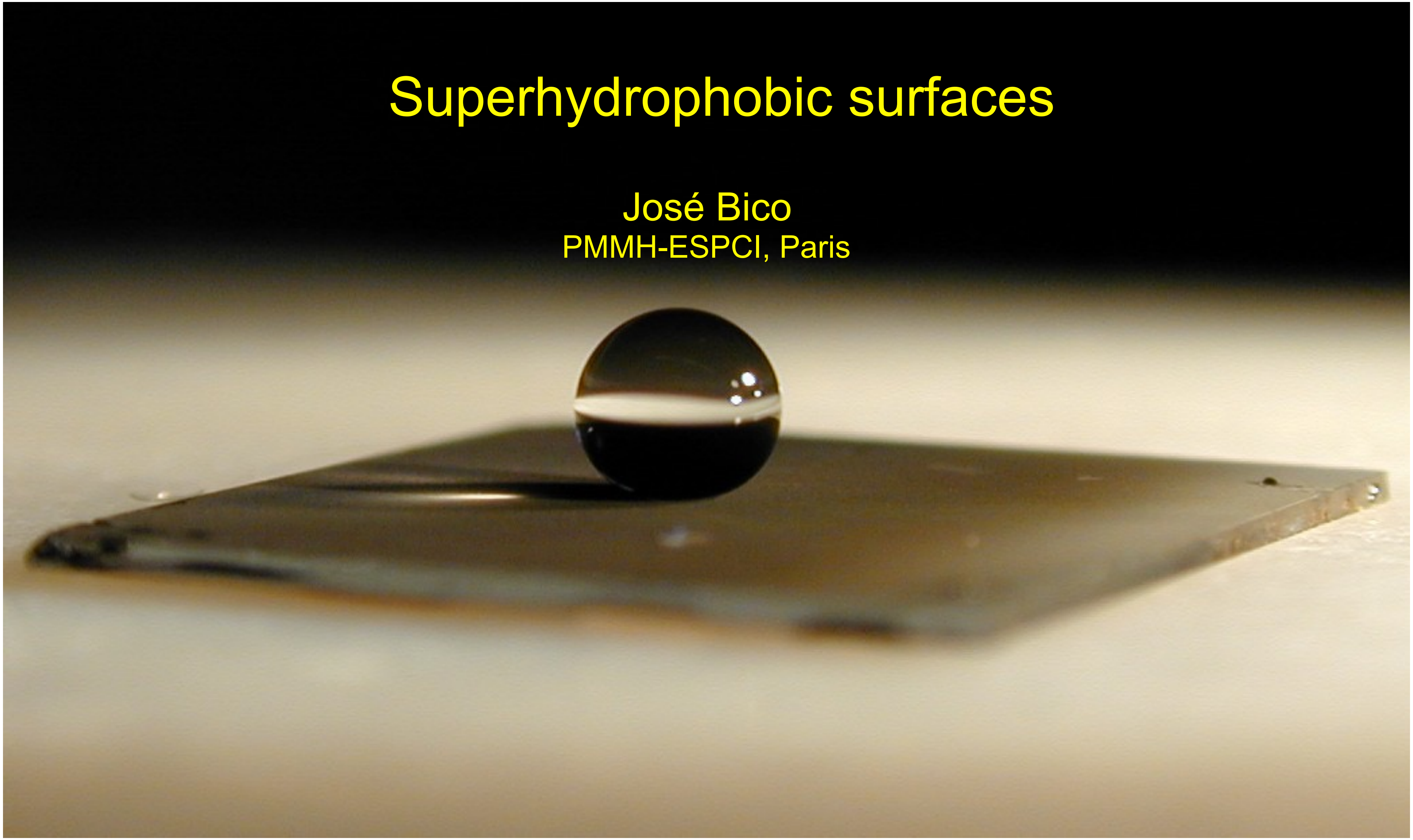
Superhydrophobic surfaces
José Bico
PMMH-ESPCI, Paris

Superhydrophobic surfaces

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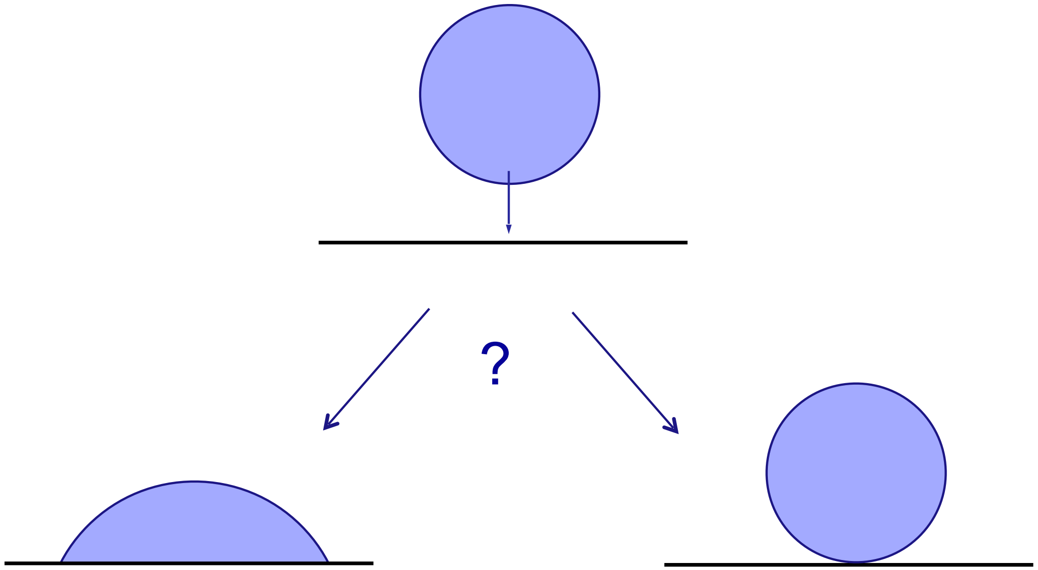
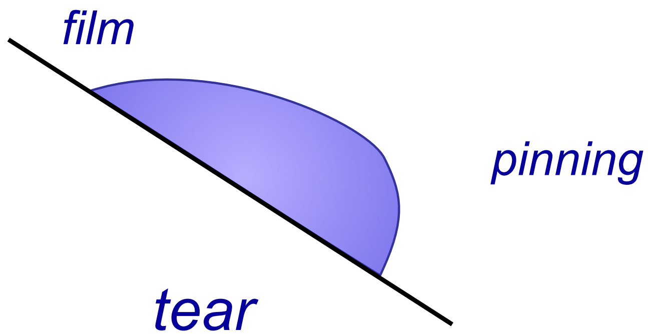
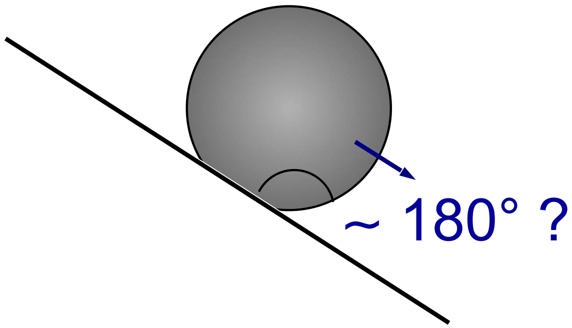
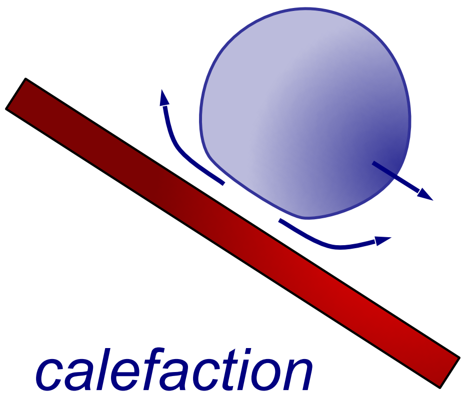
PMMH-ESPCI, Paris



Rain droplet on a window





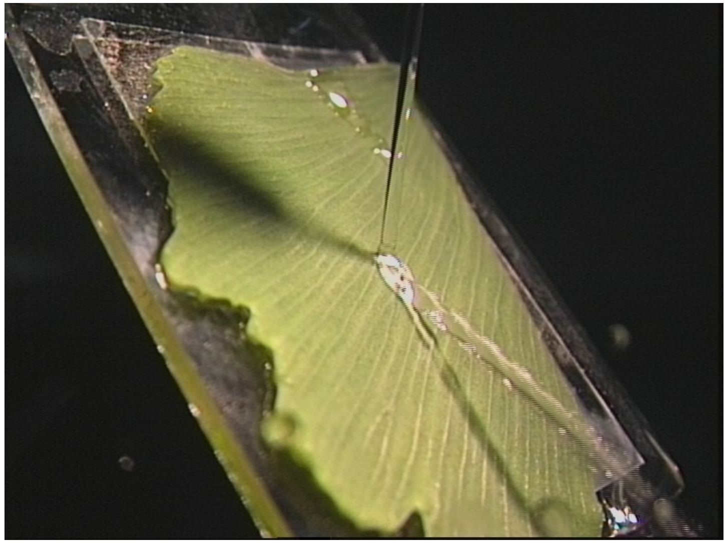


Leidenfrost point, T = 150°C

Anne-Laure Biance
Christophe Clanet,
David Quéré

"Lotus" effect

Setcreasea



Ginkgo Biloba

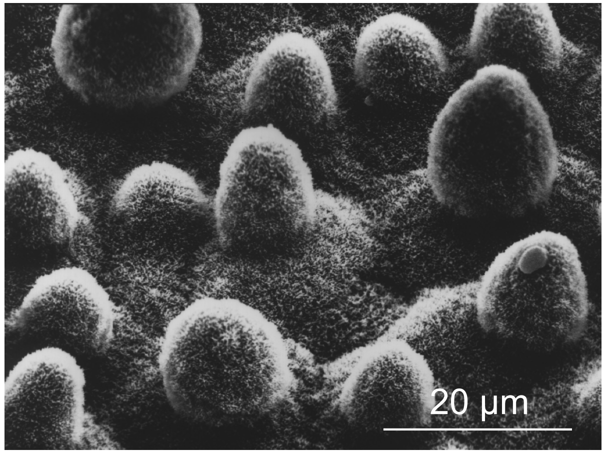
Natural water-repellent surfaces:

some plant leaves
insect wings
water spiders silk nests…

Impacts

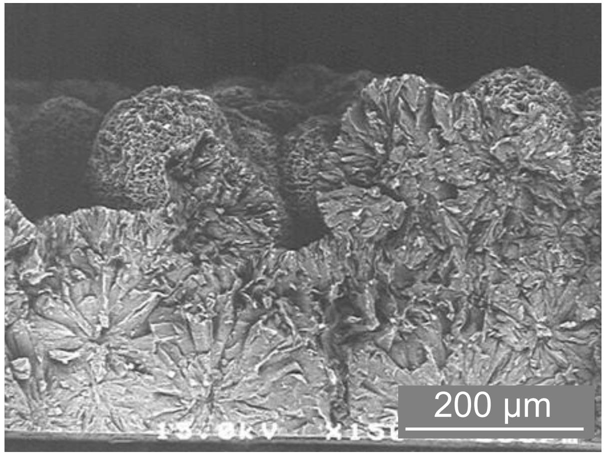
Ingredients for super-hydrophobicity

Chemical hydrophobicity + Taylored surface



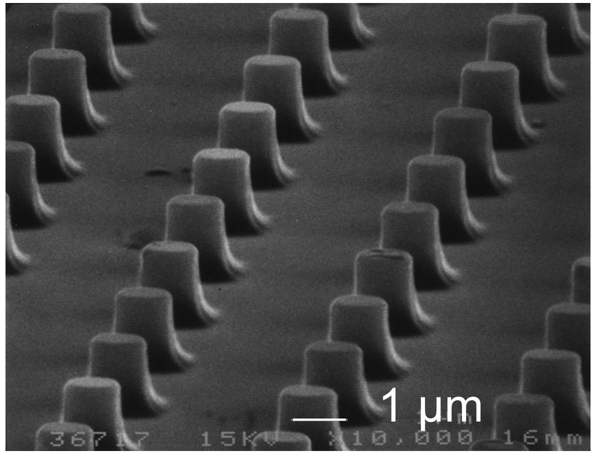
Lotus leaf

Barthlott & Neinhuis (1997)



hydrophobic wax

Onda et al. (1996)

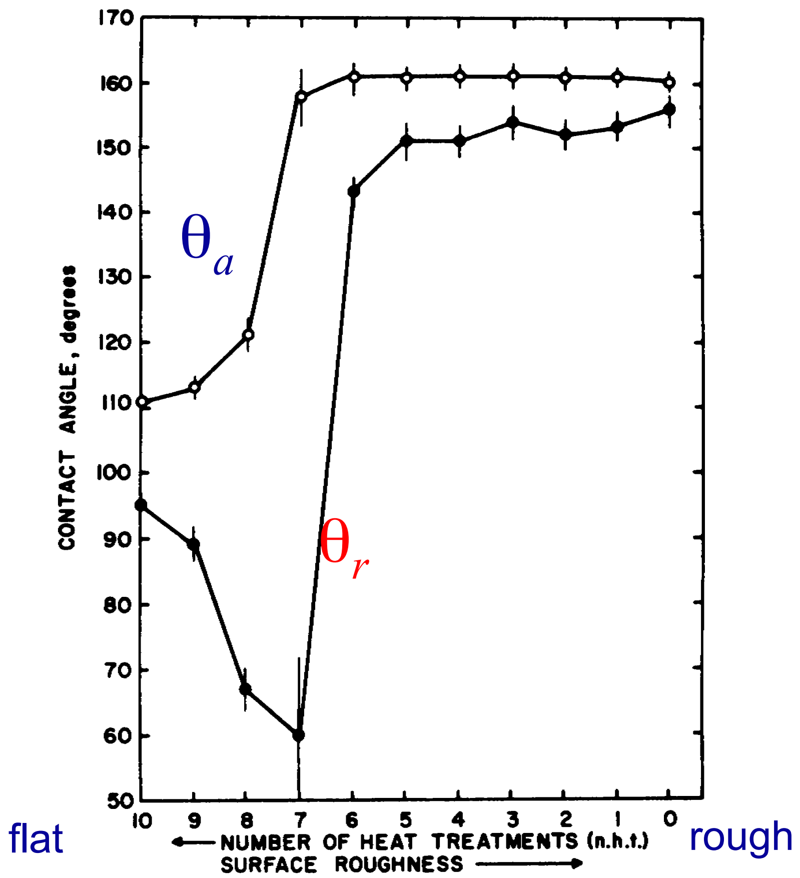


textured surfaces

with C.Marzolin & D.Quéré

recent insights: Mathilde Reyssat

hysteresis ↔ heterogeneities?

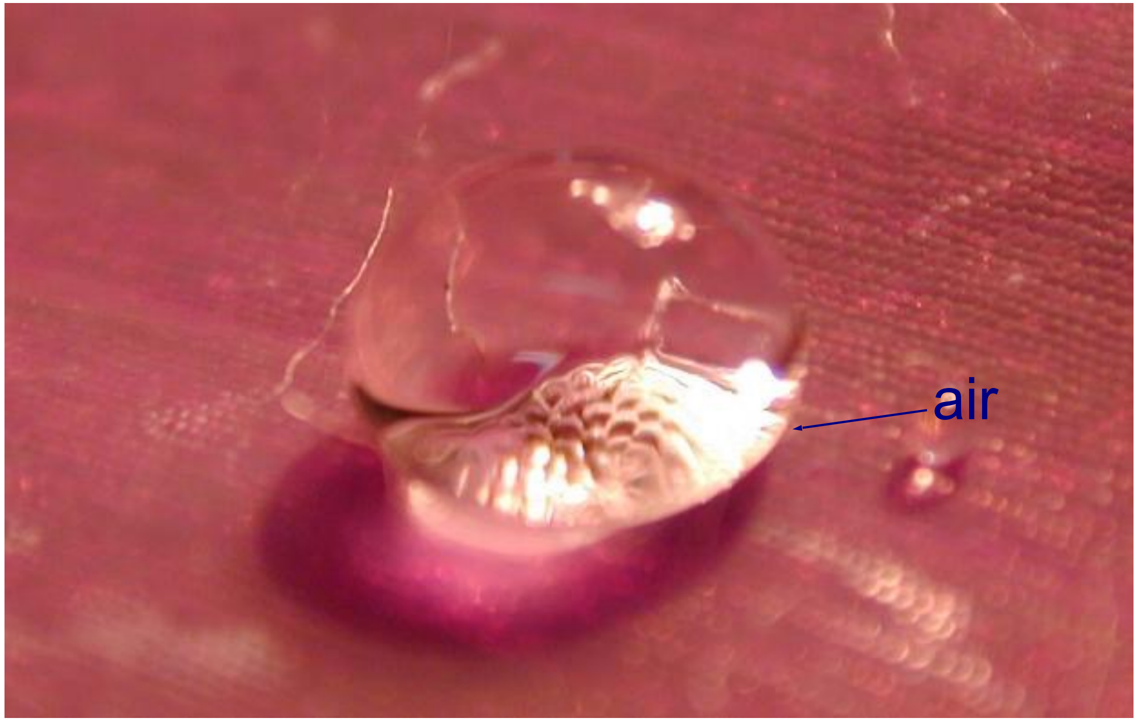


wax surface

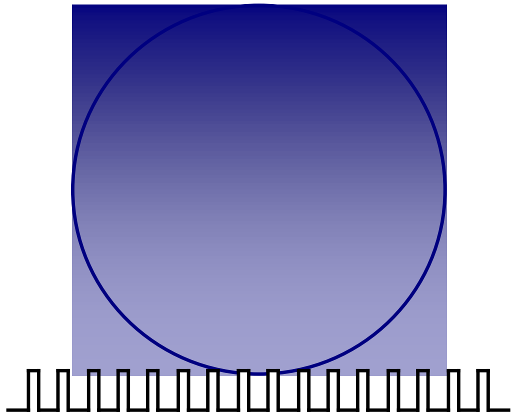
initially rough, then progressively heated up
to smooth it down by partial melting

Dettre & Johnson (1964)

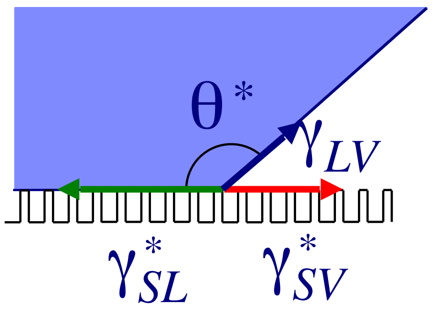
Mechanism: fakir carpet



air trapped under the liquid



Macroscopic contact angle



$$\phi_S = \frac{\text{top of asperities}}{\text{apparent area}}$$

"effective solid" = ϕ_S solid + (1-ϕ_S) air

$$\begin{cases} \gamma^*_{SV} = \phi_S \gamma_{SV} + \cancel{(1-\phi_S)\gamma_{VV}} \\ \gamma^*_{SL} = \phi_S \gamma_{SL} + (1-\phi_S)\gamma_{LV} \end{cases}$$

$$\cos\theta^* = \frac{\gamma^*_{SV} - \gamma^*_{SL}}{\gamma_{LV}}$$

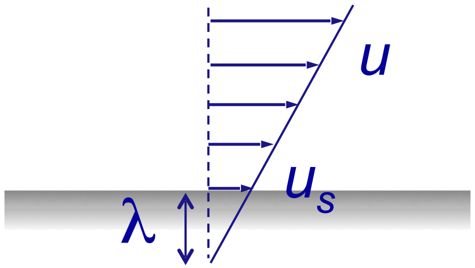
$$\cos\theta^* = -1 + \phi_S (1 + \cos\theta)$$

Cassie & Baxter (1944)

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

angle on a flat surface
of the same material

Slippery surfaces



classical experimental facts: $u_s = 0$

Navier's concept of possible slip (1823):

$$u_s = \lambda \left.\frac{\partial u}{\partial z}\right)_{surf}$$

λ: slip length

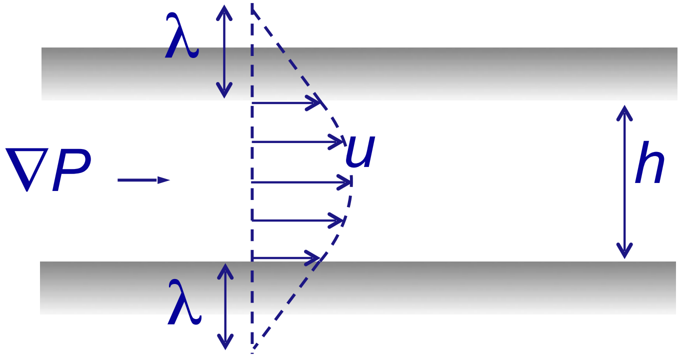
recent experiments and molecular dynamics simulations

- on smooth hydrophobic surfaces: λ ~ nm
- on textured super-hydrophobic surfaces: λ ~ texture size (μm)

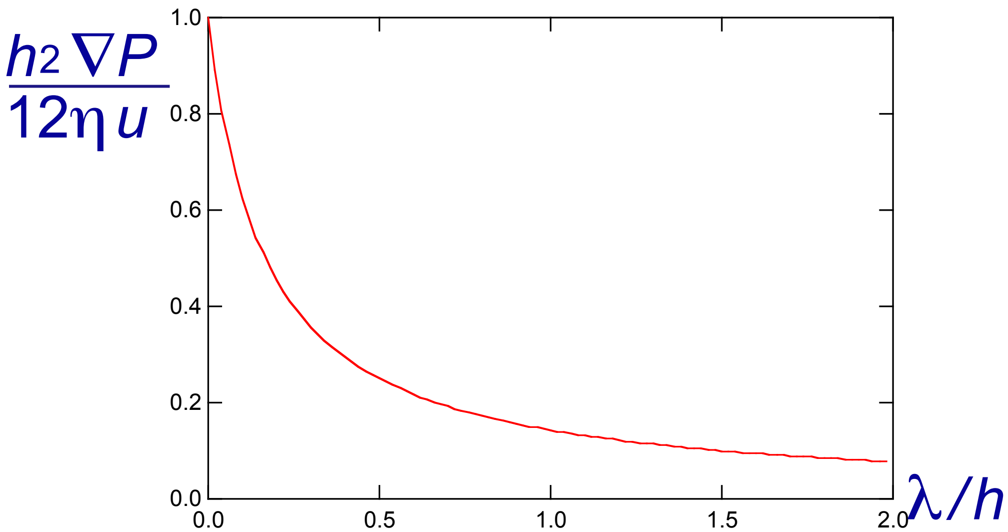
review J.Rothstein (2009)

Drag reduction ?

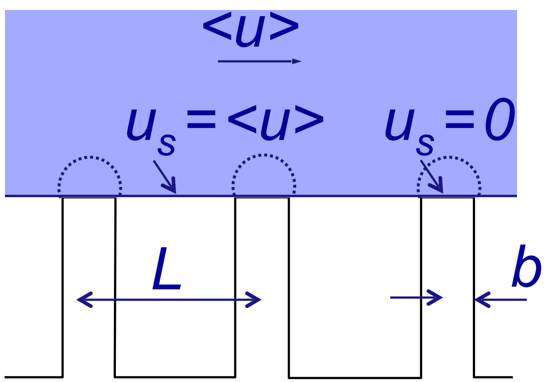
ex: Poiseuille flow between 2 plates



$$\nabla P = \frac{12\eta u}{h^2} \frac{h}{h+6\lambda}$$



Slip length on textured surfaces



dilute pillars:

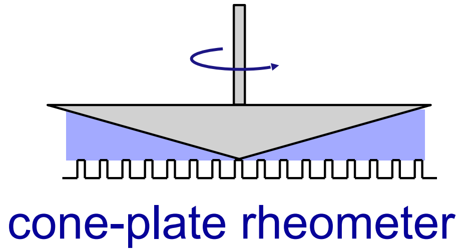
$$\langle\sigma\rangle \sim \phi_S \eta \frac{\langle u\rangle}{b} \sim \eta \frac{\langle u\rangle}{\lambda_{eff}}$$

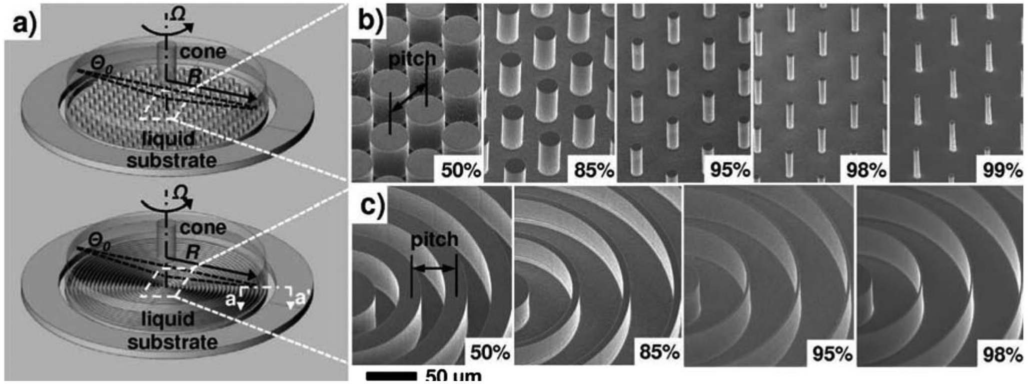
low Reynolds numbers
⇒ Stokes flow (laplacian) ⇒ scale ~ *b*

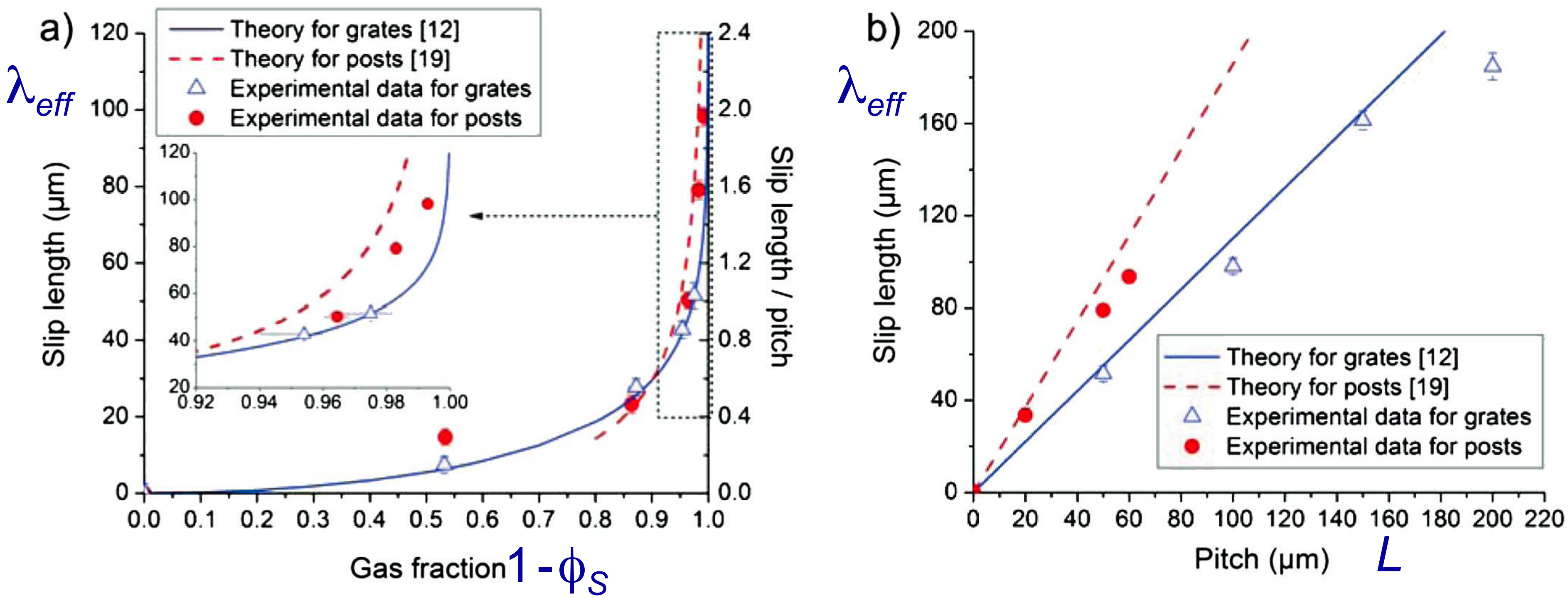
$$\lambda_{eff} \sim \frac{b}{\phi_S} \sim \frac{L}{\sqrt{\phi_S}}$$

Ybert & al. (2007)
see also Lauga & al.

Slip length on textured surfaces



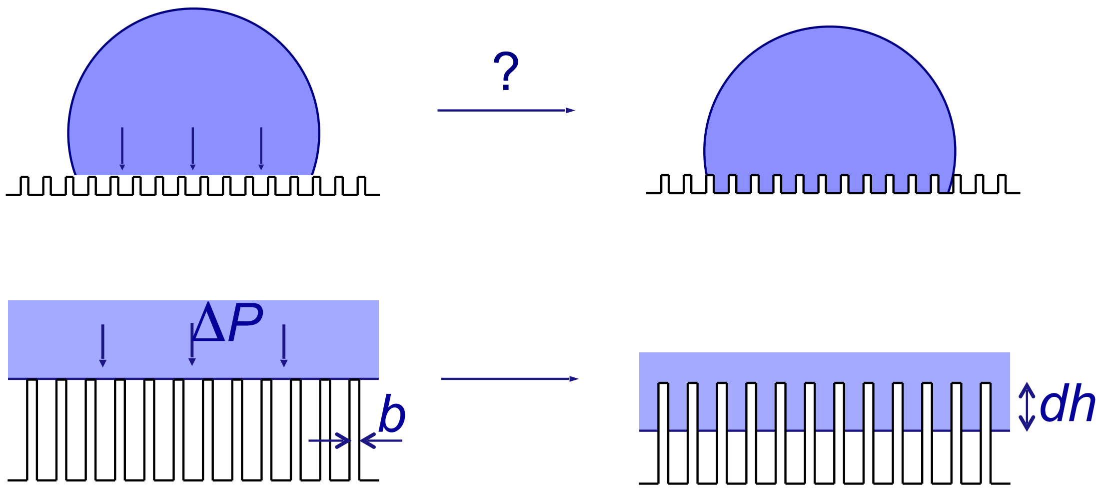




Lee & al. (2008)

also PIV measurements e.g. P.Tsai & al. (2009)

"Fat fakir"



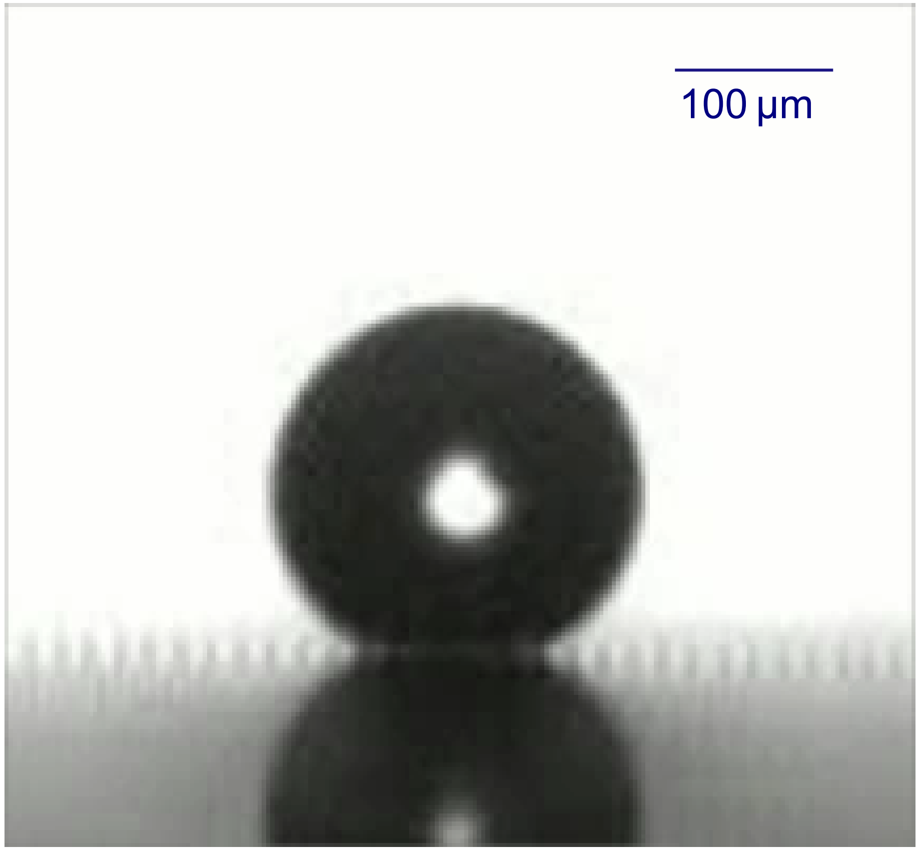
$$dV = A(1-\phi_S)\,dh$$

$$dS = 2A\frac{\phi_S}{b}dh \text{ (pillars surface)}$$

$$\Delta P\,dV = (\gamma_{SL} - \gamma_{SV})\,dS = \gamma\cos\theta\,dS$$

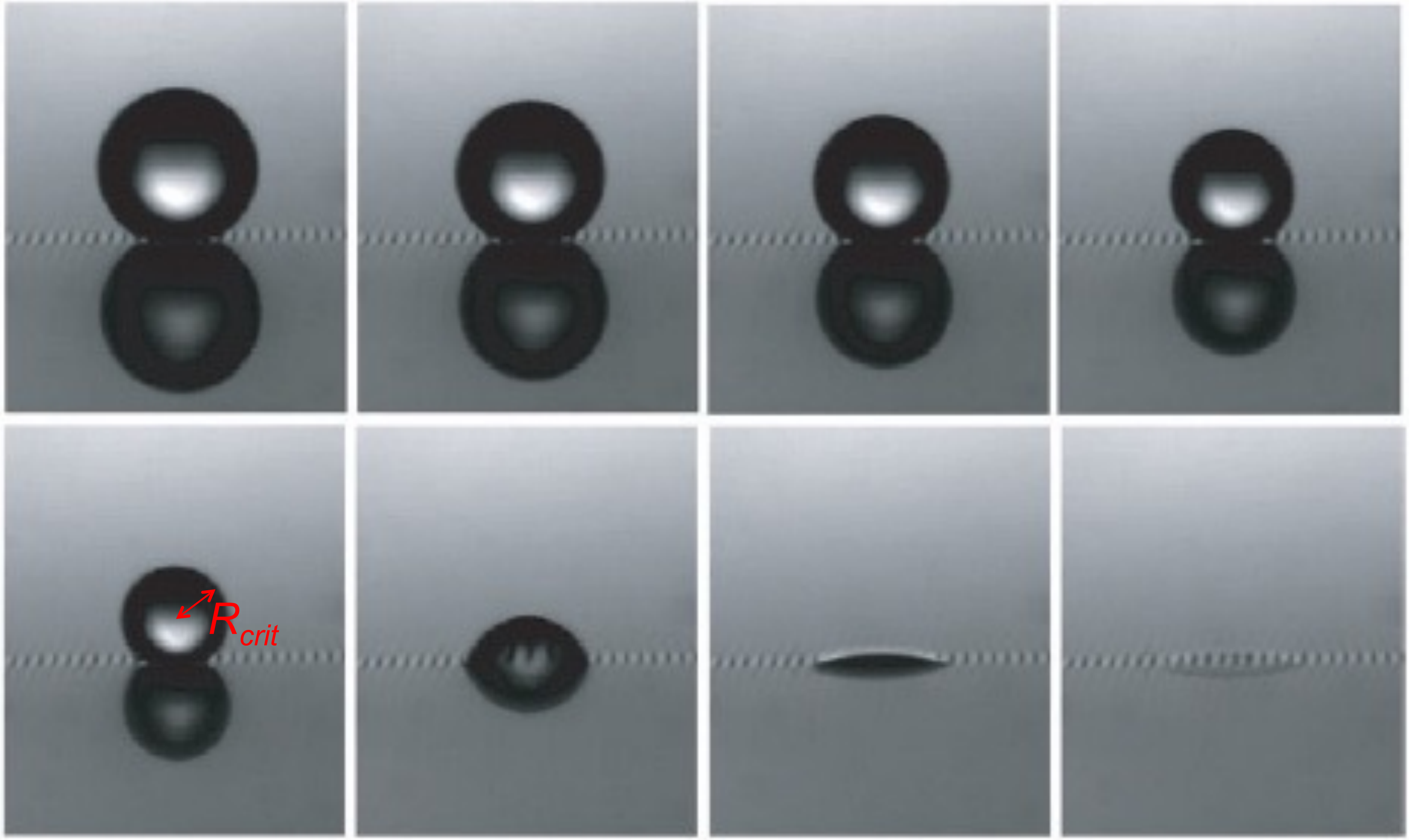
$$\Delta P_{crit} = \frac{2\gamma}{b}\frac{\phi_S}{1-\phi_S}$$

From big to skinny fakirs



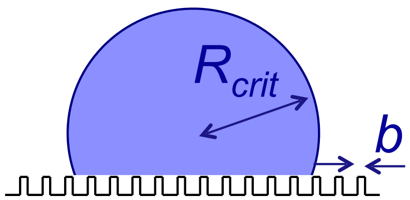
Mathilde Reyssat et al. (2008)

Critical radius



2 scenarios

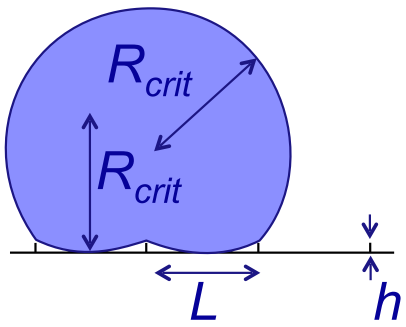
Critical pressure



$$\frac{2\gamma}{R_{crit}} = \Delta P_{crit} \ ? \quad \rightarrow \quad \boxed{R_{crit} = b\,\frac{1-\phi_S}{\phi_S}}$$

usually too small

Touch down

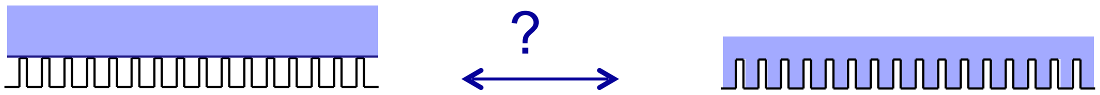


$$R_{interface} = R_{macroscopic}$$

$$\boxed{R_{crit} \sim \frac{L^2}{h}}$$

Reyssat et al. (2008)

A metastable state ?



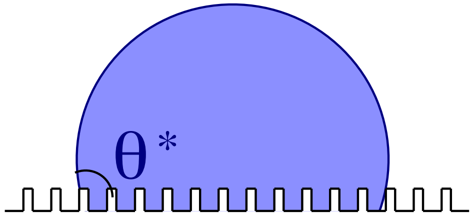
roughness factor: $r = \frac{\text{actual area}}{\text{apparent area}}$

$$\Delta E_S = (r - \phi_s)(\gamma_{SL} - \gamma_{SV}) - (1 - \phi_s)\gamma_{LV}$$

$\Delta E_S < 0$ if $\theta < \theta_c$, $\cos\theta_c = -\frac{1 - \phi_s}{r - \phi_s}$

with U.Thiele & D.Quéré

Wenzel regime



liquid inside the roughness
⇒ actual surface amplified

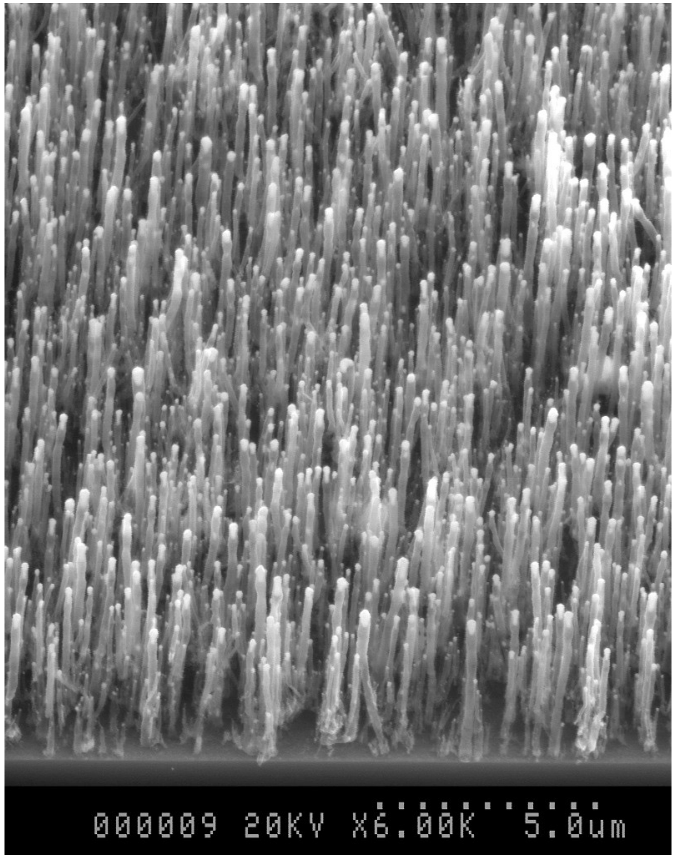
"effective solid" = *r* solid

$$\begin{cases} \gamma_{SV}^{*} = r\,\gamma_{SV} \\ \gamma_{SL}^{*} = r\,\gamma_{SL} \end{cases}$$

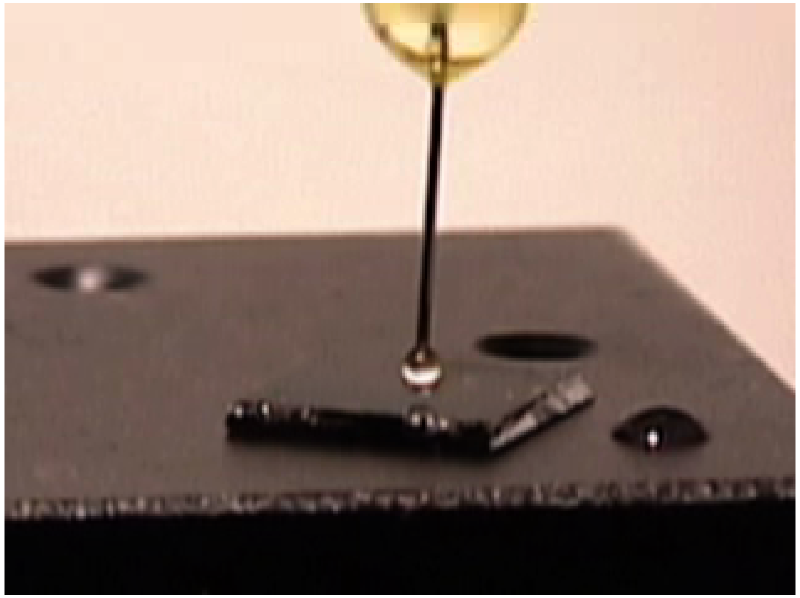
$$\cos\theta^{*} = r\cos\theta$$

Wenzel (1949)

Super-hydrophilic surfaces ?



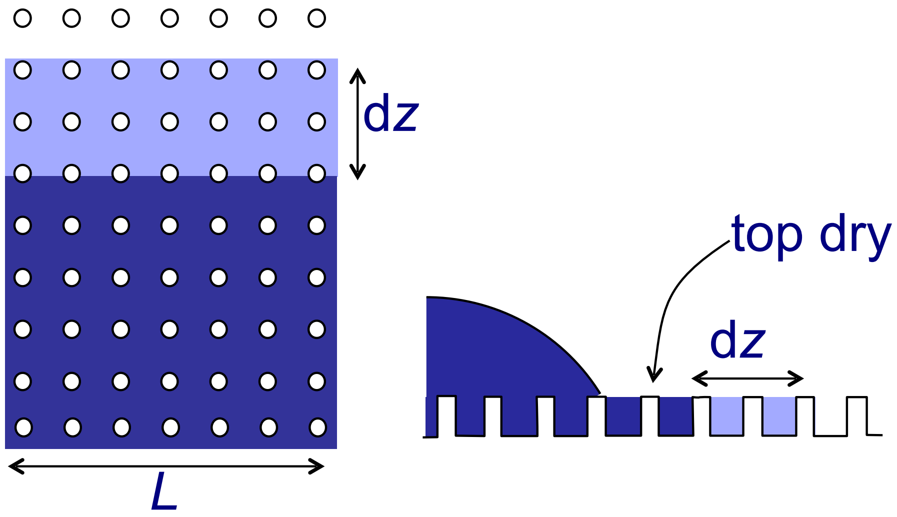
Nanotubes forests



with K.Teo, K.Lau, M.Chhowalla, G.A.G. Amaretunga, W.I. Milne, G.McKinley & K.Gleason

imbibition dynamics ⇒ Mathilde & Étienne Reyssat

Condition for imbibition



$$\phi_S = \frac{\text{top of asperities}}{\text{apparent area}}$$

$$r = \frac{\text{real area}}{\text{apparent area}}$$

$$dE_S/L = (r - \phi_S)\,(\gamma_{SL} - \gamma_{SV})\,dz + (1 - \phi_S)\,\gamma_{LV}\,dz$$

top dry $\quad \gamma_{SL}\cos\theta$

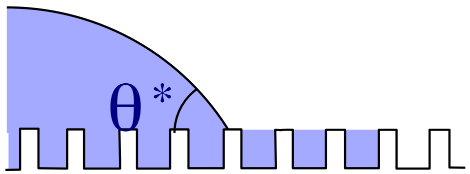
imbibition if $dE_S < 0 \Leftrightarrow \theta < \theta_c$

$$\cos\theta_c = \frac{1 - \phi_S}{r - \phi_S}$$

$r \to \infty$ porous media: rise if $\theta < 90°$

$r \to 1$ flat surface: rise if $\theta = 0$

Contact angle on an imbibed surface

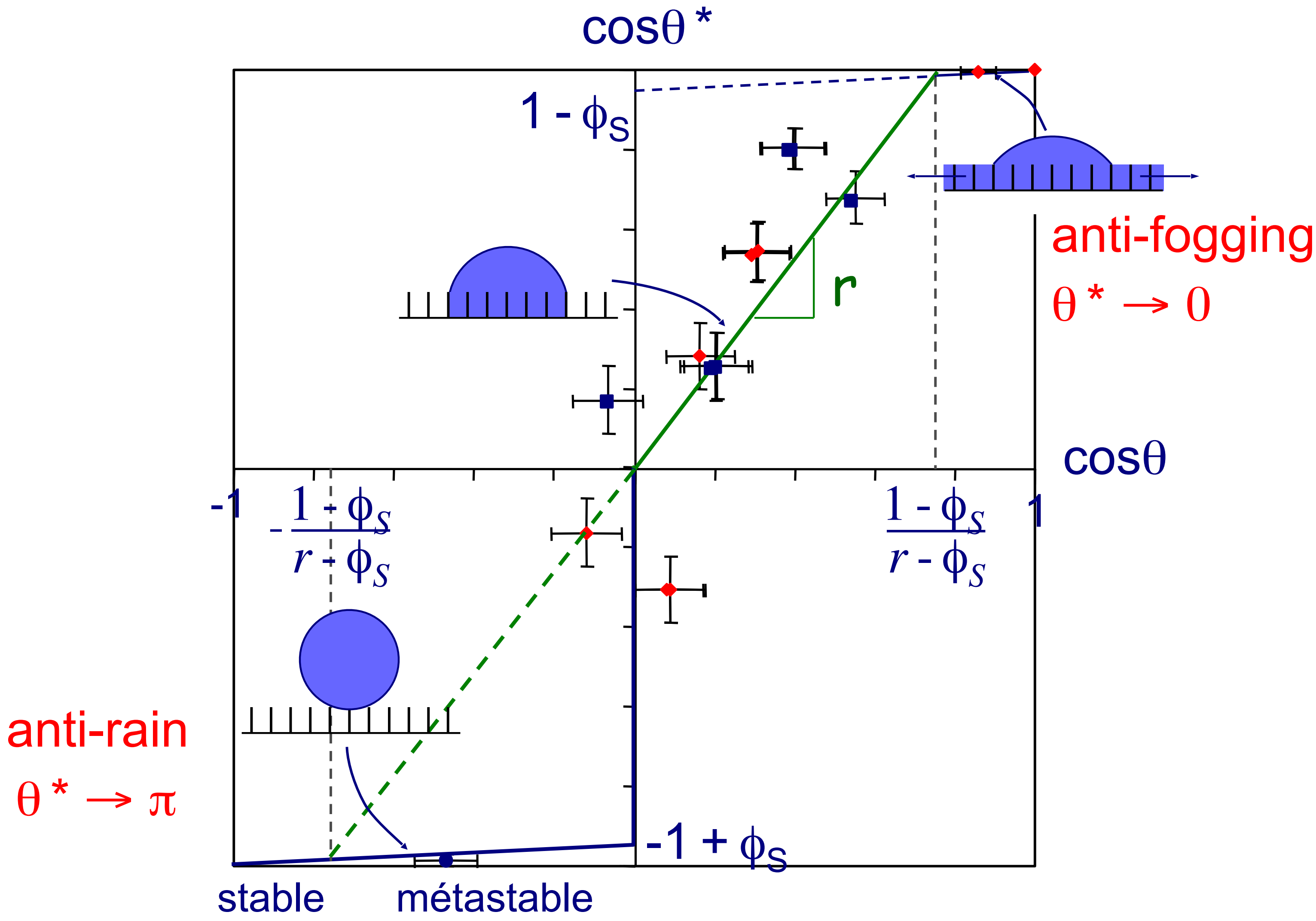


"effective solid" = ϕ_S solid + (1-ϕ_S) liquid

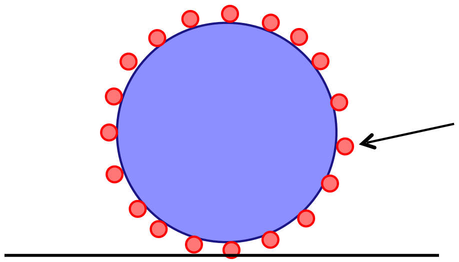
$$\begin{cases} \gamma_{SV}^{*} = \phi_S \gamma_{SV} + (1-\phi_S)\gamma_{LV} \\ \gamma_{SL}^{*} = \phi_S \gamma_{SL} + \cancel{(1-\phi_S)\gamma_{LL}} \end{cases}$$

$$\cos\theta^{*} = 1 - \phi_S (1 - \cos\theta)$$

From anti-rain to anti-fog materials



Coated droplets



hydrophobic particles, $\theta > 90°$

(if $\theta < 90°$, particles immersed in the liquid)

Adhesion of the particles?

$$\Delta E_S/S = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta) > 0$$

$\Rightarrow$ always some adhesion

Liquid marbles

shape: centrifuge forces / surface tension

$$\underbrace{\text{centrifuge forces}}_{\rho R^2 \omega^2} \;/\; \underbrace{\text{surface tension}}_{\gamma / R}$$

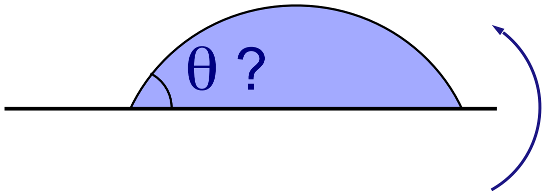
$$\Omega = \frac{\rho R^2 \omega^2}{\gamma}$$

$\Omega << 1 \Rightarrow$ sphere $\Omega \sim 1 \Rightarrow$ peanut, doughnut $\Omega >> 1 \Rightarrow$ breakup

Pascale Aussillous

[redacted]

A well defined contact angle?



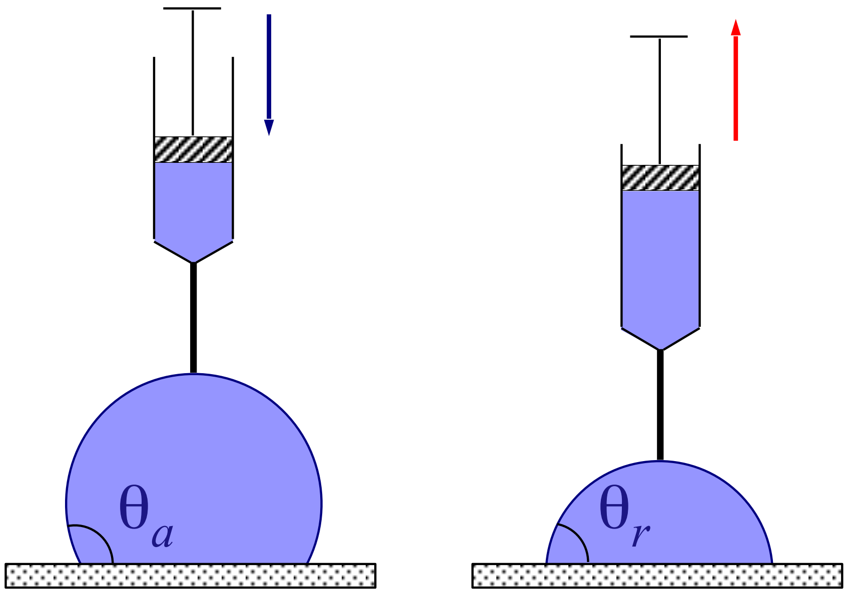
Young's relation:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

D.Quéré, C. Clanet, M. Fermigier

Contact angle hysteresis

D.Quéré, C. Clanet, M. Fermigier

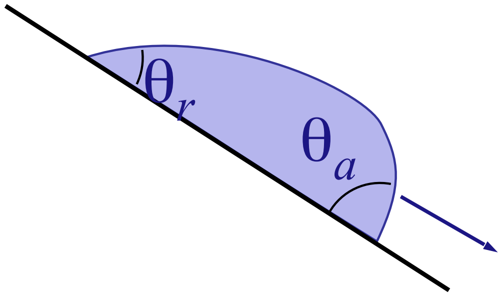


$$\theta_a > \theta_{Young} > \theta_r$$

$\longrightarrow$ hysteresis

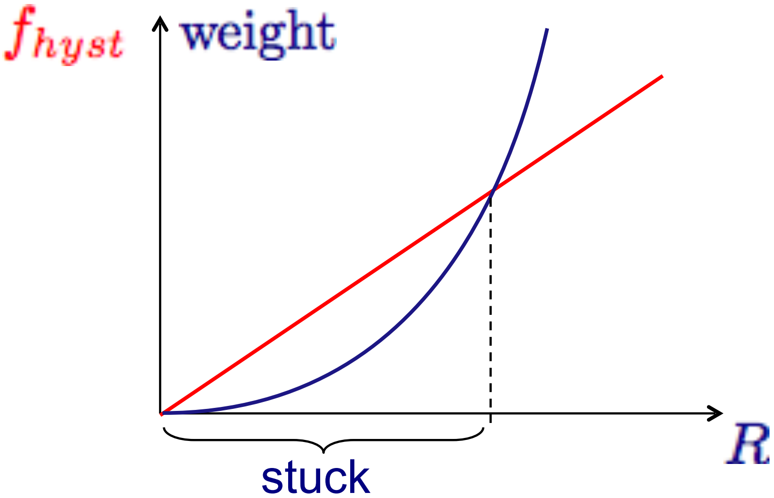
"clean" surface: $\theta_a - \theta_r \sim 5°$

Droplet sticking on a window

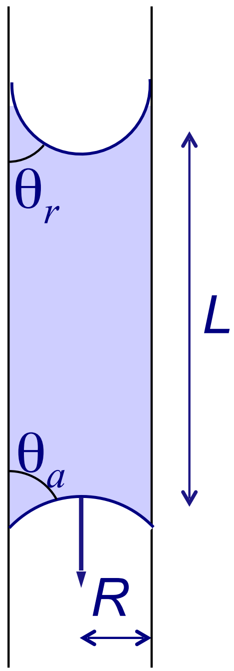


$$f_{hyst} \sim R\gamma\,(\cos\theta_r - \cos\theta_a)$$

$$\text{weight} \sim R^3 \rho g \sin\alpha$$



Index in a straw



balance for:

$$2\pi R\gamma\left(\cos\theta_r - \cos\theta_a\right) = \pi R^2 \rho g L$$

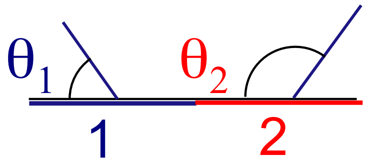
moves if:

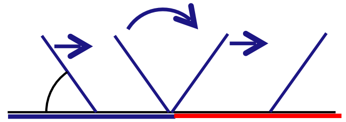
$$L > \frac{2\gamma}{\rho g R}\left(\cos\theta_r - \cos\theta_a\right)$$

Origin of hysteresis

heterogeneities on surfaces:

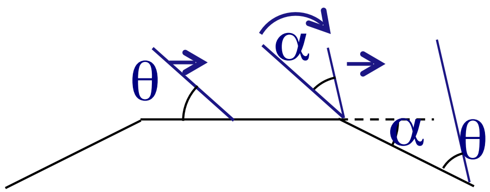
→ chemistry



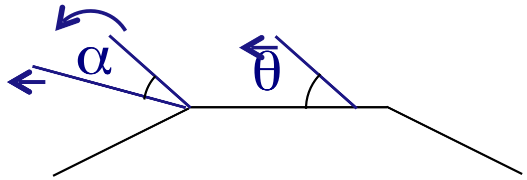


$$\begin{cases} \theta_a = \theta_2 \\ \theta_r = \theta_1 \end{cases}$$

→ geometry



$$\theta_a = \theta + \alpha$$



$$\theta_a = \theta - \alpha$$