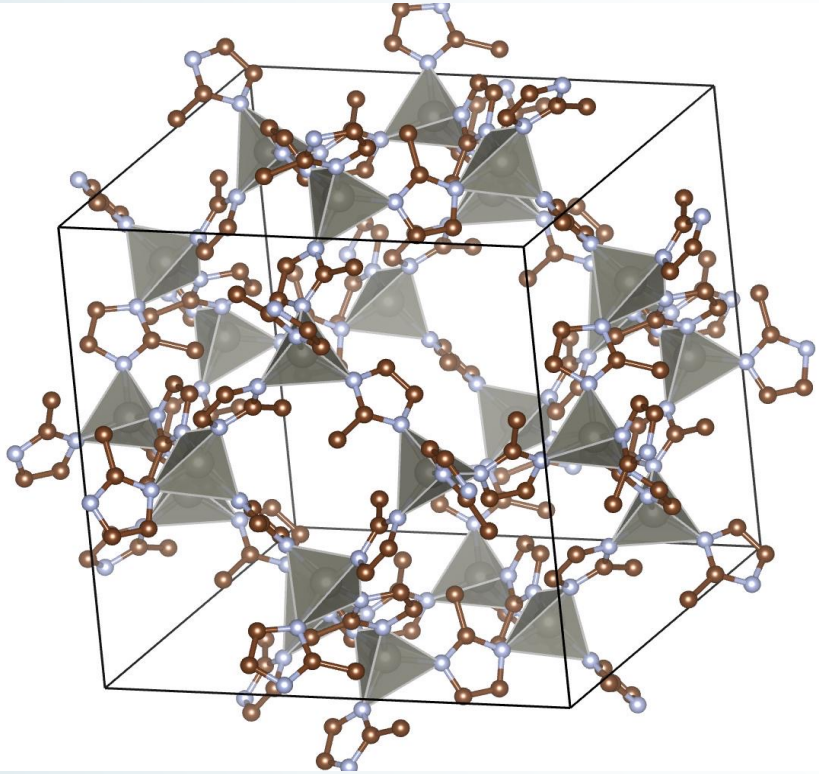
Heat pump 2.0

$$\Delta E_{hyst} + \Delta Q + \mathrm{E}_{elec} = 0$$

Cyclic intrusion/extrusion large dissipated energy to convert

ELECTRO INTRUSION

Hydrophobic Nanoporous-based triboelectric nanogenerators: Electro-Intrusion



Suitable materials: MOFs, COFs and other porous materials with large internal area (100-10000 m^2/g): the larger is the internal area, the larger is the liquid/solid contact area upon intrusion, the larger is the total electrification

ELECTRO INTRUSION

Electro-Intrusion Scientific challenges

- Basic laws/design principles to control intrusion/extrusion pressure
- Laws governing hysteresis
- Laws governing thermal energy fluxes
- Effect of thermodynamic conditions
- Contact electrification
- Chemical and mechanical stability.

ELECTRO INTRUSION

Nano Lett. 21, 2848, 2021

Electro-Intrusion Scientific challenges

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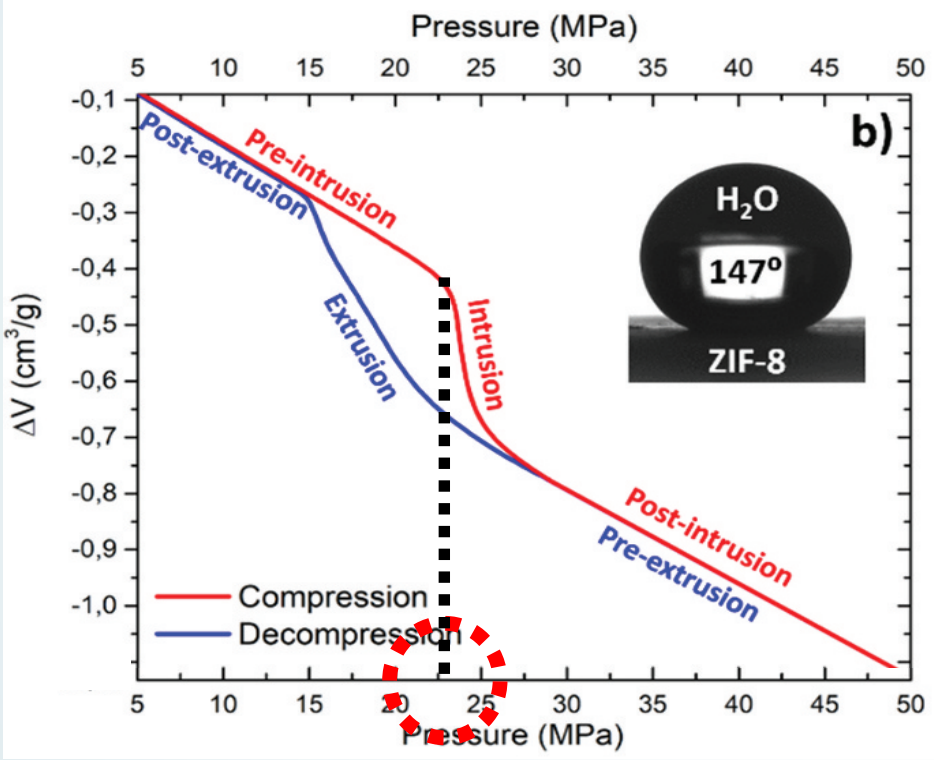
ELECTRO INTRUSION

Nano Lett. 21, 2848, 2021

Electro-Intrusion



- laws/design principles to control intrusion/extrusion pressure...
  - ...needed to identify suitable/best materials
  - Intrusion presume must be within the operative range, ~10-30 Mpa
  - Extrusion must be spontaneous, i.e., must occur at positive pressures

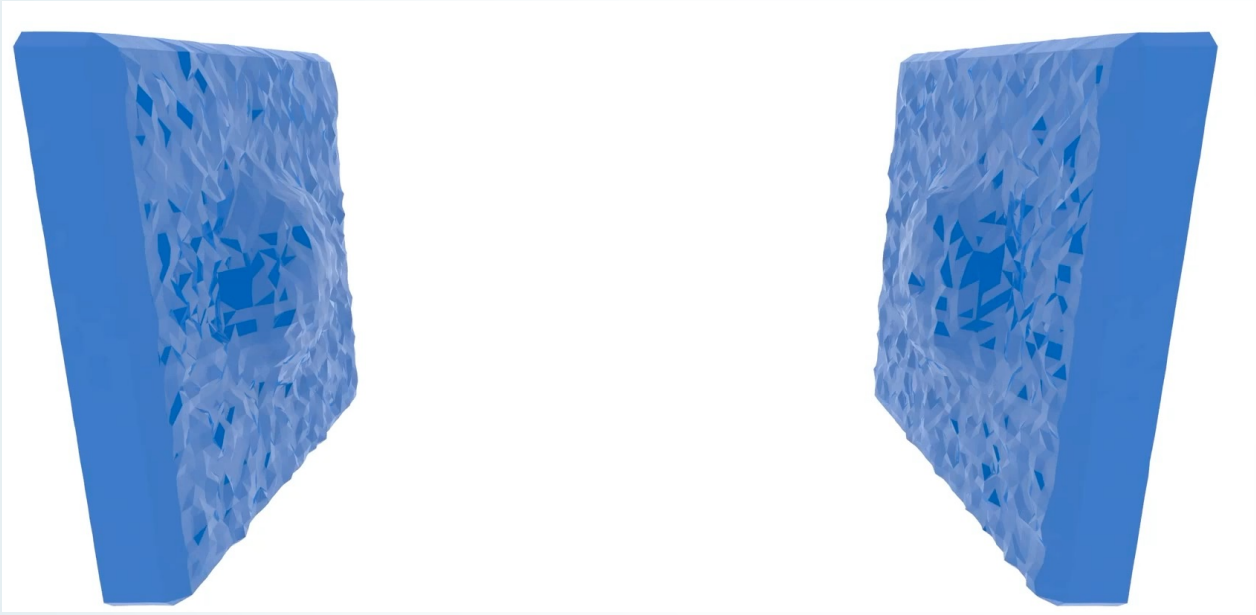
Young-Laplace

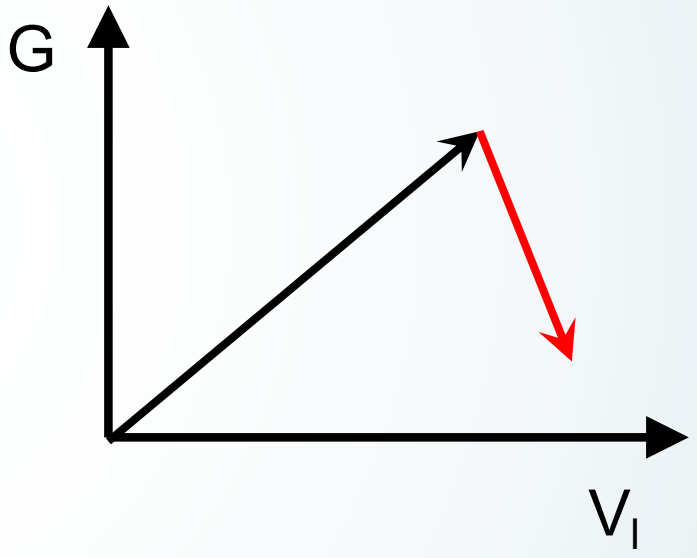
$$P_{int} = -\frac{2\gamma \cos\theta}{r} > 300MPa$$

ELECTRO INTRUSION

Nano Lett. 21, 2848, 2021

Intrusion/extrusion in hydrophobic porous materials: a thought experiment





ELECTRO INTRUSION

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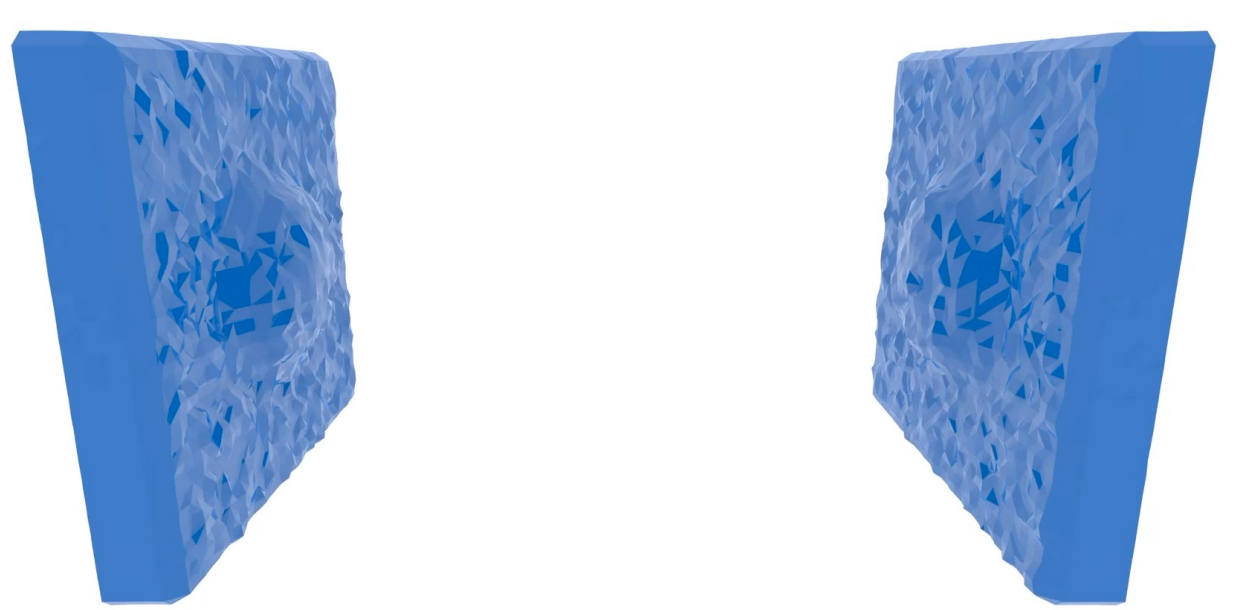
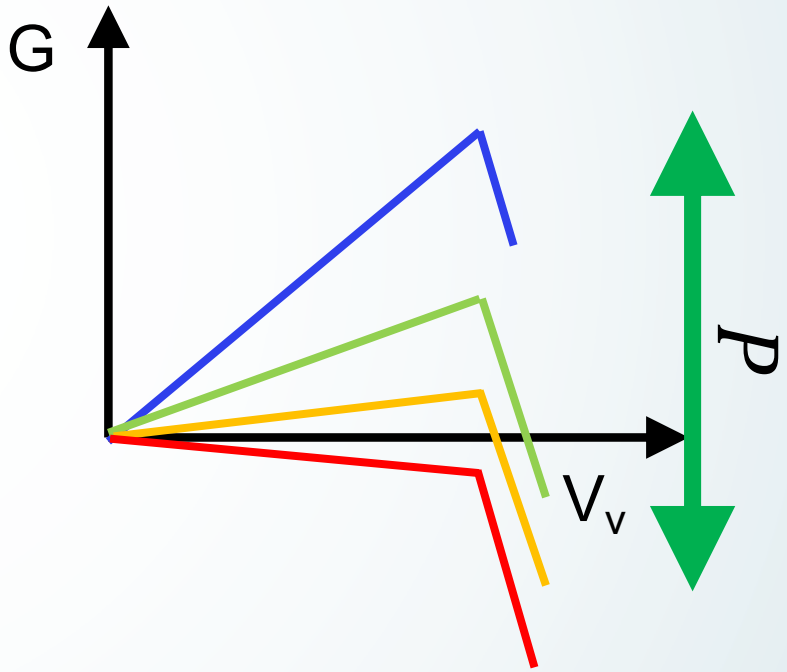


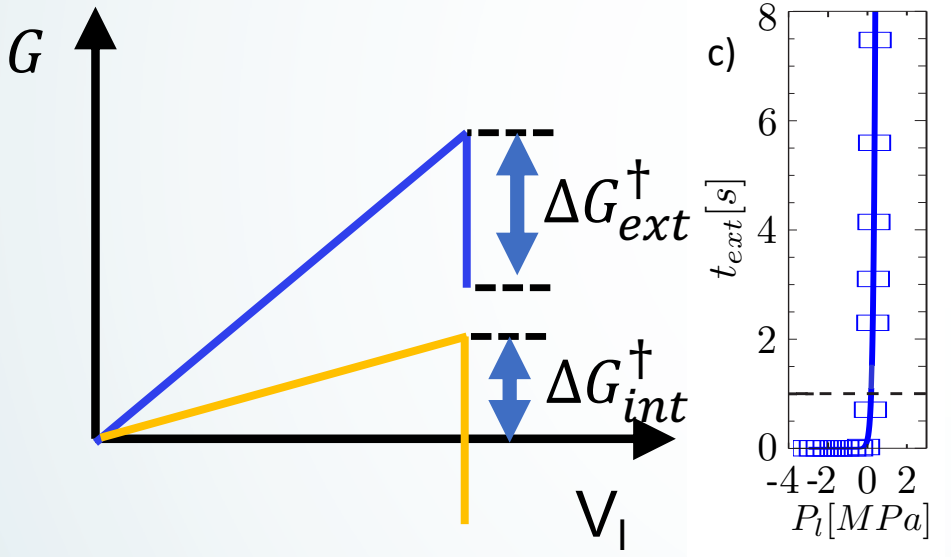


ELECTRO INTRUSION

Intrusion and extrusion pressure and hysteresis

TST
Kramers theory
…

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



Confined Classical nucleation Theory
cCNT

- Hysteresis originates from the over/underpressure you must apply for the barrier to become ~1 k_BT
- One can control P_{int}/P_{ext} and hysteresis by tuning the intrusion extrusion barrier

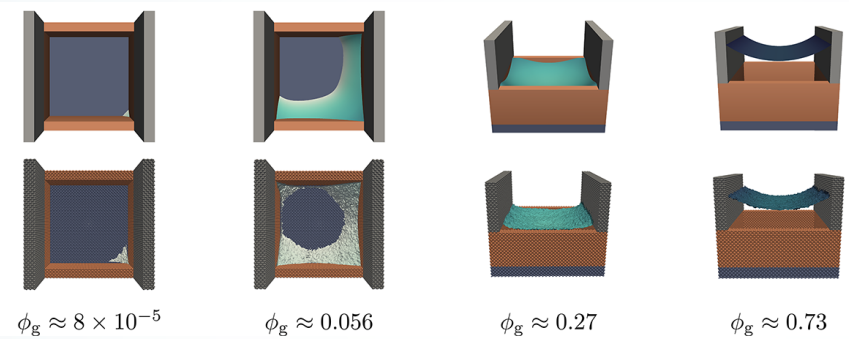
ELECTRO INTRUSION

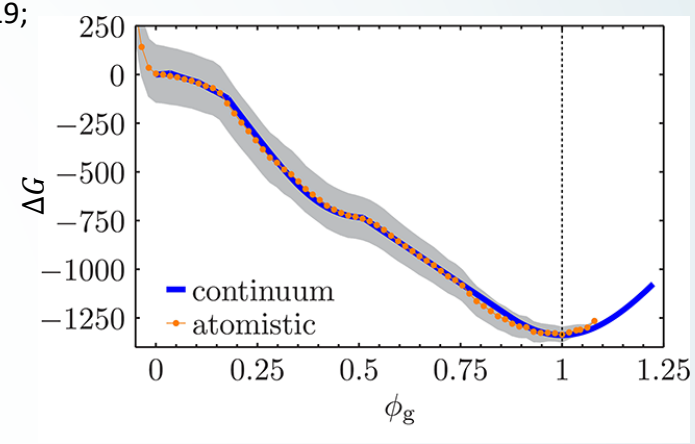
Continuum intrusion/extrusion theory

PRL **109**, 226102, 2012; *Langmuir* **29**, 14873, 2013; ACS Nano **12**, 359, 2018;Nanoscale **11**, 21458, 2019;

Atomistic

Continuum

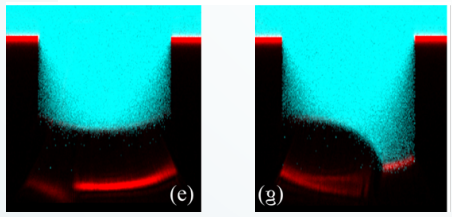




J. Chem. Phys. 2015, **142**, 104701;

Intrusion

Langmuir 2015, **31**, 1248,

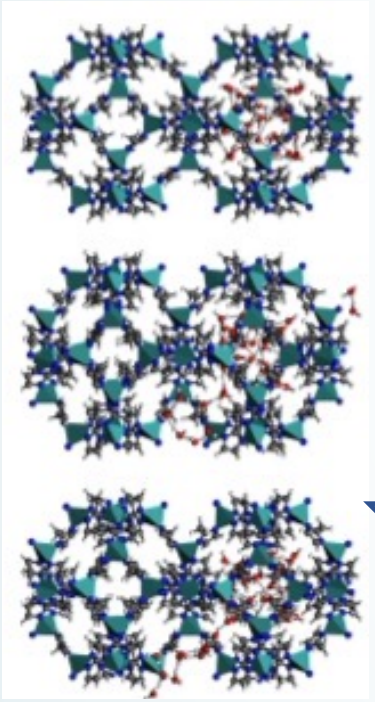


- continuum theory is a mere extension of Young-Laplace to complex geometries and **extrusion**

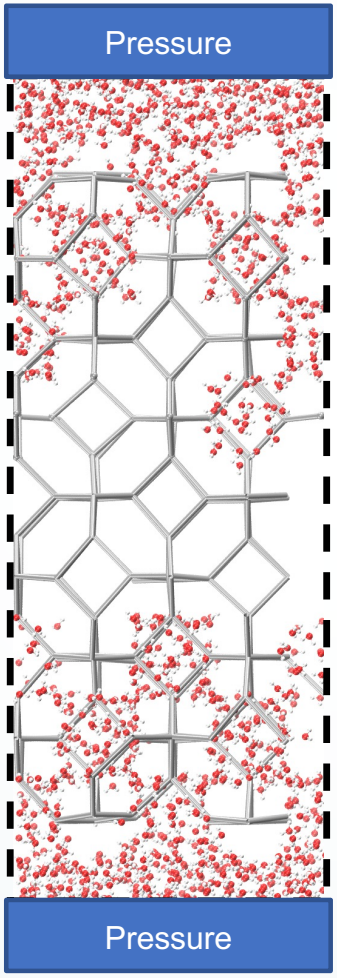
Still wrong order of magnitude P_{int} of P_{ext} of MOFs

ELECTRO INTRUSION

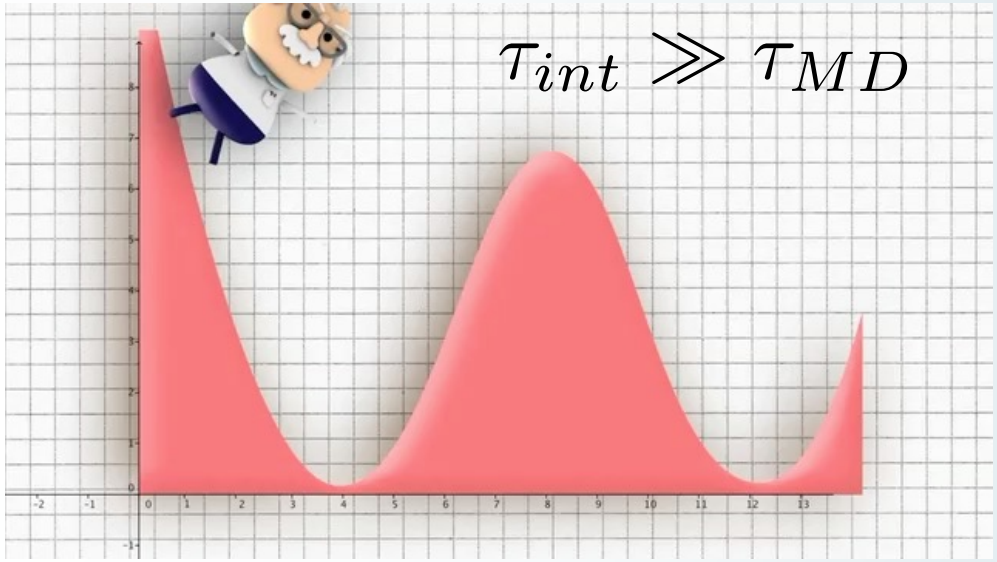
Mechanism and free energetics of intrusion in ZIF-8



MD time



Courtesy of P. Ciccotti



RMD: forces the system to visit improbably states, e.g., the barrier region

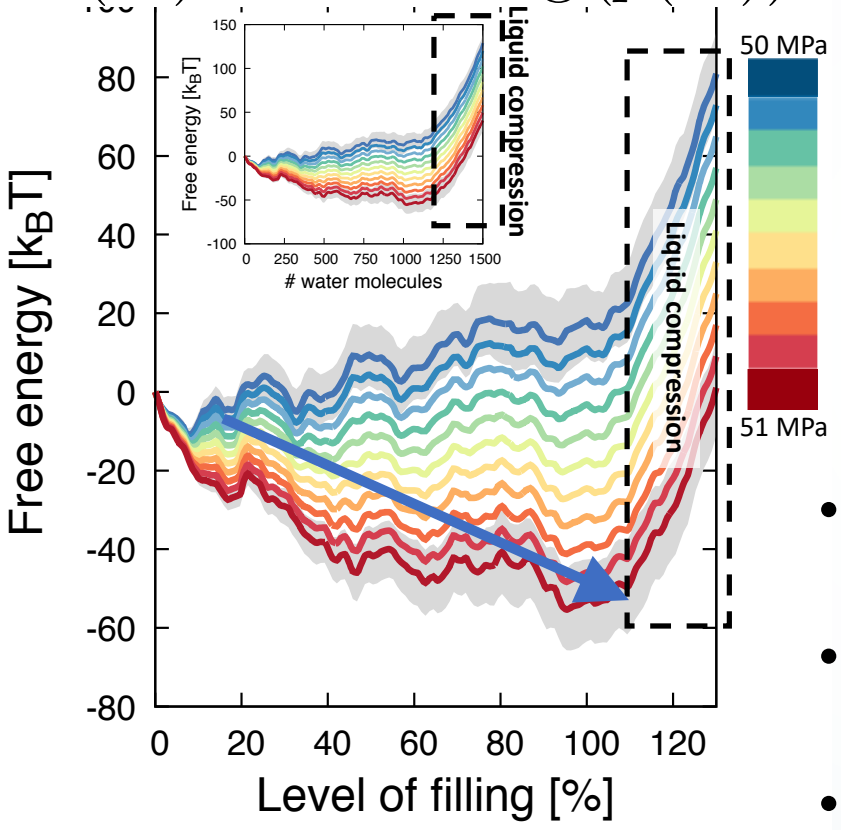
Nat. Materials 2021, **20**, 1015
Nano Letters 2021, **21**, 2848
Chem. Phys. 2018, **148,** 064706
Nano Letters 2023

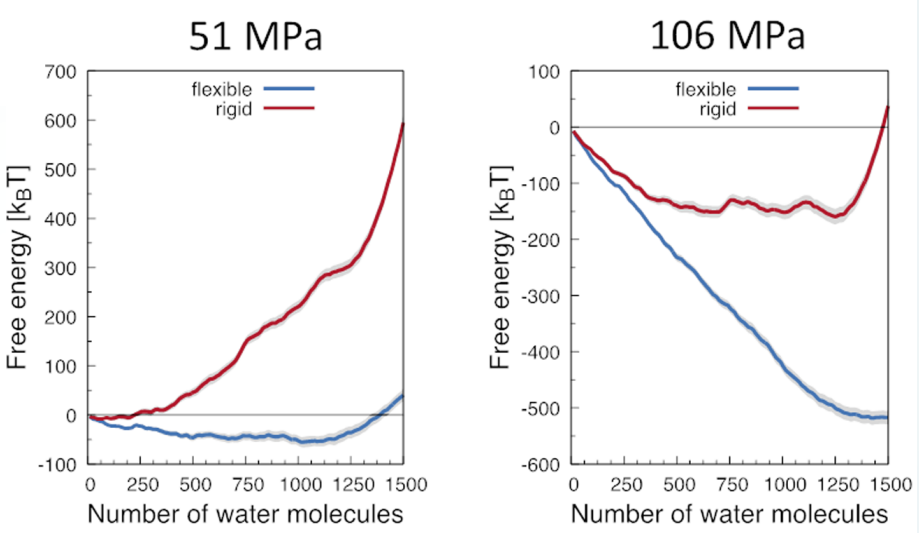
Chemical Physics Letters 2006, **426**, 168
Phys. Chem. Chem. Phys., 2011,**13**, 5952
Eur. Phys. J. B, 2012, **85**, 97

ELECTRO INTRUSION

Mechanism and free energetics of intrusion in ZIF-8

$$\Omega(N) = -k_B T \log\left(p(N)\right)$$



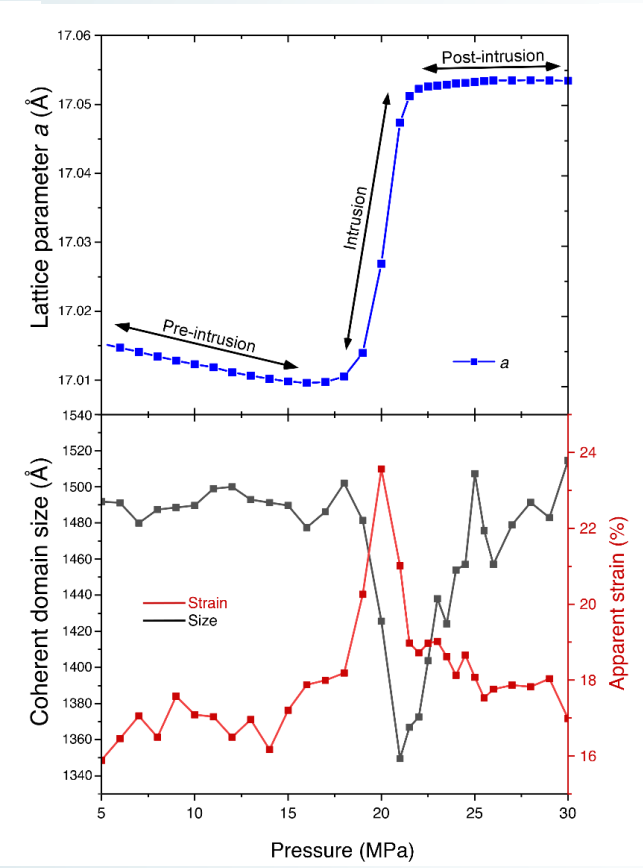


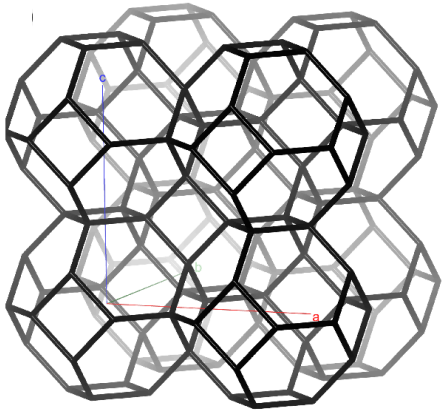
- Predicted intrusion pressure consistent with the experimental value.
- Mechanism is percolation-like, not capillary condensation
- Flexibility plays a crucial role

ELECTRO INTRUSION

Nano Letters 2021, 21, 2848; ACS Appl. Mater. Interfaces 2022, 14, 26699; Nano Letters accepted for 2023

Mechanism and free energetics of intrusion in ZIF-8



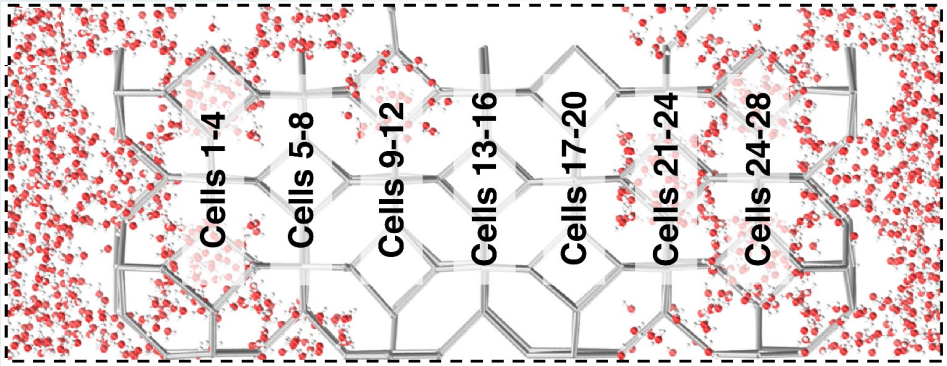


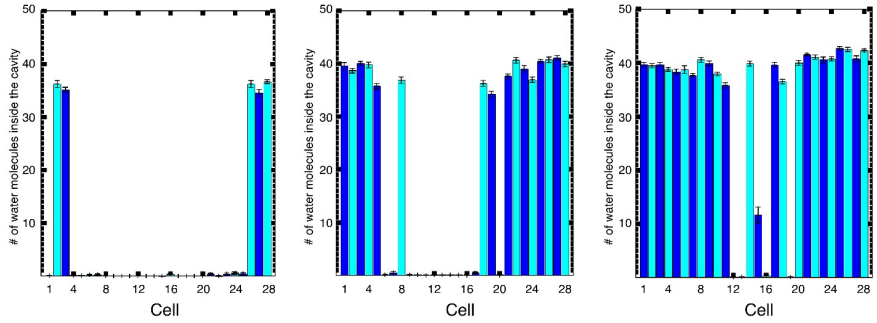
- One observes i) a strain in the lattice and ii) a initial growth and then shrink of the smallest domain
- This is conflicting with the classical model of intrusion (capillary theory)

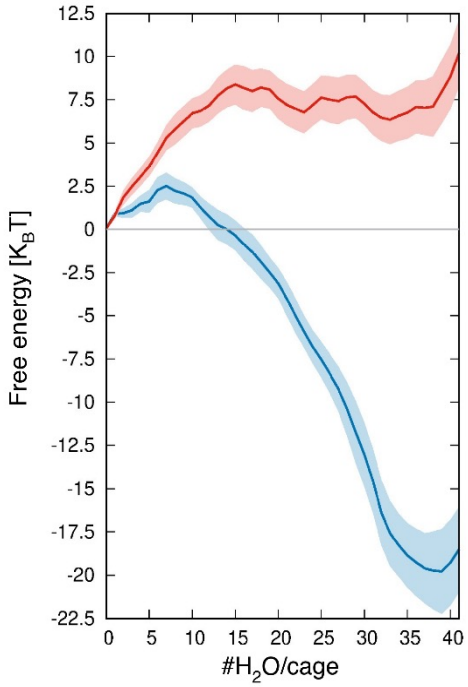
ELECTRO INTRUSION

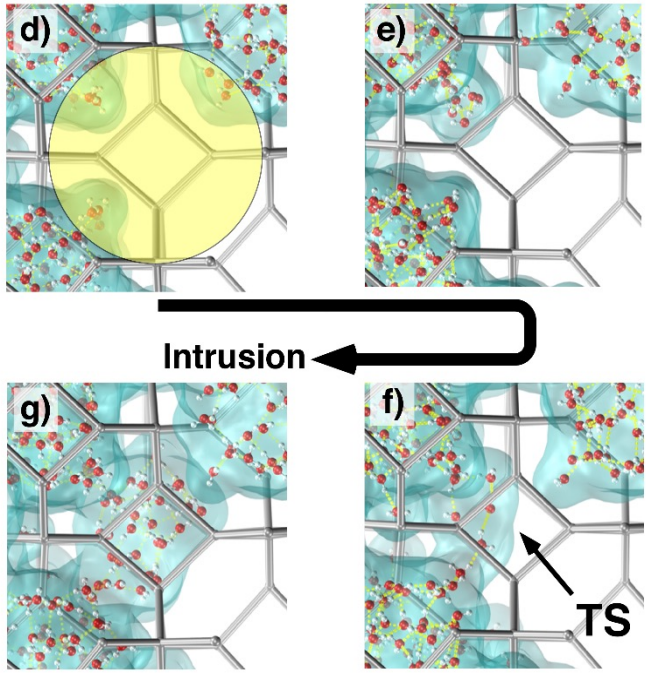
Nano Letters 2021, **21**, 2848; ACS Appl. Mater. Interfaces 2022, **14**, 26699; Nano Letters accepted for 2023
Nat. Materials 2021, **20**, 1015;

Mechanism and free energetics of intrusion in ZIF-8





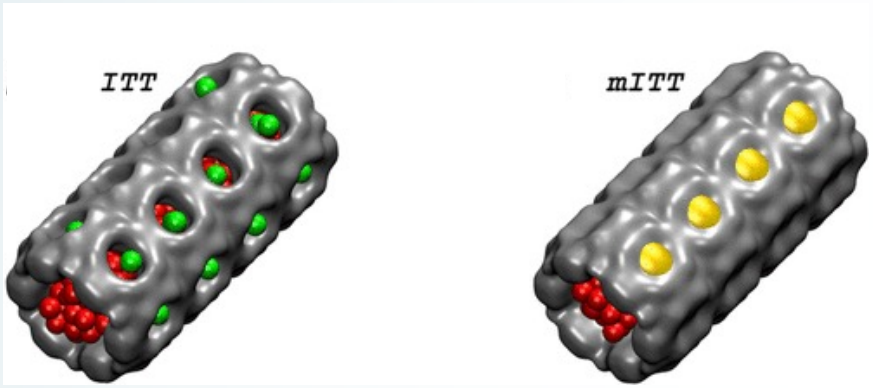


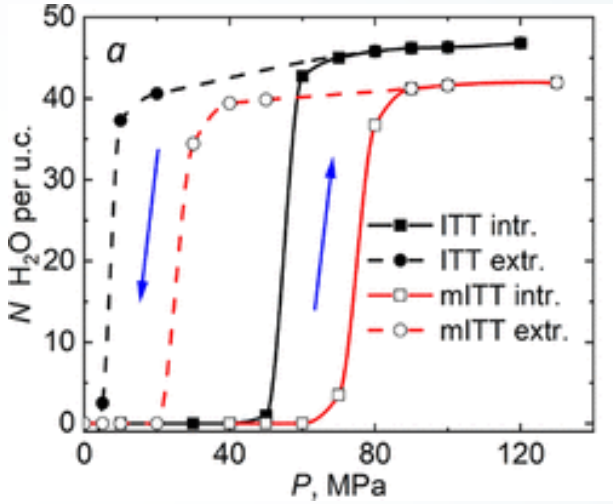


ELECTRO INTRUSION

Nano Letters accepted for 2023

Effect of secondary subnanometric features of porous systems





Effect of secondary apertures opposite than standard theories:
The system present an Anti Cassie-Baxter/Wenzel, shallow lateral apertures reduces hydrophobicity, **with the effective contact angle going from $\theta = 114°$ to $\theta = 106°$**

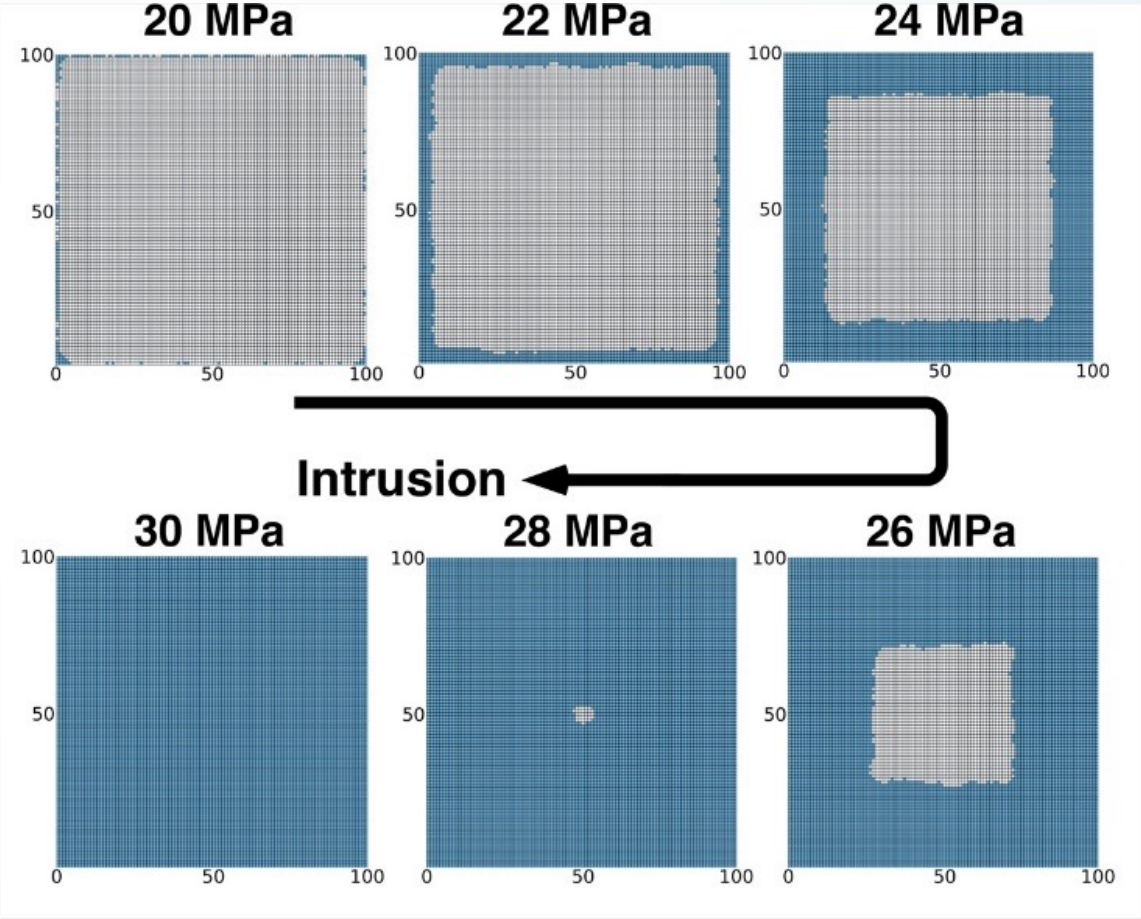
ELECTRO INTRUSION

Nano Lett. 2022, 22, 6, 2164−2169

Mechanism and free energetics of intrusion in ZIF-8

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

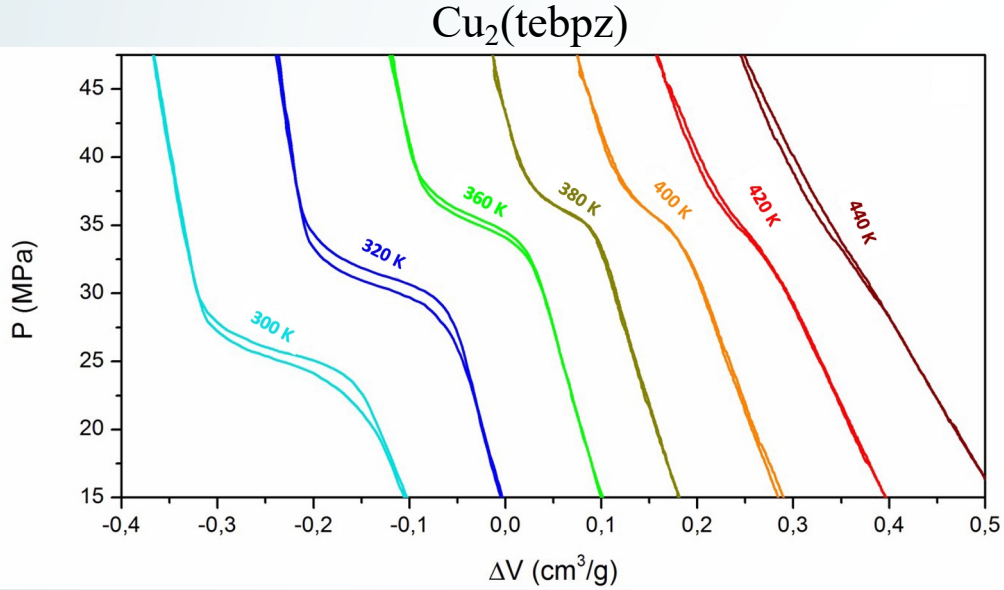
$$t_e = t_e^0 e^{\frac{\Omega_e}{k_B T}}$$

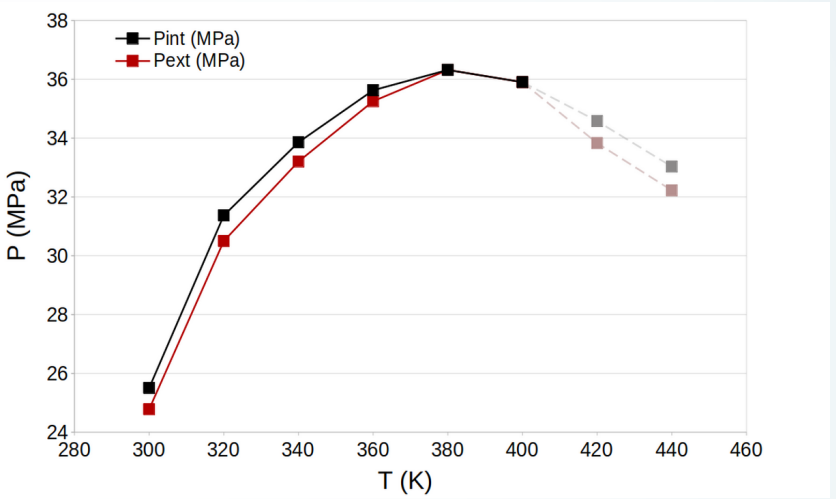


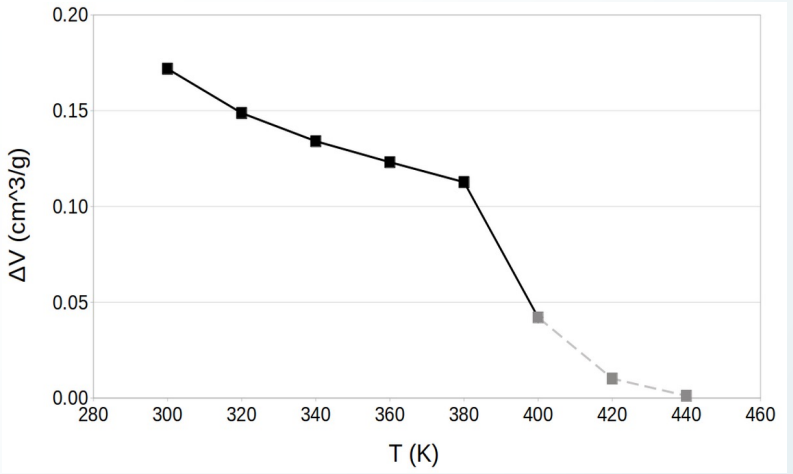
ELECTRO INTRUSION

Nano Letters accepted for 2023

Other (selected) bizarreness of highly confined liquids

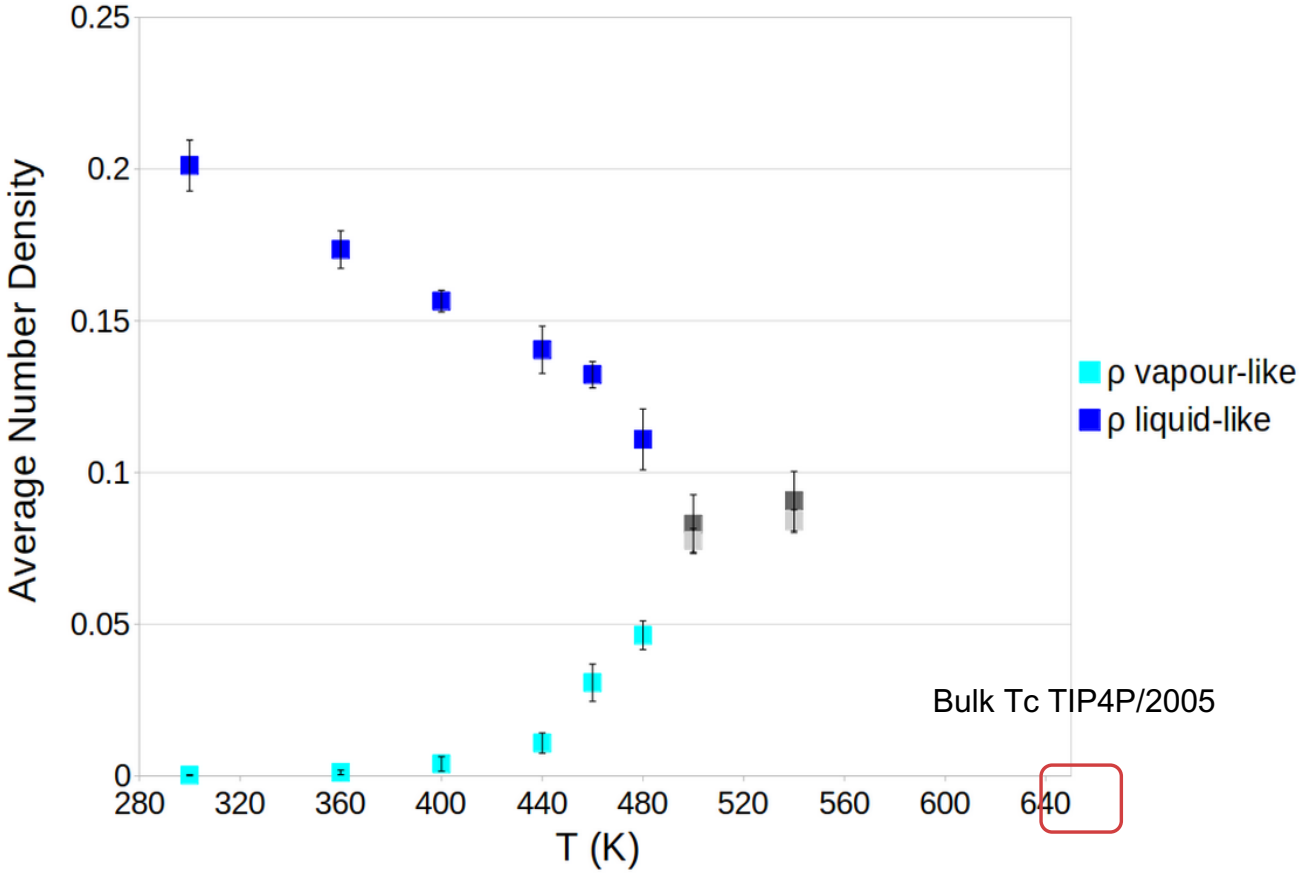


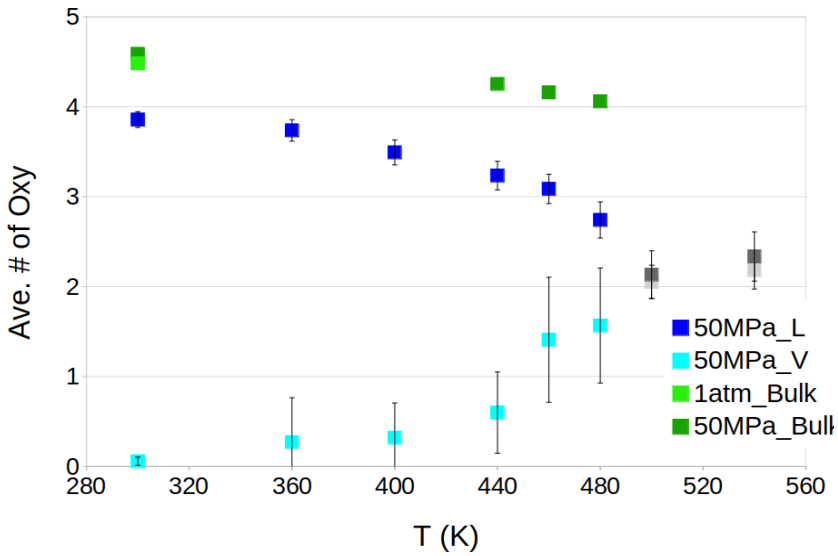




ELECTRO INTRUSION

Giant reduction of the critical temperature





ELECTRO INTRUSION

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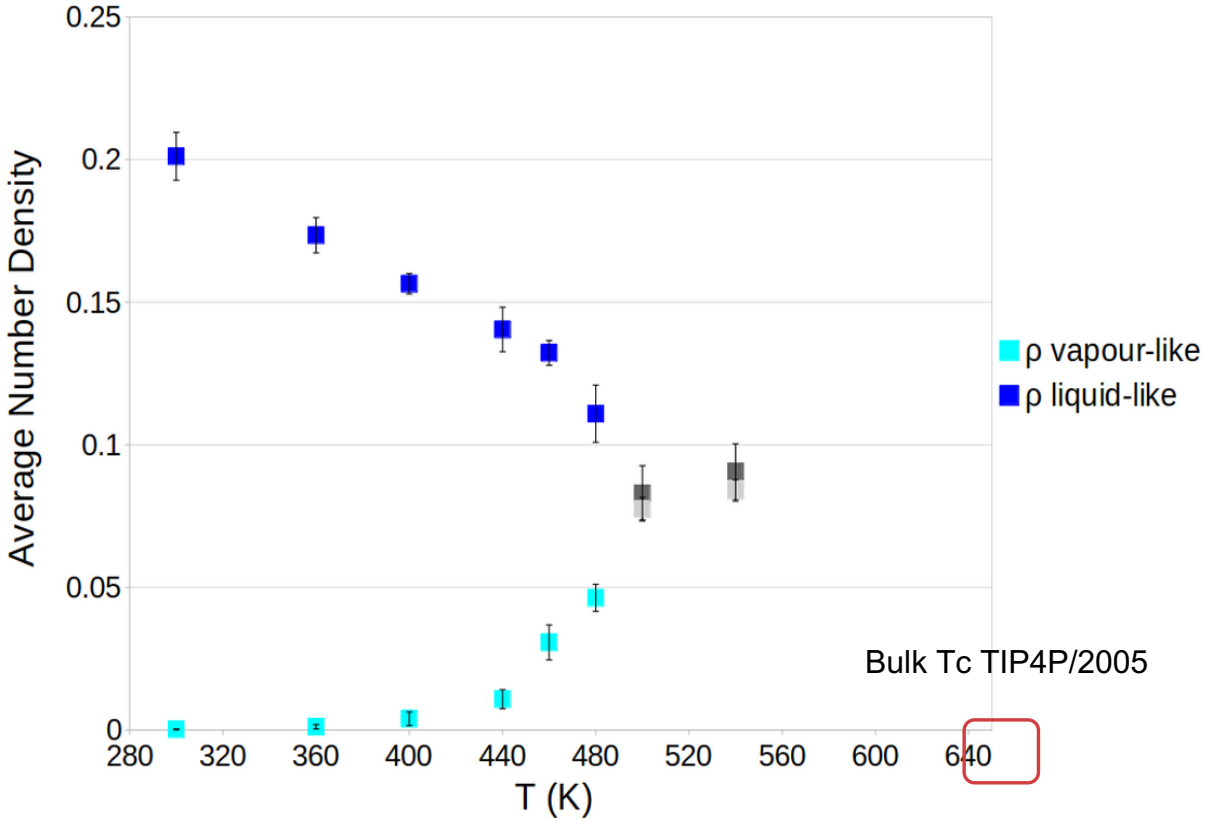
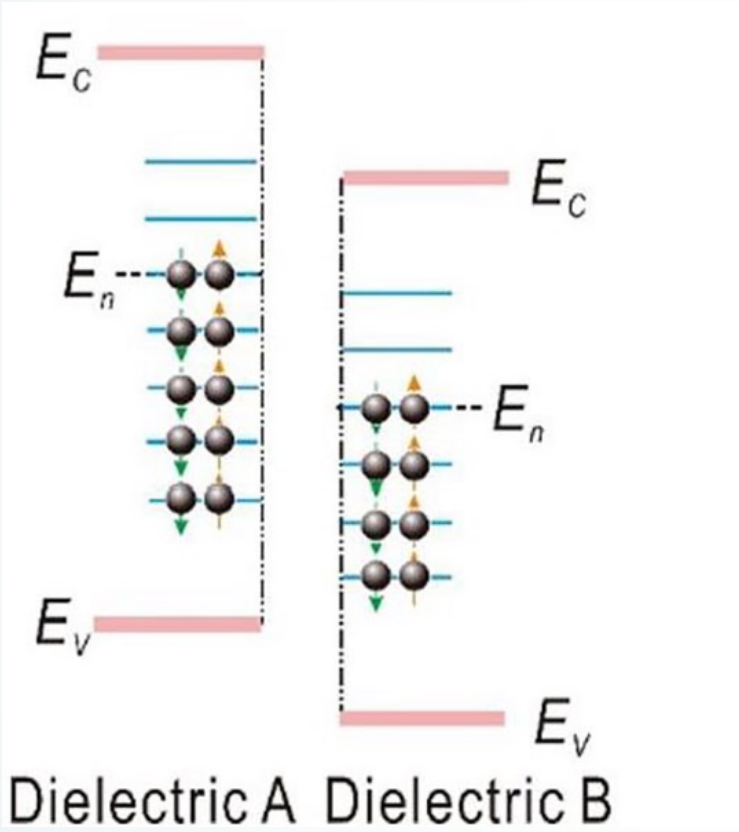


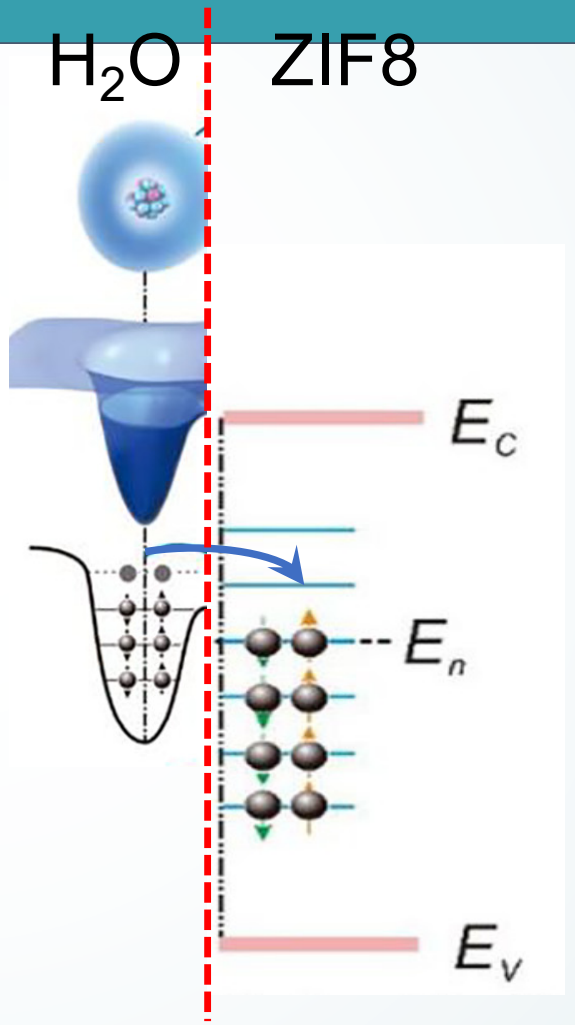
Possible technological uses:

- Cooling thanks to the higher heat capacity of supercritical fluids
- Supercritical solvents for chemical reactions
- Thermal-to-mechanical energy conversion
- Actuation

ELECTRO INTRUSION

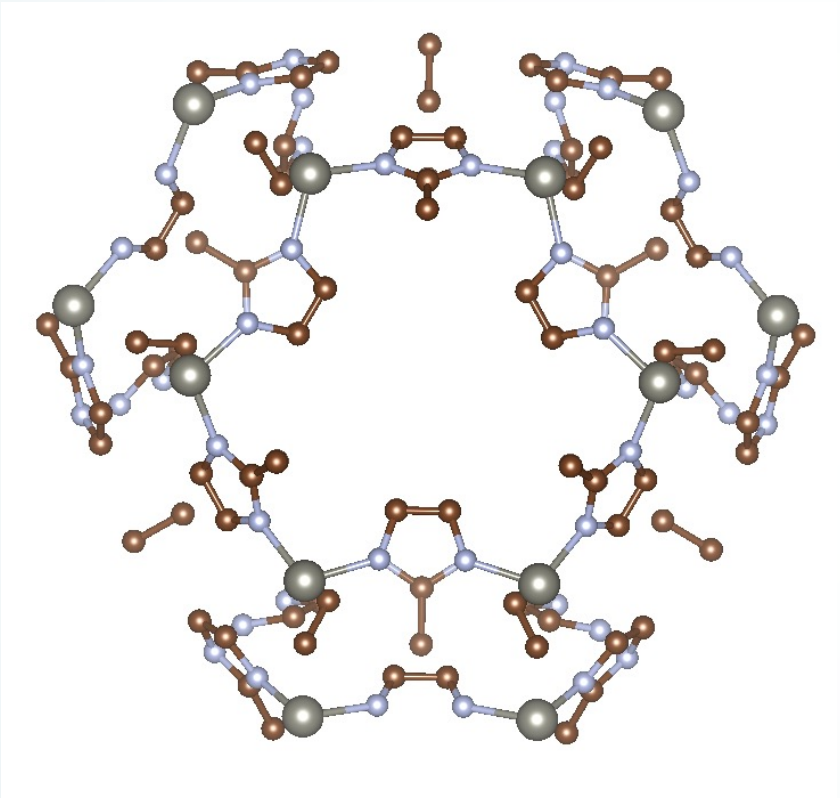
Crash course on contact electrification

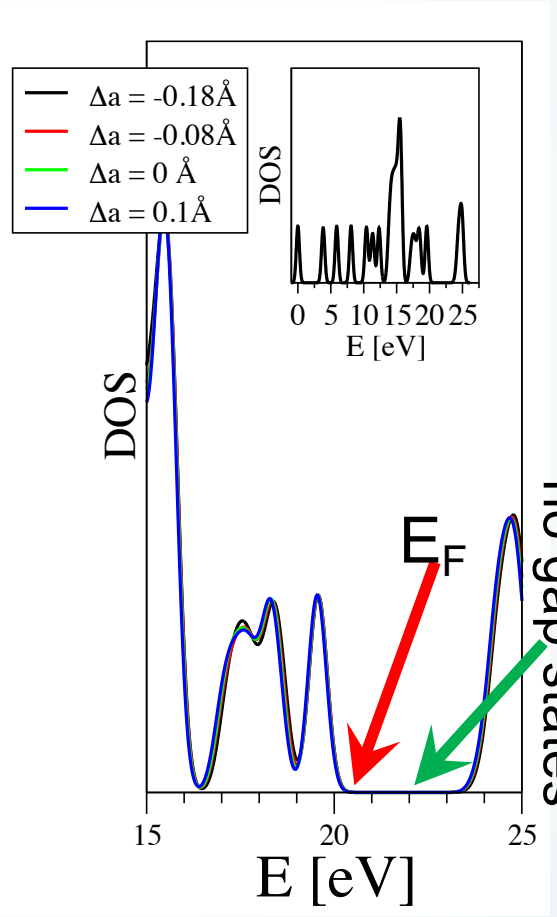




ELECTRO INTRUSION

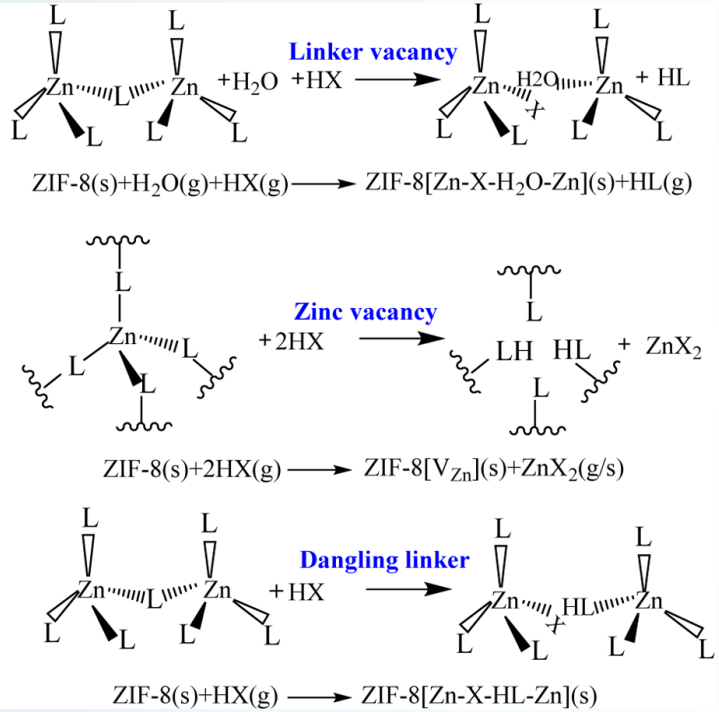
Challenges with internal surfaces of MOFs

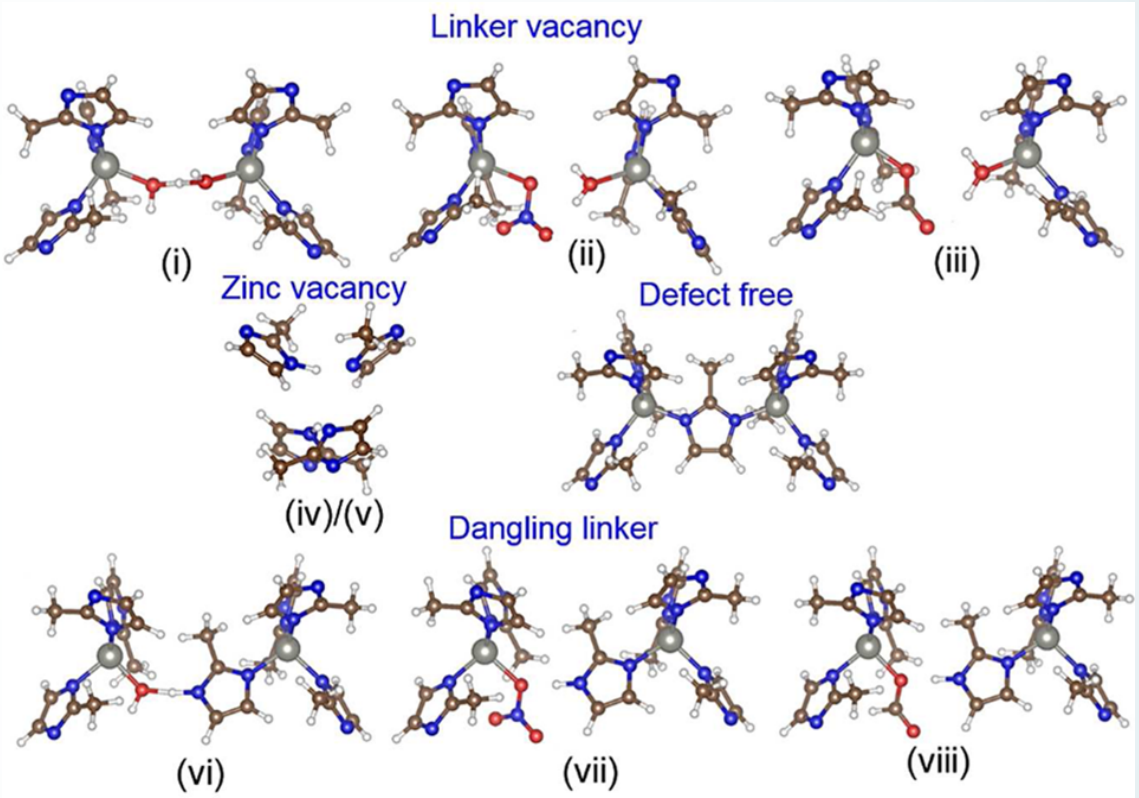




ELECTRO INTRUSION

Is contact electrification possibly due to defects?

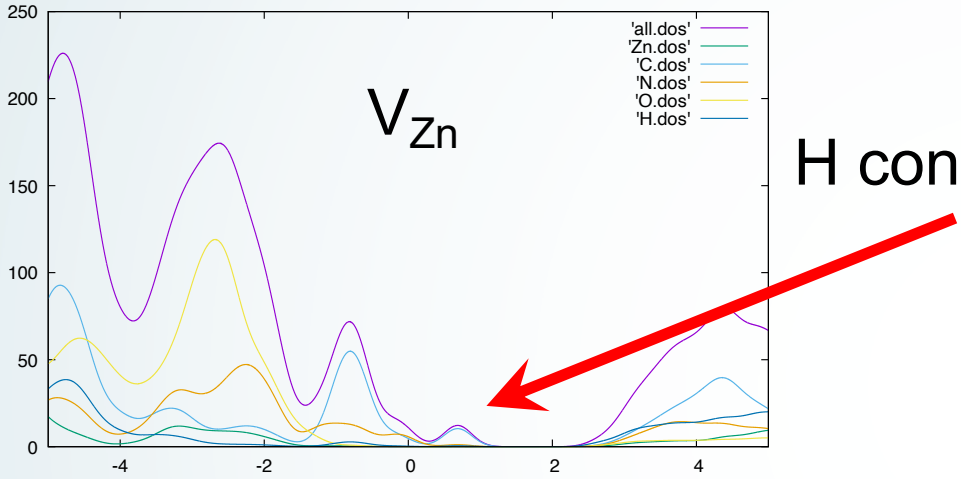




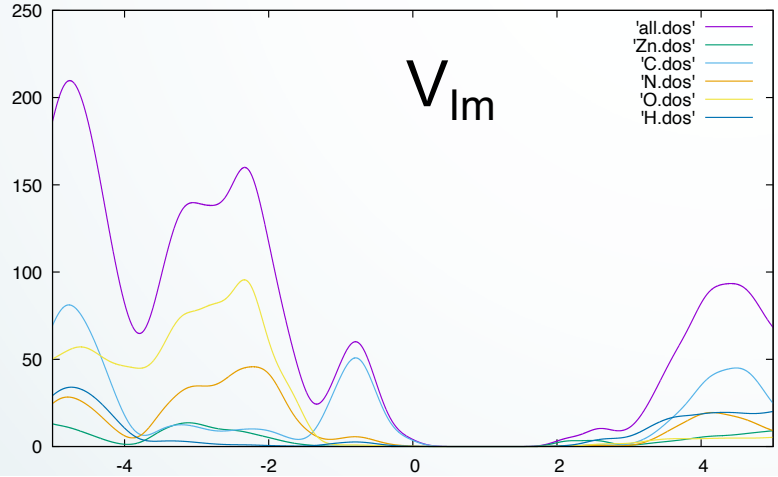
J. Phys. Chem. Lett. 2018, 9, 4037−4044

J. Phys. Chem. Lett. 2016, 7, 459−464

Defected ZIF-8/water contact eòectrification



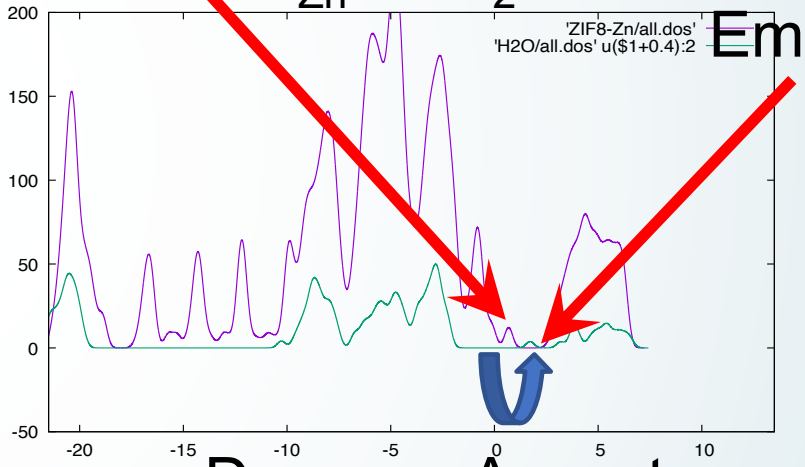
H contribution



Occupied

V_{Zn} vs H_2O

Empty



Donor ⇢ Acceptor

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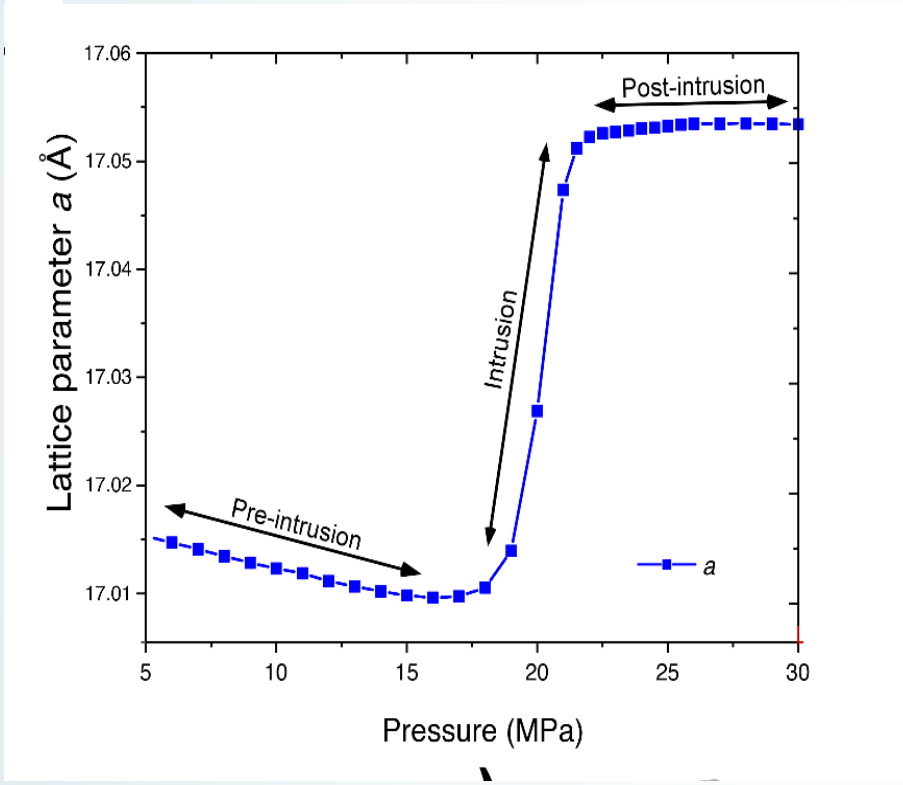
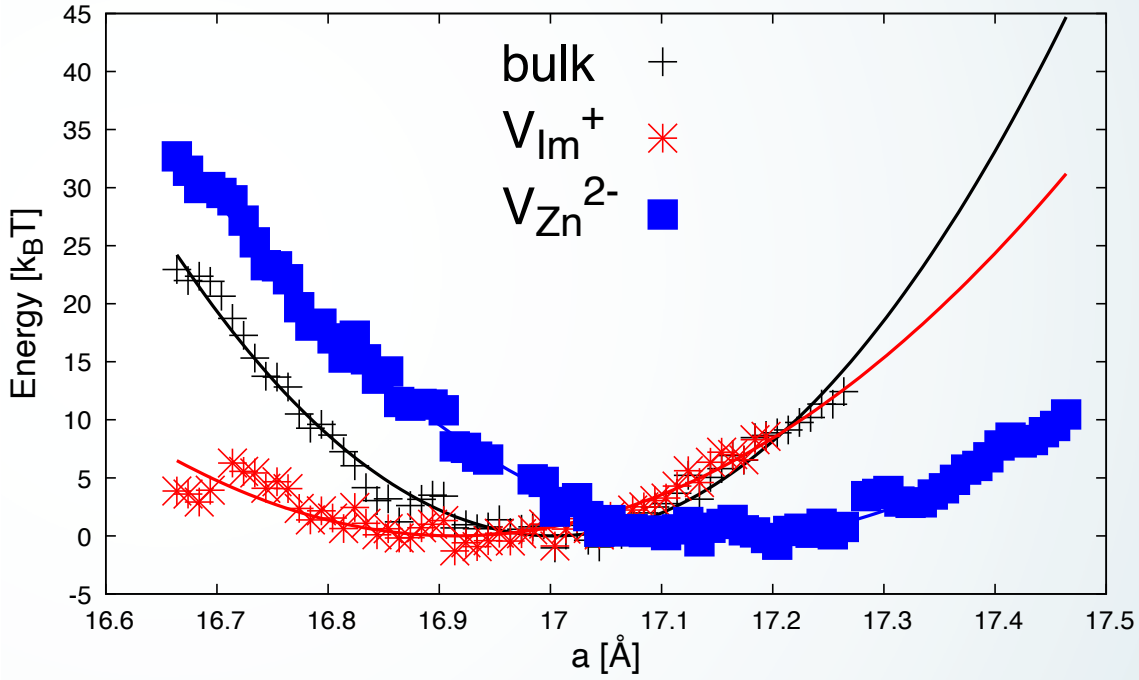
Negative compressibility & defect formation





ELECTRO INTRUSION

Conclusions

- We plan to develop a technology to recover energy dispersed in vibrations using intrusion/extrusion-based TENGs
- This requires understanding many fundamental chemical and physical phenomena
- Here, I focused only on liquid intrusion/extrusion in nanoporous materials…
  - which do not obey to classical laws
- …, *Exotic* properties of highly confined liquid in non-trivial porosities…
  - No cylindrical or slit structures
- And shortly touched contact electrification

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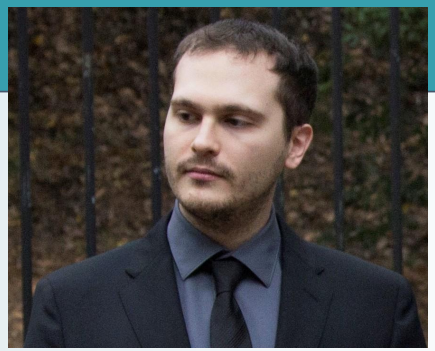
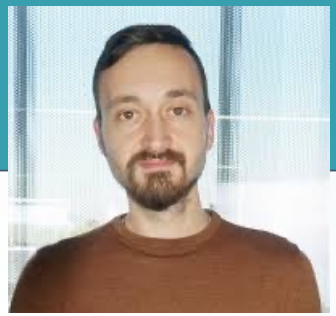
Acknowledgements



Marco Tortora

Seb Merchiori



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Alberto Giacomello

Carlo Massimo Casciola

Andrea Le Donne

Josh Littlefair

H2020-FET Electro-Intrusion

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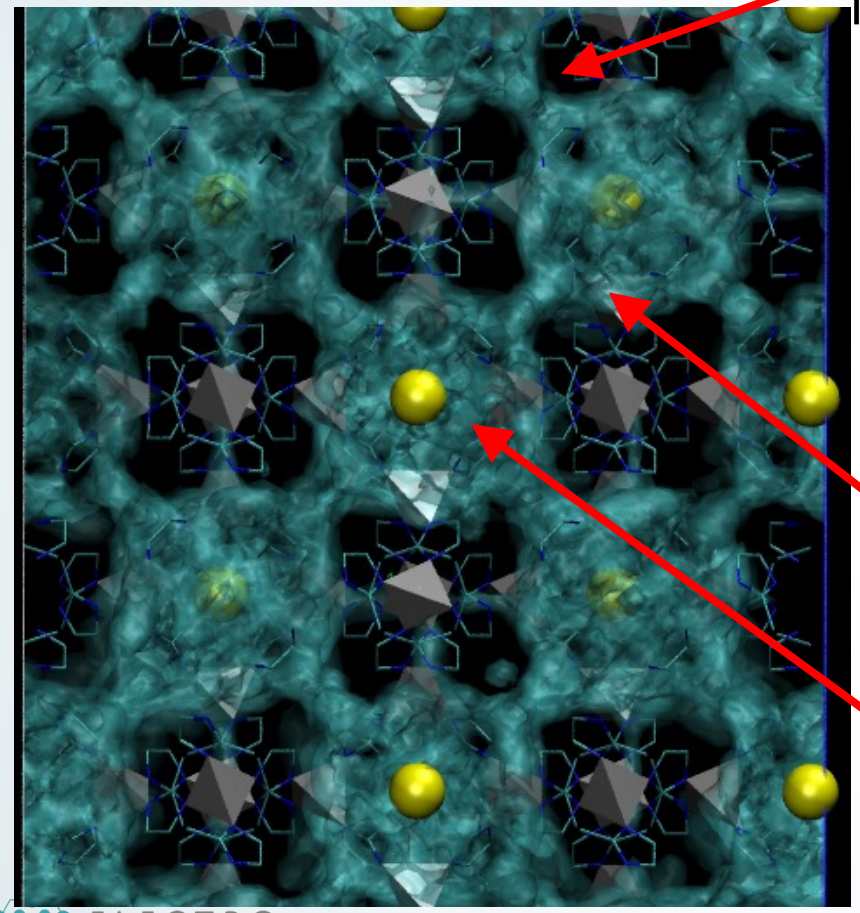
Thanks for your attention!

ELECTRO INTRUSION

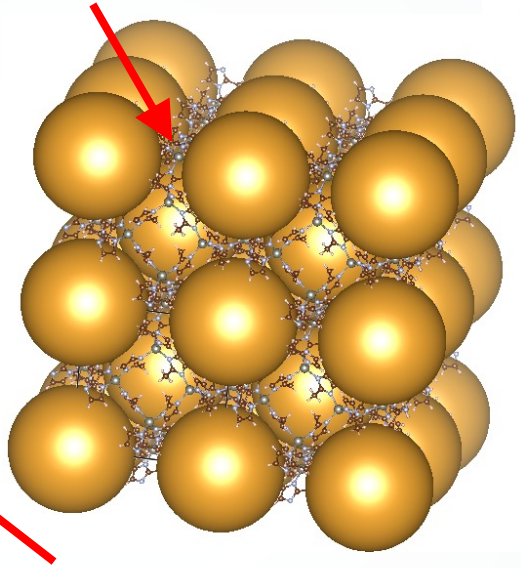
Backup

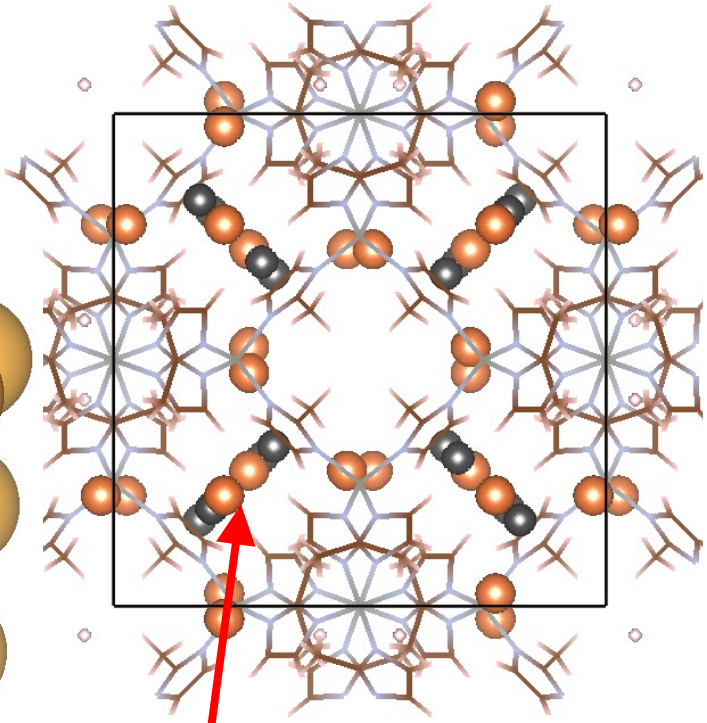
H2020-FET

ELECTRO INTRUSION



Secondary interconnections





Crystal-like and liquid-like water

Water sites with Fractional occupation

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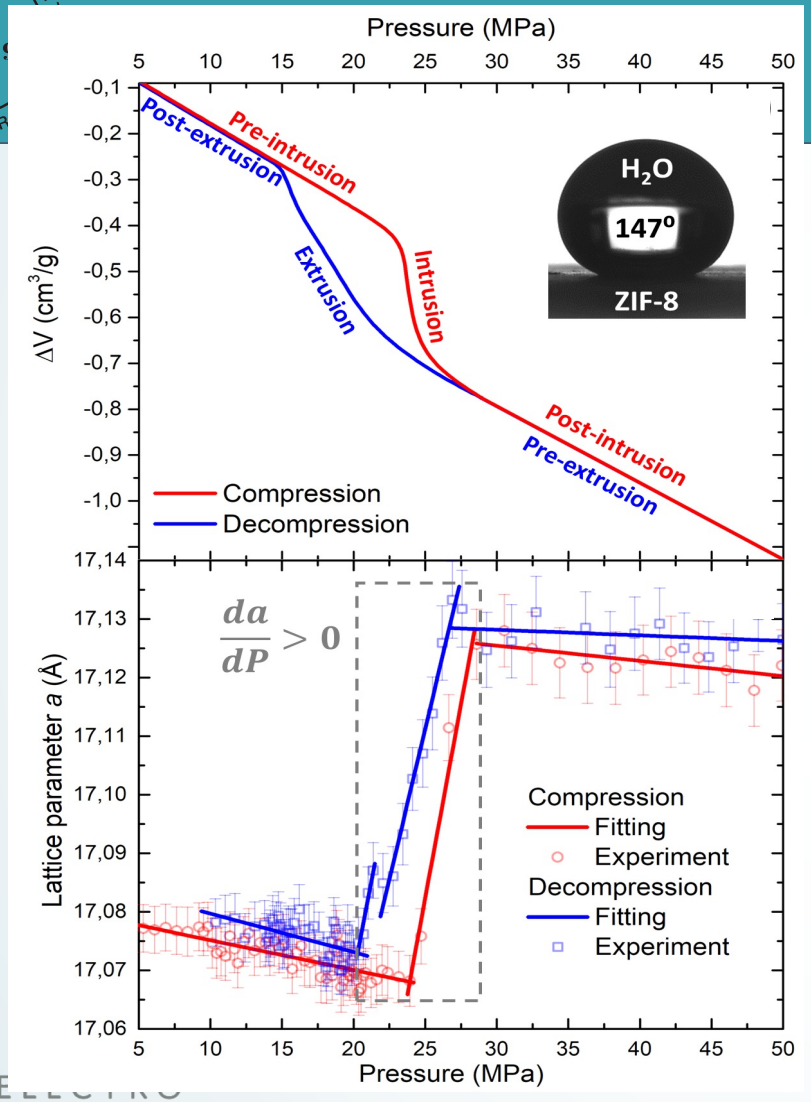
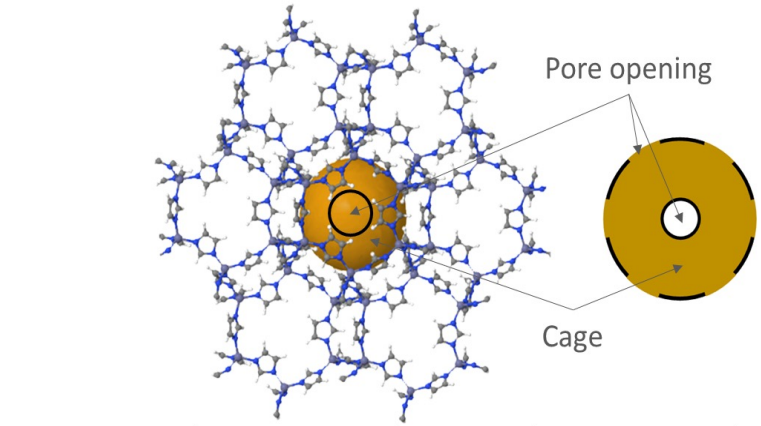
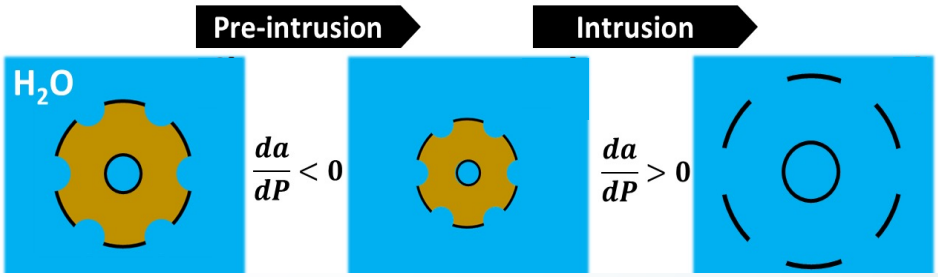
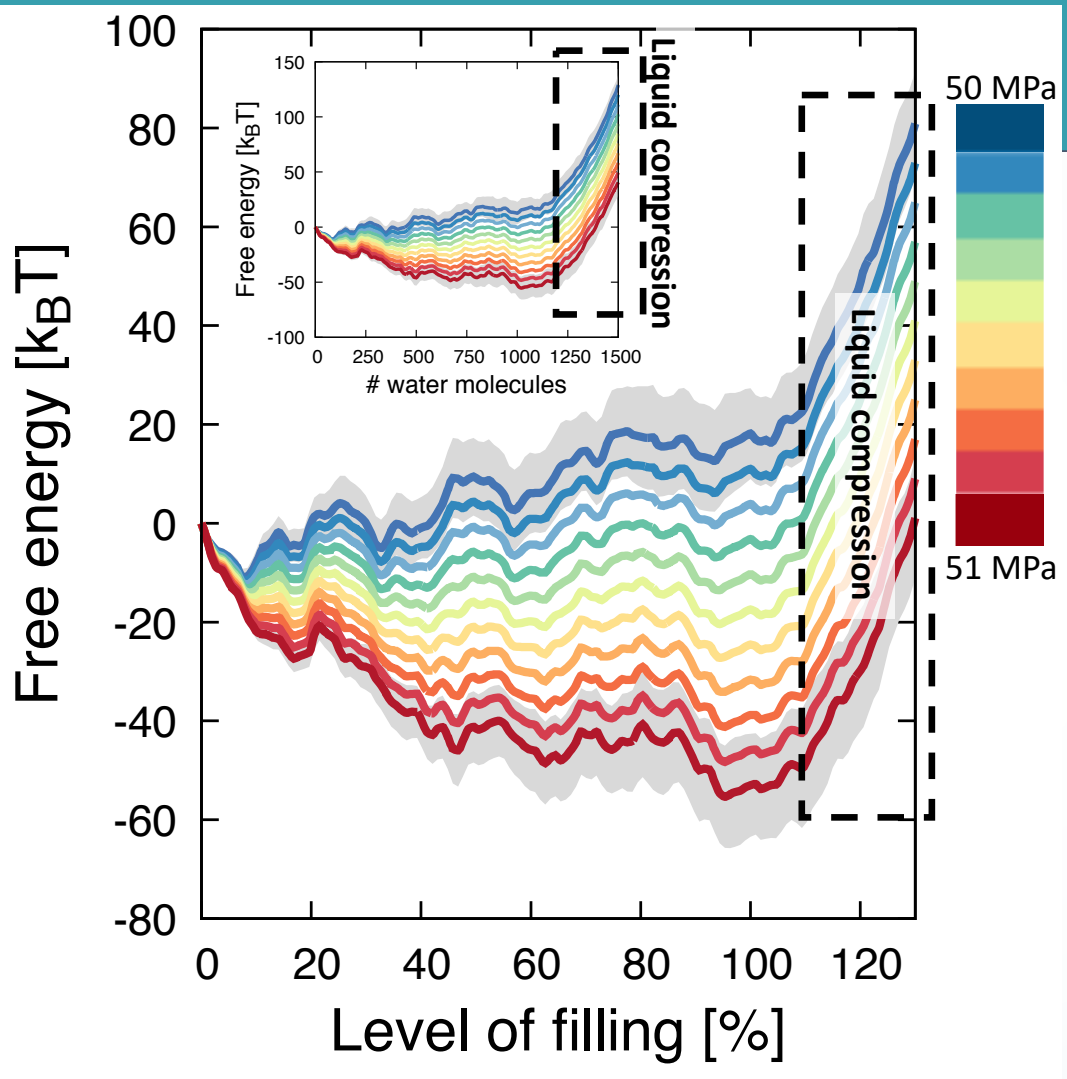
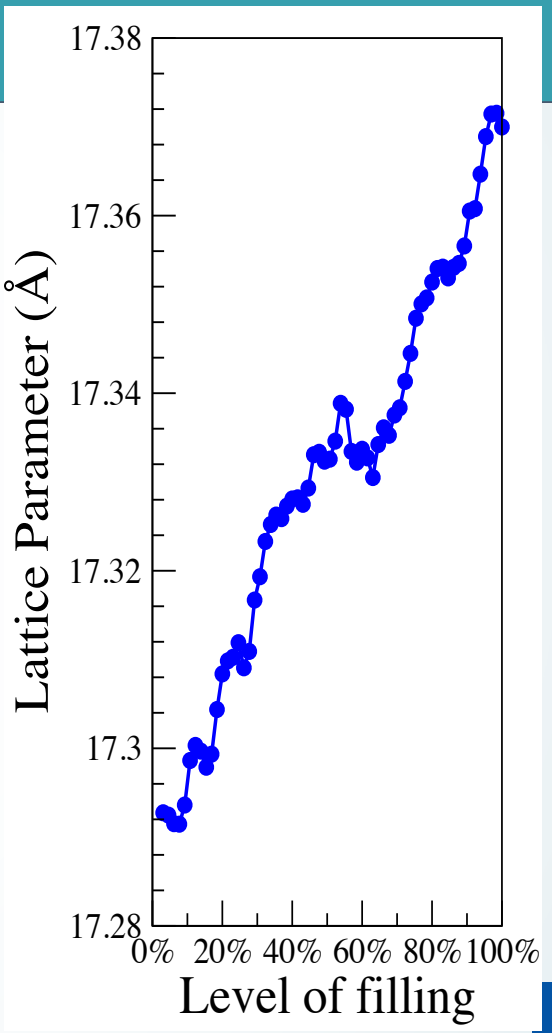

Pressure (MPa)
ΔV (cm³/g)
Post-extrusion
Pre-intrusion
Extrusion
Intrusion
Post-intrusion
Pre-extrusion
H₂O
147°
ZIF-8
Compression
Decompression
Lattice parameter a (Å)
da/dP > 0
Compression
Fitting
Experiment
Decompression
Fitting
Experiment
Pressure (MPa)

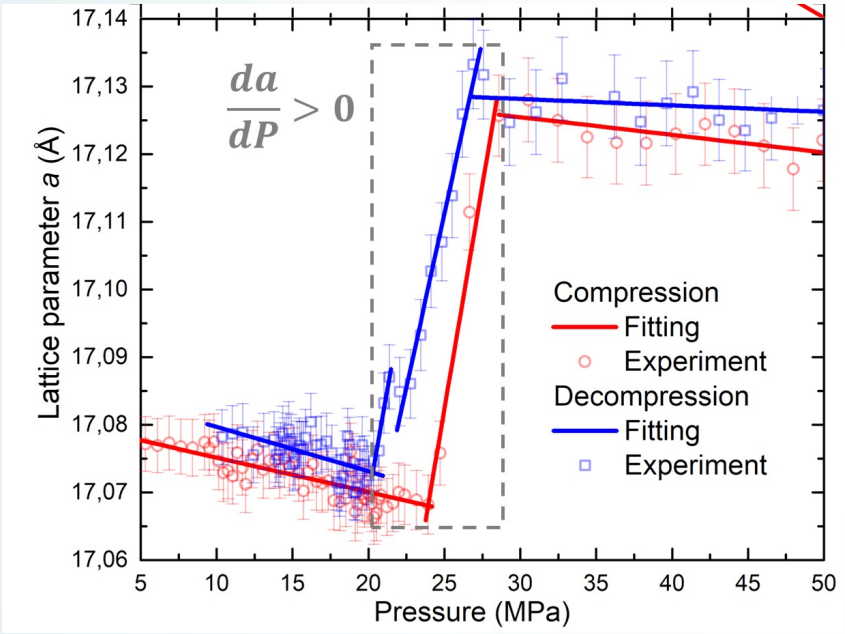

Pore opening
Cage

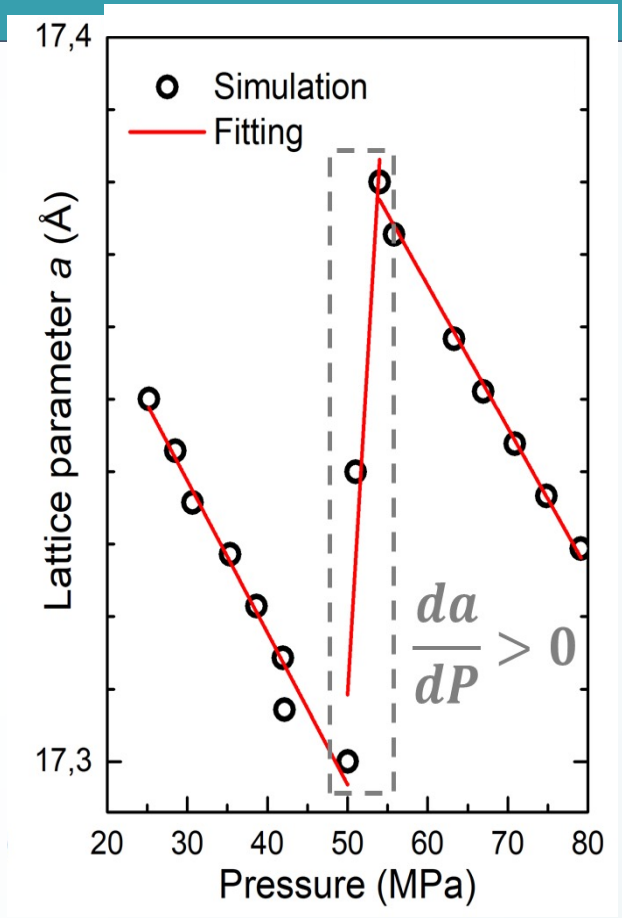

Pre-intrusion
Intrusion
H₂O
da/dP < 0
da/dP > 0

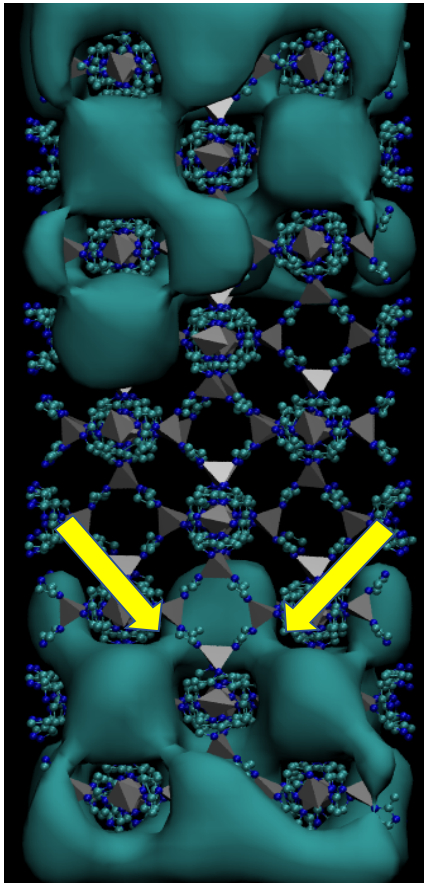


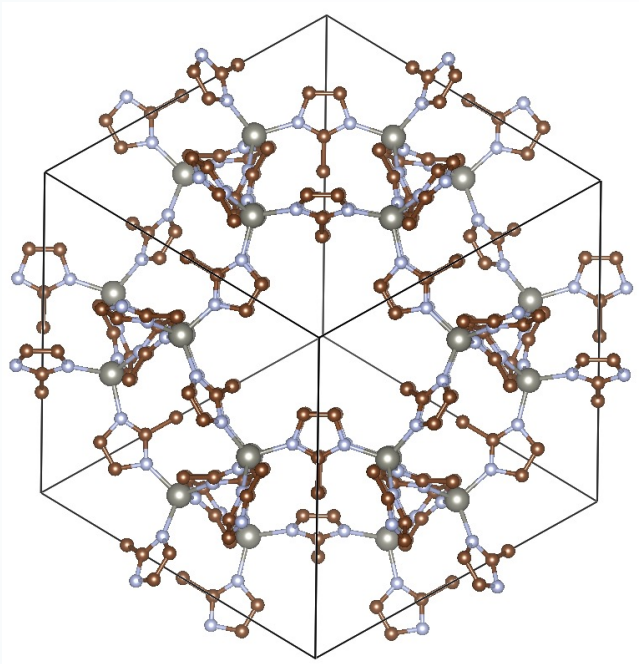


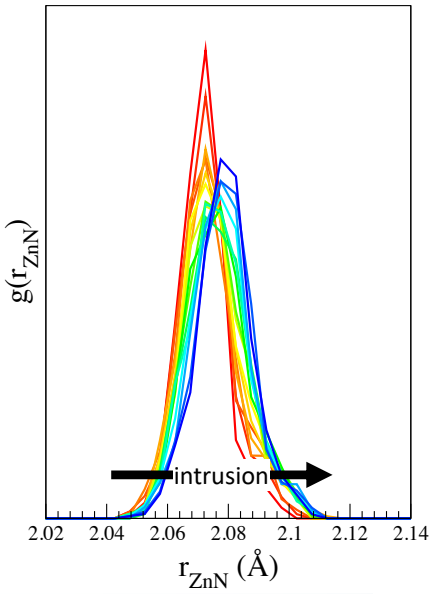
ELECTRO INTRUSION

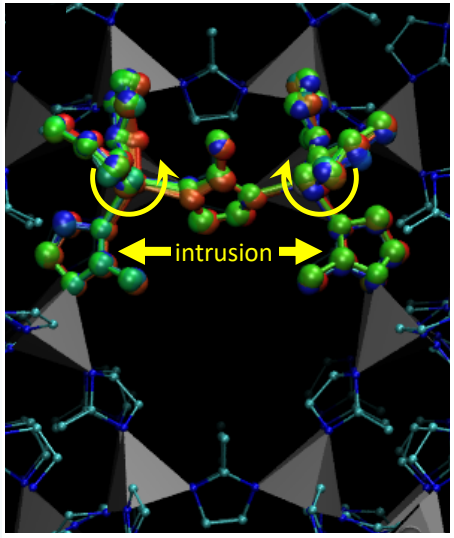

17,14
17,13
17,12
17,11
17,10
17,09
17,08
17,07
17,06
Lattice parameter a (Å)
5
10
15
20
25
30
35
40
45
50
Pressure (MPa)
$\frac{da}{dP} > 0$
Compression
Fitting
Experiment
Decompression
Fitting
Experiment


17,4
17,3
Lattice parameter a (Å)
20
30
40
50
60
70
80
Pressure (MPa)
Simulation
Fitting
$\frac{da}{dP} > 0$

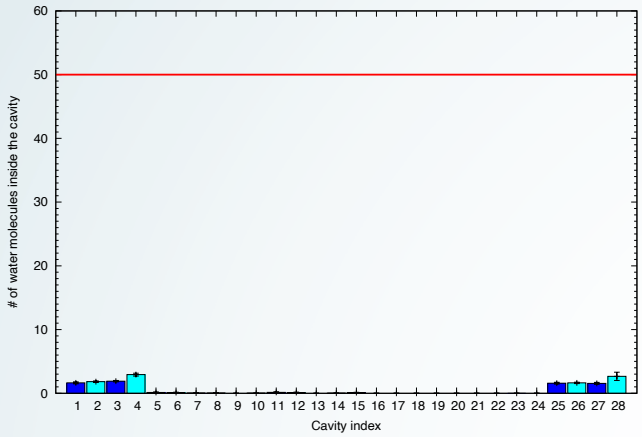


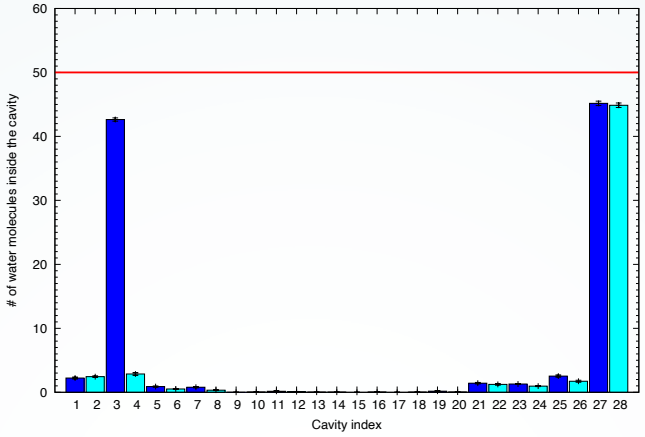


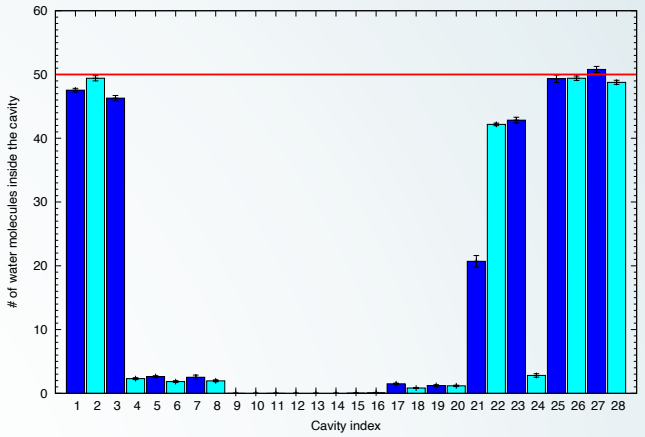




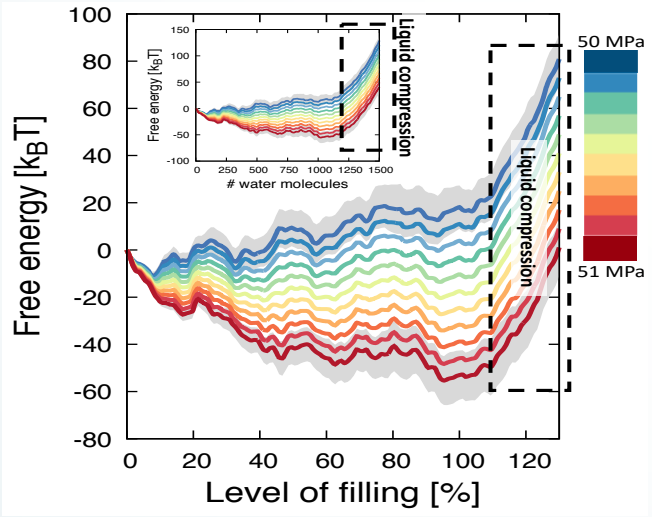
ELECTRO INTRUSION

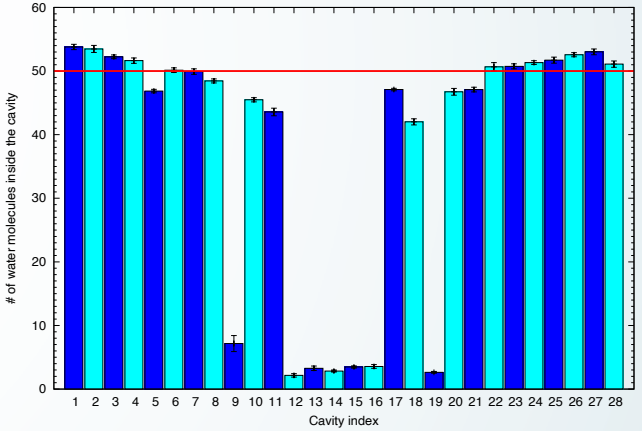






Intrusion





ELECTRO INTRUSION