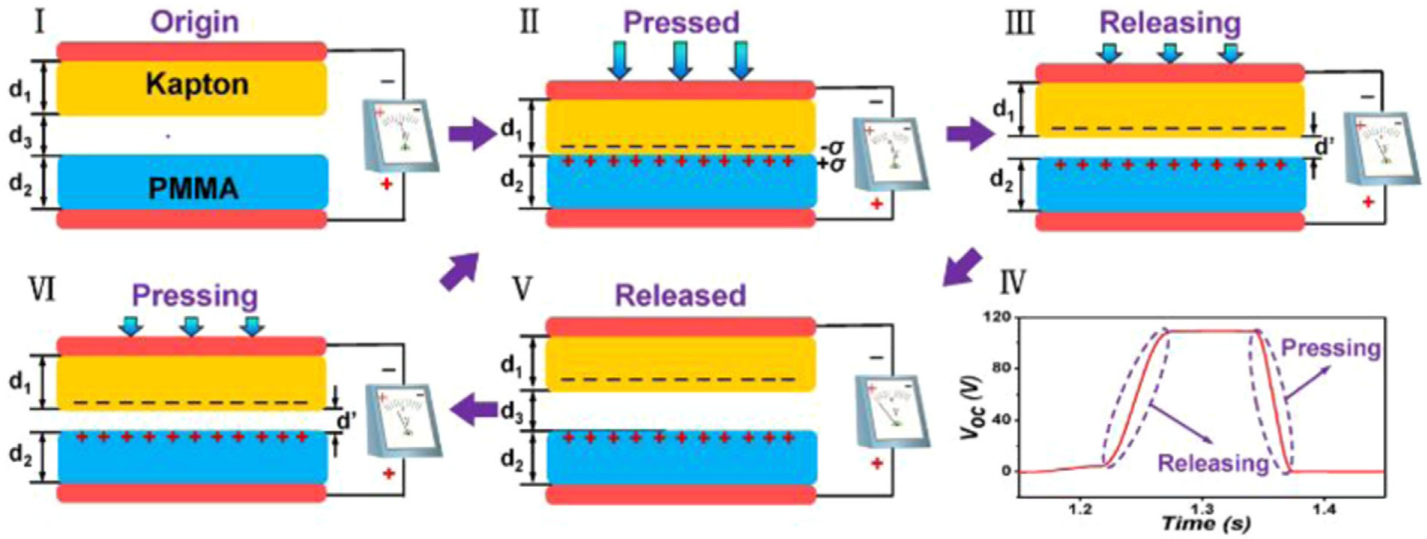
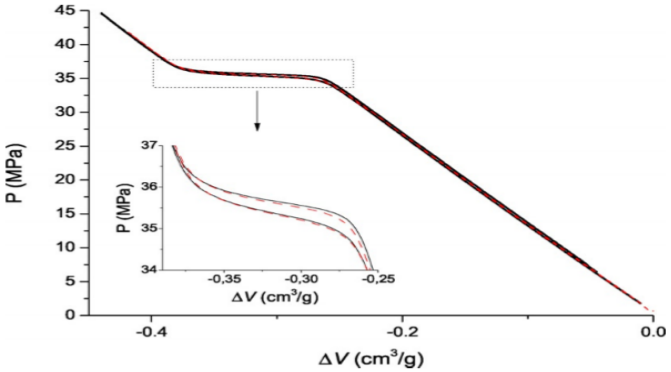
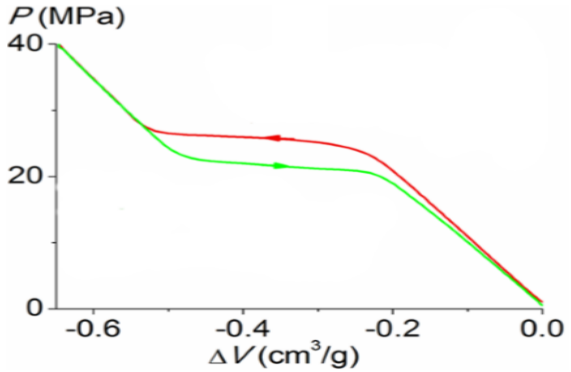
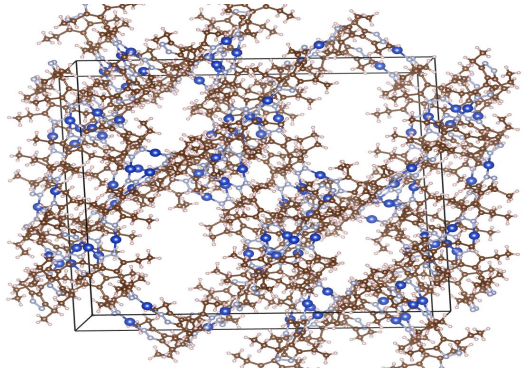
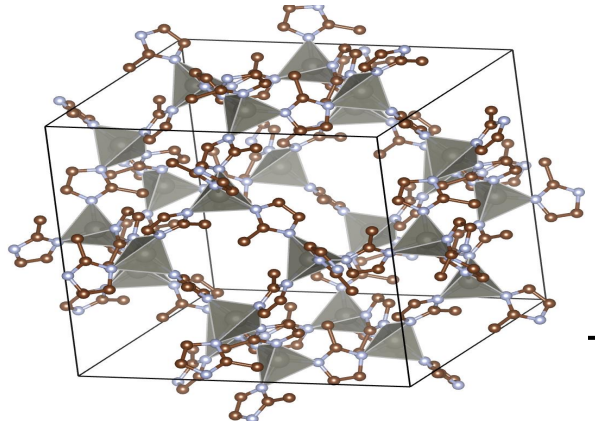
Getting liquids in and out porous materials: a theoretical point of view

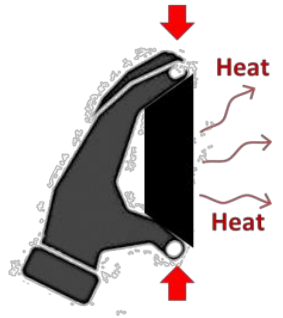




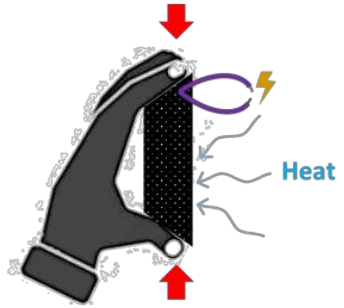






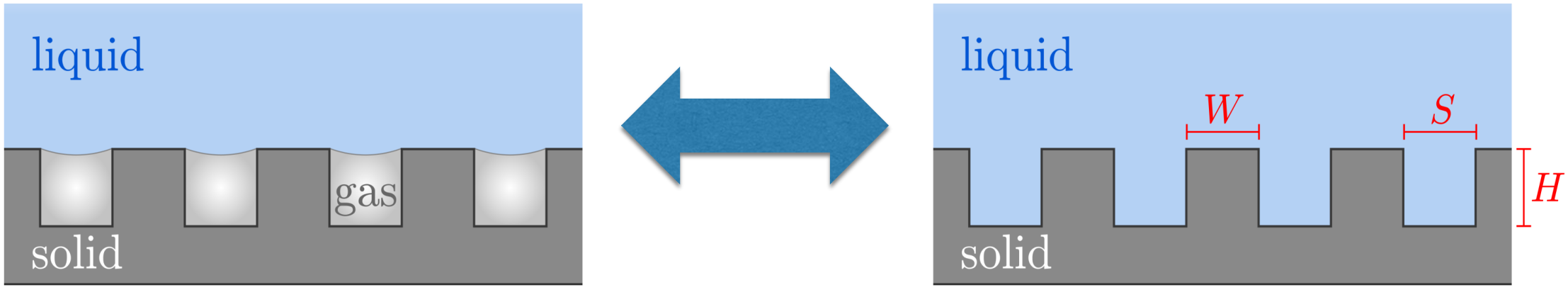


Work → Heat



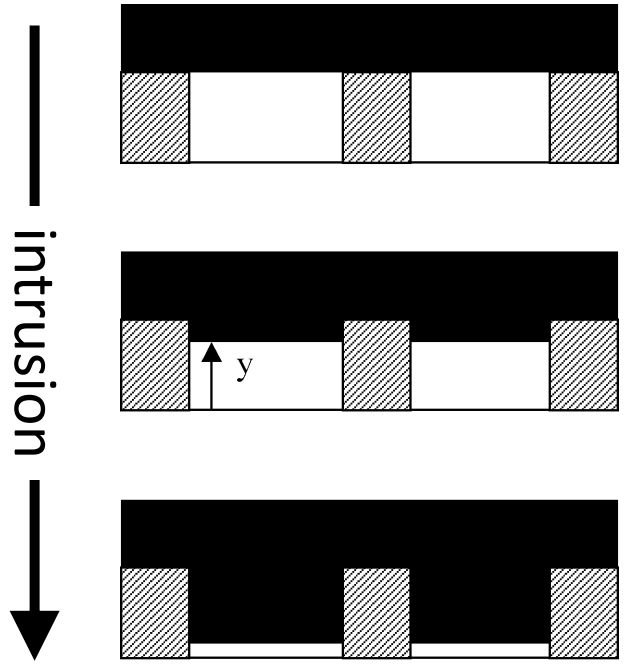
Work
+ **→ Electricity**
ambient Heat

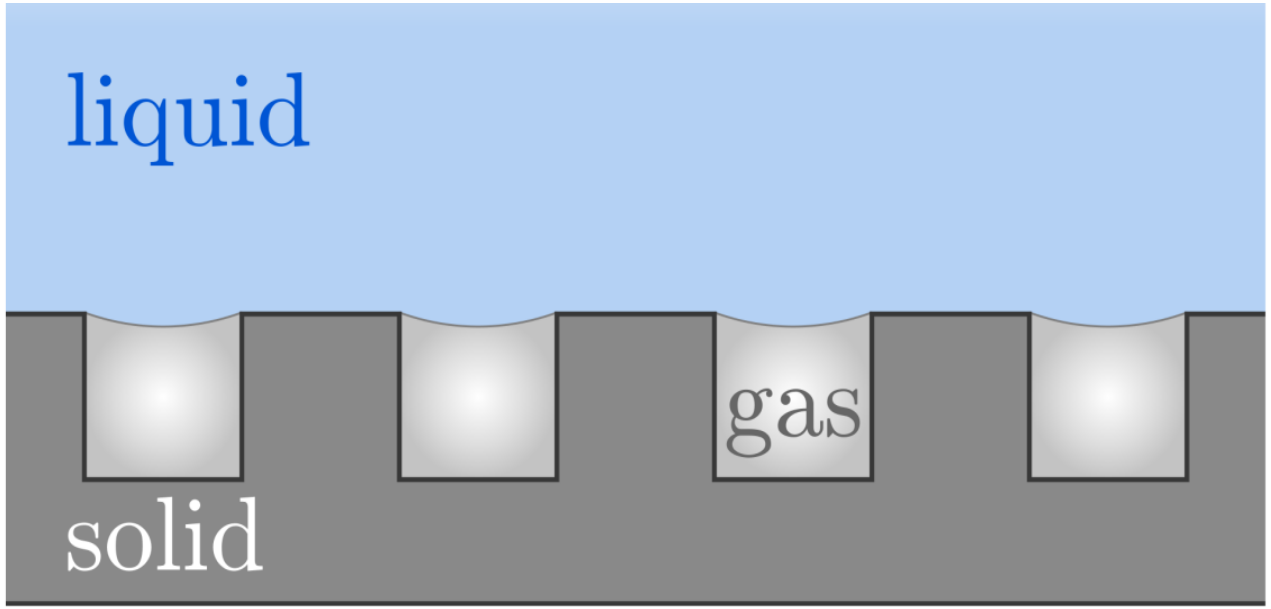
Liquid intrusion/extrusion: a thought experiment



Self-recovery superhydrophobic surfaces: Modular design Lisi, Amabili, SM, Giacomello, Casciola ACS nano 12 (1), 359-367

Liquid intrusion/extrusion: a thought experiment





$$\Omega = \Delta P V_v + \gamma A_{lv} + \gamma_{sv} A_{sv} + \gamma_{sl} A_{sl}$$

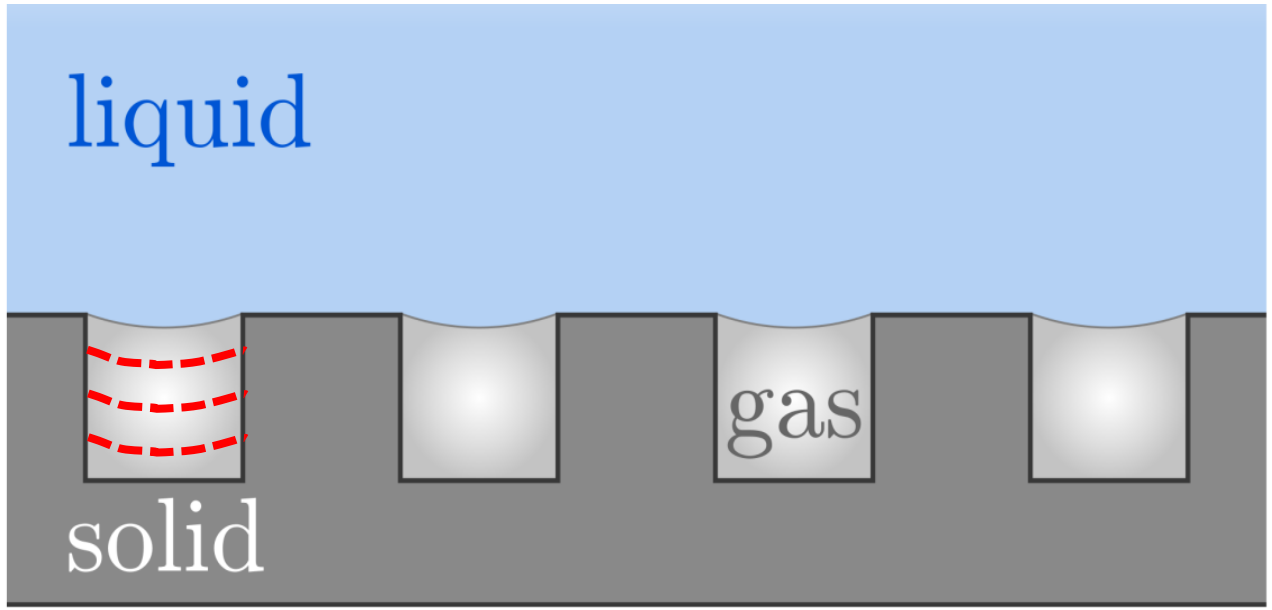
$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right) \qquad \cos(\theta) = \left(\gamma_{sv} - \gamma_{sl} \right) / \gamma_{lv}$$

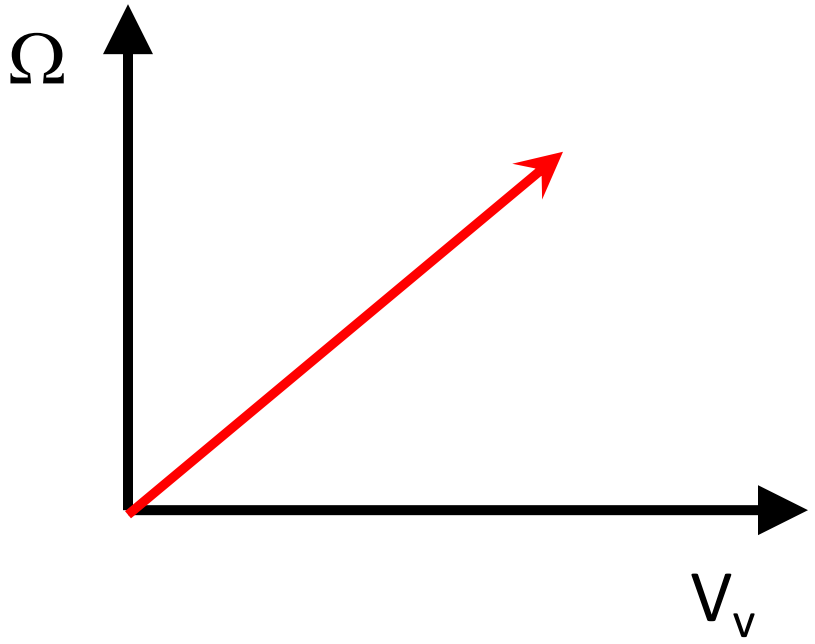
Bulk coexistence conditions

Langmuir, 2004, **20**, 2004

Liquid intrusion/extrusion: a thought experiment

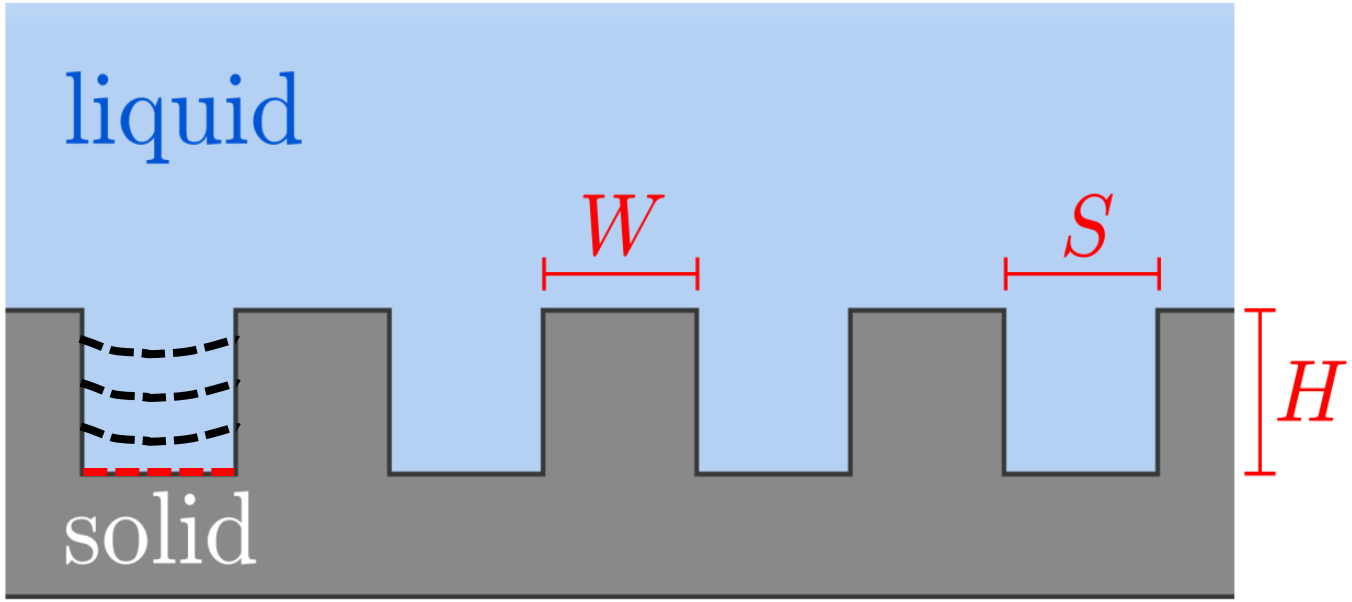
$$\Omega = \cancel{\Delta P} V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

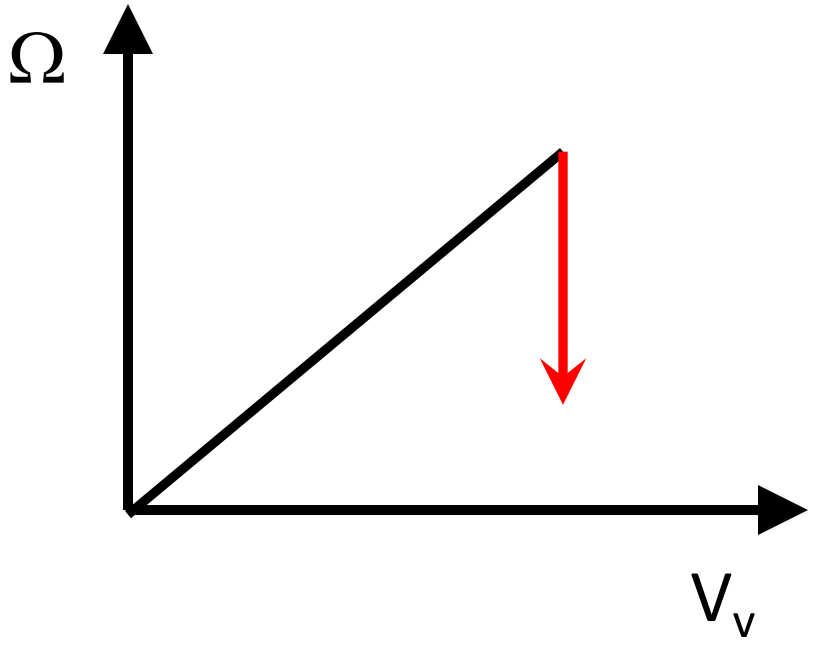




Liquid intrusion/extrusion: a thought experiment

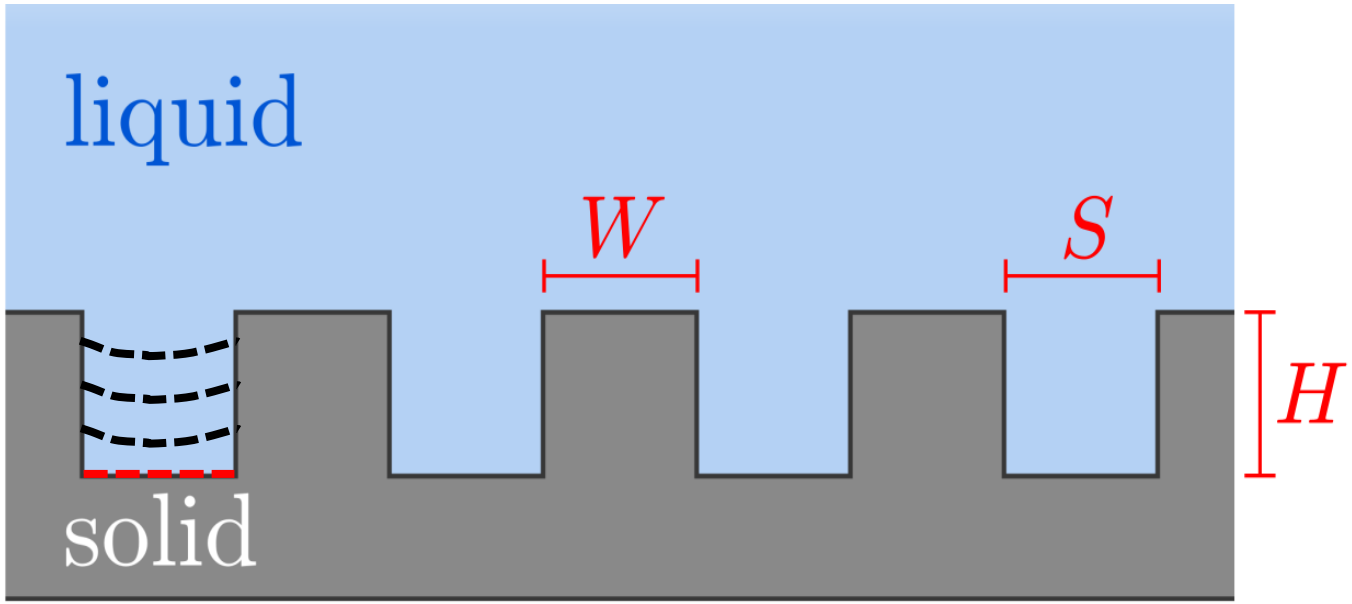
$$\Omega = \Delta P V_v + \gamma A_{lv} + \gamma_{sv} A_{sv} + \gamma_{sl} A_{sl}$$

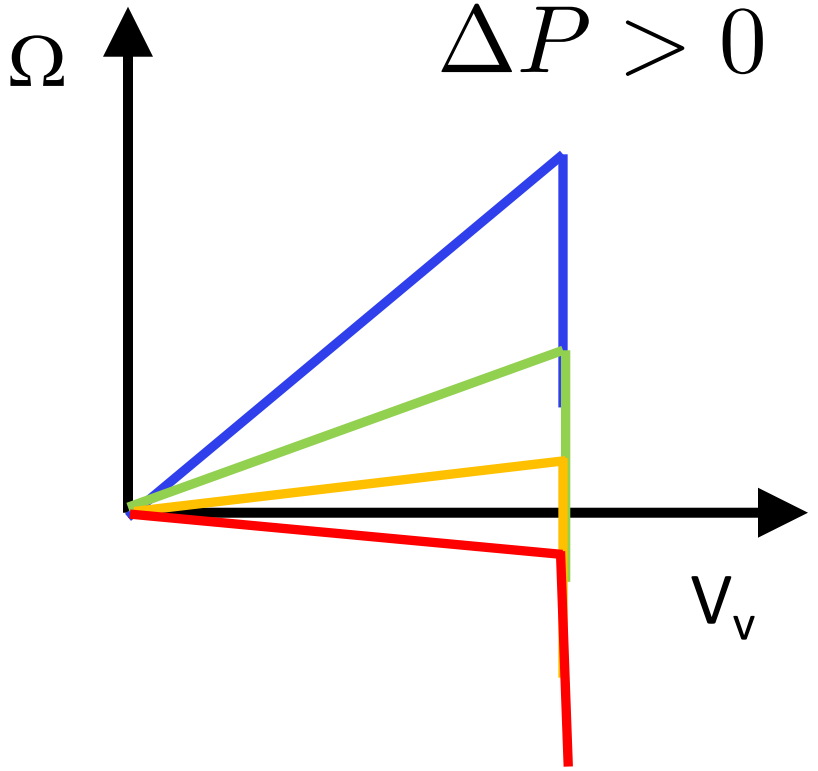




Liquid intrusion/extrusion: a thought experiment

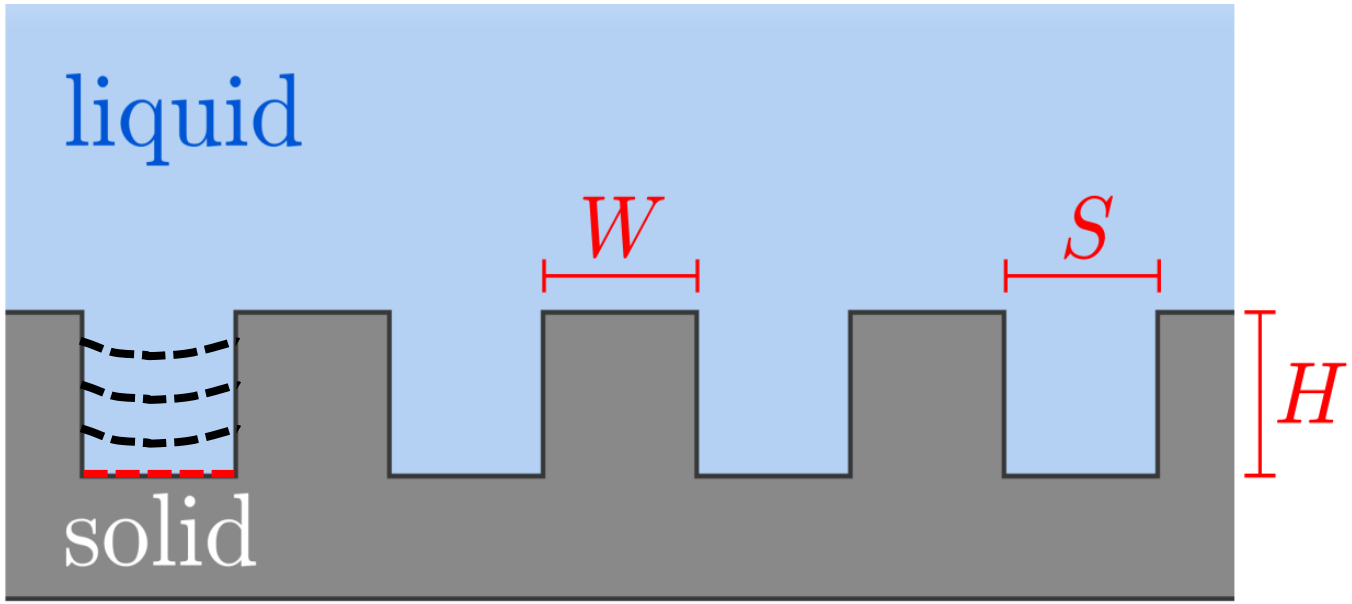
$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

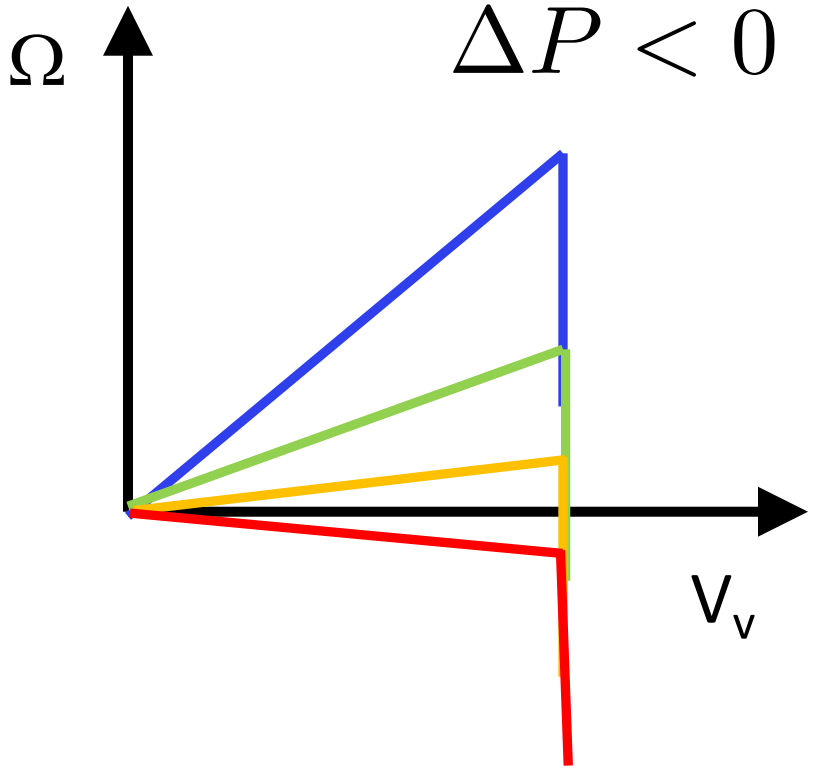




Liquid intrusion/extrusion: a thought experiment

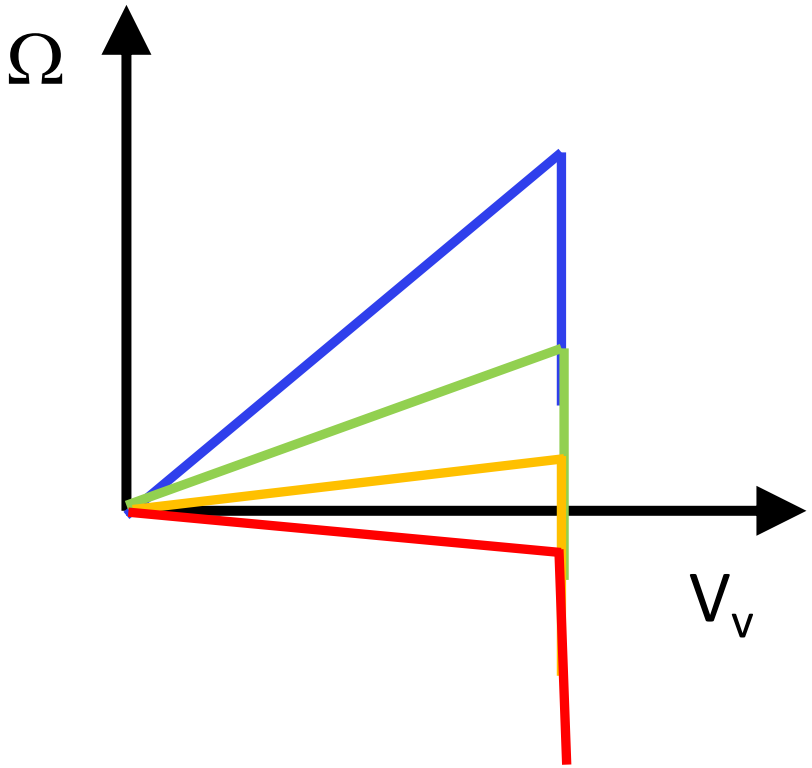
$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

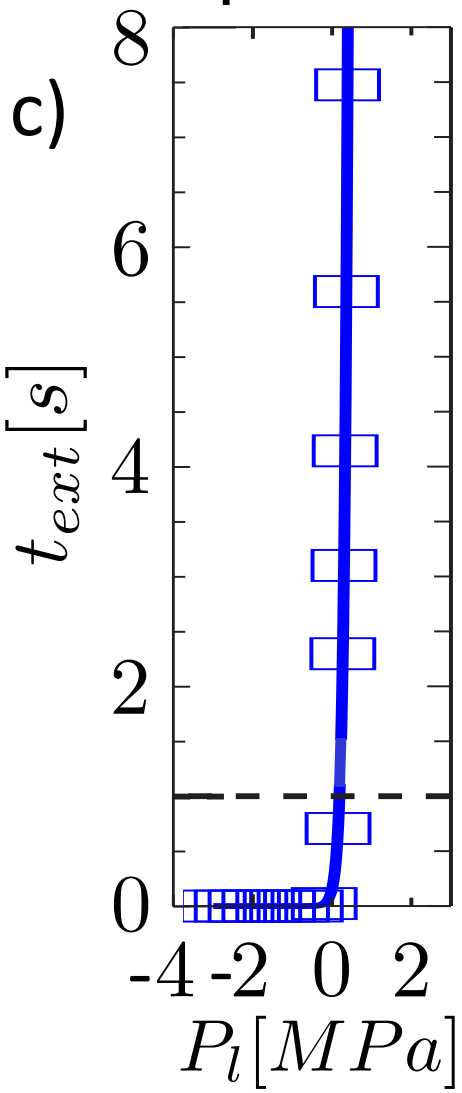




Liquid intrusion/extrusion: a thought experiment

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

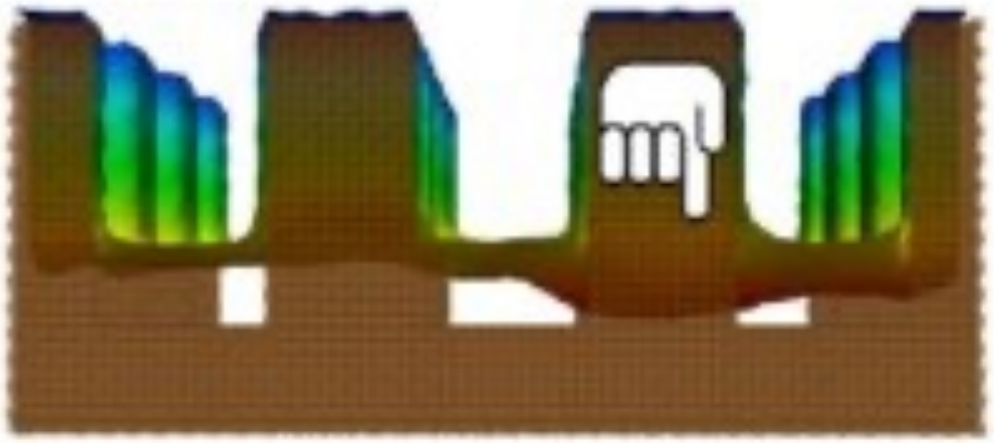


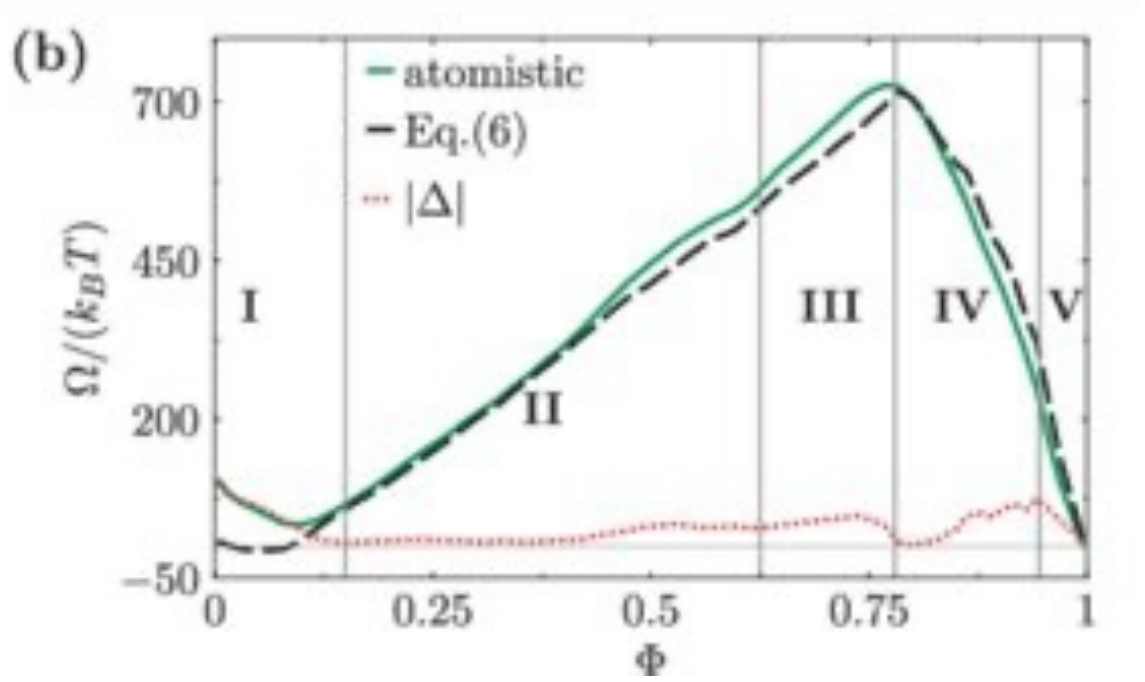


$$\Omega = \Delta P V_v + \gamma A_{lv} + \gamma_{sv} A_{sv} + \gamma_{sl} A_{sl}$$

+

Confined Classical Nucleation Theory



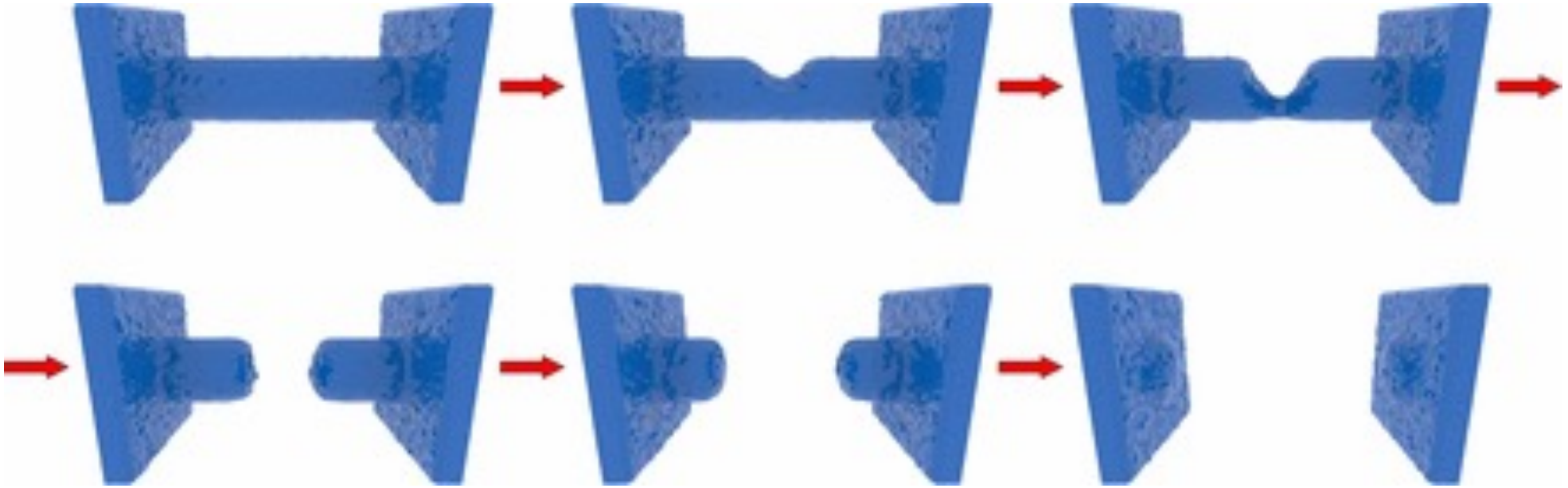


Activated wetting of nanostructured surfaces: reaction coordinates, finite size effects, and simulation pitfalls
Amabili, SM, Giacomello, Casciola, The Journal of Physical Chemistry B 122, 200-212

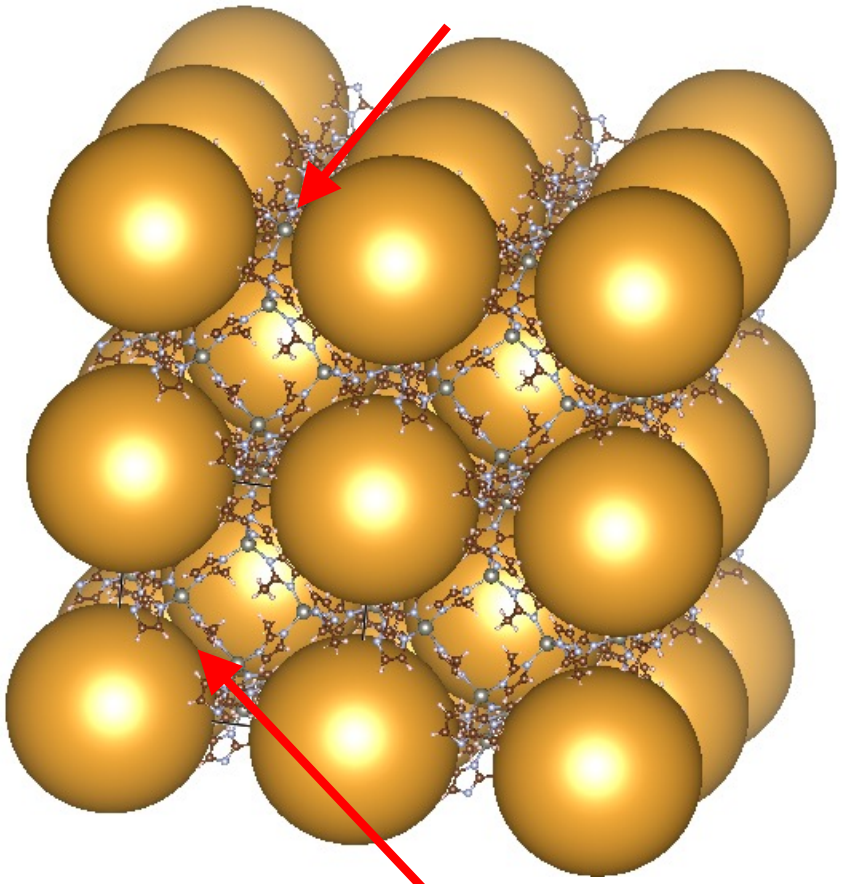
Collapse of superhydrophobicity on nanopillared surfaces Amabili, Giacomello, Meloni, Casciola, Physical Review Fluids 2, 034202

Liquid intrusion in and extrusion from non-wettable nanopores for technological applications
Giacomello, Casciola, Grosu, SM, to appear in Europhys. J. B

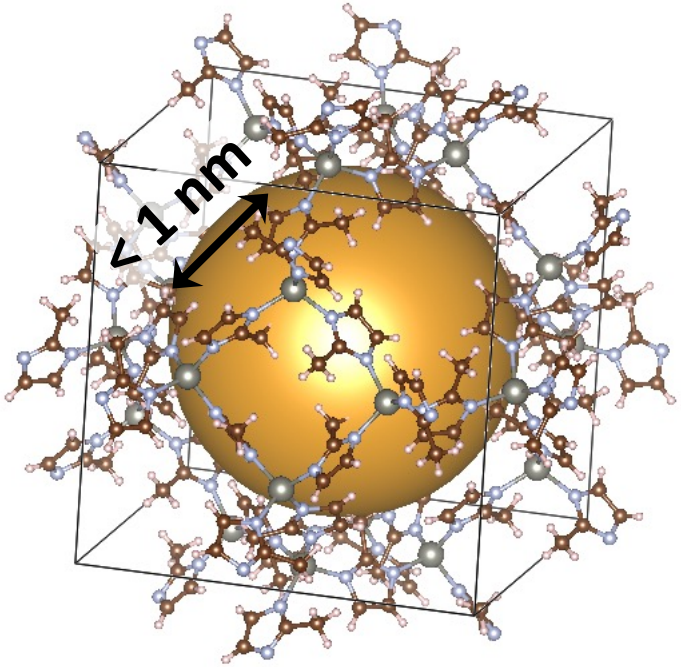
Metastable wetting on superhydrophobic surfaces: Continuum and atomistic views of the Cassie-Baxter–Wenzel transition



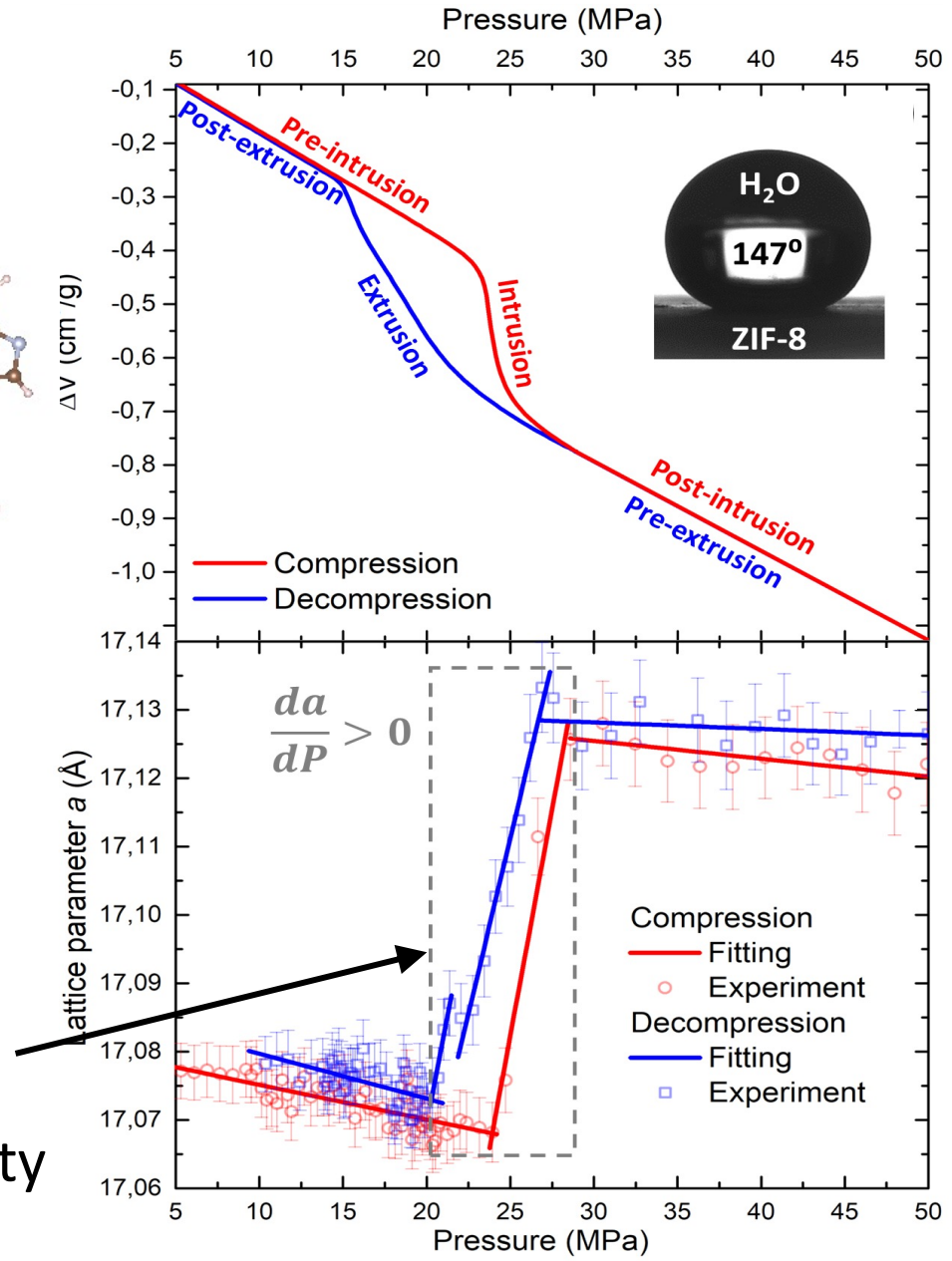
Secondary interconnections



Primary interconnections



Exceptional Negative Compressibility

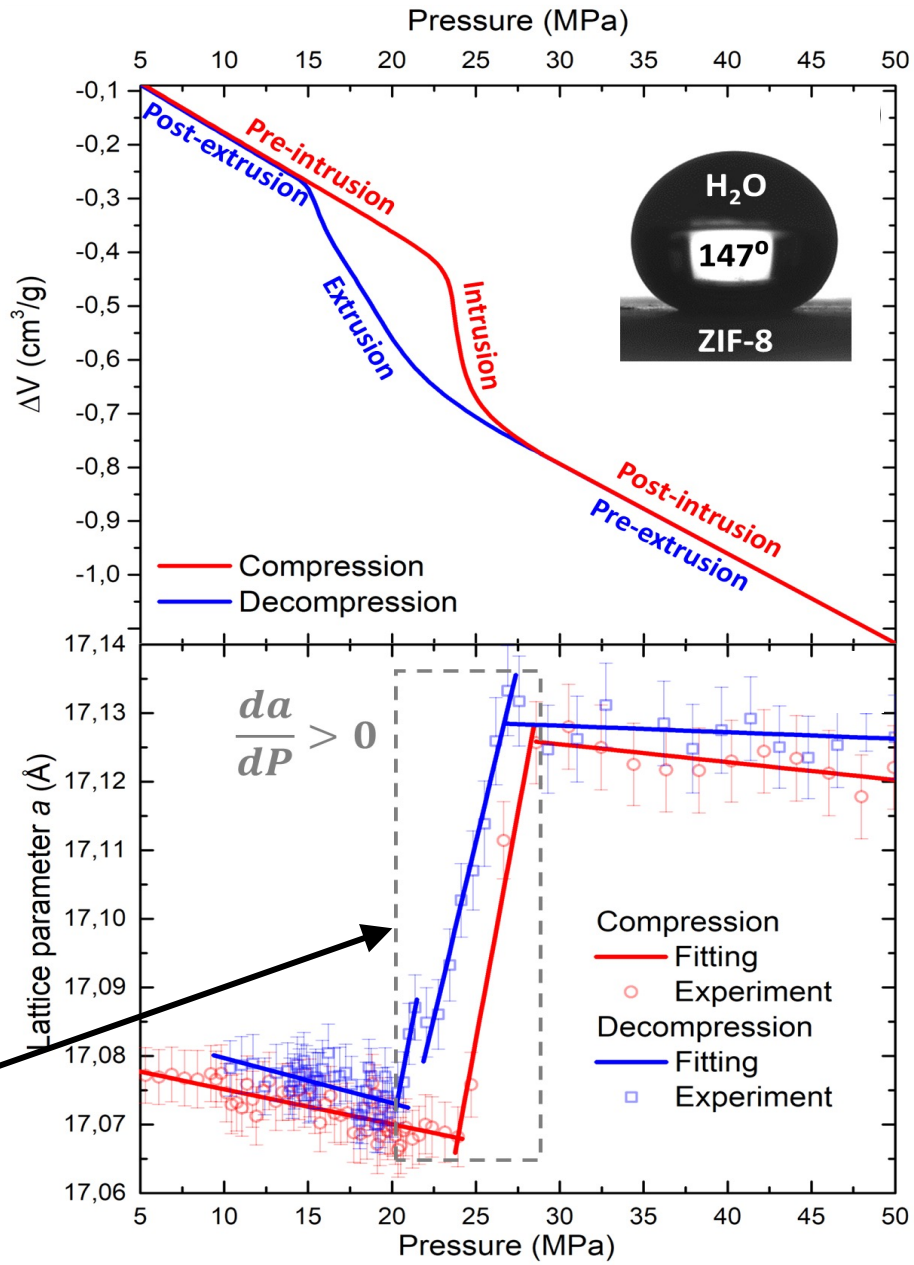


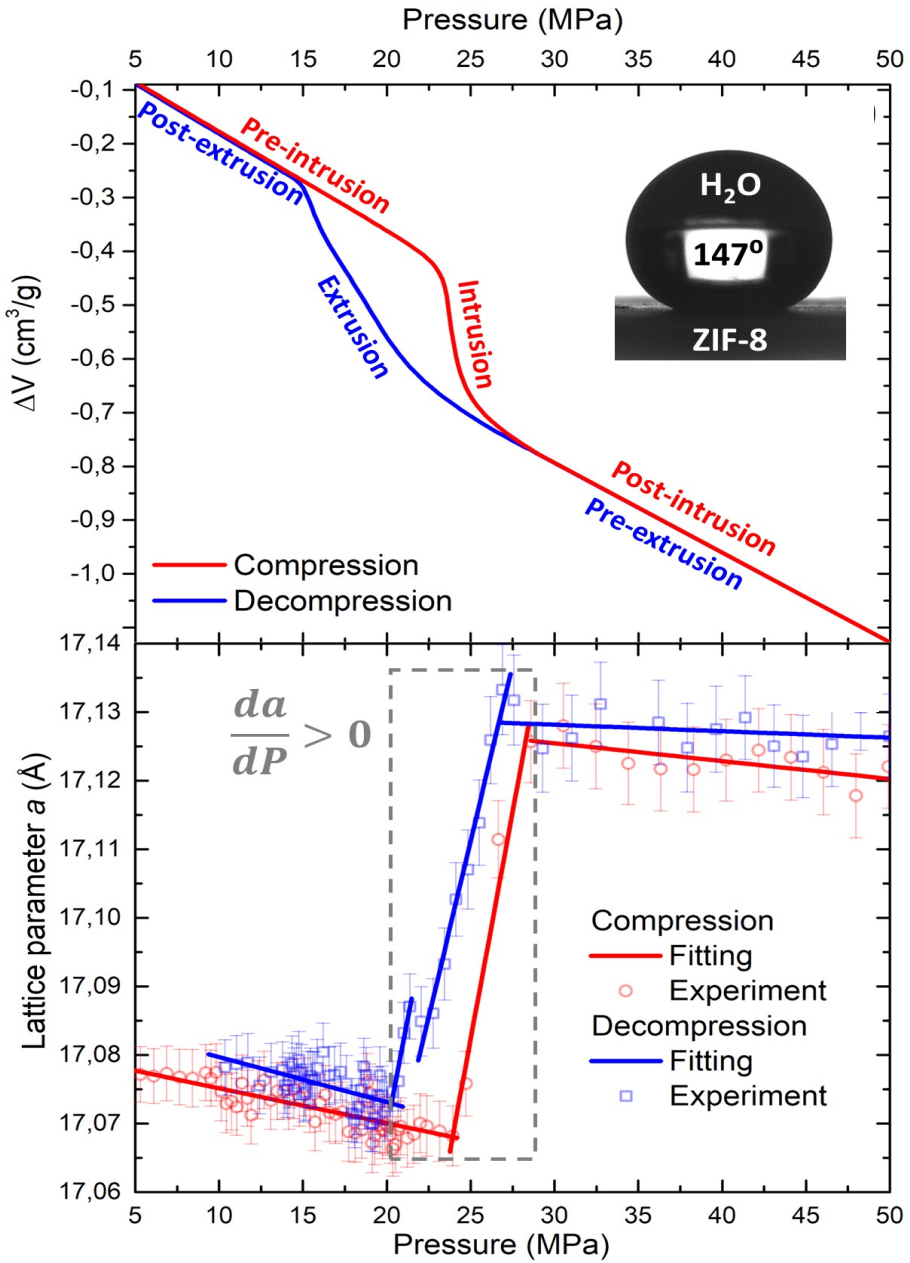
Giant Negative Compressibility by Liquid Intrusion into Superhydrophobic Flexible Nanoporous Framework Tortora et al, Nano Letters 21, 2848-2853

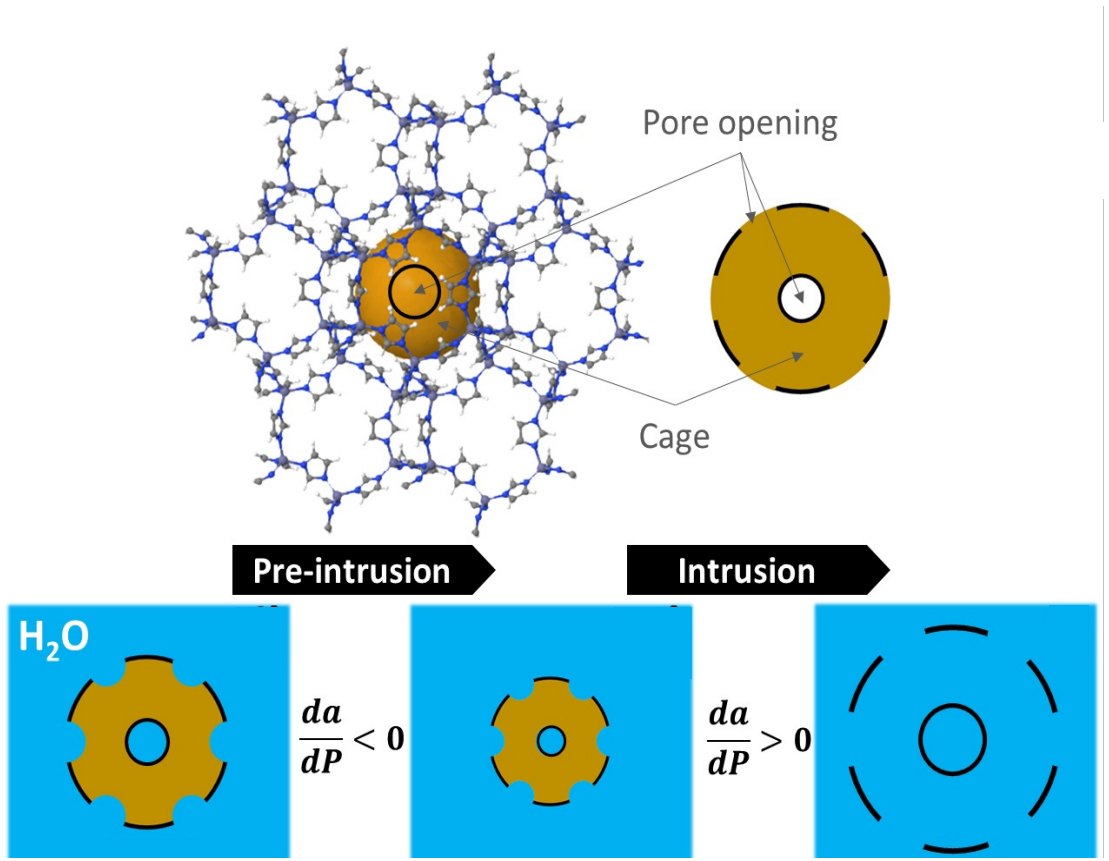
$$\kappa = \frac{-1}{V} \cdot \frac{\partial V}{\partial P}$$

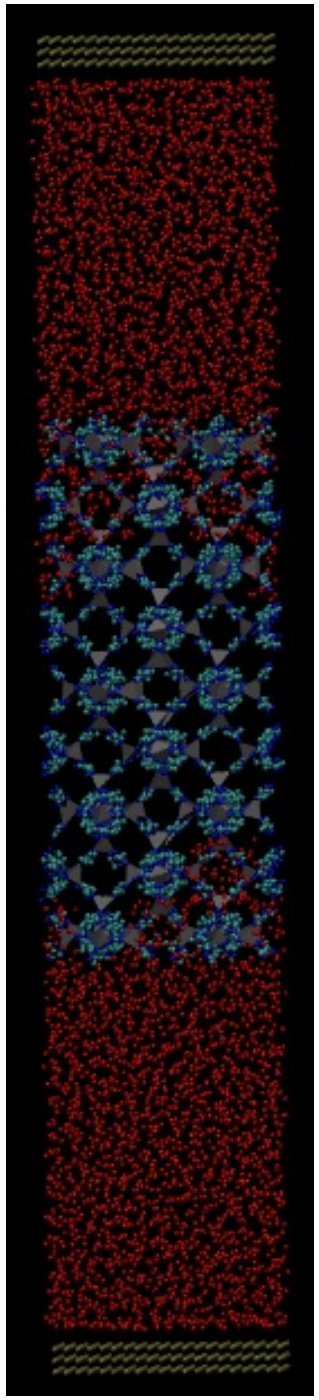
Material	κ_l, TPa^{-1}
BiB_3O_6 (0 - 5 GPa)	-6.7
BiB_3O_6 (P → 0)	-12.5
MIL-53 MOF	-28
$[Ag(en)]NO_3$	-28.4
$Zn[Au(CN)_2]_2$	-42
MCF-34 MOF	-47.3
$InH(BDC)_2$	-62.4
$[Zn(L)_2(OH)_2]_n$	-72
$Ag_3[Co(CN)_6]$	-76.9
ZIF-8 MOF (intrusion)	-1020
ZIF-8 MOF (extrusion 1)	-770
ZIF-8 MOF (extrusion 2)	-610

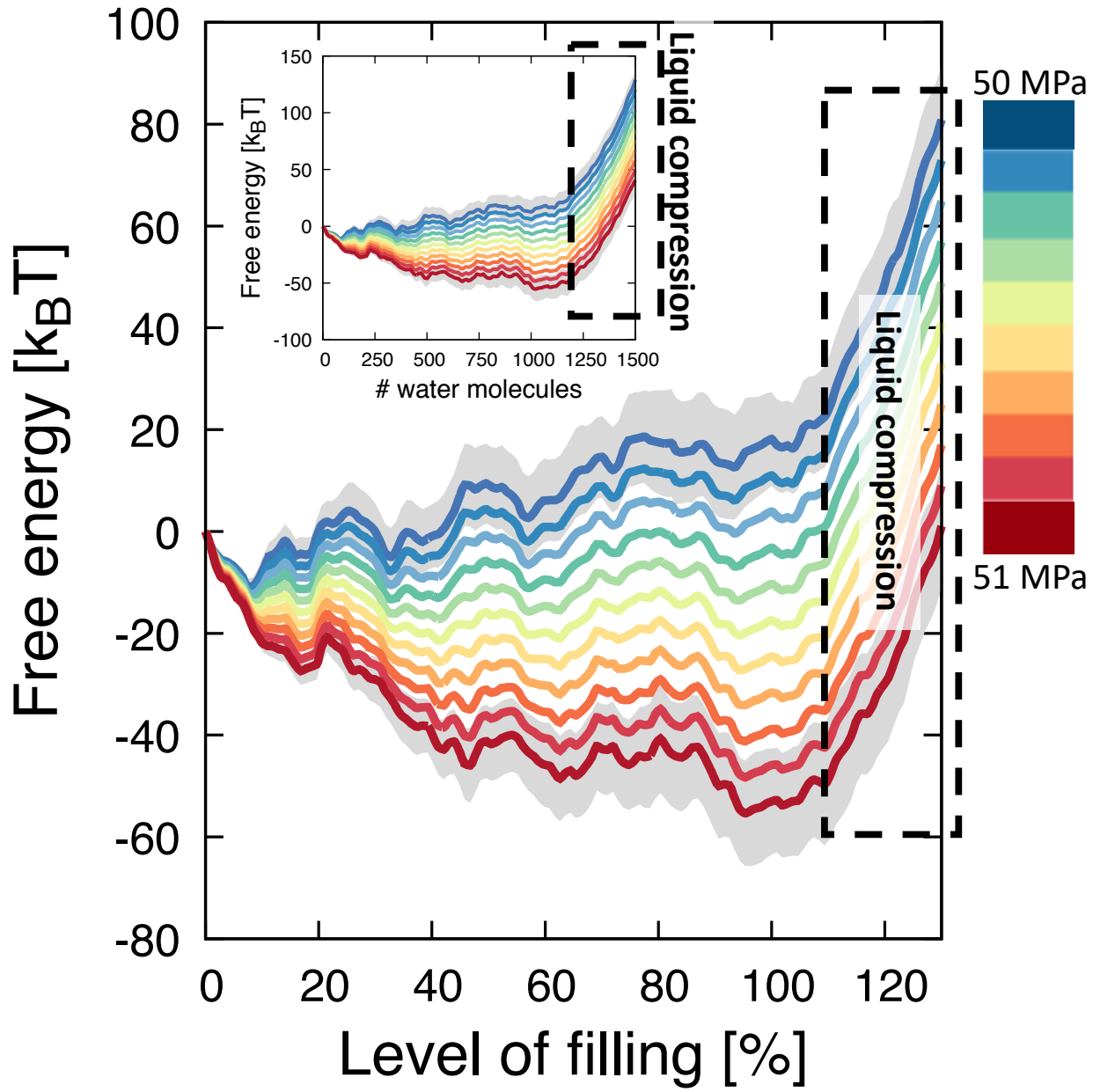
Exceptional Negative Compressibility

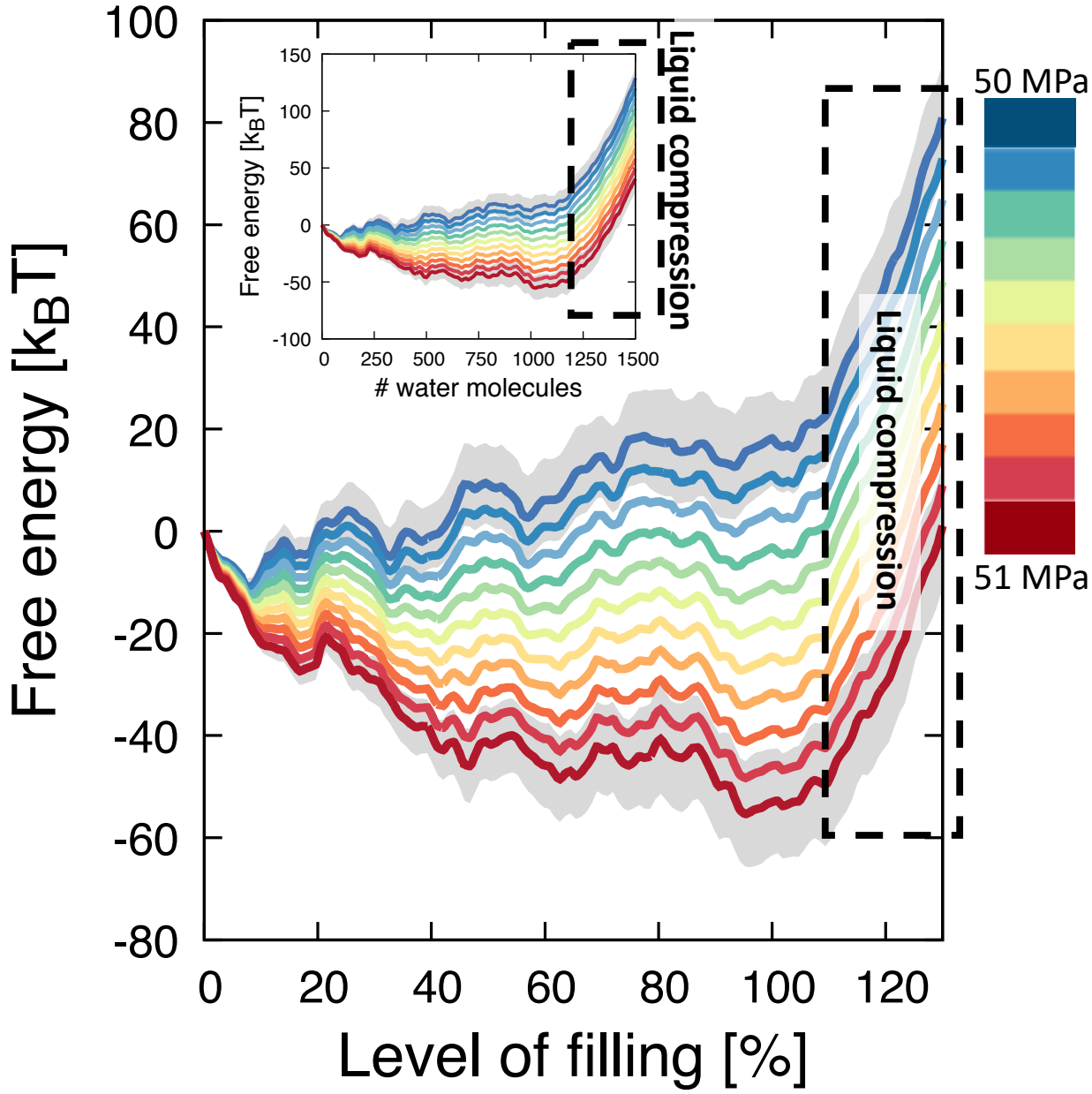


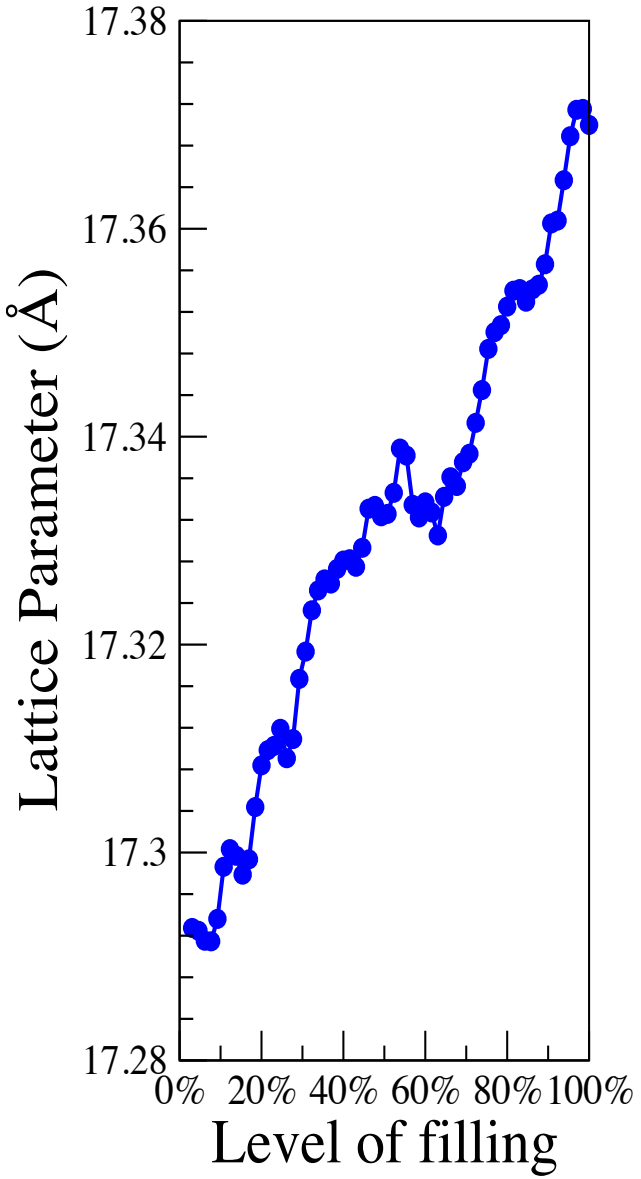

Pressure (MPa)
ΔV (cm³/g)
Pre-intrusion
Post-extrusion
Extrusion
Intrusion
Post-intrusion
Pre-extrusion
H2O
147°
ZIF-8
Compression
Decompression
Lattice parameter a (Å)
da/dP > 0
Compression
Fitting
Experiment
Decompression
Fitting
Experiment
Pressure (MPa)

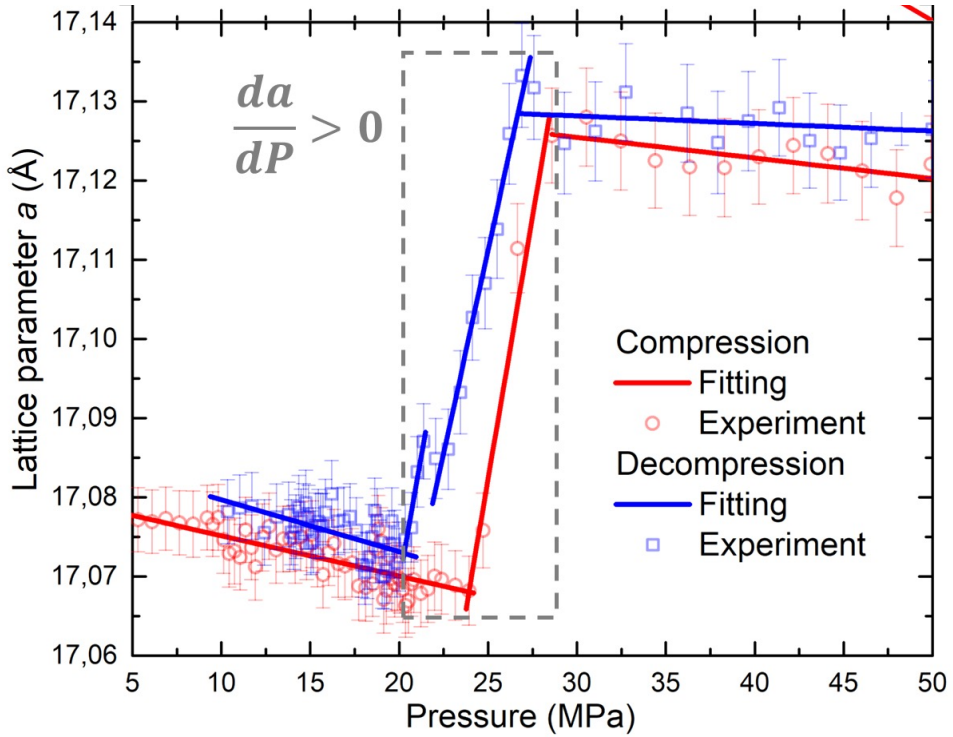

Pore opening
Cage
Pre-intrusion
Intrusion
H2O
da/dP < 0
da/dP > 0

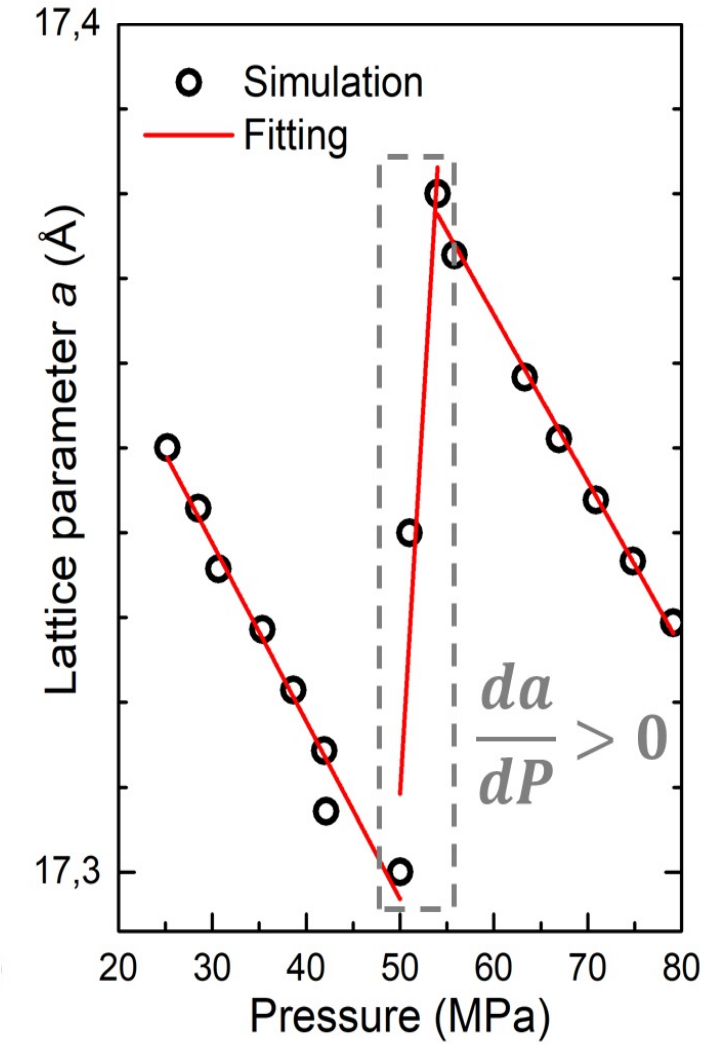


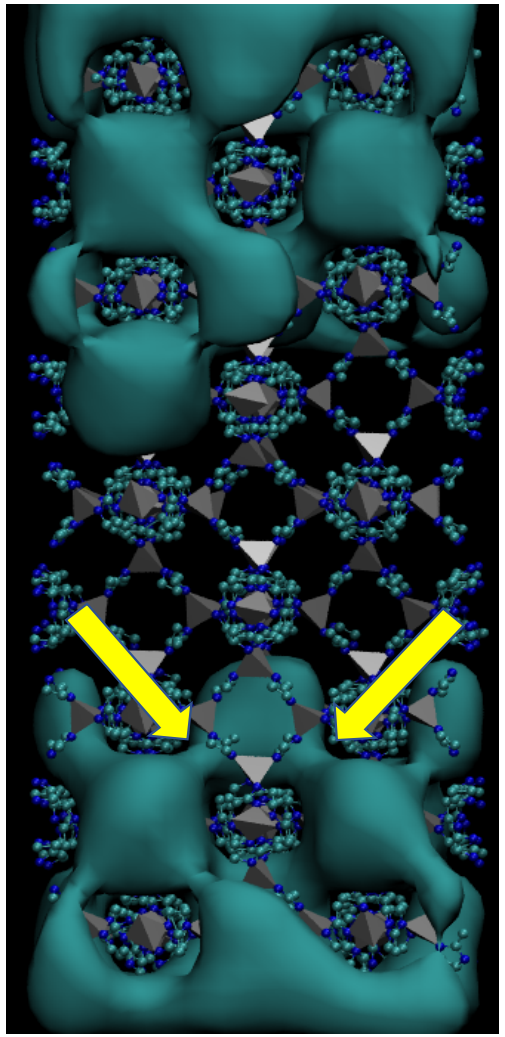

Free energy [$k_B T$]
Level of filling [%]
100
80
60
40
20
0
-20
-40
-60
-80
0
20
40
60
80
100
120
Liquid compression
Liquid compression
50 MPa
51 MPa
Free energy [$k_B T$]
water molecules
150
100
50
0
-50
-100
0
250
500
750
1000
1250
1500

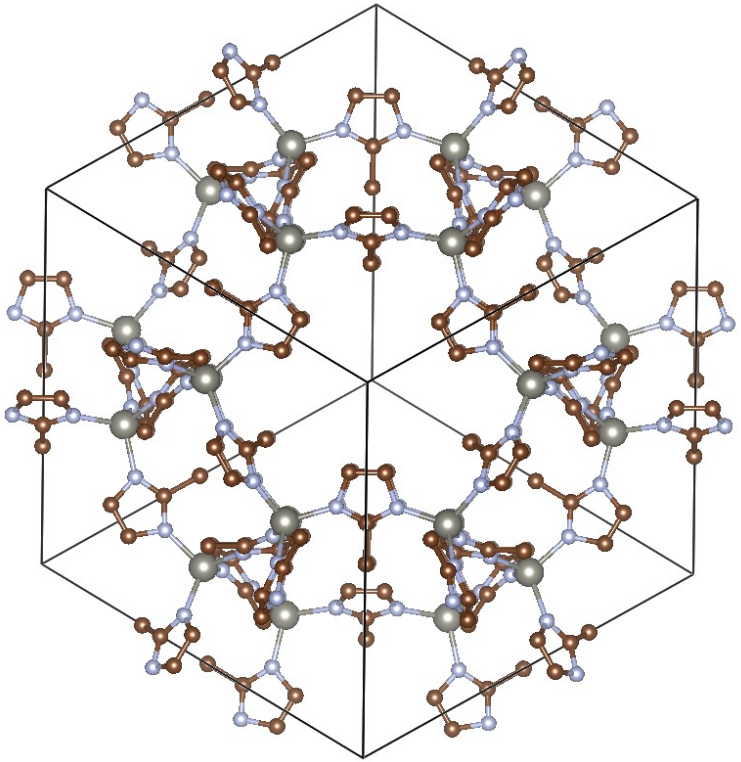

Free energy [k_BT]
Level of filling [%]
Liquid compression
Liquid compression
50 MPa
51 MPa
Free energy [k_BT]
water molecules

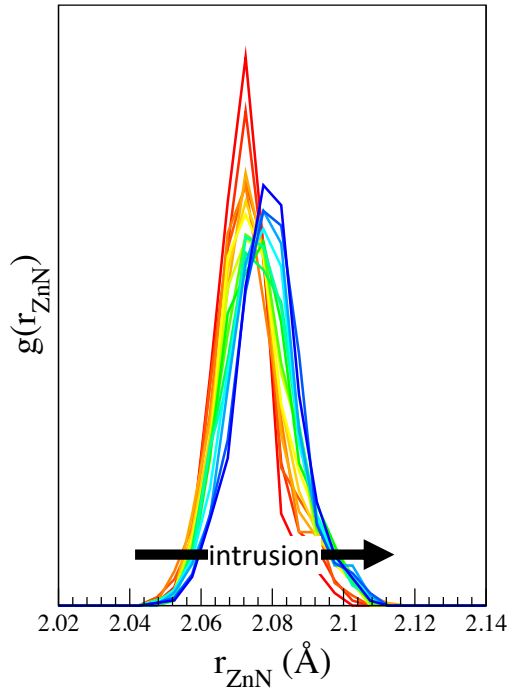

Lattice Parameter (Å)
Level of filling

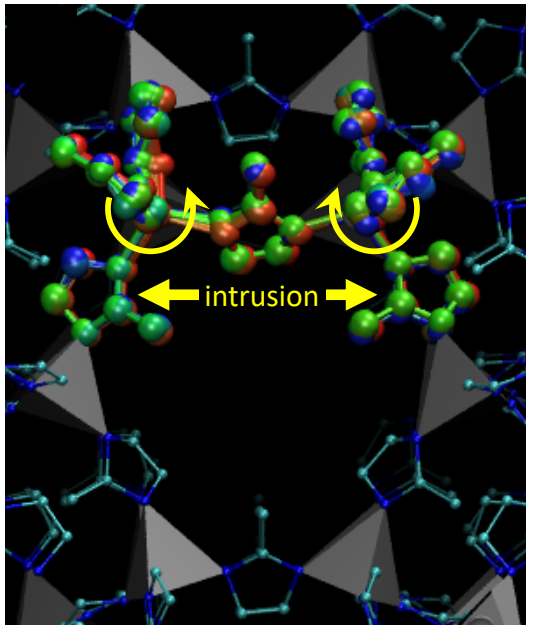

17,14
17,13
17,12
17,11
17,10
17,09
17,08
17,07
17,06
Lattice parameter a (Å)
5
10
15
20
25
30
35
40
45
50
Pressure (MPa)
$\frac{da}{dP} > 0$
Compression
Fitting
Experiment
Decompression
Fitting
Experiment

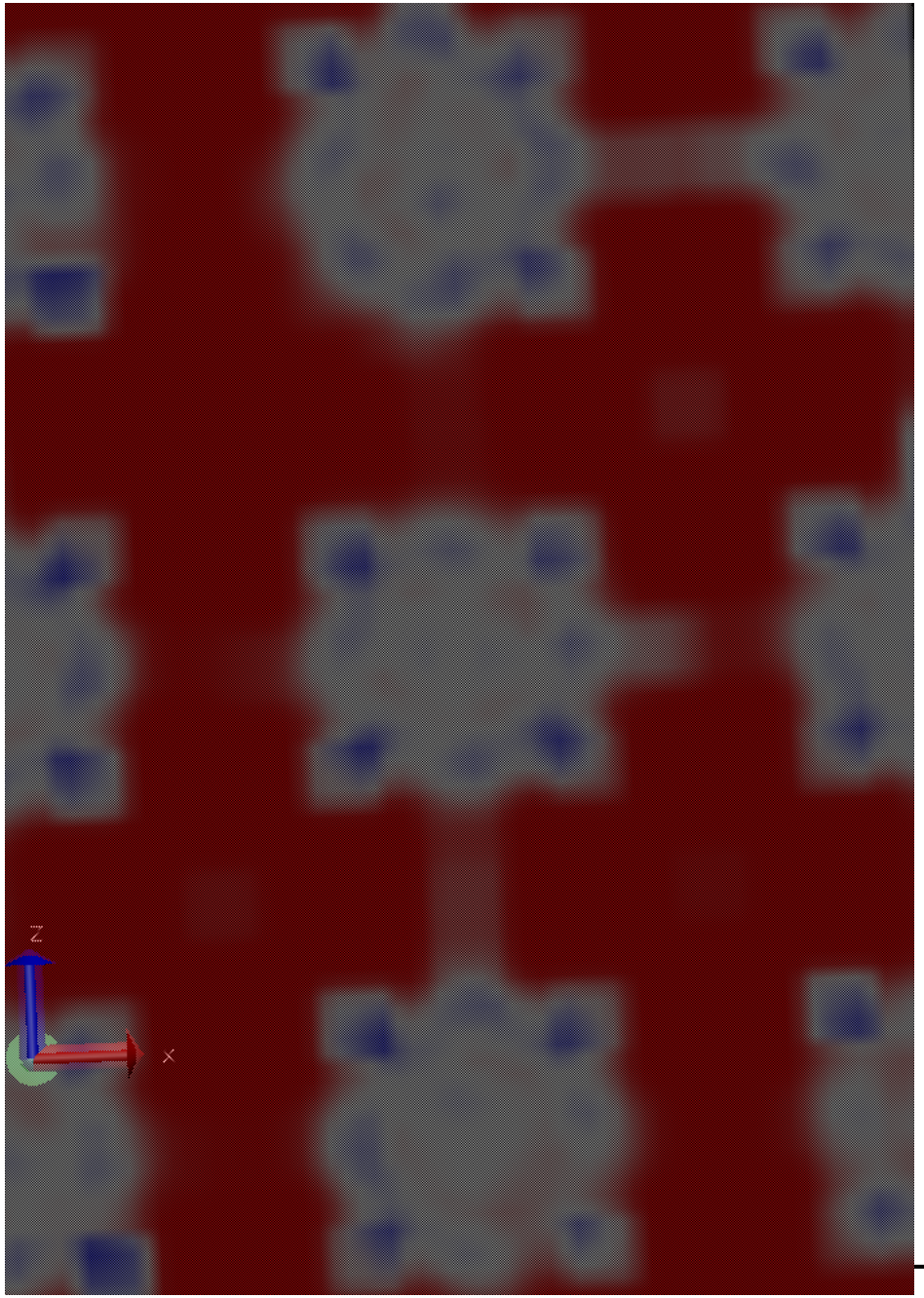

17,4
17,3
Lattice parameter a (Å)
20
30
40
50
60
70
80
Pressure (MPa)
Simulation
Fitting
$\frac{da}{dP} > 0$

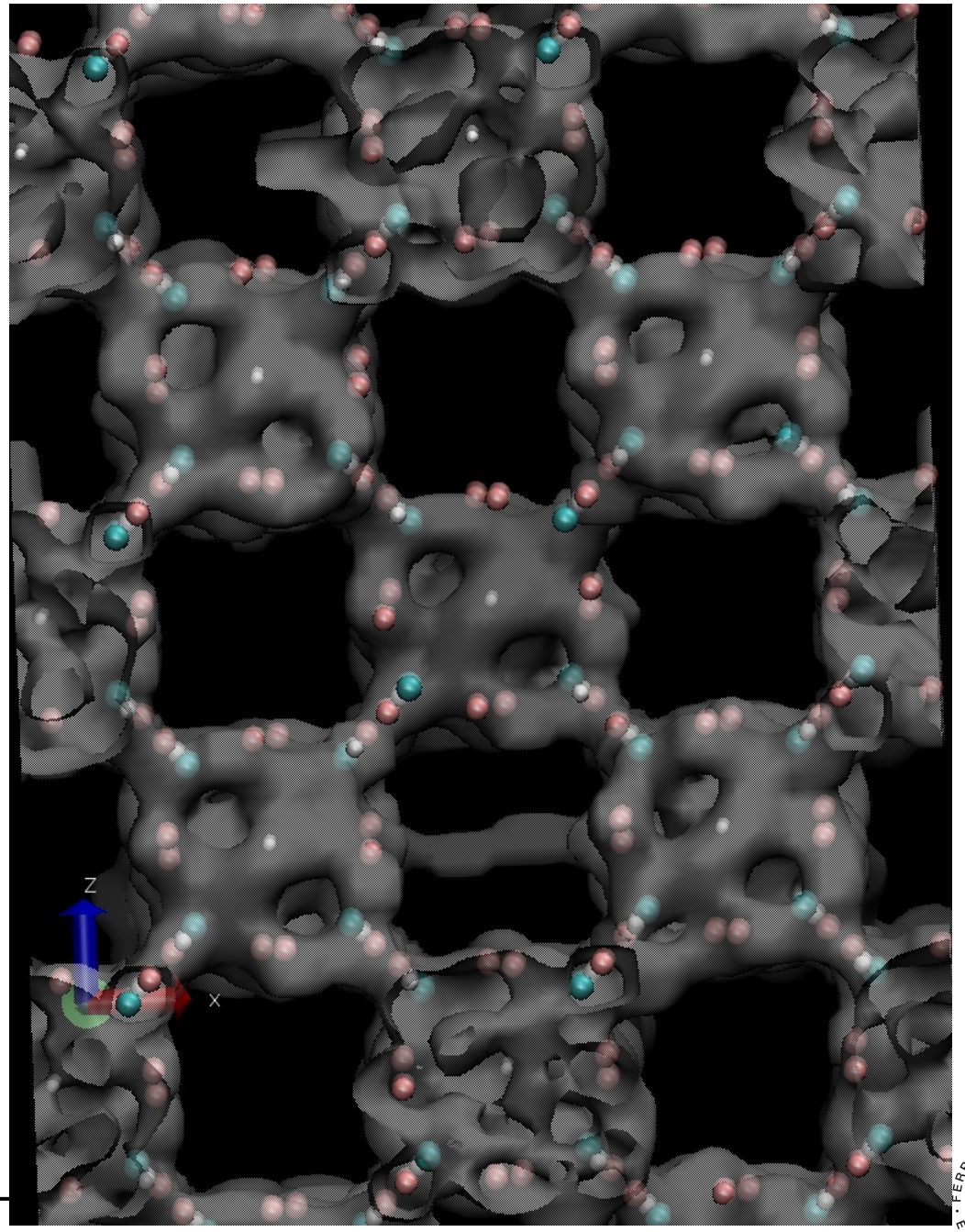





g(r_ZnN)
intrusion
2.02
2.04
2.06
2.08
2.1
2.12
2.14
r_ZnN (Å)

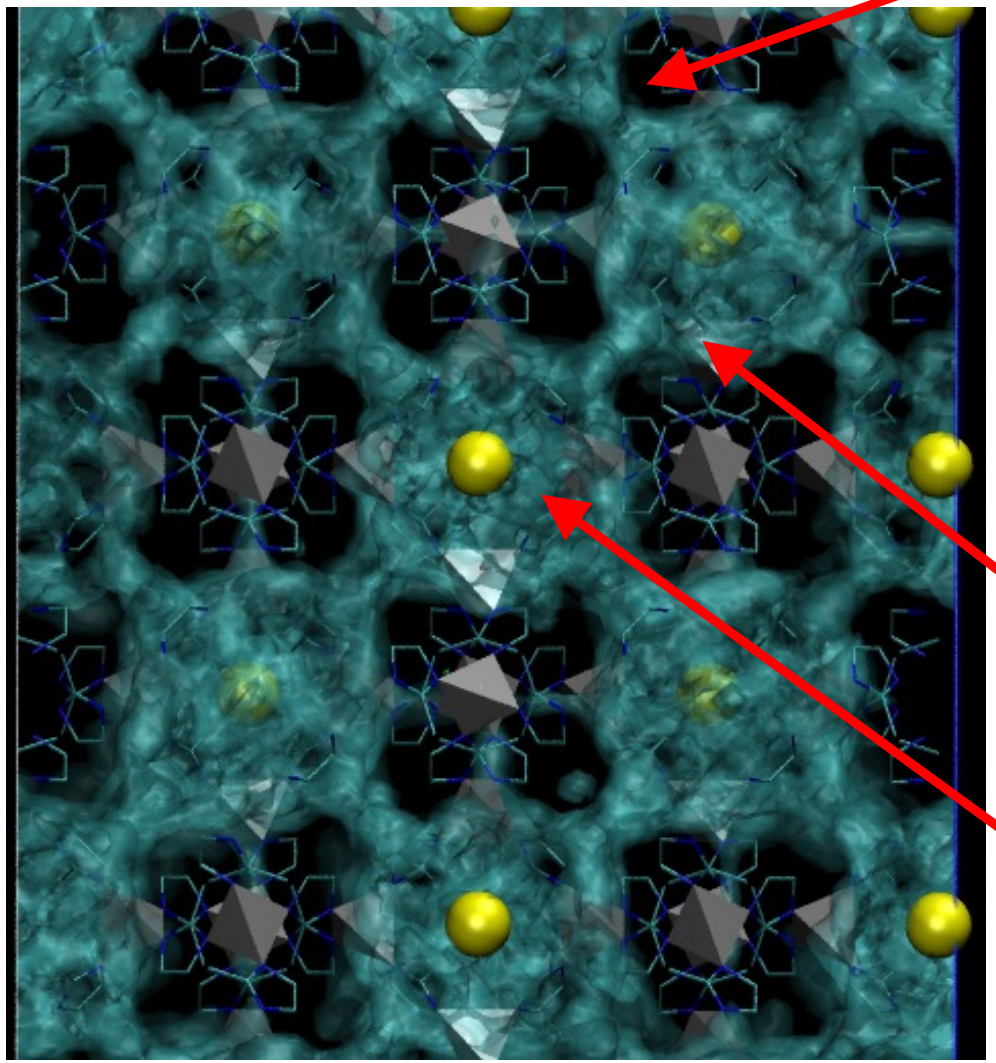

intrusion



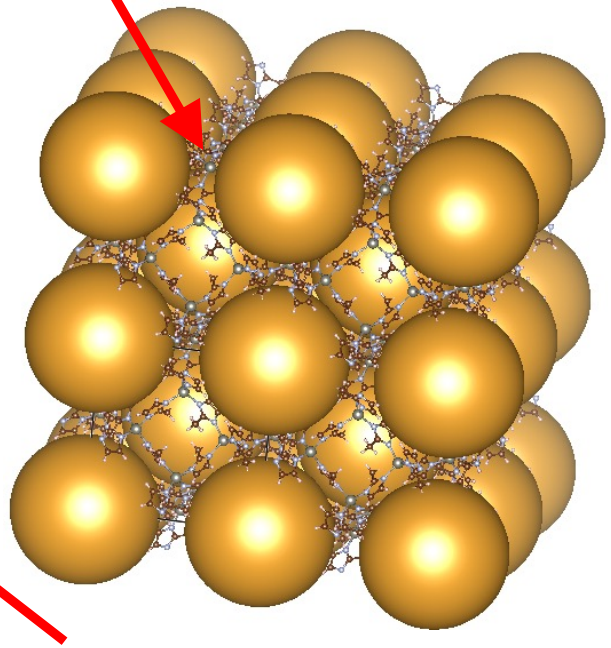


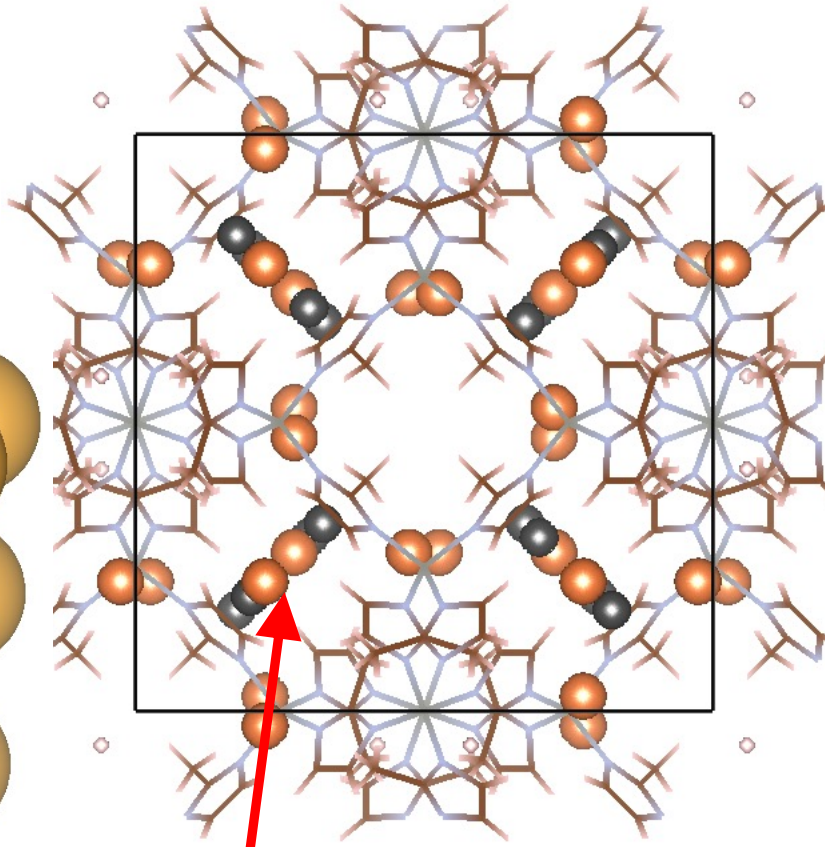
H2020-FET

ELECTRO INTRUSION



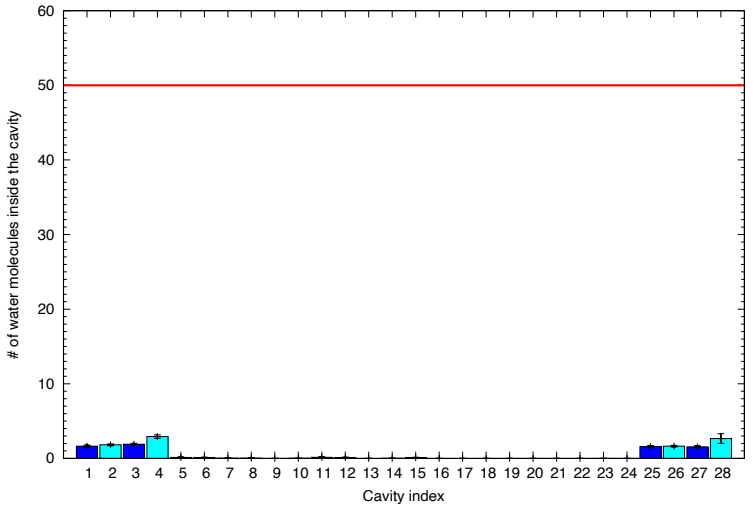
Secondary interconnections

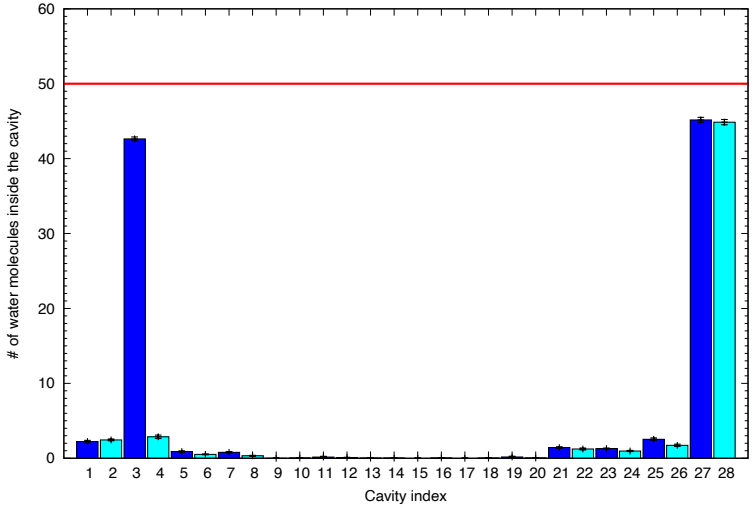


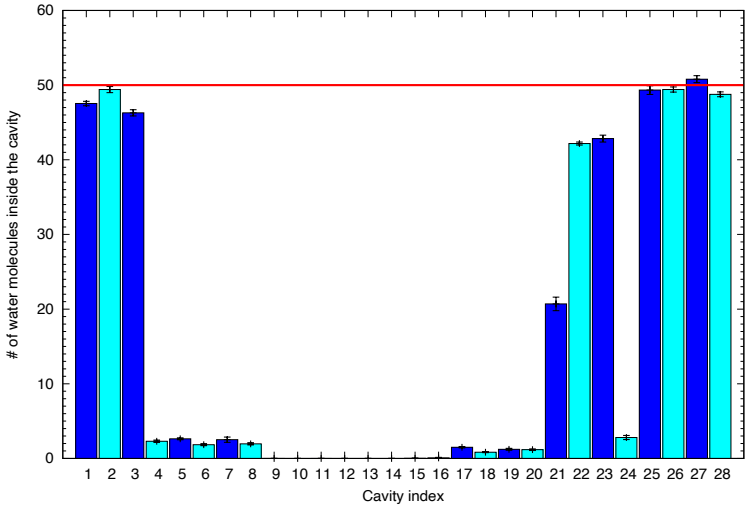


Crystal-like and liquid-like water

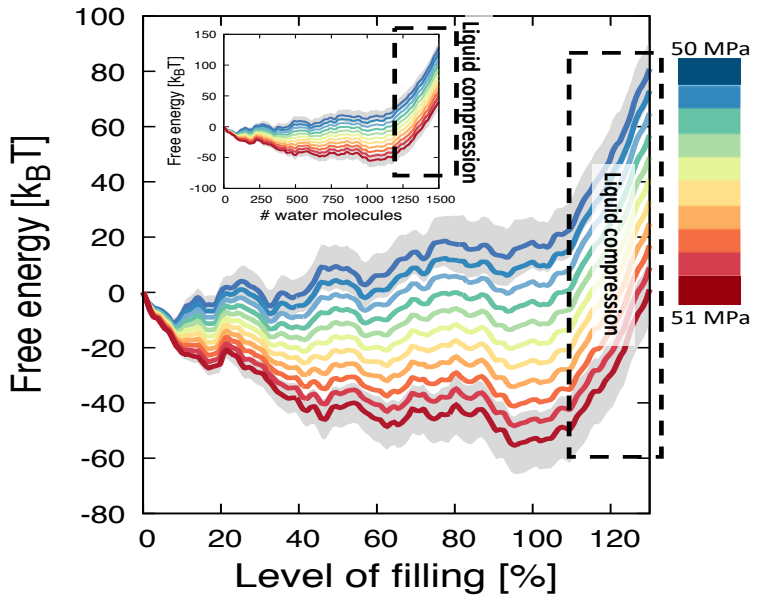
Water sites with Fractional occupation

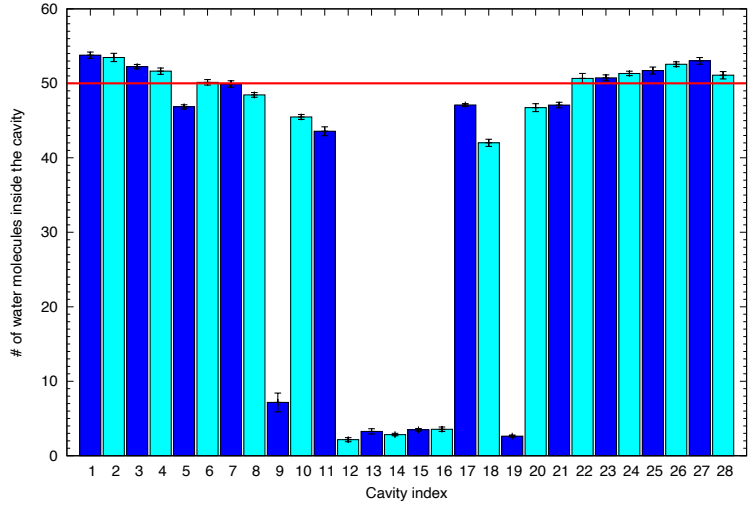

# of water molecules inside the cavity
Cavity index

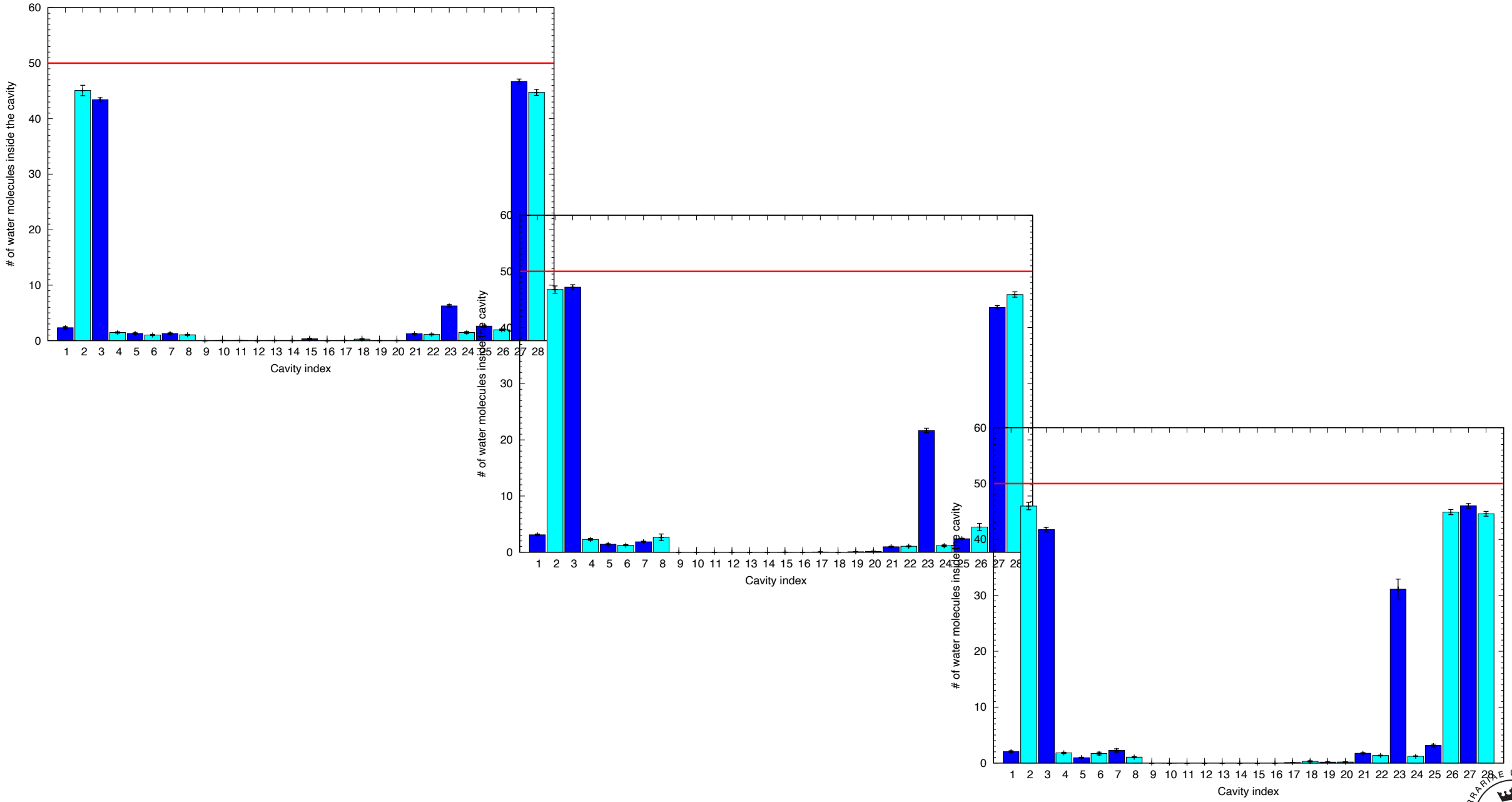

# of water molecules inside the cavity
Cavity index


# of water molecules inside the cavity
Cavity index

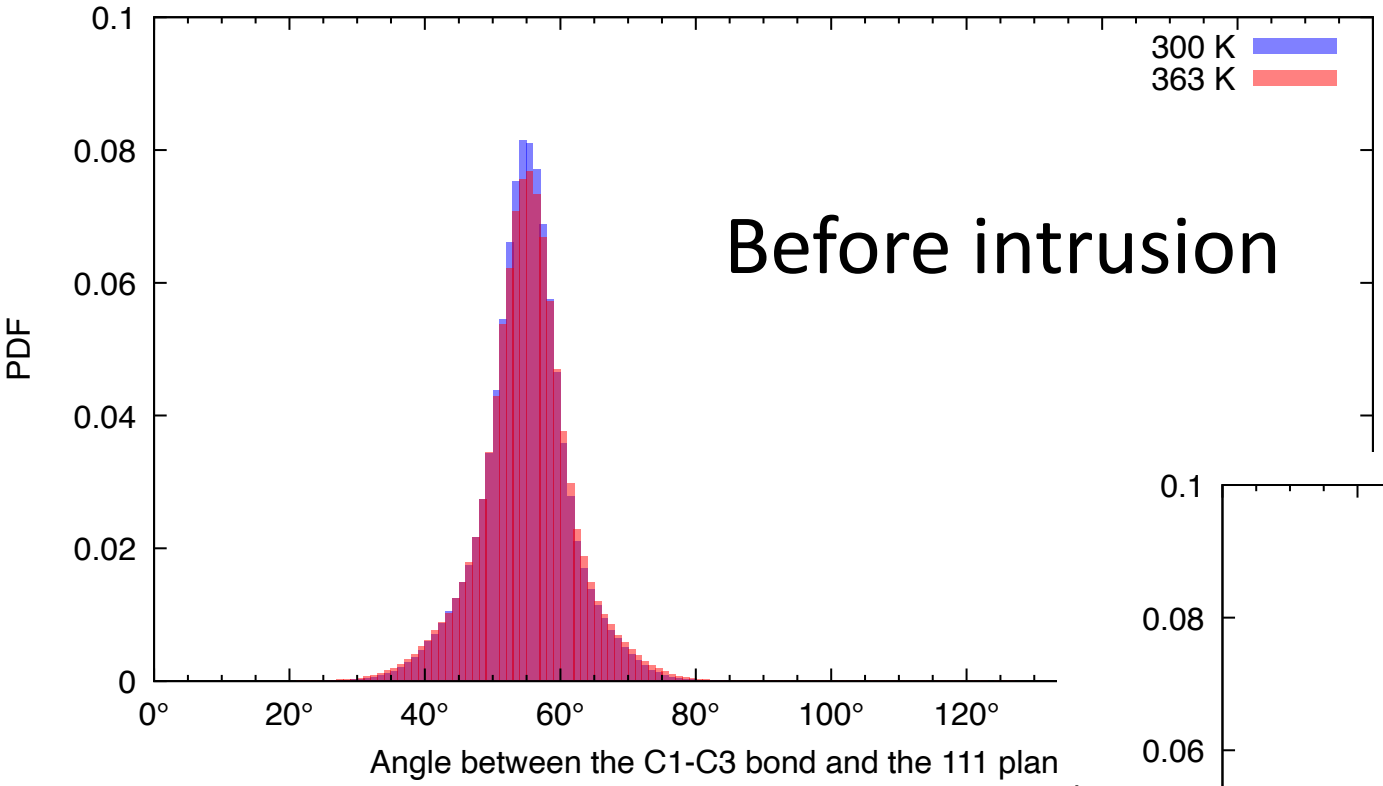
Intrusion


Free energy [kBT]
Level of filling [%]
Free energy [kBT]
water molecules
Liquid compression
Liquid compression
50 MPa
51 MPa

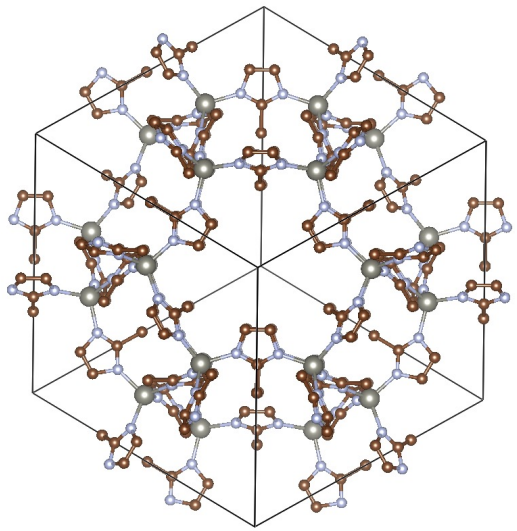

# of water molecules inside the cavity
Cavity index

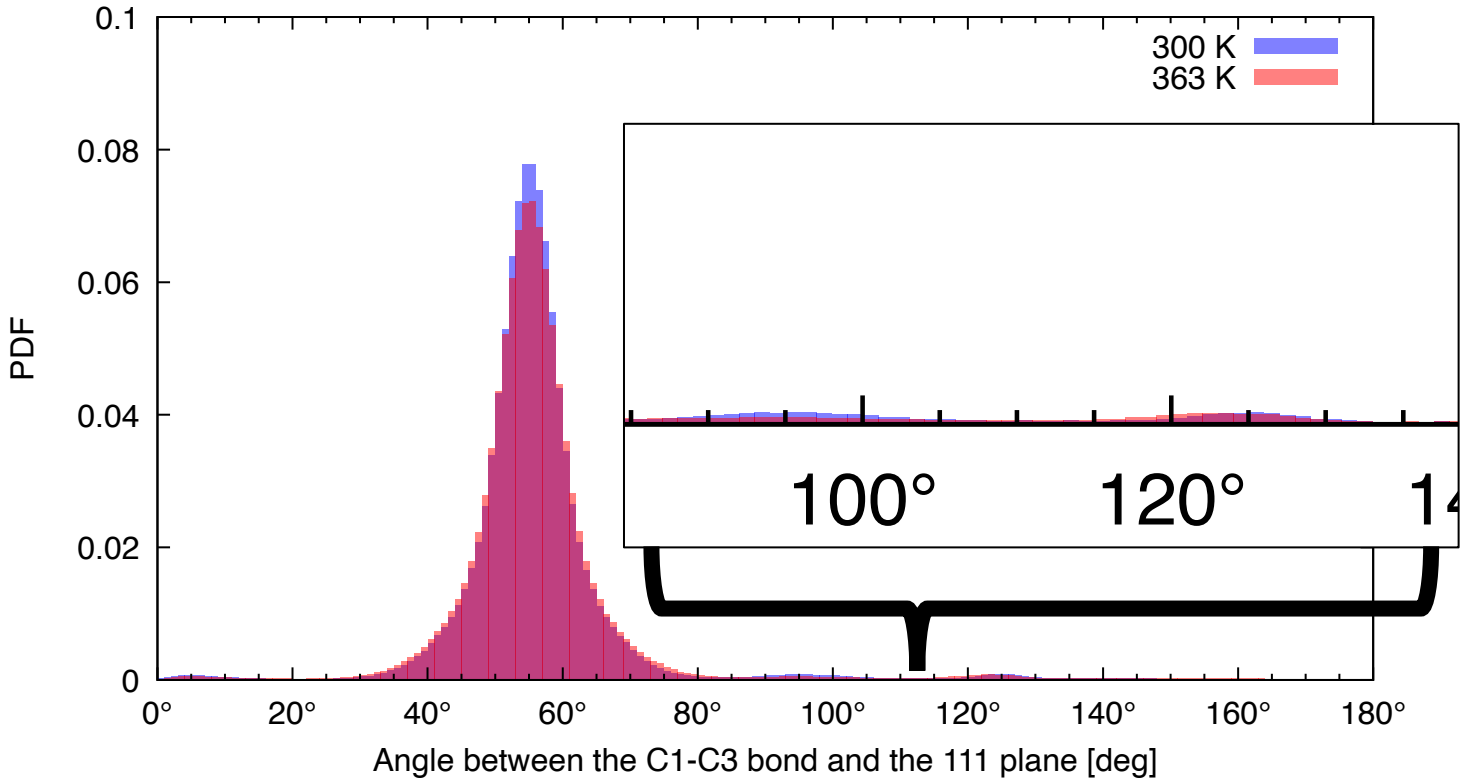

# of water molecules inside the cavity
Cavity index
# of water molecules inside the cavity
Cavity index
# of water molecules inside the cavity
Cavity index

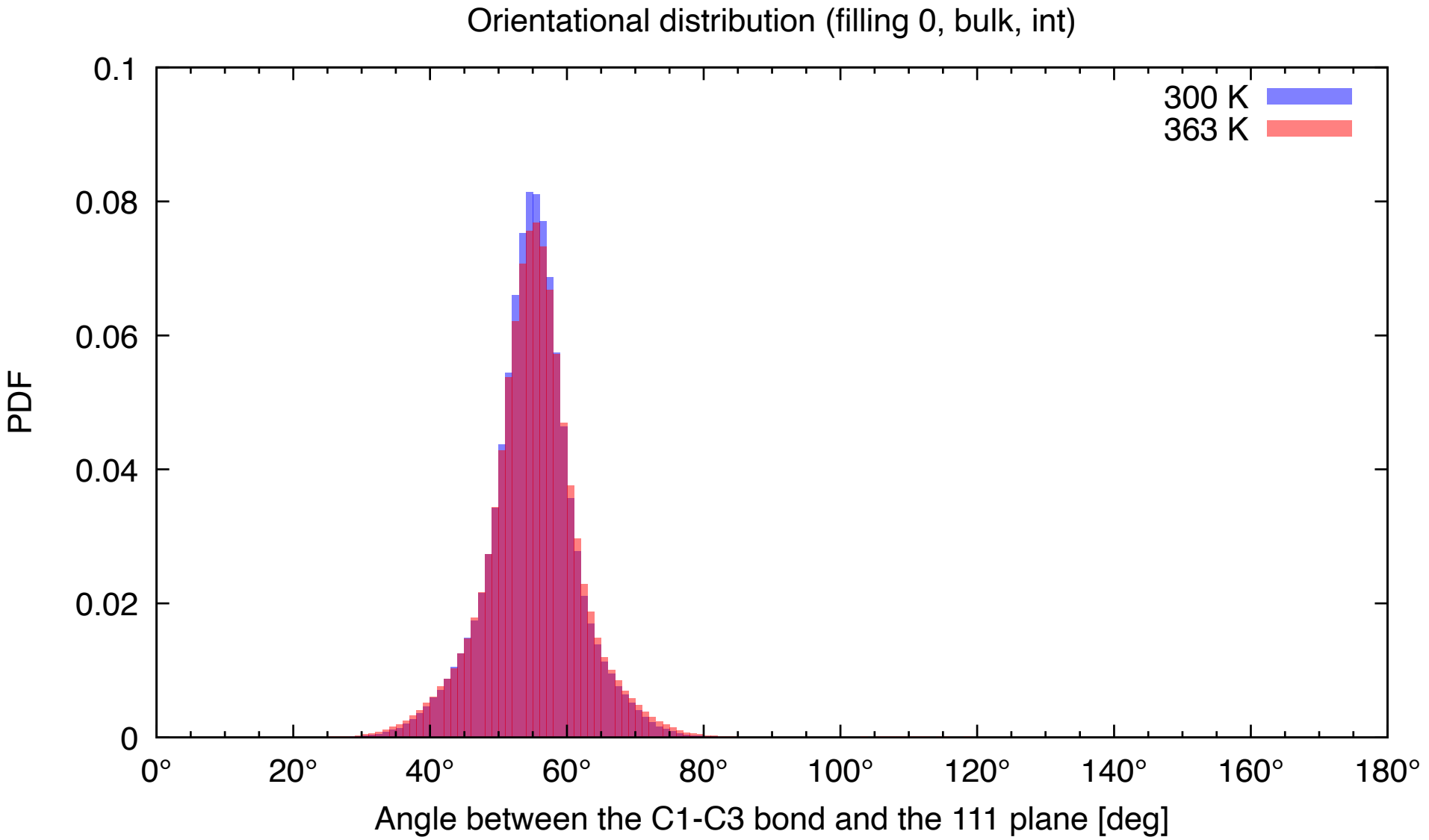
EMPTY ZIF8

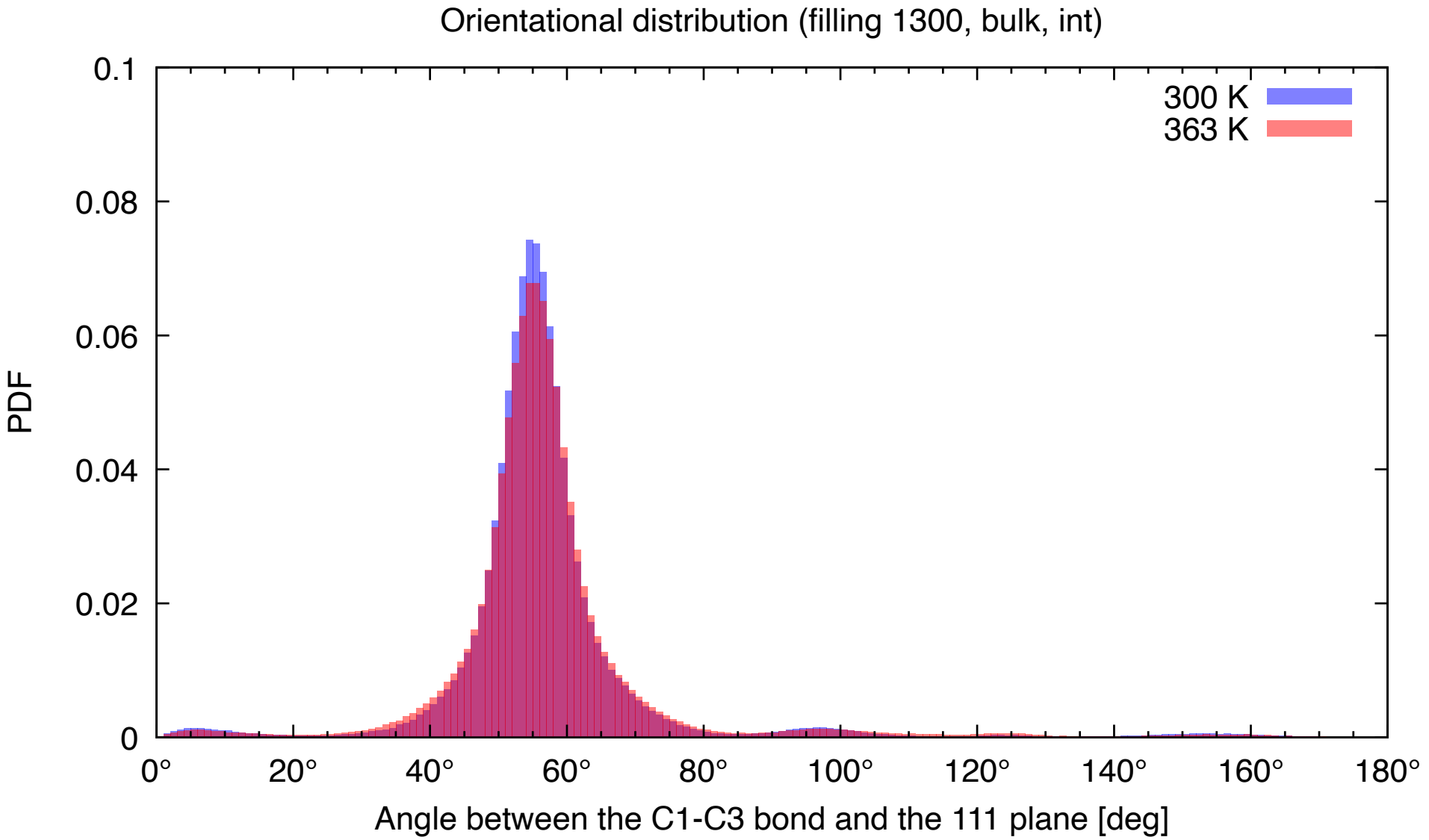


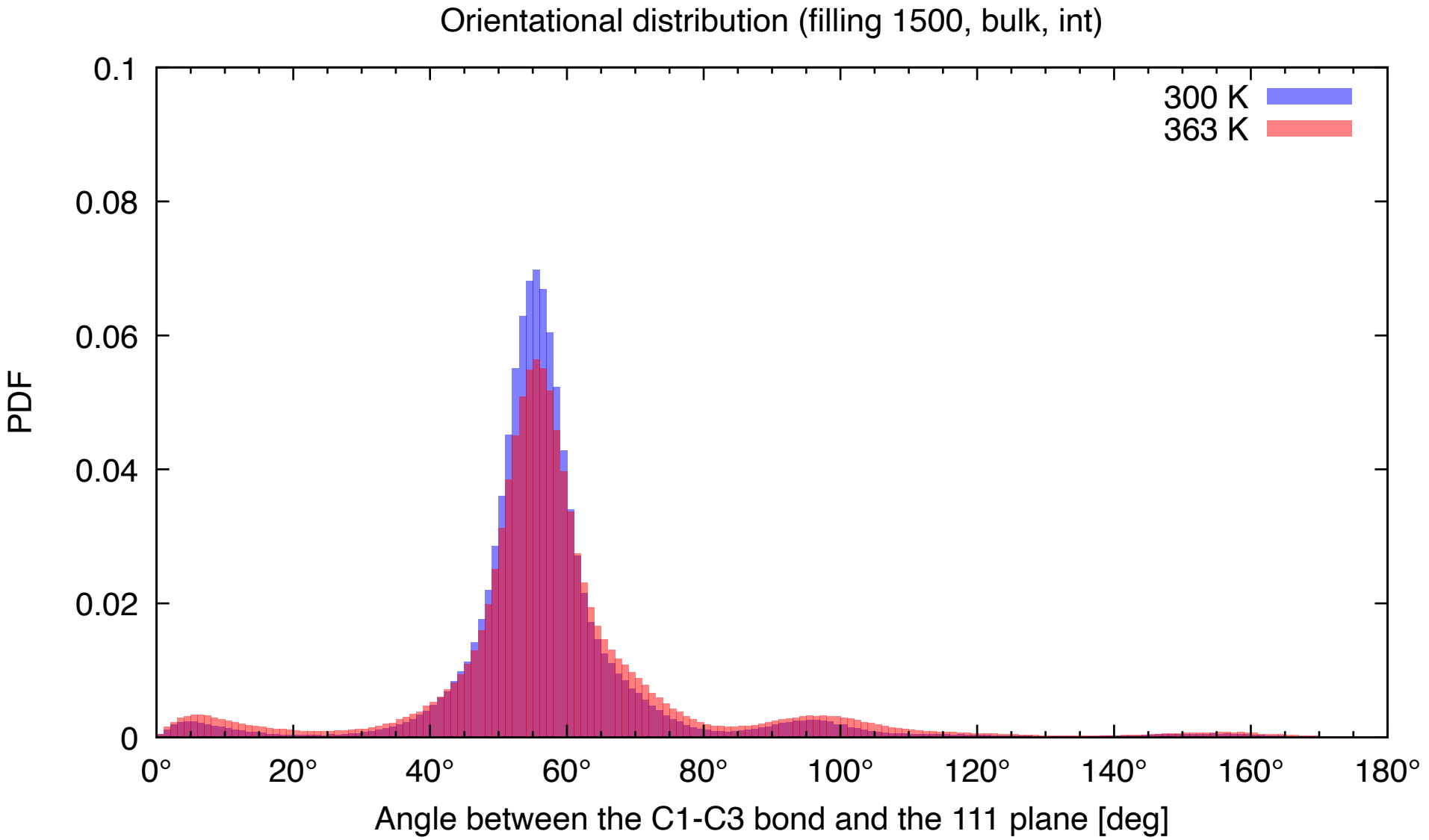
Before intrusion

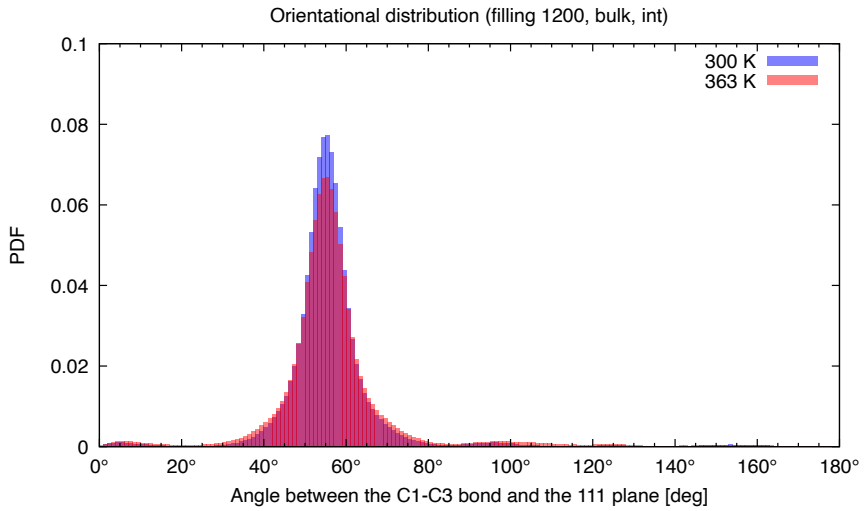


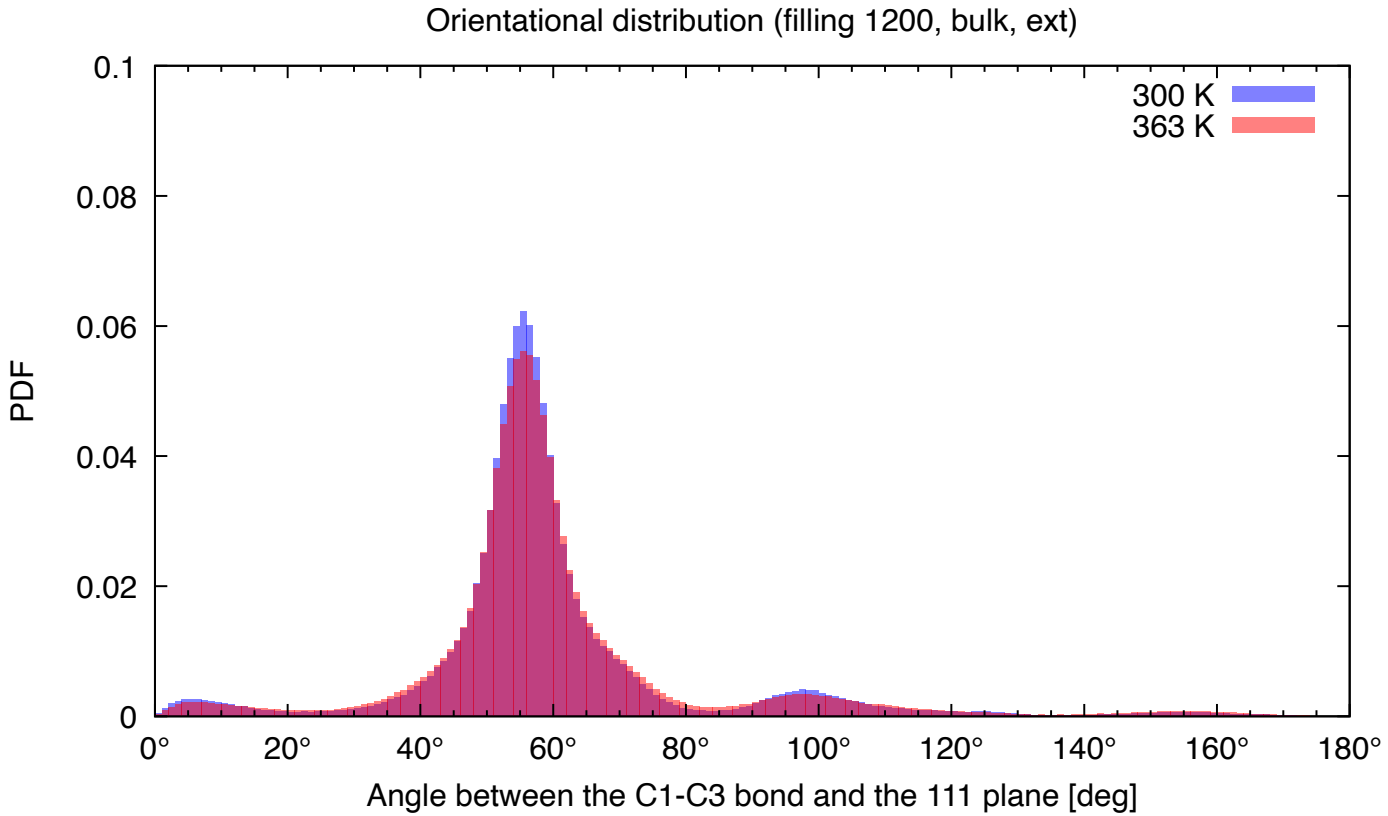


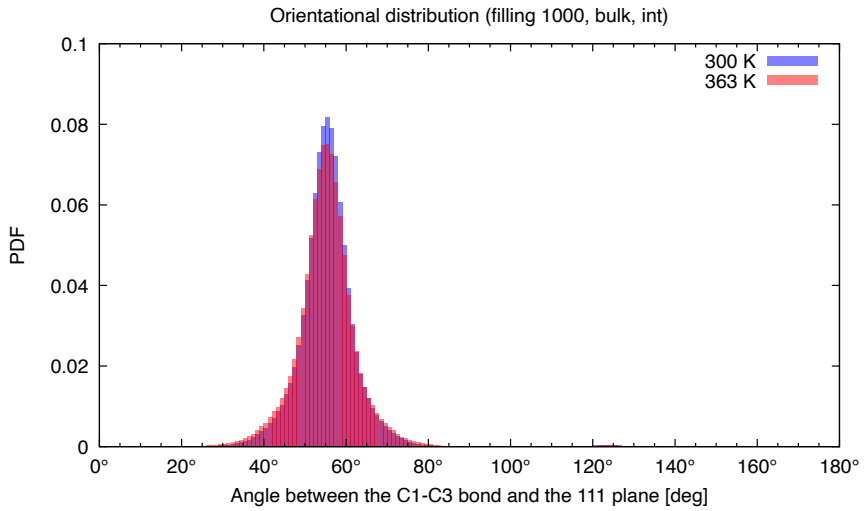

Orientational distribution (filling 0, bulk, int)
300 K
363 K
PDF
0.1
0.08
0.06
0.04
0.02
0
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]

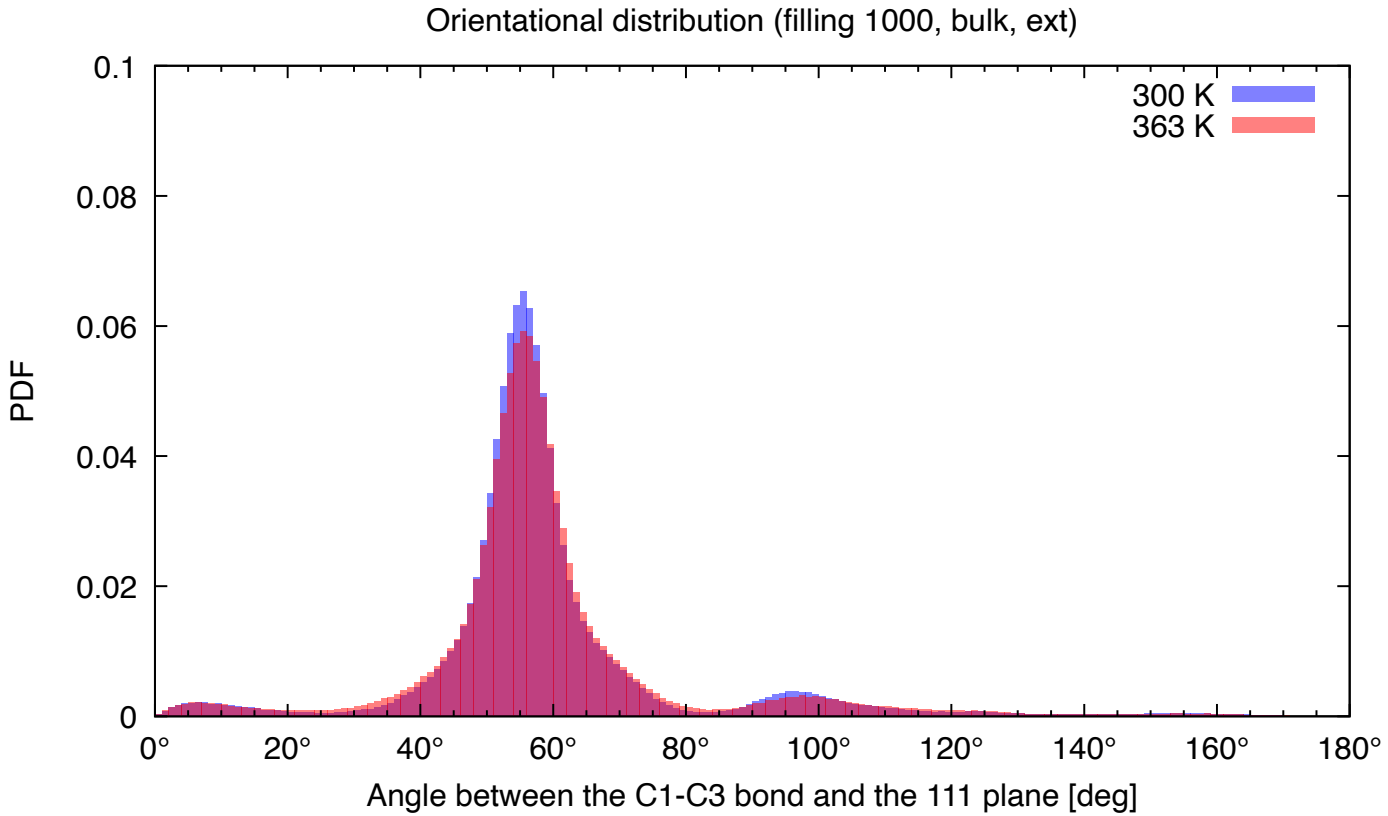

Orientational distribution (filling 1300, bulk, int)
300 K
363 K
PDF
0.1
0.08
0.06
0.04
0.02
0
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]

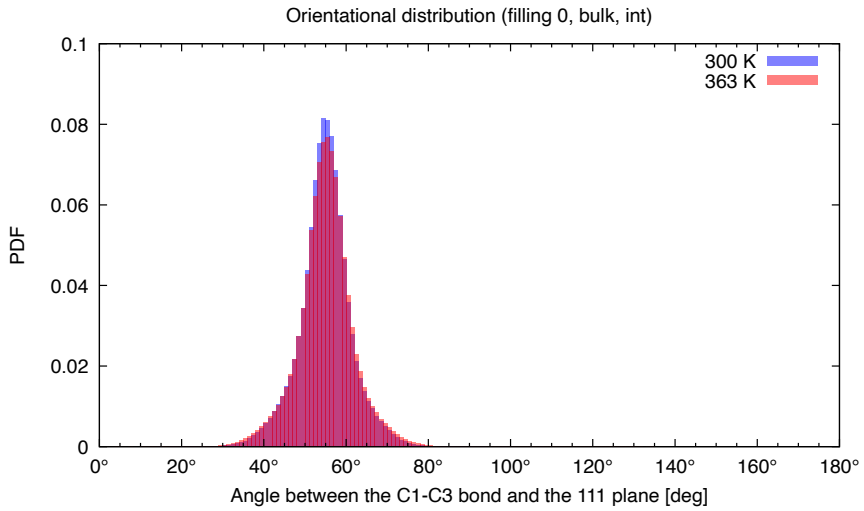

Orientational distribution (filling 1500, bulk, int)
300 K
363 K
PDF
0.1
0.08
0.06
0.04
0.02
0
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]

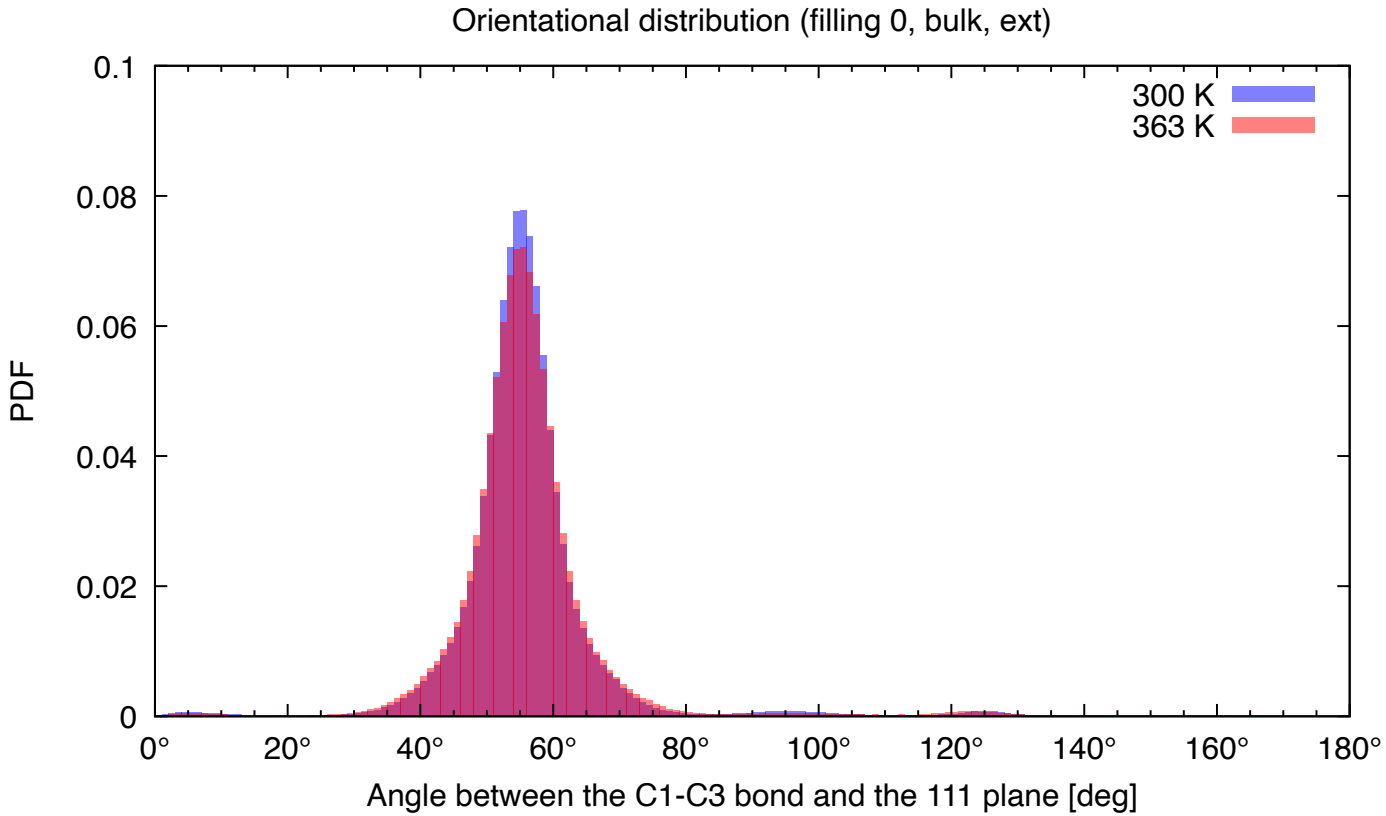

Orientational distribution (filling 1200, bulk, int)
PDF
0.1
0.08
0.06
0.04
0.02
0
300 K
363 K
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]


Orientational distribution (filling 1200, bulk, ext)
PDF
0.1
0.08
0.06
0.04
0.02
0
300 K
363 K
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]


Orientational distribution (filling 1000, bulk, int)
PDF
0.1
0.08
0.06
0.04
0.02
0
300 K
363 K
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]


Orientational distribution (filling 1000, bulk, ext)
PDF
0.1
0.08
0.06
0.04
0.02
0
300 K
363 K
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
Angle between the C1-C3 bond and the 111 plane [deg]


Orientational distribution (filling 0, bulk, int)
PDF
Angle between the C1-C3 bond and the 111 plane [deg]
300 K
363 K
0.1
0.08
0.06
0.04
0.02
0
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°


Orientational distribution (filling 0, bulk, ext)
PDF
Angle between the C1-C3 bond and the 111 plane [deg]
300 K
363 K
0.1
0.08
0.06
0.04
0.02
0
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°

Conclusions

- Intruision of liquids in textured and porous materials is non trivial

- Crystalline porous materials increase the level of complexity
  - Flexibility
  - Ordering of liquid inside cavities (breakdown of the sharp interface model?)
  - Multiple levels of metastabilities: liquid state, configuration of the porous medium

Acknowledgements

Marco Tortora

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Carlo Massimo Casciola

PRACE

ELECTRO INTRUSION

H2020-FET Electro-Intrusion