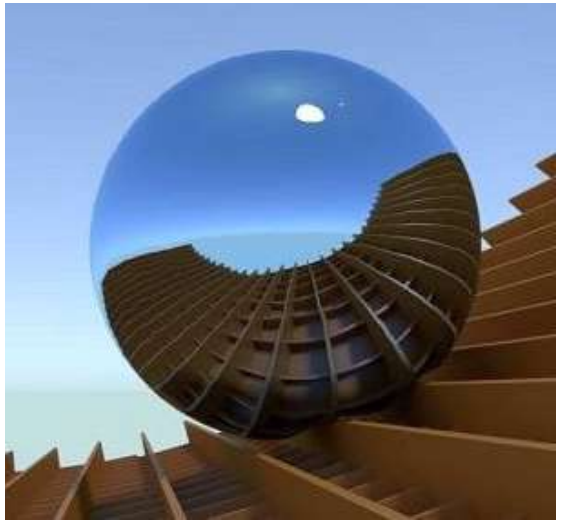
H2020-FET Electro-Intrusion

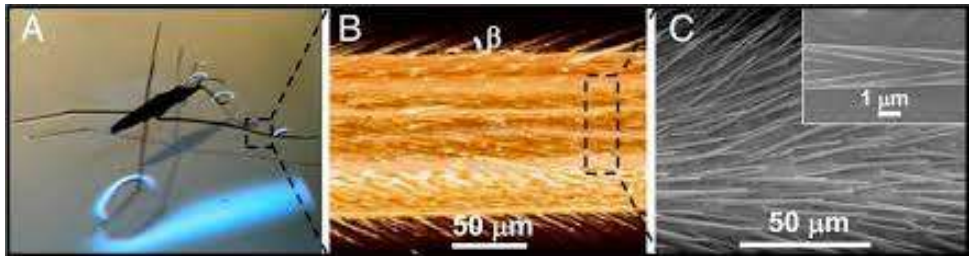
Liquid intrusion (and extrusion) in porous and textured materials

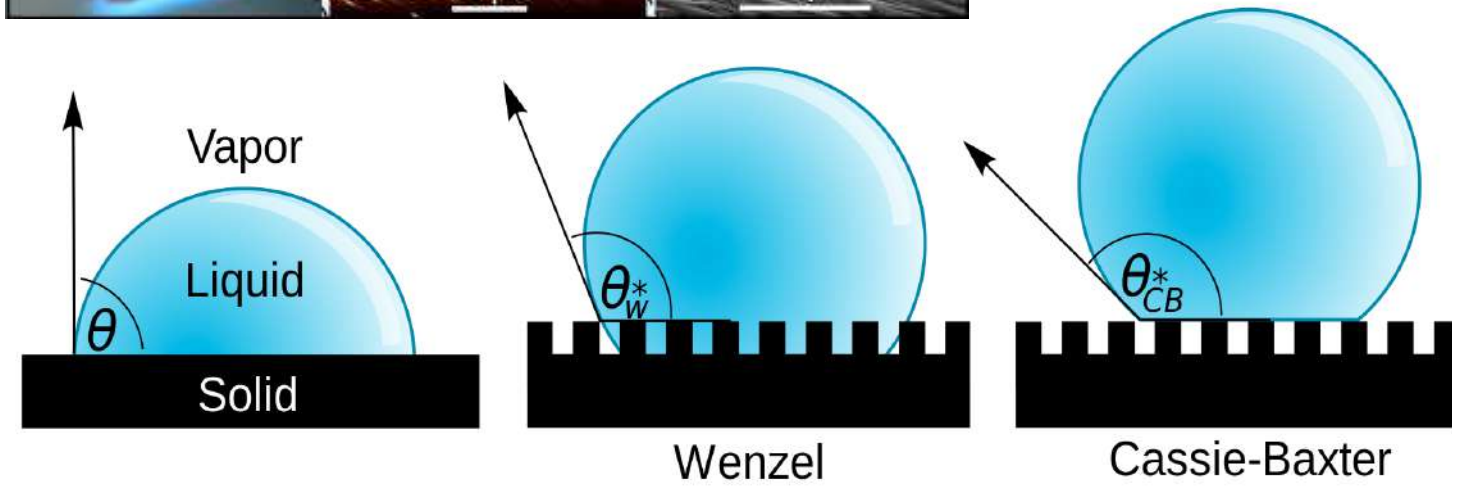
Simone.meloni@unife.it

Frontiers in ion channels and nanopores: theory, experiments, and simulation

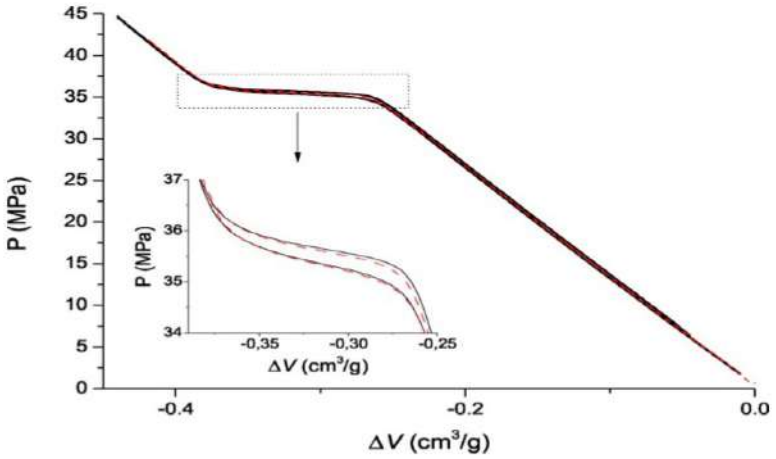
Motivation

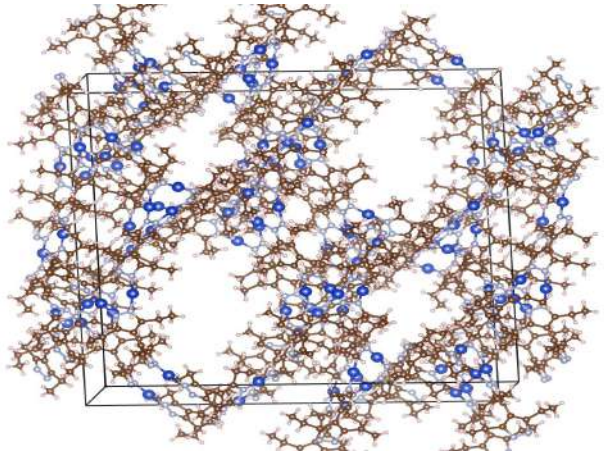


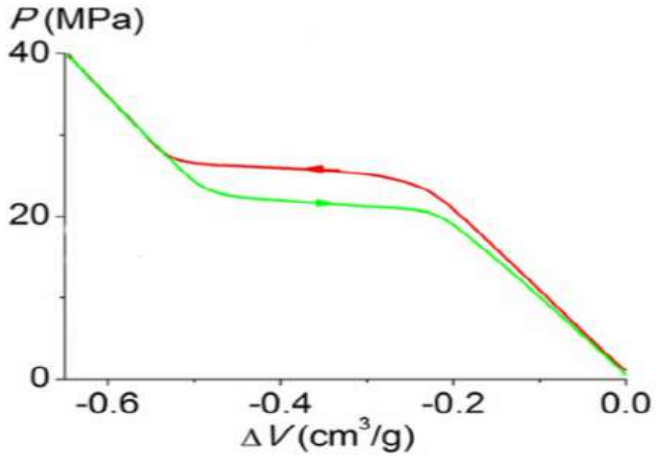

A
B
β
C
1 μm
50 μm
50 μm

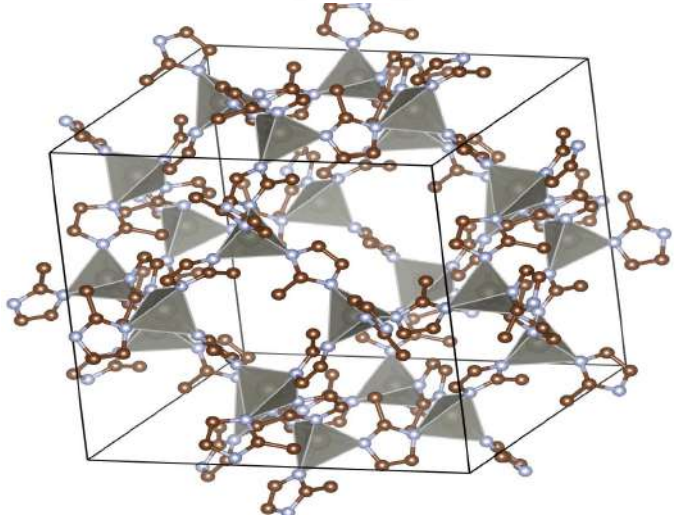

Vapor
Liquid
θ
Solid
θ*w
Wenzel
θ*CB
Cassie-Baxter

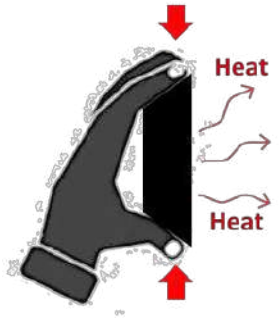
Motivation



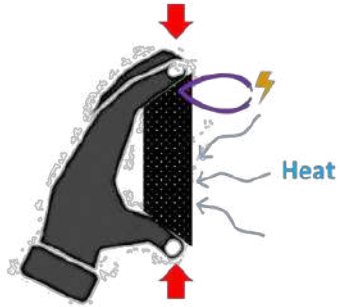






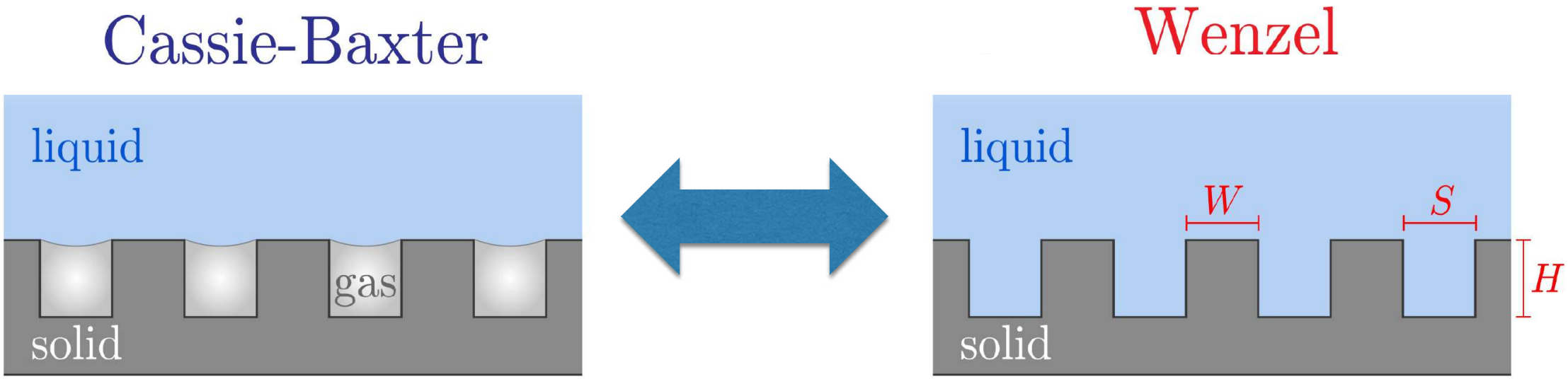


Work → Heat

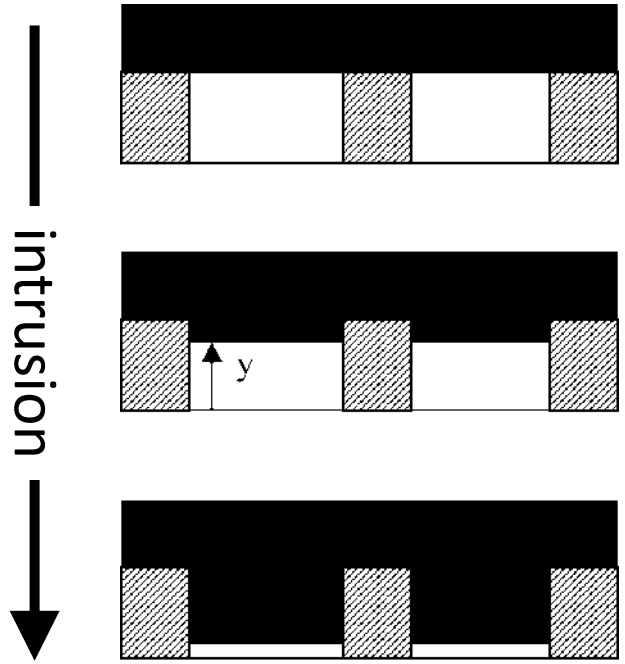


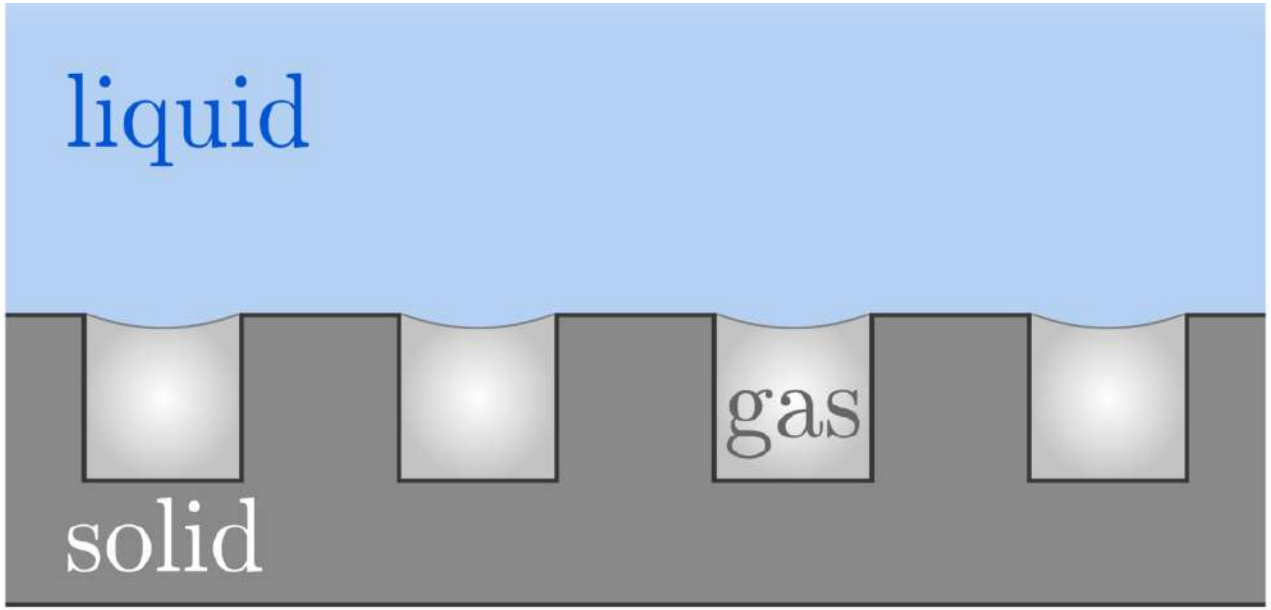
Work
+ → Electricity
ambient Heat

Liquid intrusion/extrusion: a thought experiment



Liquid intrusion/extrusion: a thought experiment





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

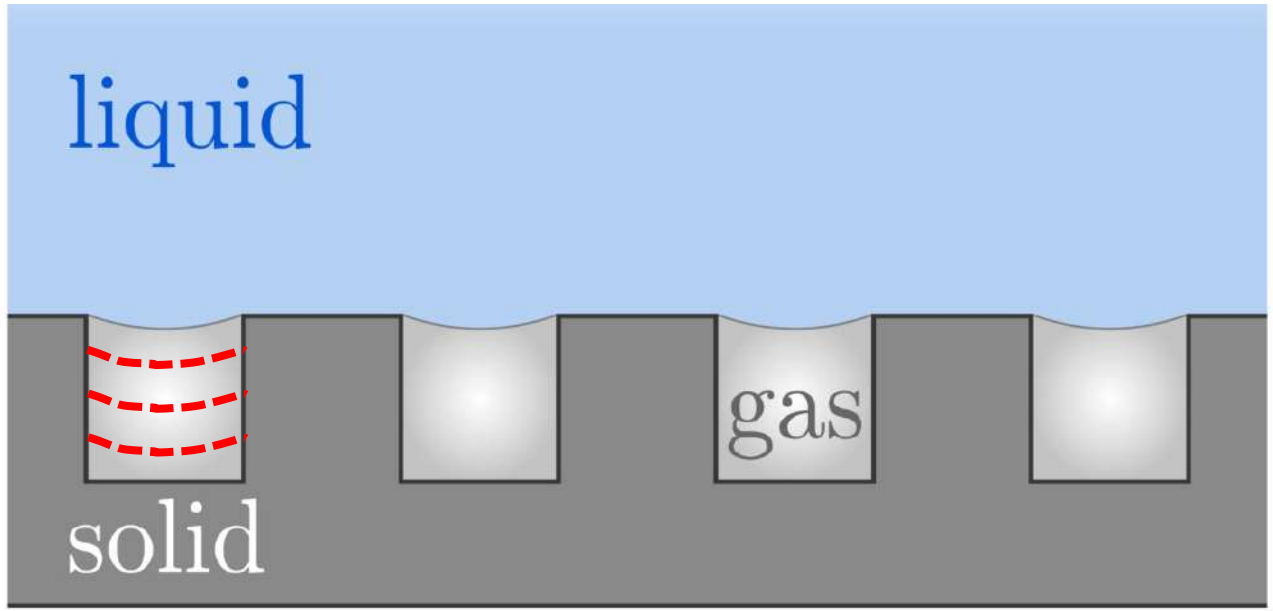
$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right) \qquad \cos(\theta) = \left(\gamma_{sv} - \gamma_{sl} \right) / \gamma_{lv}$$

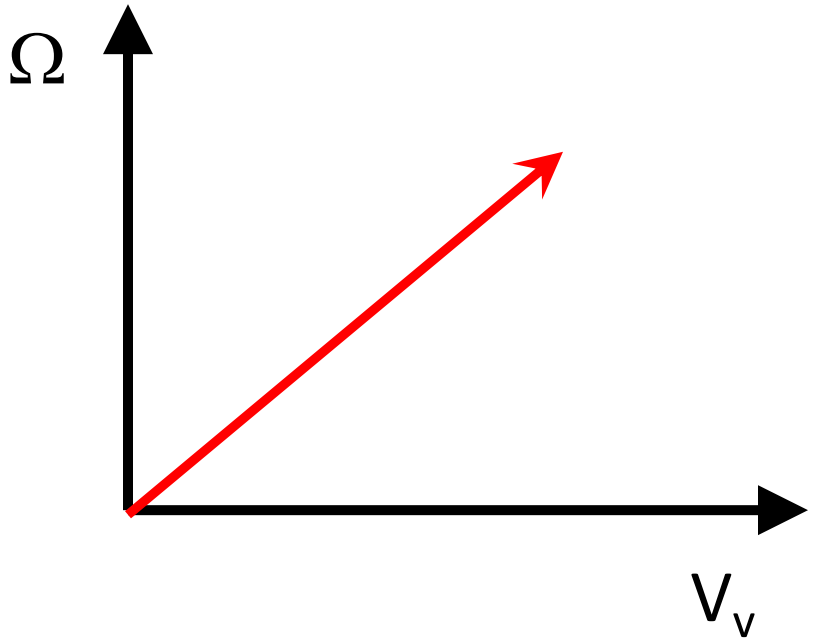
Bulk coexistence conditions

Langmuir, 2004, **20**, 2004

Liquid intrusion/extrusion: a thought experiment

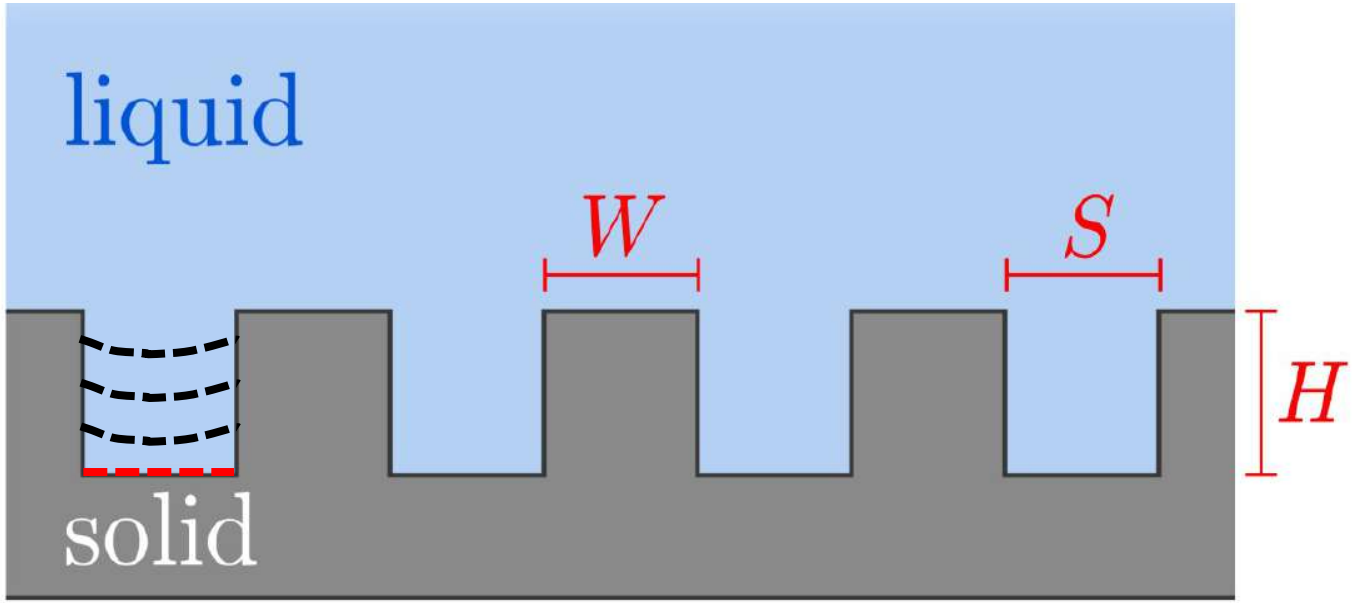
$$\Omega = \cancel{\Delta P} V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

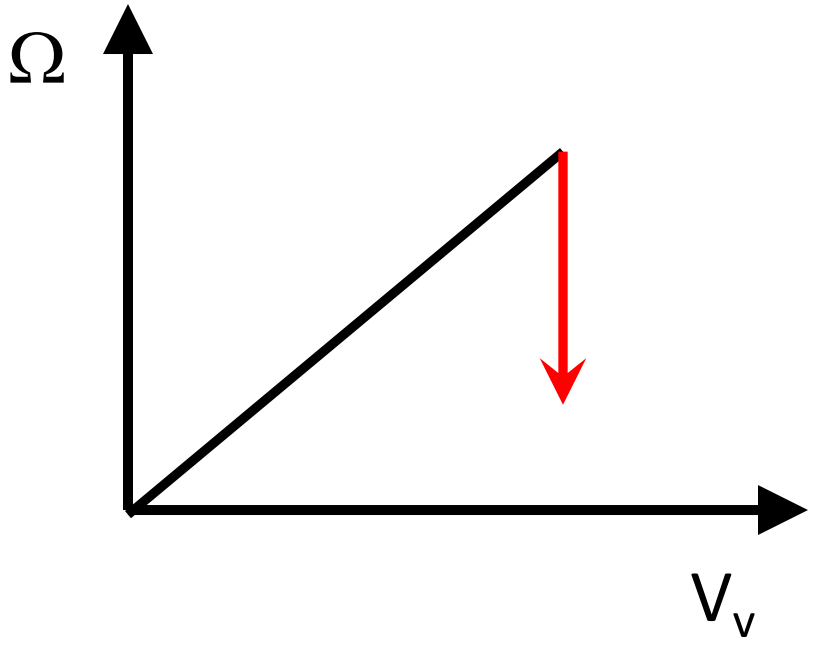




Liquid intrusion/extrusion: a thought experiment

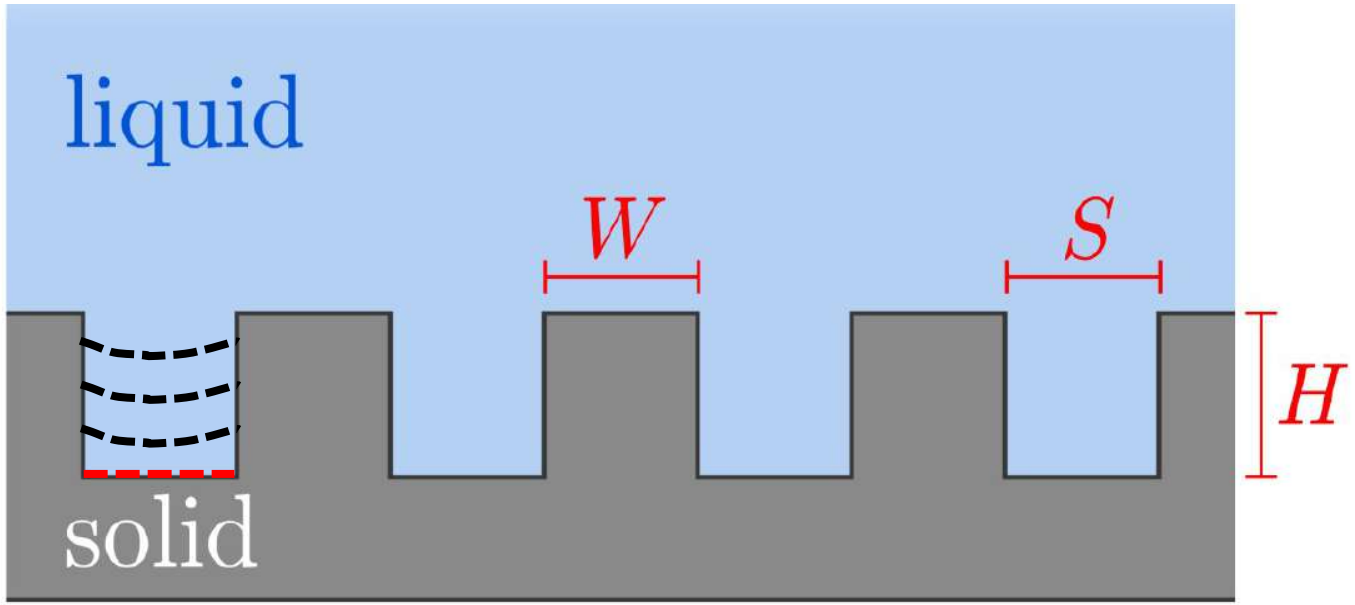
$$\Omega = \Delta P V_v + \gamma A_{lv} + \gamma_{sv} A_{sv} + \gamma_{sl} A_{sl}$$

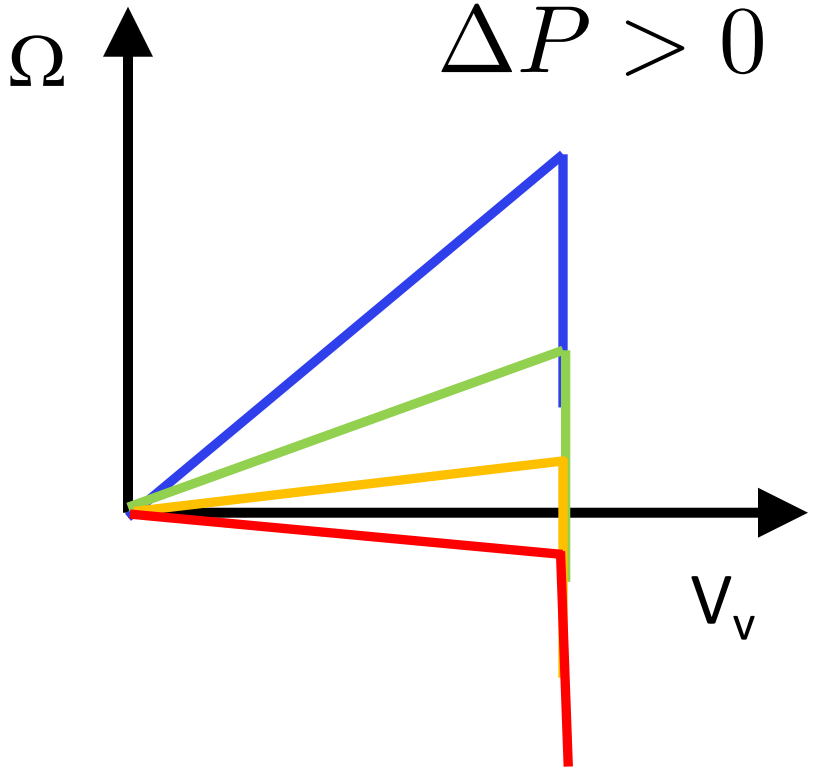




Liquid intrusion/extrusion: a thought experiment

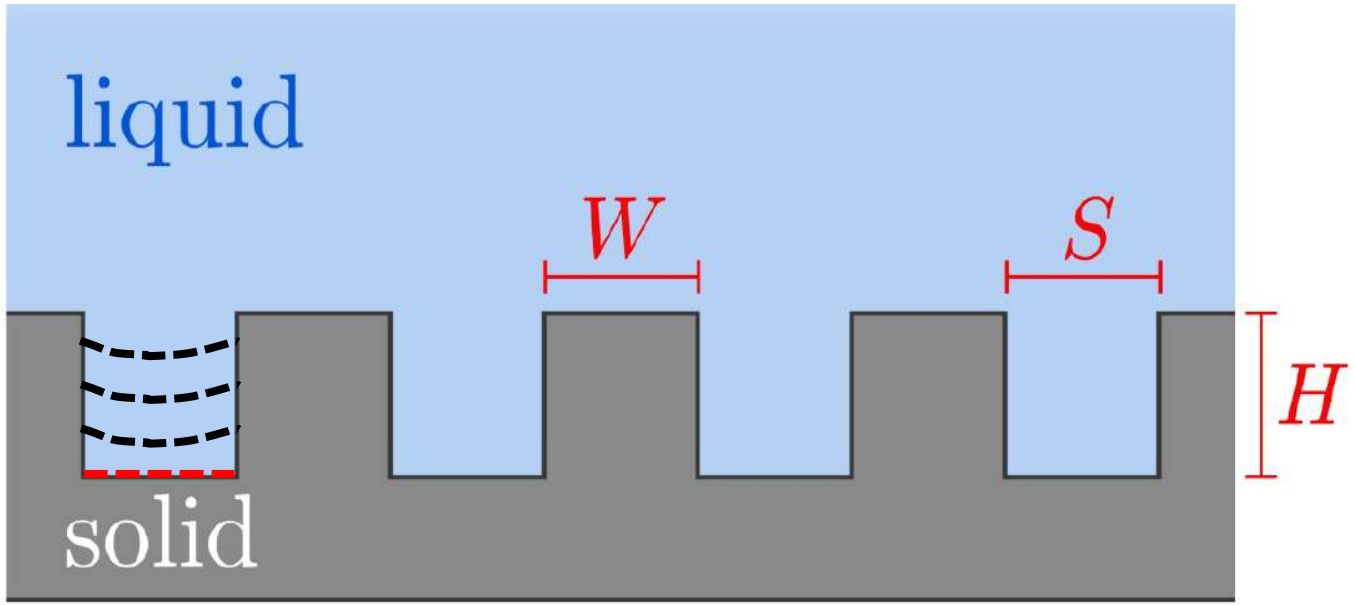
$$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$$

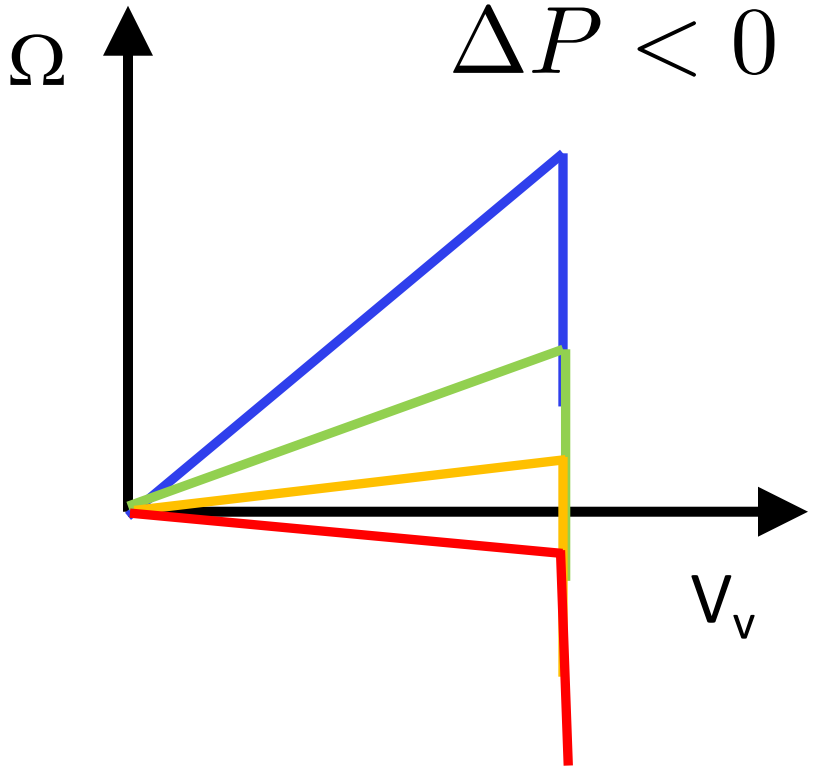




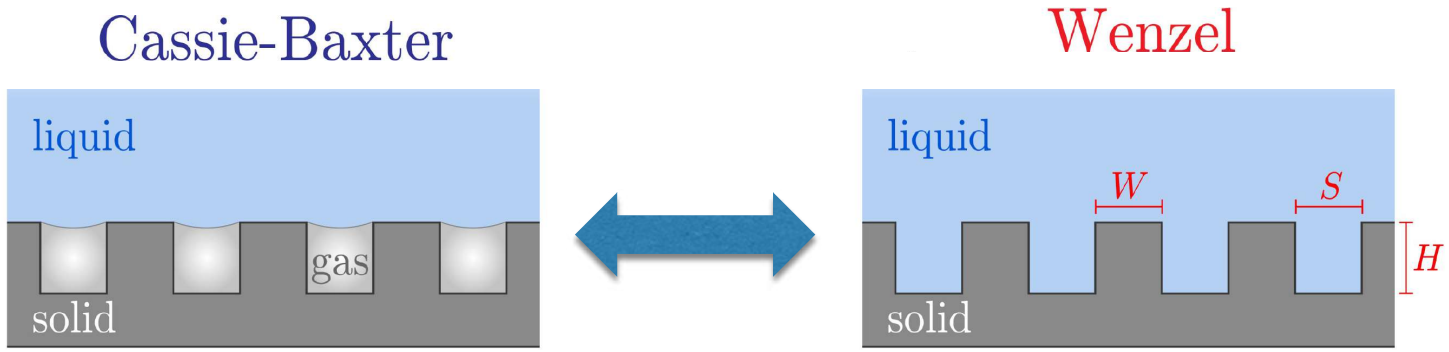
Liquid intrusion/extrusion: a thought experiment

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

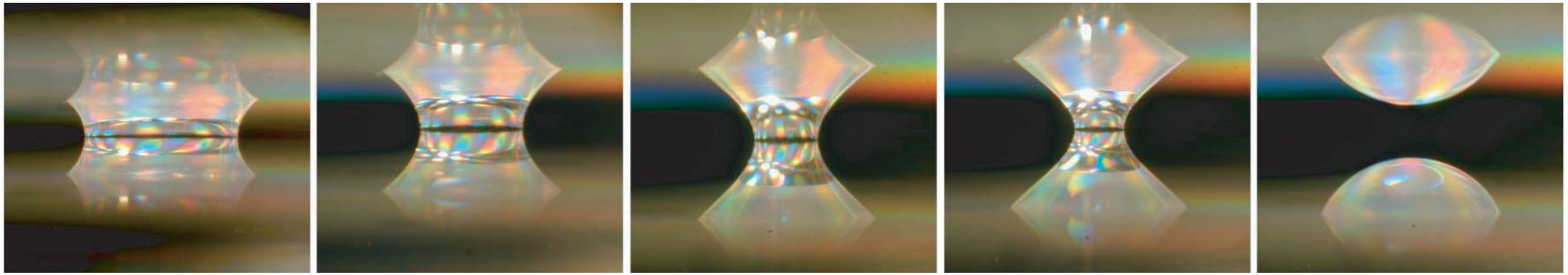




Comparison with experiments



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

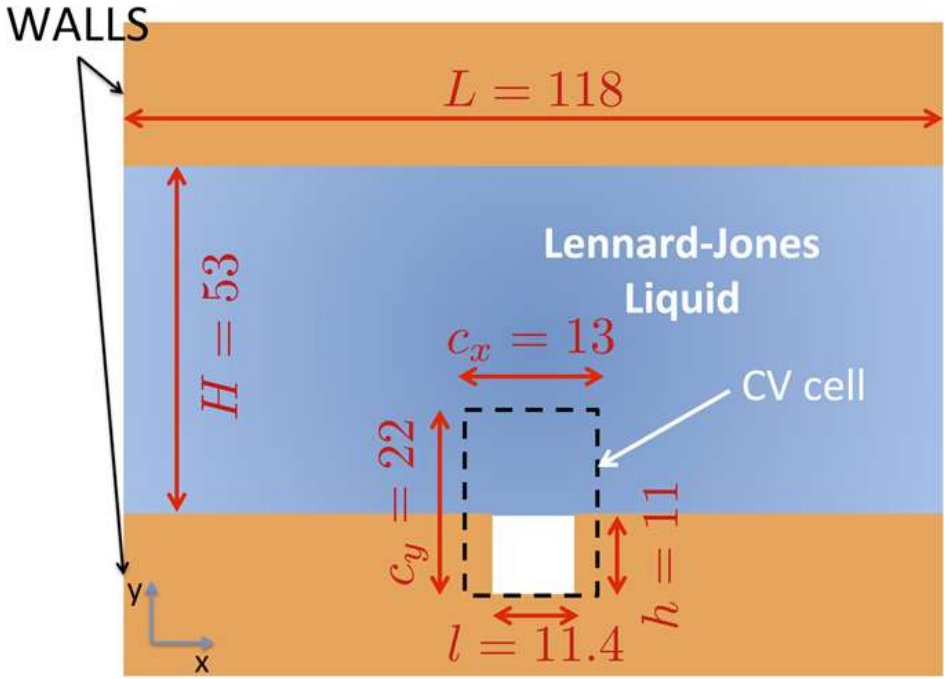


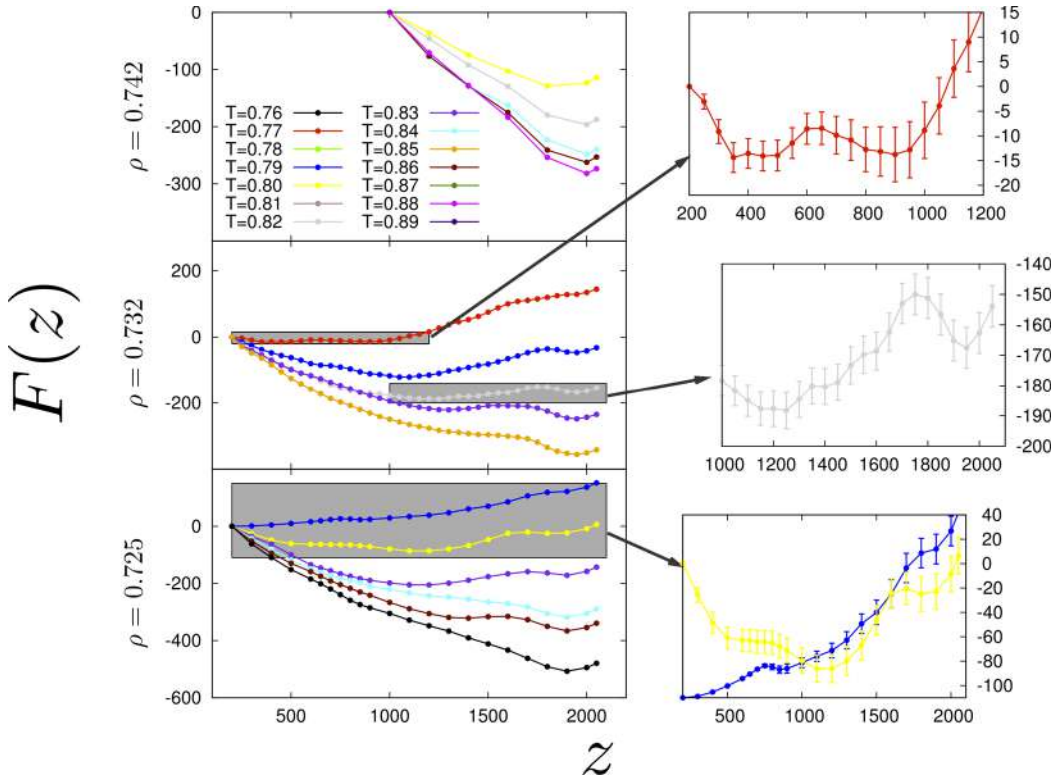
Nat. Mat., 2003, **2**, 457

Atomistic Mechanism

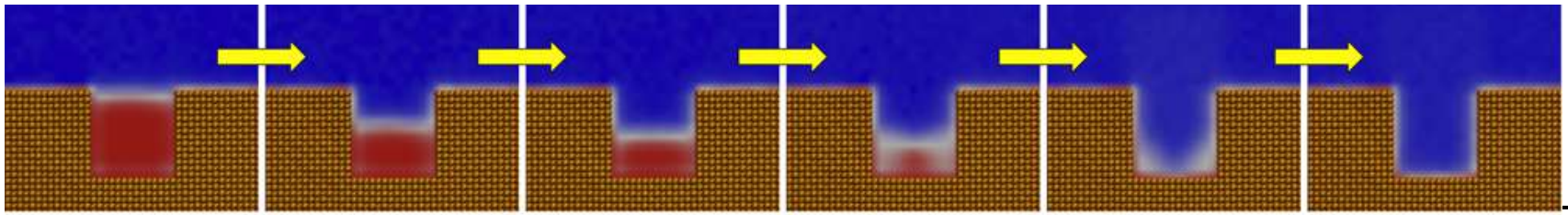
$$P(z) = \frac{\int d\mathbf{r}\ exp[-\beta V(\mathbf{r})]\delta(N(\mathbf{r}) - z)}{\int d\mathbf{r}\ exp[-\beta V(\mathbf{r})]}$$

$$F(z) = -k_B T \log P(z)$$





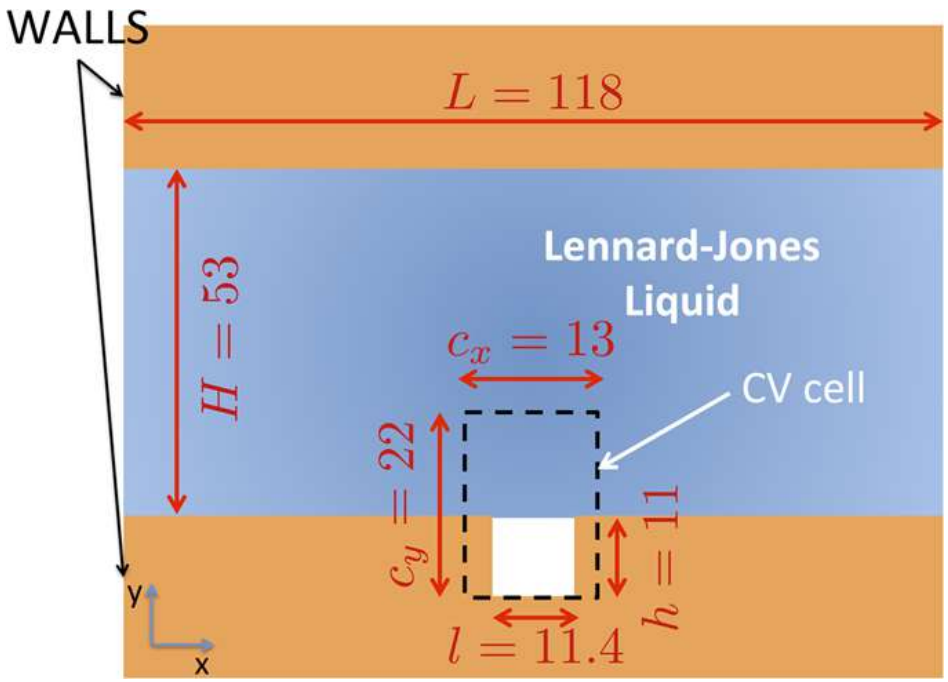
$$\mu(\mathbf{r}; z) = \frac{exp[-\beta V(\mathbf{r})]\delta(N(\mathbf{r}) - Z)}{\int d\mathbf{r}\ exp[-\beta V(\mathbf{r})]\delta(N(d\mathbf{r}) - z)}$$



$z = 1200$ $z = 1500$ $z = 1600$ $z = 1700$ $z = 1800$ $z = 1900$

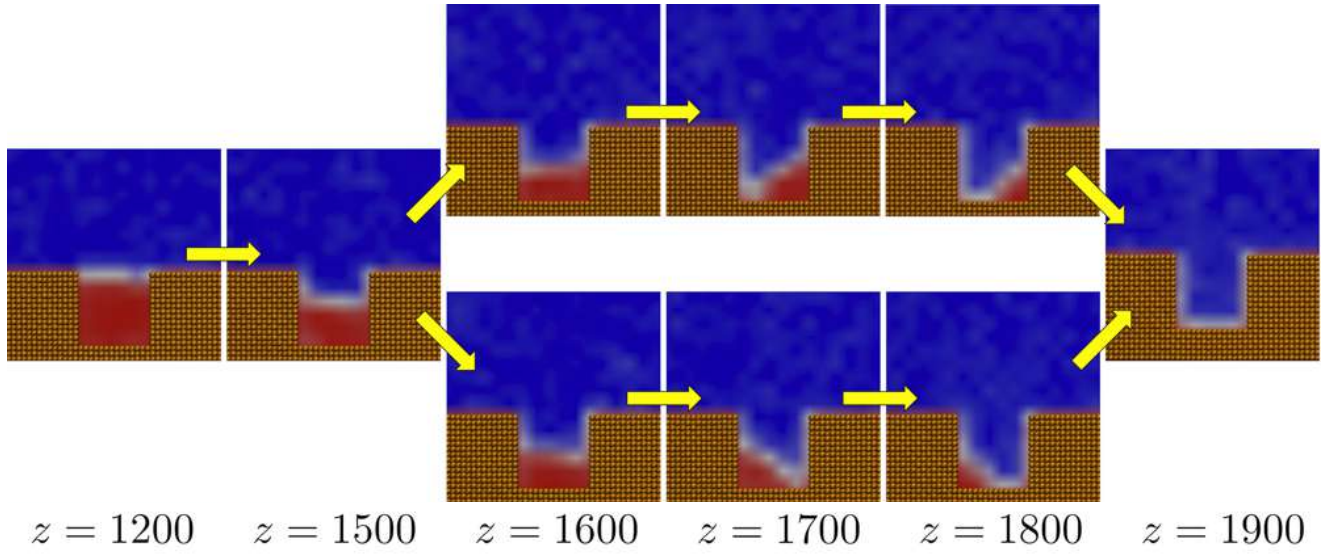
Langmuir 2012, **28**, 10764
Chem. Phys. Lett. 2006, **426**, 168

Atomistic Mechanism



$$\mu(\mathbf{r}; z) = \frac{exp[-\beta V(\mathbf{r})]\delta(N(\mathbf{r}) - Z)}{\int d\mathbf{r}\ exp[-\beta V(\mathbf{r})]\delta(N(d\mathbf{r}) - z)}$$

\+ cluster analysis



Langmuir 2012, **28**, 10764

Continuum analysis

CNT

$$I(\Sigma; V_l) = \Omega(\Sigma; V_l) - \lambda(V_l - Z)$$

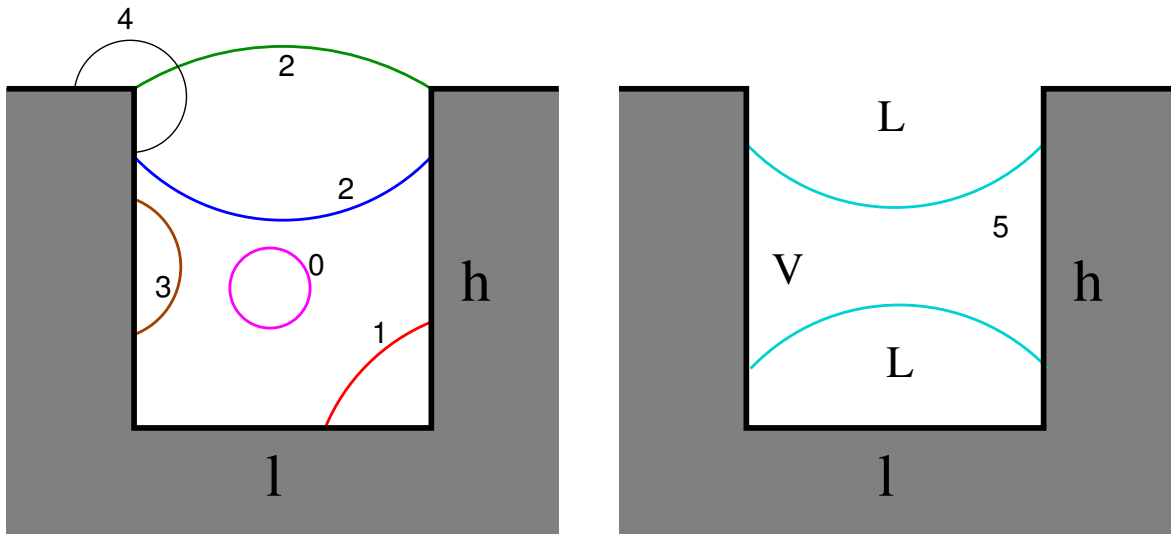
$$\delta I(\Sigma; V_l) = 0$$

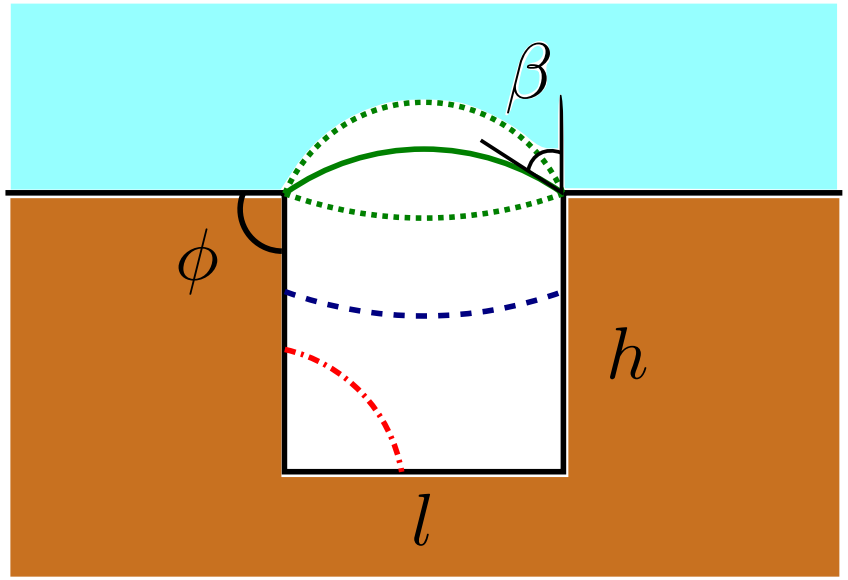
Generalized Laplace

$$p_l - p_v + \lambda = J\gamma_{lv}$$

Young

$$\cos\theta = (\gamma_{sg} - \gamma_{sl})/\gamma_{lg}$$

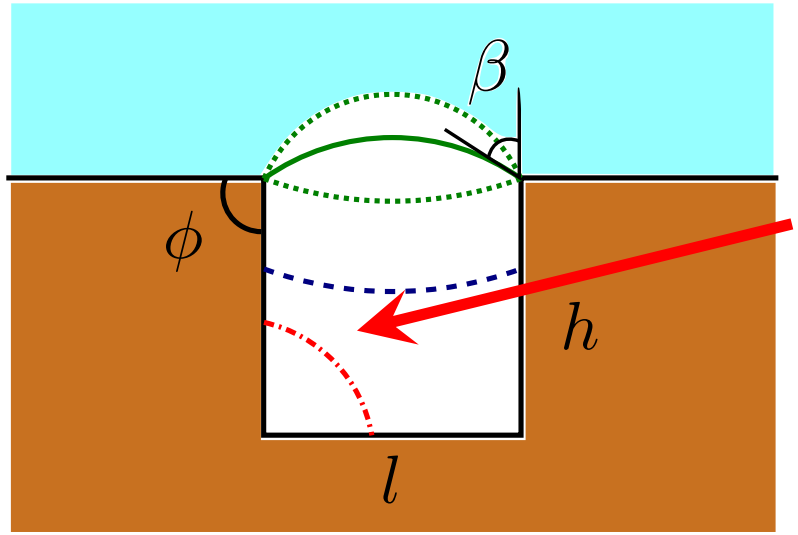




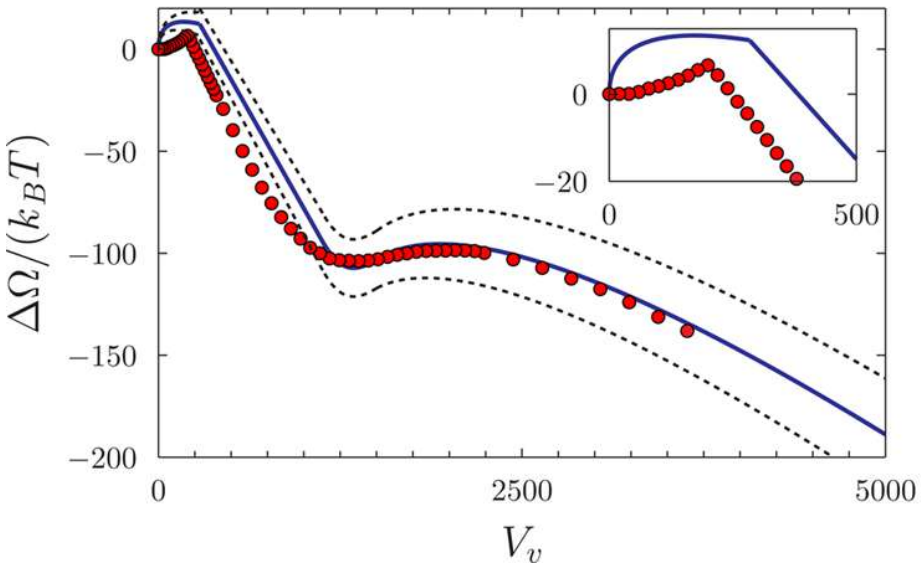
Constant curvature morphologies

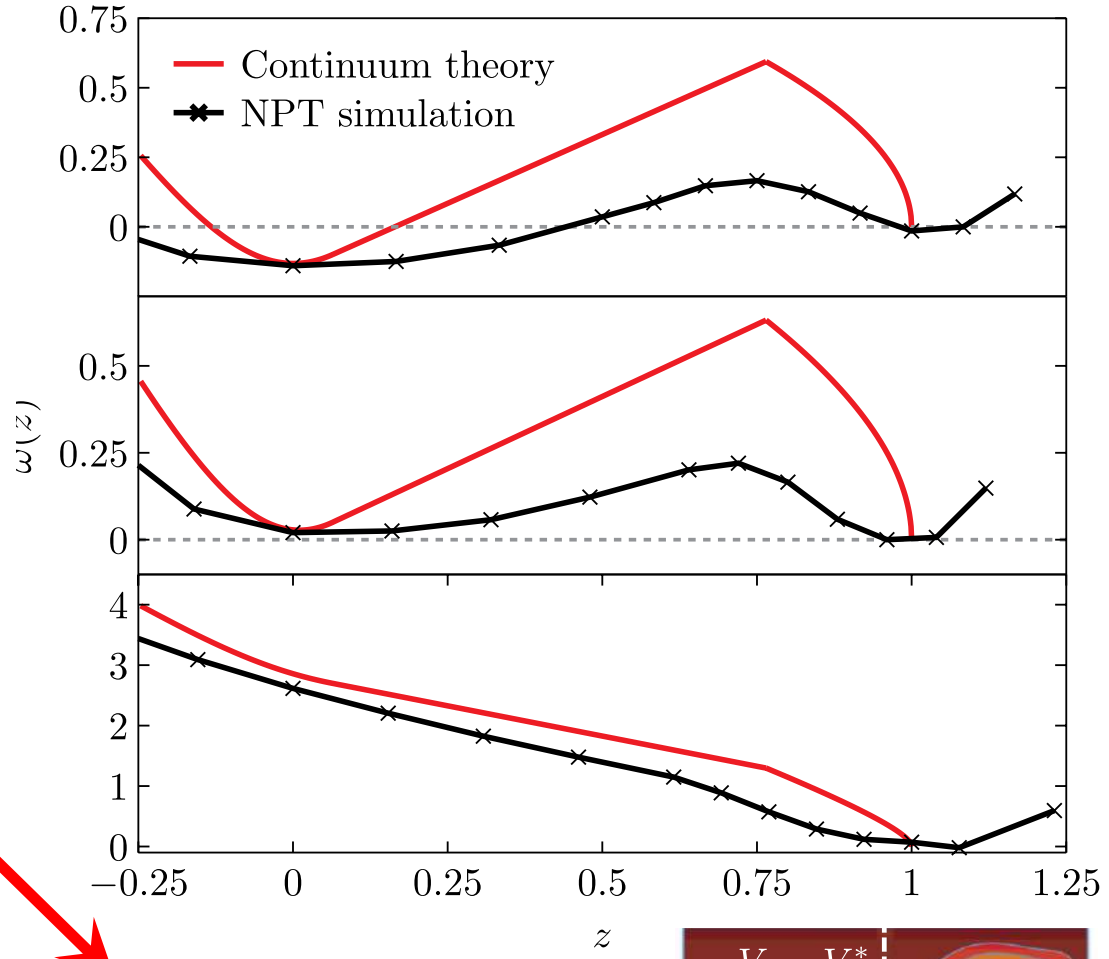
PRL 2012, **109**, 226102

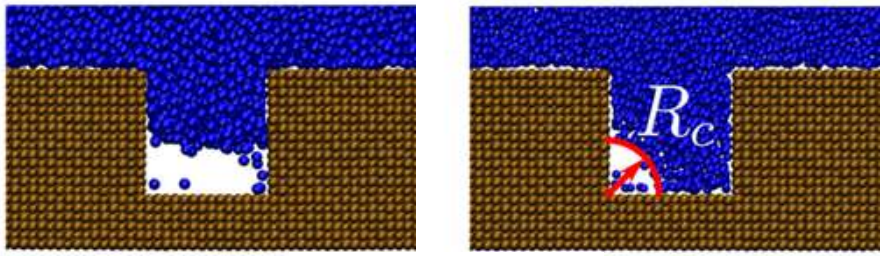
Continuum vs atomistic analysis



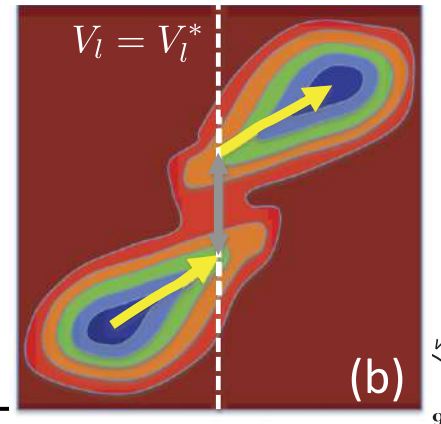
Change of morphology of Σ







Intrusion



Langmuir 2013, **29**, 14873

Suitable descriptors of intrusion

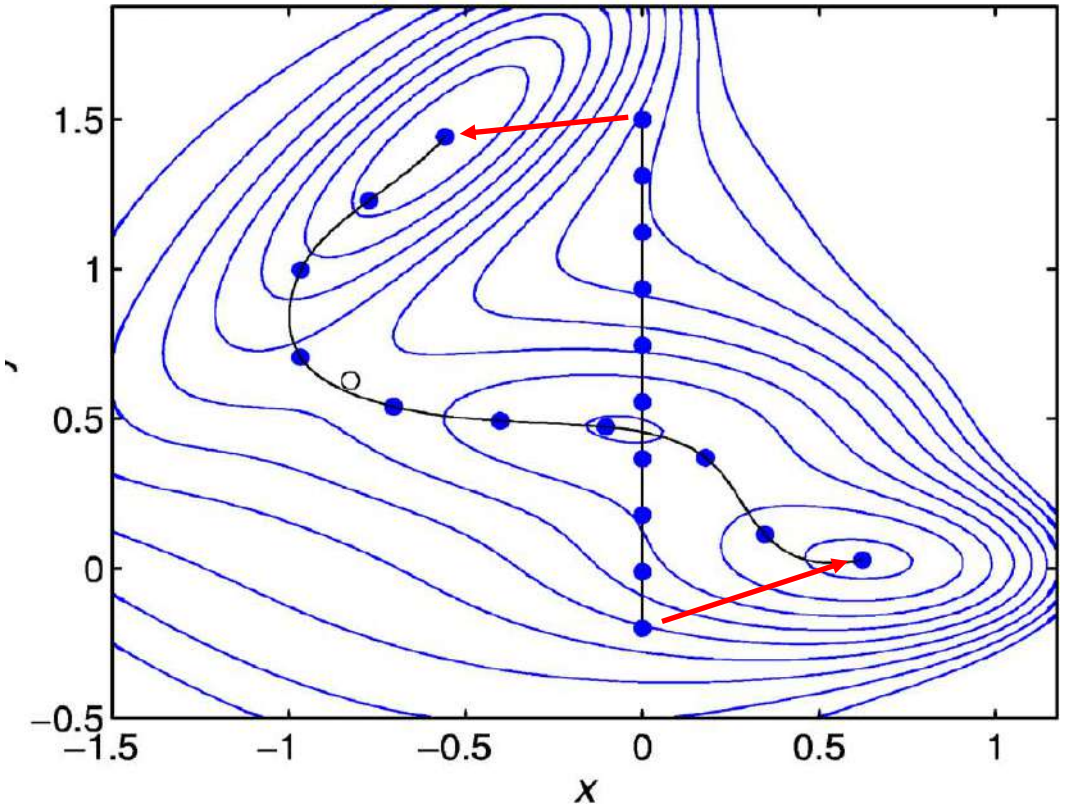
$$\left[g(\alpha) \nabla_{\boldsymbol{z}} \Omega(\alpha) \right]_{\perp} = 0$$

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

$$+ \left[\gamma_{sl} - (\gamma_{lv} + \gamma_{sv}) \right] A_{sl}^{bottom}$$

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

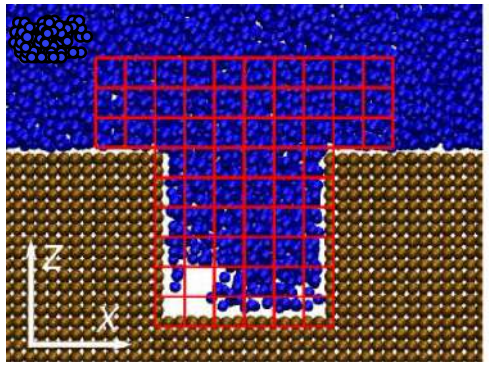
$$- \gamma_{lv} \left(1 + \cos(\theta) \right) \int dx \, f(h(x)/\delta)$$

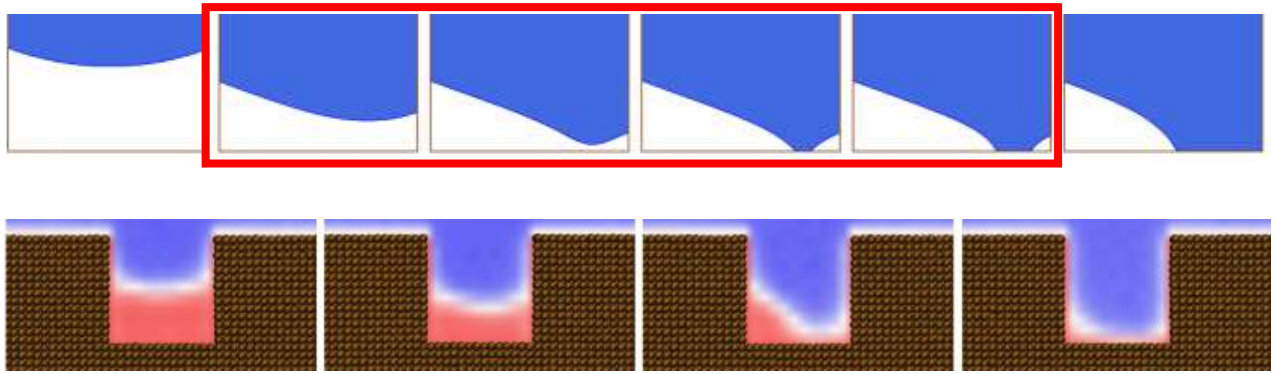


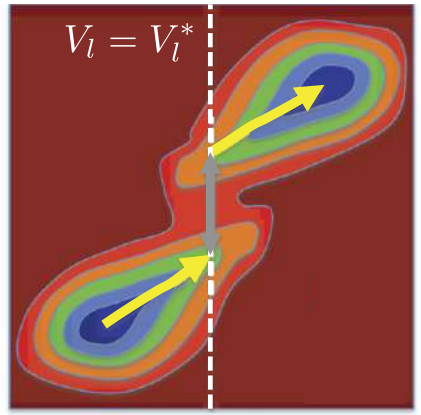
Switching function
of characteristic length δ

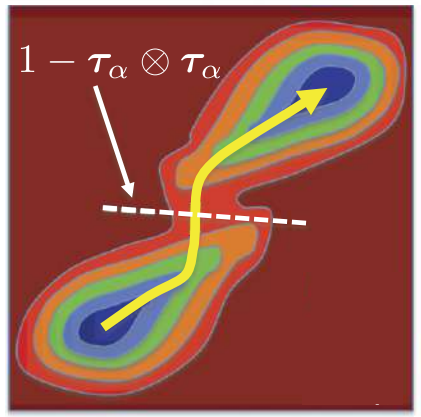
J. Chem. Phys. 2006, **125**, 024106; J. Chem. Phys. 2015, **142**, 104701;

Suitable descriptors of intrusion

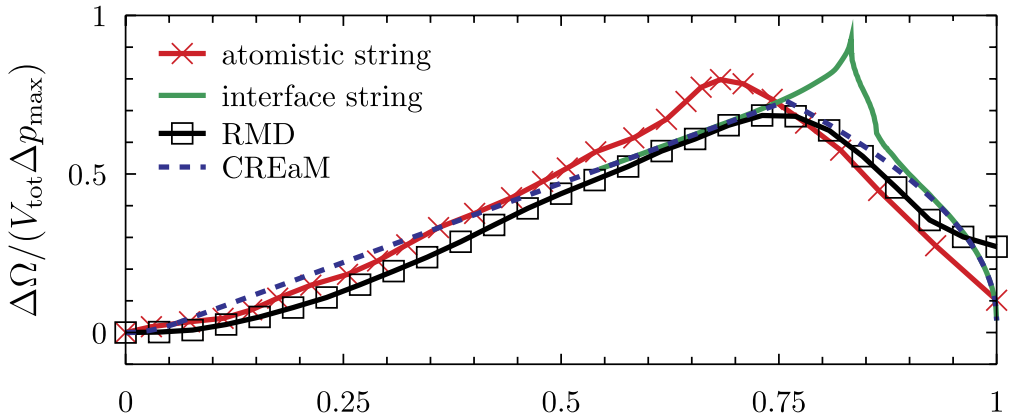


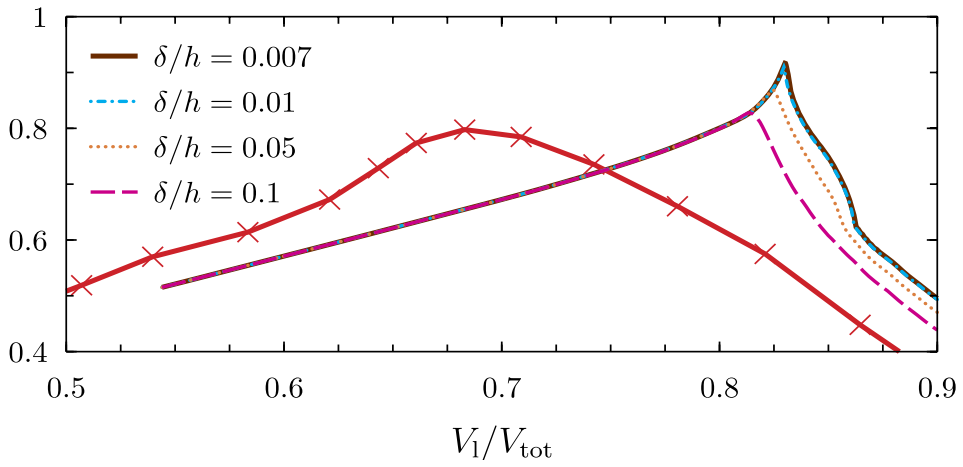


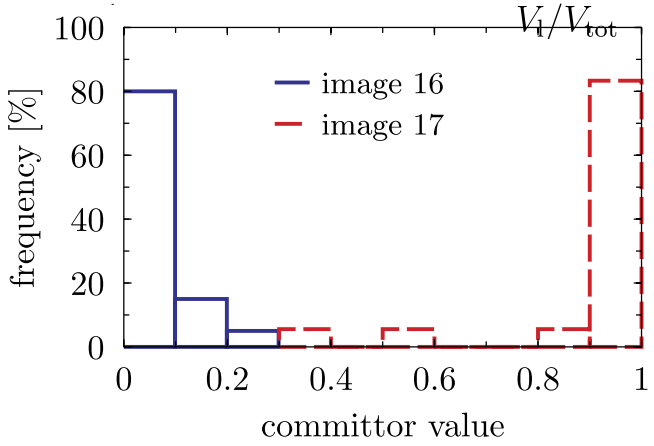




V_l

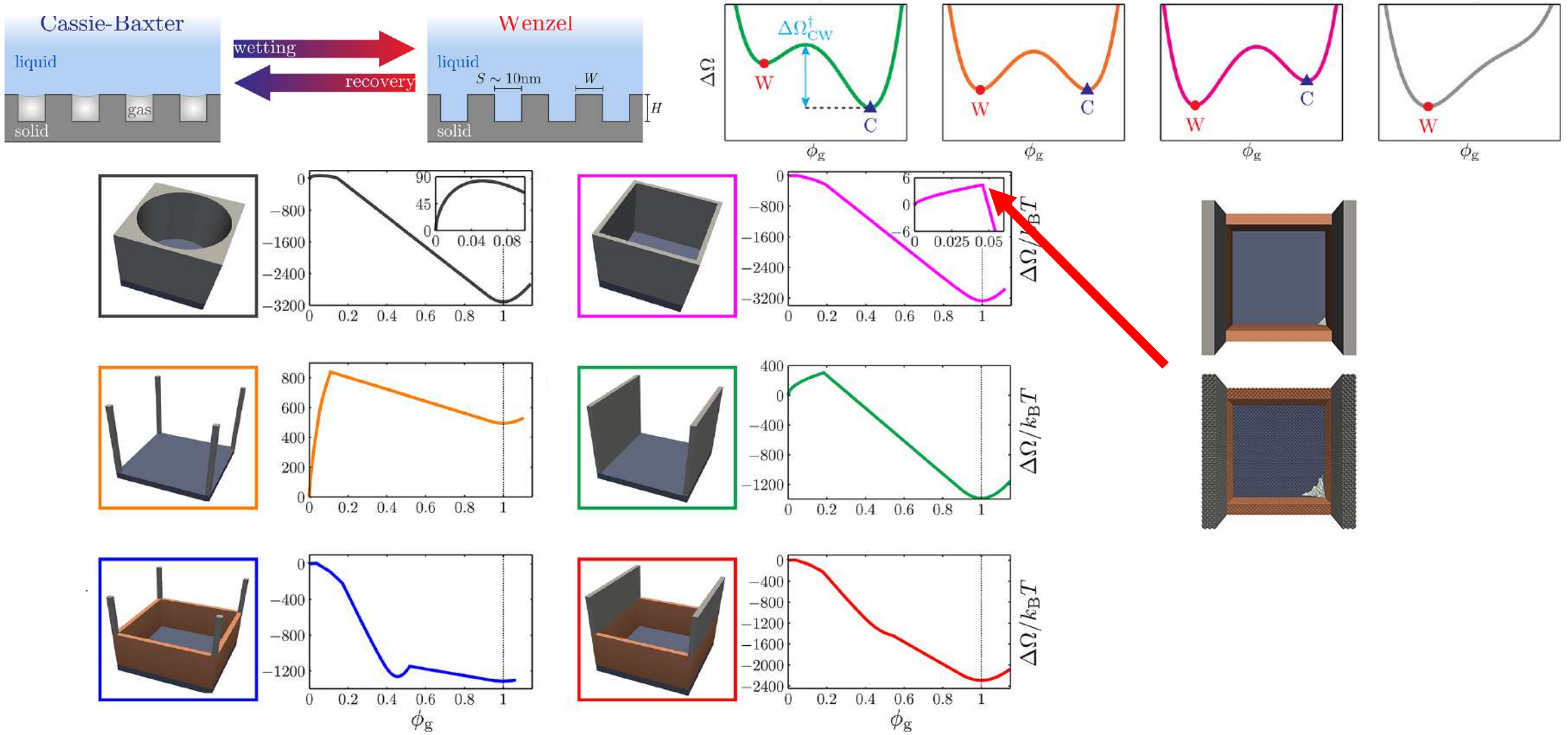






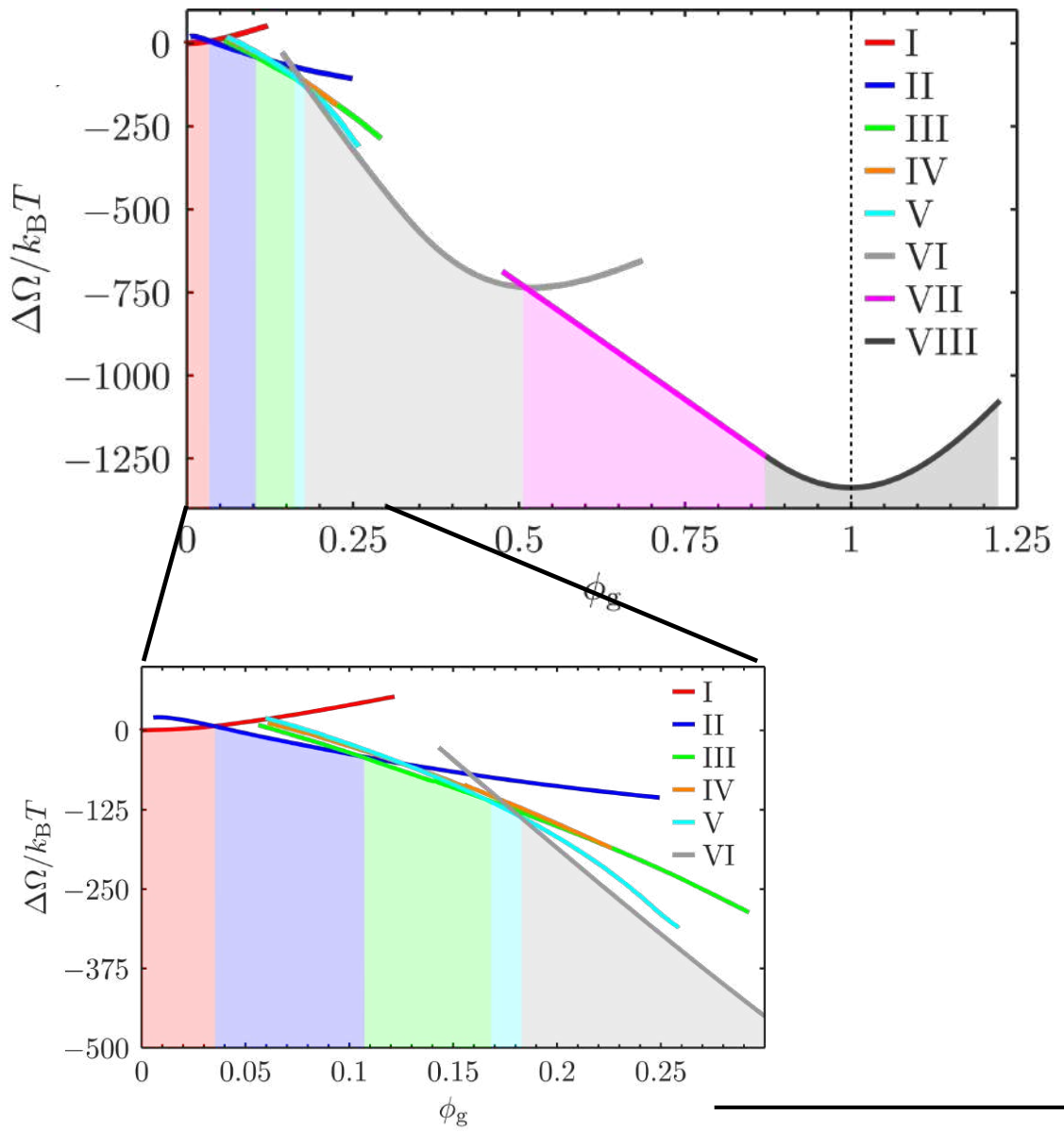
J. Chem. Phys. 2015, **142**, 104701; PNAS 2007, **104**, 14559

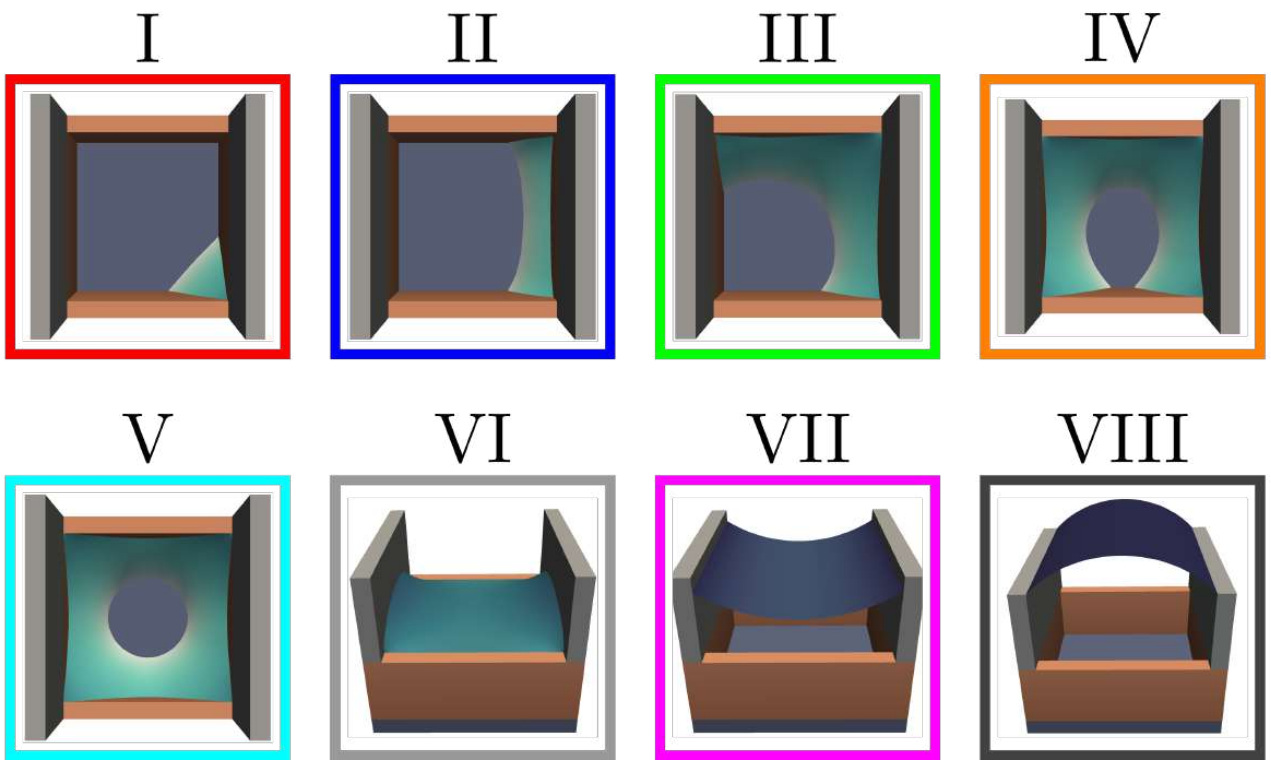
Experiments and applications



ACS Nano 2018, **12**, 359

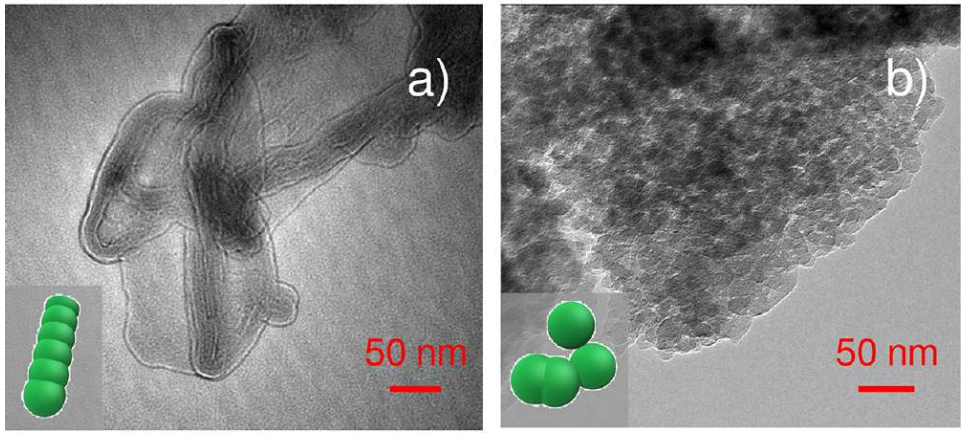
Experiments and applications

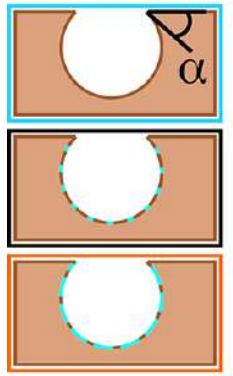


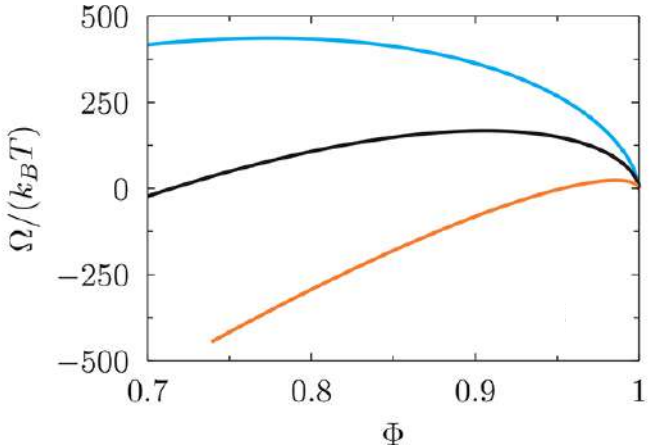


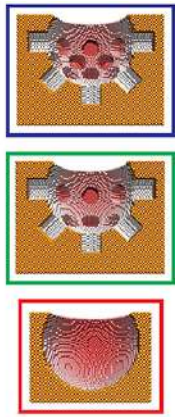
ACS Nano 2018, **12**, 359

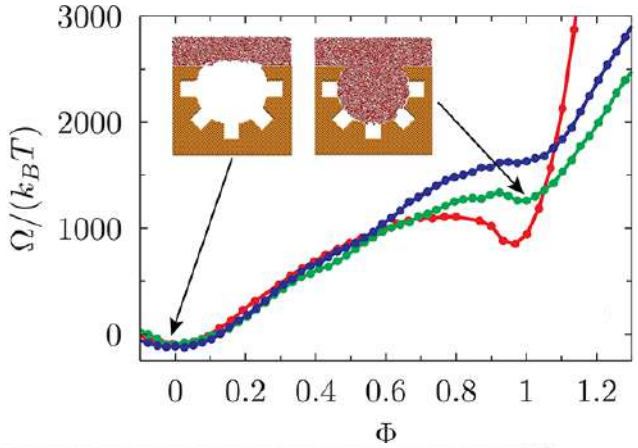
Experiments and applications

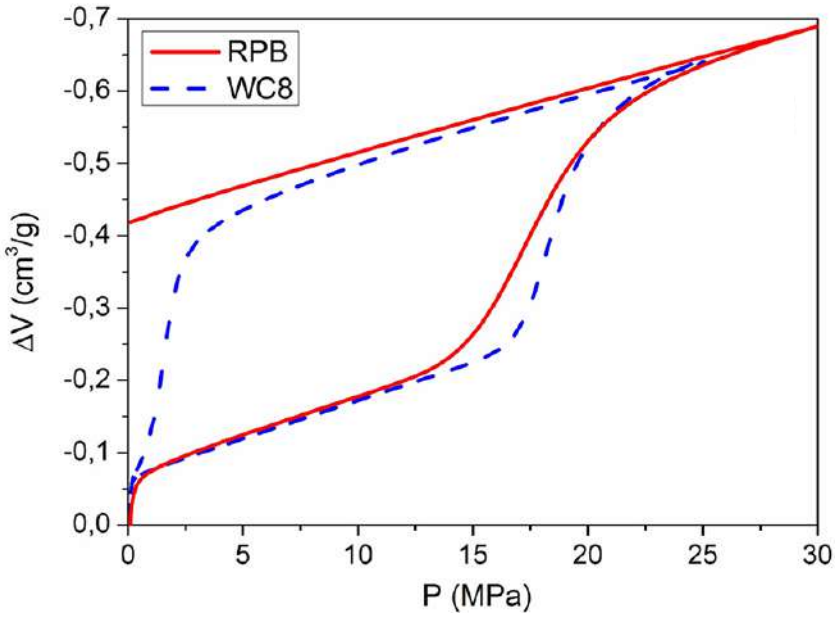


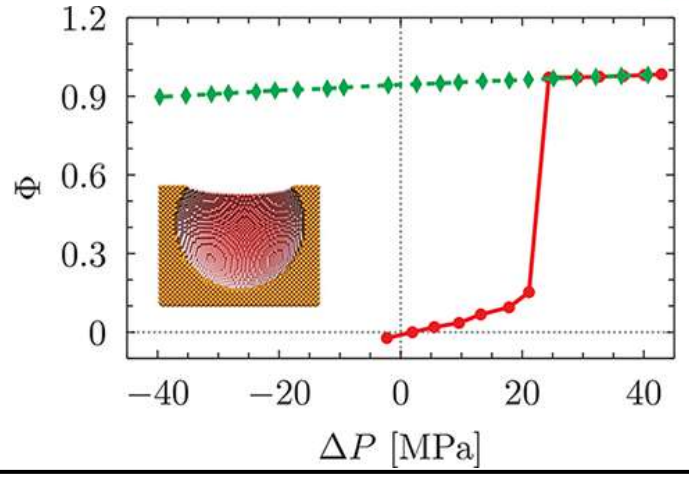


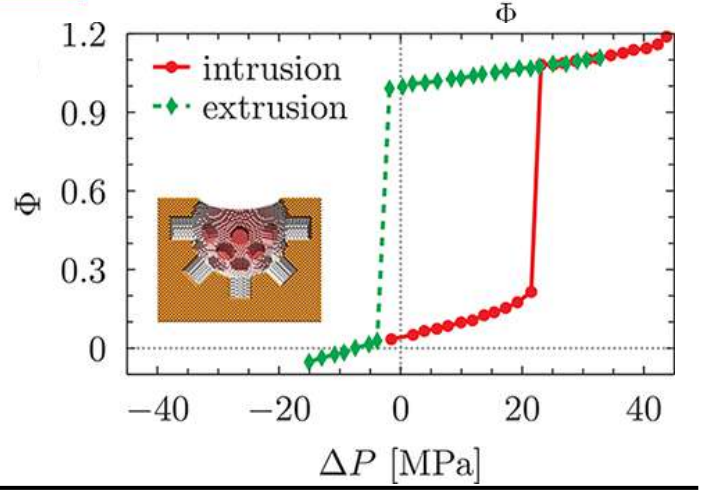








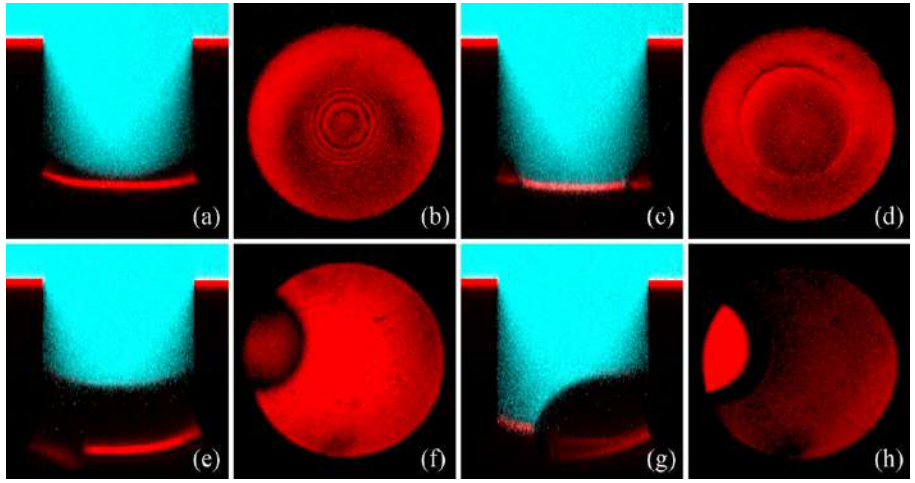


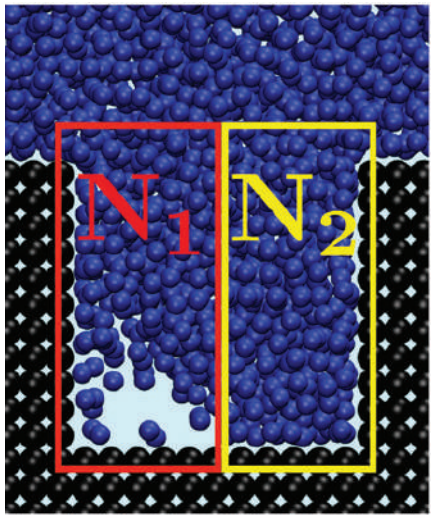


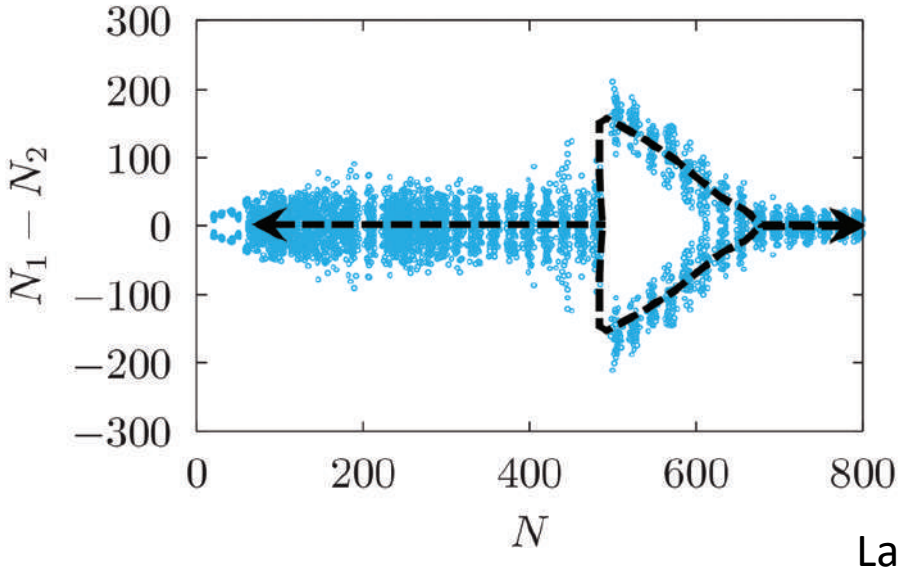
ACS Nano 2019, **13**, 1728

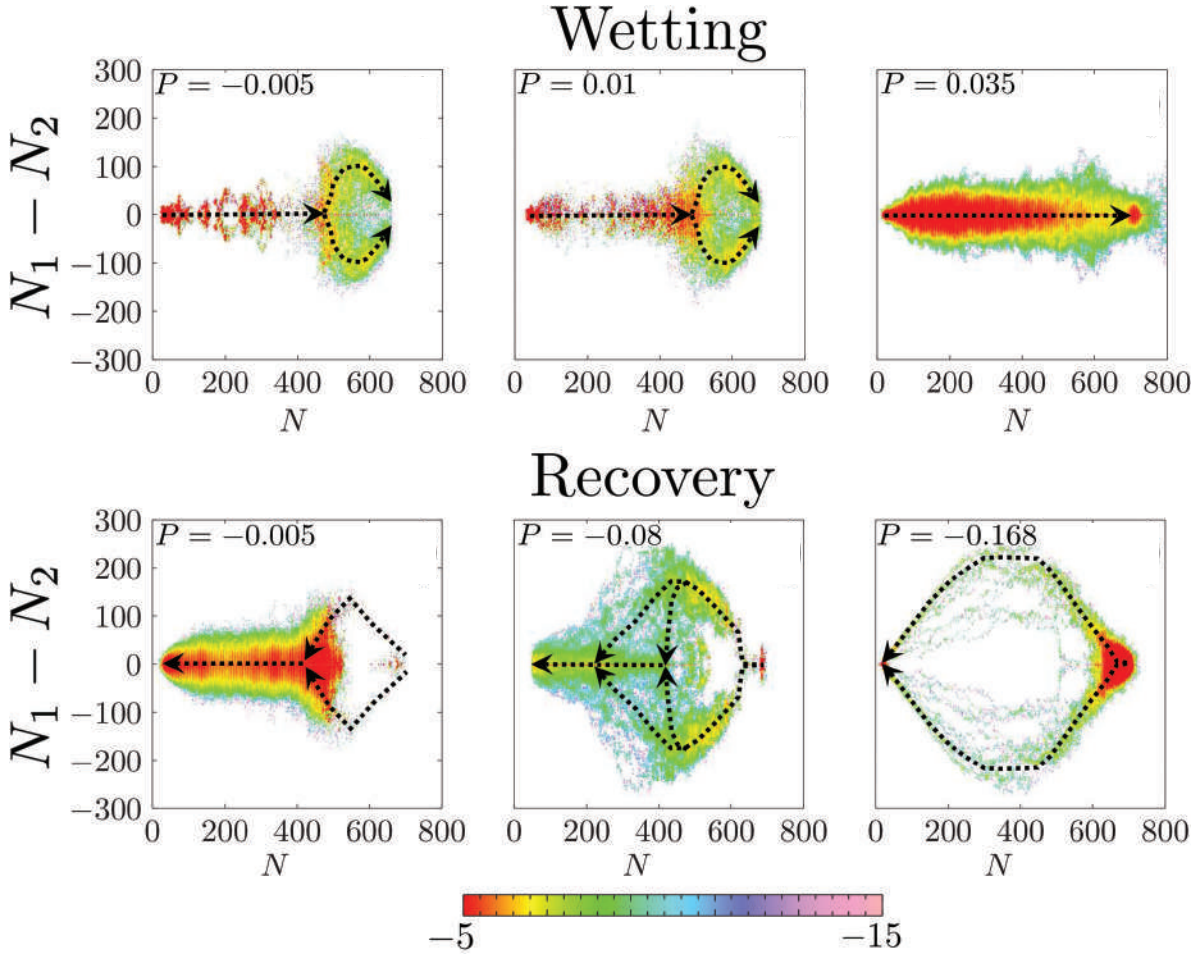
Comparison with experiments

Intrusion





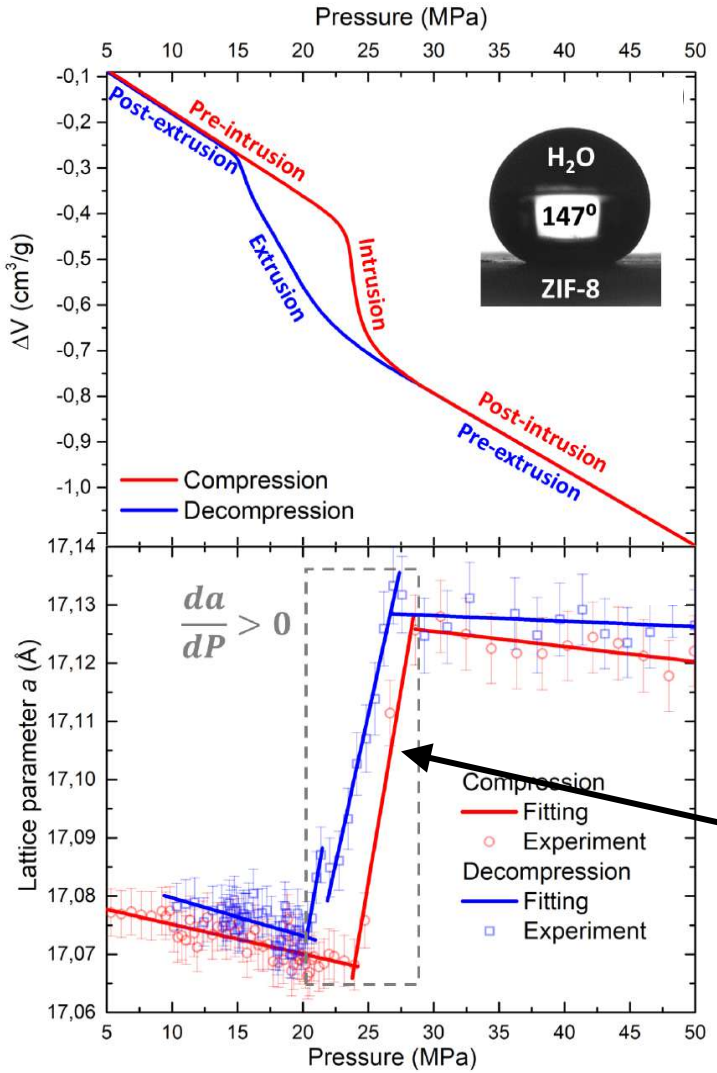


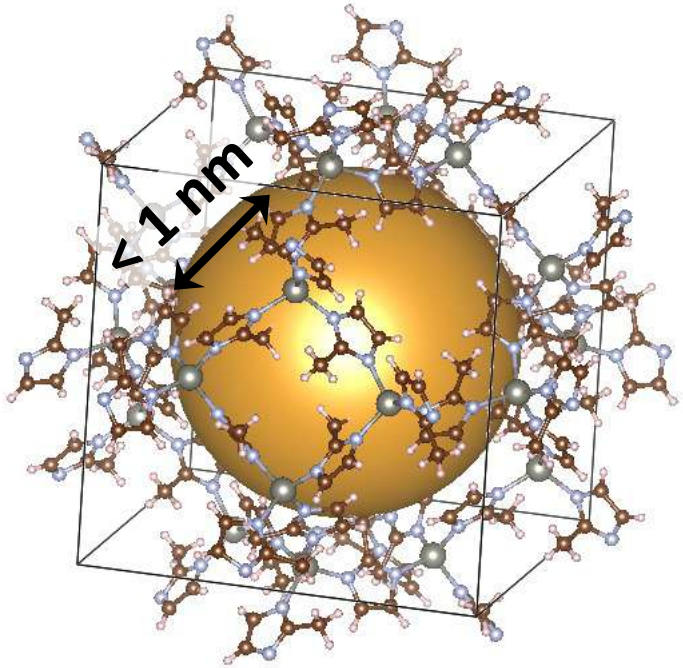


Langmuir 2015, **31**, 1248, Nanoscale 2019, **11**, 21458

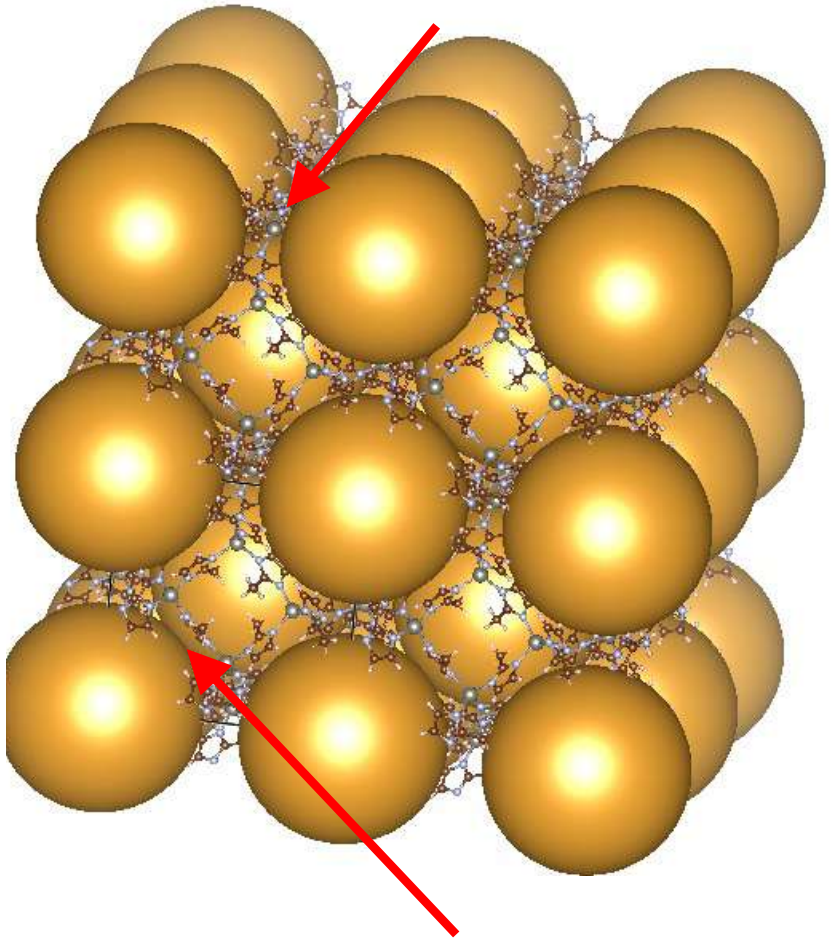
Future challenges: crystalline porous materials

Low P_{int}



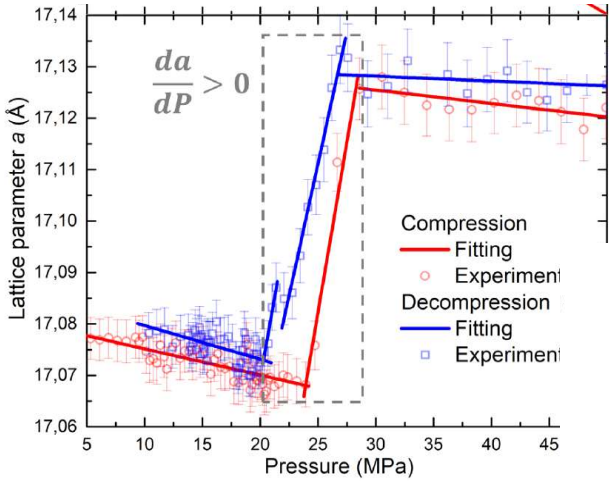


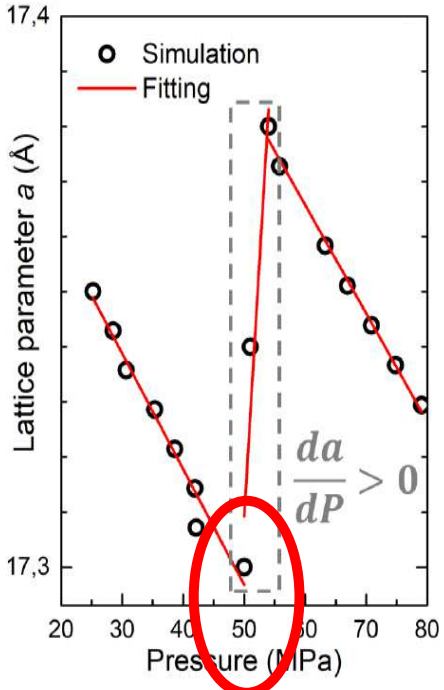
Exceptional Negative Compressibility

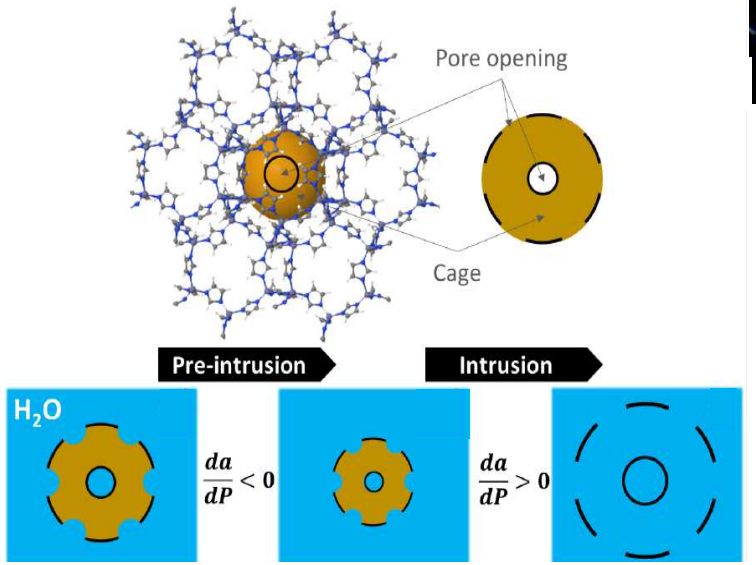


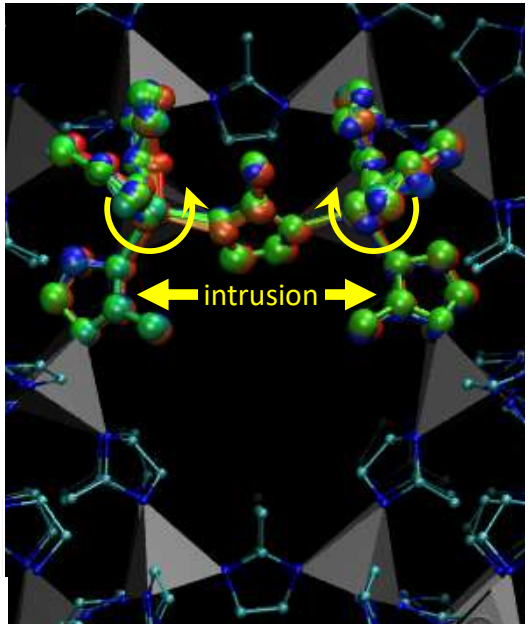
Manuscript submitted

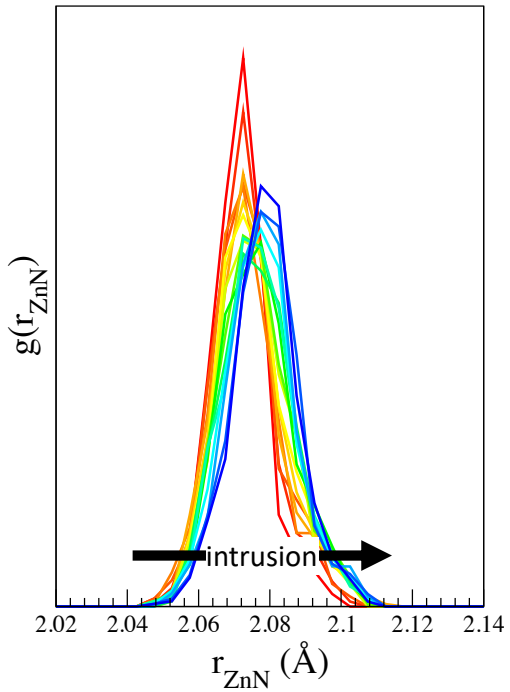
Future challenges: crystalline porous materials

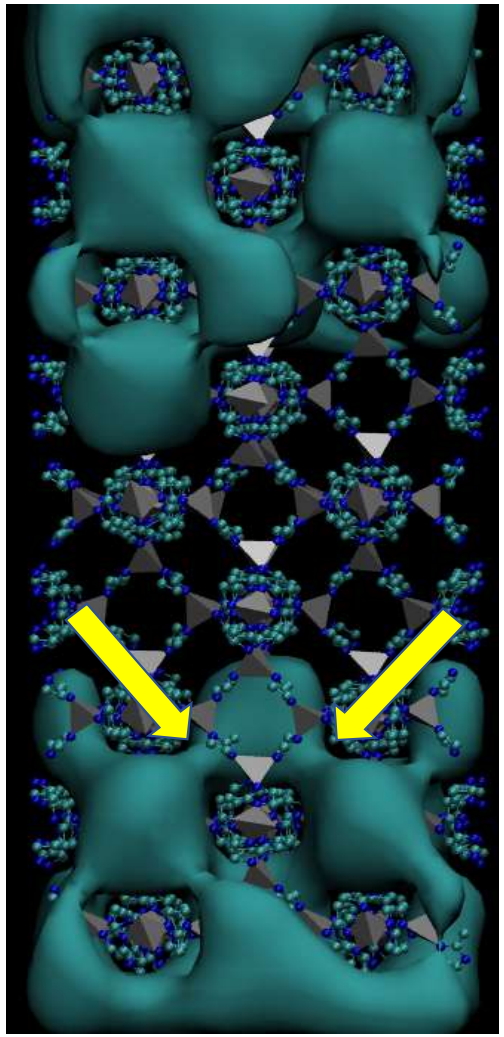












Conclusions

- Intruision of liquids in textured and porous materials is non trivial
- Continuum models are adequate at predicting the general features of the process in relatively simple system
  - Semi-quantitative conclusions can be drawn from continuum modeling
- Dynamics/inertia effects must be included
- Crystalline porous materials increase the level of complexity
  - Flexibility
  - Multiple levels of metastabilities
  - Hierarchy of cavities
  - …

Acknowledgements

Matteo Amabili

Emanuele Lisi

Chiara Marchio

Marco Tortora

Yaroslav Grosu

Mauro Chinappi

Marcus Müller

Alberto Giacomello

Antonio Tinti

Carlo Massimo Casciola

FP7-ERC BIC

H2020-FET Electro-Intrusion

European Union's Horizon 2020 research and innovation programme. grant agreement No 101017858