The Super-hydroprepellence of fractal surfaces

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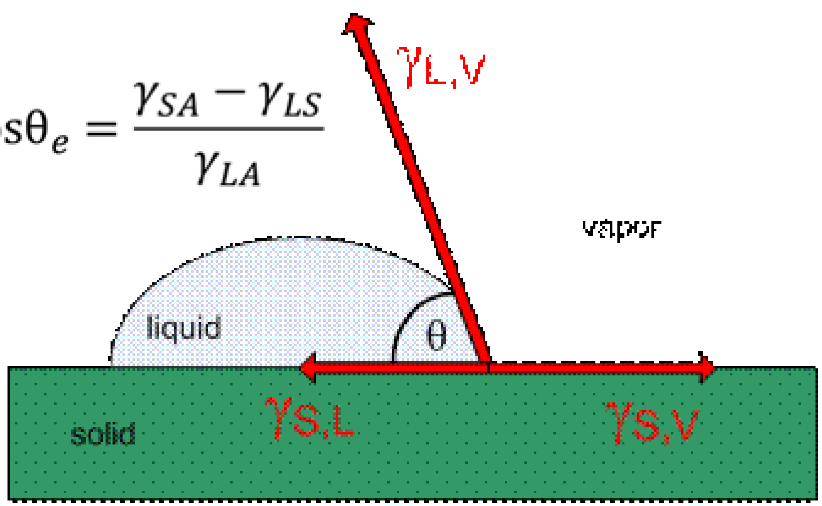
Surface tension and contact angle

✓ When a drop is placed on a flat substrate, the contact angle at the triple line is determined by Young's equation

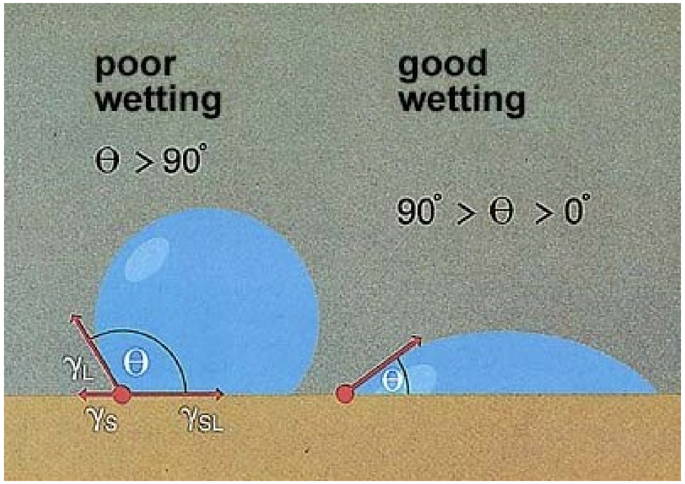
$$\gamma_{LA}\cos\theta_e + \gamma_{LS} - \gamma_{SA} = 0$$

Equilibrium equation at triple line

$$\cos\theta_e = \frac{\gamma_{SA} - \gamma_{LS}}{\gamma_{LA}}$$



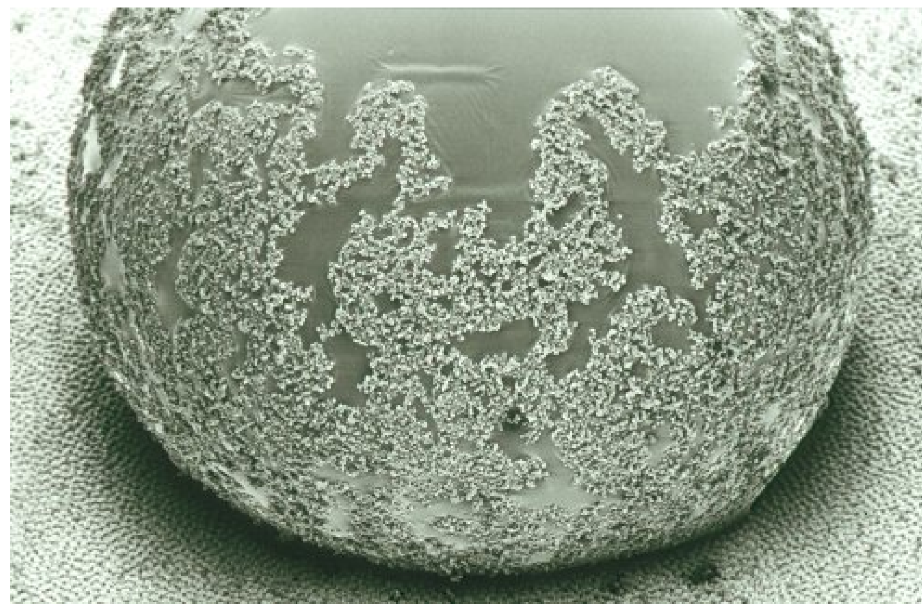
Tipically on flat surfaces: $\theta_e \leq 120°$



What is super-hydrorepellence?

- When a drop is placed on a properly rough surface the macroscopic contact angle (CA) is largely increased resulting in:
  - ✓ an almost spherical drop
  - ✓ a self-cleaning surface

Pearl drops:
A super-hydrophobic spray on wood (BASF)

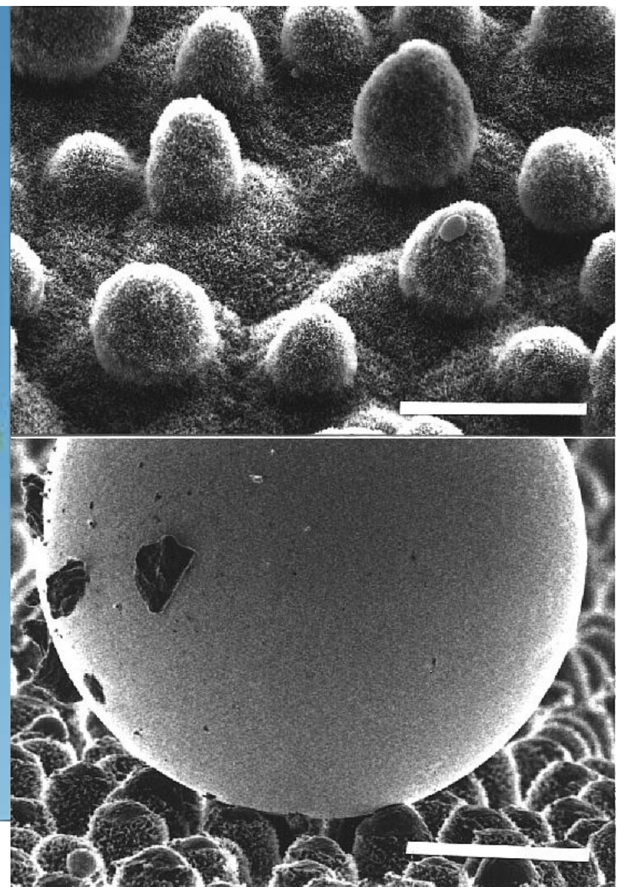


Self-cleaning effect:
The drop, not being able to adhere to the underlying surface, captures dirt particles during its rolling motion

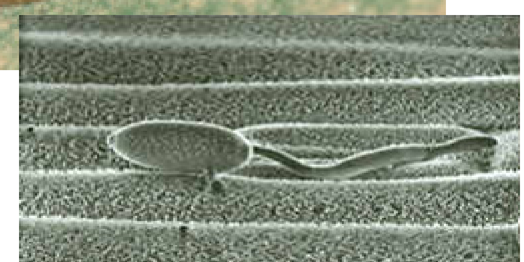
The Nature lesson

- ✓ The biologist Barthlott was the first who observed roughness induced super-hydrophobicity in 1997 on the leaf of Lotus plant.
- ✓ Since then, this phenomenon has been called Lotus-Effect®.

The Lotus leaf

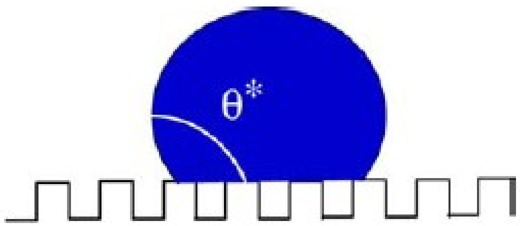


The micro structure of the Lotus leaf: Water repellence is produced by epidermal cells (papillae) and superimposed epicuticular waxes. Bar-length = 20 µm (adapted from *Barthlott, W; Neinhuis, C. Planta. 1997, 202, 1-8*).

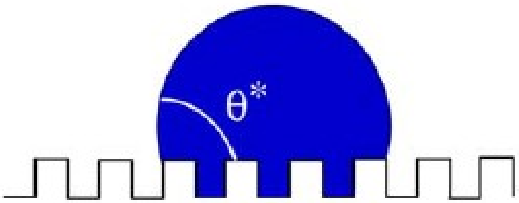


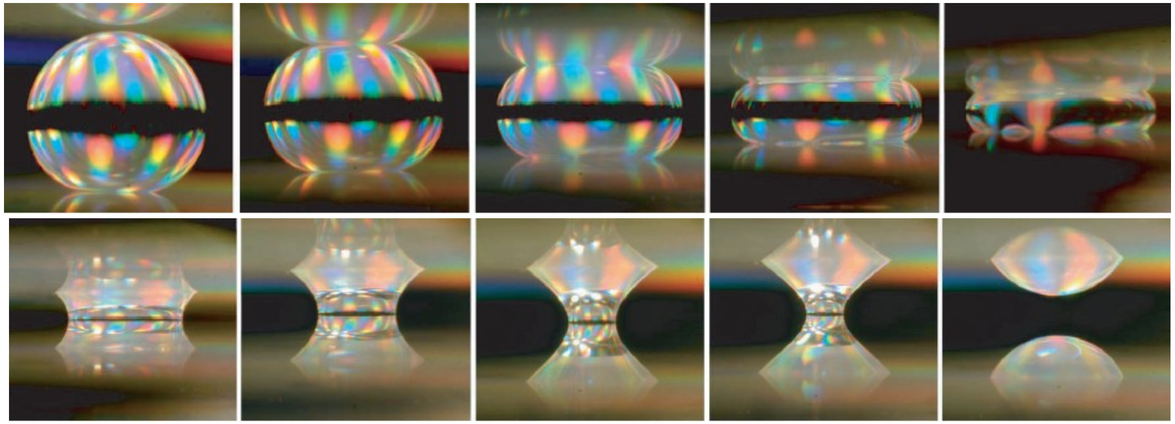
The Cassie and the Wenzel states

- **Cassie state**
  - ✓ Very high contact angle up to 174°
  - ✓ The drop does not stick to the surface: **self-cleaning**



- **Wenzel state**
  - ✓ Contact angle up to 155°
  - ✓ Sticky drop: **no self-cleaning effect**





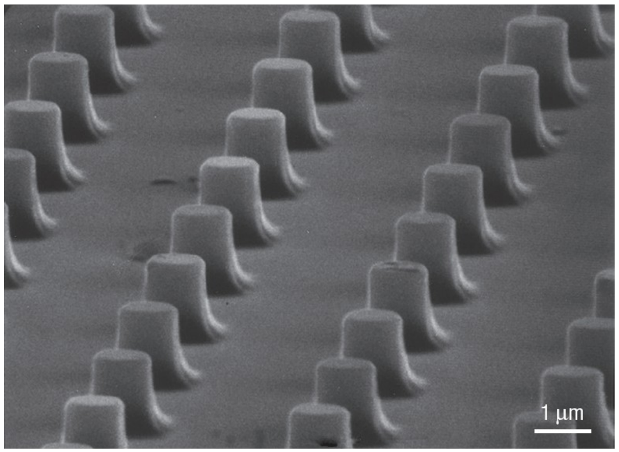
← Cassie state

Increasing the drop pressure beyond a certain critical value may cause an irreversible transition from the Cassie to the Wenzel state.

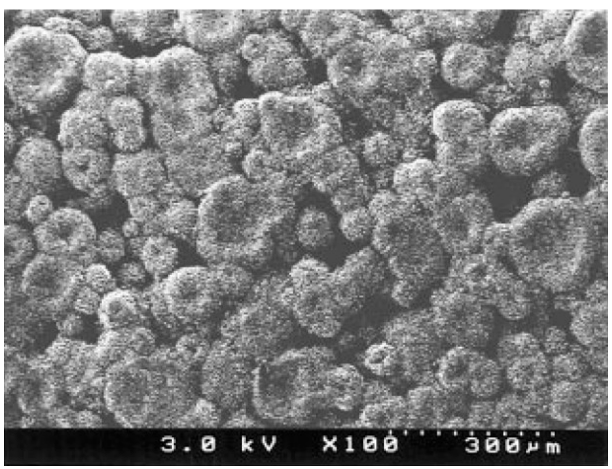
← Wenzel state

Lafuma, Quéré, Nature Materials, **2**, 457, 2003

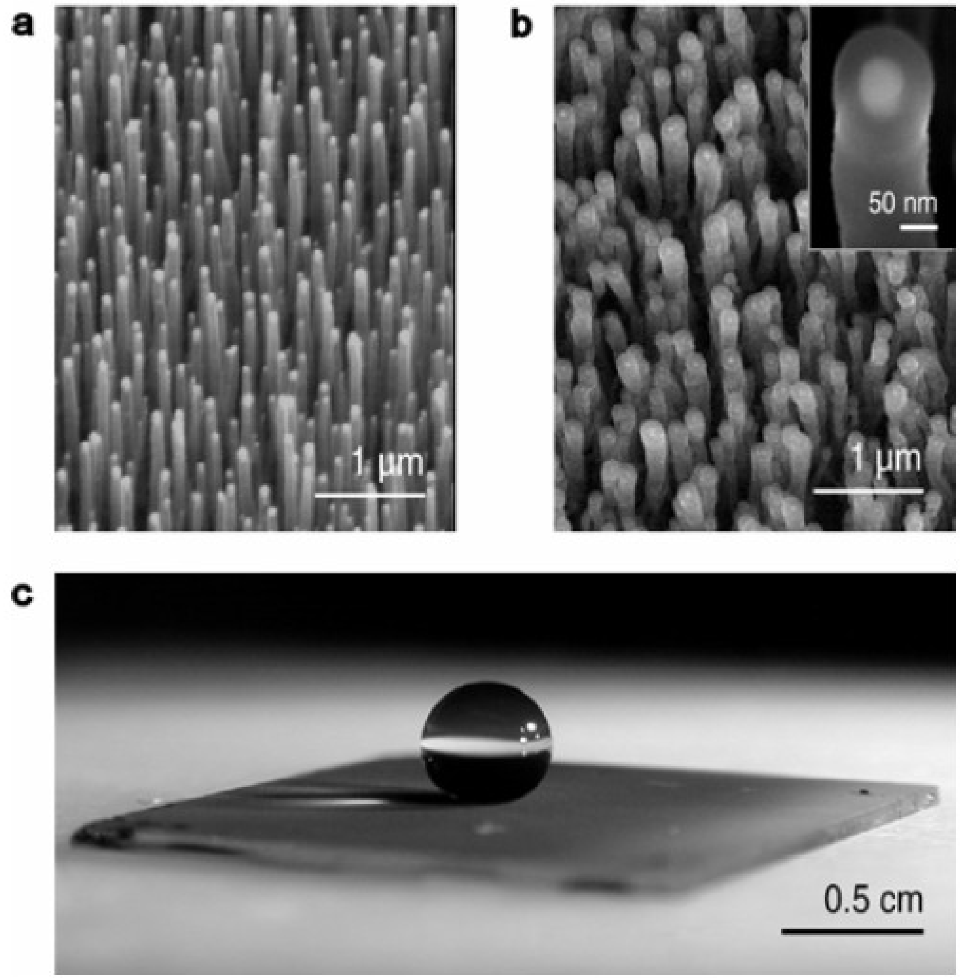
Can we mimic Nature?



A uniform array of micro-pillars



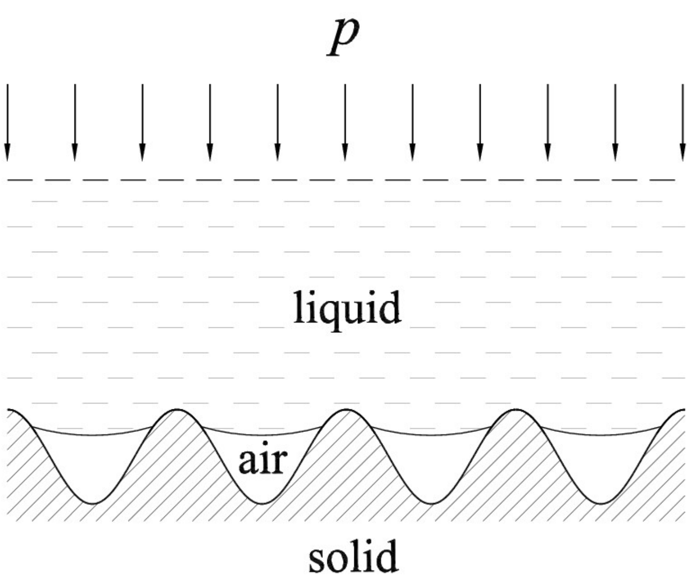
A fractal surface



A carbon nanotube forest

Mathematical insight: the one scale rough substrate

- **Physical Model**
  - ✓ A drop in contact with a sine wave profile (2-D)
  - ✓ The pressure *p* inside the drop is uniformely distribuited



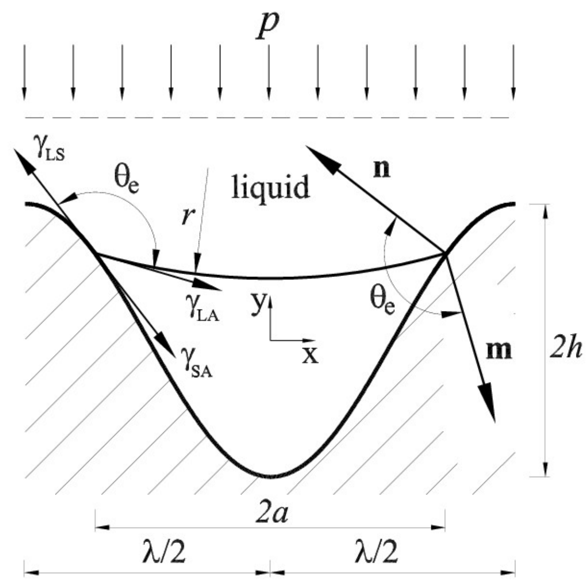
$$-\cos\theta_e = \frac{\gamma_{LS} - \gamma_{SA}}{\gamma_{LA}} > 0$$

$$r = \gamma_{LA} / p$$

$$\cos\theta_e = \mathbf{m} \cdot \mathbf{n}$$

$$\Delta = h - s_0$$

s_0 is the distance between the mean plane of the rough surface and the mean plane of the liquid profile

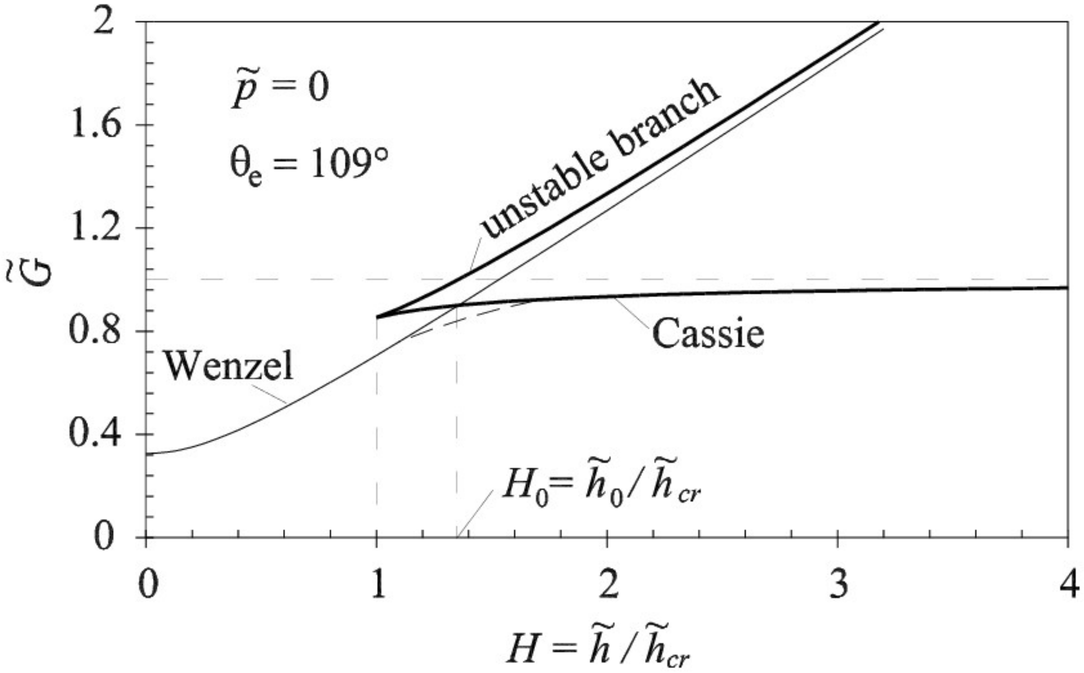


The total energy per unit thickness (Gibbs free entalpy) is ➡ $G = F - p\lambda\Delta$

The Helmholtz free energy per unit thickness is ➡ $F = (\gamma_{LS} - \gamma_{SA}) l_{LS} + \gamma_{LA} l_{LA}$

Carbone G., Mangialardi L., Eur. Phys. J. E 16, 67–76

The stability diagram at zero pressure



If $\tilde{h} = h/\lambda$ is below a critical value the only available state is the Wenzel one. A bifurcation occurs at such critical value, beyond which a stable Cassie state exists.

$$\tilde{G} = G / \lambda \gamma_{LA}$$

$$\tilde{h}_{cr} = 2\pi h_{cr} / \lambda = -\tan \theta_e$$

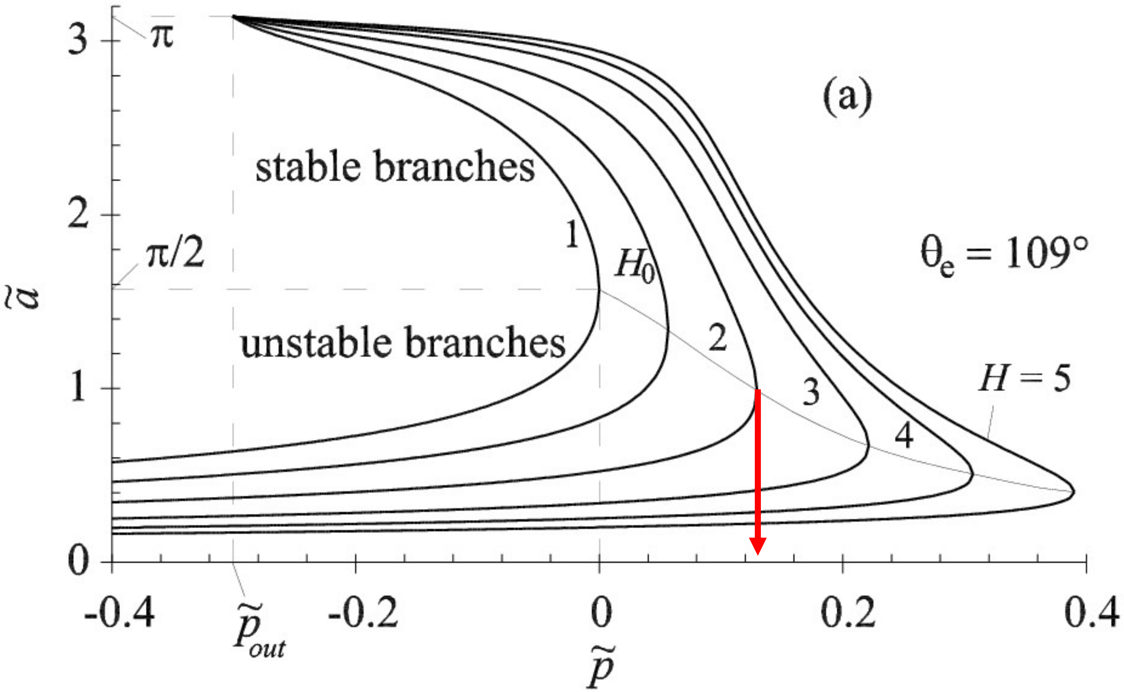
$$H = \tilde{h} / \tilde{h}_{cr}$$

The macroscopic contact angle

$$-\cos\theta = \frac{F}{\lambda \gamma_{LA}} = -\cos\theta_e \frac{l_{LS}}{\lambda} + \frac{l_{LA}}{\lambda}$$

The critical pressure p_W

- For each value of dimensionless amplitude h/λ a critical value of drop pressure p_W can be found at which the Cassie state is unstable and a transition to the Wenzel state occurs
- The critical pressure p_W increase as h/λ is increased



The dimensionless apparent half-extension of the liquid/air interface as a function of the dimensionless drop pressure.

Non dimensional quantities

$k = 2\pi / \lambda$ (dimensional)

$\tilde{p} = p / (k\gamma_{LA})$

$\tilde{a} = ka$

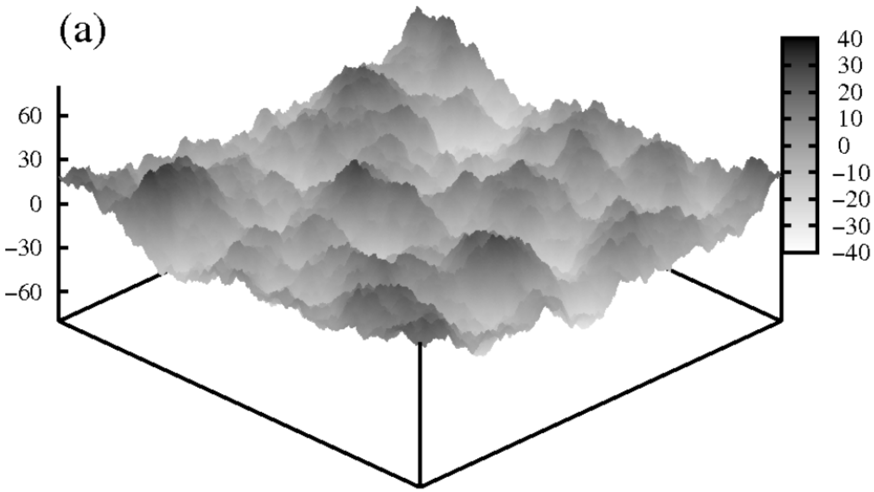
$\tilde{h} = kh$

$H = h / h_{cr}$

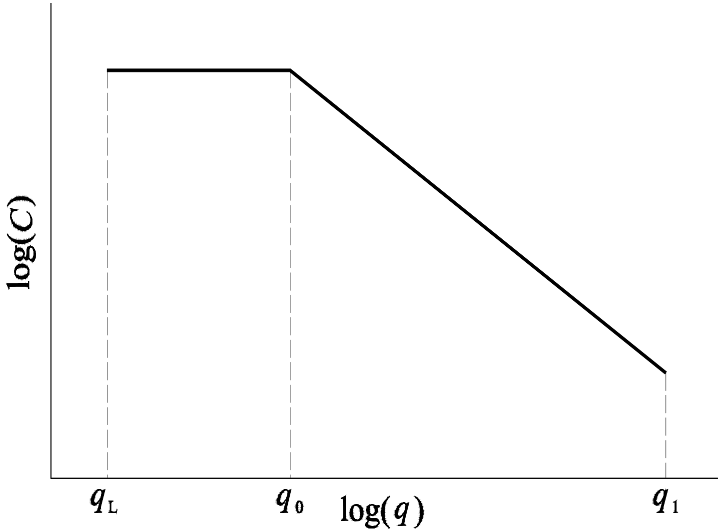
$\tilde{h}_{cr} = -\tan\theta_e$

Fractal randomly rough surfaces

- Rough surfaces often present self-affine properties which lead to fractal geometry.
- These kind of surfaces can be relatively easily produced by means of chemical or physical processes.
- Some very recent experimental investigations (S. Sarkar et al. APL, **96**, 063112 (2010)) have shown that a correlation seems to exist between the statistical properties of the fractal surface and its wettability.
- However the question is still open and it is not yet clear what is the main paramenter that should be tuned to control the hydrorepellence of such surfaces.



An numerically generated fractal surface



PSD of a self-affine fractal surface

The Self-Affine Fractal profile

- It is easy to show that the a self-affine fractal profile is completely determined once known the following three quantities

$$m_0 = \left\langle h(x)^2 \right\rangle$$

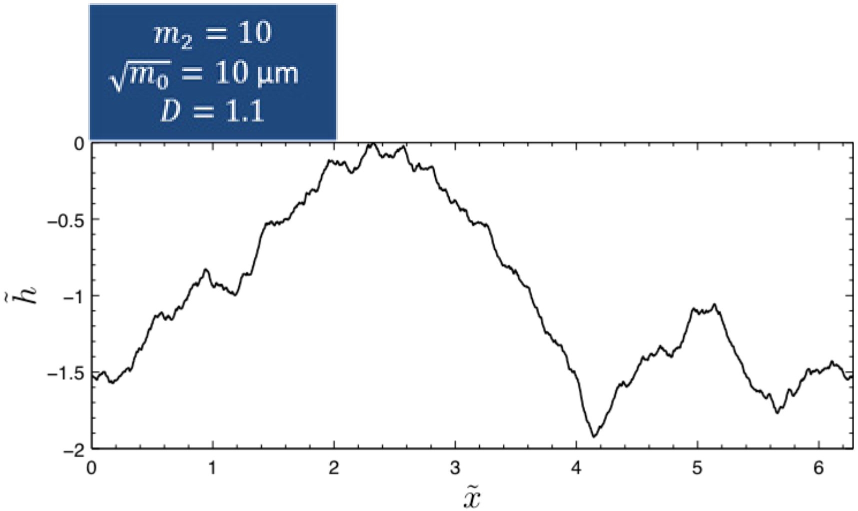
The mean square of the height distribution

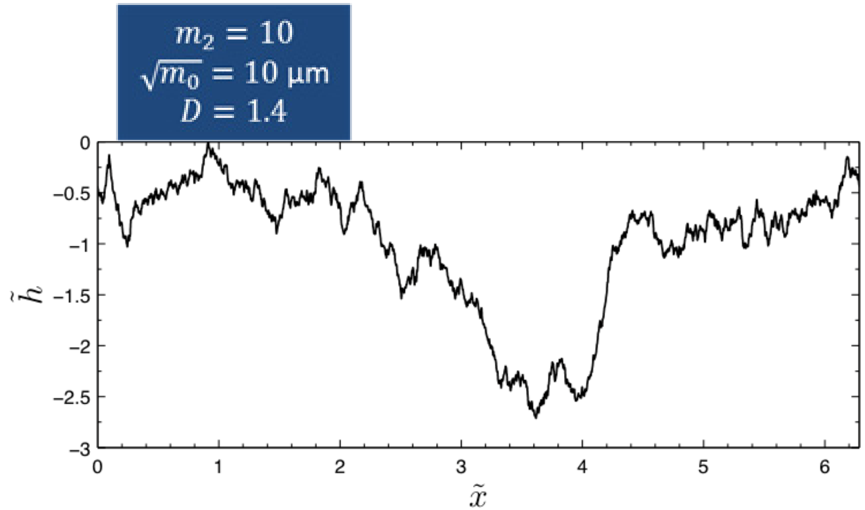
$$D$$

The fractal dimension

$$m_2 = \left\langle h'(x)^2 \right\rangle$$

The mean square of the slope distribution





Example: the effect of the fractal dimension on the shape of the profile

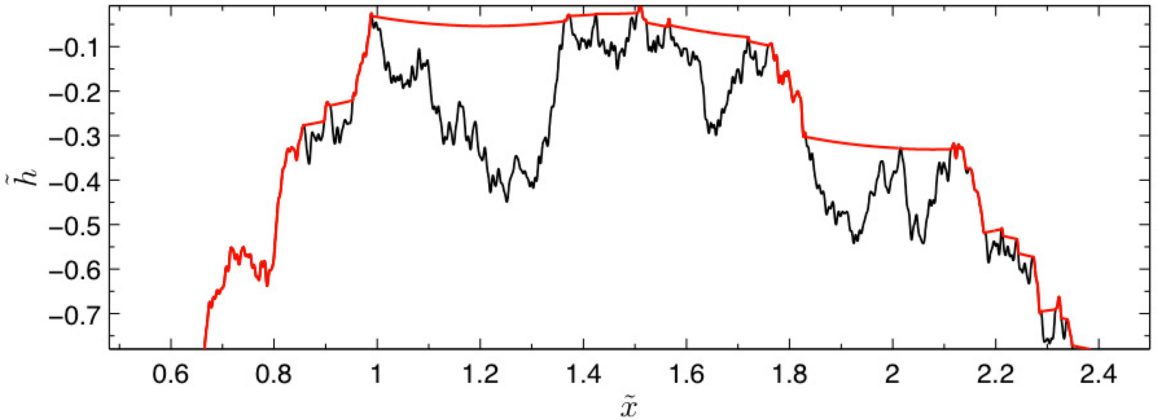
The liquid-substrate composite interface

- The liquid profile:

$$u_L(x) \begin{cases} = u_S(x) & \textit{In the contact regions} \\ = y_{c_i} - \sqrt{r^2 - (x - x_{c_i})^2} & \textit{In the non-contact regions} \end{cases}$$

- The equation of state (the liquid is considered incompressible)

$$\frac{1}{\lambda}\sum_{i=1}^{n}\left(\int_{a_i}^{b_i} u_S(x)dx + \int_{b_i}^{a_{i+1}} u_L(x)dx\right) = f(a_1, b_1, \dots, a_n, b_n, p, \Delta) = 0$$



Finding the equilibrium state

- The total energy of the system is thus the Gibbs energy (per unit thickness)

$$G(a_1, b_1, \ldots, a_n, b_n, p) = \gamma_{LA} l_{LA} + (\gamma_{LS} - \gamma_{SA}) l_{LS} - p\lambda\Delta$$

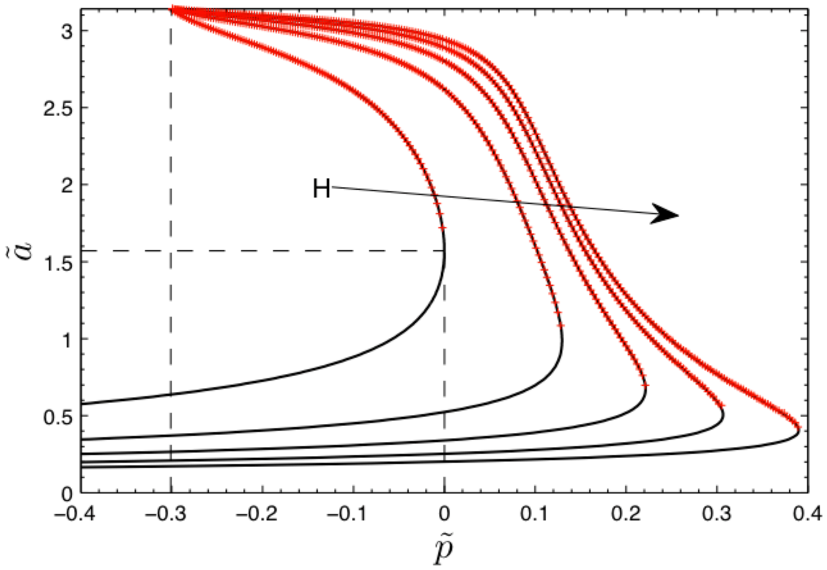
l_{LS}, l_{LA}	Liquid-Solid, Liquid-Air interfacial lengths

✓ For any given value of the contact pressure p the minimum of the Gibbs energy per unit thickness is found by means of a conjugate gradient algorithm approach.

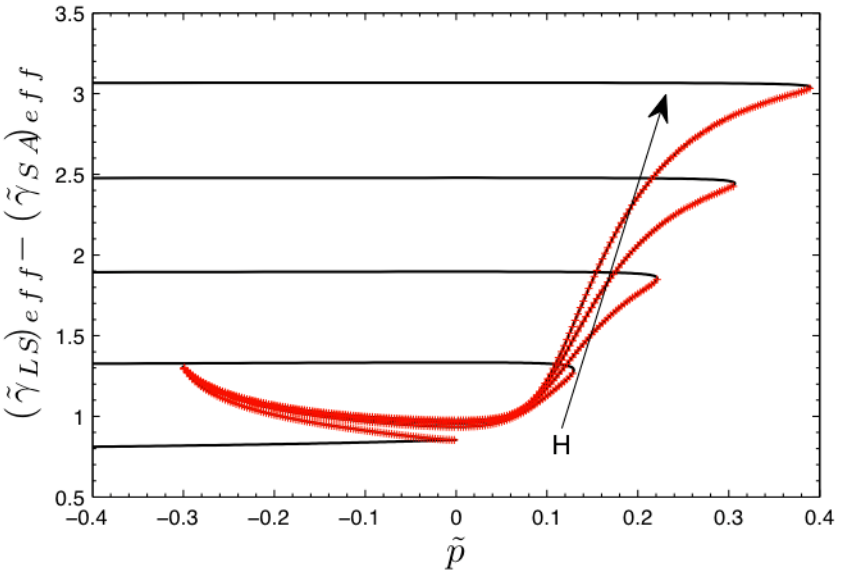
✓ The birth, death and coalescence of contact areas is taken in consideration which make the problem strongly nonlinear

✓ For any given value of the contact pressure, the mixed interface is fully characterized and the actual contact area, the penetration Δ, the actual interfacial energy and the apparent contact angle are calculated

Numerical model validation: sinusoidal profile

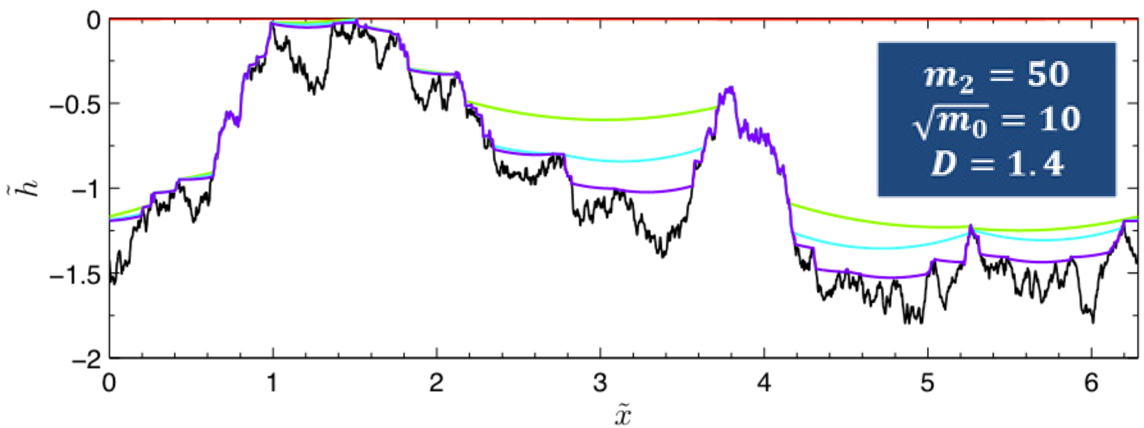


Analytical results: black continuous line
Numerical results: red markers



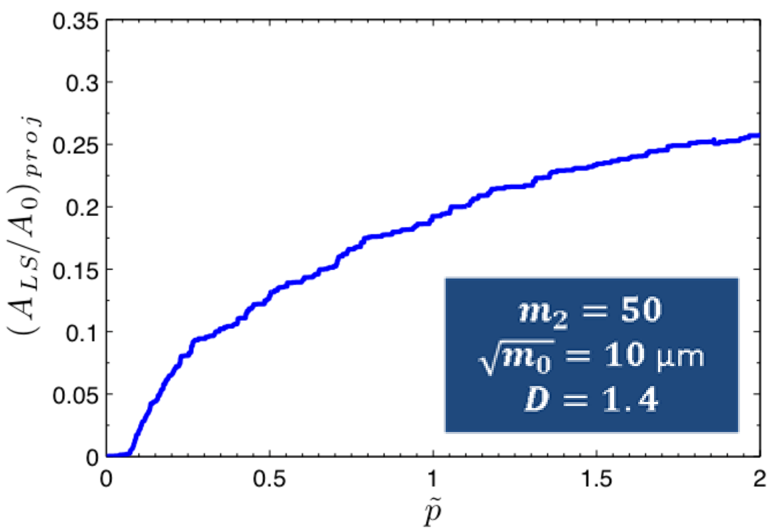
- ✓ **Only stable branches can be calculated**
- ✓ **Full matching between analytical and numerical results**
- ✓ **The agreement is excellent whatever is the dimensionless amplitude of the sinusoid.**

Numerical simulation

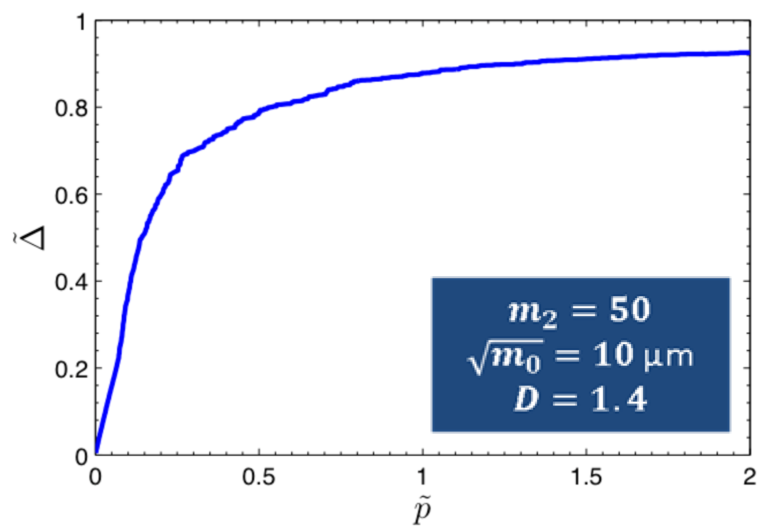


- ✓ The contact interface between the liquid (red-green-cyan lines with increasing pressures) and the rough profile.
- ✓ Each set of parameters is used to generate 30 profiles. The results are then averaged

The non dimensional contact area as a function of the non dimensional drop pressure

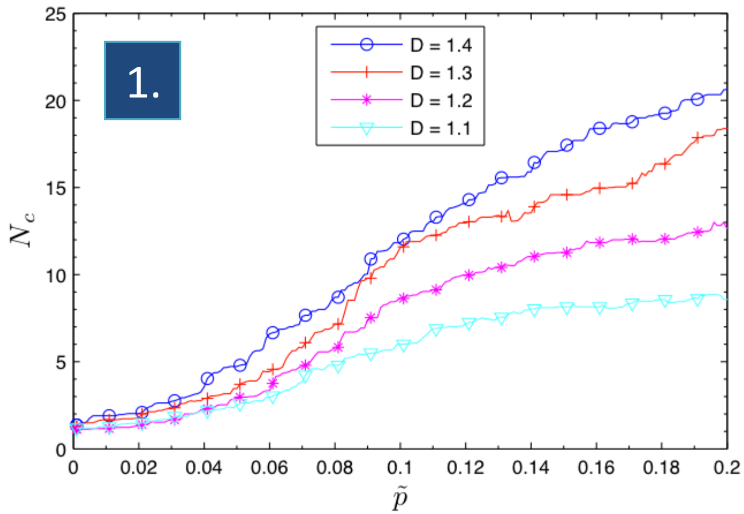


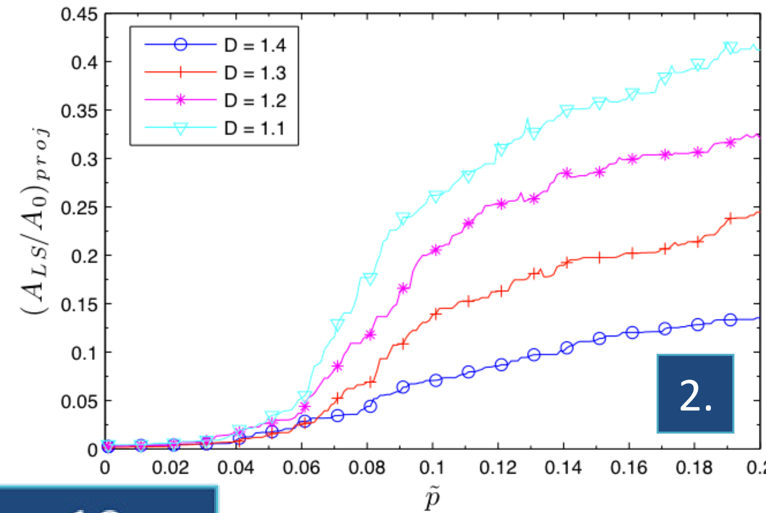
The non dimensional penetration as a function of the non dimensional drop pressure

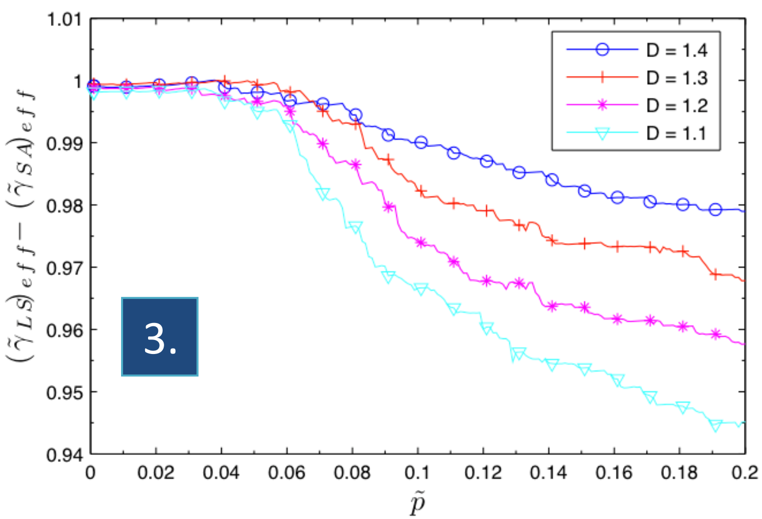


TriboLAB trasforma network

The role of the fractal dimension





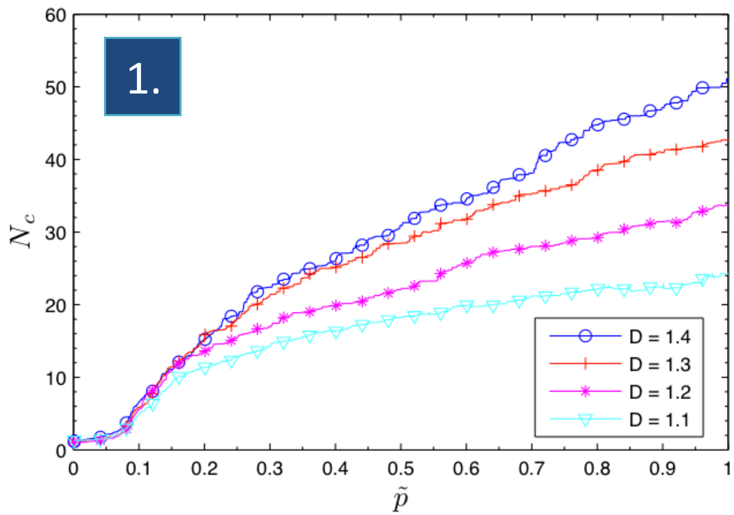


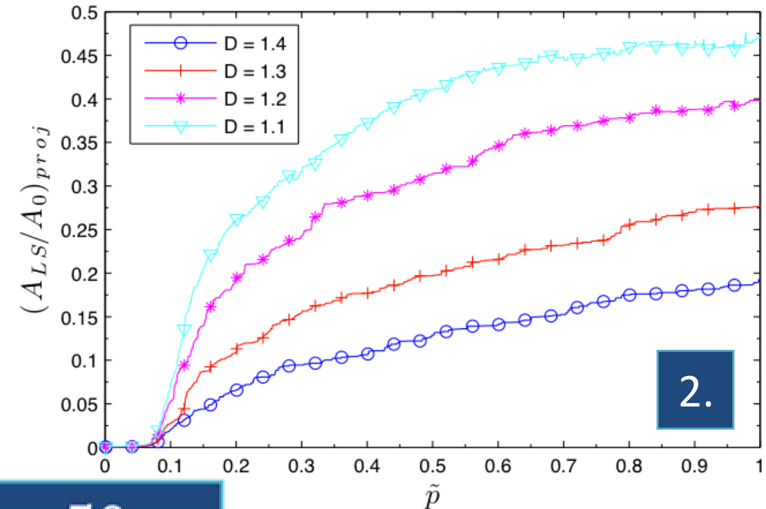
$$m_2 = 10$$
$$\sqrt{m_0} = 10\ \mu\text{m}$$

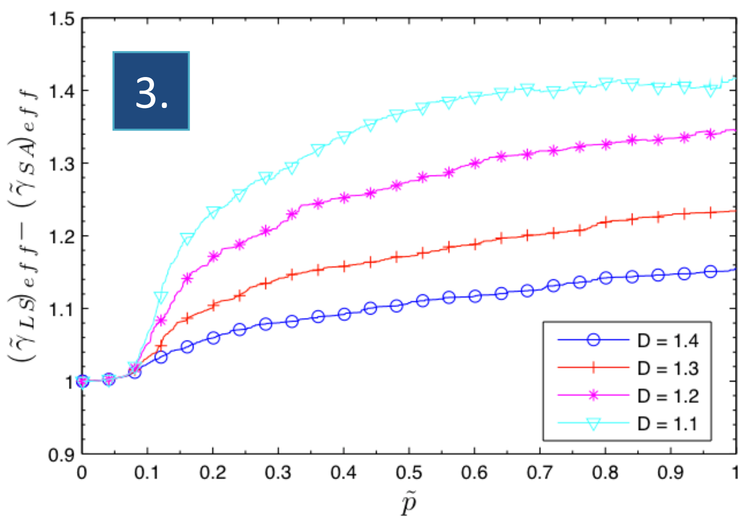
1) The number of contacts vs. dimensionless pressure
2) The contact area vs. dimensionless pressure
3) The apparent –cos(θ) vs. dimensionless pressure

$$\frac{F}{\lambda \gamma_{LA}} = (\tilde{\gamma}_{LS})_{eff} - (\tilde{\gamma}_{SA})_{eff} = -\cos(\theta) = -\cos(\theta_Y)\frac{l_{LS}}{\lambda} + \frac{l_{LA}}{\lambda}$$

The role of the fractal dimension





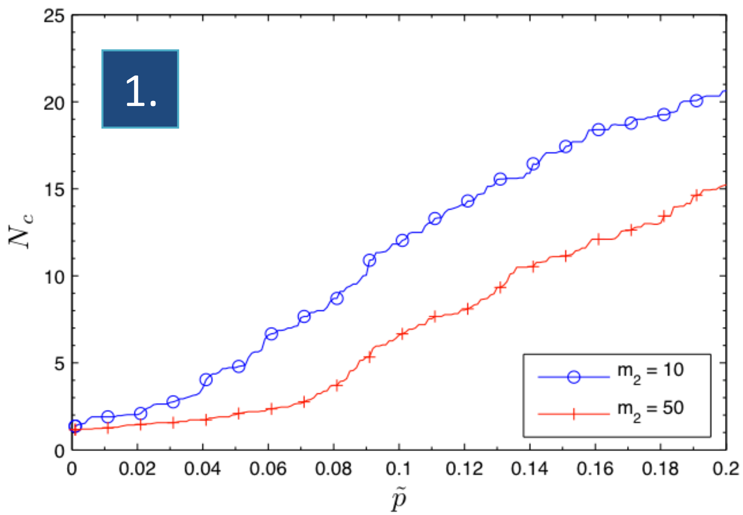


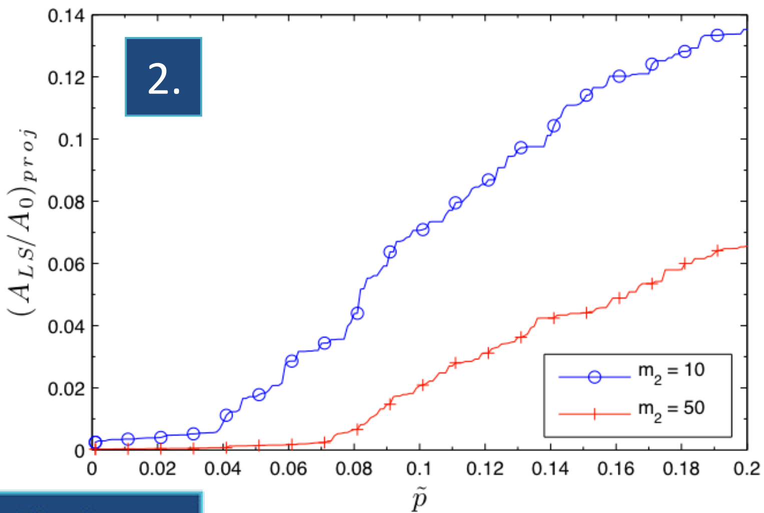
$$m_2 = 50$$
$$\sqrt{m_0} = 10\ \mu\text{m}$$

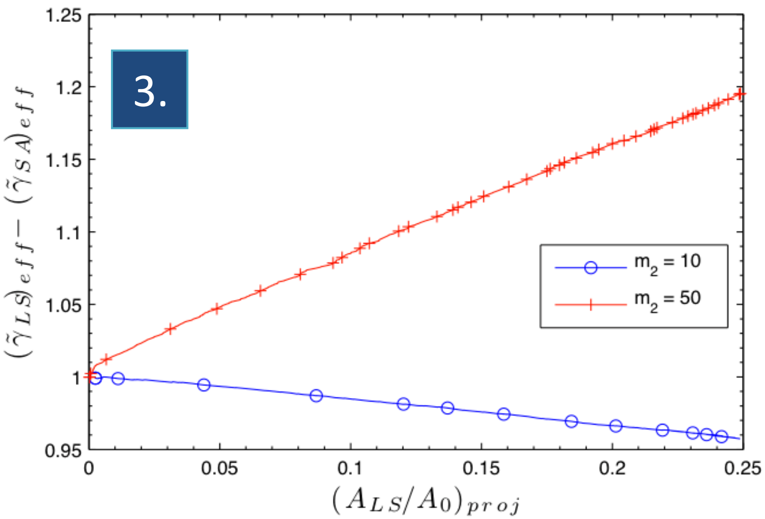
1) The number of contacts vs. dimensionless pressure
2) The contact area vs. dimensionless pressure
3) The apparent –cos(θ) vs. dimensionless pressure

$$\frac{F}{\lambda \gamma_{LA}} = (\tilde{\gamma}_{LS})_{eff} - (\tilde{\gamma}_{SA})_{eff} = -\cos(\theta) = -\cos(\theta_Y)\frac{l_{LS}}{\lambda} + \frac{l_{LA}}{\lambda}$$

The role of m_2







$$D = 1.4$$
$$\sqrt{m_0} = 10\mu m$$

1) The number of contacts vs. dimensionless pressure
2) The contact area vs. dimensionless pressure
3) The apparent –cos(θ) vs. the contact area

$$\frac{F}{\lambda \gamma_{LA}} = (\tilde{\gamma}_{LS})_{eff} - (\tilde{\gamma}_{SA})_{eff} = -\cos(\theta) = -\cos(\theta_Y)\frac{l_{LS}}{\lambda} + \frac{l_{LA}}{\lambda}$$

Conclusions

- We have developed a numerical methodology to solve the non linear problem of the contact between a liquid and a randomly rough profile.

- We have tested our methodology against the analytical results obtained by one of the authors in the case of single wavelength rough surface

- We show that the mean square slope of the surface and its fractal dimension strongly affect the hydrorepellence properties of randomly rough surface.

- In particular we have been able to demonstrate for the first time that it is possible to regulate the superhydrorepellence properties of the surface mainly by controlling the mean square slope of the surface and secondly by changing its fractal dimension.

- Our numerical methodology may be a very useful tool to design optimized randomly rough surface with superlative wetting/non-wetting properties.

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Thank you for your attention

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