The Salvinia Paradox: how hydrophilic patches help keeping its surface dry

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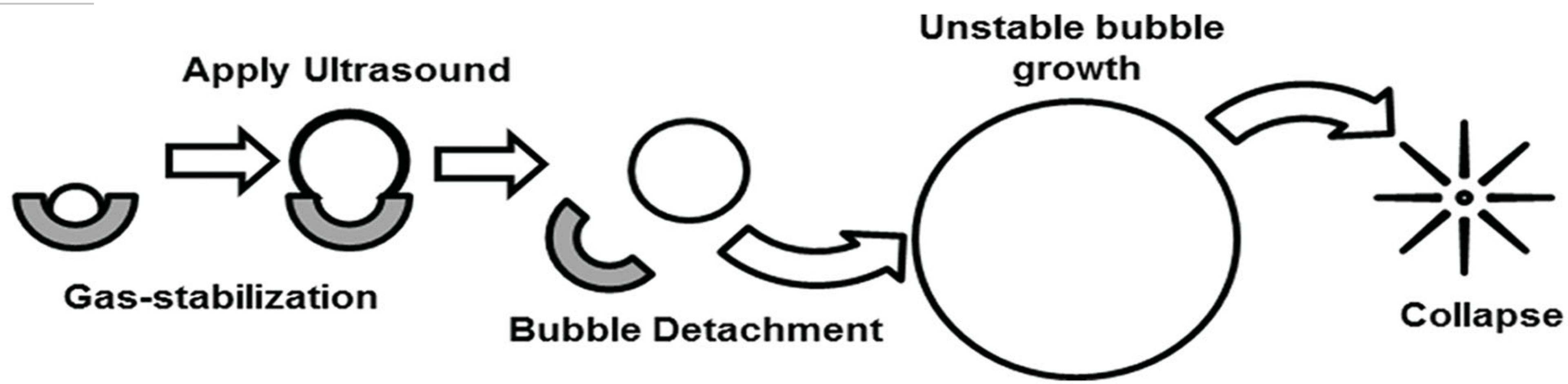
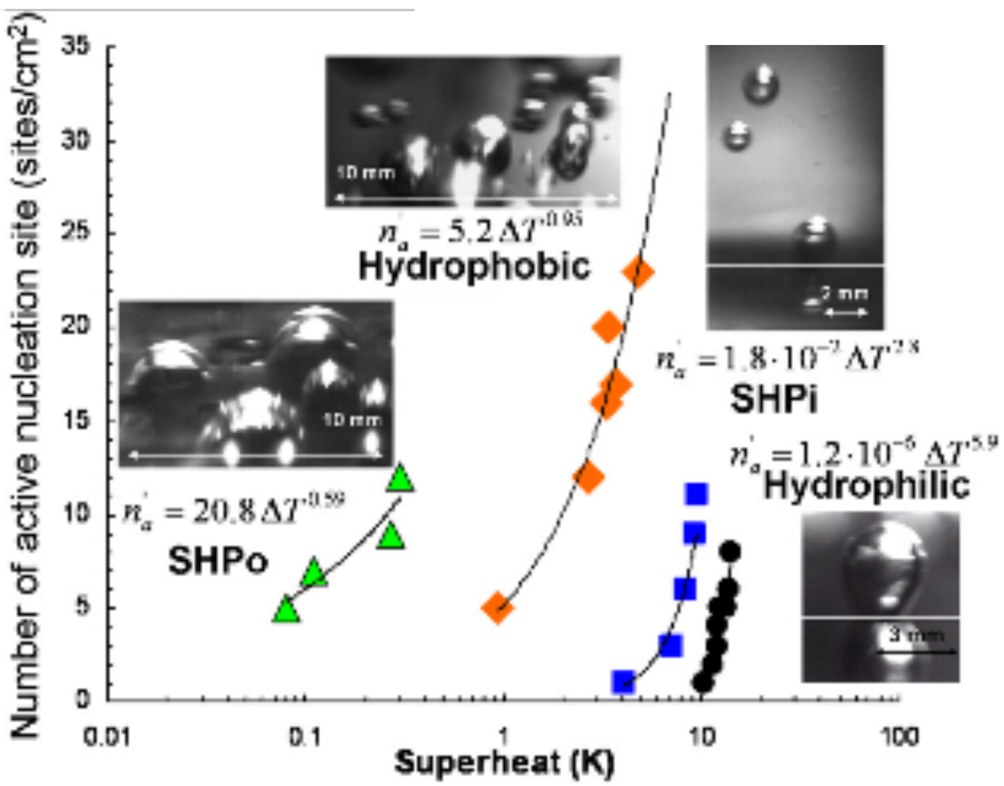
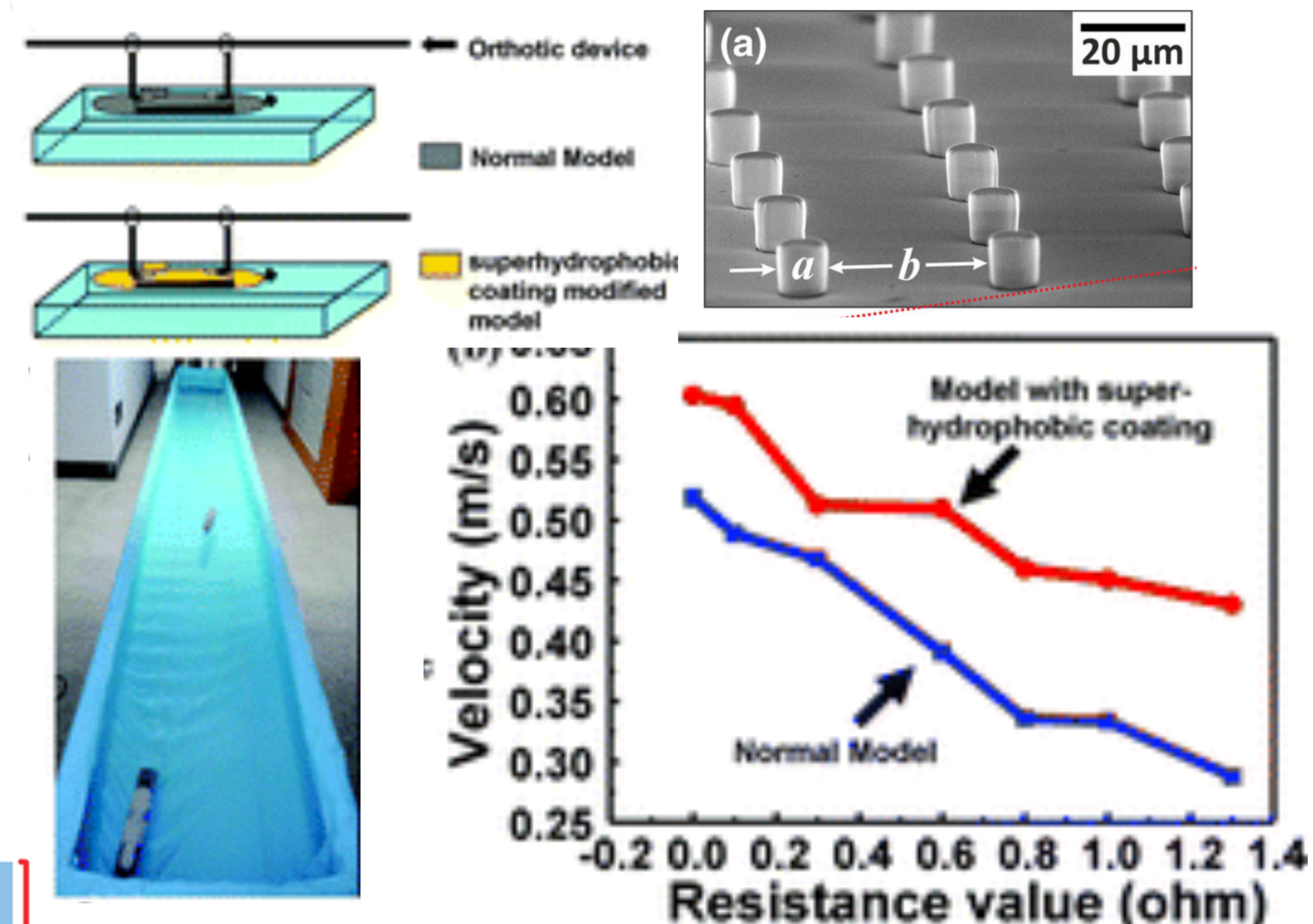
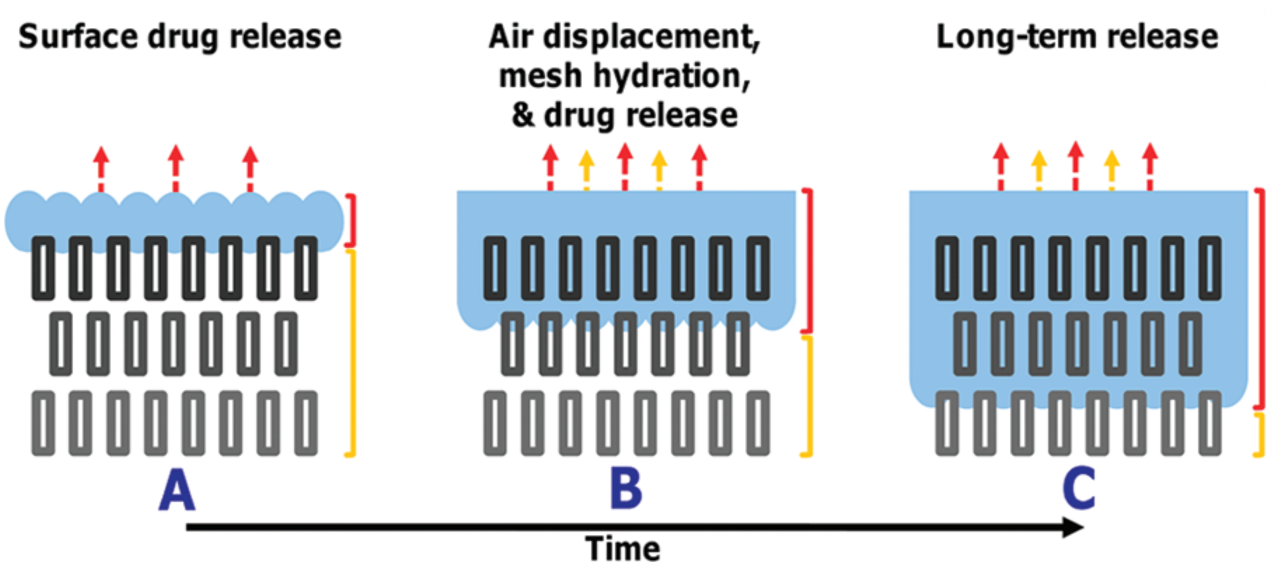
Technological applications of *textured* materials

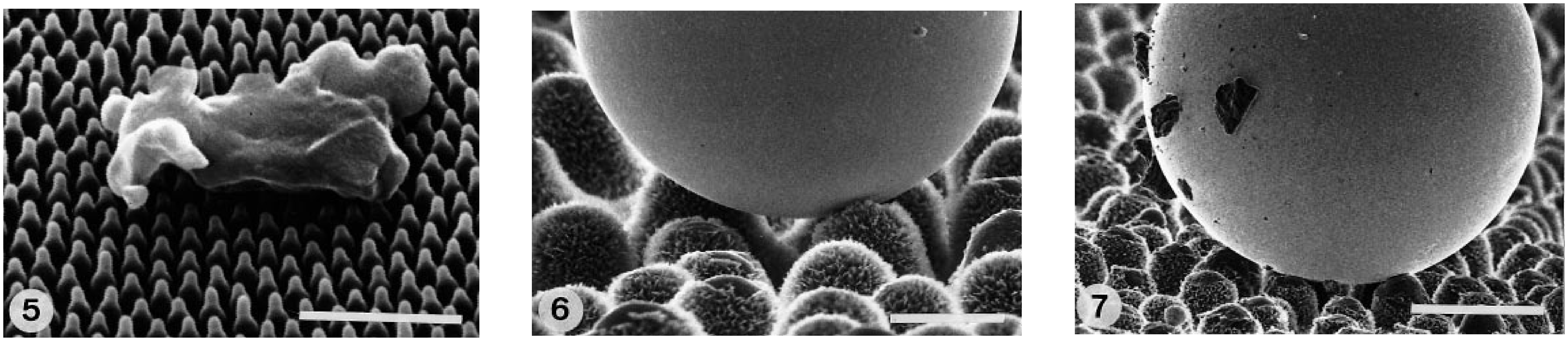




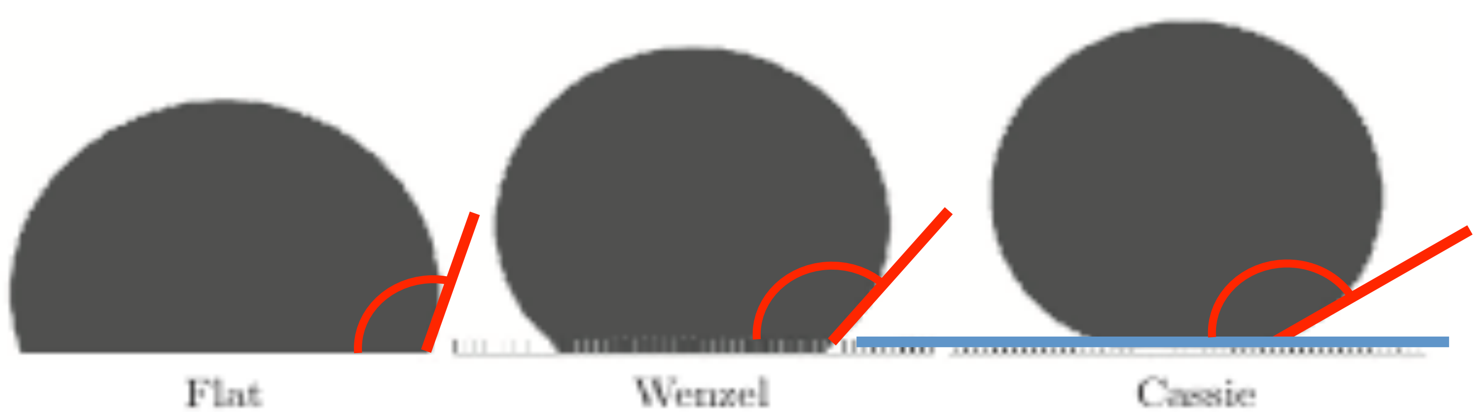


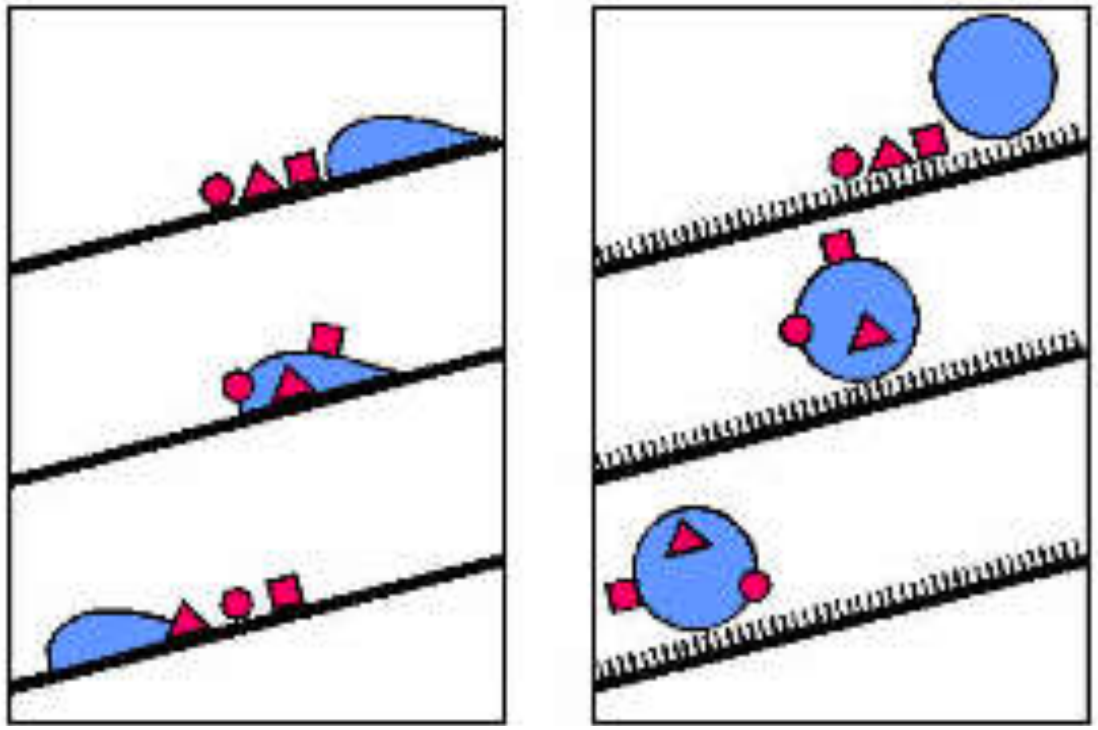


Lotus: a paradigm for “emerged” applications



$$\theta_C > \theta_W > \theta_Y$$
$$\Delta\theta_C \sim 0 - 5^\circ$$





W. Barthlott and C. Neinhuis, Planta 202: 1-8 (1997)
R. N. Wenzel, *Ind. Eng. Chem* 28(8):988-94 (1936)
A. B. D. Cassie and S. Baxter, *Transactions of the Faraday Society* 40:546-51 (1944)

Submerged applications

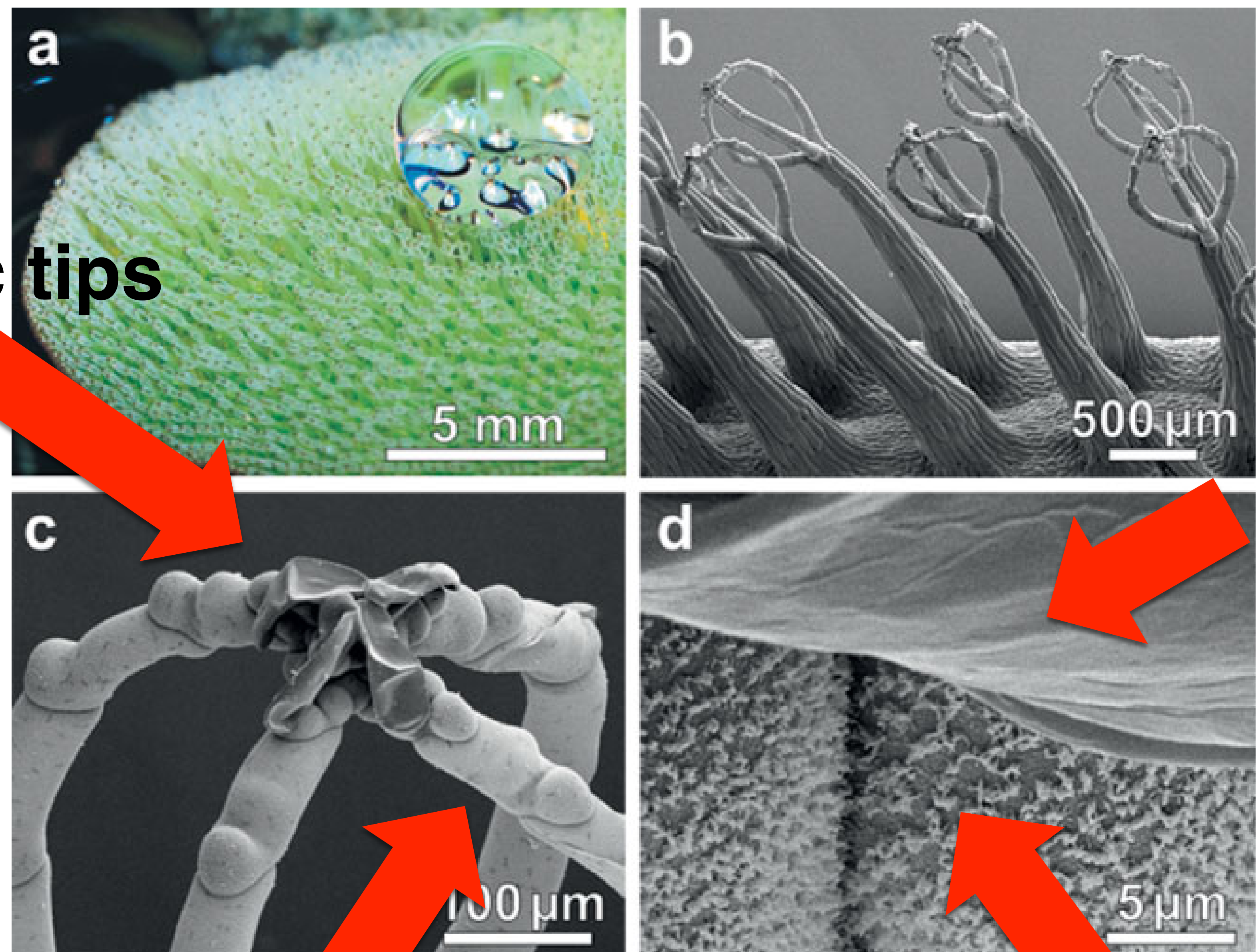
- Properties tailored for the specific application, e.g. high slippage

- **Resistant to the wetting transition**
    - **Cassie → Wenzel**

Salvinia: a paradigm for submerged gas retaining surfaces

Complex morphology and hydrophobic/hydrophilic chemistry

Hydrophilic tips



No wax

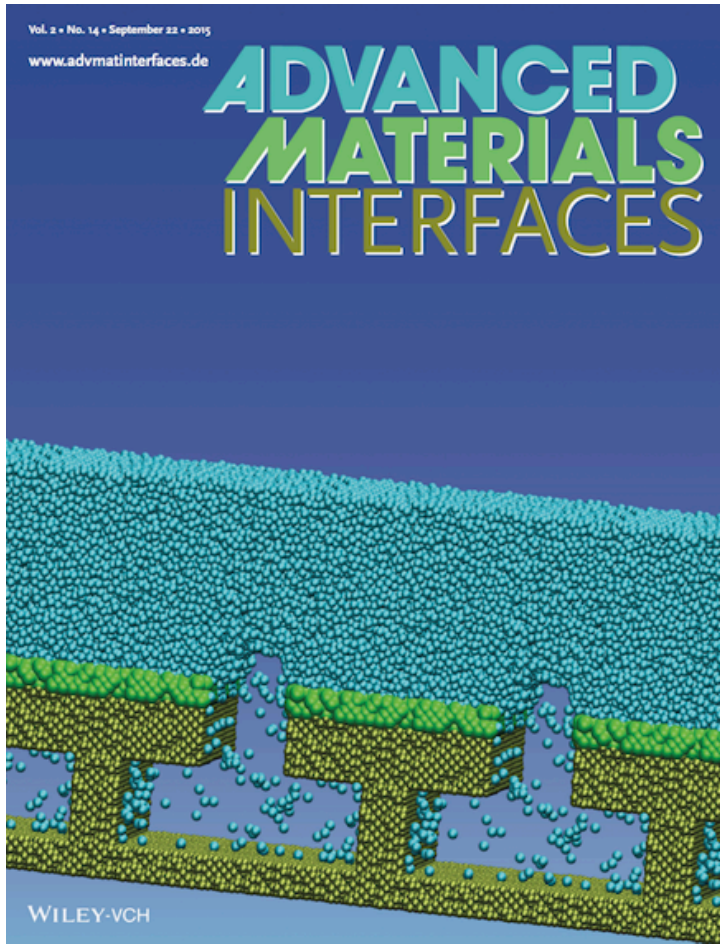
Hydrophobic hairs

Wax crystals

W. Barthlott et al., Advanced Material, 22: 2325 (2010)

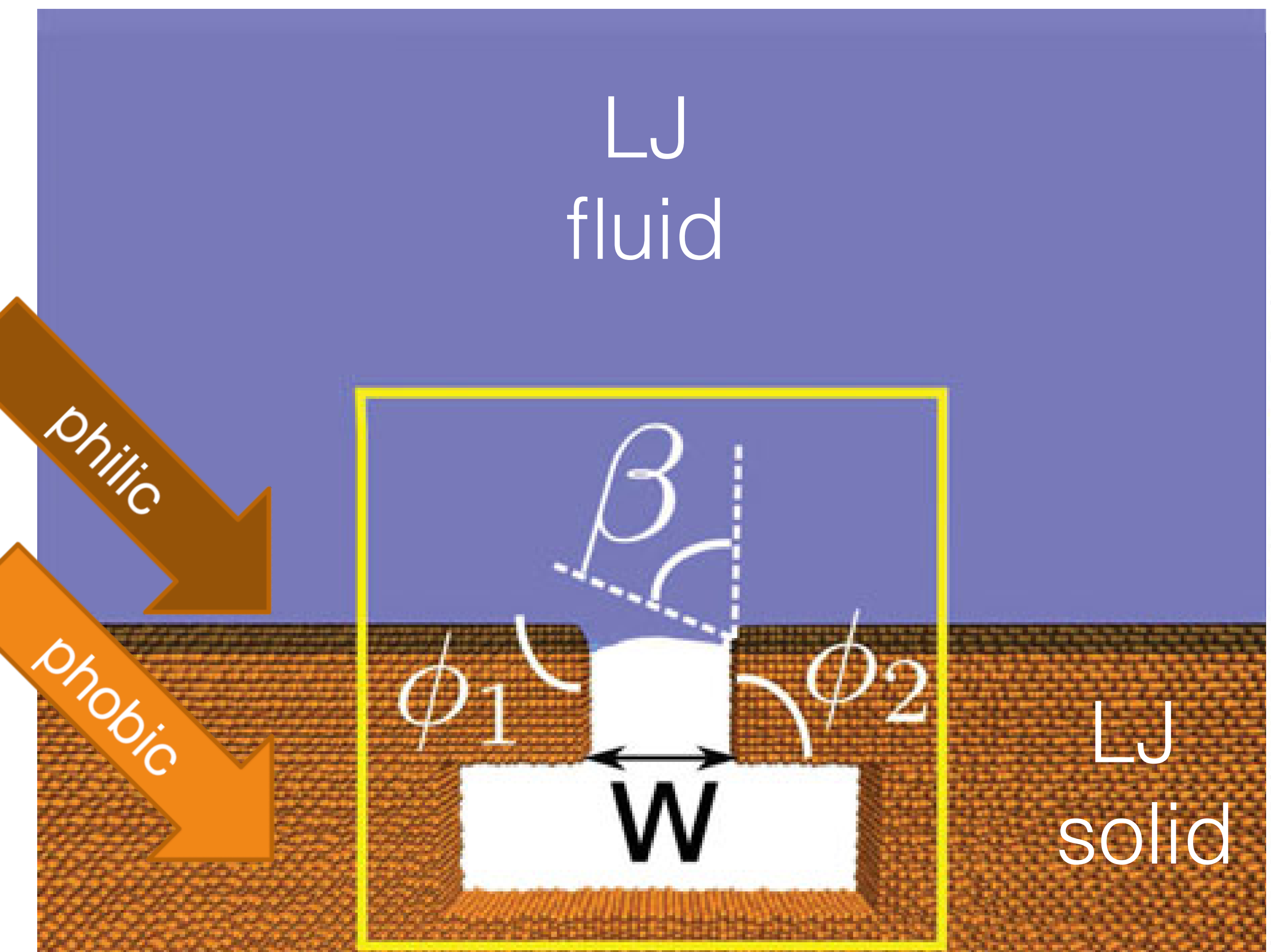
Questions

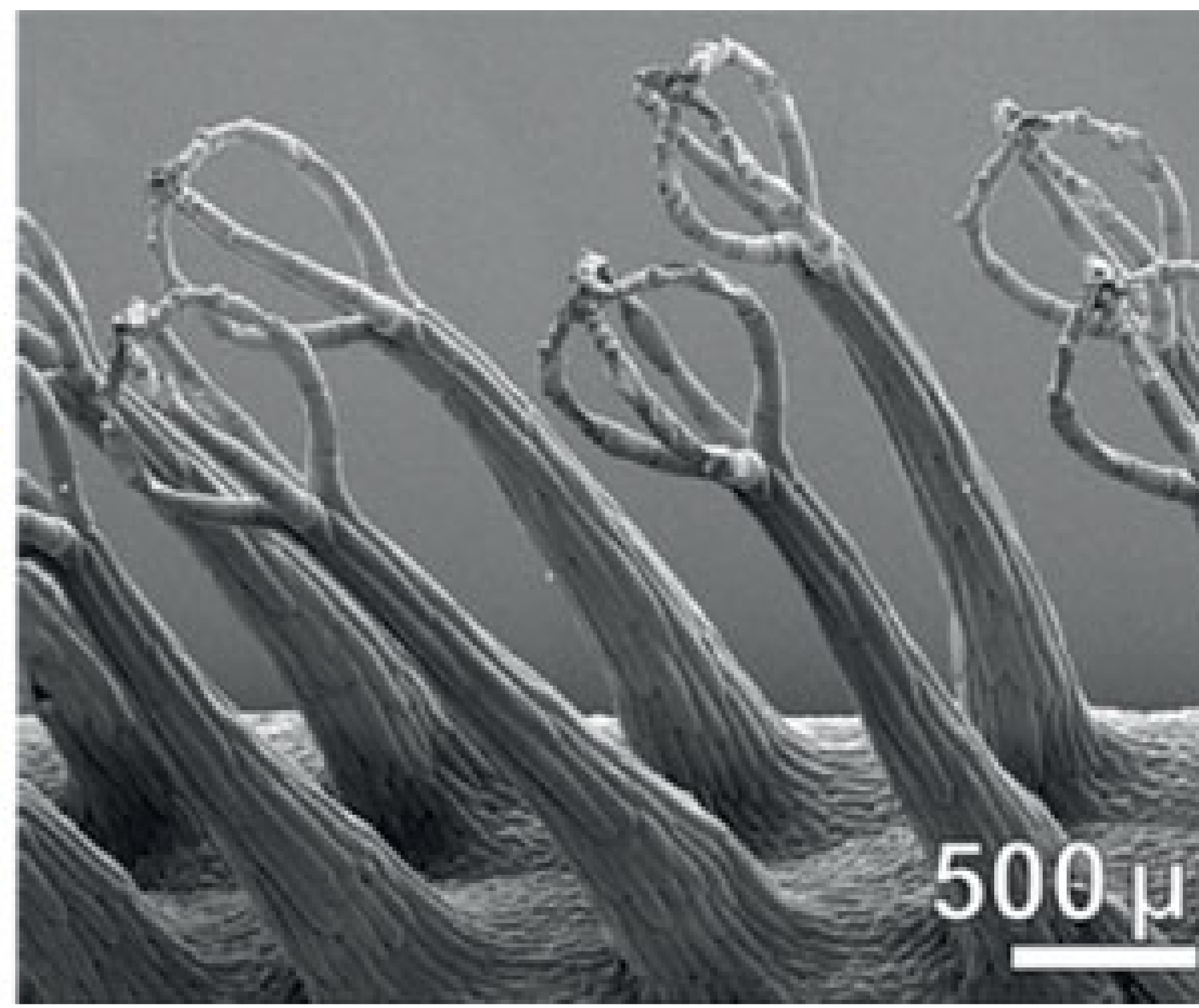
- Why has nature developed such complex morphologies/chemistry to control or prevent wetting/cavitation?
- Can one derive any general design principle for a more stable Cassie state with respect wetting/cavitation?
- How are the stability and kinetics of the wetting/cavitation transitions affected by the morphology/chemistry surfaces?



M. Amabili, A. Giacomello, SM, C. M. Casciola, Adv. Mater. Interfaces, 2: 1500248 (2015)

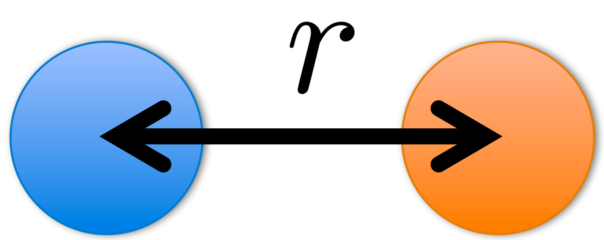
Model System



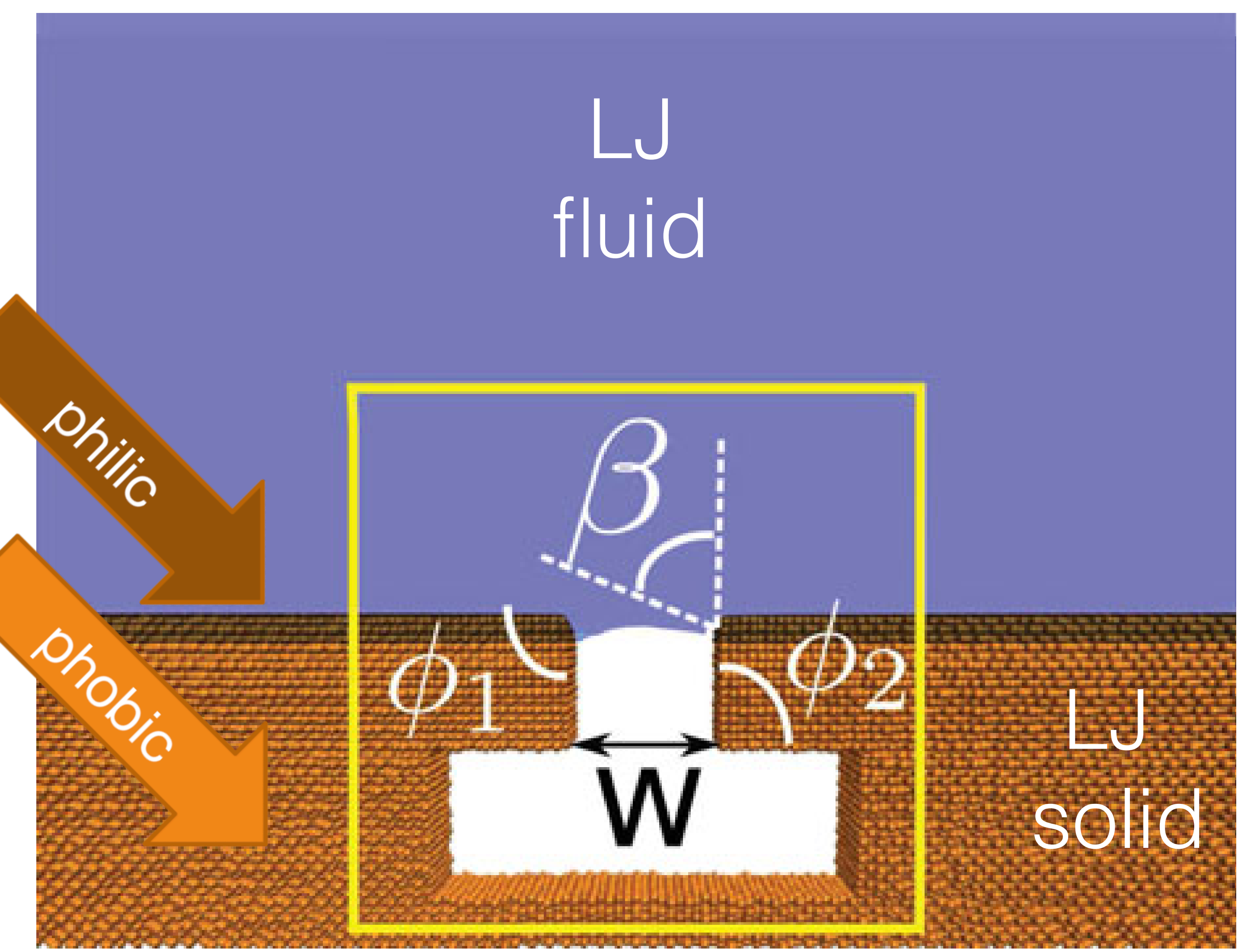


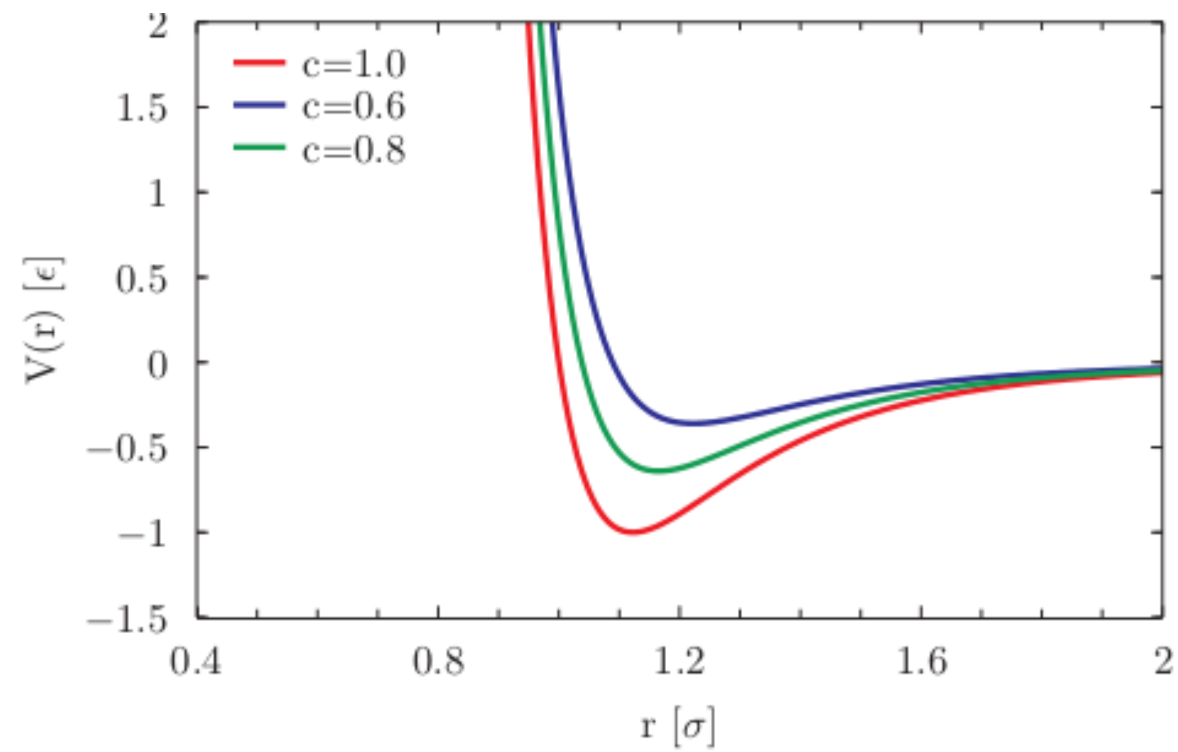
Model System

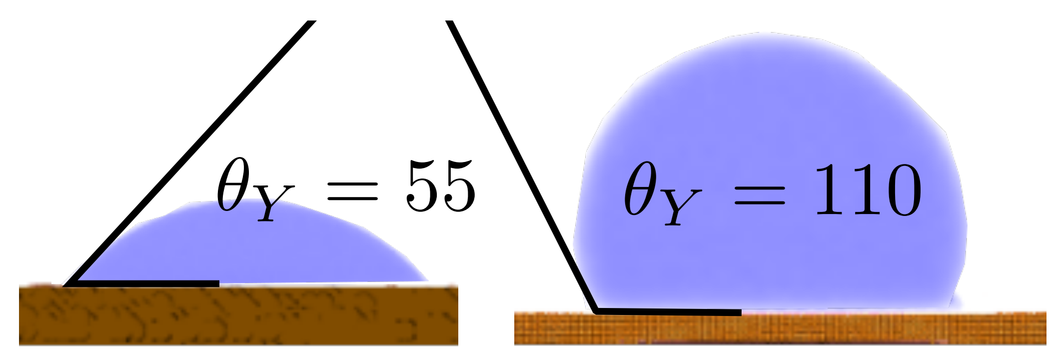
Atomistic simulations to avoid any aprioristic assumptions



$$v_{fs}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - c \left(\frac{\sigma}{r} \right)^{6} \right]$$

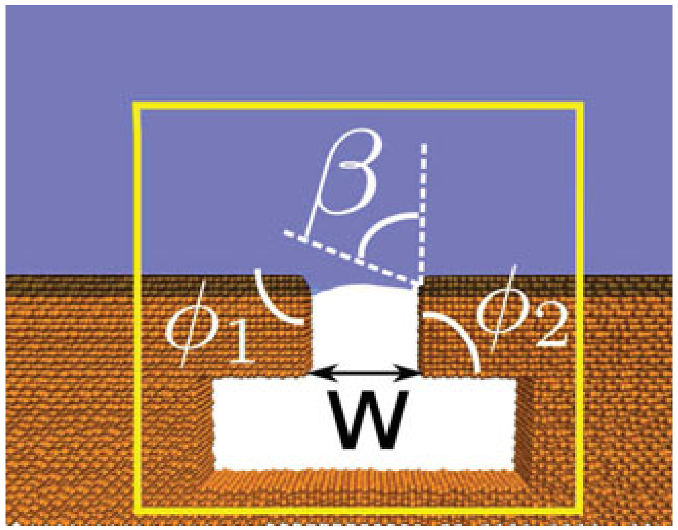




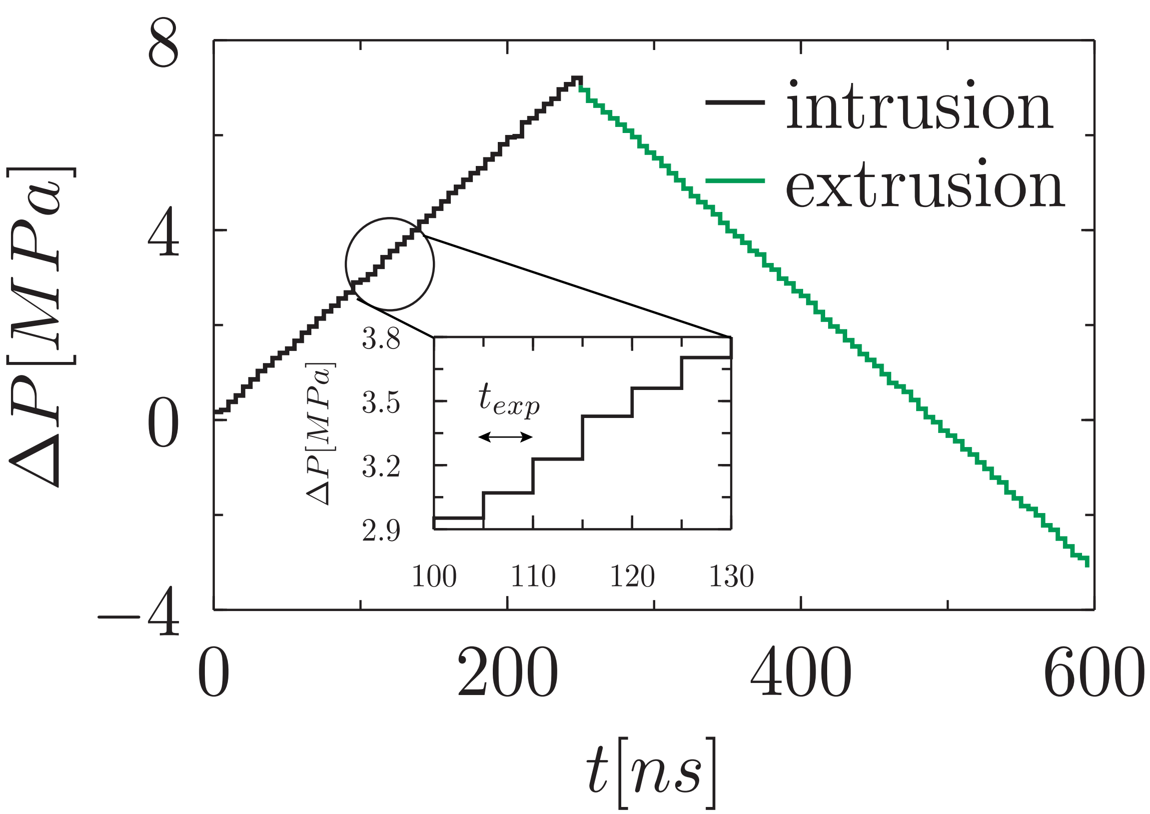


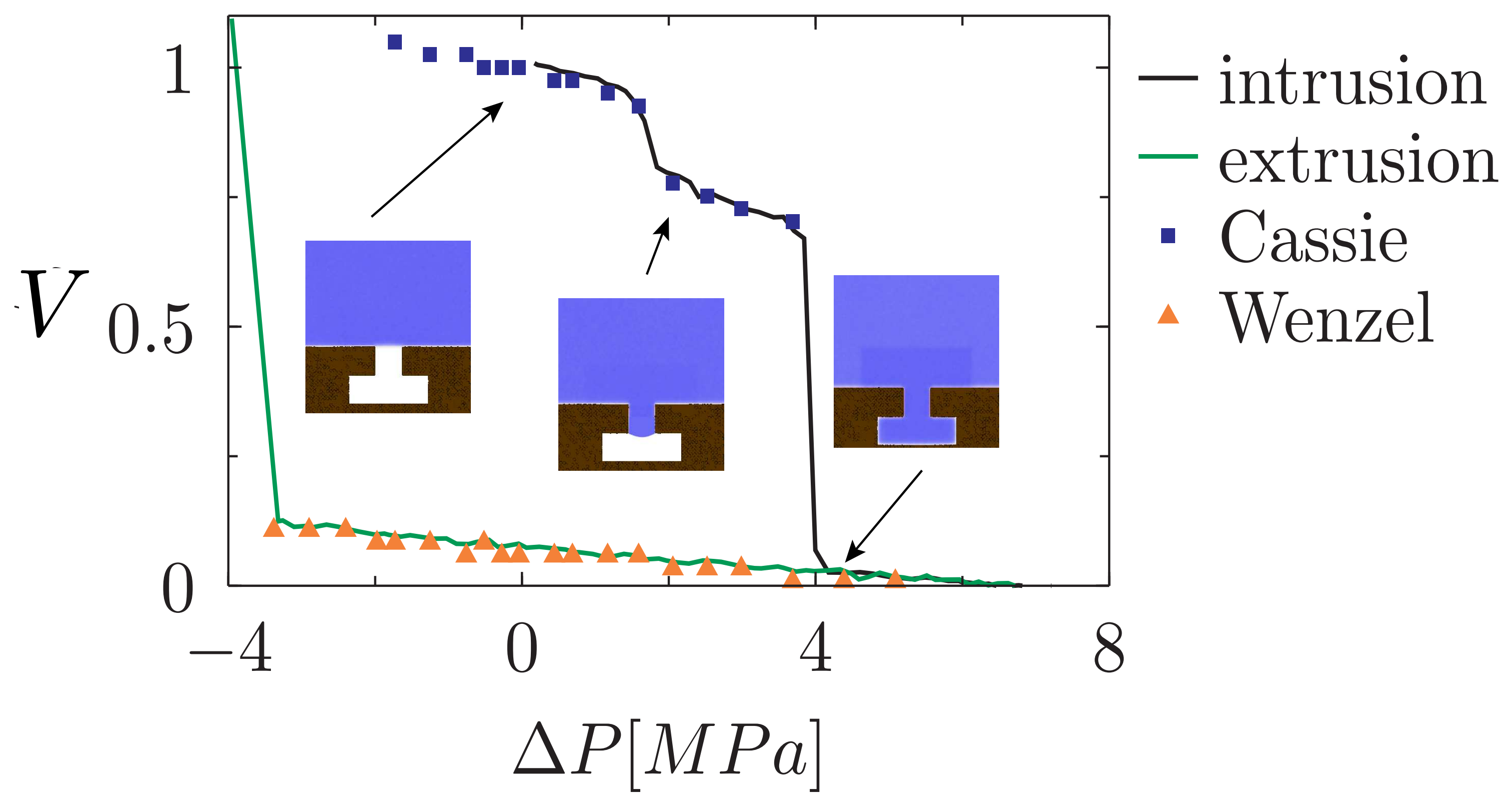
$c = 0.8$ $c = 0.6$

Intrusion/extrusion experiment on a hydrphobic surface



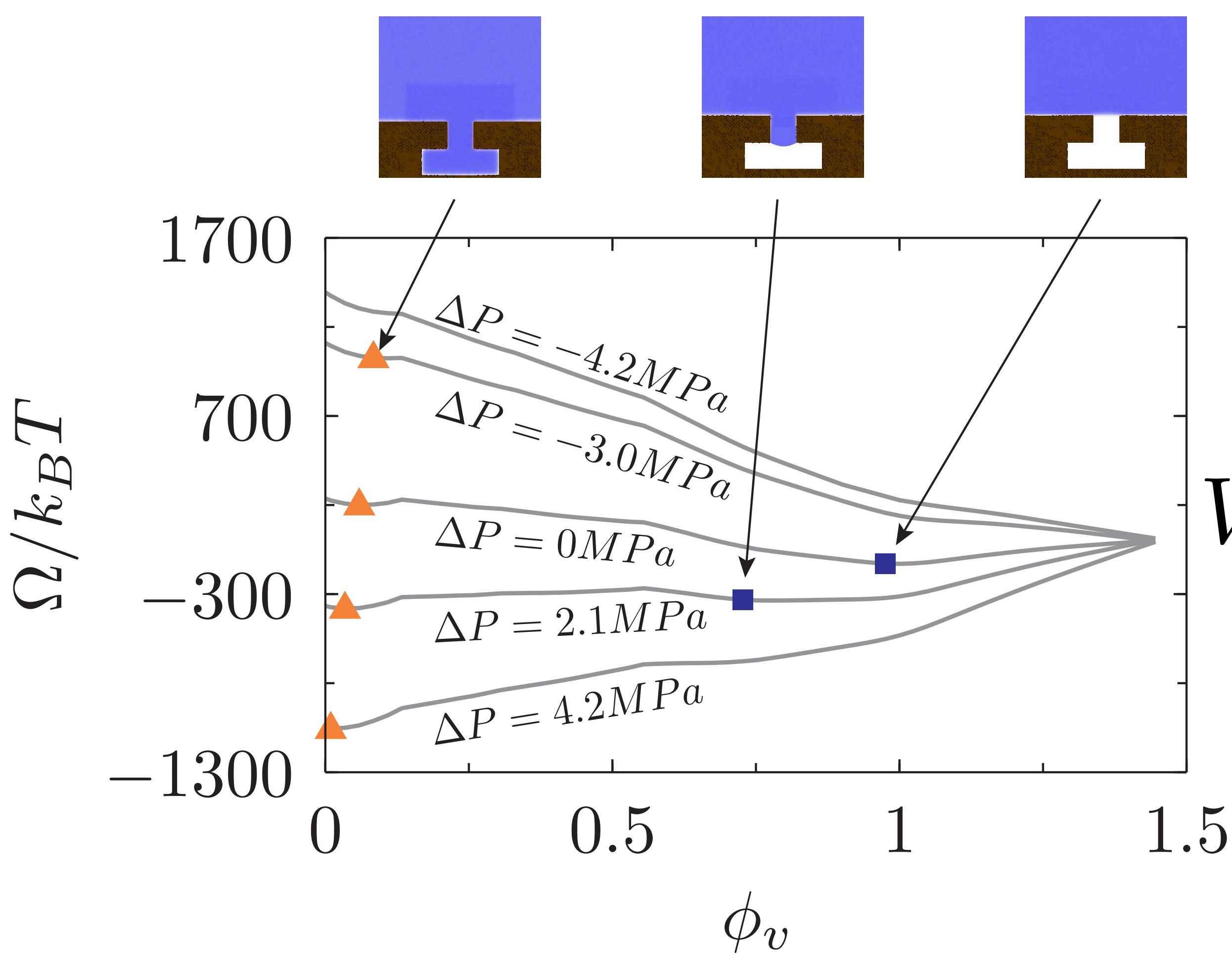
$$V = \frac{N_W - N}{N_W - N_C}$$

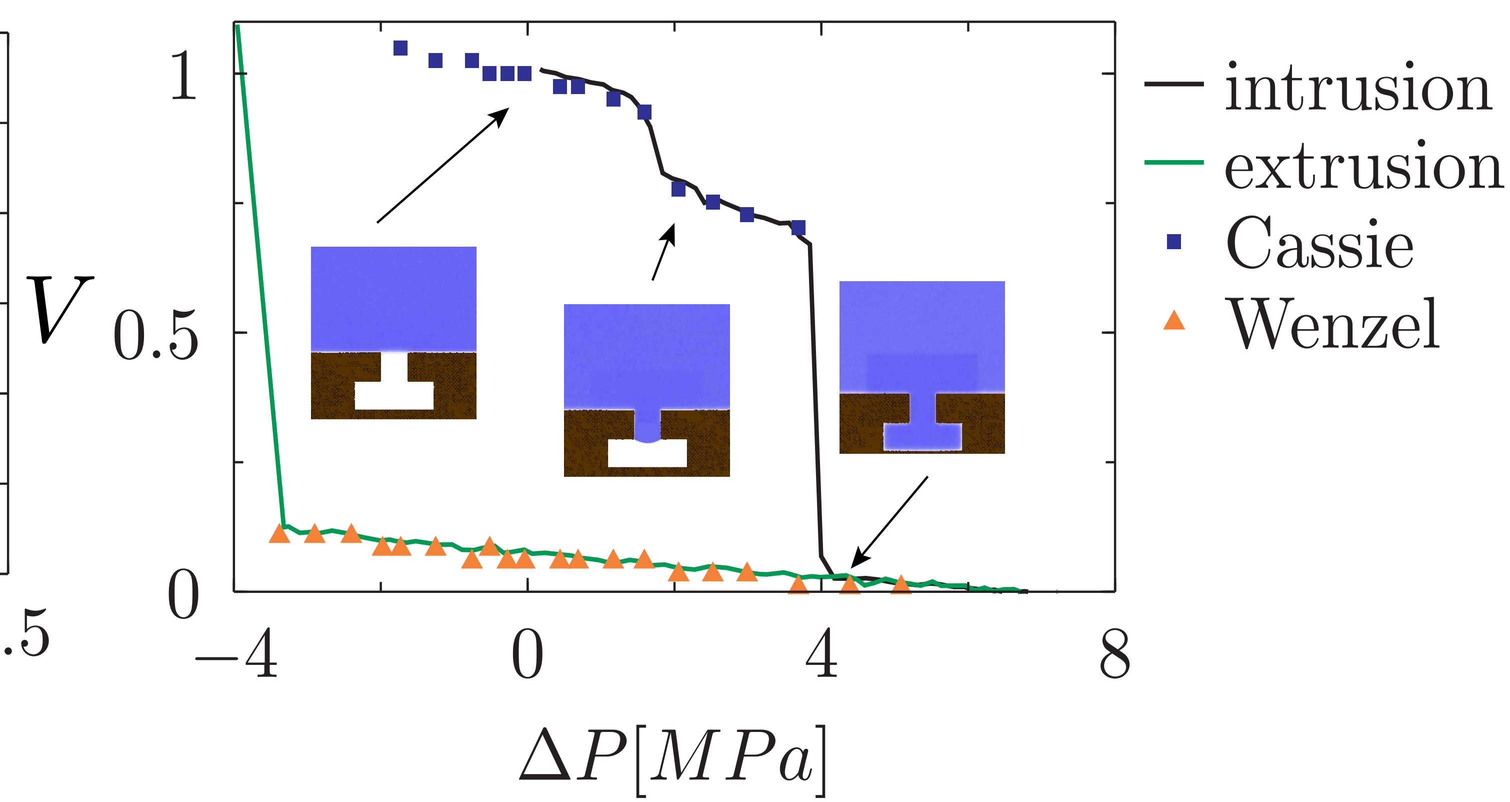




Intrusion/extrusion experiment on a hydrphobic surface

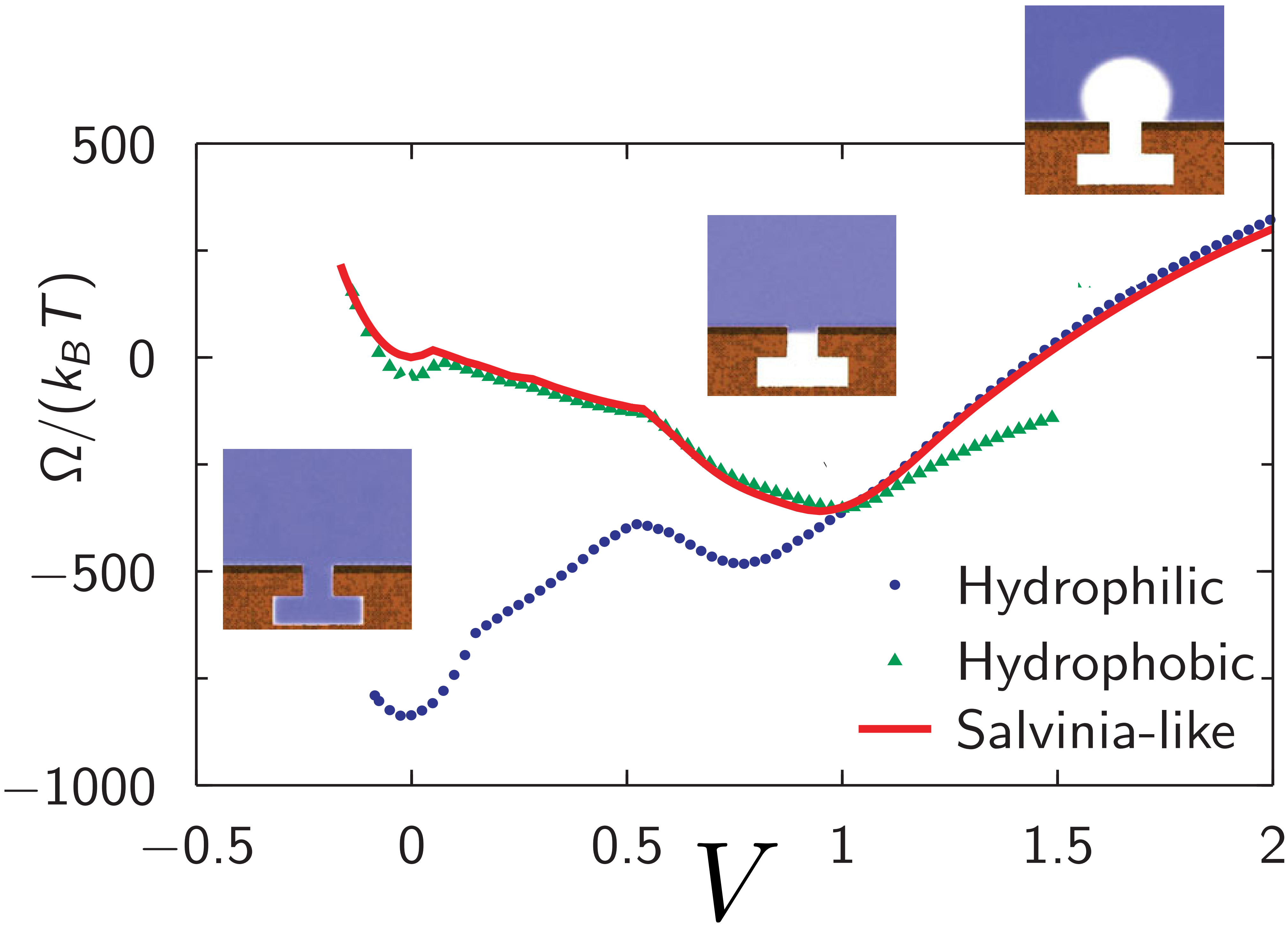
$$\tau = \tau_\infty \exp\left[\frac{\Delta\Omega(V^*)}{k_B T}\right] \qquad \tau_\infty >> \text{fs}$$





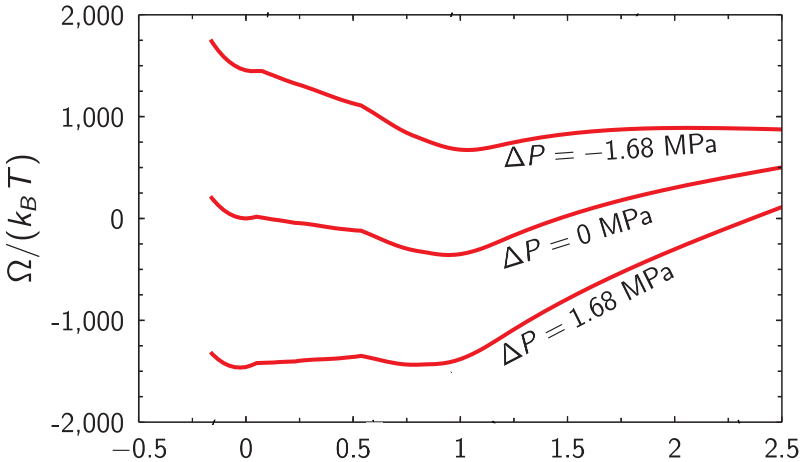
S. Meloni – Nanoinnovation 2016

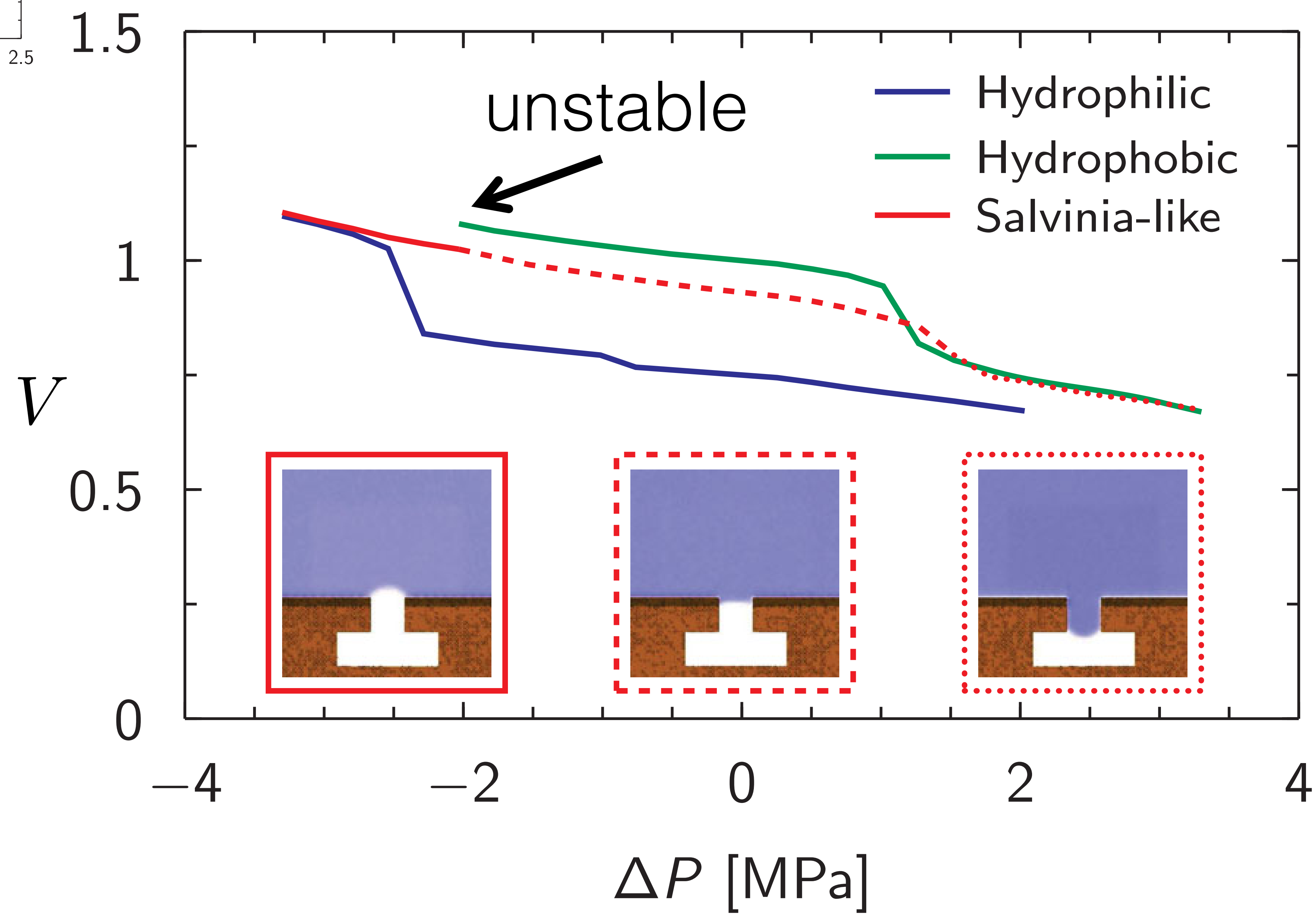
Free energy *vs* vapor volume fraction



The best characteristics of resistance to wetting and vapor nucleation of the two chemically *pure* surfaces

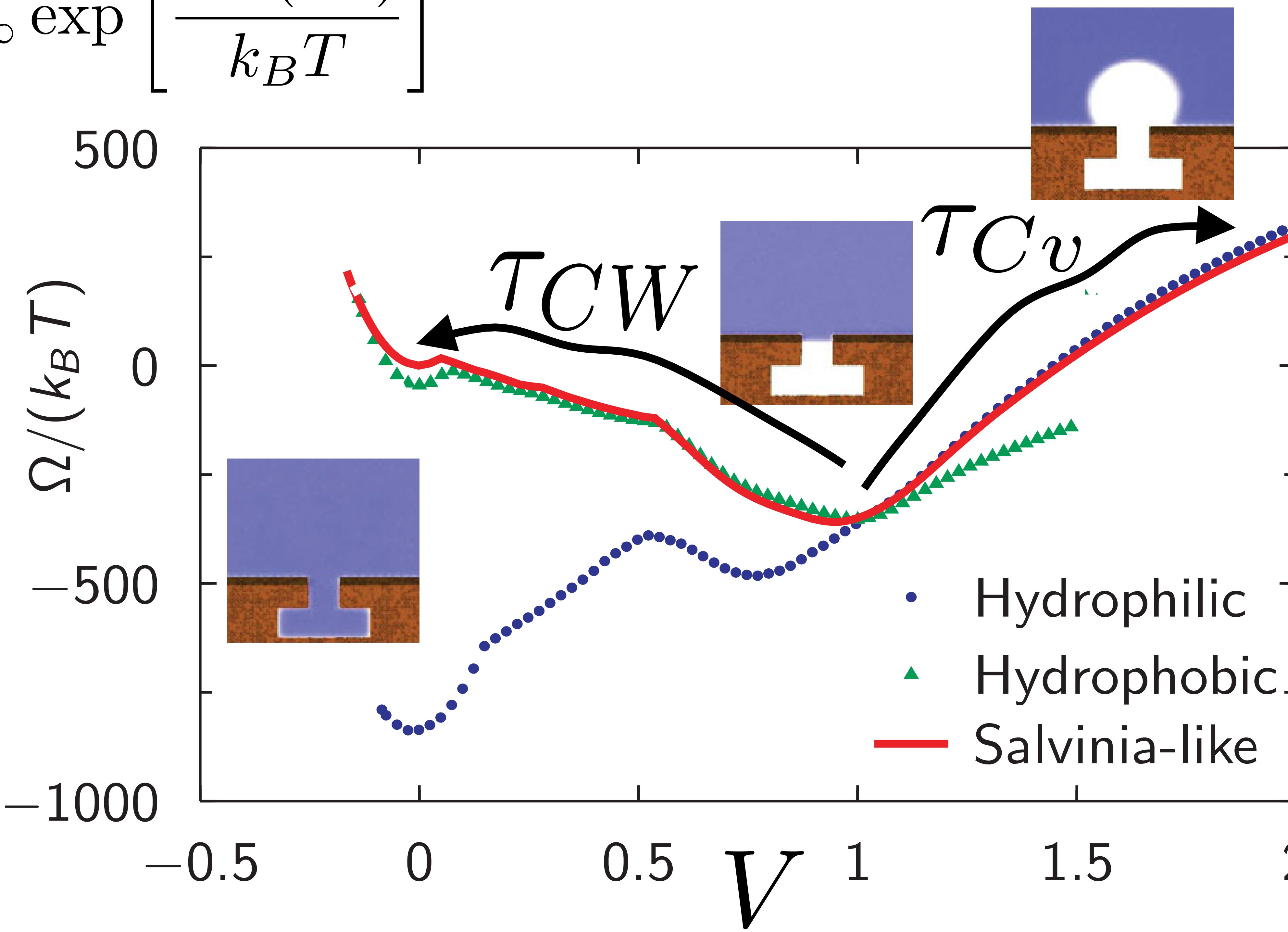
Stability of Cassie with P



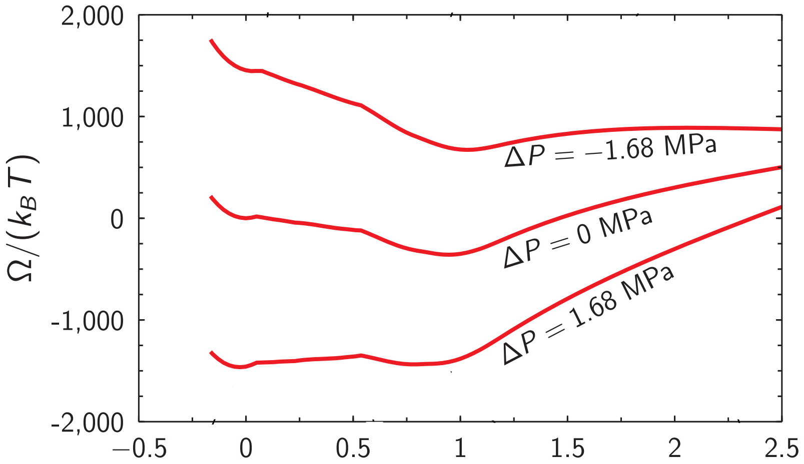


Free energy *vs* vapor volume fraction

$$\tau = \tau_\infty \exp\left[\frac{\Delta\Omega(V^*)}{k_B T}\right]$$

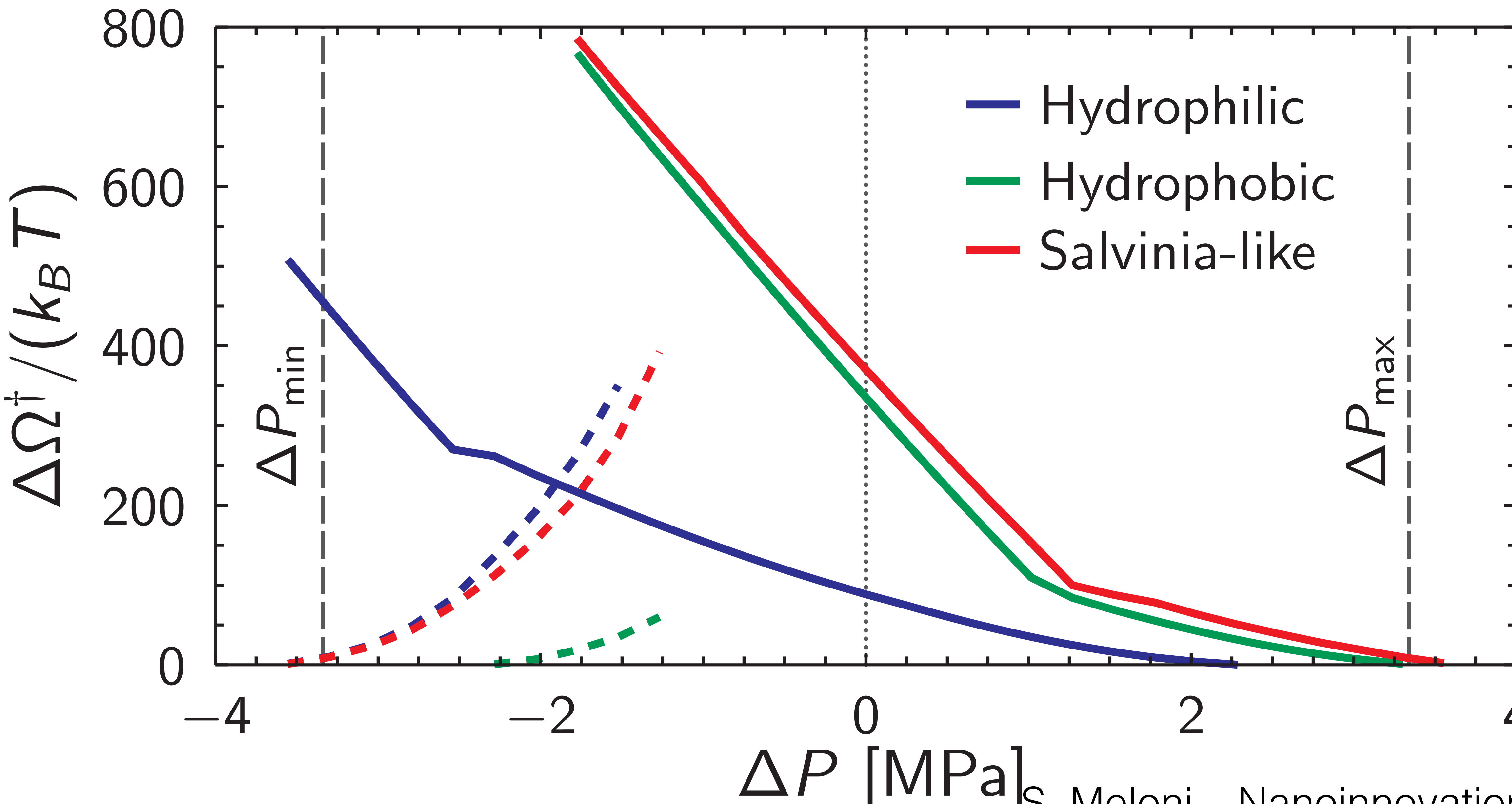


Stability of Cassie with P

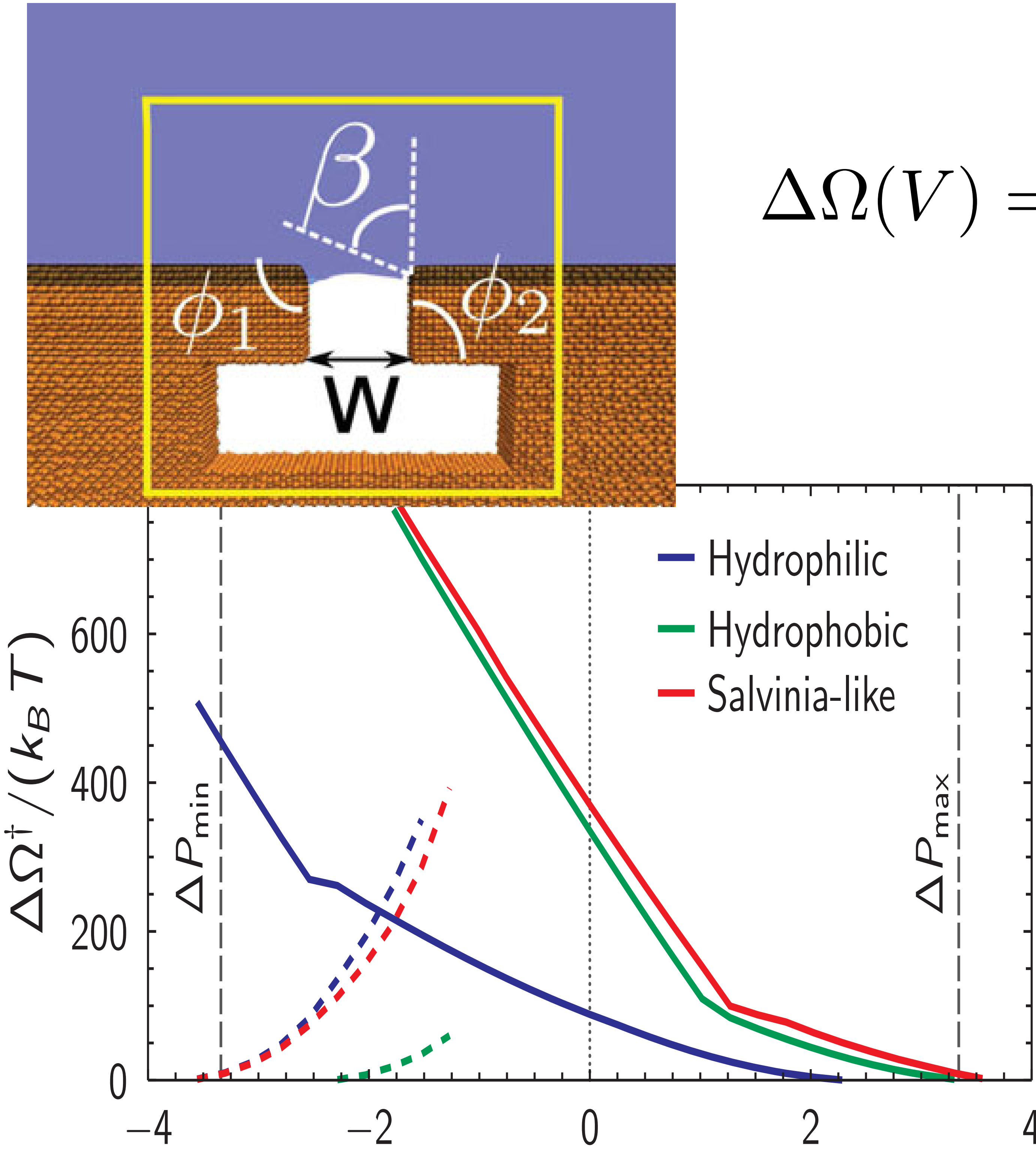


$$\tau = \tau_\infty \exp\left[\frac{\Delta\Omega(V^*)}{k_B T}\right]$$

$$\tau_\infty >> \text{fs}$$



Design principles



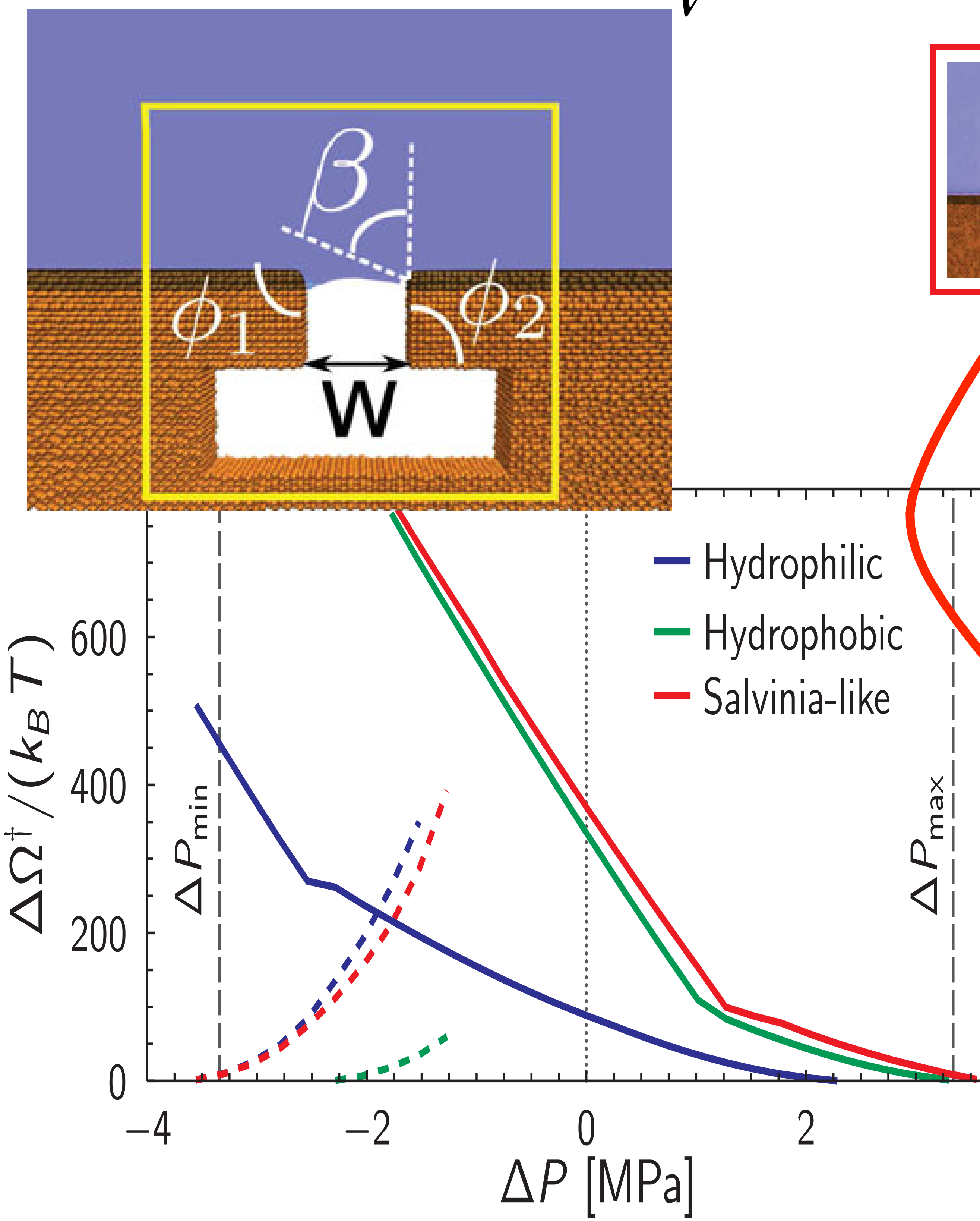
Sharp interface model

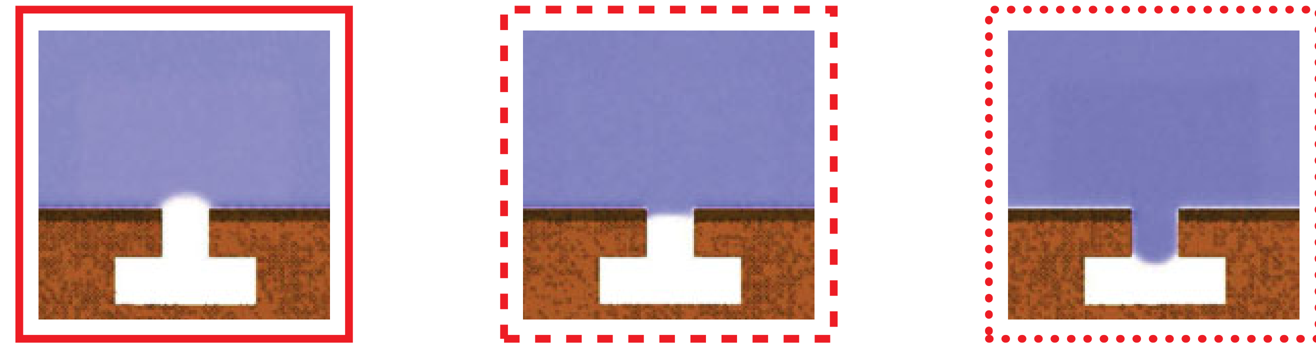
$$\Delta\Omega(V) = \Delta P\ V + \gamma_{lv}\left(\cos\theta_Y A_{vs} + A_{lv}\right)$$

$$\cos\theta_Y = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lv}}$$

Design principles

V





$$\Delta P = -\frac{2\gamma_{lv}\cos\beta}{W}$$

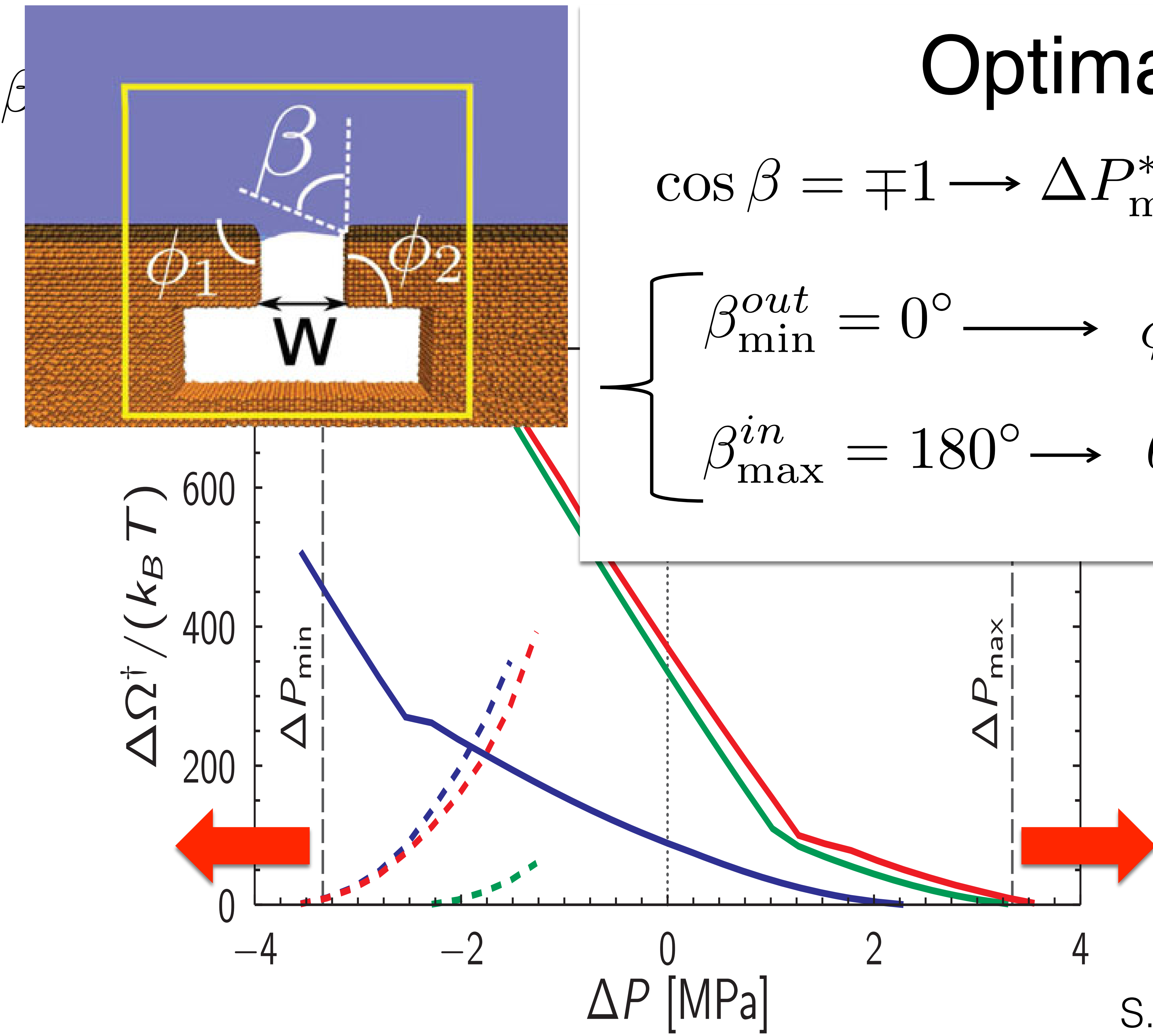
$$\Delta P_{\max\,/\,\min} = \max\,/\,\min_{\beta}\,(\Delta P)$$

$$\phi_1 + \theta_Y^{top} - 180^\circ < \beta < \theta_Y^{in}$$

$$\theta_Y^{in} < \beta < 180^\circ - \phi_2 + \theta_Y^{in}$$

Gibb's criterion

Design principles

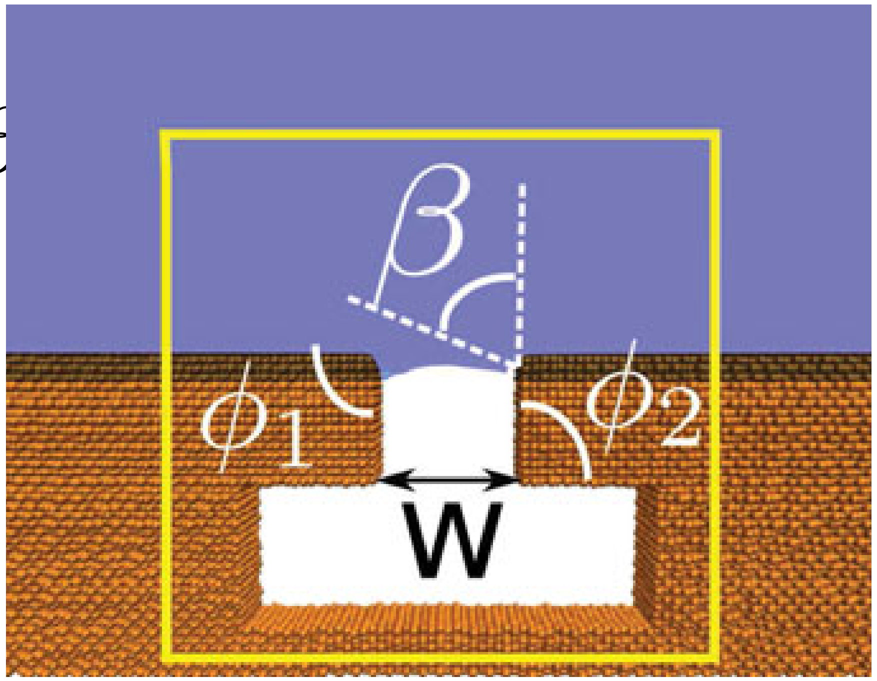


Optimal case

$$\cos\beta = \mp 1 \longrightarrow \Delta P^*_{\max\,/\,\min} = \pm \frac{2\gamma_{lv}}{W}$$

$$\left\{ \begin{array}{l} \beta^{out}_{\min} = 0° \longrightarrow \quad \phi_1 + \theta^{top}_{Y} \leq 180° \\ \beta^{in}_{\max} = 180° \longrightarrow \quad \theta^{in}_{Y} - \phi_2 \geq 0° \end{array} \right.$$

Design principles



Optimal case

$$\cos\beta = \mp 1 \longrightarrow \Delta P^{*}_{\mathrm{max}\,/\,\mathrm{min}} = \pm\frac{2\gamma_{lv}}{W}$$

$$\begin{cases} \beta^{out}_{\mathrm{min}} = 0^\circ \longrightarrow \quad \phi_1 + \theta^{top}_{\mathrm{Y}} \leq 180^\circ \\ \beta^{in}_{\mathrm{max}} = 180^\circ \longrightarrow \quad \theta^{in}_{\mathrm{Y}} - \phi_2 \geq 0^\circ \end{cases}$$

The details of the chemistry is irrelevant, it must just satisfy the condition that

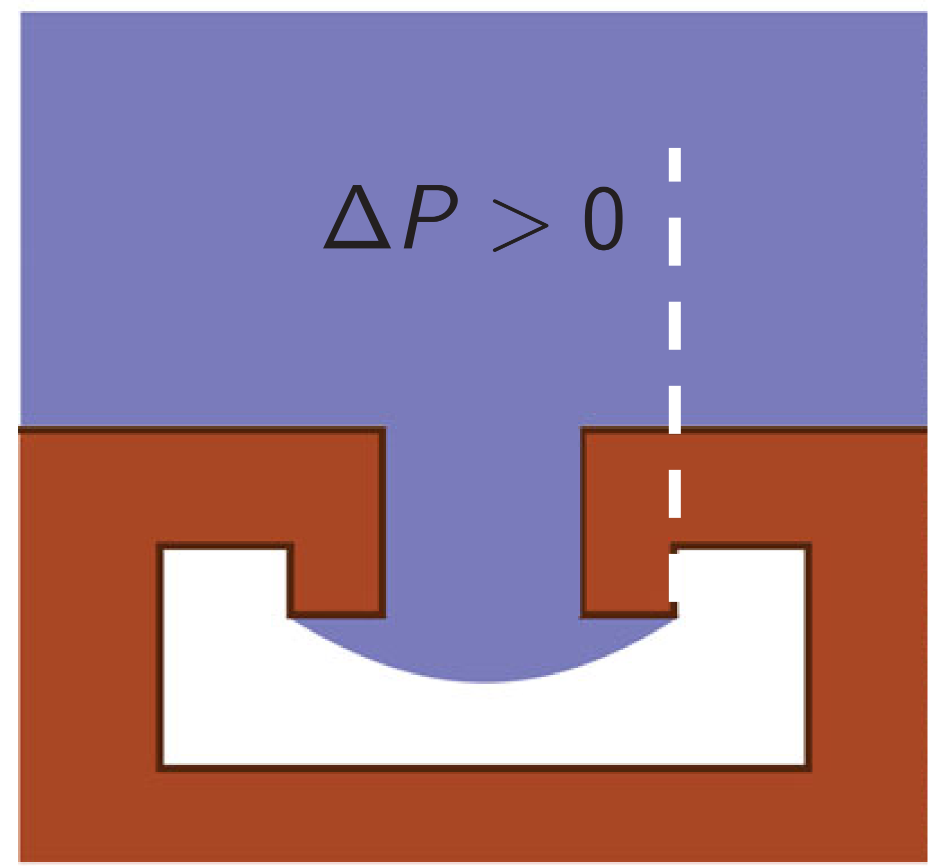
$$0 \leq \beta \leq 180^\circ$$

Design principles

Adapt ϕ_2 such the the optimal β can be still achieved:

$$\begin{cases} \beta_{\min}^{out} = 0^\circ \longrightarrow \phi_1 + \theta_Y^{top} \leq 180^\circ \\ \beta_{\max}^{in} = 180^\circ \longrightarrow \theta_Y^{in} - \phi_2 \geq 0^\circ \end{cases}$$

$$\Delta P^*_{\max\,/\,\min} = \pm = \frac{2\gamma_{lv}}{W}$$



Conclusions

- Resistance to liquid intrusion and cavitation can be tuned independently by optimizing the chemistry on interior and top of surfaces textures

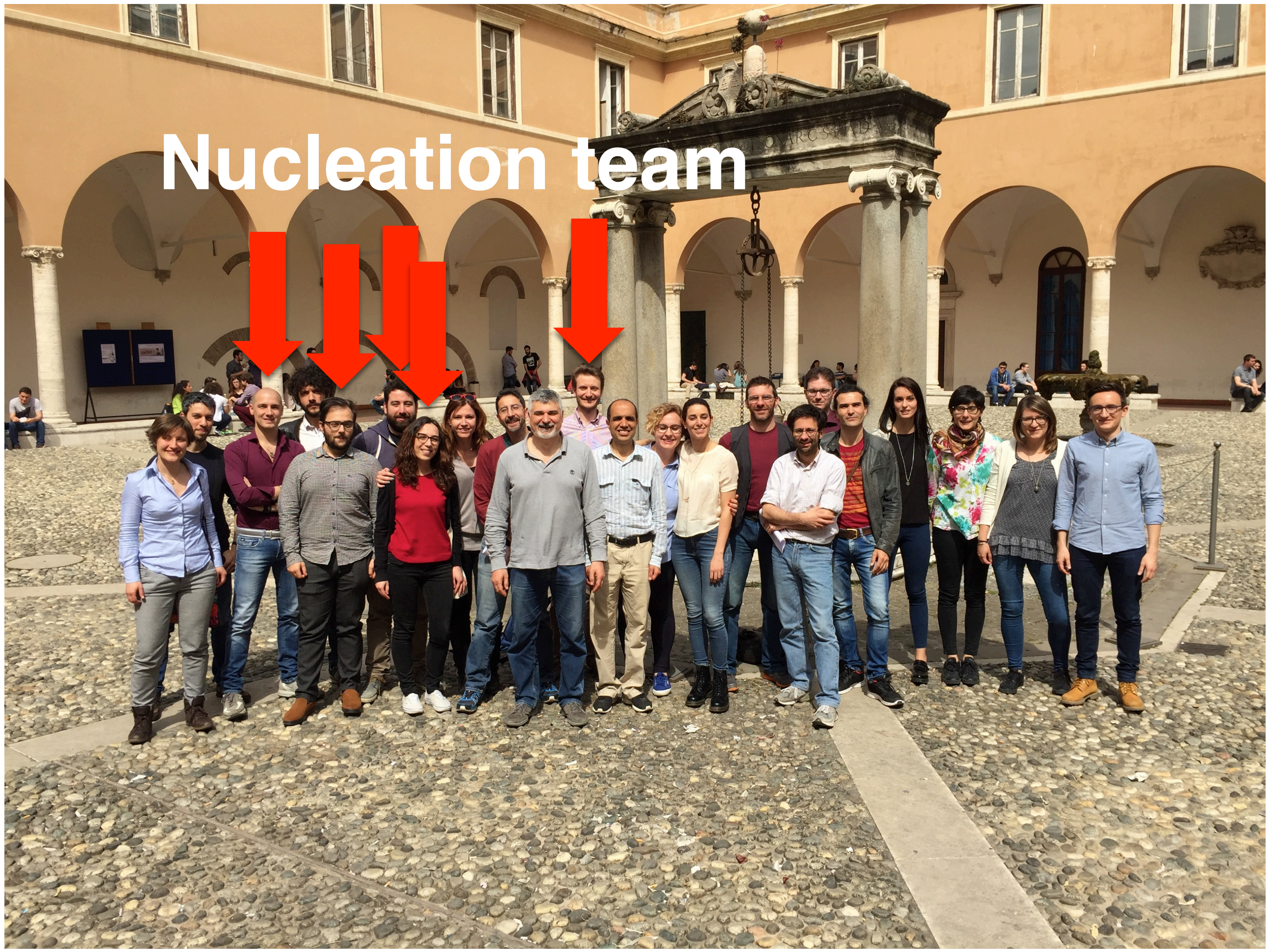
- Intrusion and cavitation barriers grow very quickly with pressure departing from P_{min} and P_{max}

  - Intrusion and cavitation pressures are the two main quantities characterizing the stability of superhydrophobic submerged surfaces

- Design principles are proposed to design surfaces with optimal resistance to wetting/cavitation

  - They depend on the topography and chemistry but not on they *fine details*

Acknowledgements



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Thank you for your attention