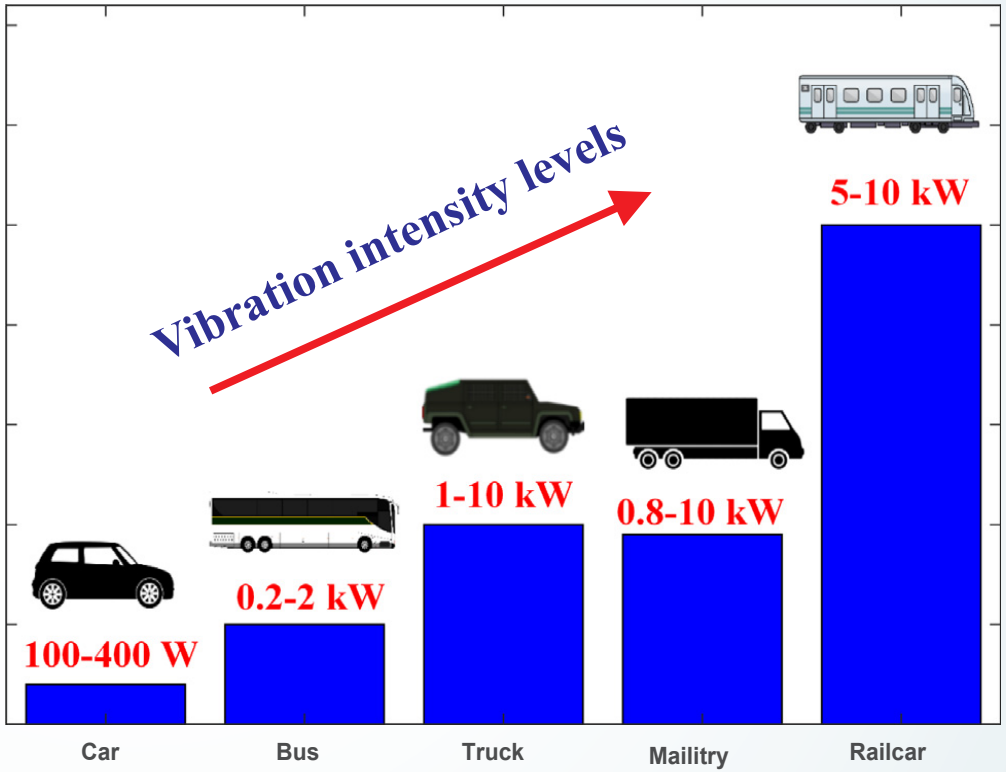

Wetting and drying of nanoporous systems:
From theoretical modeling to design
principles of novel energy materials
Simone.meloni@unife.it
ELECTRO
INTRUSION
ACS
Chemistry for Life®
AMERICAN CHEMICAL SOCIETY
MEETINGS & EVENTS
ACS FALL 2022
SUSTAINABILITY IN A CHANGING WORLD
AUGUST 21–25
Chicago, IL • Hybrid
#ACSFall2022

Energy dissipated in vibrations

1kW

50W



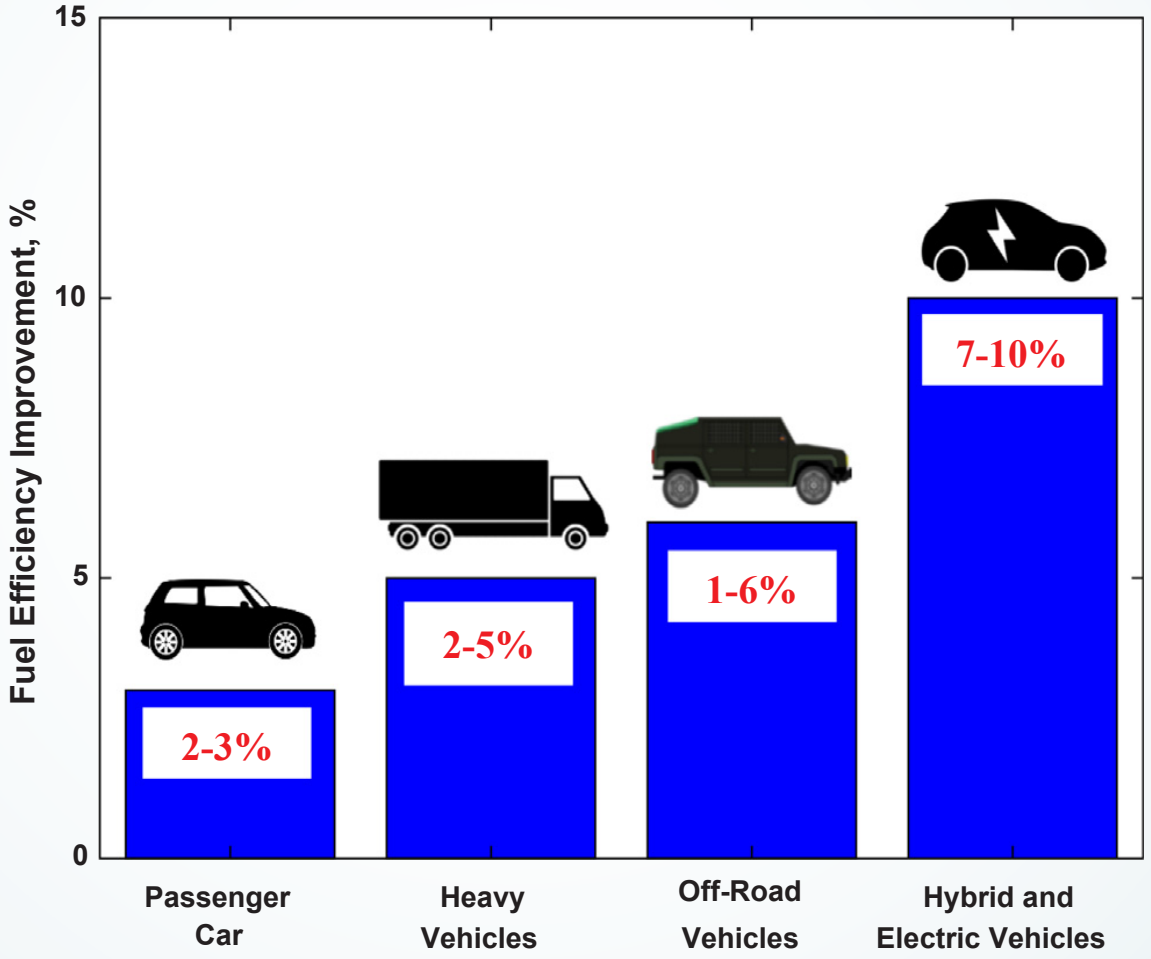
2-8 fridges **1-10 ovens** **5 fridges/10 ovens**

4 fridges/1 oven **16 fridges/10 oven**

ELECTRO INTRUSION

Applied Energy 229 (2018) 672–699

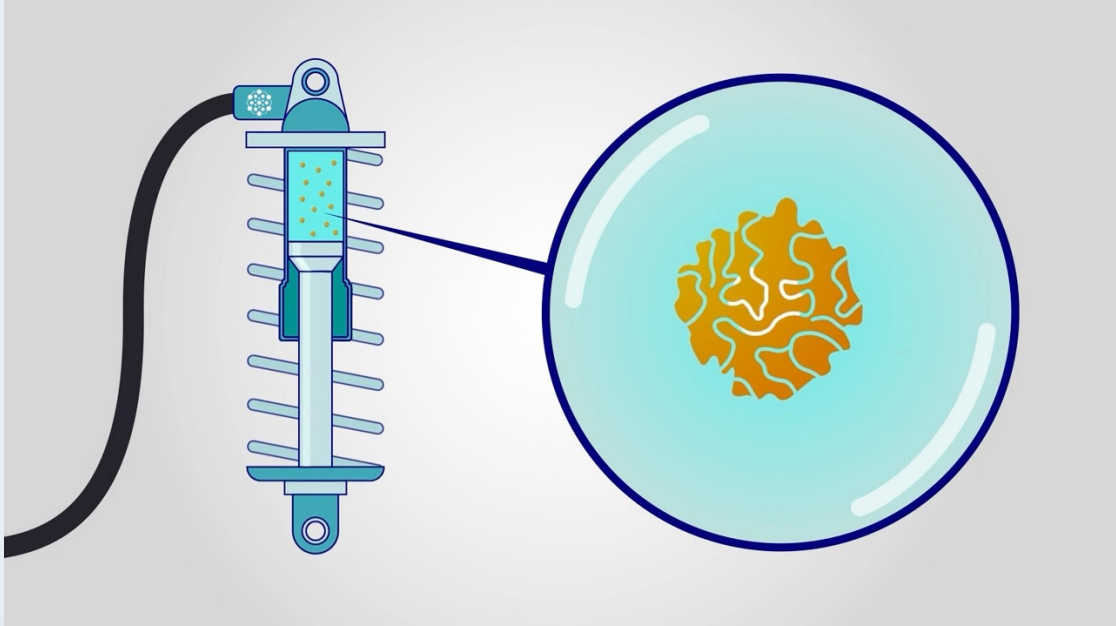
efficiency potentiality using regenerative energy shock absorbers

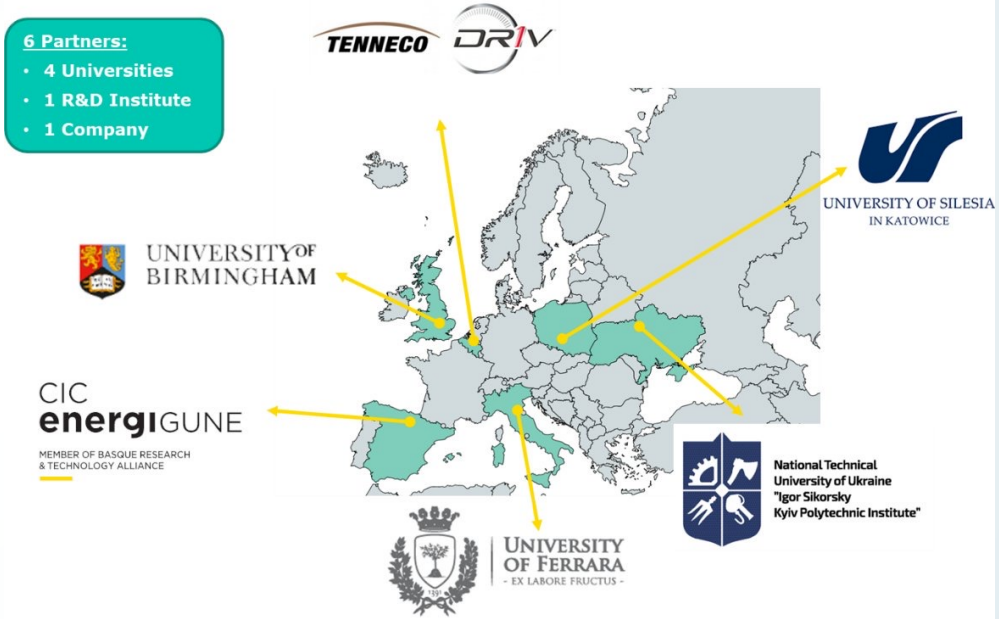


Applied Energy 229 (2018) 672–699

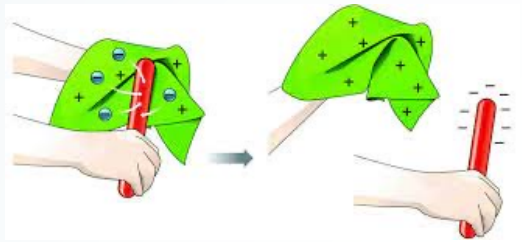
ELECTRO INTRUSION

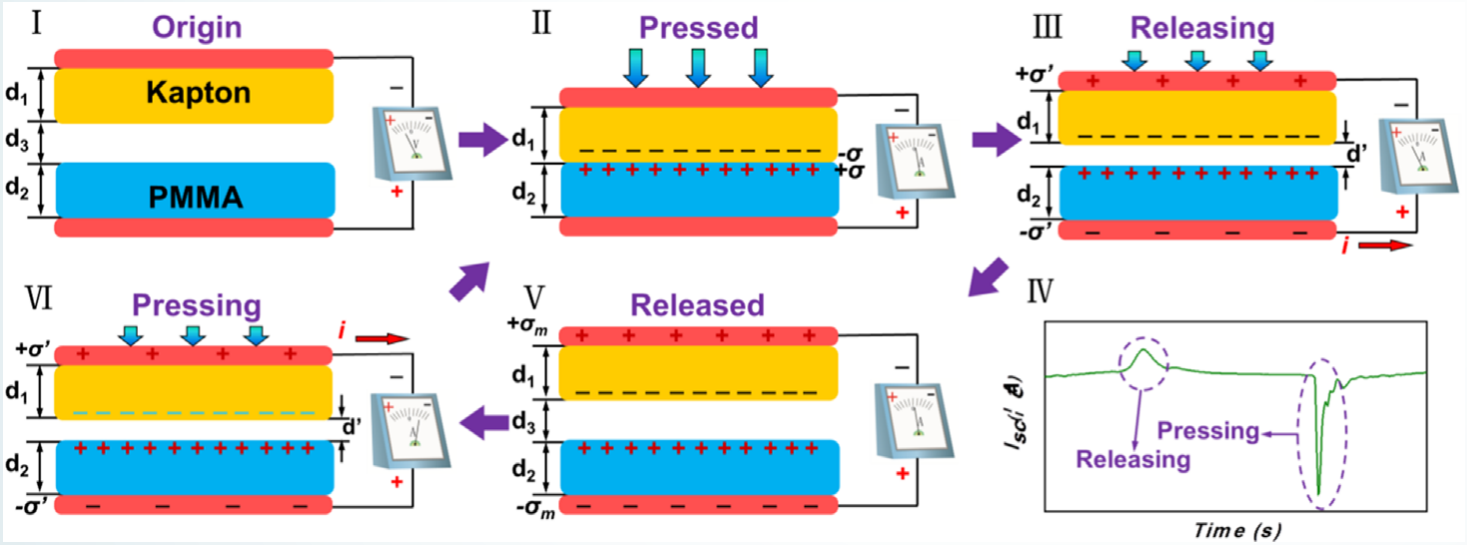
Our final goal

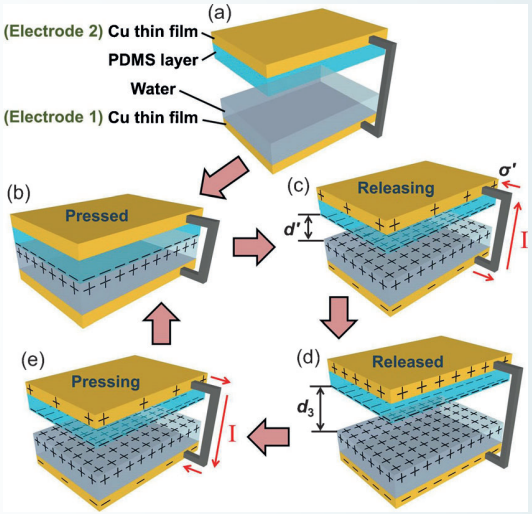




Triboelectric nanogenerators - TENGs

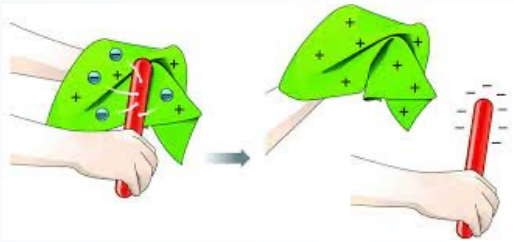


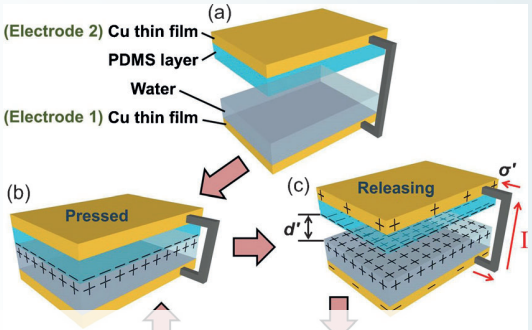


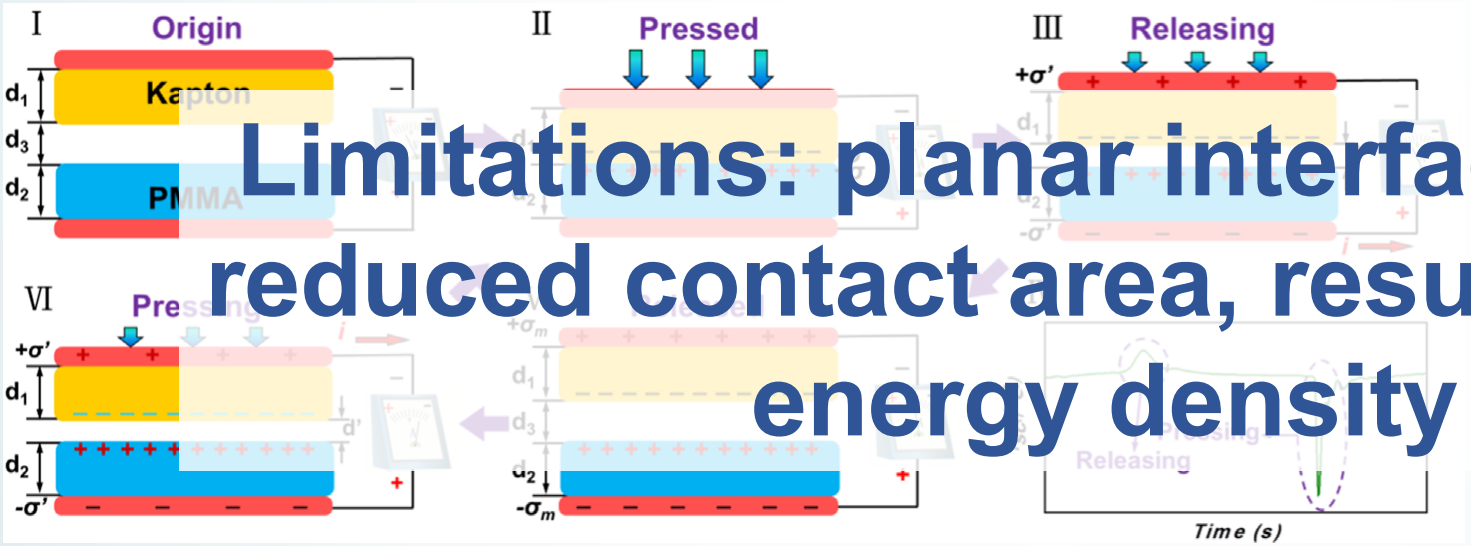


Nano Energy 14, 126, 2015
Angew. Chem. Int. Ed. 52, 12545, 2013

Triboelectric nanogenerators - TENGs







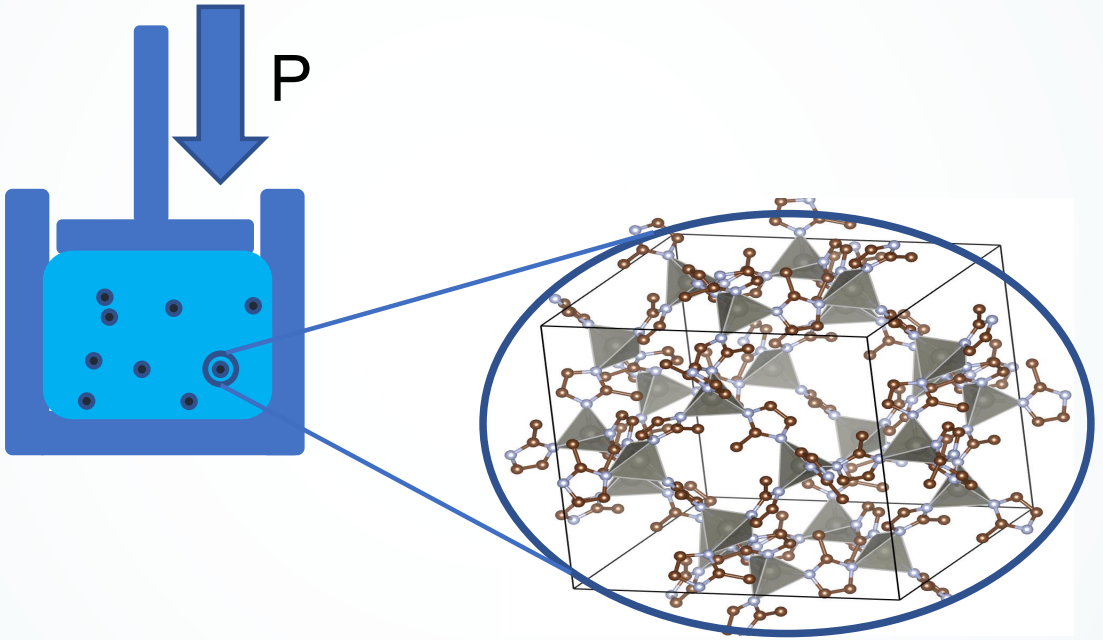
Limitations: planar interfaces have a reduced contact area, resulting in low energy density

ELECTRO INTRUSION

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

ELECTRO INTRUSION

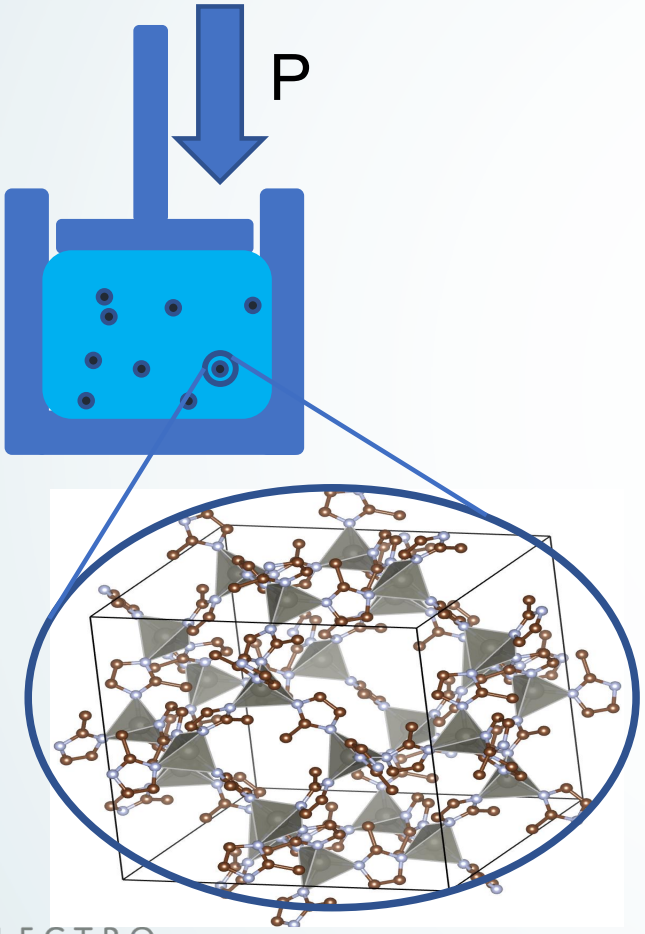
Hydrophobic Nanoporous-based triboelectric nanogenerators: Electro-Intrusion

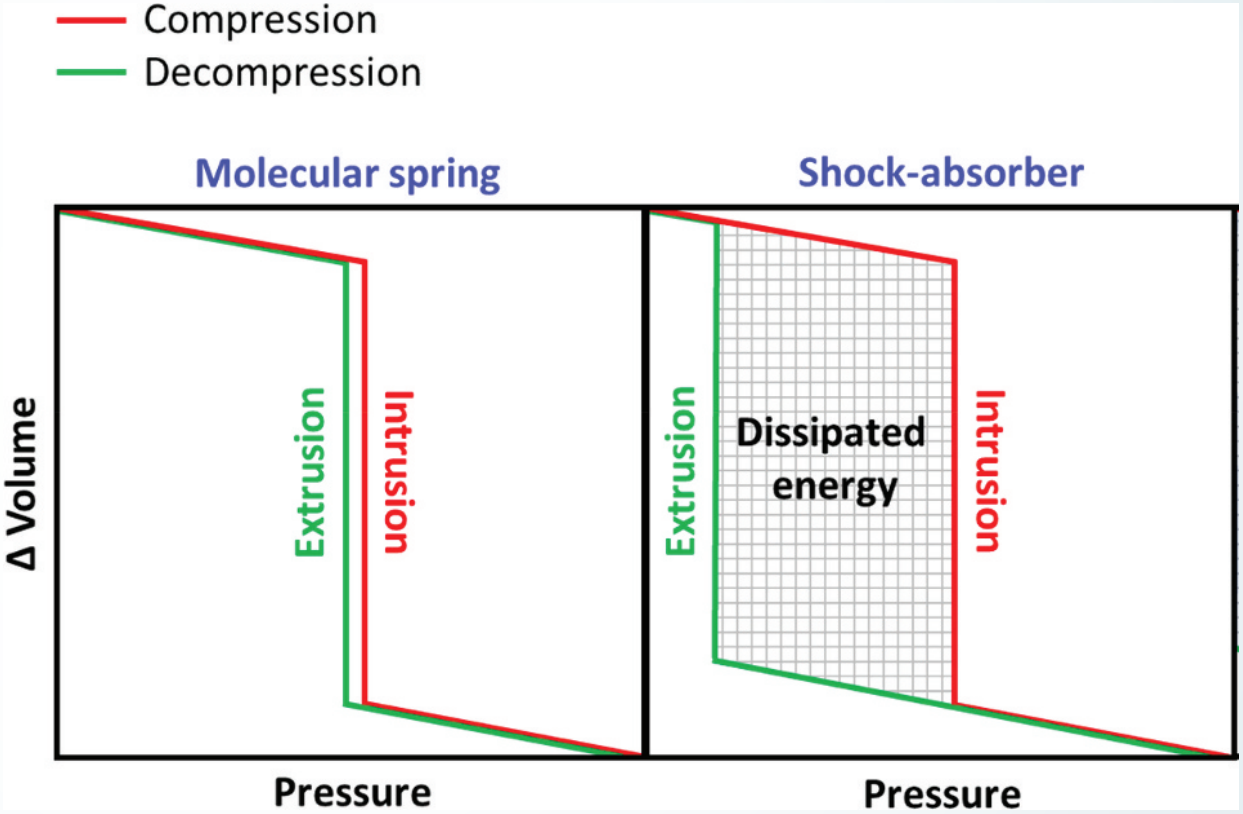


ELECTRO INTRUSION

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

Hydrophobic Nanoporous-based triboelectric nanogenerators: Electro-Intrusion

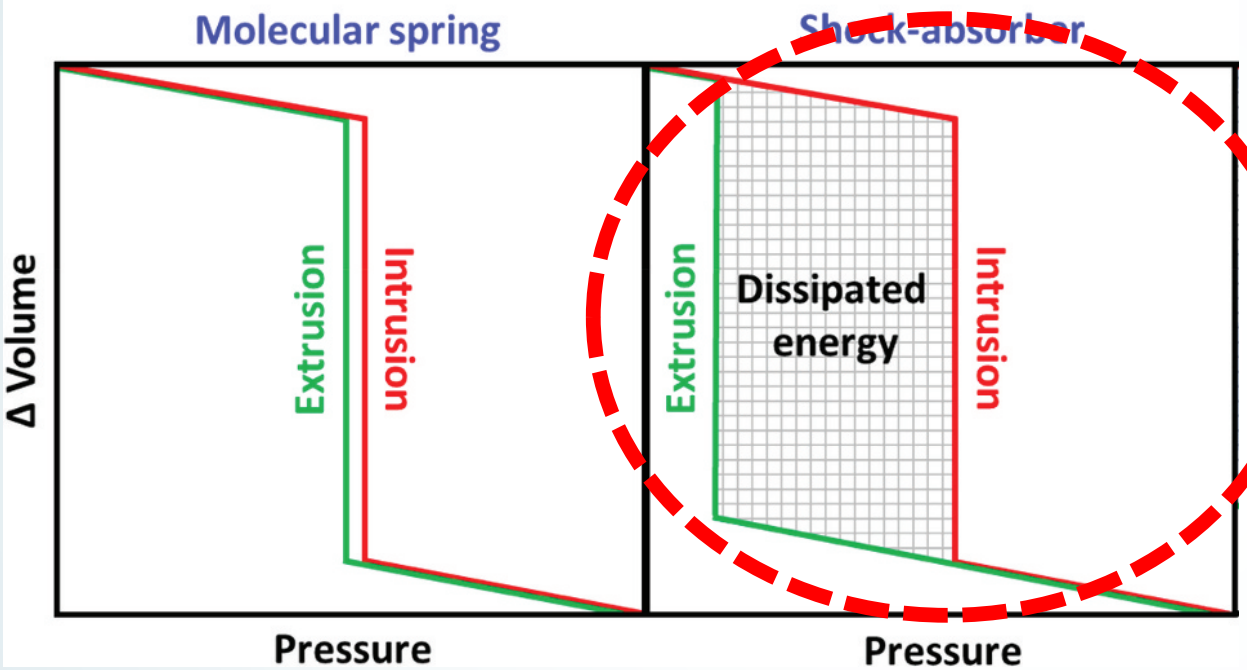


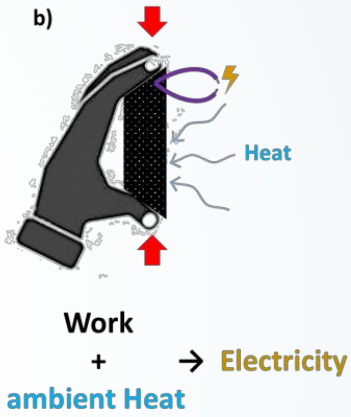


ELECTRO INTRUSION

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

Electro-Intrusion





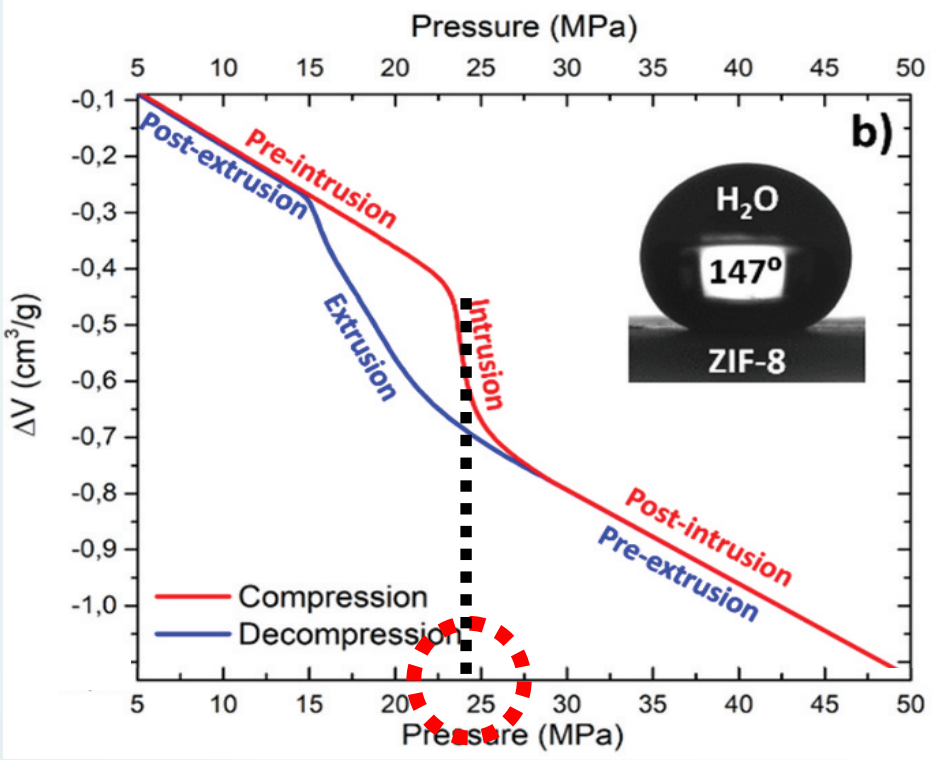
Heat pump 2.0

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

Cyclic intrusion/extrusion large dissipated energy to convert

ELECTRO INTRUSION

Electro-Intrusion



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

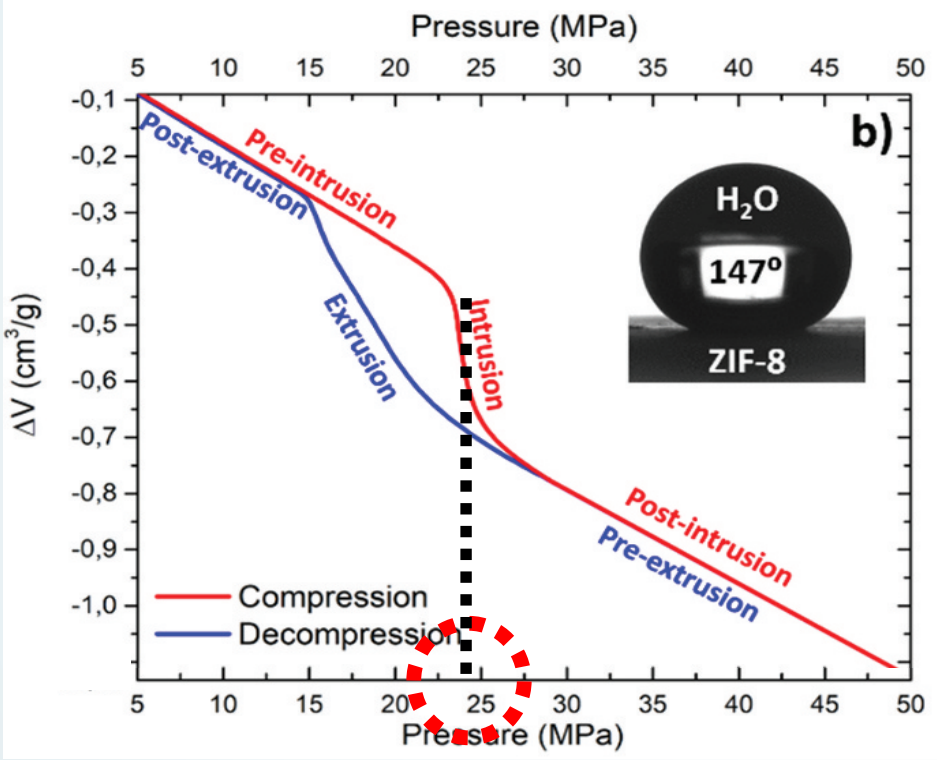
Young-Laplace

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

ELECTRO INTRUSION

Nano Lett. 21, 2848, 2021

Electro-Intrusion



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

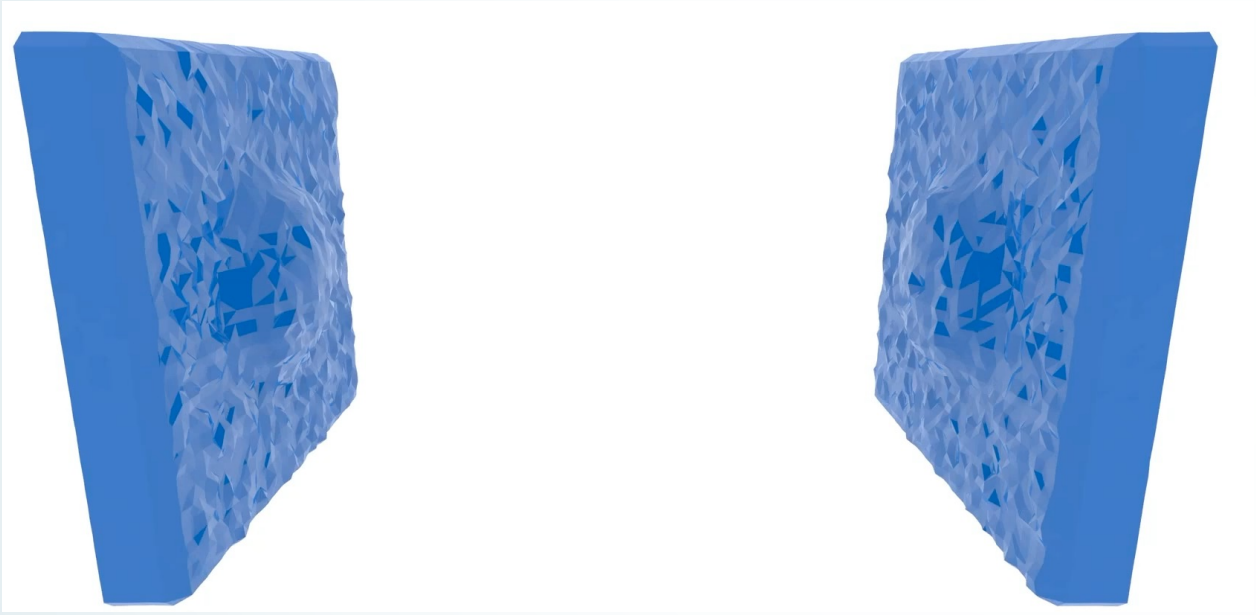
Young-Laplace

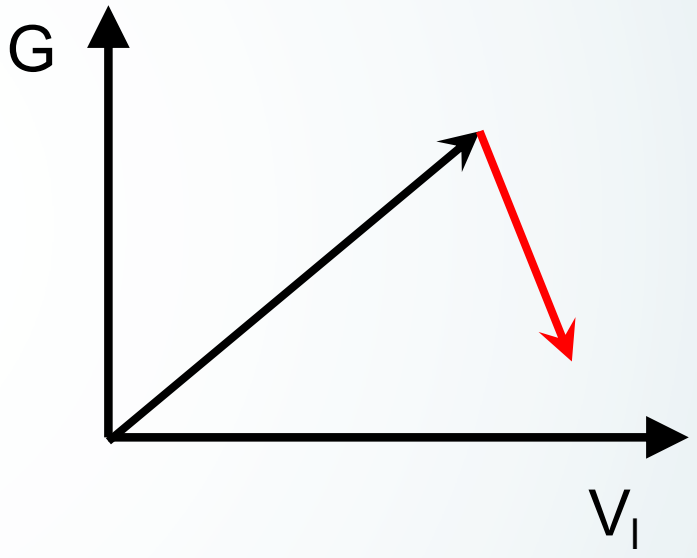
$$P_{int} = -\frac{2\gamma \cos\theta}{r} \gtrsim 300MPa$$

ELECTRO INTRUSION

Nano Lett. 21, 2848, 2021

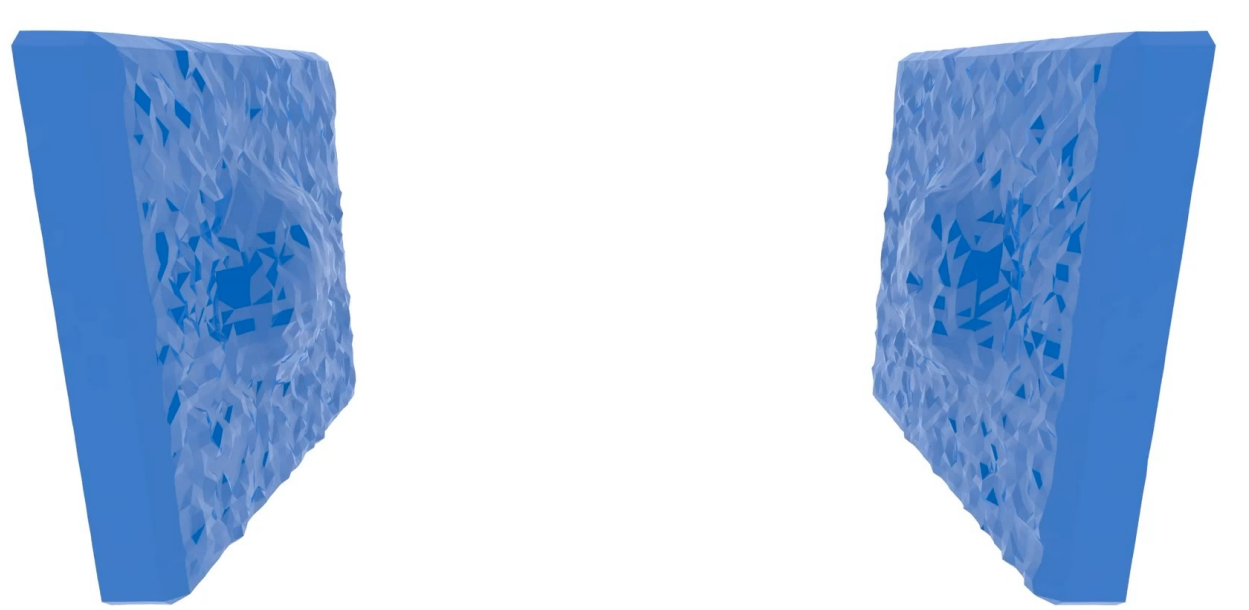
Intrusion/extrusion in hydrophobic porous materials: a thought experiment

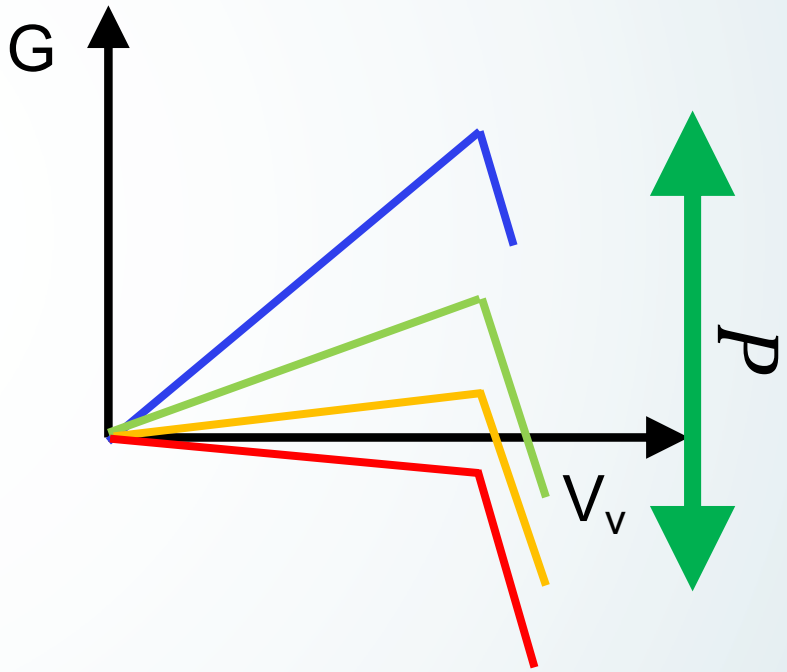




ELECTRO INTRUSION

Intrusion/extrusion in hydrophobic porous materials: a thought experiment



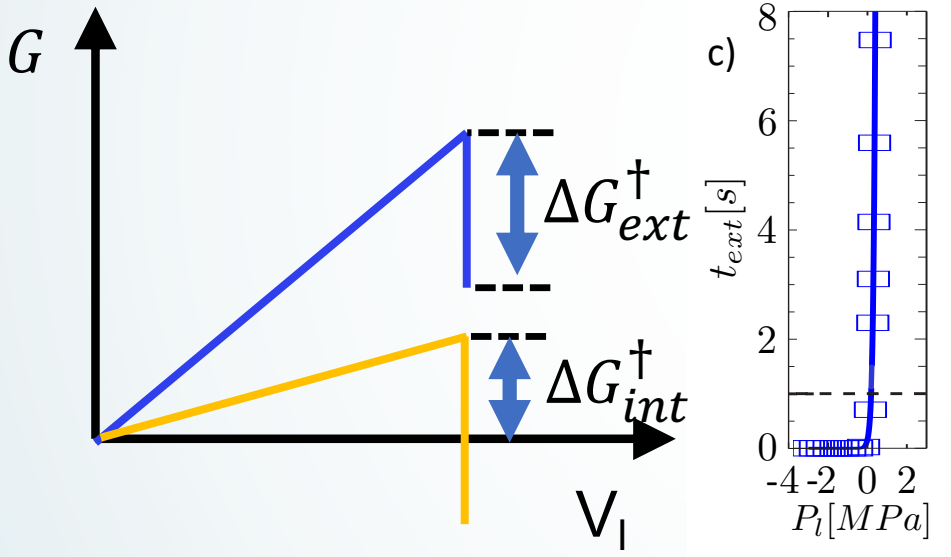


ELECTRO INTRUSION

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

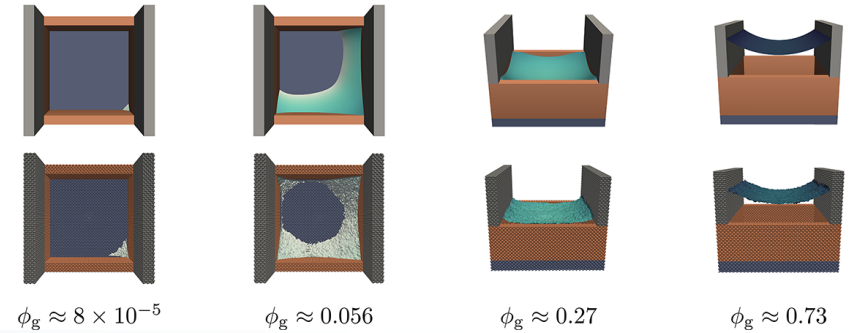
ELECTRO INTRUSION

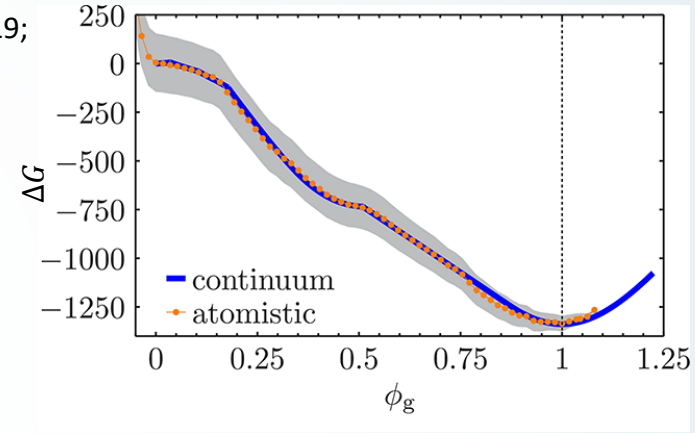
Continuum intrusion/extrusion theory

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

Atomistic

Continuum

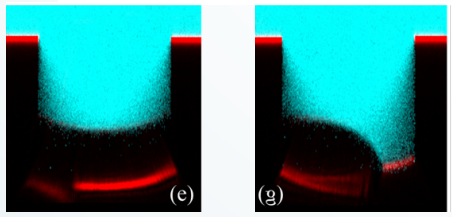




J. Chem. Phys. 2015, **142**, 104701;

Intrusion

Langmuir 2015, **31**, 1248,

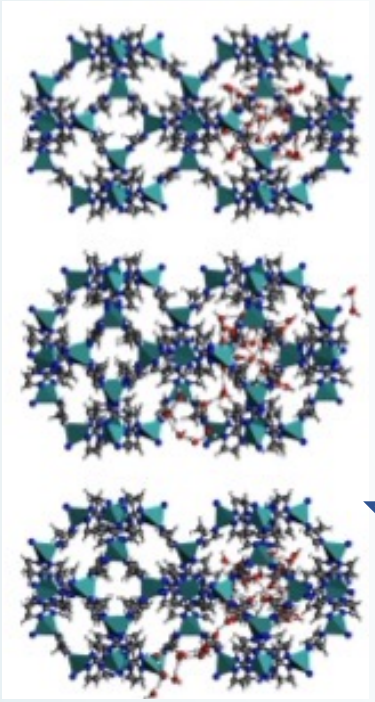


- continuum theory is a mere extension of Young-Laplace to complex geometries and **extrusion**

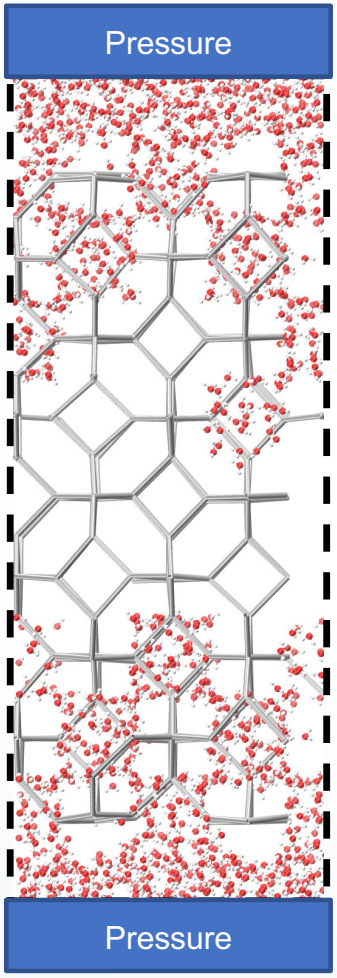
Still wrong order of magnitude P_{int} of P_{ext} of MOFs

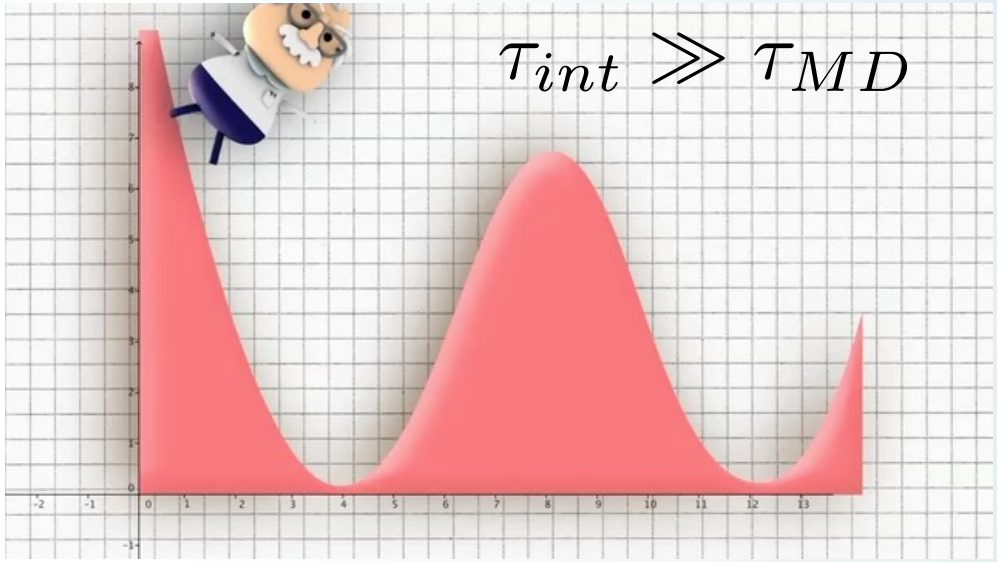
ELECTRO INTRUSION

Mechanism and free energetics of intrusion in ZIF8



MD time





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

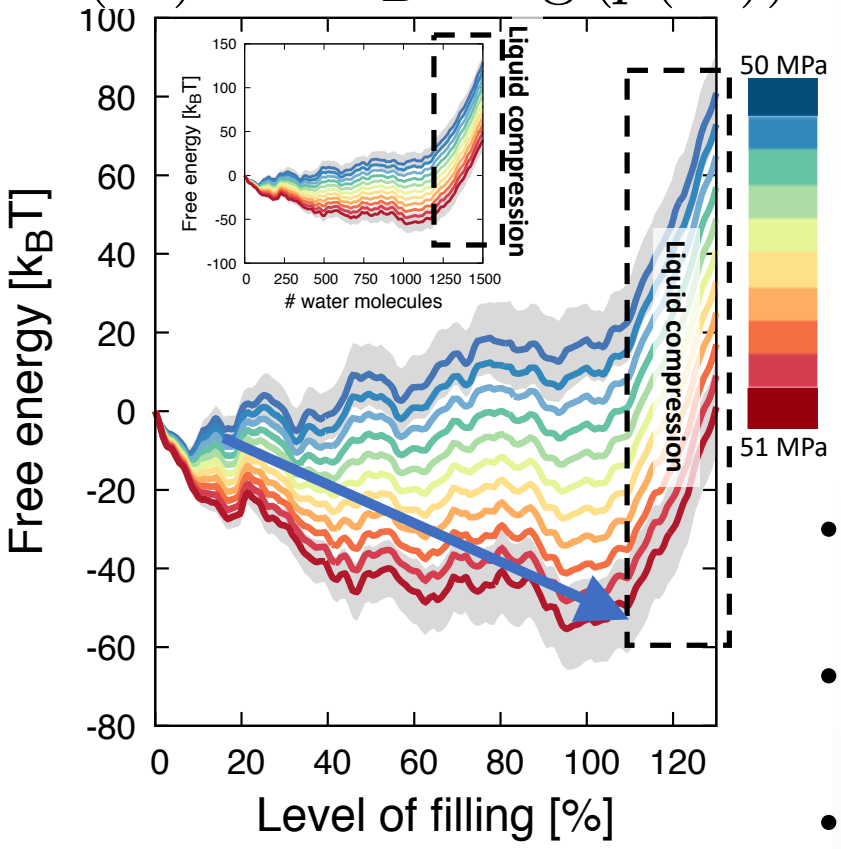
ELECTRO INTRUSION

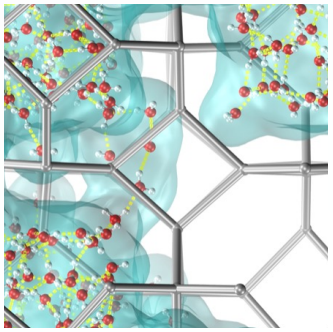
Nat. Materials 2021, **20**, 1015
Nano Letters 2021, **21**, 2848
Chem. Phys. 2018, **148,** 064706

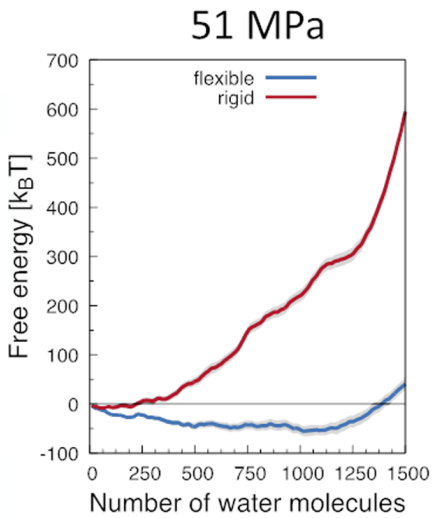
Chemical Physics Letters 2006, **426**, 168
Phys. Chem. Chem. Phys., 2011,**13**, 5952
Eur. Phys. J. B, 2012, **85**, 97

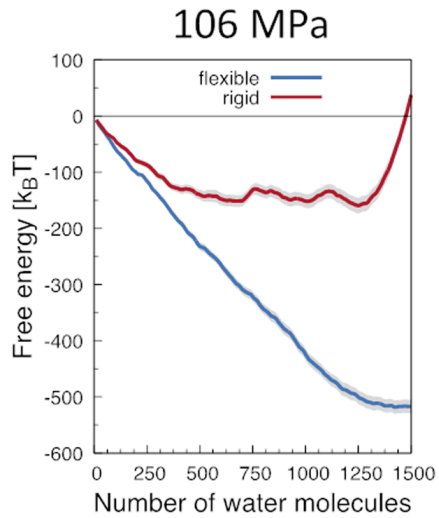
Mechanism and free energetics of intrusion in ZIF8

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







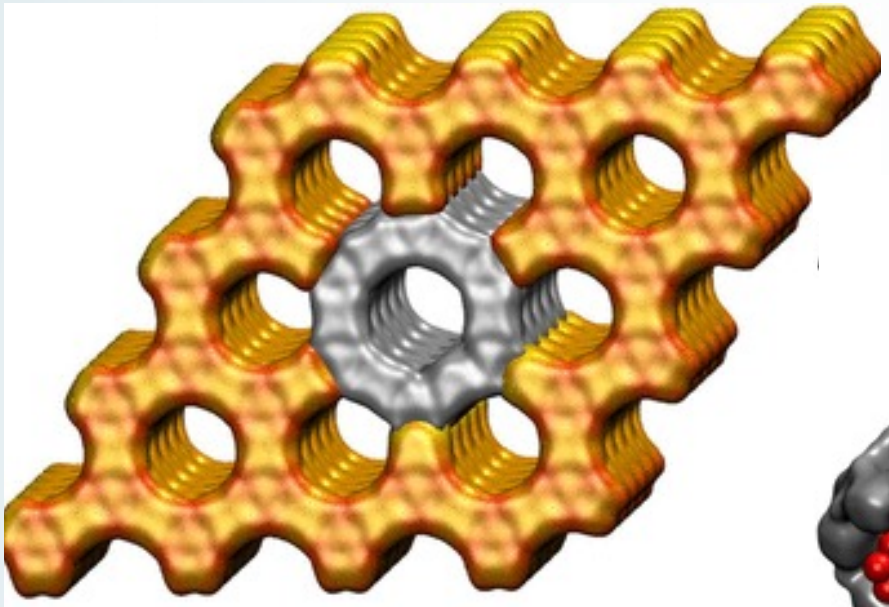


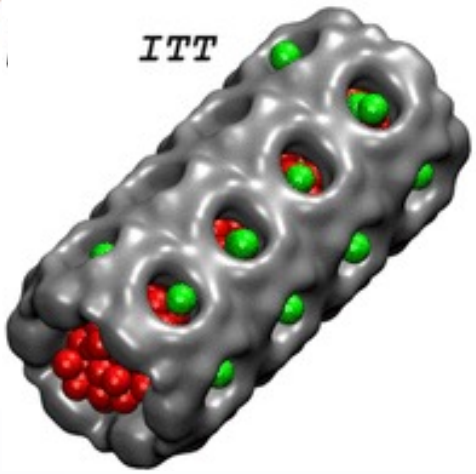
- Predicted intrusion pressure consistent with the experimental value.
- Mechanism is percolation-like, not capillary condensation
- Flexibility plays a crucial role

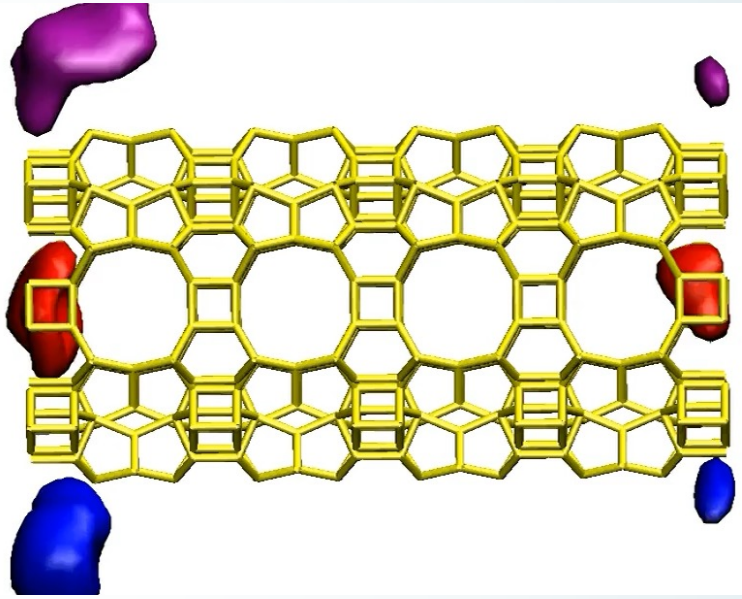
ELECTRO INTRUSION

Nano Letters 2021, 21, 2848
ACS Appl. Mater. Interfaces 2022, 14, 26699

Effect of secondary subnanometric features of porous systems





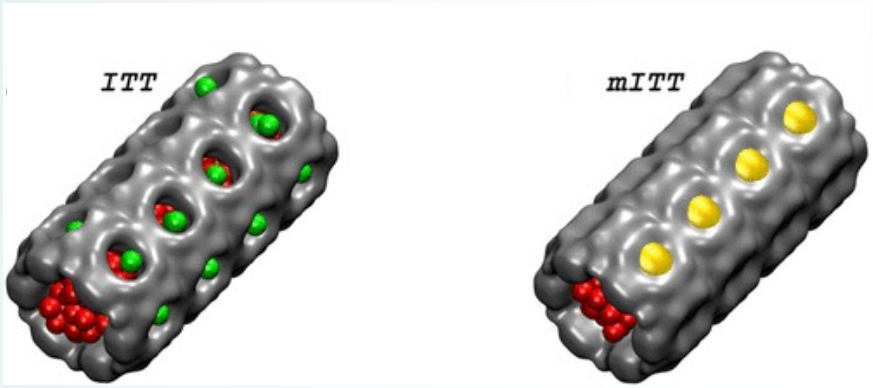


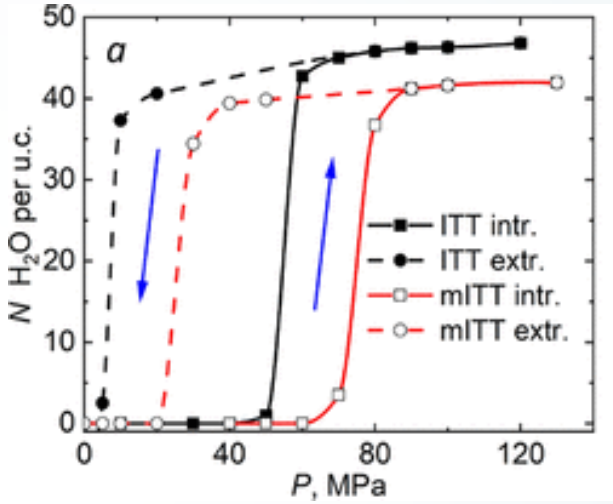
Contrary so classical predictions, Subnanometric secondary cavities are intruded to bridge water across major channels

ELECTRO INTRUSION

Nano Lett. 2022, 22, 6, 2164−2169

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

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 the liquid intrusion/extrusion in nanoporous materials, which do not obey to classical laws

We identified the fundamental phenomena determining intrusion/extrusion pressure and hysteresis and design principles for novel materials

ELECTRO INTRUSION

Acknowledgements

Marco Tortora

Yaroslav Grosu

Alberto Giacomello

Yuriy Bushuev

Carlo Massimo Casciola

PRACE

Miroslaw Chorążewski

H2020-FET Electro-Intrusion

ELECTRO INTRUSION

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101017858

ELECTRO INTRUSION

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101017858

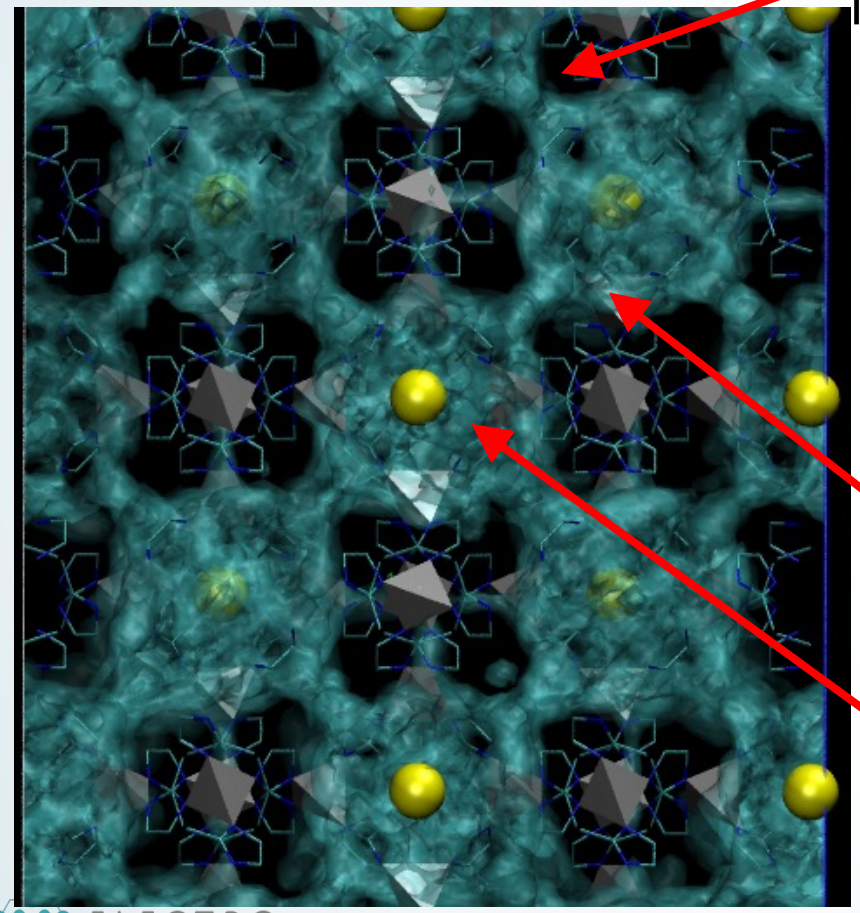
Thanks for your attention!

ELECTRO INTRUSION

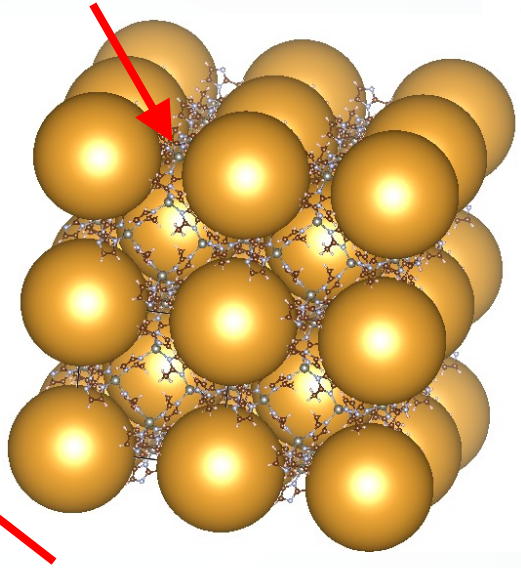
Backup

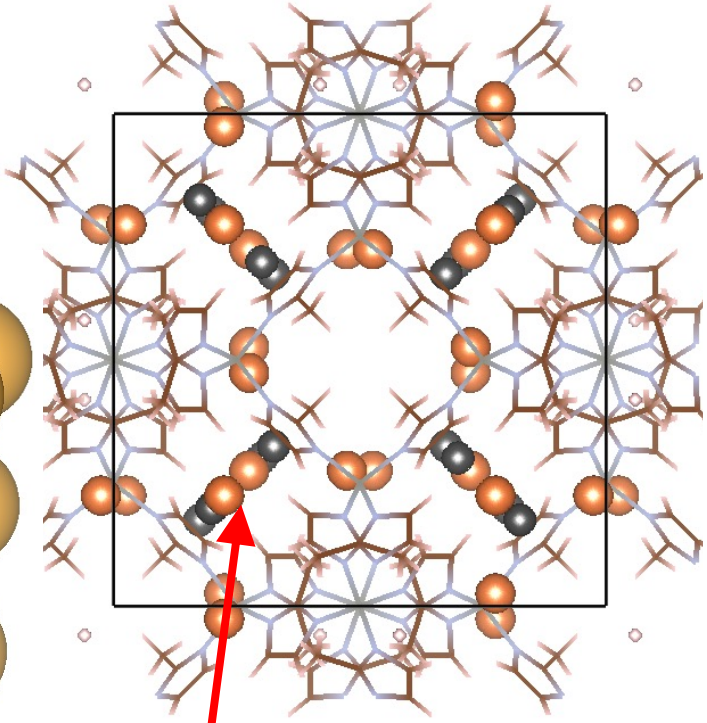
H2020-FET

ELECTRO INTRUSION



Secondary interconnections

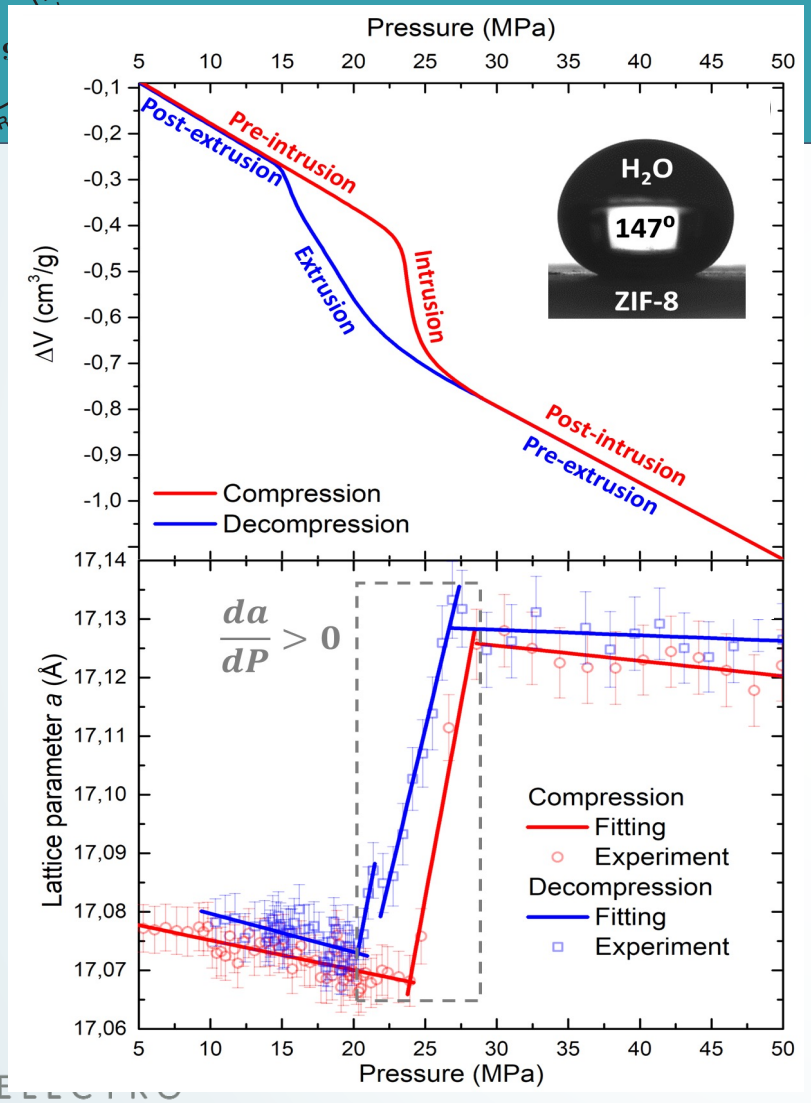


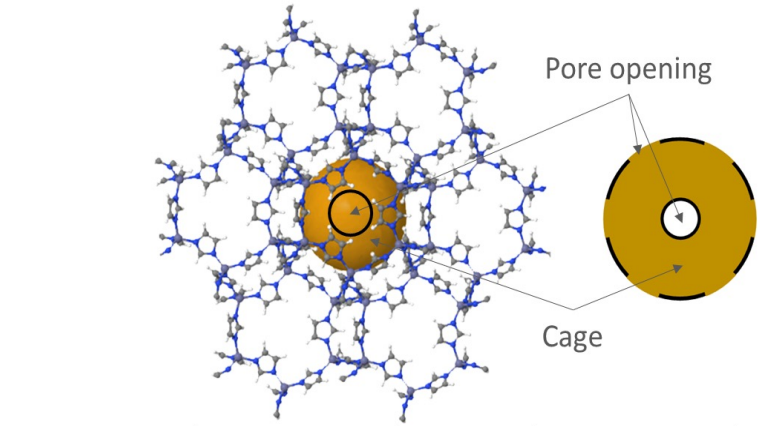


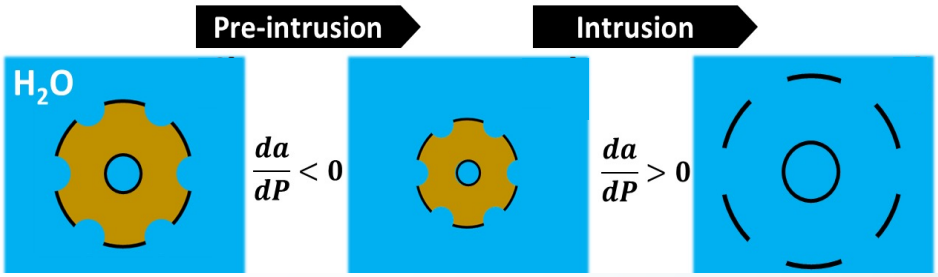
Crystal-like and liquid-like water

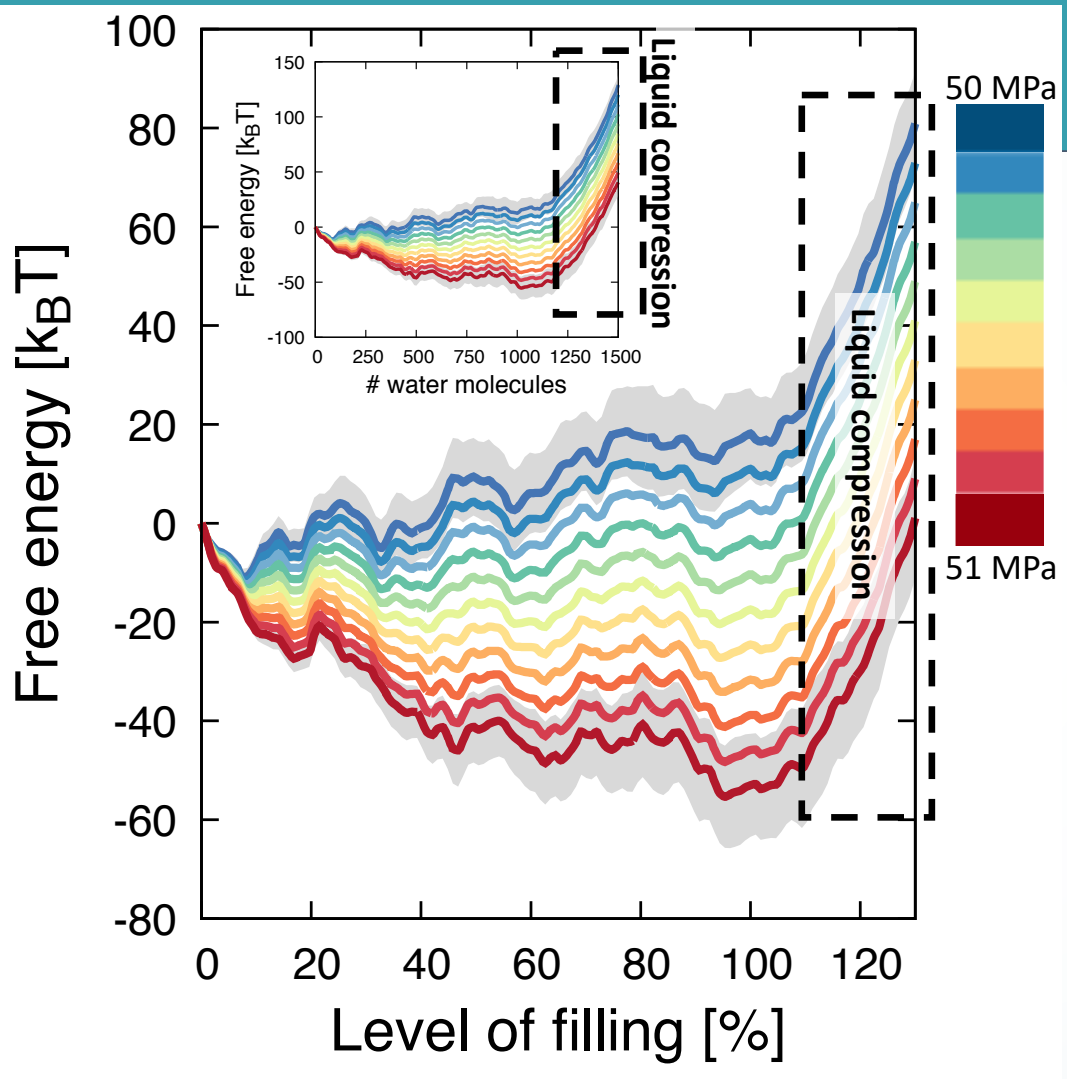
Water sites with Fractional occupation

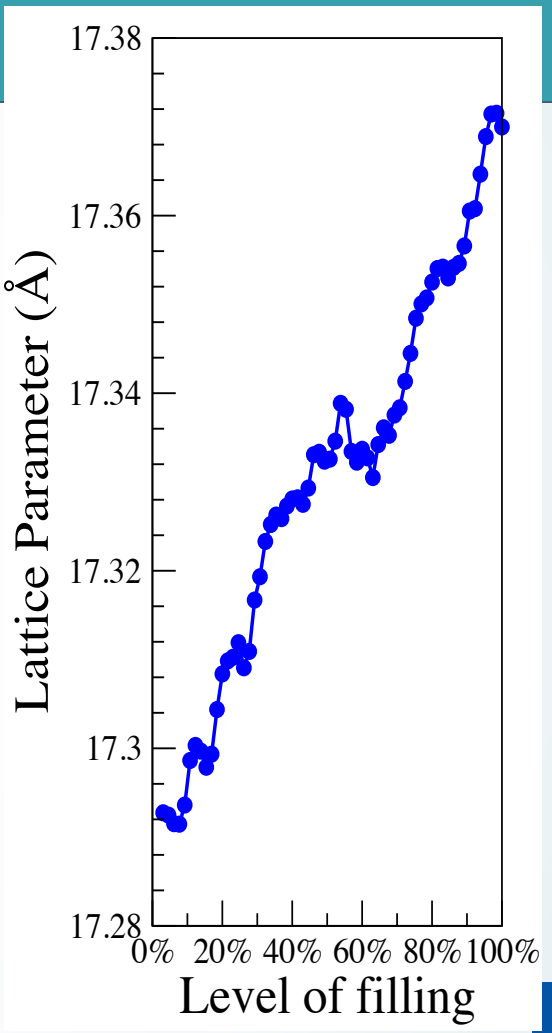
ELECTRO INTRUSION


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)

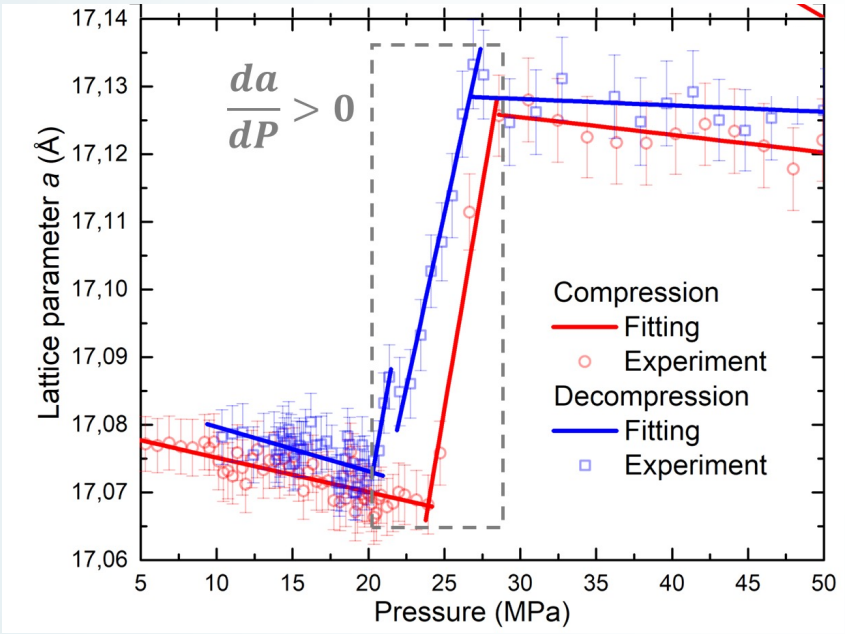

Pore opening
Cage

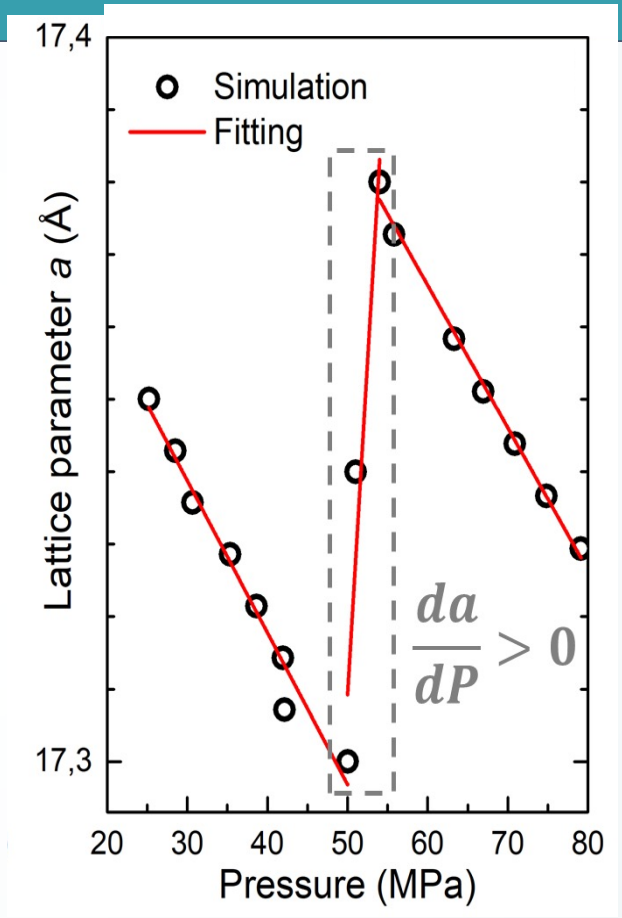

Pre-intrusion
Intrusion
H2O
da/dP < 0
da/dP > 0



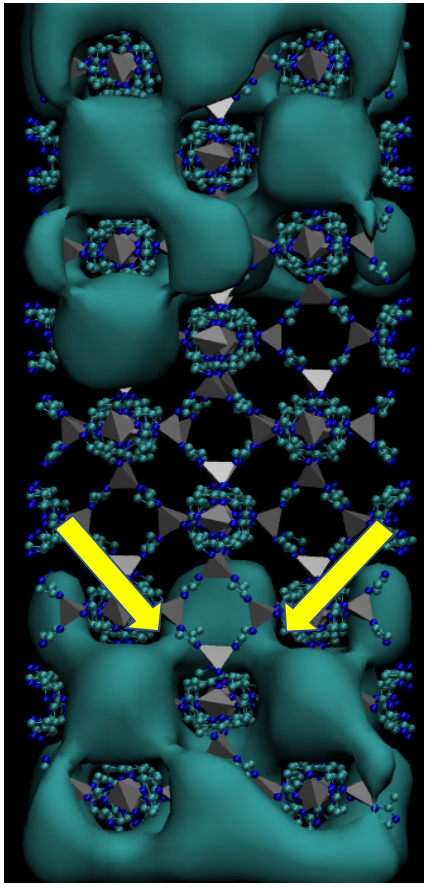


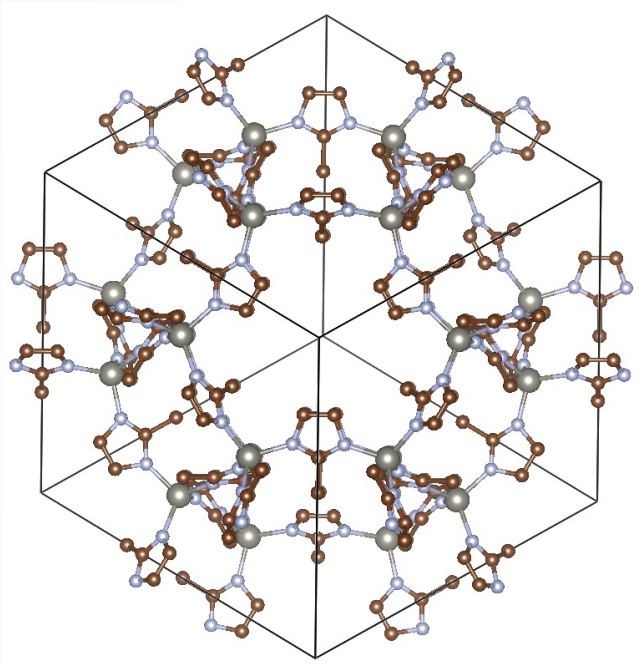
ELECTRO INTRUSION

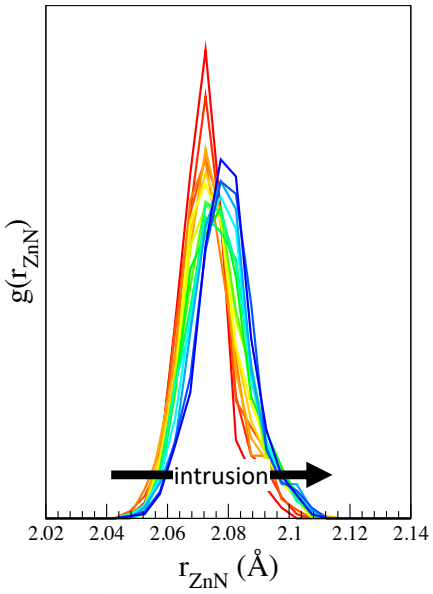


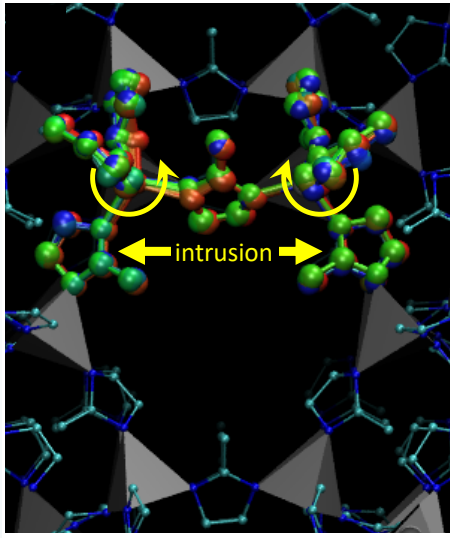


ELECTRO INTRUSION

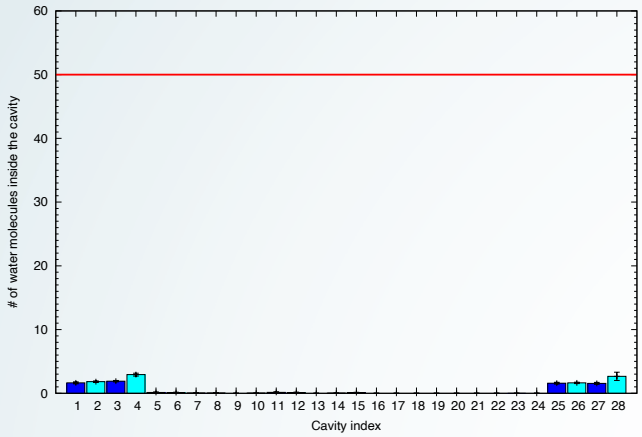


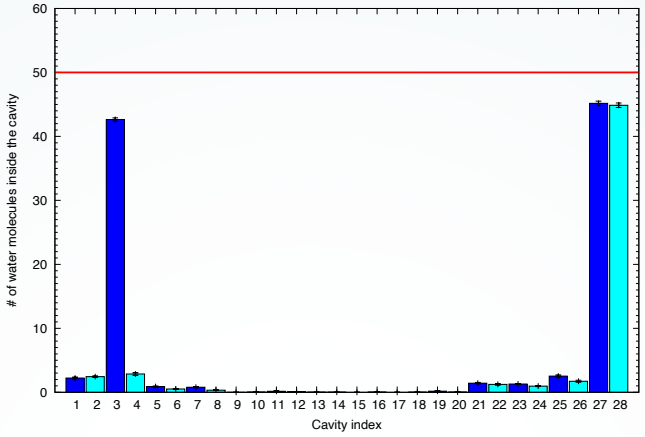


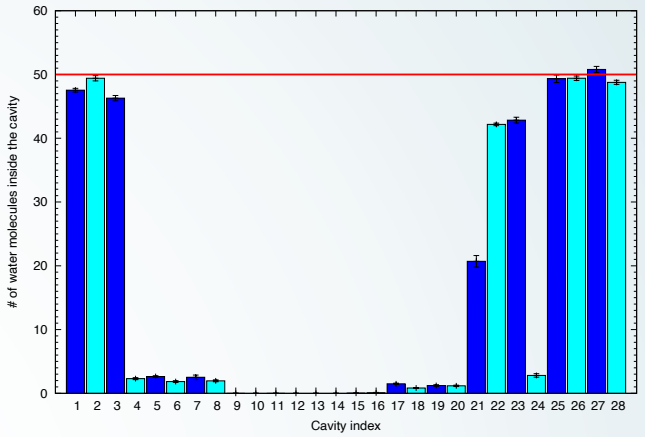




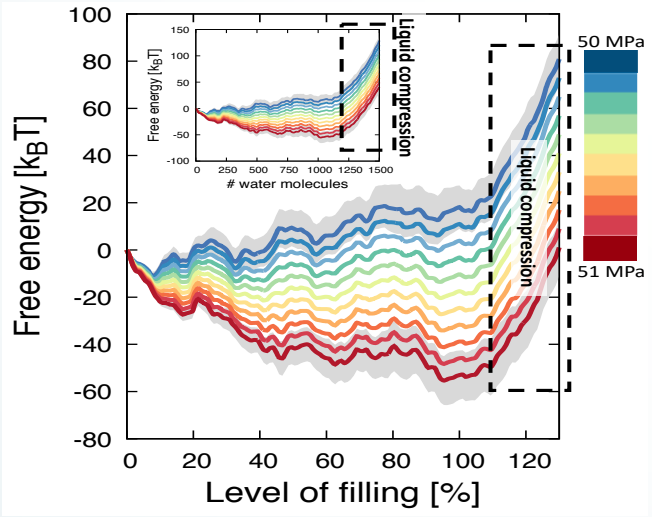
ELECTRO INTRUSION

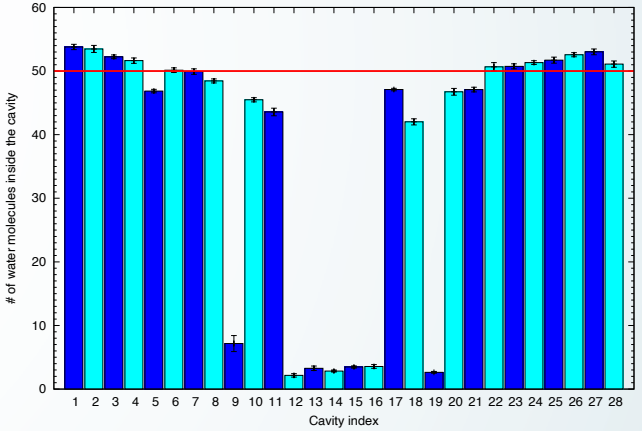






Intrusion





ELECTRO INTRUSION