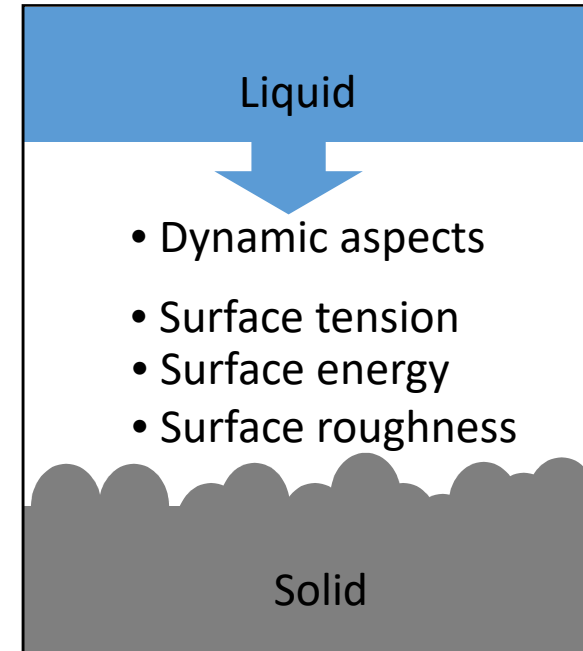




Barthlott W. and C. Neinhuis “Purity of the sacred lotus, or escape from contamination in biological surfaces” (Planta (1997) 202: 1)



Wetting/Wettability

= ability of a solid or a liquid to be wet/to maintain a contact with a liquid

Wettability

Laurent Vonna

IIS2M - Institut de Science des Matériaux de Mulhouse
Université de Haute-Alsace



1/ Surface tension and cohesive forces

2/ Wetting for a measure of the surface energy

3/ Wetting of textured surfaces

4/ Resisting wetting

5/ Liquid-infused surfaces

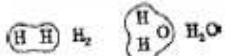

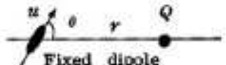
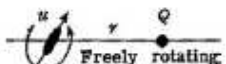
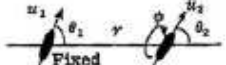
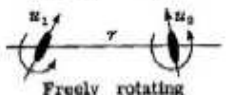
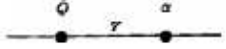
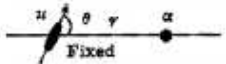
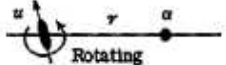

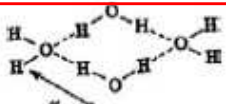


Gouttes, bulles, perles et ondes

Pierre Gilles de Gennes , Françoise Brochard-Wyart , David Quéré (Belin, 2002)

1/ Surface tension and cohesive forces

Table 2.2 Common Types of Interactions and their Pair-Potentials $w(r)$ between Two Atoms, Ions, or Small Molecules in a Vacuum ($\epsilon = 1$)^a

| Type of interaction | Interaction energy $w(r)$ |
|--|--|
| Covalent, metallic:  | Complicated, short range |
| Charge-charge:  | $+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy) |
| Charge-dipole:  | $-Qu \cos \theta/4\pi\epsilon_0r^2$ |
| Charge-dipole:  | $-Q^2u^2/6(4\pi\epsilon_0)^2kT r^4$ |
| Dipole-dipole:  | $-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$ |
| Dipole-dipole:  | $-u_1^2u_2^2/3(4\pi\epsilon_0)^2kT r^6$ (Keesom energy) |
| Charge-non-polar:  | $-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$ |
| Dipole-non-polar:  | $-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$ |
| Dipole-non-polar:  | $-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy) |
| Two non-polar molecules:  | $\frac{3}{4} \frac{h\nu\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy) |
| Hydrogen bond:  | Complicated, short range, energy roughly proportional to $-1/r^2$ |

^a $w(r)$ is the interaction free energy or pair-potential (in J); Q , electric charge (C); u , electric dipole moment (C m); α , electric polarizability ($C^2 m^2 J^{-1}$); r , distance between the centers of the interacting atoms or molecules (m); k , Boltzmann constant ($1.381 \times 10^{-23} J K^{-1}$); T , absolute temperature (K); h , Planck's constant ($6.626 \times 10^{-34} J s$); ν , electronic absorption (ionization) frequency (s^{-1}); ϵ_0 , dielectric permittivity of free space ($8.854 \times 10^{-12} C^2 J^{-1} m^{-1}$). The force $F(r)$ is obtained by differentiating the energy $w(r)$ with respect to distance r : $F = -dw/dr$. The stabilizing repulsive "Pauli exclusion" interactions (not shown) usually follow an exponential function $w(r) \propto \exp(-r/r_0)$, but for simplicity they are usually modeled as power laws: $w(r) \propto +1/r^n$ (where $n = 9-12$).

Cohesion forces in a liquid :

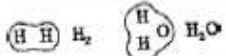

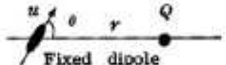
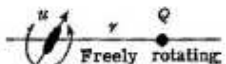
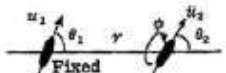
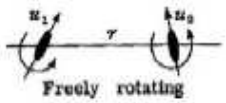
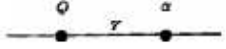
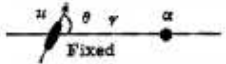
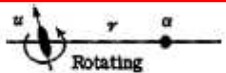

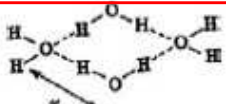
- London
- Debye
- Keesom

Van der
Walls Forces

- Hydrogen bonds

1/ Surface tension and cohesive forces

Table 2.2 Common Types of Interactions and their Pair-Potentials $w(r)$ between Two Atoms, Ions, or Small Molecules in a Vacuum ($\epsilon = 1$)^a

| Type of interaction | Interaction energy $w(r)$ |
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| Charge-non-polar:  | $-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$ |
| Dipole-non-polar:  | $-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$ |
| Dipole-non-polar:  | $-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy) |
| Two non-polar molecules:  | $\frac{3}{4} \frac{h\nu\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy) |
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Cohesion forces in a liquid :

Dispersion forces

- London

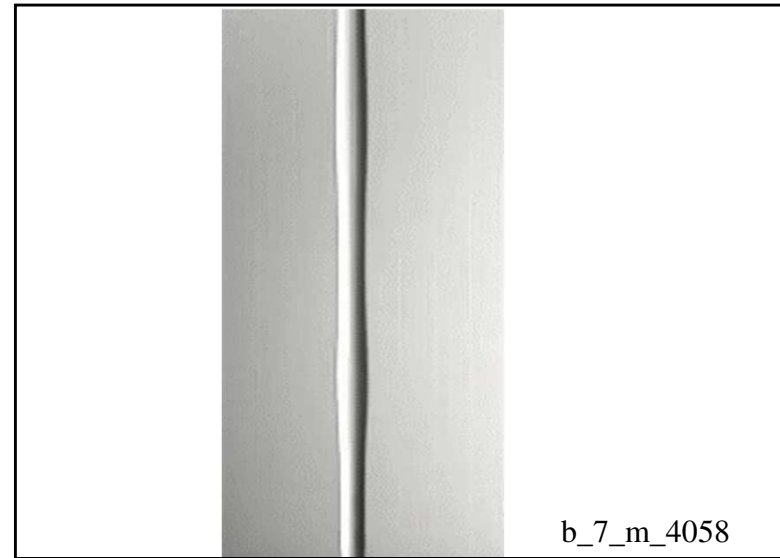
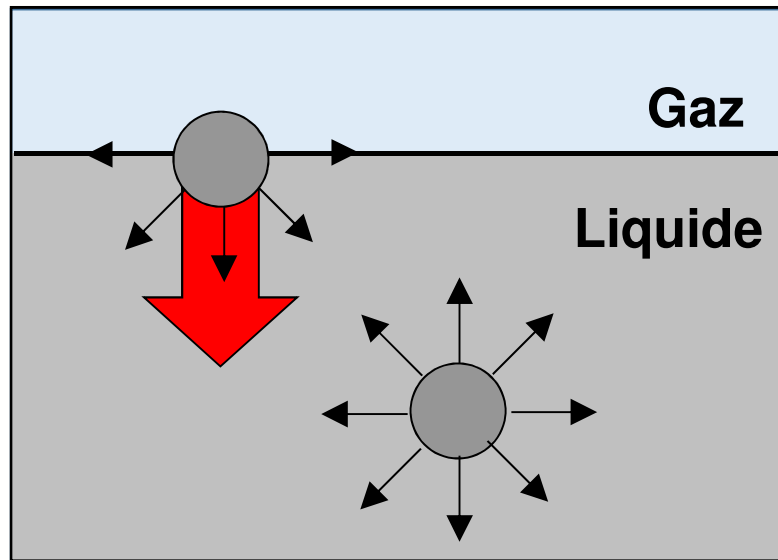
- Debye
- Keesom

- Hydrogen bonds

Polar forces

Van der
Walls Forces

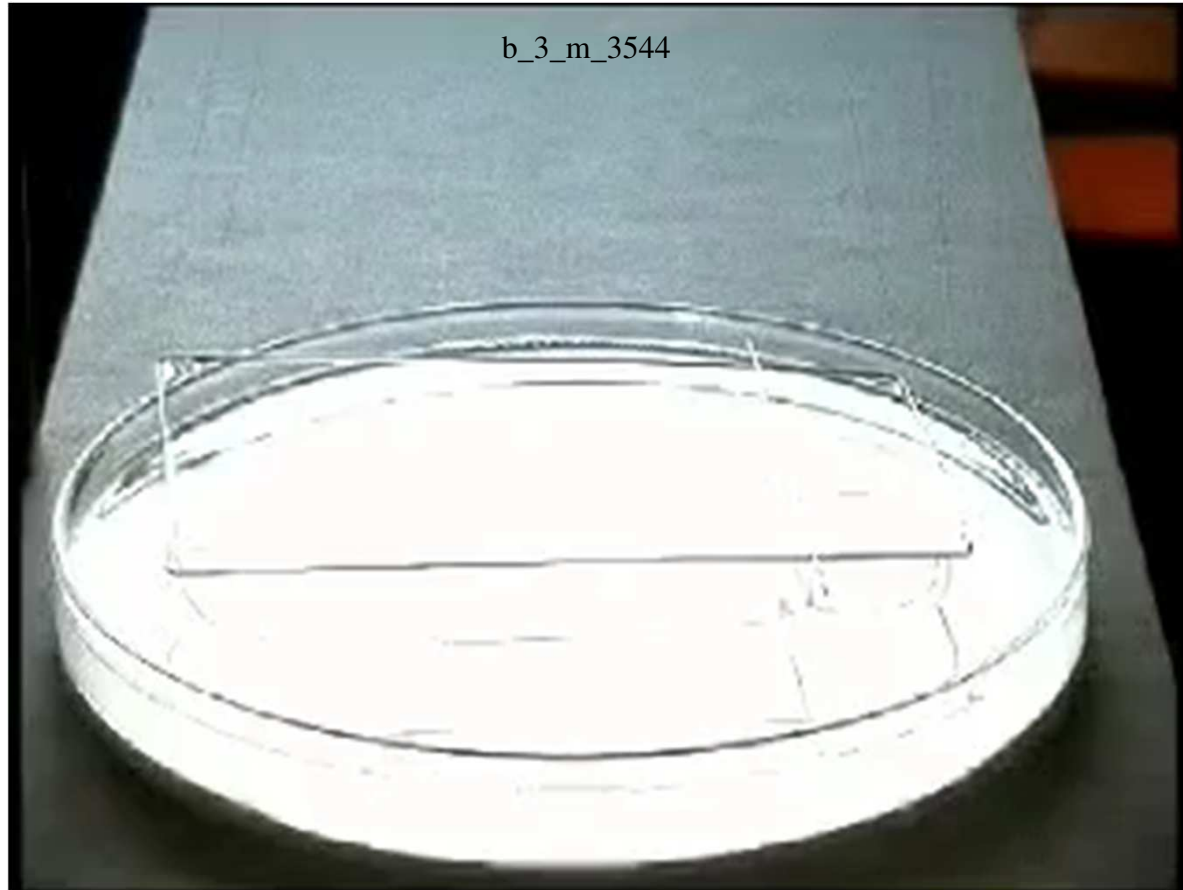
1/ Surface tension and cohesive forces



Gouttes, bulles, perles et ondes
Pierre Gilles de Gennes , Françoise Brochard-
Wyart , David Quéré (Belin, 2002)

Surface energetic penalty = reduction of the interfacial area
= decrease of the ratio surface/volume

1/ Surface tension and cohesive forces



Gouttes, bulles, perles et ondes
Pierre Gilles de Gennes , Françoise Brochard-
Wyart , David Quéré (Belin, 2002)

$$\delta W = F dx = 2 \gamma l dx$$

with γ the surface tension [$\text{mN}\cdot\text{m}^{-1}$]

1/ Surface tension and cohesive forces

Surface tension values

| Name ⁽¹⁾ ▲▲ | Mol. Formula ⁽²⁾ ▲▲ | CAS # ⁽²⁾ ▲▲ | Mol. Wt. ⁽³⁾ ▲▲ | Surface Tension ⁽⁴⁾ | | | | |
|----------------------------------|-----------------------------------|----------------------------|-------------------------------|--------------------------------|------------------------|----------------------|----------------------|--------------------|
| | | | | Total ▲ ▼ | Dispersion ▲▲ ▼▼ | Polar ▲ ▼ | Acid ▲ ▼ | Base ▲ ▼ |
| Trichloromethane (chloroform) | CHCl ₃ | 67-66-3 | 119.38 | 27.2 | 27.2 | 0.0 | 1.5 | 0.0 |
| Diiodomethane (methylene iodide) | CH ₂ I ₂ | 75-11-6 | 267.84 | 50.8 | 50.8 | 0.0 | 0.01 | 0.0 |
| Diiodomethane (methylene iodide) | CH ₂ I ₂ | 75-11-6 | 267.84 | 50.8 ⁽⁵⁾ | 49.0 ⁽⁵⁾ | 1.8 ⁽⁵⁾ | 0.01 | 0.0 |
| Diiodomethane (methylene iodide) | CH ₂ I ₂ | 75-11-6 | 267.84 | 50.8 ⁽⁶⁾ | 44.1 ⁽⁶⁾ | 6.7 ⁽⁶⁾ | 0.01 | 0.0 |
| Diiodomethane (methylene iodide) | CH ₂ I ₂ | 75-11-6 | 267.84 | 50.8 ⁽¹²⁾ | 48.5 ⁽¹²⁾ | 2.3 ⁽¹²⁾ | 0.01 | 0.0 |
| Formamide (methanamide) | CH ₃ NO | 75-12-7 | 45.04 | 58 | 39 | 19 | 2.28 | 39.6 |
| Formamide (methanamide) | CH ₃ NO | 75-12-7 | 45.04 | 58.2 ⁽⁵⁾ | 36.0 ⁽⁵⁾ | 22.2 ⁽⁵⁾ | 2.28 | 39.6 |
| Formamide (methanamide) | CH ₃ NO | 75-12-7 | 45.04 | 57.9 ⁽⁷⁾ | 34.3 ⁽⁷⁾ | 23.5 ⁽⁷⁾ | 2.28 | 39.6 |
| Formamide (methanamide) | CH ₃ NO | 75-12-7 | 45.04 | 58.2 ⁽¹²⁾ | 39.5 ⁽¹²⁾ | 18.7 ⁽¹²⁾ | 2.28 | 39.6 |
| Methanol (methyl alcohol) | CH ₄ O | 67-56-1 | 32.04 | 22.5 | 18.2 | 4.3 | 0.06 ⁽¹⁰⁾ | 77 ⁽¹⁰⁾ |
| Ethanol (ethyl alcohol) | C ₂ H ₆ O | 64-17-5 | 46.07 | 21.4 | 18.8 | 2.6 | 0.02 ⁽¹⁰⁾ | 68 ⁽¹⁰⁾ |

<https://www.accudynetest.com>

| | | | | | | | | | | |
|---|--|--|--|--------------------------|---------------------|----------------------|----------------------|---------------------|-----|------|
| Dimethyl sulfoxide (DMSO) | C ₂ H ₆ OS | 67-68-5 | 78.13 | 44 | 36 | 8 | 0.5 | 32 | | |
| Ethylene glycol | C ₂ H ₆ O ₂ | 107-21-1 | 62.07 | 48 | 29 | 19 | 3.0 | 30.1 | | |
| Ethylene glycol | C ₂ H ₆ O ₂ | 107-21-1 | 62.07 | 48.8 ⁽⁷⁾ | 32.8 ⁽⁷⁾ | 16.0 ⁽⁷⁾ | 3.0 | 30.1 | | |
| Glycerol | C ₃ H ₈ O ₃ | 56-81-5 | 92.09 | 64 | 34 | 30 | 3.92 | 57.4 | | |
| Glycerol | C ₃ H ₈ O ₃ | 56-81-5 | 92.09 | 63.4 ⁽⁵⁾ | 40.6 ⁽⁵⁾ | 22.8 ⁽⁵⁾ | 3.92 | 57.4 | | |
| Glycerol | C ₃ H ₈ O ₃ | 56-81-5 | 92.09 | 63.4 ⁽⁷⁾ | 37.0 ⁽⁷⁾ | 26.4 ⁽⁷⁾ | 3.92 | 57.4 | | |
| 2-Butanone (methyl ethyl ketone) | C ₄ H ₈ O | Cyclohexane | C ₆ H ₁₂ | 110-82-7 | 84.16 | 25.2 | 25.2 | 0.0 | 0.0 | 0.0 |
| | | Toluene | C ₇ H ₈ | 108-88-3 | 92.13 | 28.5 | 28.5 | 0.0 | 0.0 | 0.72 |
| Tetrahydrofuran | C ₄ H ₈ O | n-Heptane | C ₇ H ₁₆ | 142-82-5 | 100.20 | 20.1 | 20.1 | 0.0 | 0.0 | 0.0 |
| | | o-Xylene | C ₈ H ₁₀ | 95-47-6 | 106.17 | 30.1 | 30.1 | 0.0 | 0.0 | 0.58 |
| Ethyl acetate (ethyl ethanoate) | C ₄ H ₈ O ₂ | 1-Bromonaphthalene | C ₁₀ H ₇ Br | 90-11-9 | 207.07 | 44.4 | 44.4 | 0.0 | - | - |
| | | cis-Decahydrohaphthalene (cis-decalin) | C ₁₀ H ₁₈ | 493-01-6 | 138.25 | 32.2 | 32.2 | 0.0 | 0.0 | 0.0 |
| Diethyl ether (ethoxyethane) | C ₄ H ₁₀ O | Decane | C ₁₀ H ₂₂ | 124-18-5 | 142.28 | 23.8 | 23.8 | 0.0 | - | - |
| | | Hexadecane | C ₁₆ H ₃₄ | 544-76-3 | 226.44 | 27.5 | 27.5 | 0.0 | 0.0 | 0.0 |
| 2-Ethoxyethanol (ethylene glycol monoethyl ether) | C ₄ H ₁₀ O | Tricresyl phosphate | C ₂₁ H ₂₁ O ₄ P | 1330-78-5 ⁽⁹⁾ | 368.36 | 40.9 ⁽⁵⁾ | 39.8 ⁽⁵⁾ | 1.1 ⁽⁵⁾ | - | - |
| | | Tricresyl phosphate | C ₂₁ H ₂₁ O ₄ P | 1330-78-5 ⁽⁹⁾ | 368.36 | 40.9 ⁽⁸⁾ | 39.7 ⁽⁸⁾ | 1.2 ⁽⁸⁾ | - | - |
| | | Tricresyl phosphate | C ₂₁ H ₂₁ O ₄ P | 1330-78-5 ⁽⁹⁾ | 368.36 | 40.9 ⁽¹²⁾ | 39.2 ⁽¹²⁾ | 1.7 ⁽¹²⁾ | - | - |
| Water | H ₂ O | 7732-18-5 | 18.02 | 72.8 | 21.8 | 51.0 | 25.5 | 25.5 | | |
| Water | H ₂ O | 7732-18-5 | 18.02 | 72.8 ⁽⁵⁾ | 22.6 ⁽⁵⁾ | 50.2 ⁽⁵⁾ | 25.5 | 25.5 | | |
| Water | H ₂ O | 7732-18-5 | 18.02 | 72.8 ⁽⁶⁾ | 22.1 ⁽⁶⁾ | 50.7 ⁽⁶⁾ | 25.5 | 25.5 | | |

Polar and dispersion part of the surface tension γ_L with $\gamma_L = \gamma_L^D + \gamma_L^P$

1/ Surface tension and cohesive forces

Surface tension values

| Name ⁽¹⁾ | Mol. Formula ⁽²⁾ | CAS # ⁽²⁾ | Mol. Wt. ⁽³⁾ | Surface Tension ⁽⁴⁾ | | | | | |
|-------------------------|---------------------------------|----------------------|-------------------------|--------------------------------|------------|-------|--------------|------------|--|
| | | | | Total | Dispersion | Polar | Acid | Base | |
| Trichloro (chloro) | | | | | | | | | |
| Diiodo (methylene) | | | | | | | | | |
| Diiodo (methylene) | | | | | | | | | |
| Diiodo (methylene) | | | | | | | | | |
| Diiodo (methylene) | | | | | | | | | |
| Form (methane) | | | | | | | | | |
| Form (methane) | | | | | | | | | |
| Form (methane) | | | | | | | | | |
| Form (methane) | | | | | | | | | |
| Methan | | | | | | | | | |
| alcohol | | | | | | | | | |
| Ethanol (ethyl alcohol) | C ₂ H ₆ O | 64-17-5 | 46.07 | 21.4 | 18.8 | 2.6 | 0.02 (10) | 68 (10) | |

| | | | | | | | | |
|---------------------------|--|----------|-------|-------------|-------------|-------------|------|------|
| Dimethyl sulfoxide (DMSO) | C ₂ H ₆ OS | 67-68-5 | 78.13 | 44 | 36 | 8 | 0.5 | 32 |
| Ethylene glycol | C ₂ H ₆ O ₂ | 107-21-1 | 62.07 | 48 | 29 | 19 | 3.0 | 30.1 |
| Ethylene glycol | C ₂ H ₆ O ₂ | 107-21-1 | 62.07 | 48.8 (7) | 32.8 (7) | 16.0 (7) | 3.0 | 30.1 |
| Glycerol | C ₃ H ₈ O ₃ | 56-81-5 | 92.09 | 64 | 34 | 30 | 3.92 | 57.4 |
| | | | | 63.4 | | 22.8 | | |

| Name ⁽¹⁾ | Mol. Formula ⁽²⁾ | CAS # ⁽²⁾ | Mol. Wt. ⁽³⁾ | Surface Tension ⁽⁴⁾ | | | | |
|----------------------------------|---------------------------------|----------------------|-------------------------|--------------------------------|----------------------|--------------|------|------|
| | | | | Total | Dispersion | Polar | Acid | Base |
| Water | H ₂ O | 7732-18-5 | 18.02 | 72.8 (6) | 22.1 ⁽⁶⁾ | 50.7 (6) | 25.5 | 25.5 |
| Diiodomethane (methylene iodide) | CH ₂ I ₂ | 75-11-6 | 267.84 | 50.8 | 50.8 | 0.0 | 0.01 | 0.0 |
| Formamide (methanamide) | CH ₃ NO | 75-12-7 | 45.04 | 58.2 (12) | 39.5 ⁽¹²⁾ | 18.7 (12) | 2.28 | 39.6 |
| Decane | C ₁₀ H ₂₂ | 124-18-5 | 142.28 | 23.8 | 23.8 | 0.0 | - | - |

| | | | |
|-------------------|-------------|------|------|
| 5.2 | 0.0 | 0.0 | 0.0 |
| 8.5 | 0.0 | 0.0 | 0.72 |
| 0.1 | 0.0 | 0.0 | 0.0 |
| 0.1 | 0.0 | 0.0 | 0.58 |
| 4.4 | 0.0 | - | - |
| 2.2 | 0.0 | 0.0 | 0.0 |
| 3.8 | 0.0 | - | - |
| 7.5 | 0.0 | 0.0 | 0.0 |
| 8 ⁽⁵⁾ | 1.1 (5) | - | - |
| 7 ⁽⁸⁾ | 1.2 (8) | - | - |
| 2 ⁽¹²⁾ | 1.7 (12) | - | - |
| 1.8 | 51.0 | 25.5 | 25.5 |

| | | | | | | | | |
|-------|------------------|-----------|-------|-------------|---------------------|-------------|------|------|
| Water | H ₂ O | 7732-18-5 | 18.02 | 72.8 (5) | 22.6 ⁽⁵⁾ | 50.2 (5) | 25.5 | 25.5 |
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<https://www.accudynetest.com>

Polar and dispersion part of the surface tension γ_L with $\gamma_L = \gamma_L^D + \gamma_L^P$

Wettability

Laurent Vonna

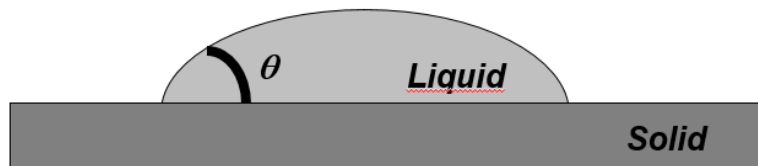
- 1/ Surface tension and cohesive forces
- 2/ Wetting for a measure of the surface energy
- 3/ Wetting of textured surfaces
- 4/ Resisting wetting
- 5/ Liquid-infused surfaces



« On a marché sur la lune »
Hergé, 1954

2/ Wetting for a measure of the surface energy

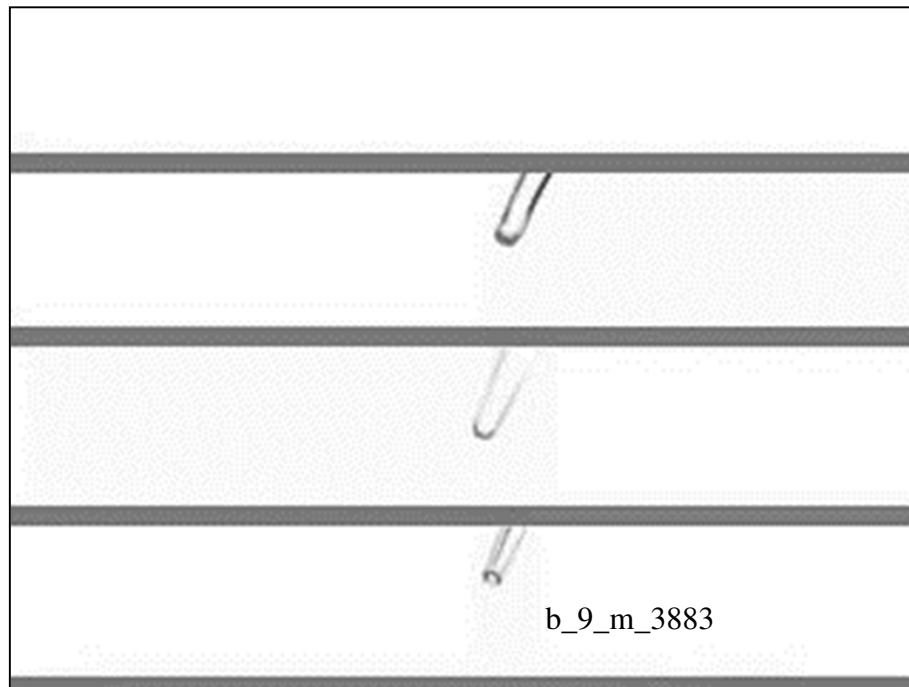
- Contact angle value of a sessile drop is a measure of the wettability



- Sessile droplet morphology (contact angle) is a way to characterize wettability

small contact angle = high wettability

large contact angle = low wettability



On dépose sur du téflon quatre gouttes de liquides différents : de haut en bas, de la perfluorodécane (de **tension superficielle** $\gamma = 12$ mN/m), du méthyl-naphtalène ($\gamma = 37$ mN/m), de l'eau ($\gamma = 72$ mN/m) et du mercure ($\gamma = 485$ mN/m). Les liquides s'étalent d'autant mieux que leur tension superficielle est faible. La condition de raccord avec le solide (ou angle de contact) est donnée par la relation de Young (éq. 1.23).

“Gouttes, bulles, perles et ondes”

Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Editions Belin)

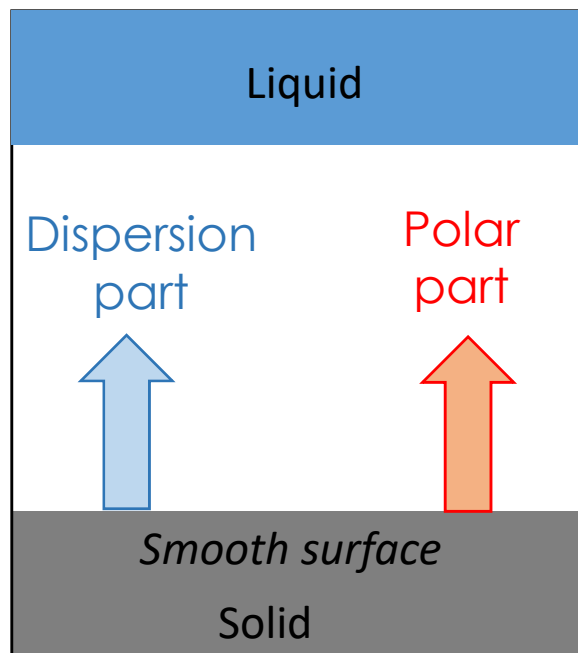
2/ Wetting for a measure of the surface energy

- **Determination of a surface energy**

$$\text{surface energy [mJ.m}^{-2}\text{]} = \text{surface tension [mN.m}^{-1}\text{]}$$

Solid

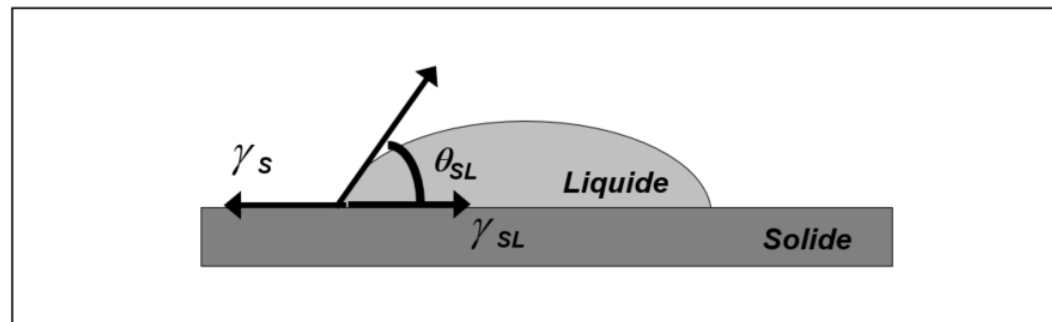
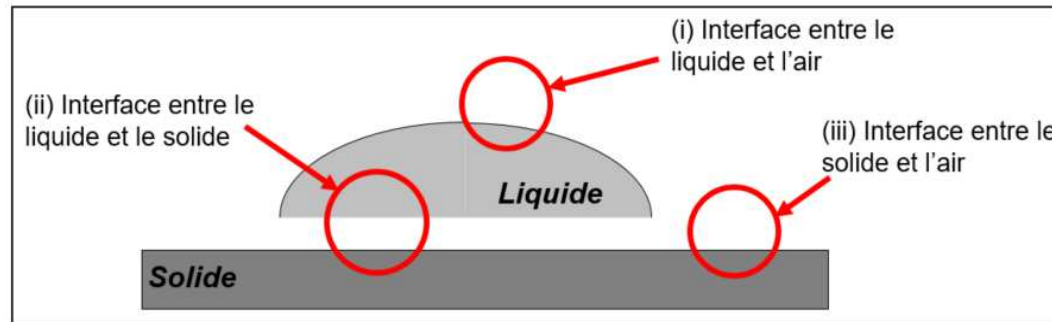
Liquid



- ➔ To qualify a surface treatment
- ➔ To predict wetting
- ➔ To predict adhesion

2/ Wetting for a measure of the surface energy

- Contact angle value of a sessile drop is a measure of the wettability



Young's equation

$$\gamma_s = \gamma_{SL} + \gamma_L \cos\theta_{SL}$$


2/ Wetting for a measure of the surface energy

- **Wettability/Contact angle, for the determination of the surface energy**


Dupré's adhesion energy

$$I_{SL} = \sigma_S + \sigma_L - \sigma_{SL}$$

State 1



State 2



+

Young's equation

$$\sigma_S = \sigma_{SL} + \sigma_L \cos \theta$$

Geometric mean assumption

- proposed by Good and Girifalco

$$I_{SL} = 2 (\sigma_L)^{1/2} (\sigma_S)^{1/2}$$

- extended by Fowkes
 - additivity of the different part of the surface tension
 - geometric mean is used for these different parts

$$I_{SL} = 2 [(\sigma_L^D)^{1/2} (\sigma_S^D)^{1/2} + (\sigma_L^P)^{1/2} (\sigma_S^P)^{1/2}]$$

$$I_{SL} = \sigma_L (\cos \theta + 1)$$

$$(\sigma_L^D)^{1/2} (\sigma_S^D)^{1/2} + (\sigma_L^P)^{1/2} (\sigma_S^P)^{1/2} = \frac{\sigma_L (\cos \theta + 1)}{2}$$

2/ Wetting for a measure of the surface energy

- **Wettability/Contact angle, for the determination of the surface energy**

$$(\sigma_L^D)^{1/2} (\sigma_S^D)^{1/2} + (\sigma_L^P)^{1/2} (\sigma_S^P)^{1/2} = \frac{\sigma_L (\cos \theta + 1)}{2}$$

- first liquid only with a dispersion part $\Rightarrow \sigma_S^D = \frac{\sigma_L (\cos \theta + 1)^2}{4}$

- second liquid with a dispersion AND a polar part $\Rightarrow \sigma_S^P$

Surface energy of a solid

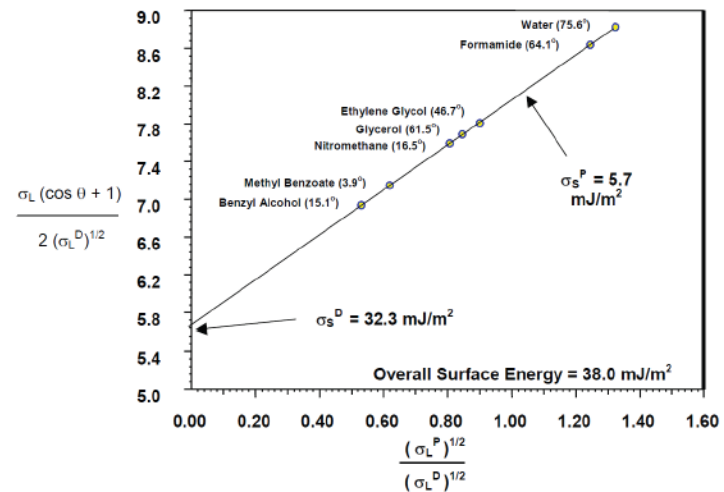
$$\sigma_S = \sigma_S^P + \sigma_S^D$$

Alternative method

$$\frac{\sigma_L (\cos \theta + 1)}{2 (\sigma_L^D)^{1/2}} = (\sigma_S^P)^{1/2} \frac{(\sigma_L^P)^{1/2}}{(\sigma_L^D)^{1/2}} + (\sigma_S^D)^{1/2}$$


$$Y = a X + b$$

With $a = (\sigma_S^P)^{1/2}$ and $b = (\sigma_S^D)^{1/2}$




2/ Wetting for a measure of the surface energy

- **Wettability/Contact angle, for the determination of the surface energy**



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International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Analysis of the results of surface free energy measurement of Ti6Al4V by different methods

Jonathan M. Schuster^{a,b*}, Carlos E. Schvezov^a, Mario R. Rosenberger^a

^a *Materials Institute of Misiones – IMAM (UNaM-Conicet), University of Misiones, 1552, Azara Street, 3300 Posadas, Argentina*
^b *Board of Development and Technological Innovation (CEDIT), 1890 Azara Street, 3300 Posadas, Argentina*

Abstract

Surface Free Energy (SFE) of solids should be calculated using theoretical models. The contact angle (CA) measurement on a surface is considered the most practical way to obtain the SFE. The results of five methods based in the models are compared: the method of Zisman (ZI), the geometric mean (GM), the harmonic mean (HM), the Lifshitz-van der Waals / Acid-Base (LW/AB) and the equation of state (ES). The SFE calculated with GM, HM and LW/AB methods change with the amount and type of liquid used, however, when water, glycerol and dimethyl sulfoxide are used together the SFE and its dispersive and polar components are similar in value for the three methods. In the case of the ES model the values of SFE change with the liquid used; finally using the ZI method the SFE values are 20% lower than the values of SFE obtained with the other methods.

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Table 3. Surface free energy (mJ/m²) of a TiO₂, calculated with the different methods using different combinations of liquids


| <i>Geometric mean method</i> | | | | |
|---|--------------|--------------|------------|-------------------------|
| Liquids | γ_s^d | γ_s^p | γ_s | γ_s^p / γ_s |
| WEGD | 17.1 ± 0.6 | 30.2 ± 1.1 | 47.3 ± 0.6 | 0.64 |
| WEG | 11.0 ± 0.8 | 37.7 ± 1.6 | 48.8 ± 0.9 | 0.77 |
| WED | 17.3 ± 0.5 | 30.1 ± 1.1 | 47.4 ± 0.6 | 0.64 |
| EGD | 29.1 ± 0.5 | 13.3 ± 0.8 | 42.5 ± 0.3 | 0.31 |
| WGD | 19.5 ± 0.5 | 28.8 ± 1.1 | 48.3 ± 0.6 | 0.60 |
| WD | 21.2 ± 0.4 | 28.0 ± 1.0 | 49.2 ± 0.6 | 0.57 |
| WG | 14.4 ± 0.8 | 34.0 ± 1.4 | 48.3 ± 0.8 | 0.70 |
| WE | 8.5 ± 0.7 | 41.0 ± 1.8 | 49.5 ± 1.1 | 0.83 |
| DG | 26.3 ± 0.5 | 18.0 ± 0.9 | 44.3 ± 0.4 | 0.41 |
| DE | 34.5 ± 0.6 | 7.5 ± 0.6 | 42.0 ± 0.1 | 0.18 |
| GE* | - | - | - | - |
| <i>Harmonic mean method</i> | | | | |
| Liquids | γ_s^d | γ_s^p | γ_s | γ_s^p / γ_s |
| WEGD | 22.3 ± 0.2 | 26.7 ± 0.6 | 49.0 ± 0.5 | 0.54 |
| WEG | 14.4 ± 0.4 | 35.9 ± 0.9 | 50.3 ± 0.7 | 0.71 |
| WED | 23.0 ± 0.2 | 27.2 ± 0.6 | 50.2 ± 0.5 | 0.54 |
| EGD | 29.0 ± 0.1 | 15.6 ± 0.4 | 44.6 ± 0.3 | 0.35 |
| WGD | 24.6 ± 0.2 | 26.0 ± 0.6 | 50.7 ± 0.5 | 0.51 |
| WD | 25.8 ± 0.1 | 27.5 ± 0.6 | 53.2 ± 0.5 | 0.52 |
| WG | 17.5 ± 0.4 | 32.8 ± 0.8 | 50.3 ± 0.6 | 0.65 |
| WE | 13.7 ± 0.3 | 36.4 ± 0.9 | 50.1 ± 0.7 | 0.73 |
| DG | 28.3 ± 0.1 | 17.4 ± 0.4 | 45.6 ± 0.3 | 0.38 |
| DE | 32.3 ± 0.2 | 9.9 ± 0.4 | 42.2 ± 0.1 | 0.23 |
| GE* | - | - | - | - |
| <i>Lifshitz-van der Waals/ Acid-Base method</i> | | | | |
| Liquids | γ_s^d | γ_s^p | γ_s | γ_s^p / γ_s |
| WEGD | 26.9 ± 0.9 | 15.7 ± 1.1 | 42.7 ± 0.2 | 0.37 |
| WEG* | - | - | - | - |
| WED | 39.1 ± 1.2 | 3.4 ± 1.2 | 42.5 ± 0.2 | 0.08 |
| EGD* | - | - | - | - |
| WGD | 20.5 ± 0.8 | 23.4 ± 1.1 | 43.9 ± 0.4 | 0.53 |

Ref: W: Water – E: Ethylene glycol – G: Glycerol – D: Dimethyl sulfoxide
*result without physical meaning


- five different methods: the Zisman method, the geometric mean method, the harmonic mean method, the Lifshitz-van der Waals / Acid-Base method and the equation of state method
- calculated values of σ_s which are similar, between 42 and 50 mJ/m²

2/ Wetting for a measure of the surface energy

- **Wettability/Contact angle, for the determination of the surface energy**



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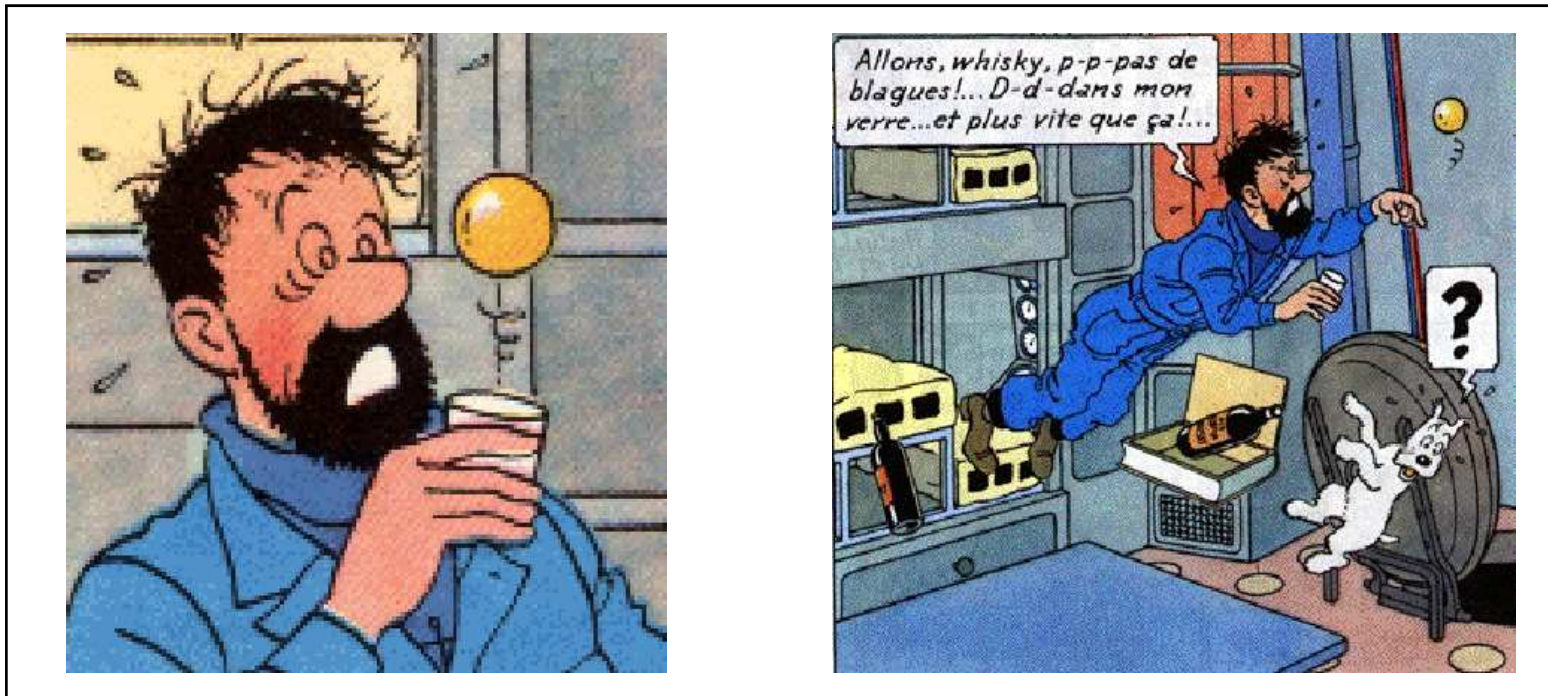
Ref: W: Water – E: Ethylene glycol – G: Glycerol – D: Dimethyl sulfoxide
 *result without physical meaning

- Determining the surface energy of a solid using the contact angle suppose
 - to choose a method
 - to know the polar and dispersion part of the surface tension of the test liquids
 - to use liquids that are compatible with the solid
 - To avoid rough and porous substrate

2/ Wetting for a measure of the surface energy

- **Wettability/Contact angle, for the determination of the surface energy**

Hergé's assumption



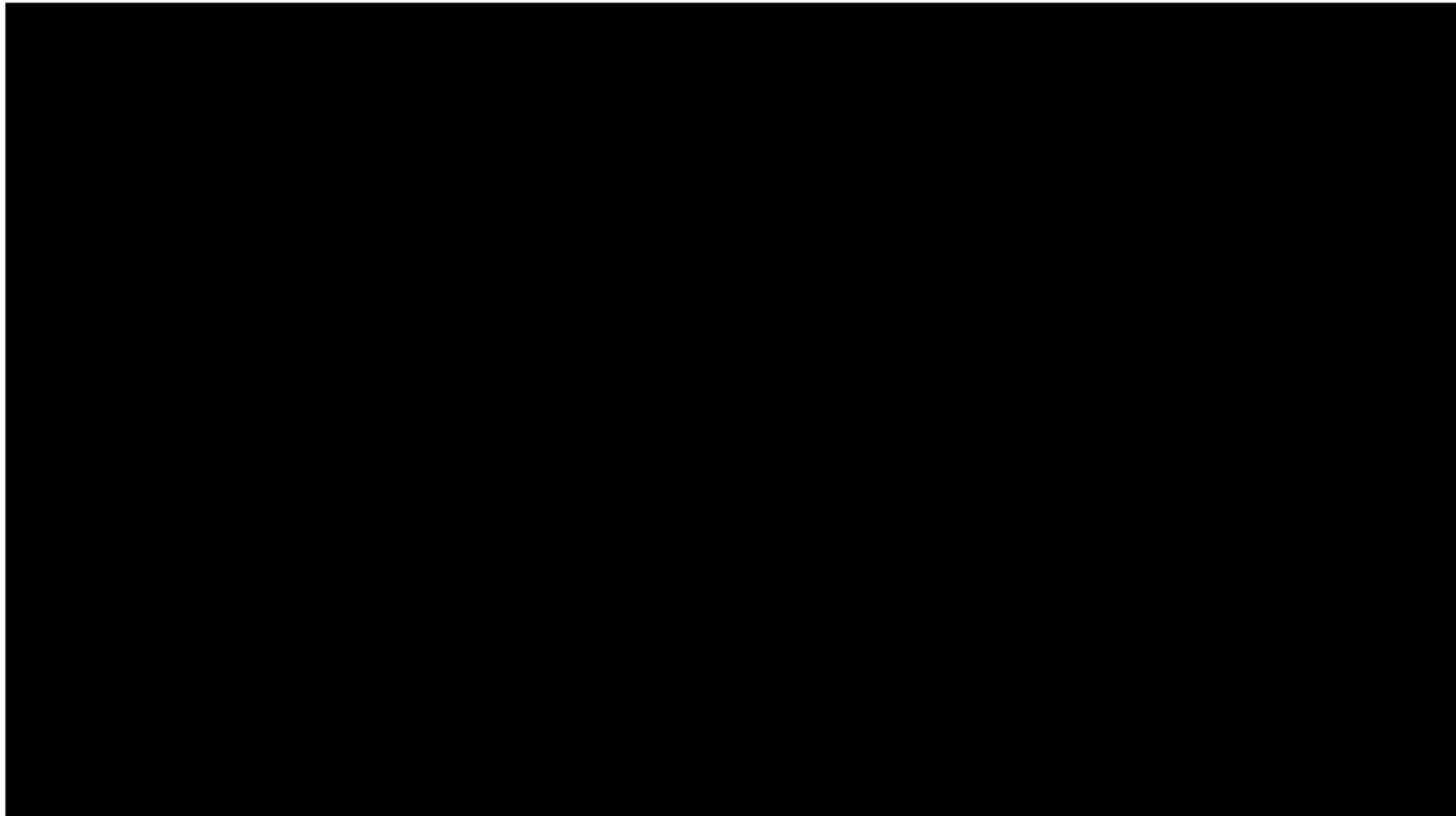
« On a marché sur la lune », Hergé, 1954

2/ Wetting for a measure of the surface energy



Wringing out Water on the ISS - for Science!
<https://www.youtube.com/watch?v=o8TssbmY-GM>
Canadian Space Agency (2013)

2/ Wetting for a measure of the surface energy



Wringing out Water on the ISS - for Science!
<https://www.youtube.com/watch?v=o8TssbmY-GM>
Canadian Space Agency

Wettability

Laurent Vonna

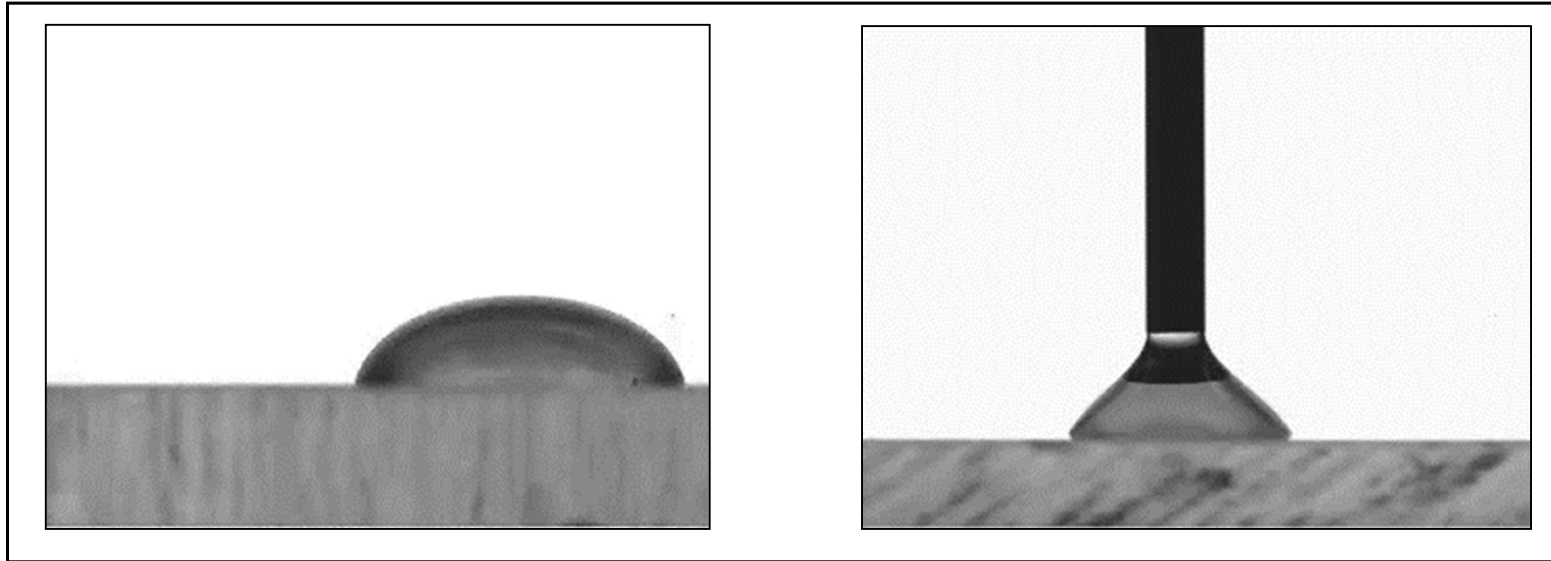
- 1/ Surface tension and cohesive forces
- 2/ Wetting for a measure of the surface energy
- 3/ Wetting of textured surfaces
- 4/ Resisting wetting
- 5/ Liquid-infused surfaces



<https://www.usgs.gov/>

3/ Wetting of textured surfaces

- **The contact angle hysteresis**



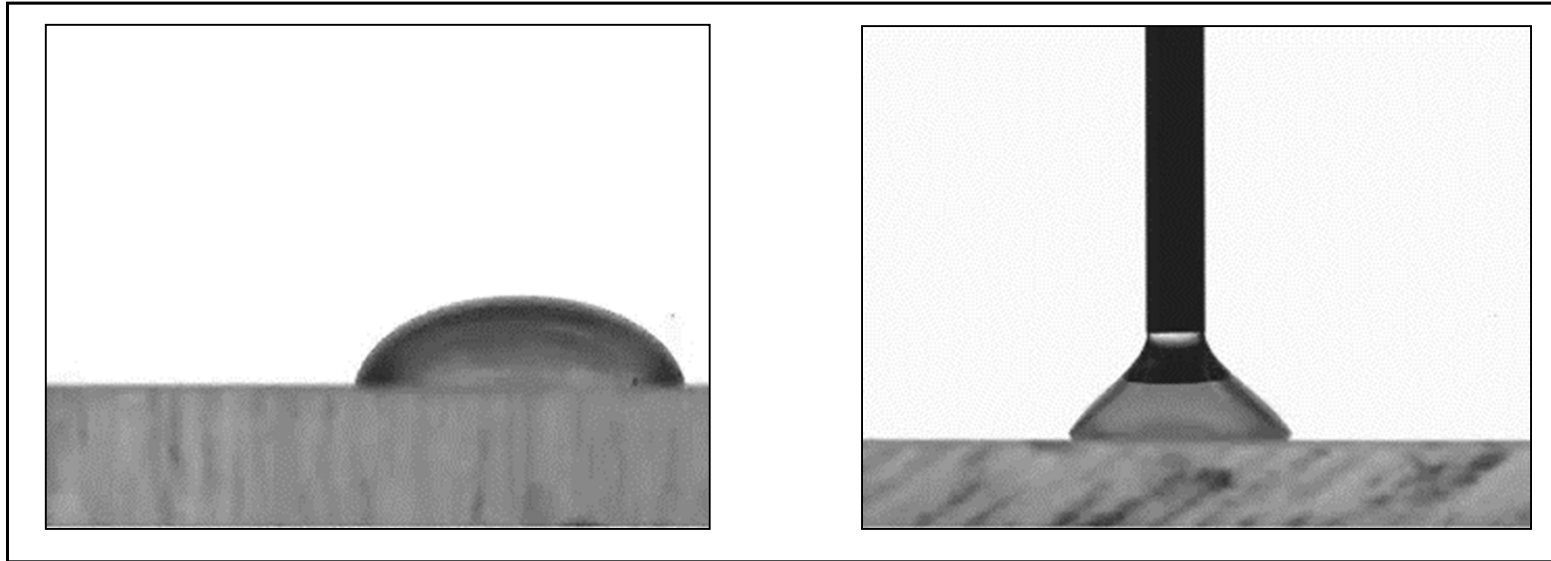
“Gouttes, bulles, perles et ondes” Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Éditions Belin)

$$H = \cos \theta_a - \cos \theta_r$$

- H gives an idea of the adhesion of a liquid on a surface
- The pinning is produced by
 - Chemical heterogeneities
 - Physical heterogeneities

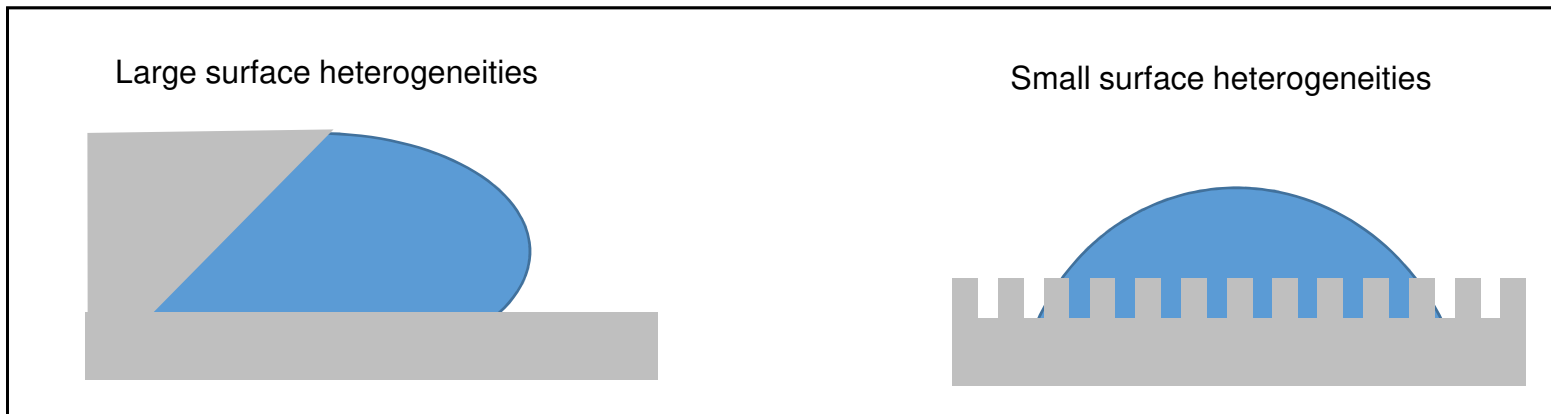
3/ Wetting of textured surfaces

- **The contact angle hysteresis**



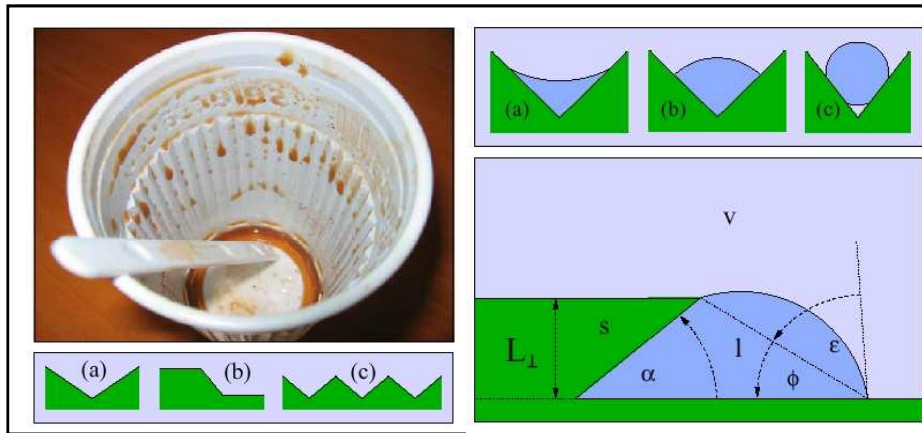
“Gouttes, bulles, perles et ondes” Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Éditions Belin)

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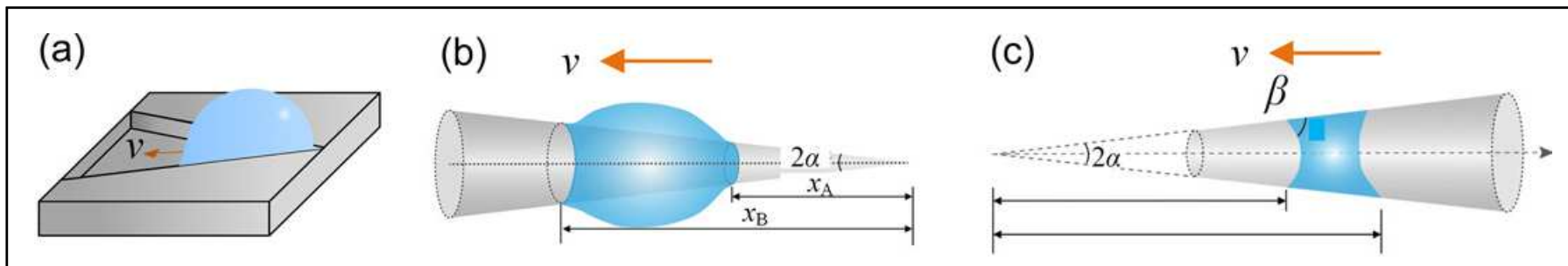


3/ Wetting of textured surfaces

- Large asymmetric structures for directed wetting



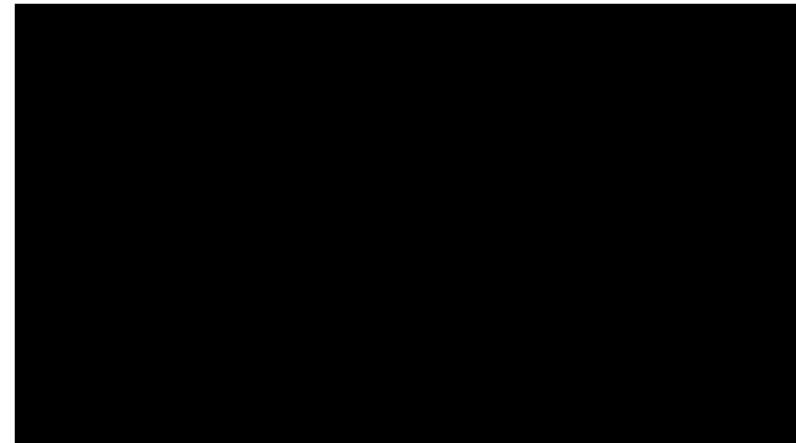
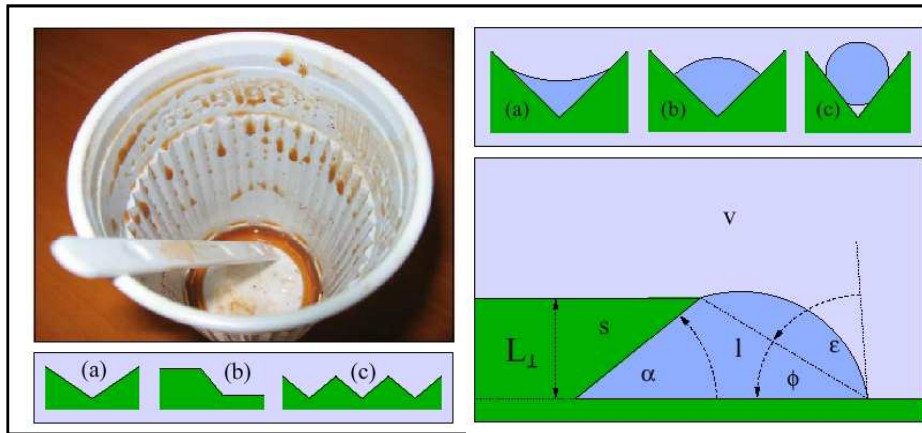
« Blobs, channels and “cigars”: Morphologies of liquids at a step » M.Brinkmann and R.Blossey
Eur.Phys.J.E 14 ,79 –89 (2004)



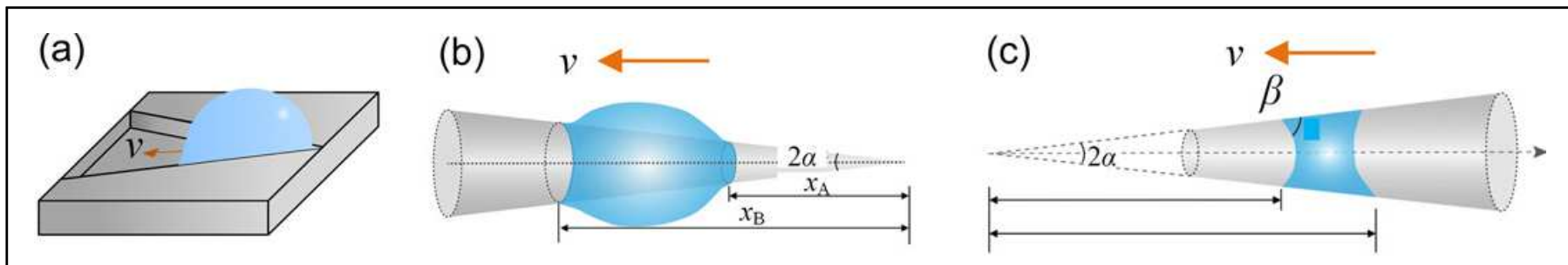
« Bioinspired materials for droplet manipulation: Principles, methods and applications »
Jinkai Xu, Siyu Xiu, Zhongxu Lian, Huadong Yu, Jiaji Cao, Droplets, 2022, <https://doi.org/10.1002/dro2.12>Citations: 7

3/ Wetting of textured surfaces

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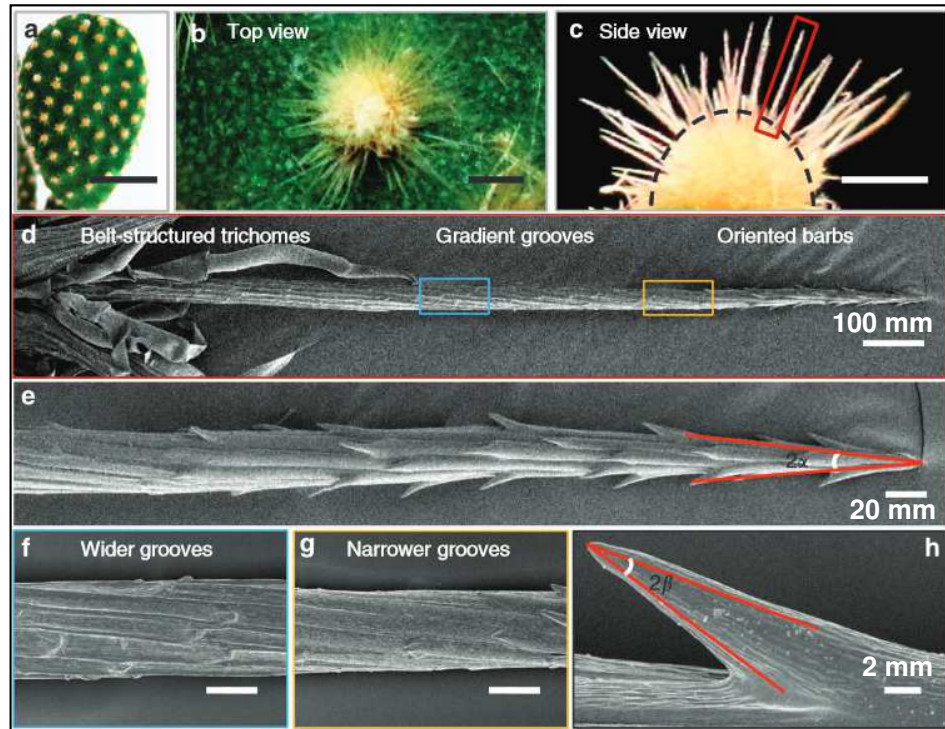


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3/ Wetting of textured surfaces

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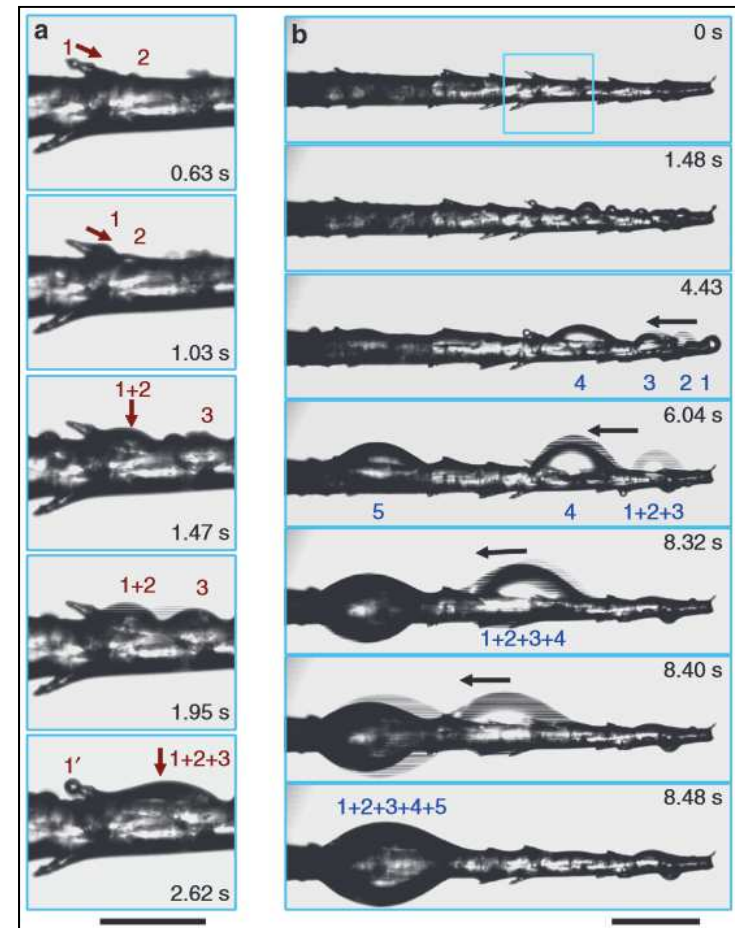
The cactus *Opuntia microdasys*



Appearance and surface structures of the cactus. (a) Optical image of a plant of *O. microdasys* stem covered with well-distributed clusters of spines and trichomes. (b,c) Magnified optical images of a single cluster with spines growing from the trichomes in the top (b) and side (c) view. (d) SEM image of a single spine divided into three regions, the tip (e) with an apex angle ($2a$) and oriented barbs, the middle (f,g) with gradient grooves, and the base with belt-structured trichomes. (f,g) Magnified images of regions near the base and tip of the cactus spine, respectively. The microgrooves near the base are wider and sparser than those near the tip. (h) Magnified image of a single barb with an apex angle ($2b$) covering the tip of the spine (e). Scale bars, 5 cm (a), 500 mm (b,c), 100 mm (d), 20 mm (e–g) and 2 mm (h).

J. Ju, H. Bai, Y. Zheng, Ti. Zhao, R. Fang, and L. Jianga. A multi-structural and multi-functional integrated fog collection system in cactus. *Nat Commun.* 3: 1247, 2012.

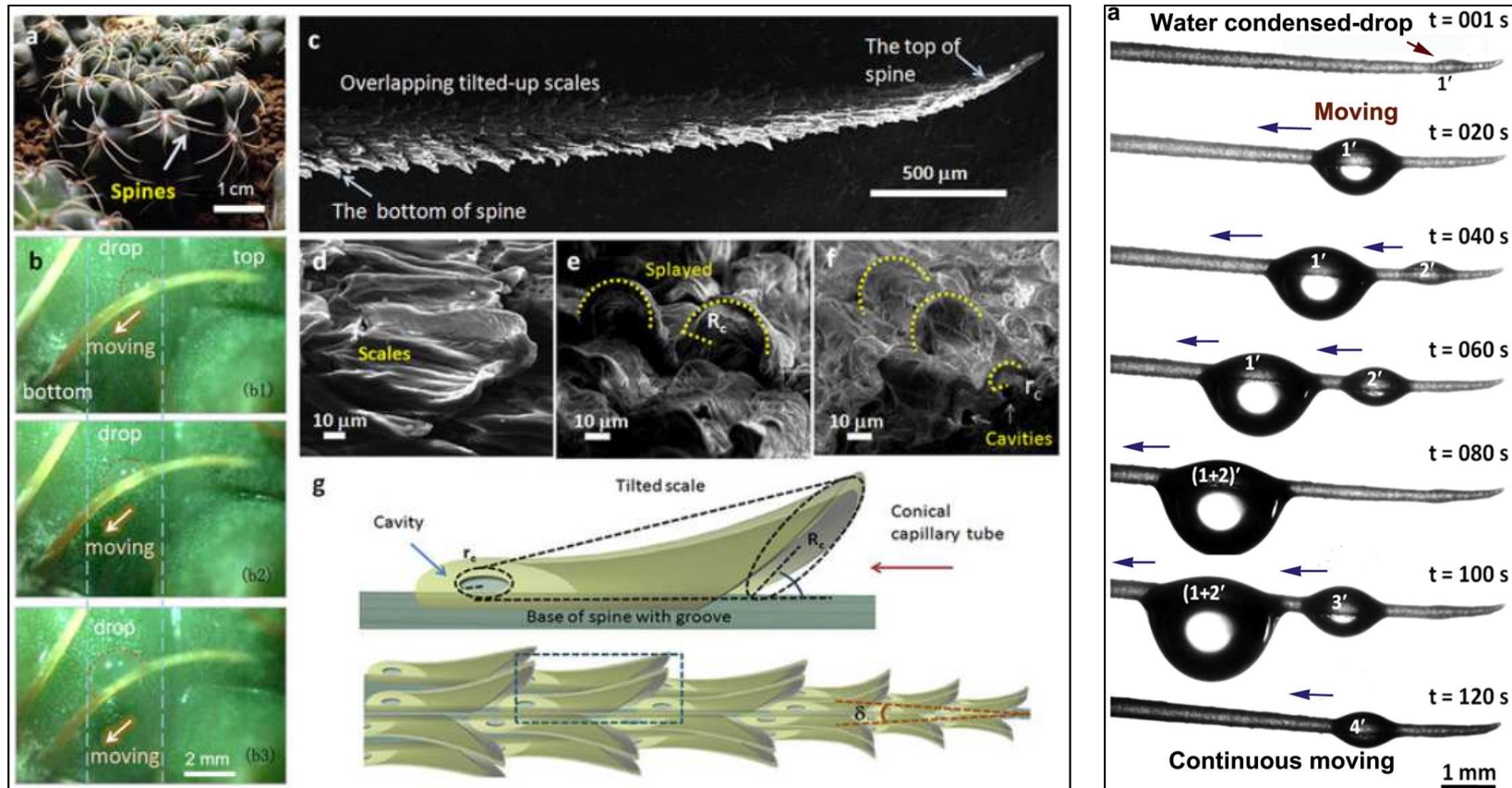
In situ optical microscopic observation of the detailed water collection process on a single horizontal spine and two adjacent spines with trichomes. (a) Continuous deposition of the water drops on the barbs and the spine. Initially, tiny water drops 1 and 2 were deposited concomitantly on the barb and the spine, respectively. Drop 1 moved toward the base of the barb with the volume increasing and coalesced with drop 2, forming larger drop 1+2. As the deposition proceeded, drop 1+2 further coalesced with drop 3 on the adjacent barb. A new cycle started when a subsequent small water drop 1 0 deposited at the same location of initial drop 1. (b) Directional collection of the water drops on the spine. The deposited drop (1) and the coalesced drops (2–4) combine, moving directionally along the spine (black arrows) to form a large drop (1+2+3+4+5).



3/ Wetting of textured surfaces

- Large asymmetric structures for directed wetting

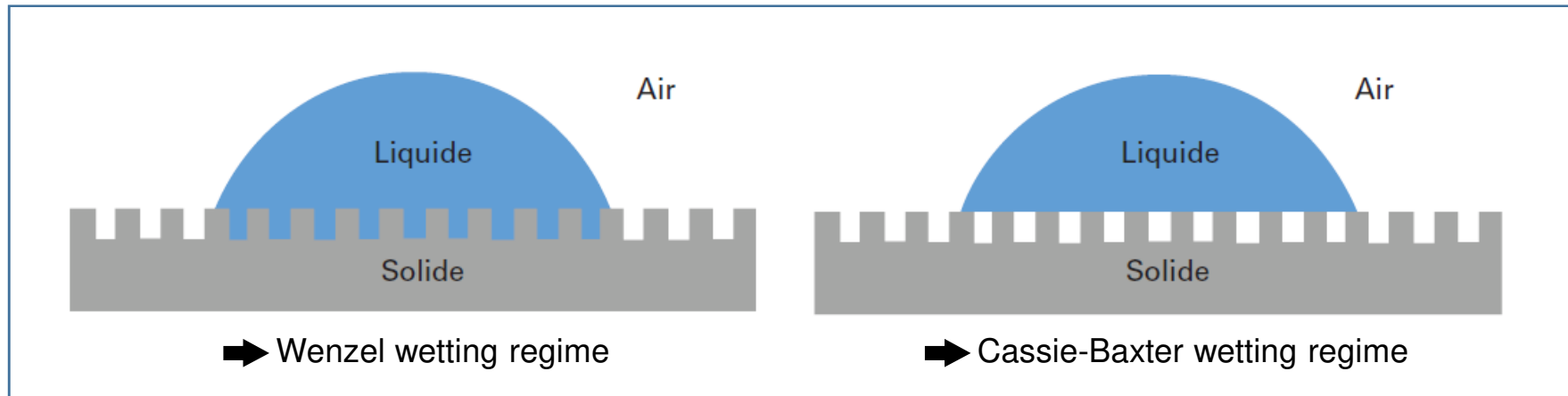
The cactus *Gymnocalycium baldianum*



« Effective directional self-gathering of drops on spine of cactus with splayed capillary arrays » Chengcheng Liu, Yan Xue, Yuan Chen, Yongmei Zheng
 Scientific Reports 5, : 17757 (2015)

3/ Wetting of textured surfaces

- **Small surface heterogeneities**



Intimate liquid/solid interface

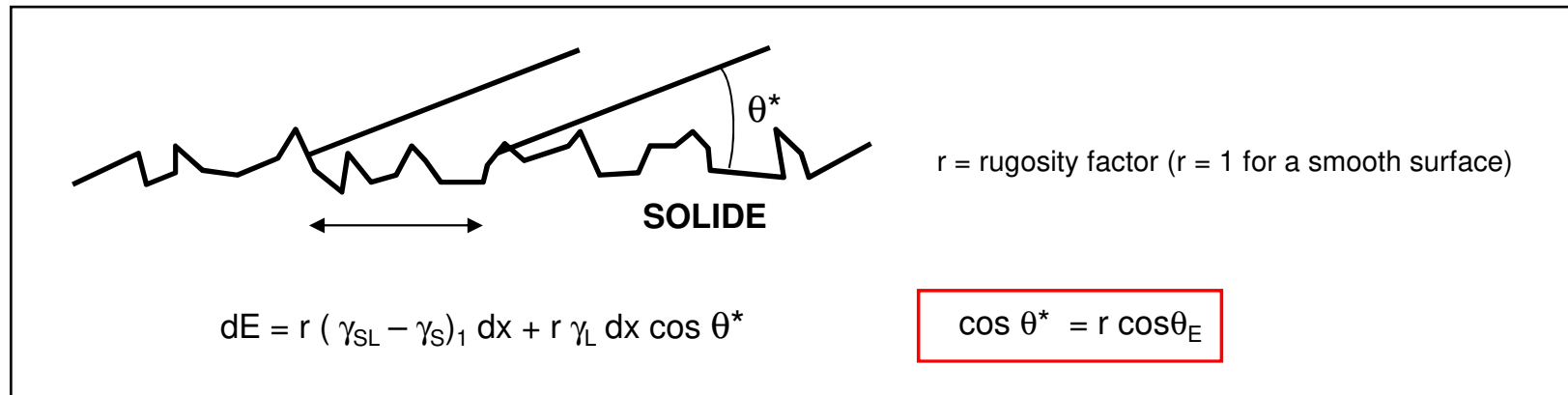


Composite interface with air trapped in between the liquid and the solid

3/ Wetting of textured surfaces

- **Small surface heterogeneities**

The Wenzel wetting regime



For an hydrophilic solid ($\theta_E < 90^\circ$) on a $\theta^* < \theta_E$

For a hydrophobic solid ($\theta_E > 90^\circ$) on a $\theta^* > \theta_E$



Roughness modifies the contact angle !



Roughness modifies the calculation of the surface energy

3/ Wetting of textured surfaces

- **Small surface heterogeneities**

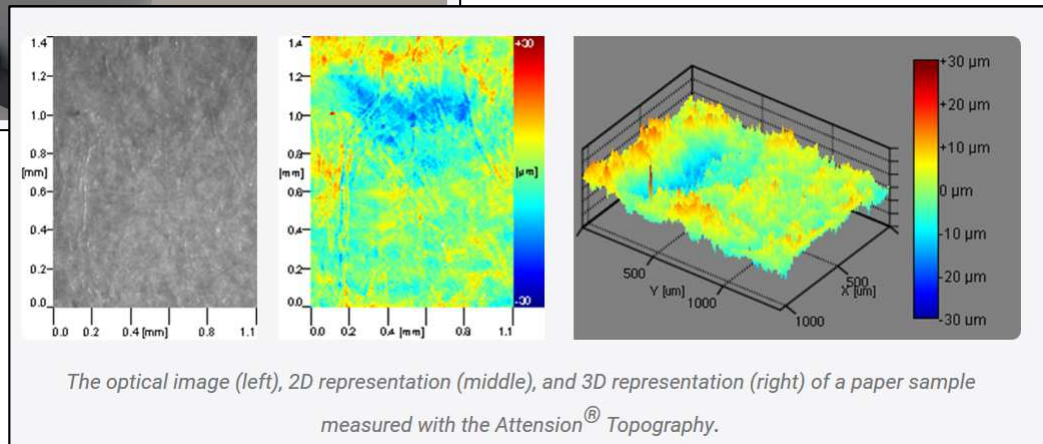
The Wenzel wetting regime



Considering r for a correction of the contact angle?

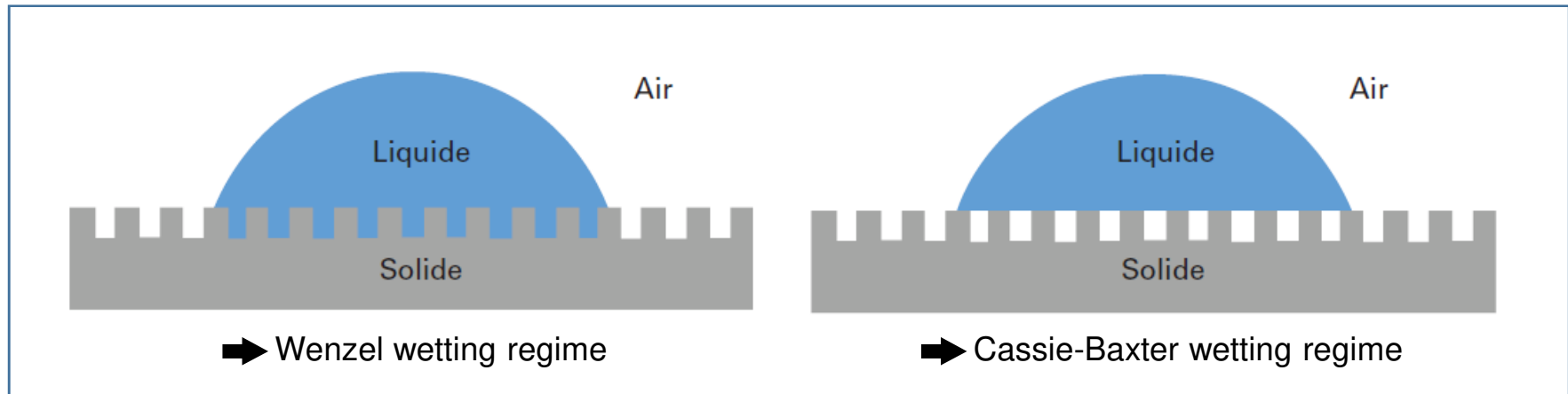


$$\cos\theta_E = (1/r) \cos\theta^*$$



3/ Wetting of textured surfaces

- **Small surface heterogeneities**



Intimate liquid/solid interface



Composite interface with air trapped in between the liquid and the solid

3/ Wetting of textured surfaces

- Superhydrophobicity + superoleophobicity = superomniphobicity

Neinhuis and Barthlott (1997)

Annals of Botany 79: 667–677, 1997

AP

Characterization and Distribution of Water-repellent, Self-cleaning Plant Surfaces

C. NEINHUIS and W. BARTHLOTT

Botanisches Institut und Botanischer Garten der Universität, Meckenheimer Allee 170, D-53115 Bonn, Germany

Received: 23 October 1996 Accepted: 23 January 1997

During the last 20 years, a wealth of data dealing with scanning electron microscopy of plant surfaces has been published. The ultrastructure of epidermal surfaces has been investigated with respect to taxonomic, as well as functional aspects. Within the latter, water-repellency has received much attention and has been well documented. Water-repellency is based on surface roughness caused by different microstructures (trichomes, cuticular folds and wax crystals), together with the hydrophobic properties of the epicuticular wax. In addition, contaminating particles are carried away by water droplets, resulting in a cleaned surface (Lotus-effect). Therefore, rough, waxy leaves are not only water-repellent but anti-adhesive with respect to particulate contamination. Based on 200 water-repellent plant species, the present paper surveys micromorphological characteristics of anti-adhesive plant surfaces. Leaves that are permanently water-repellent can be differentiated by distinctively convex to papillose epidermal cells and a very dense layer of epicuticular waxes. Leaves that are water-repellent for only a limited period of time have only slightly convex epidermal cells and often have a less dense wax layer. Finally, an overview is given on the occurrence of water-repellency among different life forms and within different habitats. Water-repellency is concentrated in herbaceous species, while it is rare in trees. Among different habitats, subtropical regions, wetlands and disturbed areas appear to have more species with water-repellent leaves. The importance of roughness and water-repellency, respectively, as the basis of an anti-adhesive, self-cleaning surface, in comparison to other functions of microstructures, is discussed.

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- ➡ High contact angles
- ➡ Low adhesion
- ➡ Surface micro and nanotexture

668 *Neinhuis and Barthlott—Water-repellent, Self-cleaning Plant Surfaces*

TABLE 1. Contact angles (CA), epidermal relief and epicuticular wax crystals (ECW) of the investigated species in respect to the characterization of water repellent surfaces

| Species | CA (°) | Epidermis | ECW |
|----------------------------------|--------|-----------|-------------------|
| <i>Abies alba</i> | 157 | Convex | Tubules |
| <i>Acacia dealbata</i> | 160 | Papillose | Tubules |
| <i>Acacia glaucoptera</i> | 162 | Convex | Platelets |
| <i>Acantholimon spec.</i> | 158 | Papillose | Ribbons |
| <i>Adiantum andicola</i> | 162 | Convex | Platelets |
| <i>Aethionema grandiflora</i> | 159 | Papillose | Coiled rodlets |
| <i>Agathis australis*</i> | 158 | Convex | Tubules |
| <i>Agathis robusta*</i> | 159 | Convex | Tubules |
| <i>Akebia quinata*</i> | 158 | Convex | Tubules |
| <i>Akebia trifoliata*</i> | 160 | Convex | Tubules |
| <i>Alchemilla diplophylla</i> | 162 | Papillose | Tubules |
| <i>Allium cyathophorum</i> | 161 | Convex | Platelets |
| <i>Alopecurus pratensis</i> | 158 | Convex | Platelets |
| <i>Alstroemeria aurantiaca</i> | 161 | Convex | Platelets |
| <i>Amelanchier lamarkii*</i> | 158 | Convex | Tubules |
| <i>Antherisia nobilis*</i> | 160 | Convex | Platelets |
| <i>Apocynum cannabinum*</i> | 153 | Convex | Platelets |
| <i>Aquilegia chrysantha</i> | 158 | Papillose | Tubules |
| <i>Aquilegia longissima</i> | 158 | Papillose | Tubules |
| <i>Argemone mexicana</i> | 157 | Convex | Tubules |
| <i>Aristolochia cymbifera*</i> | 160 | Convex | Rodlets |
| <i>Aristolochia grandiflora*</i> | 161 | Convex | Rodlets |
| <i>Ariemisia tridentata</i> | — | Hairy | — |
| <i>Arthropodium cirratum</i> | 162 | Convex | Platelets |
| <i>Asphodeline lutea</i> | 155 | Convex | Rodlets |
| <i>Asphodelus aestivus</i> | 158 | Convex | Rodlets |
| <i>Astragalus falcatus</i> | 160 | Papillose | Platelets |
| <i>Astragalus ponticus</i> | 157 | Papillose | Platelets |
| <i>Astragalus galegiformis</i> | 159 | Papillose | Platelets |
| <i>Atriplex patula</i> | 158 | Convex | Platelets |
| <i>Azolla filiculoides</i> | — | Papillose | Rodlets |
| <i>Belamcanda chinensis*</i> | 160 | Papillose | Platelets |
| <i>Berberis thunbergii*</i> | 157 | Convex | Tubules |
| <i>Bomarea spec.*</i> | 169 | Convex | Platelets |
| <i>Brassica oleracea</i> | 161 | ± Smooth | Dendritic |
| <i>Buxus sempervirens*</i> | 159 | Convex | Coiled rodlets |
| <i>Callistemon sieberi*</i> | — | Hairy | — |
| <i>Callistemon citrinus*</i> | — | Hairy | — |
| <i>Canarina canariensis</i> | 158 | Convex | Platelets/threads |
| <i>Canna glauca</i> | 159 | Papillose | Platelets |
| <i>Cercidiphyllum japonicum</i> | 152 | Papillose | Tubules |
| <i>Cladium mariscus</i> | 150 | Convex | Platelets |
| <i>Cleome arborea</i> | 159 | Papillose | Threads |
| <i>Colocasia esculenta</i> | 164 | Papillose | Platelets |
| <i>Comarum palustre</i> | 159 | Convex | Ribbons |
| <i>Comolobus cnoosum</i> | — | Hairy | Platelets |

Barthlott W. and C. Neinhuis “Purity of the sacred lotus, or escape from contamination in biological surfaces” (*Planta* (1997) 202: 1)

C. Neinhuis and Barthlott W. “Characterization and Distribution of Water-repellent, Self-cleaning Plant Surfaces” *Annals of Botany*, Volume 79, Issue 6, June 1997, Pages 667–677, <https://doi.org/10.1006/anbo.1997.0400>

3/ Wetting of textured surfaces

- **Superhydrophobicity + superoleophobicity = superomniphobicity**

Neinhuis and Barthlott (1997)

Annals of Botany 79: 667–677, 1997

AP

Characterization and Distribution of Water-repellent, Self-cleaning Plant Surfaces

C. NEINHUIS and W. BARTHLOTT

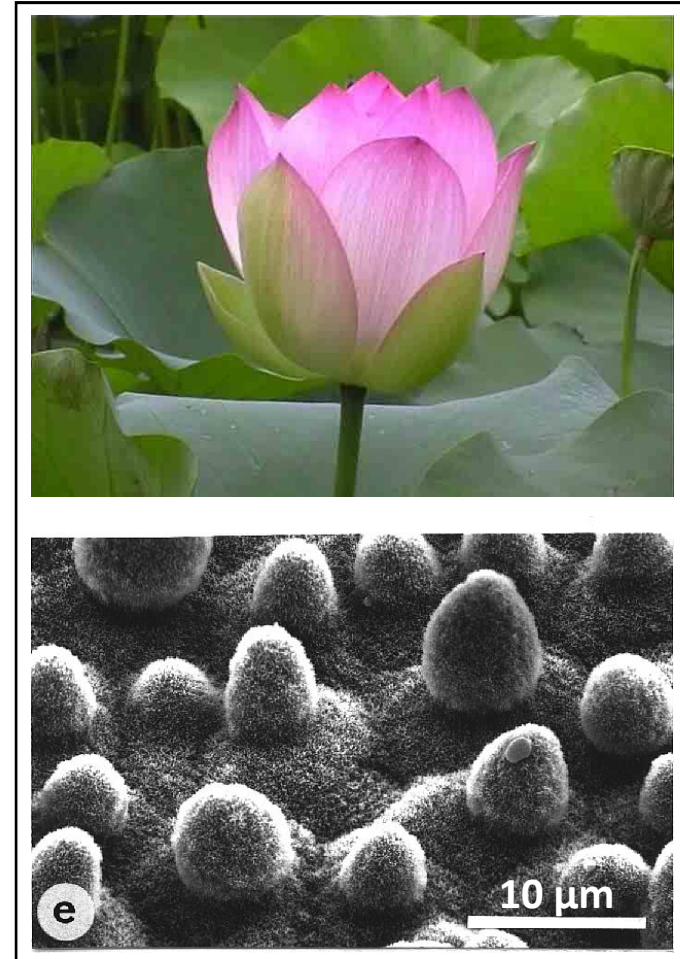
Botanisches Institut und Botanischer Garten der Universität, Meckenheimer Allee 170, D-53115 Bonn, Germany

Received: 23 October 1996 Accepted: 23 January 1997

During the last 20 years, a wealth of data dealing with scanning electron microscopy of plant surfaces has been published. The ultrastructure of epidermal surfaces has been investigated with respect to taxonomic, as well as functional aspects. Within the latter, water-repellency has received much attention and has been well documented. Water-repellency is based on surface roughness caused by different microstructures (trichomes, cuticular folds and wax crystals), together with the hydrophobic properties of the epicuticular wax. In addition, contaminating particles are carried away by water droplets, resulting in a cleaned surface (Lotus-effect). Therefore, rough, waxy leaves are not only water-repellent but anti-adhesive with respect to particulate contamination. Based on 200 water-repellent plant species, the present paper surveys micromorphological characteristics of anti-adhesive plant surfaces. Leaves that are permanently water-repellent can be differentiated by distinctively convex to papillose epidermal cells and a very dense layer of epicuticular waxes. Leaves that are water-repellent for only a limited period of time have only slightly convex epidermal cells and often have a less dense wax layer. Finally, an overview is given on the occurrence of water-repellency among different life forms and within different habitats. Water-repellency is concentrated in herbaceous species, while it is rare in trees. Among different habitats, subtropical regions, wetlands and disturbed areas appear to have more species with water-repellent leaves. The importance of roughness and water-repellency, respectively, as the basis of an anti-adhesive, self-cleaning surface, in comparison to other functions of microstructures, is discussed.

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- ➡ High contact angles
- ➡ Low adhesion
- ➡ Surface micro and nanotexture



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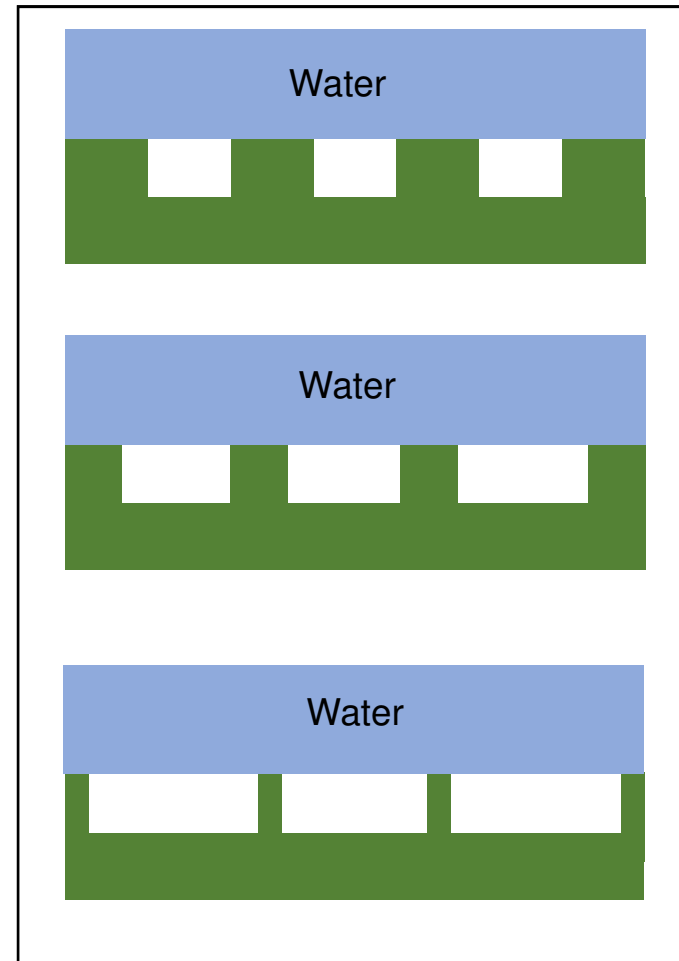
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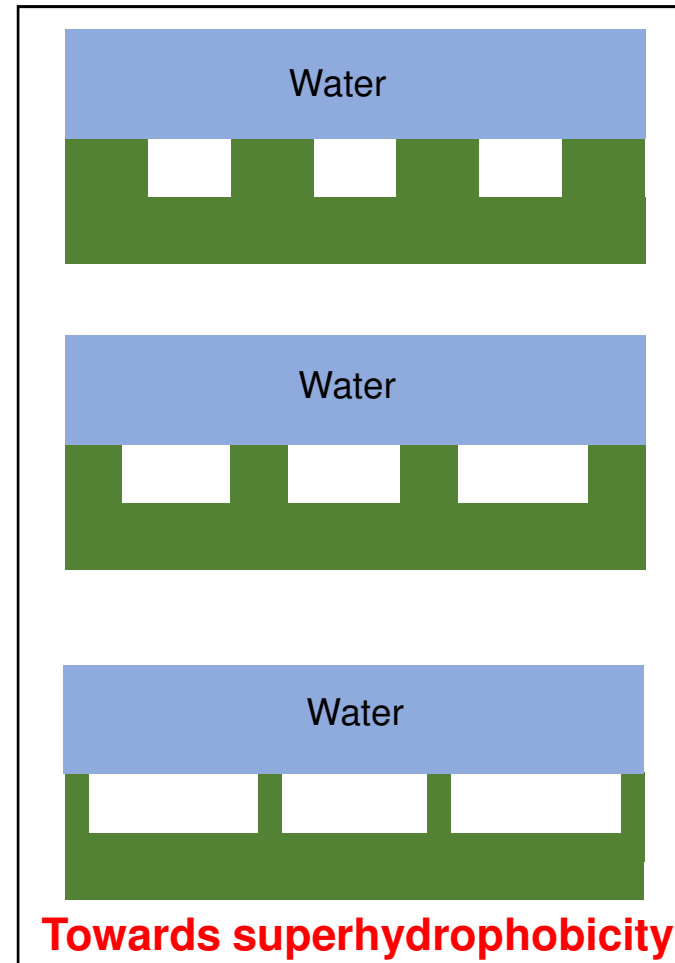
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The Cassie Baxter wetting regime (1945)

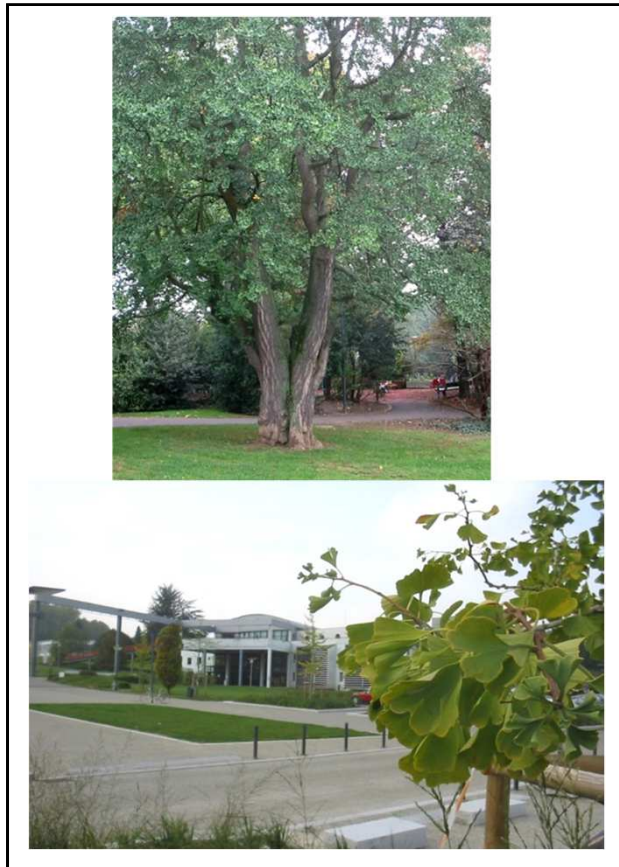
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3/ Wetting of textured surfaces

- **Superhydrophobicity + superoleophobicity = superomniphobicity**

Ginkgo Biloba



« Biomimetic Approach for the Elaboration of Highly Hydrophobic Surfaces: Study of the Links between Morphology and Wettability »
Quentin Legrand, Stephane Benayoun and Stephane Valette
Biomimetics 2021, 6(2), 38; <https://doi.org/10.3390/biomimetics6020038>

Gerris remigis (2014)

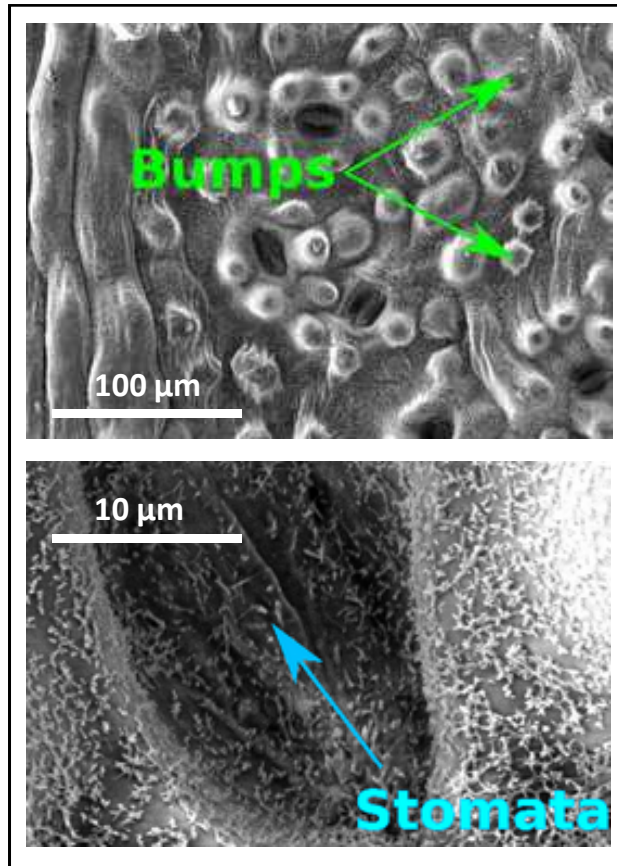


"Biophysics: Water-repellent legs of water striders"
Xuefeng Gao and Lei Jiang,
Nature 432, 36, 4, November 2004

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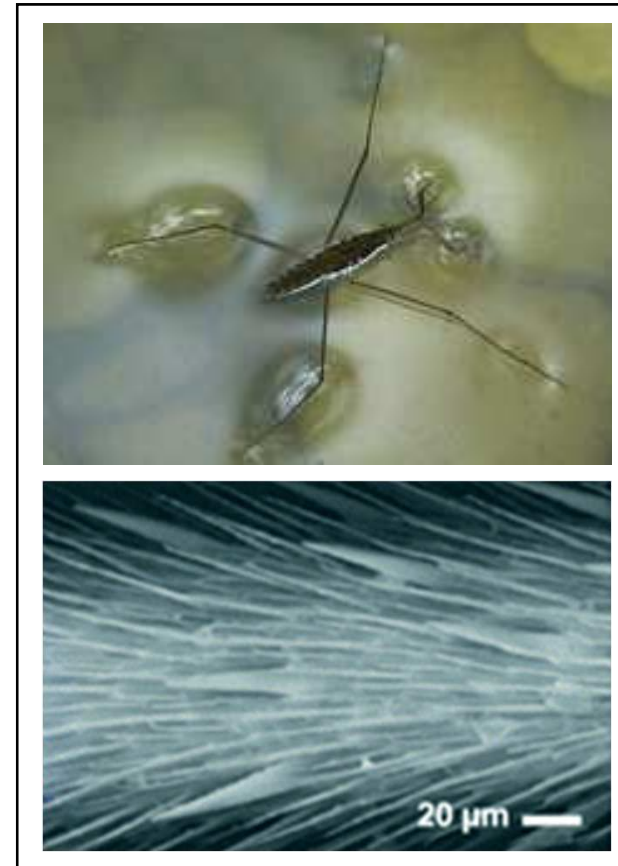
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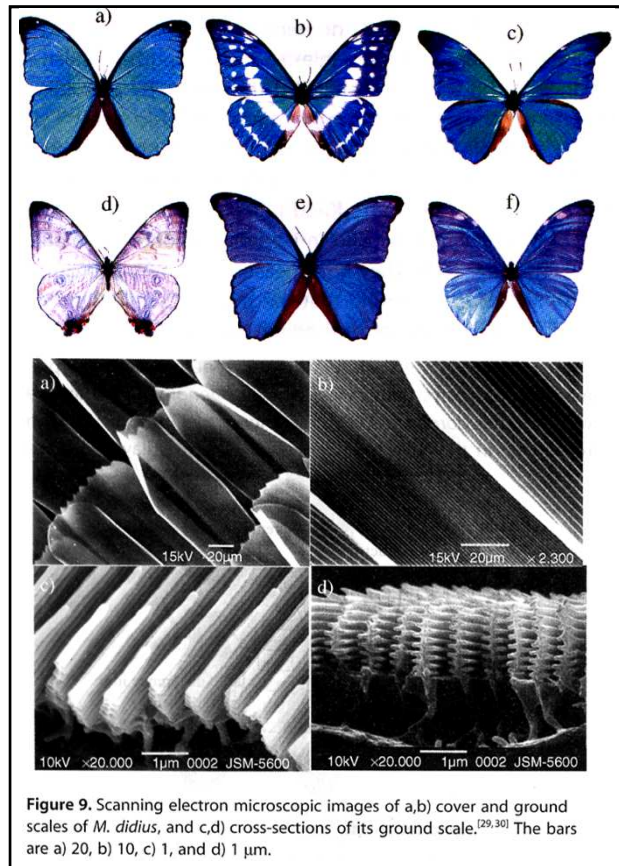


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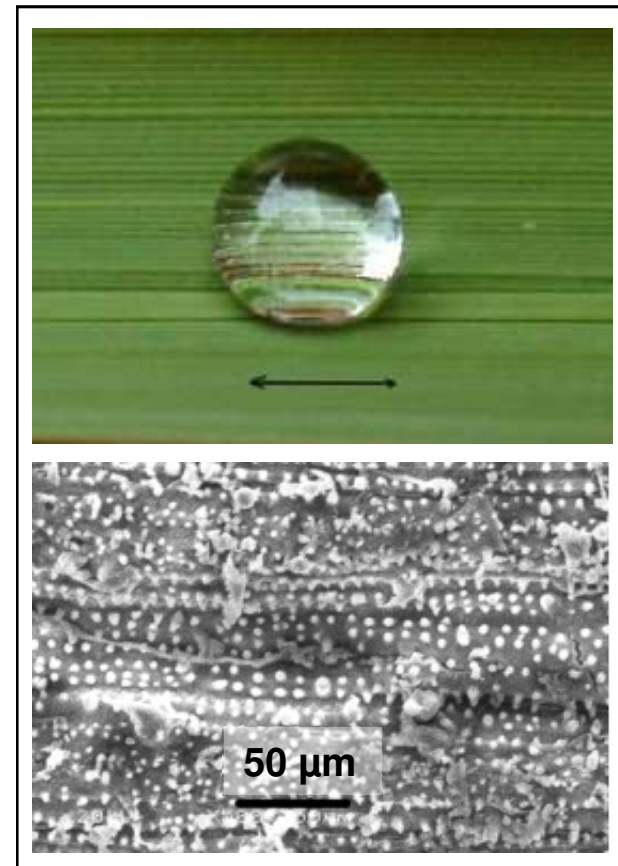
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Butterfly wings (2007)



« Directional adhesion of superhydrophobic butterfly wings » Yongmei Zheng, Xuefeng Gao and Lei Jiang, *Soft Matter*, 2007,3, 178-182

Rice leaf (2007)



« Biomimic from the superhydrophobic plant leaves in nature: Binary structure and unitary structure » Zhiguang Guo, Weimin Liu, *Plant Science* Volume 172, Issue 6, June 2007, Pages 1103-1112

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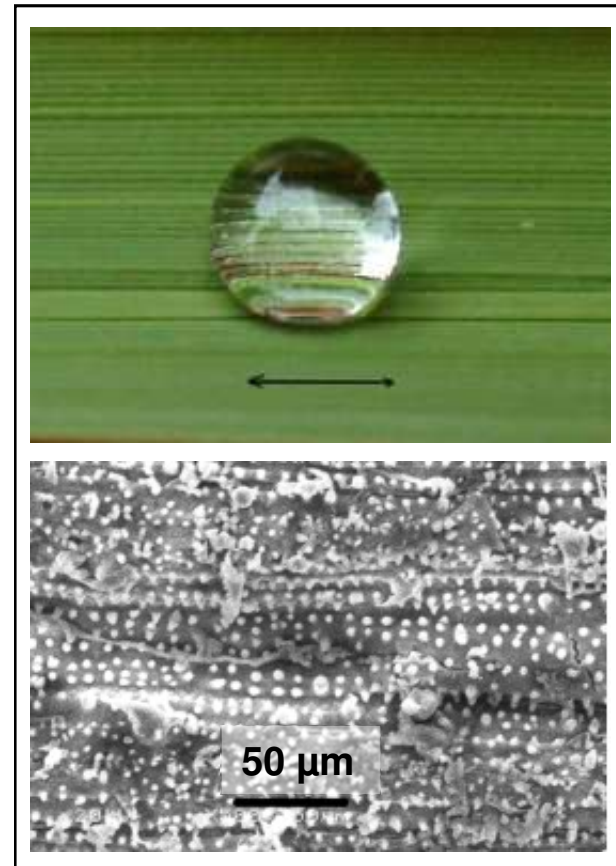
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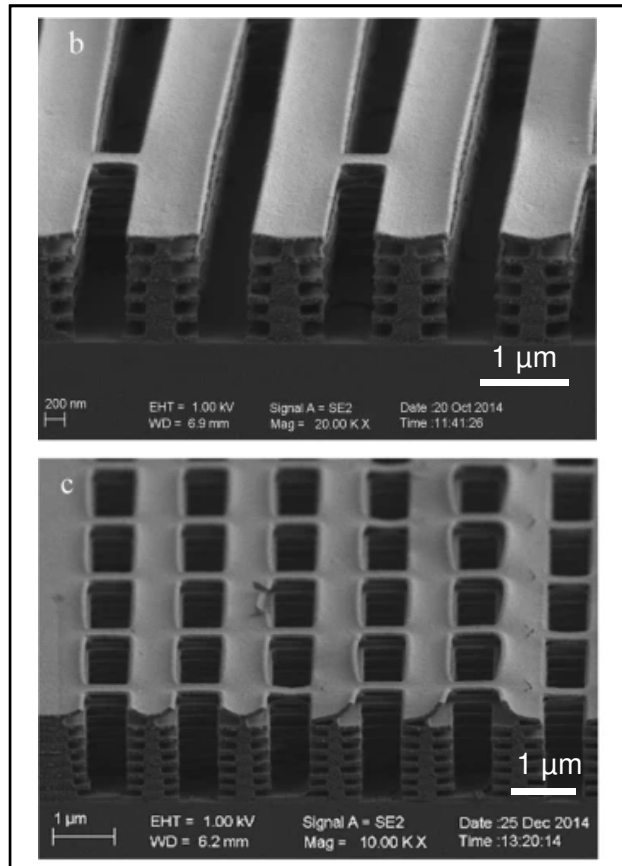


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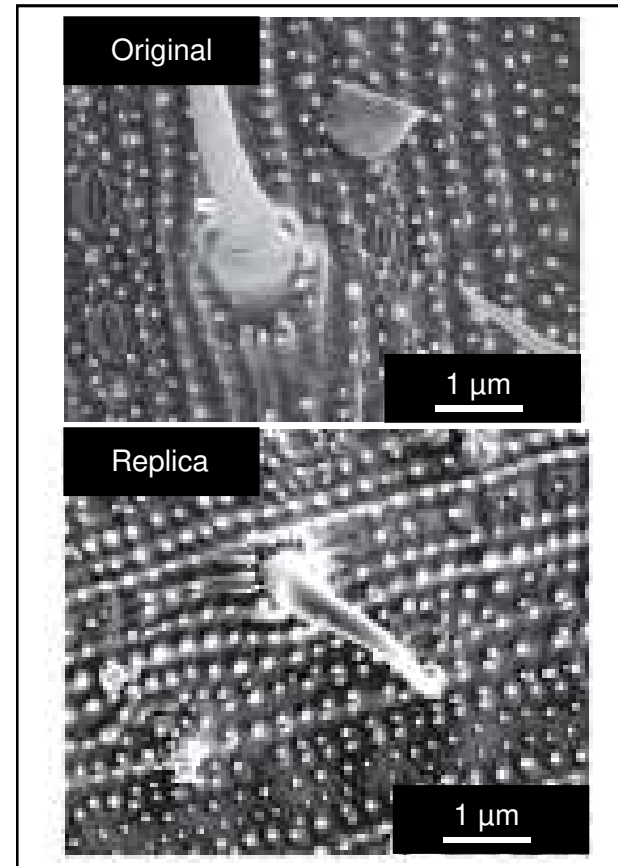
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Electron beam lithography (2015)



“Nanofabrication and coloration study of artificial Morpho butterfly wings with aligned lamellae layers” Sichao Zhang & Yifang Chen, Scientific Reports volume 5, Article number: 16637 (2015)

Molding (2021)

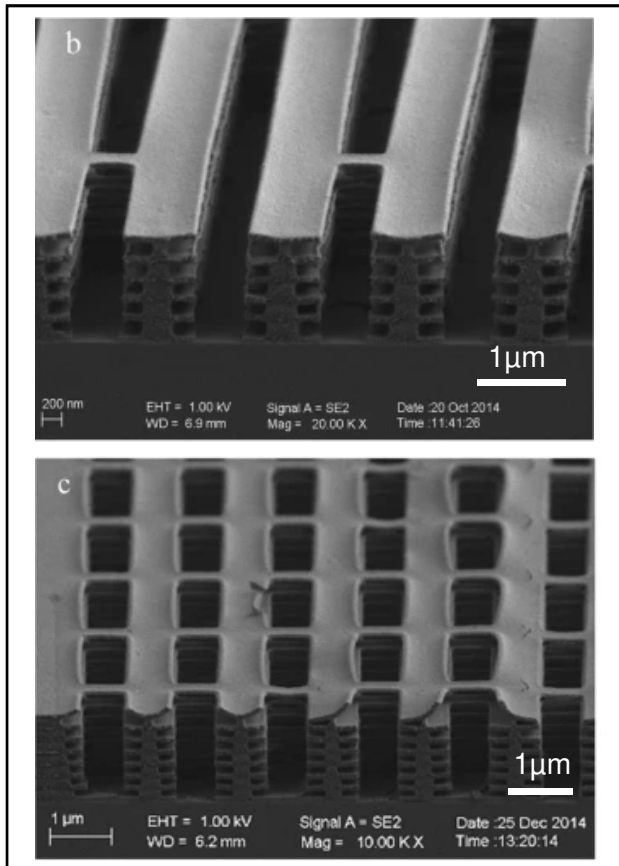


« Mimicking the surface mechanical properties of rice (*Oryza sativa*) leaf using PDMS soft lithography » Nicholas Bohlim, Donghee Lee, Sangjin Ryu & Richard A. Wilson JMST Advances volume 3, pages 11–17 (2021)

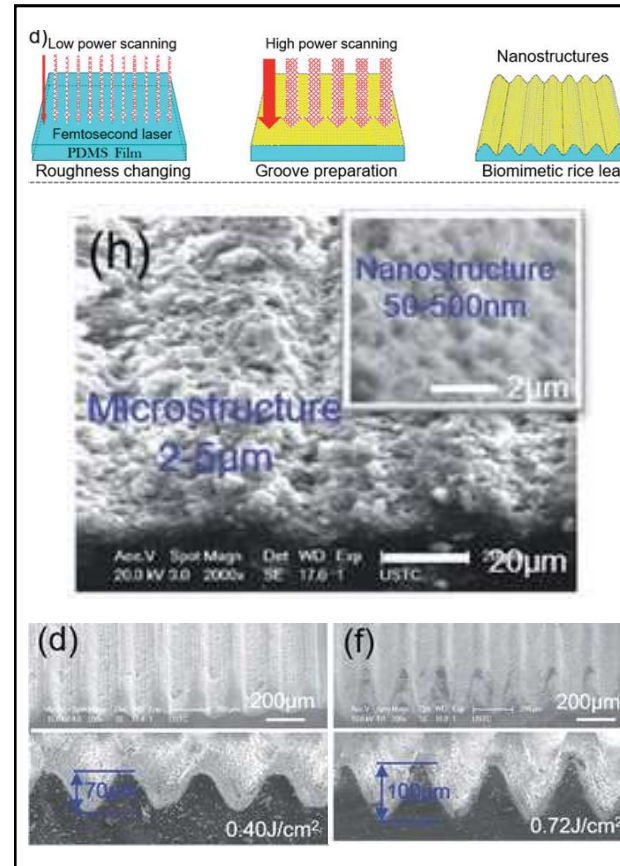
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Electron beam lithography (2015)



Femtosecond laser (2017)



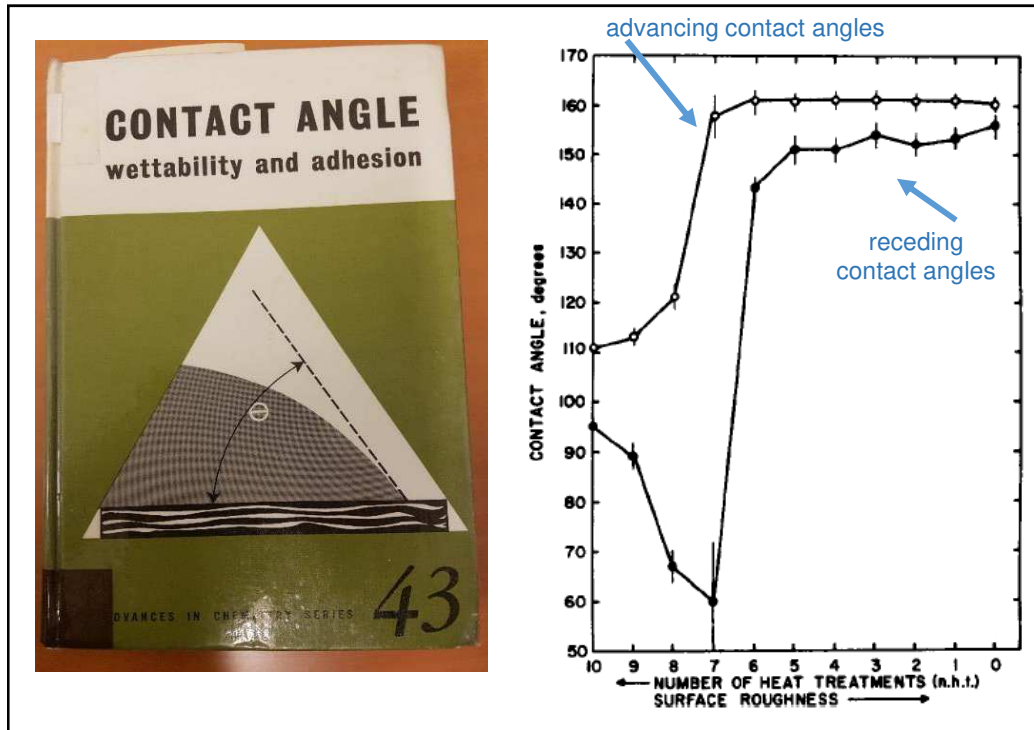
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« Biomimetic surfaces with anisotropic sliding wetting by energy-modulation femtosecond laser irradiation for enhanced water collection » Yang Lu et al. (2017) Materials Science RSC Advances

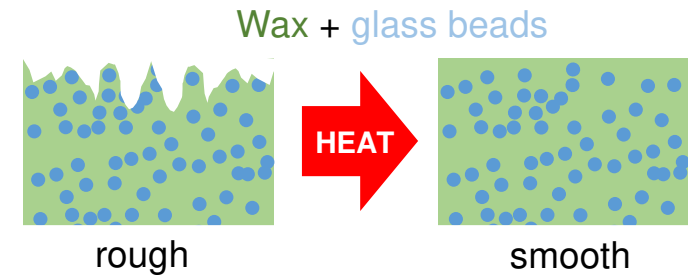
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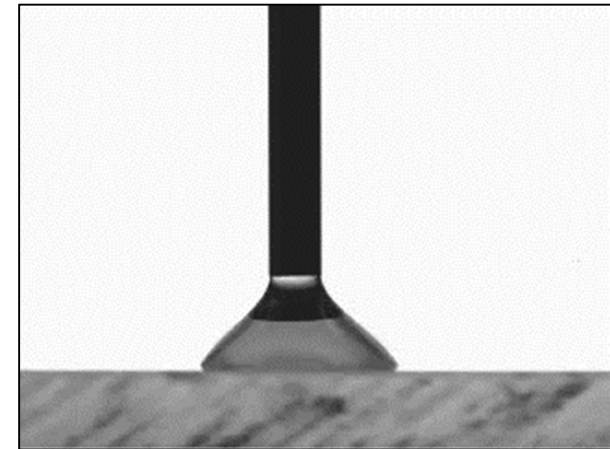
Dettre and Johnson (1964)



II. Contact Angle Measurements on Rough Surfaces R. H. DETTRE and R. E. JOHNSON JR.
Contact Angle, Wettability, and Adhesion, Editor(s): Frederick M. Fowkes Volume 43
Chapter 8, pp 136-144 DOI: 10.1021/ba-1964-0043.ch008



➔ Advancing and receding contact angles



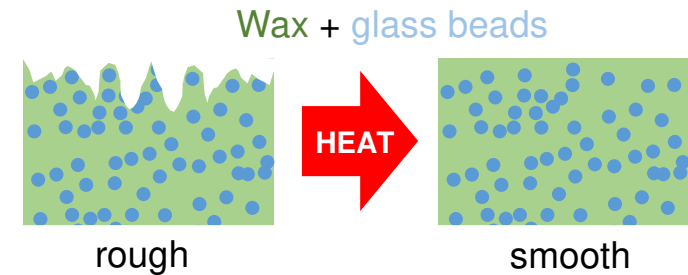
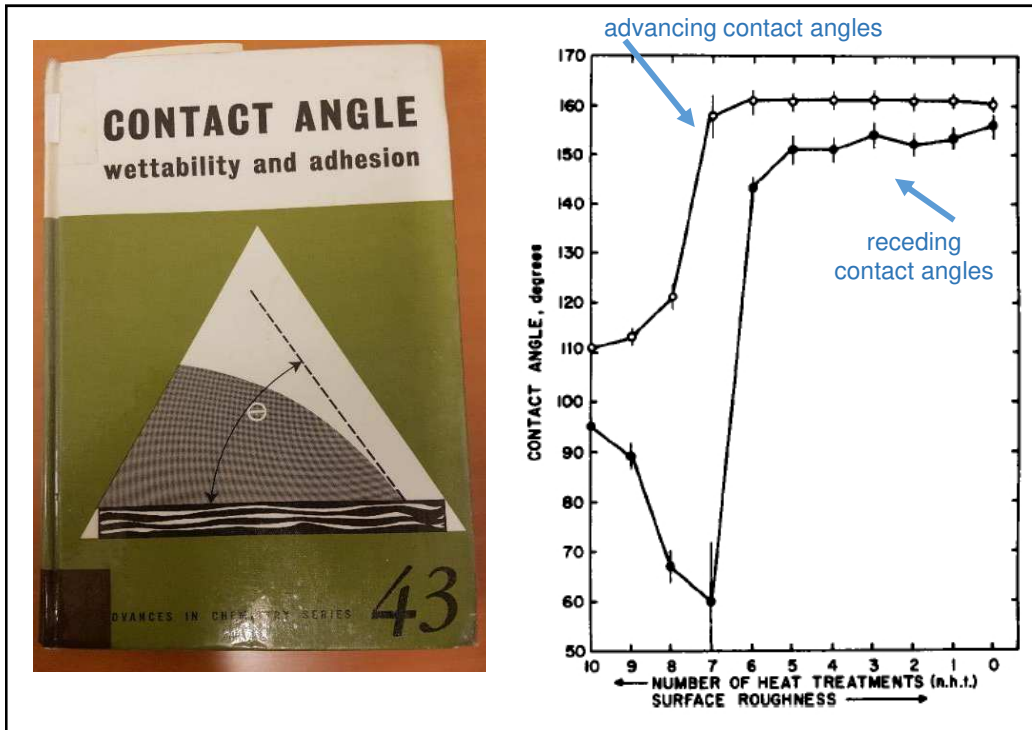
“Gouttes, bulles, perles et ondes” Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Éditions Belin)

Superhydrophobic state is characterized by a high contact angle AND low contact angle hysteresis

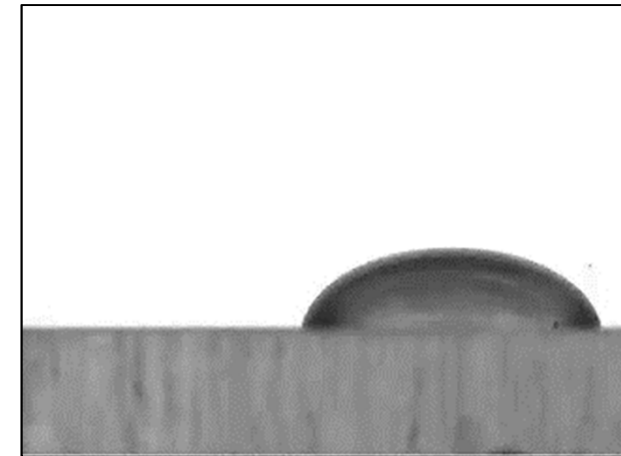
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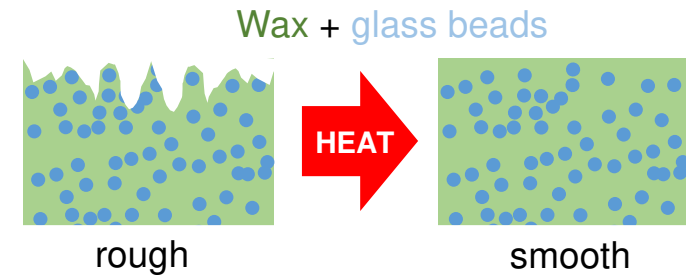
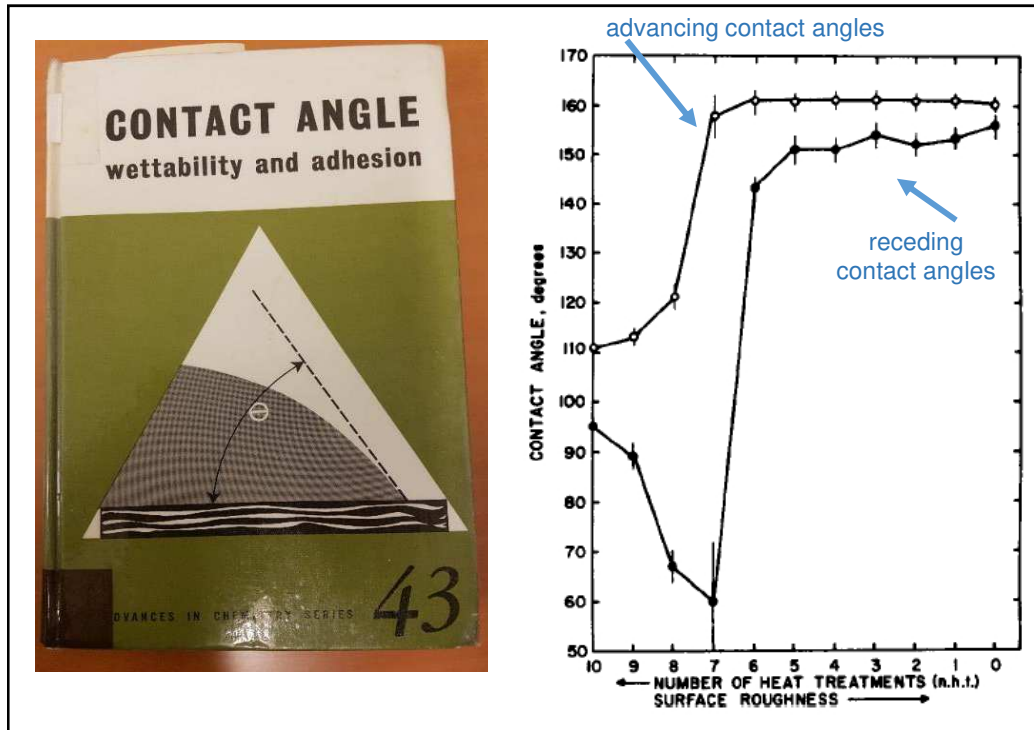
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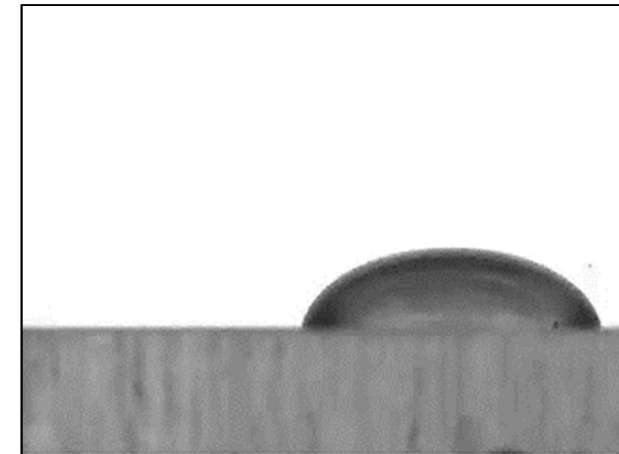
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Dettre and Johnson (1964)



➔ Advancing and receding contact angles



$$\theta_a - \theta_r = \text{hysteresis}$$

Hysteresis = adhesion

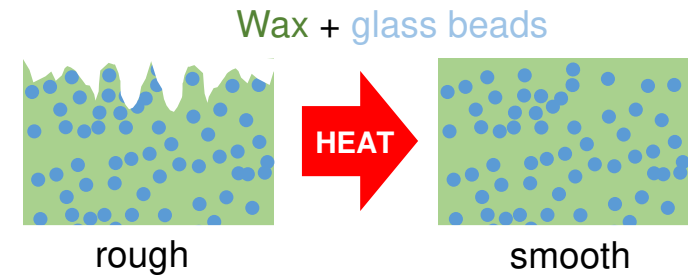
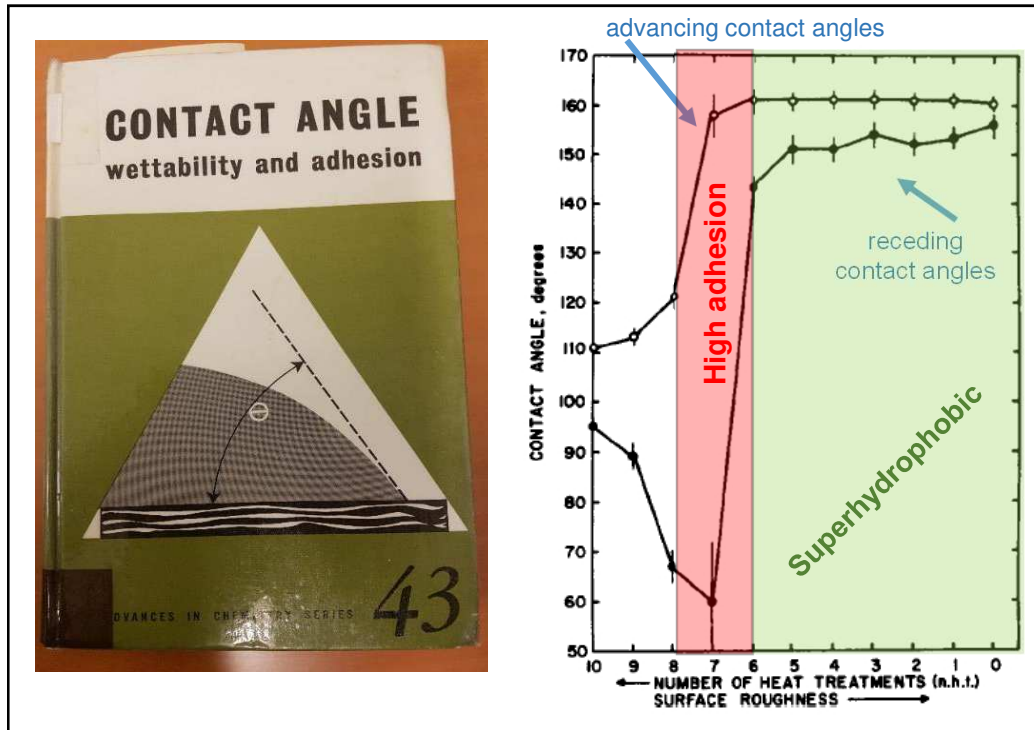
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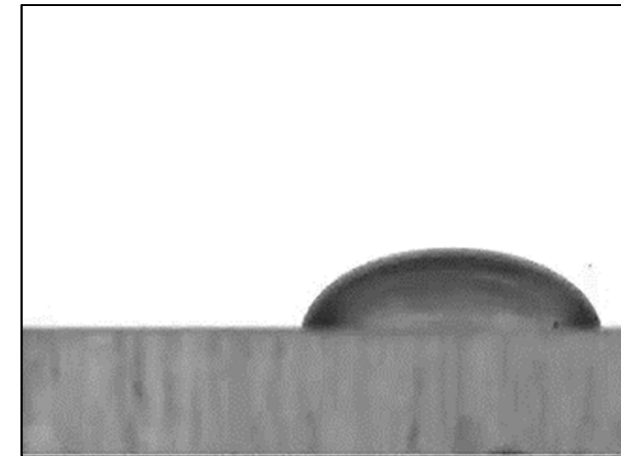
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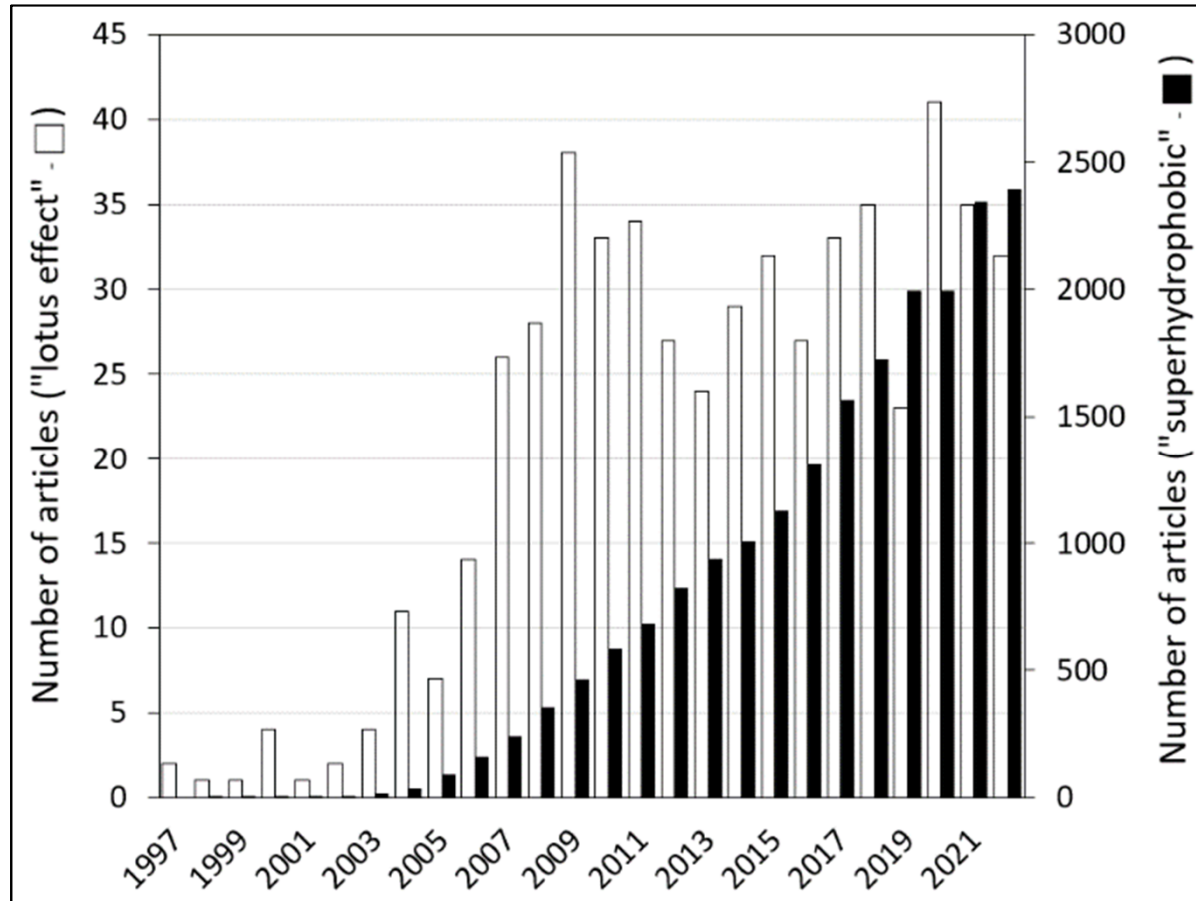
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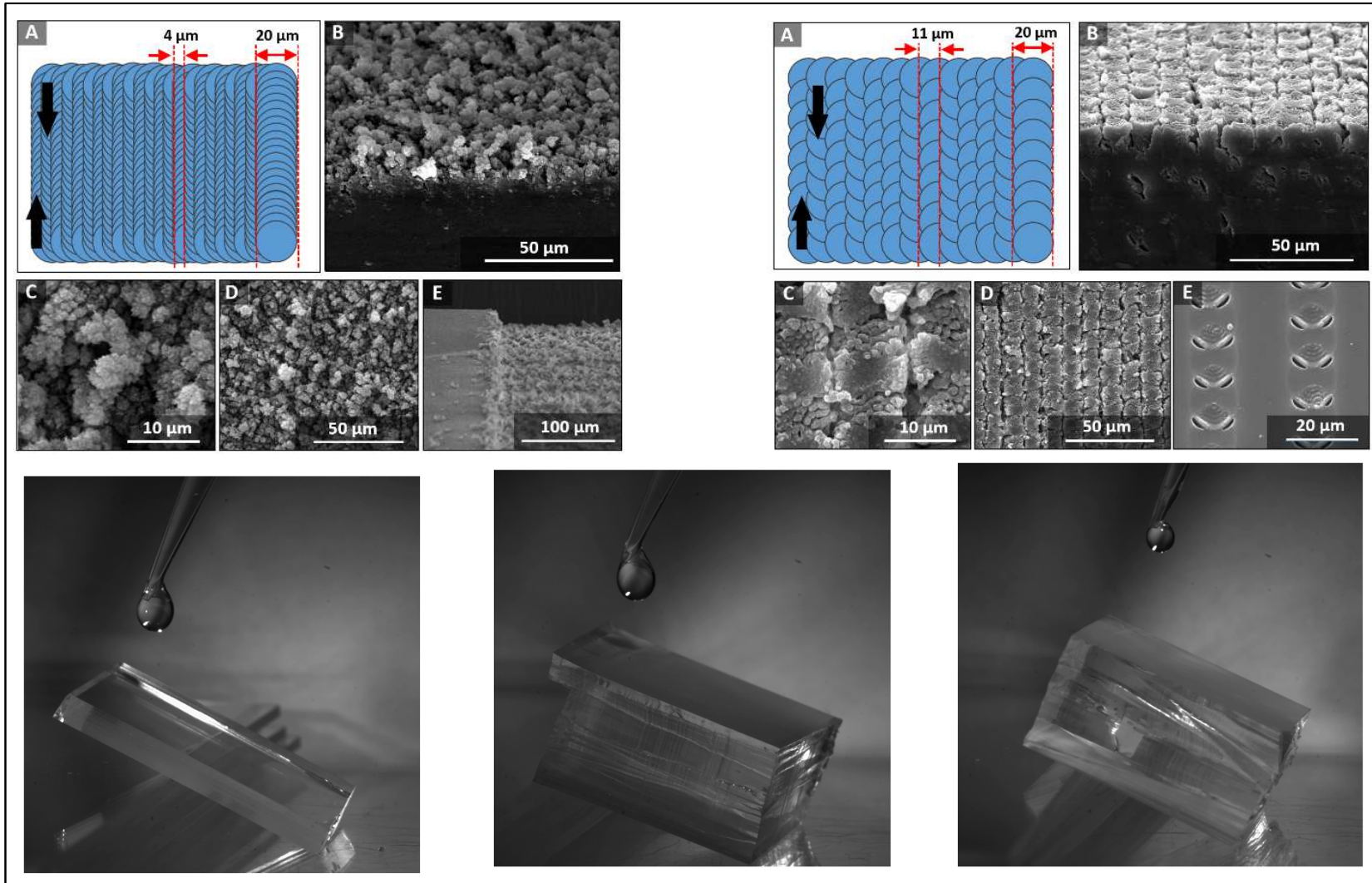


Occurrence of the terms "lotus effect" and "superhydrophobic" since 1997 according to Web of science-Clarivate (for the search fields "Title", "Abstract" and "Keywords". Using this bibliographic tool, the term "superhydrophobic" already appeared 6 times before 1997 in the field of chemical engineering and cell science.

Surfaces not wetted by liquids even of low surface tension = sessile drop method is not suited anymore

3/ Wetting of textured surfaces

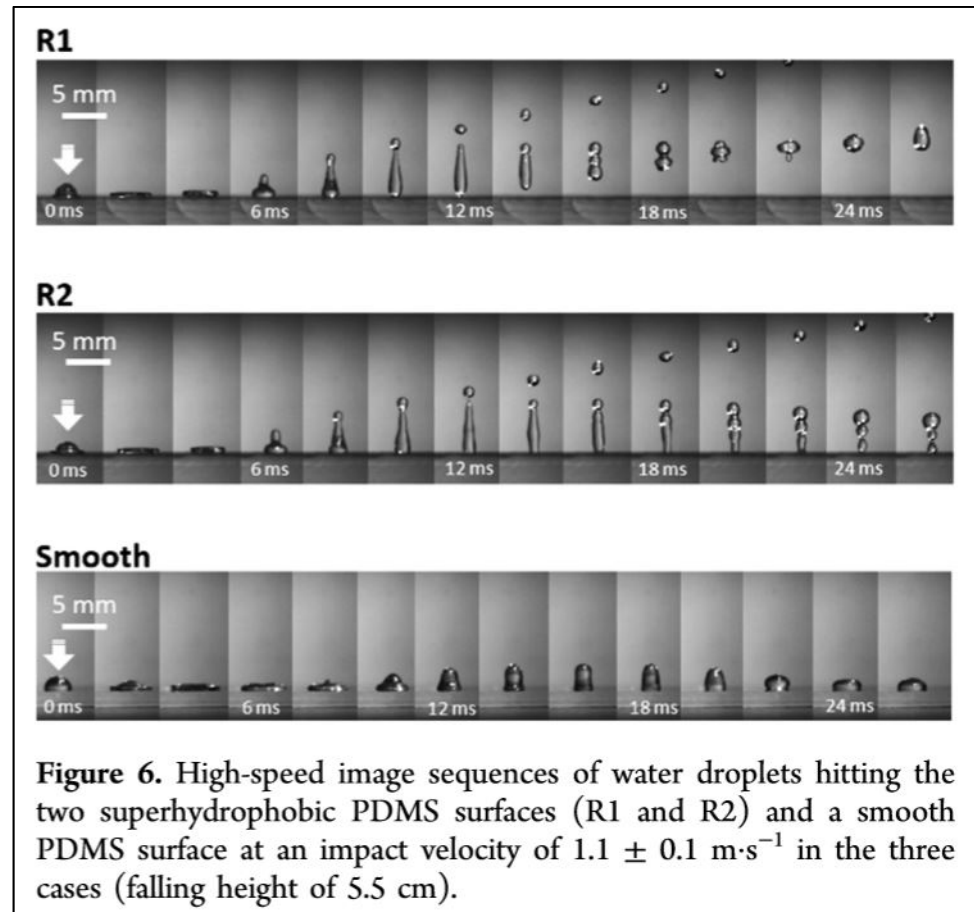
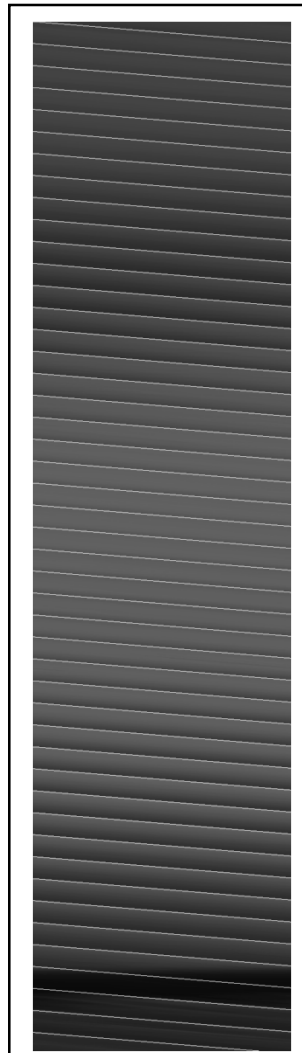
- Advanced techniques for characterizing the wetting... of non-wetting surfaces



V Hisler, H Jendoubi, C Hairaye, L Vonna, V Le Houérou, F Mermet, M Nardin, H Haidara *Tensiometric Characterization of Superhydrophobic Surfaces As Compared to the Sessile and Bouncing Drop Methods*, *Langmuir* **32** (31), 7765-7773 (2016)

4/ Resisting wetting

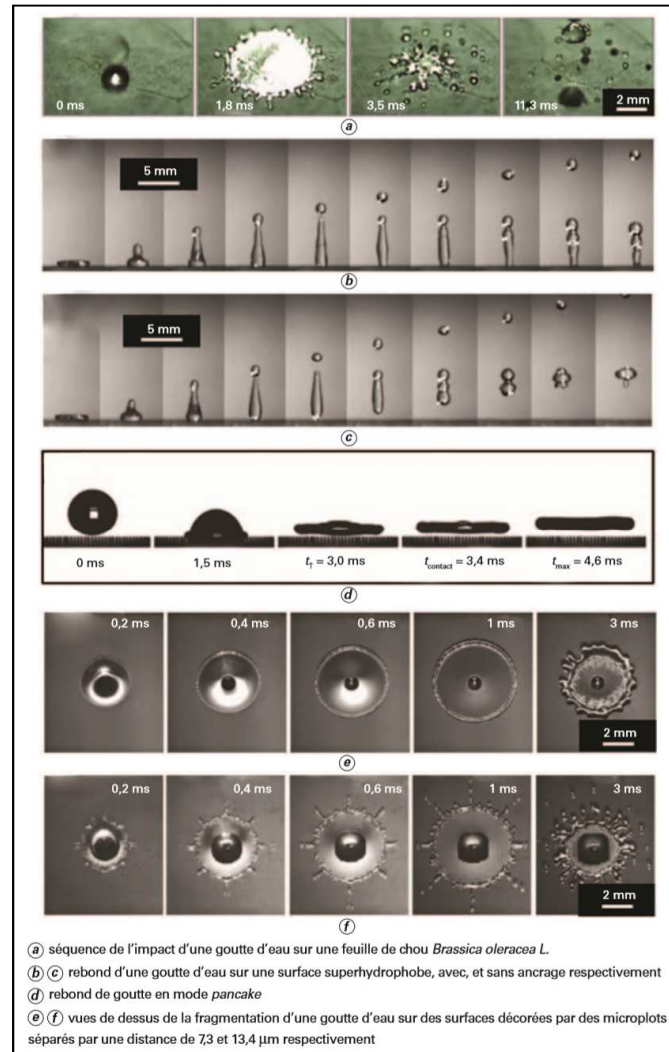
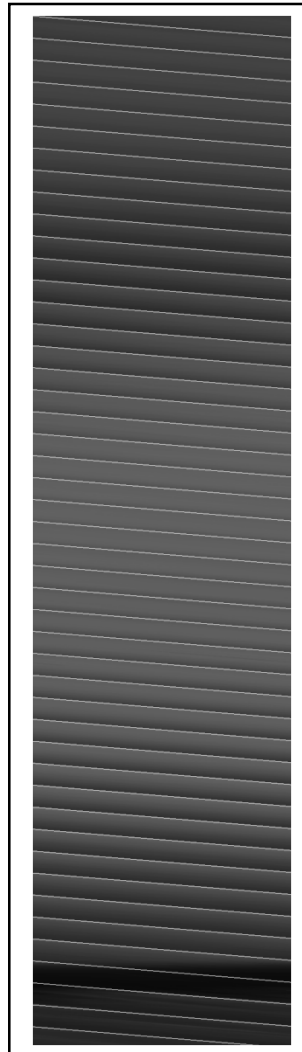
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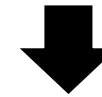
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4/ Resisting wetting

- Advanced techniques for characterizing the wetting... of non-wetting surfaces



The falling drop



Inertia to force wetting

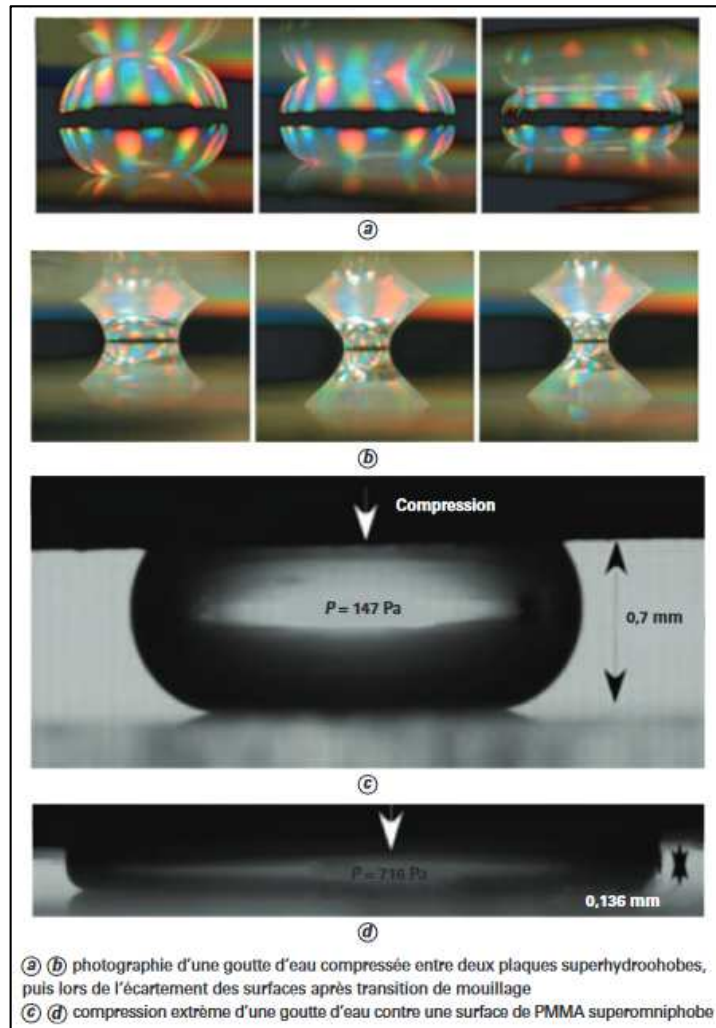
SONG (M.), JU (J.) et LUO (S.), et al.– Controlling liquid splash on superhydrophobic surfaces by a vesicle surfactant. *Sci Adv* 3 : 1-8. doi: 10.1126/sciadv.1602188 (2017).

LIU (Y.), MOEVIUS (L.) et XU (X.), et al.–Pancake bouncing on superhydrophobic surfaces. *Nat Phys* 10 : 515-519. doi: 10.1038/NPHYS2980 (2014).

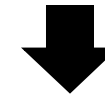
TSAI (P.), HENDRIX (M.H.W.) et DIJKSTRA (R.R.M.), et al.–Microscopic structure influencing macroscopic splash at high Weber number. *Soft Matter* 7 : 11325. doi: 10.1039/c1sm05801k (2011).

4/ Resisting wetting

- **Advanced techniques for characterizing the wetting... of non-wetting surfaces**



The squeezed droplet



Critical pressure to induced
the forced wetting

Lafuma A. and Quéré D.
Superhydrophobic states. *Nat Mater* 2 : 457-60. doi:10.1038/nmat924
(2003)

Gnanappa A.K., Papageirgiu D.P. and Gogolides E. et al.
Hierarchical, plasma nanotextured, robust superamphiphobic polymeric
surfaces structurally stabilized through a wetting-drying cycle. *Plasma
Process Polym* 9 : 304-315. doi: 10.1002/ppap.201100124 (2012)

Wettability

Laurent Vonna

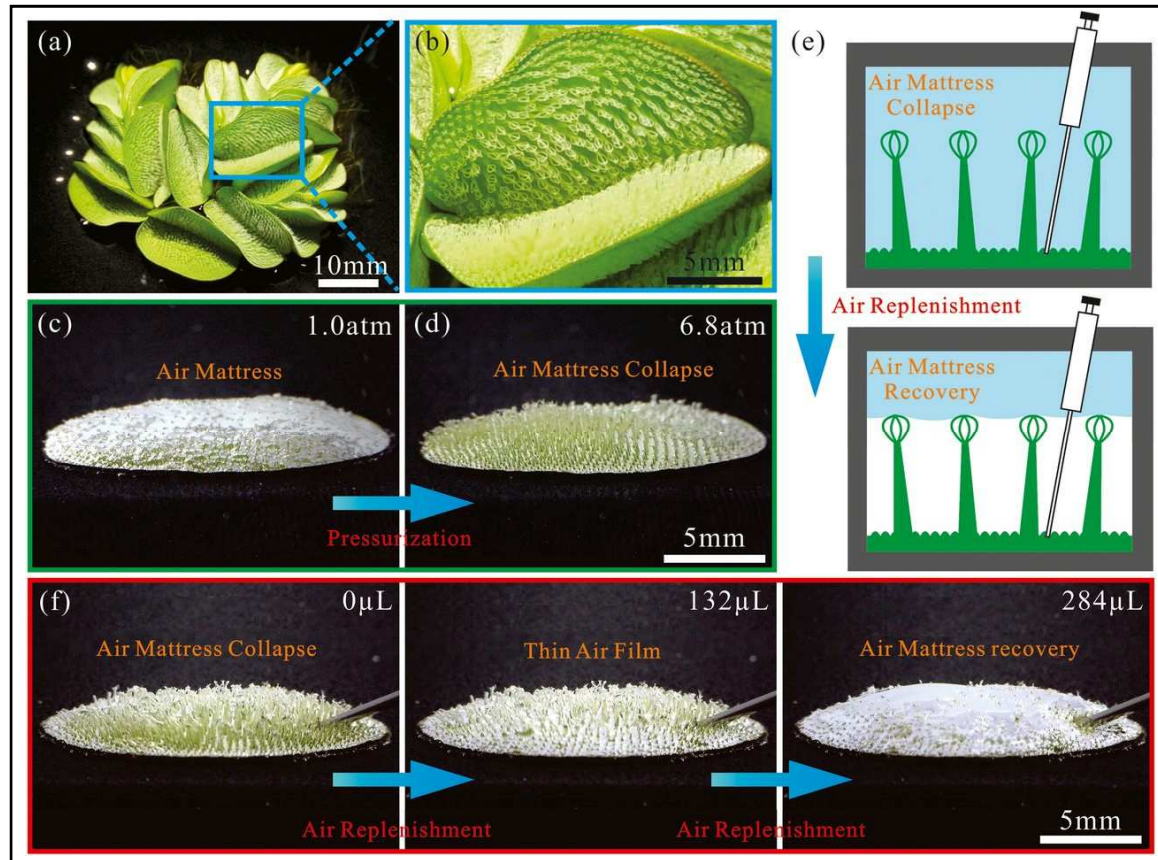
- 1/ Surface tension and cohesive forces
- 2/ Wetting for a measure of the surface energy
- 3/ Wetting of textured surfaces
- 4/ Resisting wetting
- 5/ Liquid-infused surfaces



« Stability of the volume of air trapped on the abdomen of the water spider *Argyroneta aquatica* » Dietrich Neumann and Dietrich Woermann, Springerplus. 2013; 2: 694 doi: 10.1186/2193-1801-2-694

4/ Resisting wetting

- Stability of an air layer at the surface of immersed *Salvinia molesta* leaves



➡ Stable air mattress
➡ = plastron

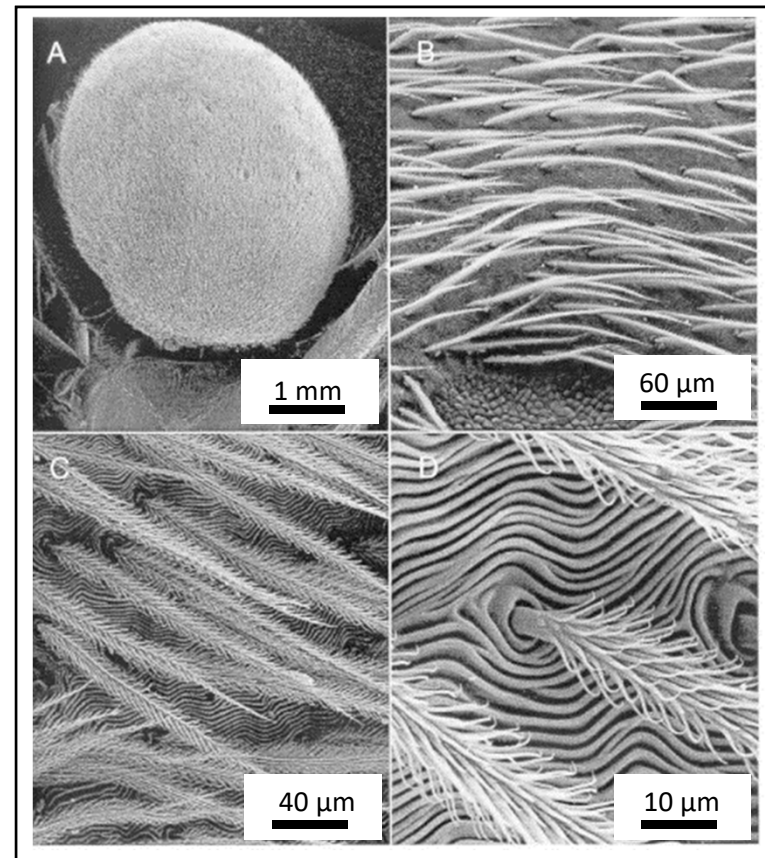
- ➡ Resist biofouling
- ➡ Resist bacterial adhesion
- ➡ Reduce drag

4/ Resisting wetting

- The water spider *Argyroneta aquatica*



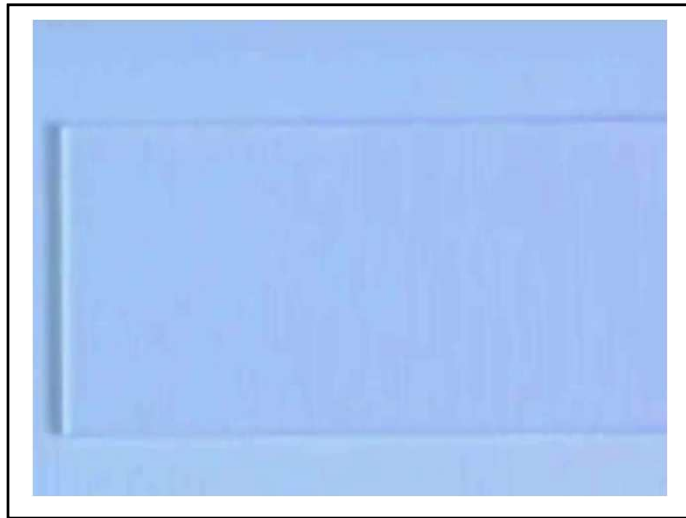
- ➔ Stable air mattress
- ➔ Stabilized by an abdomen covered with hairs



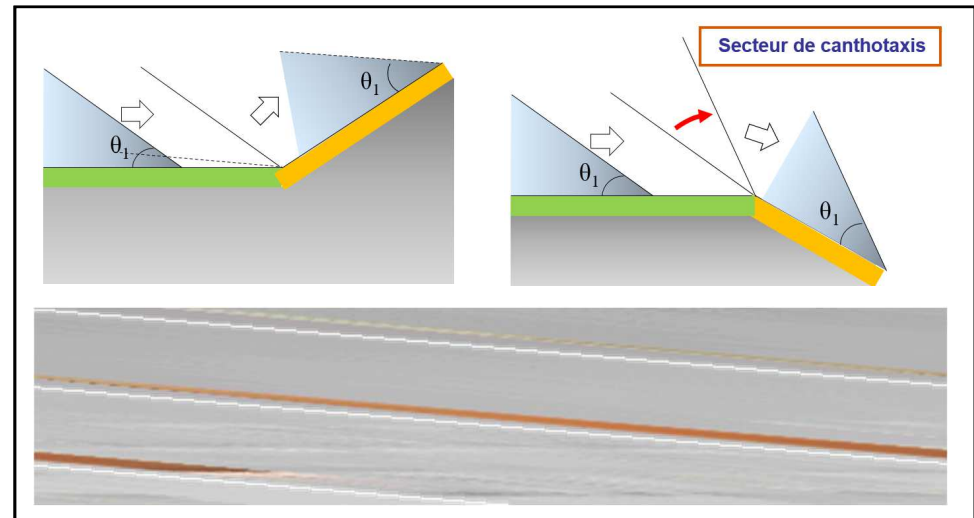
« Stability of the volume of air trapped on the abdomen of the water spider *Argyroneta aquatica* » Dietrich Neumann and Dietrich Woermann, Springerplus. 2013; 2: 694 doi: 10.1186/2193-1801-2-694

4/ Resisting wetting

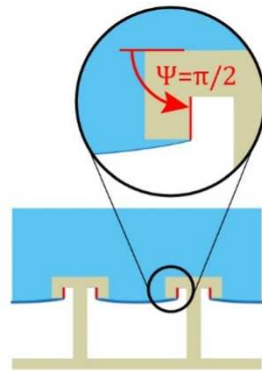
- **Pinning of the moving contact line using re-reentrant morphologies**



“Free-Running Droplets” Fabrice Domingues Dos Santos and Thierry Ondarçuhu Phys. Rev. Lett. 75, 2972 – Published 16 October 1995



“Gouttes, bulles, perles et ondes” Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Éditions Belin)



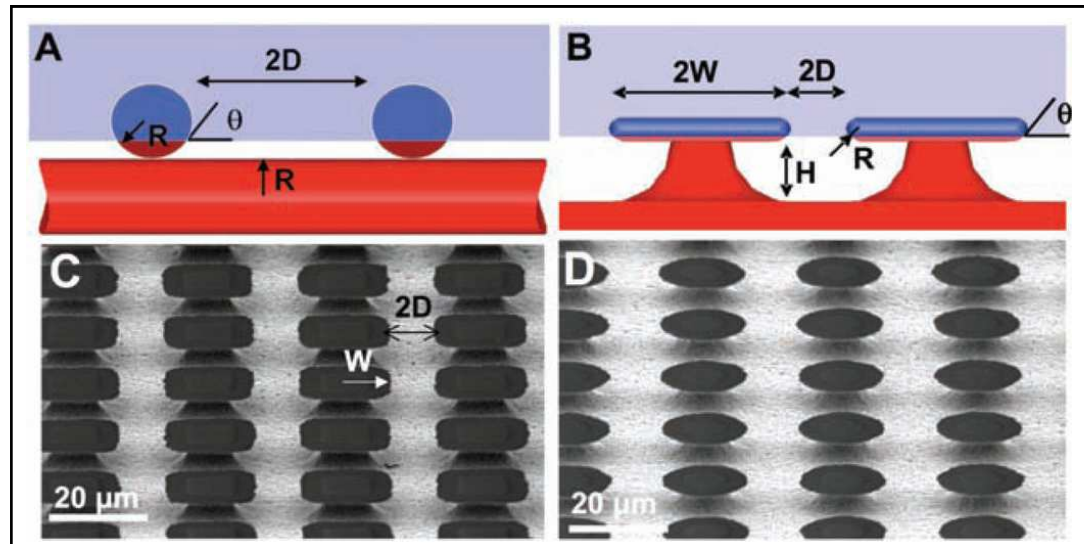
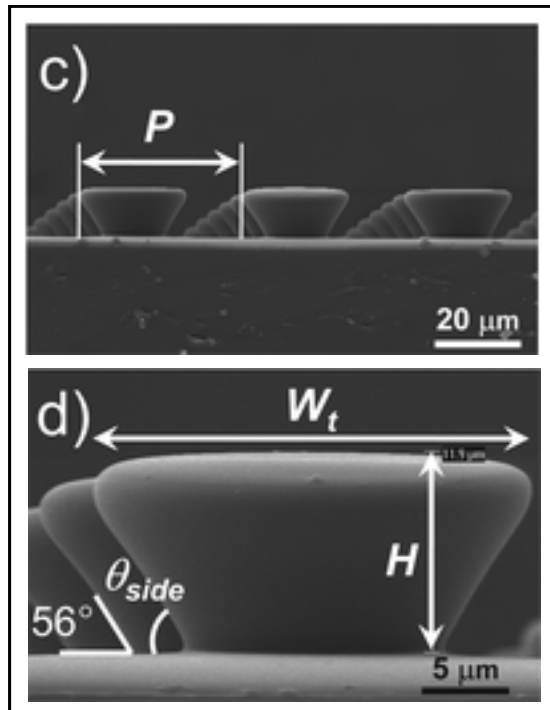
- ➔ Re-entrant textures at the microscopic scale
- ➔ Resist wetting even with liquids of low surface tension
- ➔ Superoleophobic surfaces

« Why re-entrant surface topography is needed for robust oleophobicity » Michael Nosonovsky, B. Bhushan, 2016, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences DOI:10.1098/rsta.2016.0185

4/ Resisting wetting

- Pinning of the moving contact line using re-reentrant morphologies

Artificial re-entrant surface textures

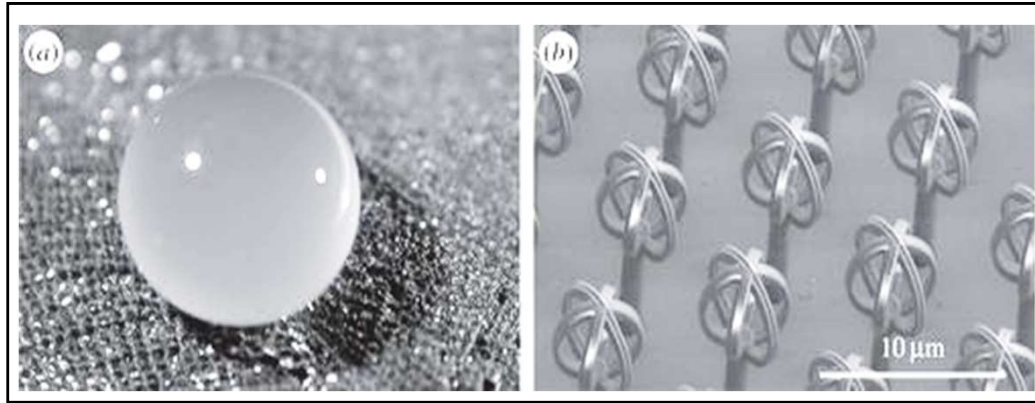


« Design parameters for superhydrophobicity and superoleophobicity ». Tuteja, A.; Choi, W.; McKinley, G.H.; Cohen, R.E.; Rubner, M.F. *MRS Bull.* 2008, 33, 752–758.

« A robust superhydrophobic and superoleophobic surface with inverse-trapezoidal microstructures on a large transparent flexible substrate » Maesoon Im, Hown Im, Joo-Hyung Lee, Jun-Bo Yoon and Yang-Kyu Choi *Soft Matter*, 2010,6, 1401-1404

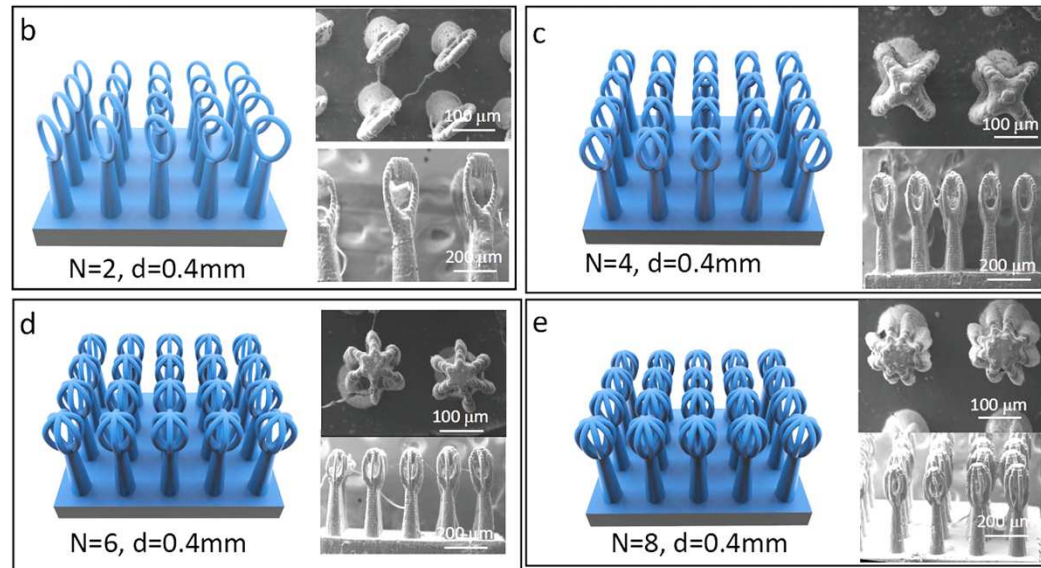
The rose petal effect

3D printed salvinia-like microtextures (2015)



Tricinci O, Terencio T, Mazzolai B, Pugno NM, Greco F, Mattoli V.
« 3D micropatterned surfaces inspired by *Salvinia molesta* via direct laser lithography ». (2015) *ACS Appl. Mater. Interfaces* 7, 25 560–25 567.
([doi:10.1021/acsami.5b07722](https://doi.org/10.1021/acsami.5b07722))

(2018)



« 3D-Printed Biomimetic Super-Hydrophobic Structure for Microdroplet Manipulation and Oil/Water Separation » Yang Yang, Xiangjia Li, Xuan Zheng, Zeyu Chen, Qifa Zhou, Yong Chen
2018 *Materials Science, Engineering Advanced Materials*

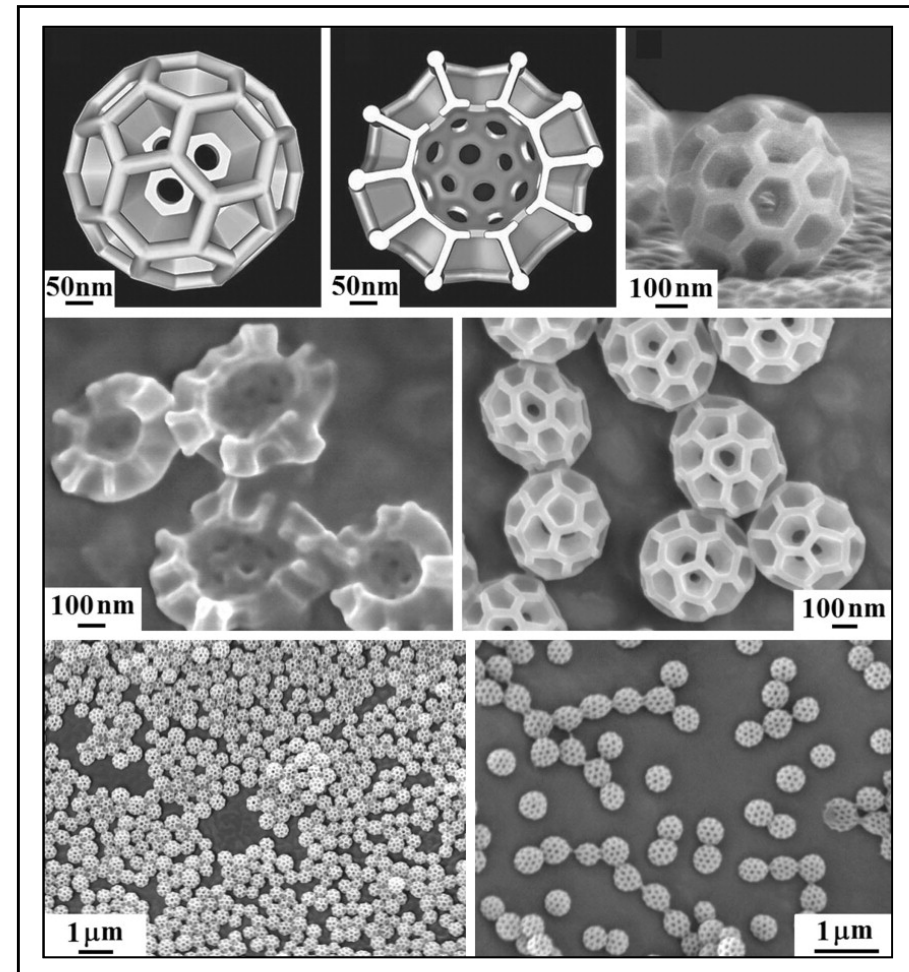
4/ Resisting wetting

- Pinning of the moving contact line using re-reentrant morphologies

Re-entrant surface textures in nature



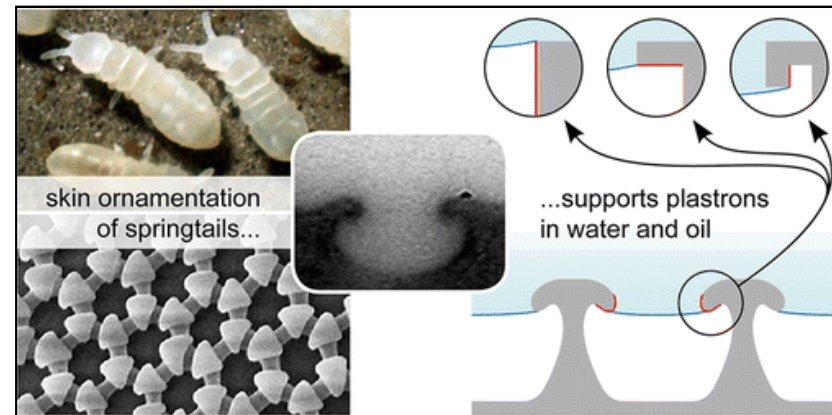
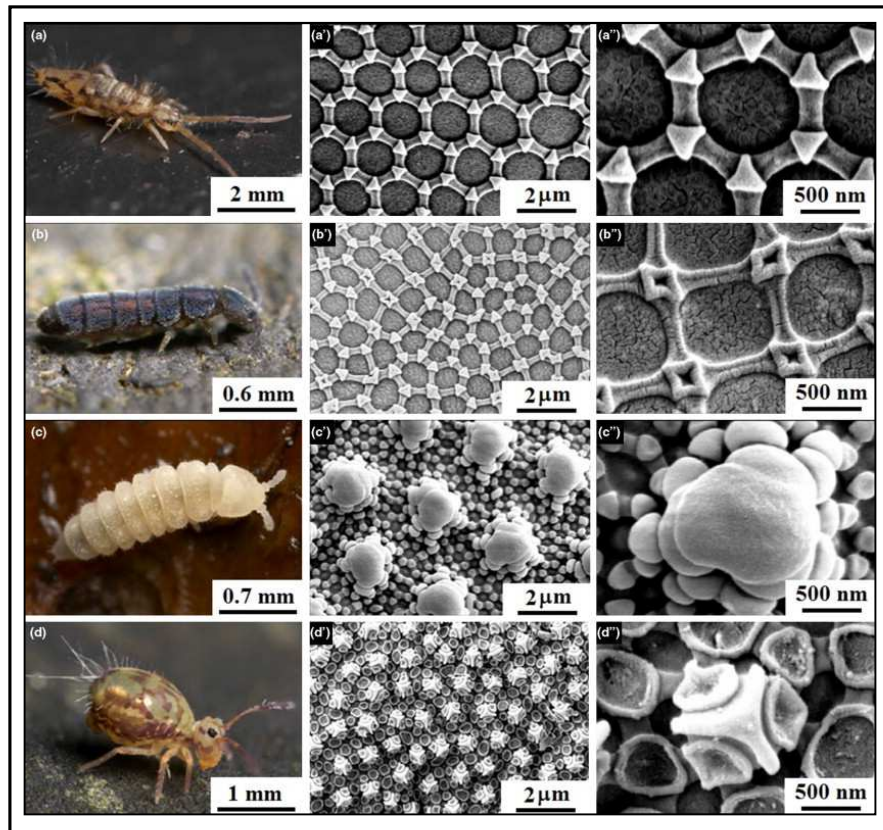
« Brochosomal coats turn leafhopper (Insecta, Hemiptera, Cicadellidae) integument to superhydrophobic state » Roman Rakitov, Stanislav N. Gorb
Proceedings of the Royal Society B 80:
20122391 (2013)



4/ Resisting wetting

- Pinning of the moving contact line using re-reentrant morphologies

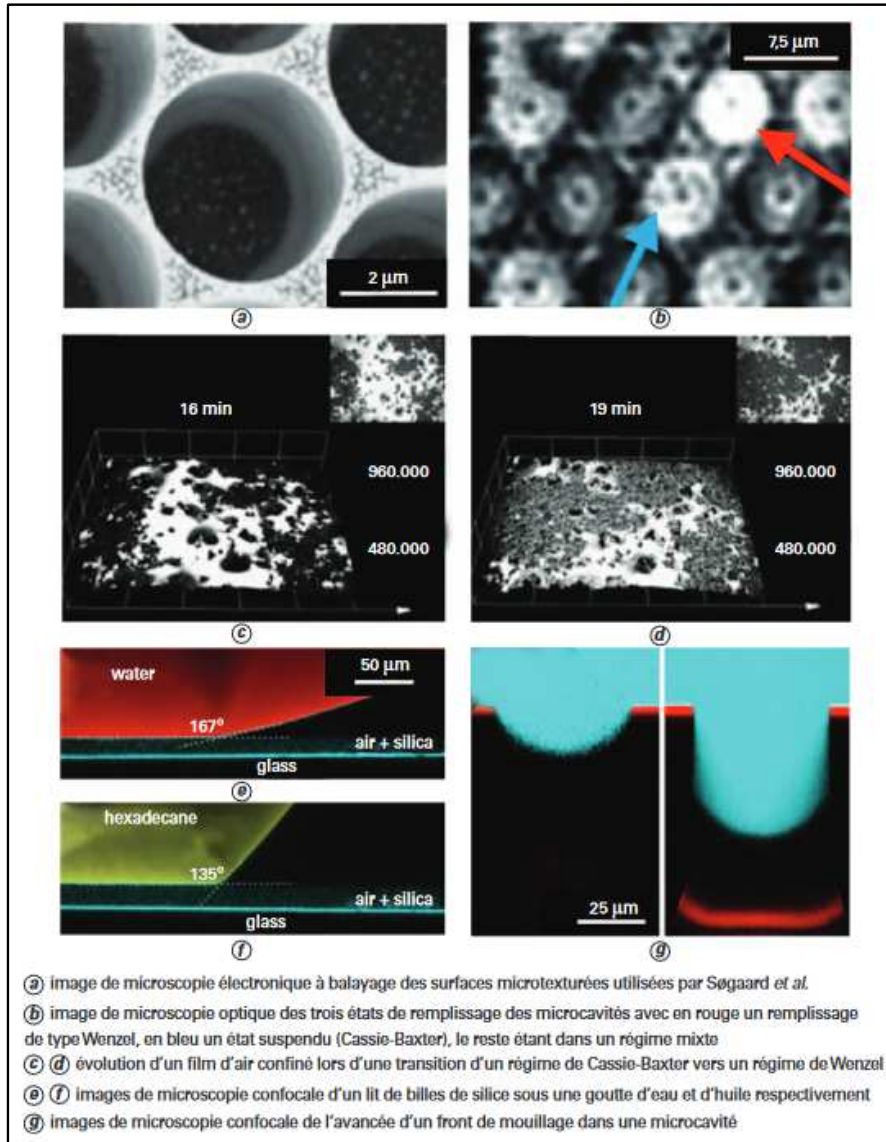
Re-entrant surface textures in nature



« Wetting Resistance at Its Topographical Limit: The Benefit of Mushroom and Serif T Structures »
René Hensel, Ralf Helbig, Sebastian Aland, Hans-Georg Braun, Axel Voigt, Christoph Neinhuis, and
Carsten Werner Langmuir, 2013, 29 (4), pp 1100–1112

4/ Resisting wetting

- Advanced techniques for characterizing the wetting... of non-wetting surfaces



Optical techniques



For the stability and the morphology of the air cushion

Sogaard, E. et al. Study of Transitions between Wetting States on Micro-cavity Arrays by Optical Transmission Microscopy. *Langmuir* 30 : 12960-12968. doi: DOI: 10.1021/la502855g (2014).

Lei, L.I., Shi, J., and Chen, Y. Diffraction patterns of a water-submerged superhydrophobic grating under pressure. *Langmuir* 26 :3666-3669 doi:10.1021/la903150h (2010).

Luo, C. et al. – Direct three-dimensional imaging of the buried interfaces between water and superhydrophobic surfaces *AngewChemie-IntEd* 49 :9145148 doi:10.1002/anie.201002470 (2010).

Papadopoulos, P. et al. Electrokinetics on superhydrophobic surfaces. *JPhysCondens Matter* 24:464110 doi:10.1088/0953-8984/24/46/464110 (2012).

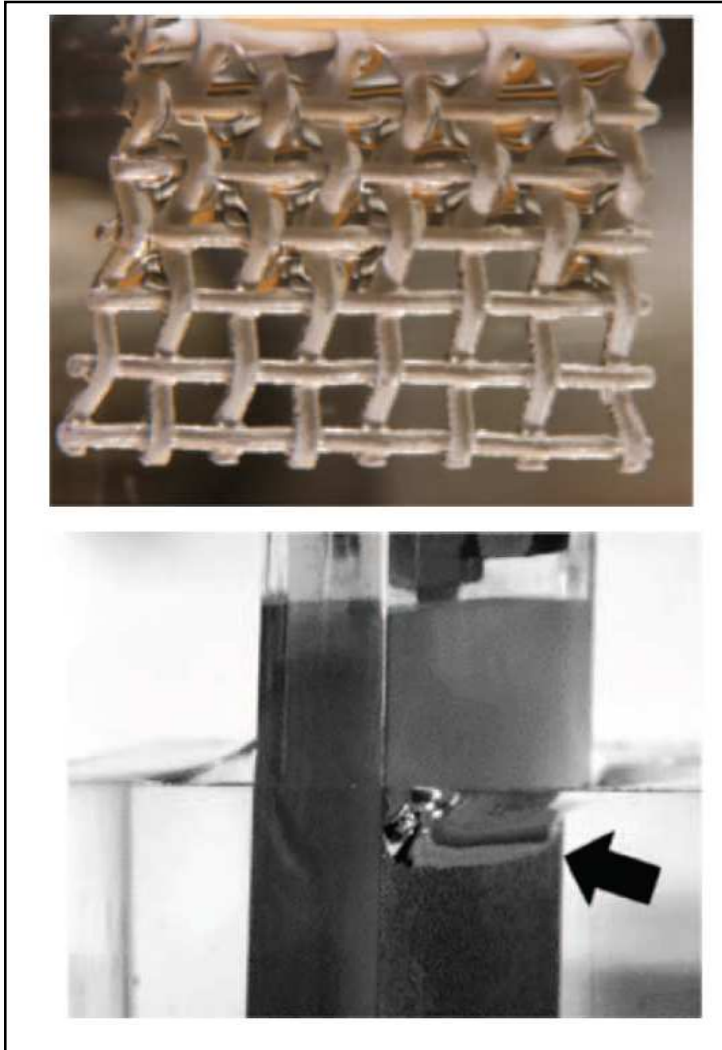
Lu, P. et al. – Metastable states and wetting transition of submerged superhydrophobic structures. *PhysRevLett* 112:1-5 doi:10.1103/PhysRevLett.112.196101 (2014).



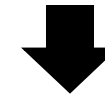
What is the ability of a surface to resist wetting (hydrostatic pressure, biological conditions,...)

4/ Resisting wetting

- **Advanced techniques for characterizing the wetting... of non-wetting surfaces**



Wilheemy plate



Adhesion under immersion

Kleingartner, J.A. et al. Utilizing Dynamic Tensiometry to Quantify Contact Angle Hysteresis and Wetting State Transitions on Nonwetting Surfaces. *Langmuir* 29 : 13396-13406
doi: DOI: 10.1021/la4022678 (2013).

Kim, J.-H. et al. Dynamic contact angle measurements on superhydrophobic surfaces. *Phys Fluids* 27 : 032107
doi: 10.1063/1.4915112 (2015).

V Hisler, H Jendoubi, C Hairaye, L Vonna, V Le Houérou, F Mermet, M Nardin, H Haidara
Tensiometric Characterization of Superhydrophobic Surfaces As Compared to the Sessile and Bouncing Drop Methods, *Langmuir* 32 (31) ,7765-7773 (2016)



What is the ability of a surface to resist wetting (hydrostatic pressure, biological conditions,...)

Wettability

Laurent Vonna

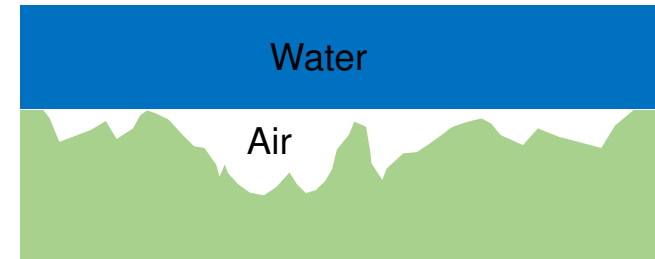
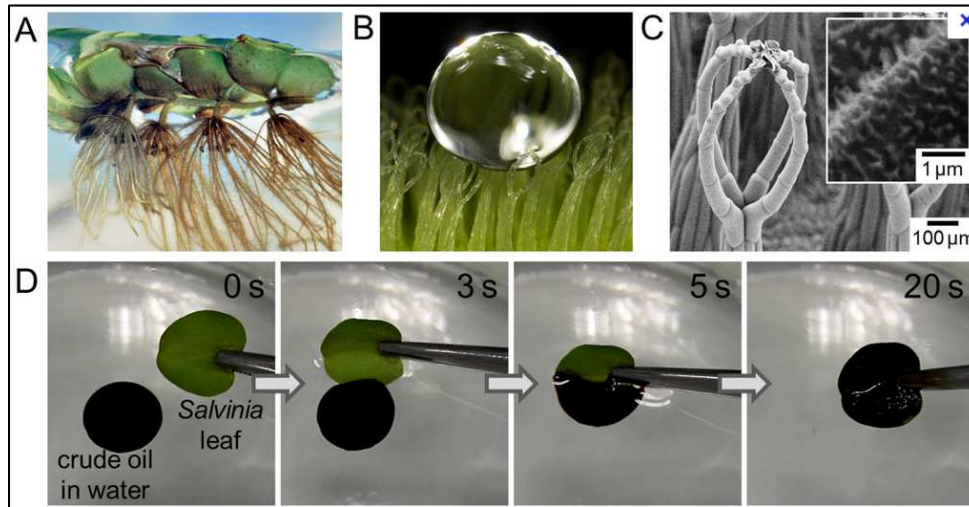
- 1/ Surface tension and cohesive forces
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<http://especies-exotiques-envahissantes.fr/espece/salvinia-molesta/>

5/ Liquid infused surfaces

- Replacement of the plastron by oil



- ➔ Liquid-infused surface
- ➔ Stable liquid layer

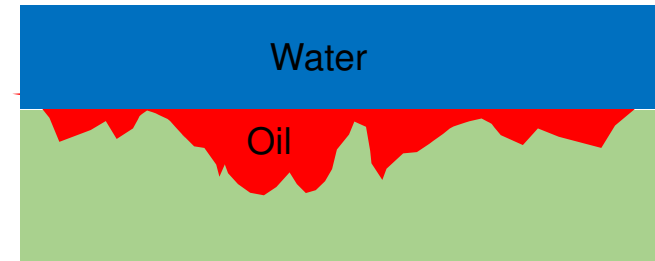
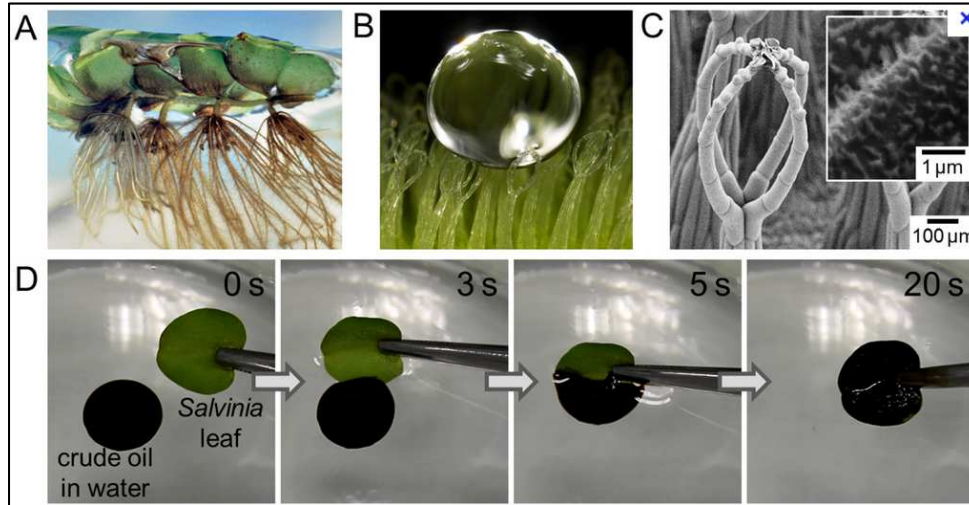


Microstructures of superhydrophobic plant leaves - inspiration for efficient oil spill cleanup materials Claudia Zeiger, Isabelle C Rodrigues da Silva, Matthias Mail, Maryna N Kavalenka, Wilhelm Barthlott and Hendrik Hölscher *Bioinspiration & Biomimetics*, Volume 11, Number 5

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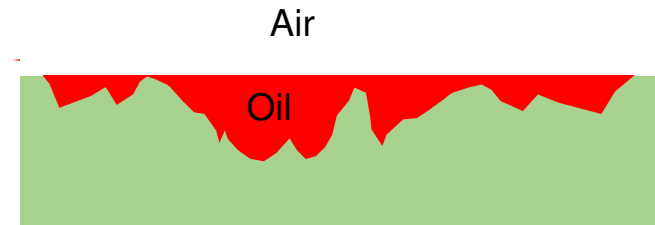
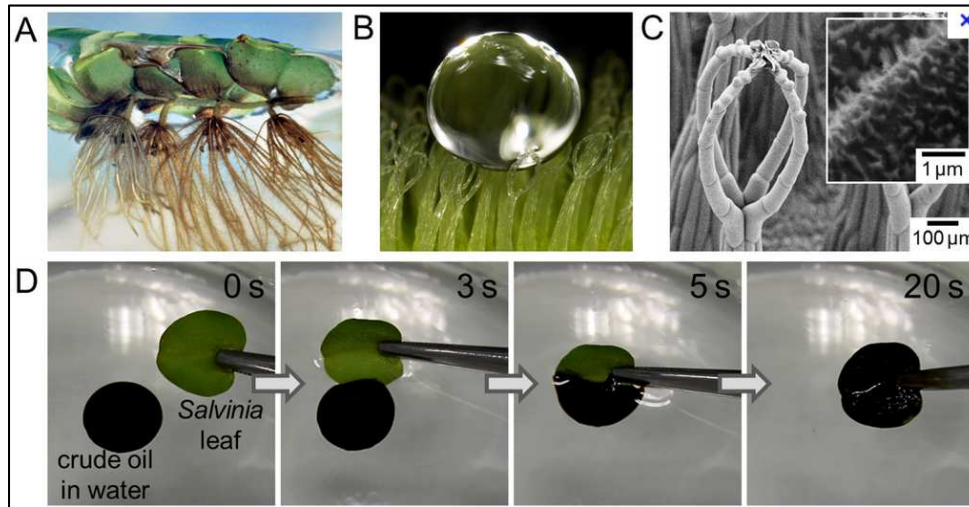


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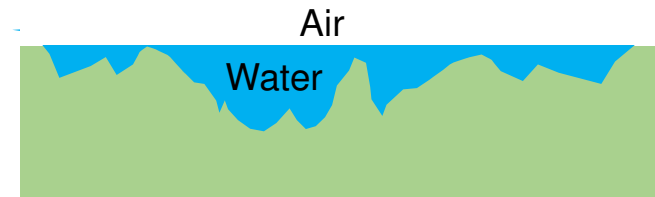
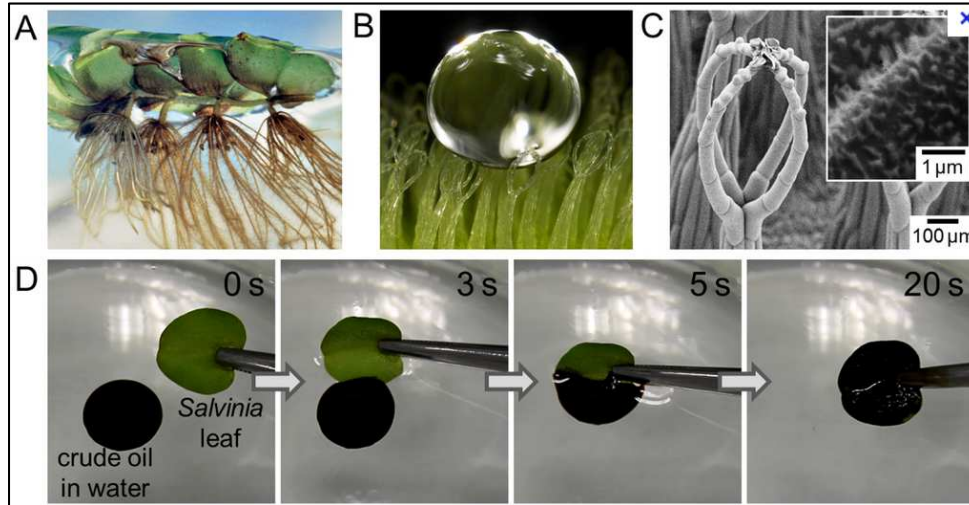


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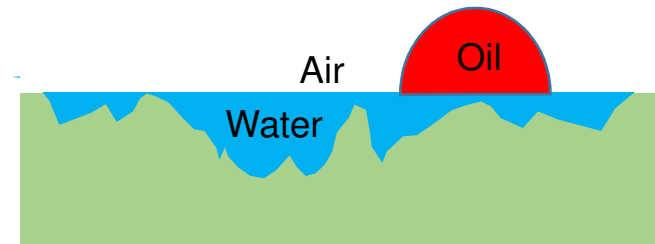
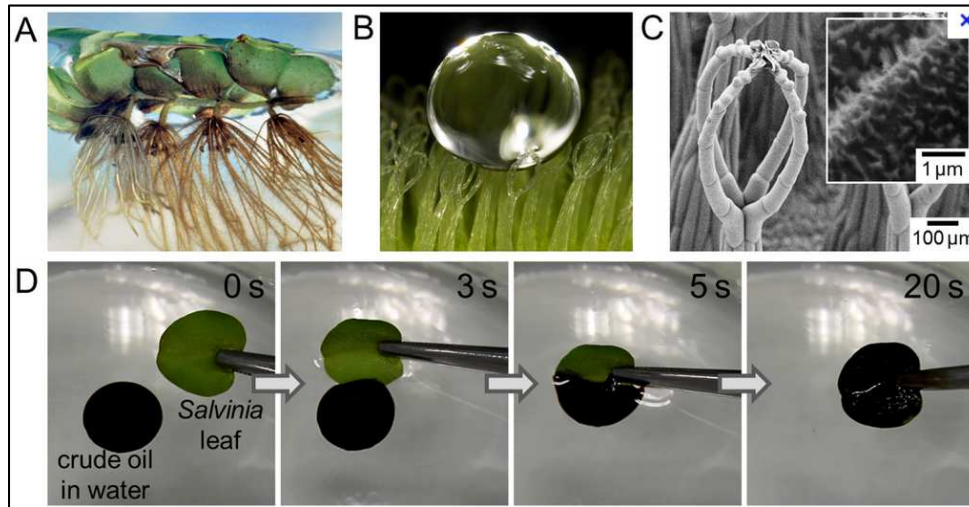


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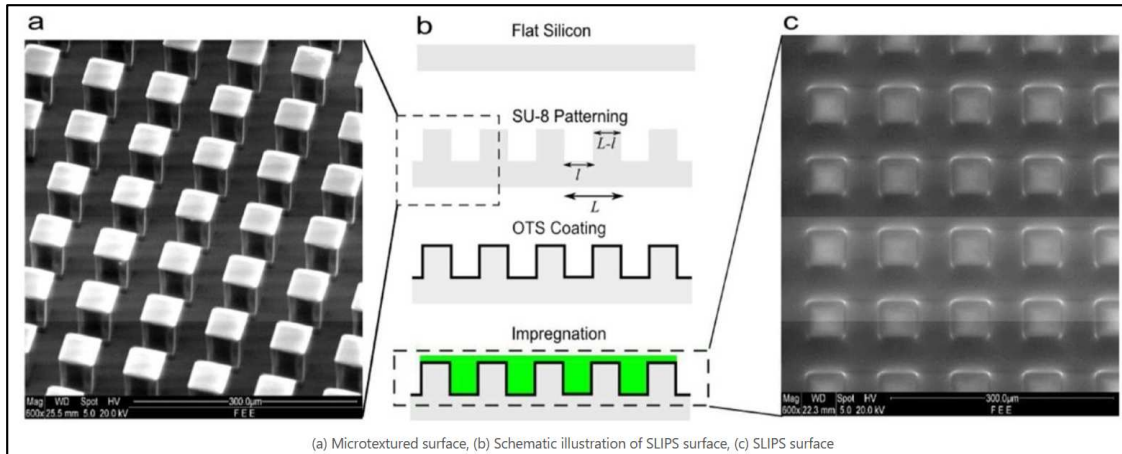
Microstructures of superhydrophobic plant leaves - inspiration for efficient oil spill cleanup materials Claudia Zeiger, Isabelle C Rodrigues da Silva, Matthias Mail, Maryna N Kavalenka, Wilhelm Barthlott and Hendrik Hölscher *Bioinspiration & Biomimetics*, Volume 11, Number 5

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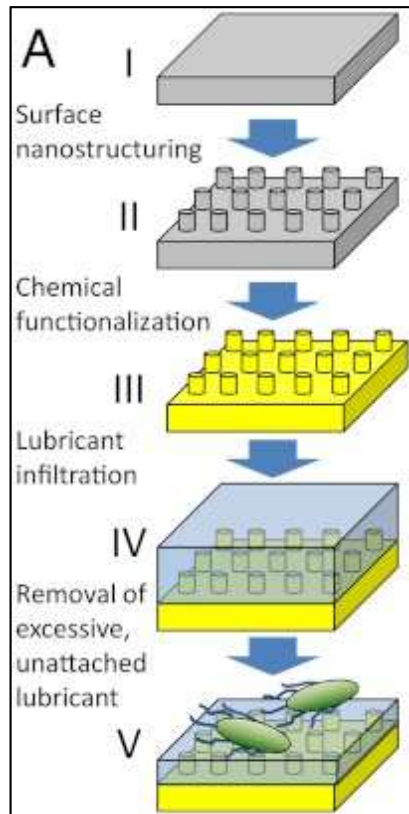
Lubricated surfaces



« Droplet mobility on lubricant-impregnated surfaces » J. David Smith, Rajeev Dhiman, Sushant Anand, Ernesto Reza-Garduno, Robert E. Cohen, Gareth H. McKinley and Kripa K. Varanasi *Soft Matter*, 6, 2013

5/ Liquid infused surfaces

• Replacement of the plastron by oil



Anti-adhesive surfaces (against bacteria)

Slippery Liquid-Infused Porous Surfaces (SLIPS) prevent

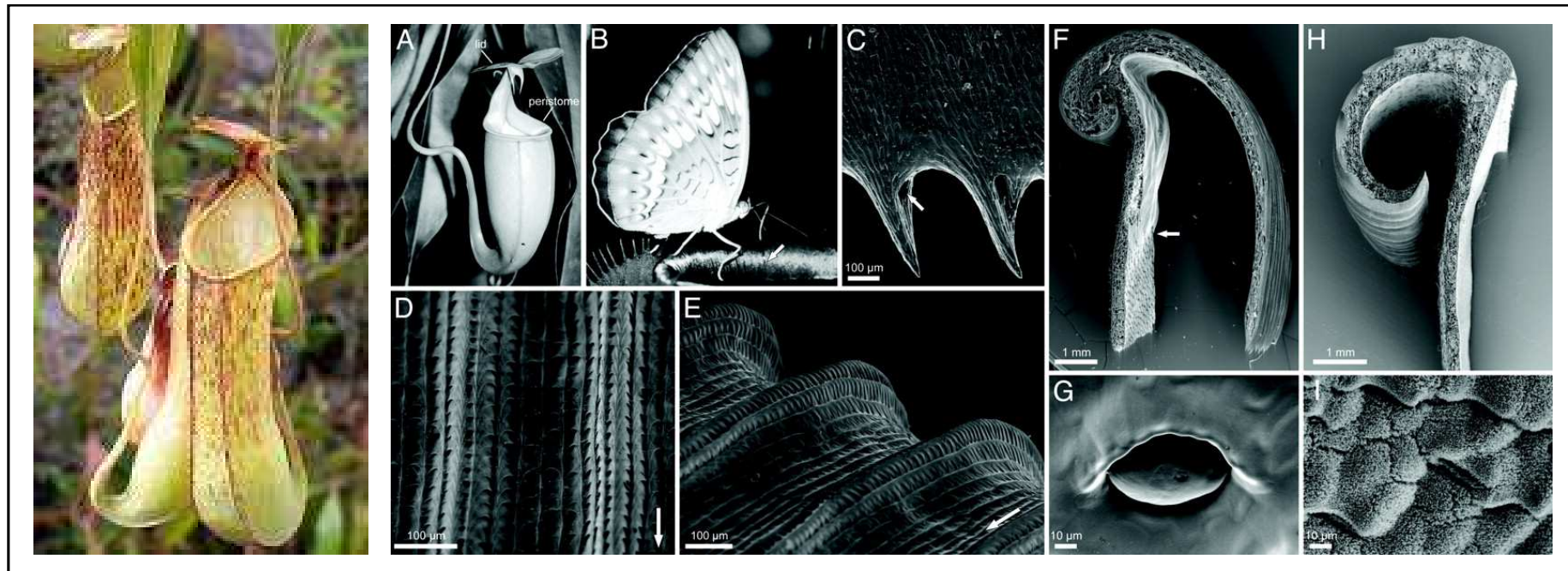
- 99.6% of *Pseudomonas aeruginosa* biofilm attachment
- 97.2 % of *Staphylococcus aureus* biofilm attachment
- 96 % of *Escherichia coli* biofilm attachment

under both static and physiologically realistic flow conditions.

Proc Natl Acad Sci U S A. 2012 Aug 14;109(33):13182-7. doi: 10.1073/pnas.1201973109. Epub 2012 Jul 30 **Liquid-infused structured surfaces with exceptional anti-biofouling performance.** Epstein AK¹, Wong TS, Belisle RA, Boggs EM, Aizenberg J.

5/ Liquid infused surfaces

- **Nepenthes pitcher plants capture strategy**



« Insect aquaplaning: *Nepenthes* pitcher plants capture prey with the peristome, a fully wettable water-lubricated anisotropic surface »
Holger F Bohn and Walter Federle 2004 ,Sep 28;101(39):14138-43.
doi: 10.1073/pnas.0405885101

5/ Liquid infused surfaces

- **Nepenthes pitcher plants capture strategy**



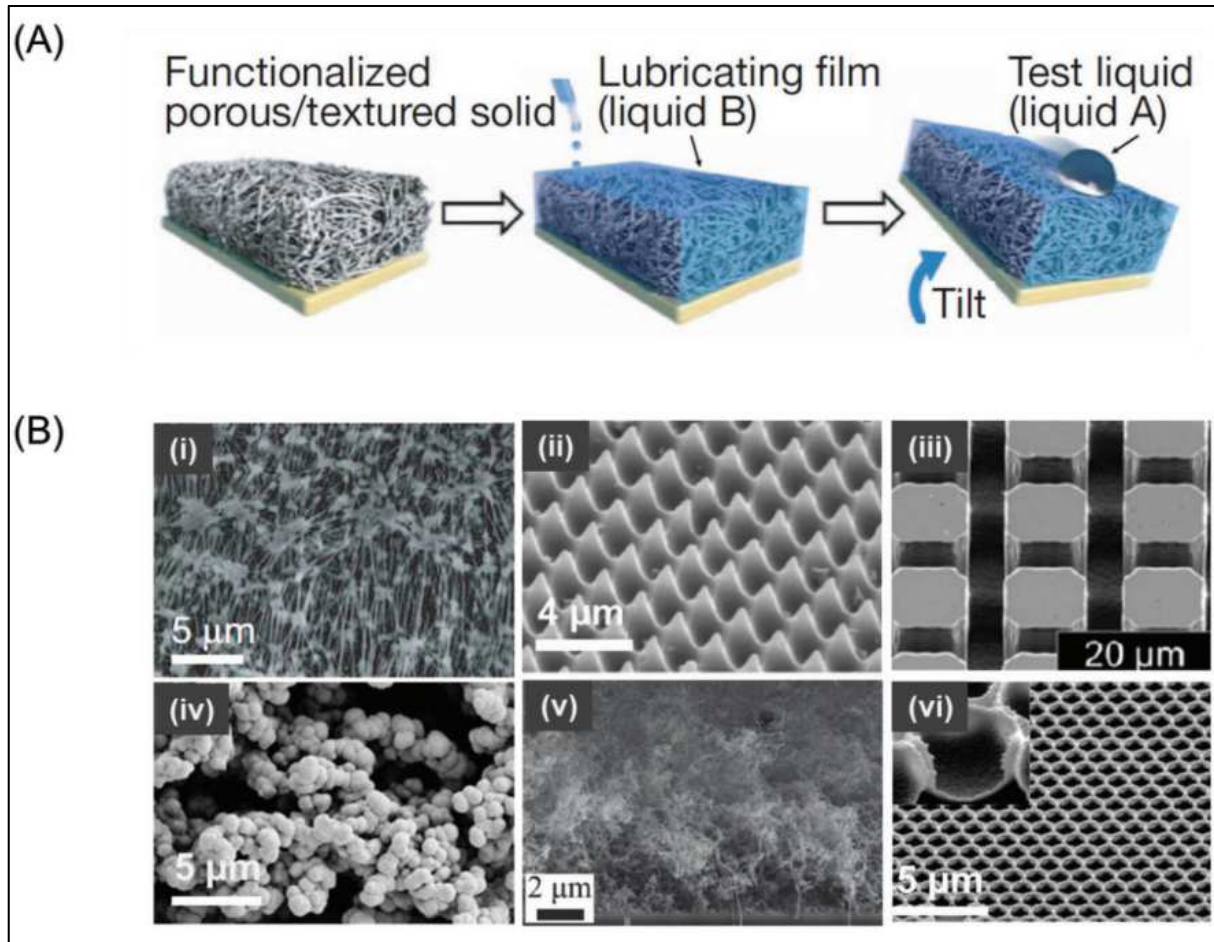
« Insect aquaplaning: Nepenthes pitcher plants capture prey with the peristome, a fully wettable water-lubricated anisotropic surface »

Holger F Bohn and Walter Federle 2004 ,Sep 28;101(39):14138-43.

doi: 10.1073/pnas.0405885101

5/ Liquid infused surfaces

• Synthetic liquid infused surfaces

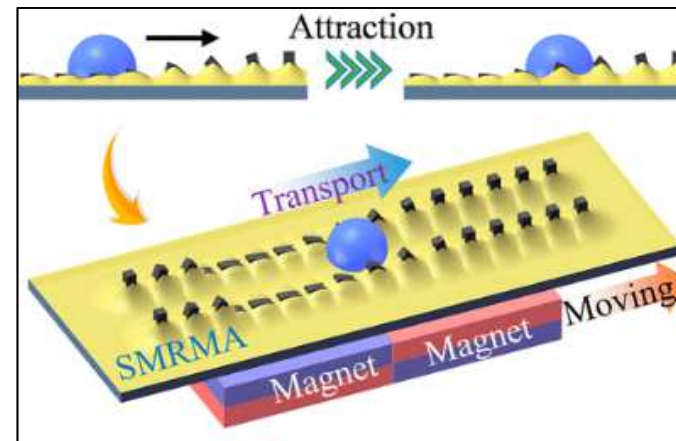


Slippery Lubricant-Infused Surfaces: Properties and Emerging Applications
Junsheng Li, Erica Ueda, Dorothea Paulssen, Pavel A. Levkin
Advanced Functionnal Materials 2018
<https://doi.org/10.1002/adfm.201802317>

Figure 1. A) Scheme showing the fabrication of a lubricant-infused surface. Reproduced with permission.^[9a] Copyright 2011, Springer Nature. B) SEM images of representative porous substrates used to fabricate SLIPS: (i) porous Teflon. Reproduced with permission.^[9a] Copyright 2011, Springer Nature. (ii) Ordered polyacrylate. Reproduced with permission.^[9a] Copyright 2011, Springer Nature. (iii) Silicon nanoarray. Reproduced with permission.^[29] Copyright 2013, American Chemical Society. (iv) porous poly(butyl methacrylate-co-ethyleneglycol dimethacrylate). Reproduced with permission.^[22] Copyright 2013, American Chemical Society. (v) porous silicone nanofilament, Reproduced with permission.^[30] Copyright 2014, Wiley-VCH. (vi) inverse colloidal monolayer. Reproduced with permission.^[28] Copyright 2013, the Authors, published by Springer Nature.

To conclude

- **Combining a liquid-infused surface and active macrostructures (2023)**



The droplet transports in the direction of magnetic field

“Gouttes, bulles, perles et ondes” Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré (Éditions Belin)

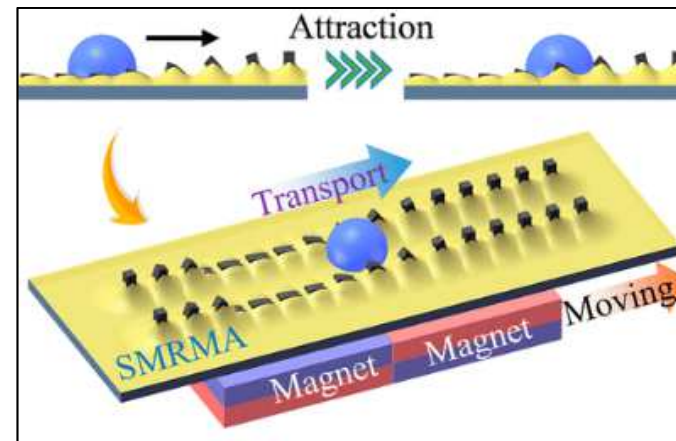
« Active Droplet Transport Induced by Moving Meniscus on a Slippery Magnetic Responsive Micropillar Array » Yubin Peng, Chuanzong Li, Yunlong Jiao, Suwan Zhu, Yanlei Hu, Wei Xiong, Yaoyu Cao, Jiawen Li, Dong Wu, Langmuir, 2023 Apr 25;39(16):5901-5910. doi: 10.1021/acs.langmuir.3c00396

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To conclude

Thank you for your attention

Laurent Vonna

IIS2M - Institut de Science des Matériaux de Mulhouse
Université de Haute-Alsace



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