Drops on Homogeneous and Non-homogeneous Surfaces

The Shape of Micro-drops

1 mm   1 cm   h

Comparison of the shape between micro-drops and macro-drops

$$\frac{\Delta P_{\text{Laplace}}}{\Delta P_{\text{hydrostatic}}} \approx \frac{\frac{\gamma}{\ell}}{\rho g \ell}$$

The two pressures are of the same order when $\qquad \ell \approx \sqrt{\dfrac{\gamma}{\rho g}}$

"l" is called the **capillary length**. A drop of dimension smaller than the capillary length has a shape resembling that of a spherical cap. A drop larger than the capillary length is flattened by gravity.
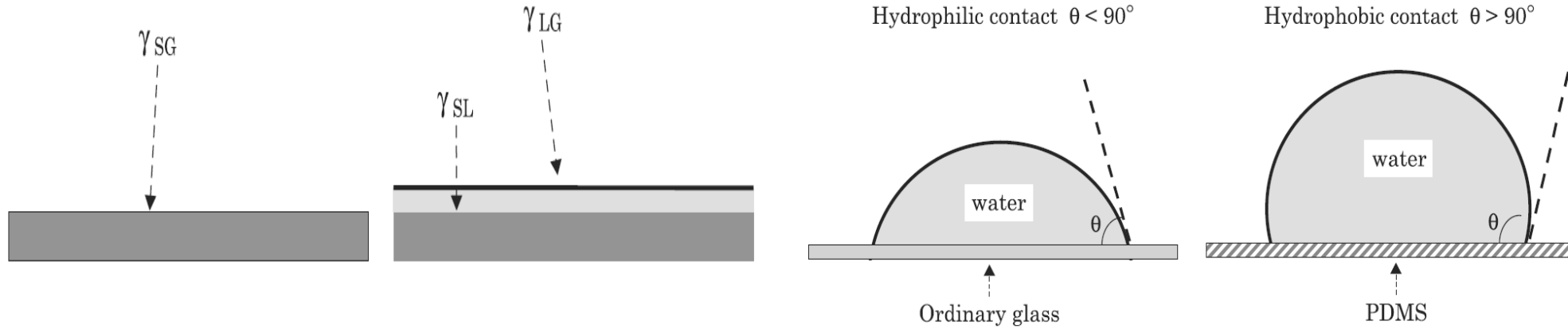
Bond Number

$$Bo = \frac{\rho g R^2}{\gamma}$$

R is of the order of the drop radius. If Bo < 1, the drop is spherical (microscopic drops), or else the gravitational force flattens the drop on the solid surface (large drops).

The capillary length is of the order of 2 mm for most liquids, even for mercury.

These equations are valid for a **perfectly flat surface**.

Wetting: Partial or Total Wetting

A liquid spreads on a substrate in a film **if the energy of the system is lowered by the presence of the liquid film** .
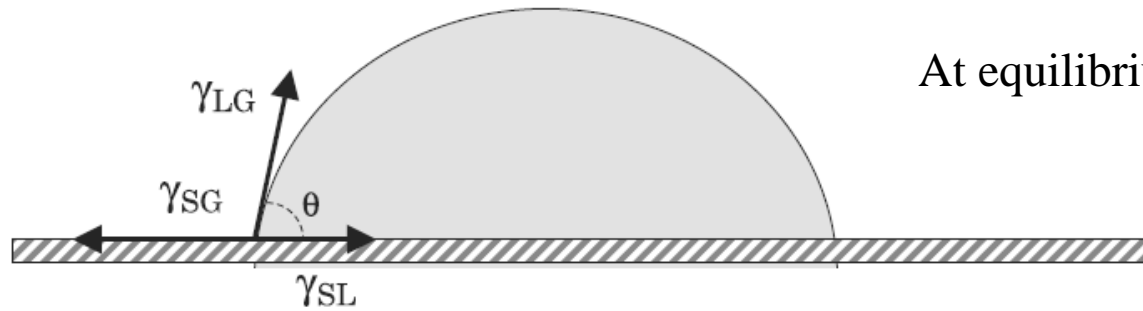
The surface energy per unit surface of the dry solid surface is γ_{SG}; the surface energy of the wetted solid is $\gamma_{SL}+\gamma_{LG}$.

The spreading parameter S determines the type of spreading (total or partial)

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

If $S > 0$, the liquid spreads on the solid surface; if $S < 0$ the liquid forms a droplet.
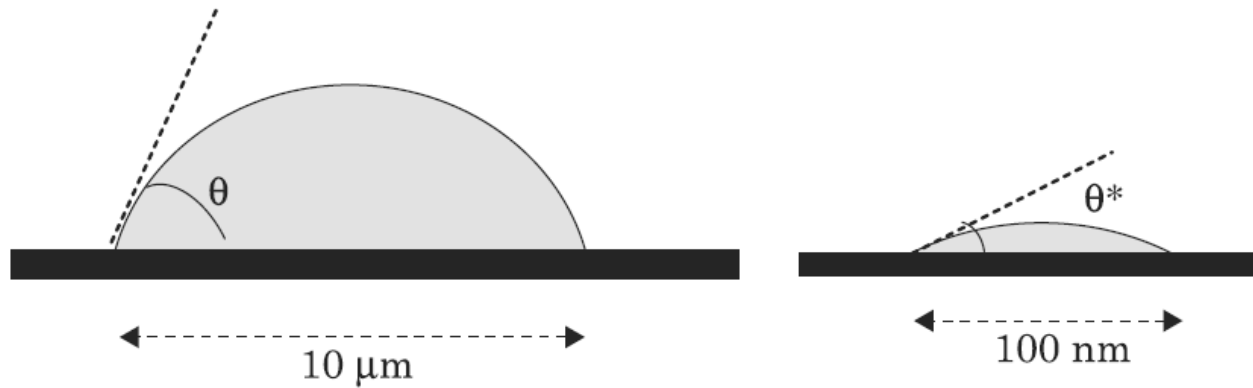
Contact Angle—Young's Law

At equilibrium, the resultant of the forces must be zero.

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}$$

Schematic of forces at the contact line

Nano-bubbles and droplets

10 μm

100 nm

θ^* is the real contact angle, r is the contact radius

Recent measurements have shown that nano-bubbles have very flat profiles—the base radius is 5–20 times larger than the height —because the contact angle of the bubble is much smaller than the macroscopic contact angle of the bubble on the same substrate

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}$$

Modified Young's Law at Nanoscale

Surface tension
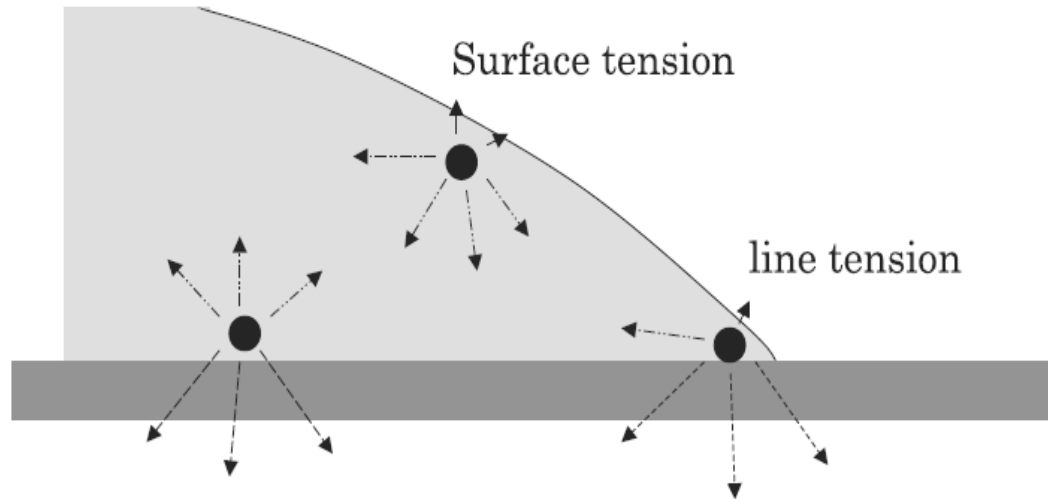
line tension

The molecules close to the triple line experience a different set of interactions than at the interface. To take into account this effect, a line tension term has been introduced in Young's law

$$\gamma_{\text{SG}} = \gamma_{\text{SL}} + \gamma_{\text{LG}} \cos \theta^* + \frac{\gamma_{\text{SLG}}}{r} \qquad \cos \theta^* = \cos \theta - \frac{\gamma_{\text{SLG}}}{r \gamma_{\text{LG}}}$$

Where r is the contact radius, γ_{SLG} the line tension (unit N), and θ^* the real contact angle.

For droplet contact radius larger than 10 μm, the effect of the line tension is negligible; the value of the second term i*s of the order of 10^{-4}* . But it is not the case for nano-drops and nano-bubbles.

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}$$

Young's law can be more rigorously derived from free energy minimization.
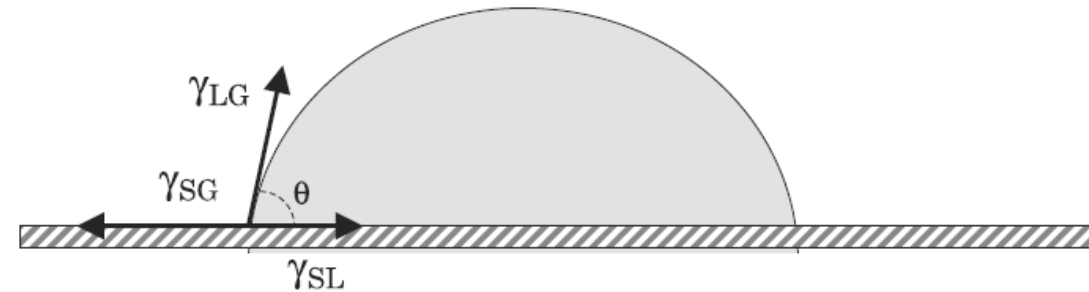
Consider a sessile droplet large enough for the effect of the triple line to be neglected. The change of free energy due to a change in droplet size can be written as

$$dF = \gamma_{SL} dA_{SL} - \gamma_{SG} dA_{SG} + \gamma_{LG} dA_{LG}$$

$$= (\gamma_{SL} - \gamma_{SG} + \gamma_{LG} \cos \theta)\, dA_{SL}$$

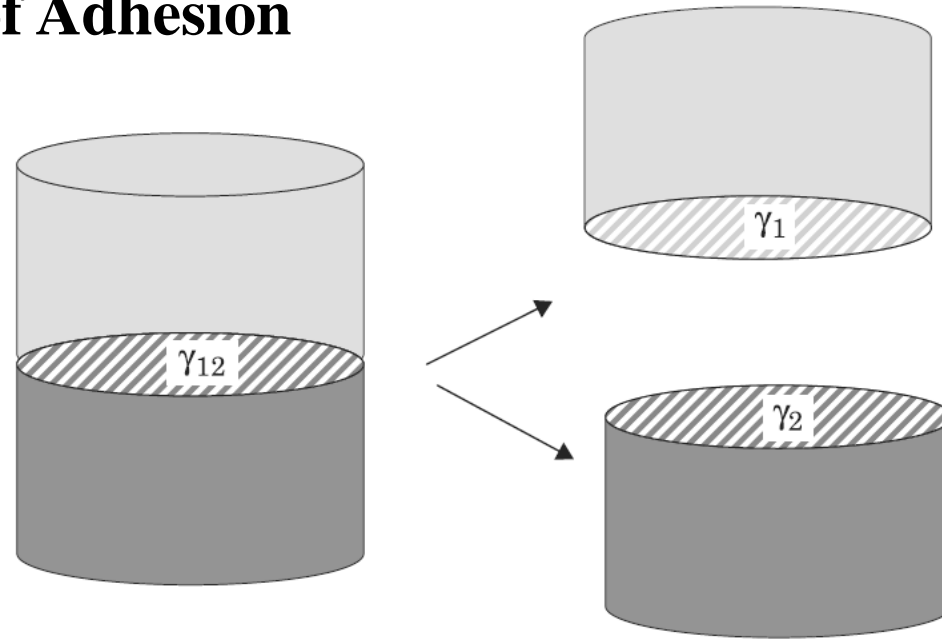where θ is the contact angle.

At mechanical equilibrium $dF = 0$ and

$$\gamma_{SL} - \gamma_{SG} + \gamma_{LG} \cos \theta = 0.$$

Work of Adhesion

Imagine a body contacting another body on a surface S. The surface energy of S when there is contact is

$$E_{12} = \gamma_{12}\, S$$

The work of adhesion is the work required to separate the two bodies. After separation, the surface energies are
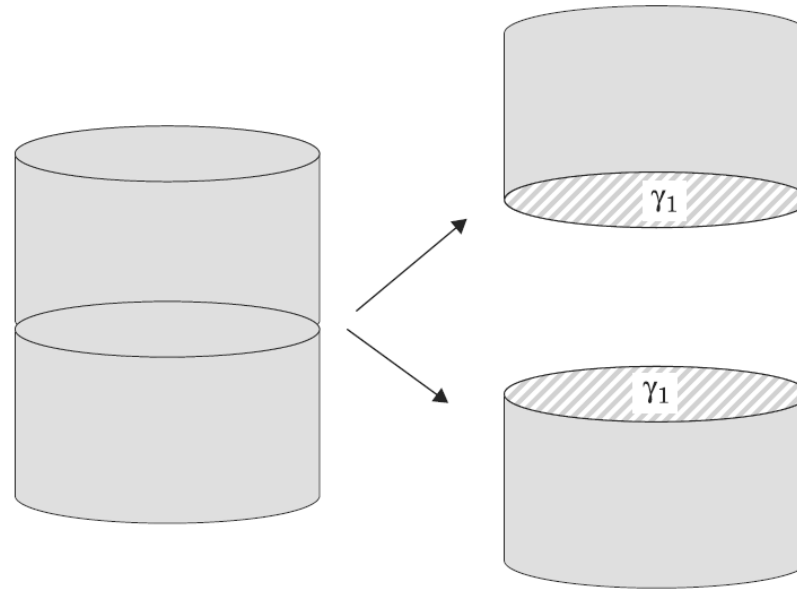
$$E = E_1 + E_2 = (\gamma_1 + \gamma_2)\, S$$

The work of adhesion (per unit area) is then

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12}$$
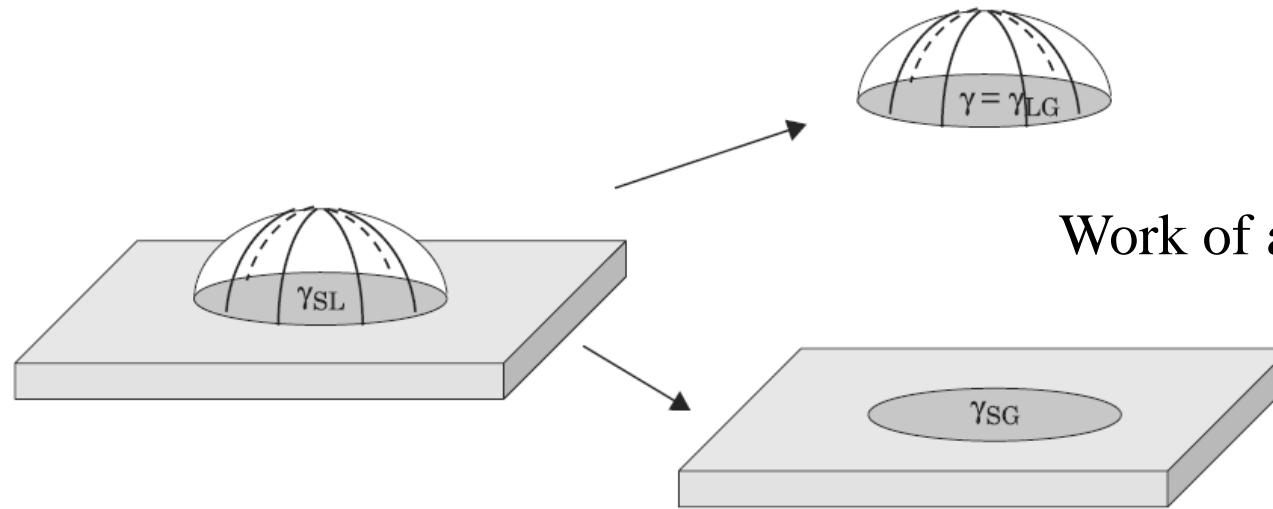
Work of Cohesion

The work of cohesion is obtained similarly, but this time the body being split is homogeneous. The same reasoning yields

$$W_c = 2\gamma_1$$

In other words, the surface energy is half the work of cohesion

Work of Adhesion - <mark>Young–Dupr´e Equation</mark>

$\gamma = \gamma_{LG}$

γ_{SL}

γ_{SG}

Work of adhesion for a liquid and a solid

Using the work of adhesion $W_a = \gamma_1 + \gamma_2 - \gamma_{12}$

with the surface tensions $\gamma_1 = \gamma_{LG} = \gamma$, $\gamma_2 = \gamma_{SG}$, and $\gamma_{12} = \gamma_{SL}$, we obtain

$$W_a = \gamma + \gamma_{SG} - \gamma_{SL}$$

$$W_a = \gamma + \gamma_{SG} - \gamma_{SL} \qquad\qquad \gamma_{LG} \cos\theta = \gamma_{SG} - \gamma_{SL}$$

Work of Adhesion - Young–Dupŕe Equation

Upon substitution of Young's law [$\gamma_{LG} \cos\theta = \gamma_{SG} - \gamma_{SL}$], one can obtain the Young–Dupŕe equation for the work of adhesion as

$$W_a = \gamma \, (1 + \cos\theta)$$

For a super-hydrophobic contact, $\theta = \pi$; $W_a = 0$: *no work is required to separate a super-hydrophobic liquid from a solid.*

Thus, a droplet of water rolls freely over a super-hydrophobic surface.

The more hydrophobic is the contact between a liquid and a solid, the smaller is the work of adhesion.

Drops on Inhomogeneous Surfaces

Young's law should be corrected to take into account the imperfections of the surface.

Roughness amplifies the hydrophilic or hydrophobic character of the contact.

θ^* is the angle with the surface with roughness and θ the angle with the smooth surface.

The size of the roughness is very small, so that the molecules of the liquid are macroscopically interacting with a plane surface but microscopically with a rough surface.

Liquid-fluid interface

Few nm to few μm

liquid

θ^*

dx

Solid (rough) surface
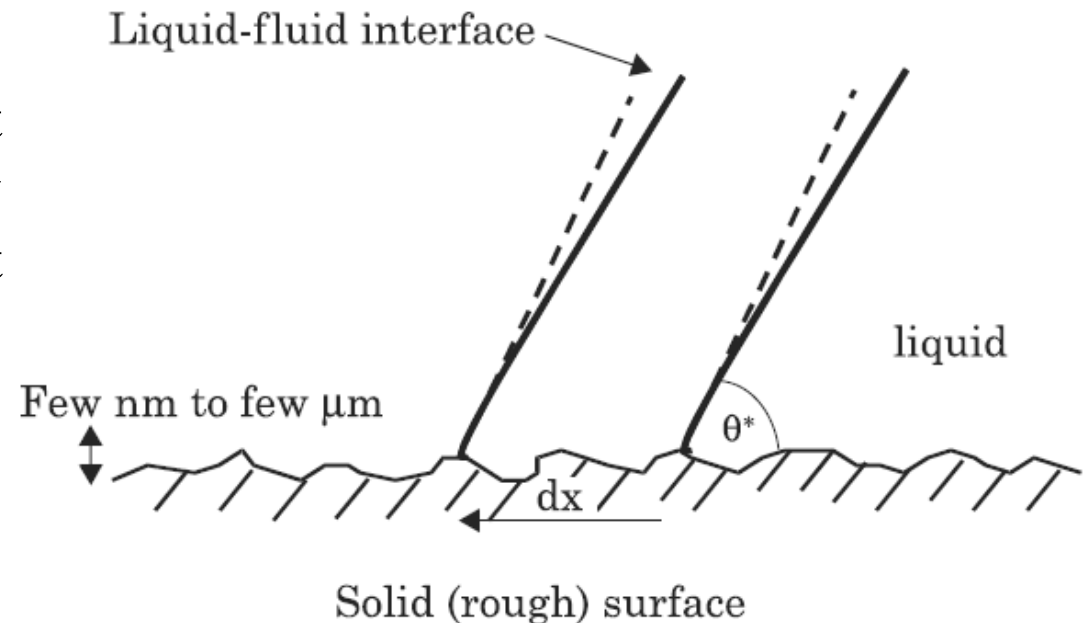
$$[\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}] \qquad W_a = \gamma + \gamma_{SG} - \gamma_{SL} \qquad S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$
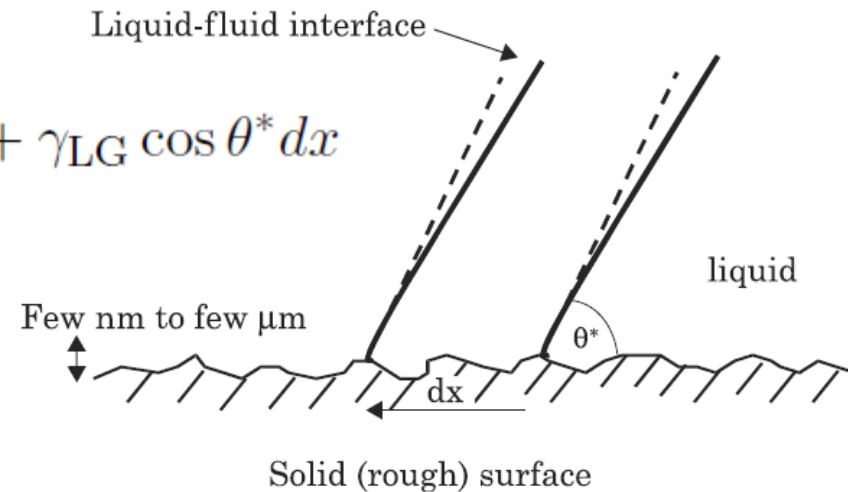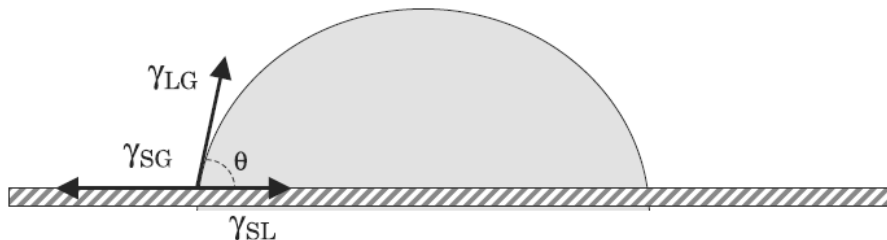
For a very small displacement of the contact line, the work of the different forces acting on the contact line is given by

$$dW = \sum \vec{F}.\vec{dl} = \sum F_x dx = (\gamma_{SL} - \gamma_{SG})\, r dx + \gamma_{LG} \cos \theta^* dx$$

where r is the roughness (rdx is the real distance on the solid surface when the contact line is displaced by dx). Therefore, by definition, r > 1.

Thus the change in energy is

$$dE = dW = (\gamma_{SL} - \gamma_{SG})\, r dx + \gamma_{LG} \cos \theta^* dx$$

Liquid-fluid interface

liquid

Few nm to few μm

θ^*

dx

Solid (rough) surface
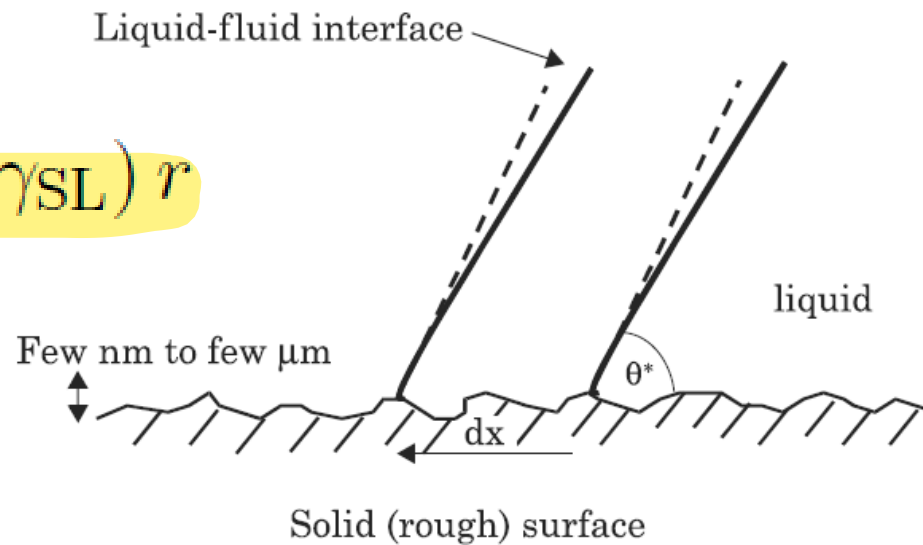
γ_{LG}

γ_{SG}

θ

γ_{SL}

13

The drop finds its equilibrium state after the small perturbation dx, it finally stops at a position where its energy is minimum, so

$$\frac{dE}{dx} = 0$$

Therefore,

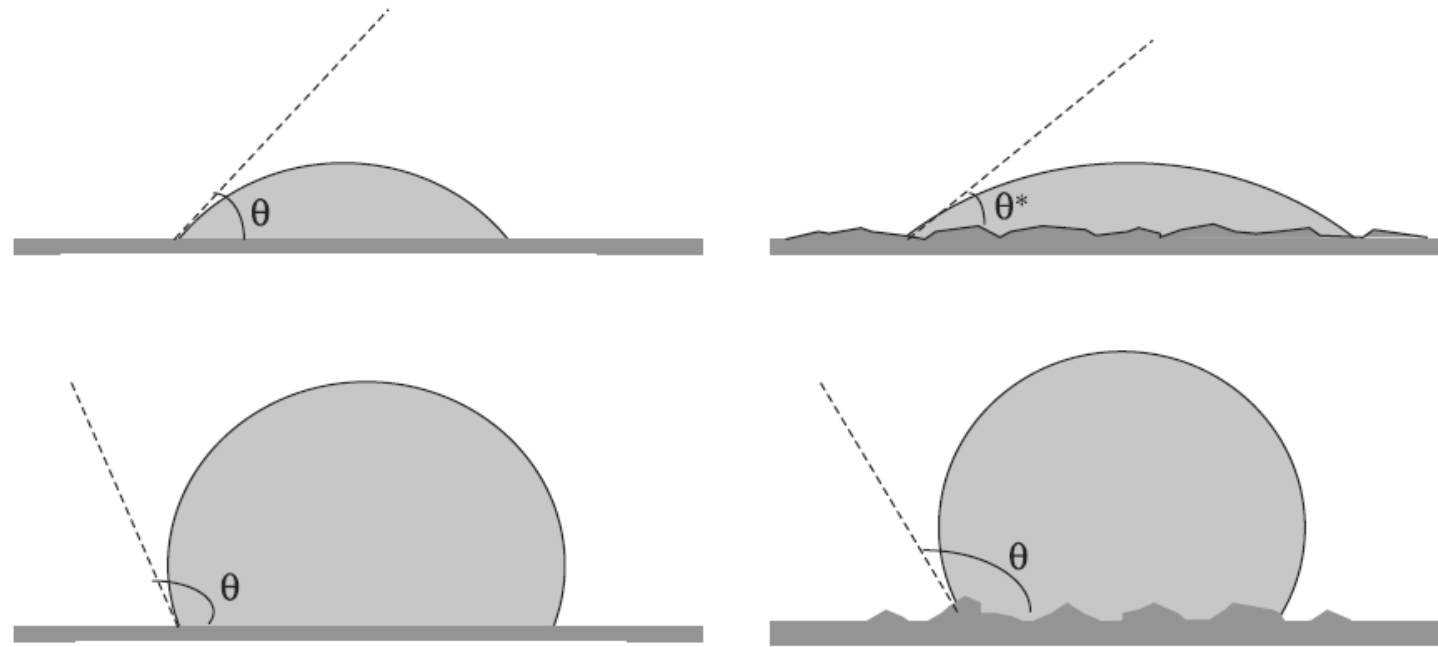$$\gamma_{LG} \cos \theta^* = (\gamma_{SG} - \gamma_{SL}) \, r$$

Liquid-fluid interface

liquid

Few nm to few μm

θ^*

dx

Solid (rough) surface

14

$$\gamma_{\mathrm{LG}} \cos \theta^* = (\gamma_{SG} - \gamma_{\mathrm{SL}})\, r$$

Young's law for a smooth surface $\qquad \gamma_{\mathrm{LG}} \cos \theta = \gamma_{SG} - \gamma_{\mathrm{SL}}$

Substitution gives Wenzel's Law $\qquad \cos \theta^* = r \cos \theta$

As r > 1, this relation implies that $\qquad |\cos \theta^*| > |\cos \theta|$

$$|\cos \theta^*| > |\cos \theta|$$

If θ is larger than 90° (hydrophobic contact), then θ∗ > θ and the contact is still more hydrophobic due to the roughness.

If θ is smaller than 90◦ (hydrophilic contact), then θ* < θ and the contact is still more hydrophilic.

Surface roughness increases the wetting character.

Cassie–Baxter Law

Interface liquid/fluid

Gas / fluid

liquid

θ^*

θ^*

Solid surface
Chemically heterogeneous

dx
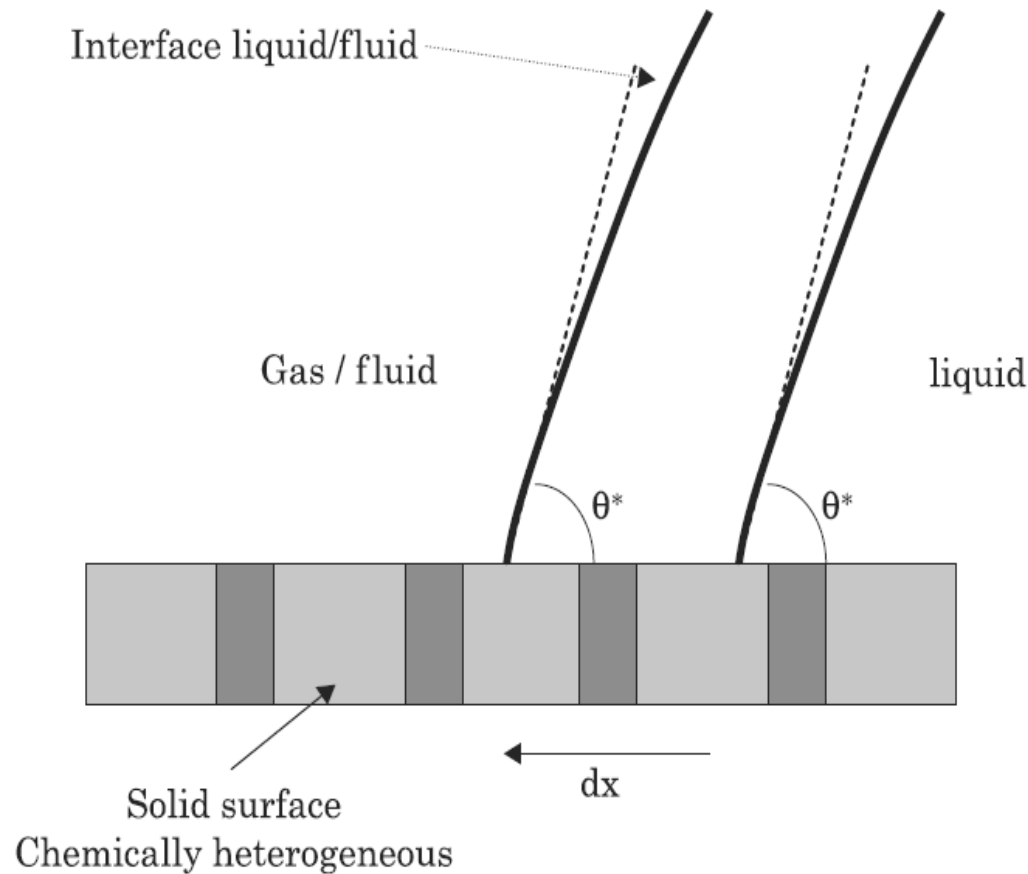
Chemically inhomogeneous solid surfaces.

Small size heterogeneities compared to interaction size between the liquid and the solid wall.

A solid wall constituted by microscopic inclusions of two different materials.

θ_1 and θ_2 are the contact angles for each material at a macroscopic size, and f_1 and f_2 are the surface fractions of the two materials.

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}$$

The energy to move the interface by dx is

$$dE = dW = (\gamma_{\mathrm{SL}} - \gamma_{SG})_1 \, f_1 dx + (\gamma_{\mathrm{SL}} - \gamma_{SG})_2 \, f_2 dx + \gamma_{\mathrm{LG}} \cos \theta^* \, dx$$

Minimizing dE

$$\gamma_{\mathrm{LG}} \cos \theta^* = (\gamma_{SG} - \gamma_{\mathrm{SL}})_1 \, f_1 + (\gamma_{SG} - \gamma_{\mathrm{SL}})_2 \, f_2$$

Using Young's Law $\qquad \gamma_{\mathrm{LG}} \cos \theta = \gamma_{SG} - \gamma_{\mathrm{SL}}$

Casey-Baxter Relaion $\quad \cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2$

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \qquad f_1 + f_2 = 1 \quad \text{or} \quad \sum_i f_i = 1$$

The Cassie–Baxter law explains some unexpected experimental results.

Sometimes during micro-fabrication—a microfabricated surface may present chemical inhomogeneity and the wetting properties are not those that were intended.

For example, if a uniform layer of Teflon is deposited on a rough substrate, the surface should become hydrophobic.

However, if the layer is too thin, the Teflon layer may be porous and the coating inhomogeneous; the wetting properties are then modified according to the Cassie–Baxter law and the gain in hydrophobicity may not be as large as expected.

The scale of change of the different chemical materials of the solid surface is *very small compared to that of the drop*

Topographically patterned surfaces

(a)

(b)
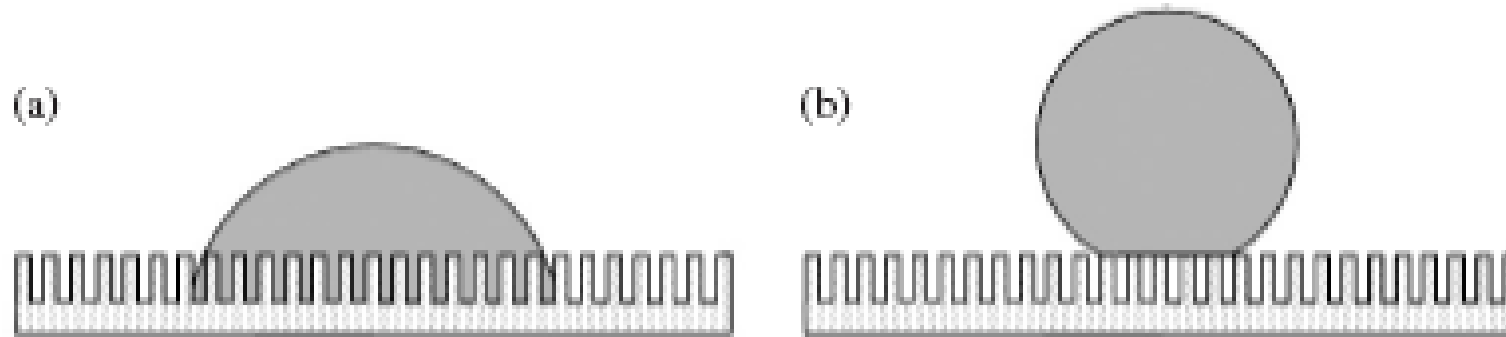
Droplets wetting rough surfaces

(a) **Wenzel state** with enhanced solid–liquid interfacial area

(b) **Cassie–Baxter state** with entrapped air underneath the droplet.

In Fig. (a), roughness increases the actual solid–liquid interfacial area A_{sl} *with respect to the apparent, projected one* $A_{sl,p}$.

Lessons from nature

Microfabricated Substrate - Case of Hydrophobic Contact

Contact angle of a sessile drop sitting on microfabricated pillars

If the drop penetrates between the pillars, one can write the Wenzel angle as

$$\cos \theta_W = r \cos \theta$$

If the drop stays on top of the pillars, one can write the Cassie law

$$\cos \theta_C = f \cos \theta + (1 - f) \cos \theta_0$$

θ_C is the "Cassie" contact angle, θ_0 the contact angle with the layer of air, and f the ratio of the contact surface (top of the pillars) to the total horizontal surface.

Wenzel's law

$$\cos \theta = r \cdot \cos \theta_Y \;\; with \; r = A_{sl}/A_{sl,\,p}.$$

Quantitatively, the validity of the picture turns out to be limited to a range of $\theta_C < \theta_Y < 90°$, with θ_C depending on the surface roughness .

As a result, the contact angle on a rough surface will be **increased** or (**decreased**) as compared to the contact angle on a smooth surface of the same material, depending on whether $\theta_Y > 90°$ *or* ($\theta_Y < 90°$), respectively.
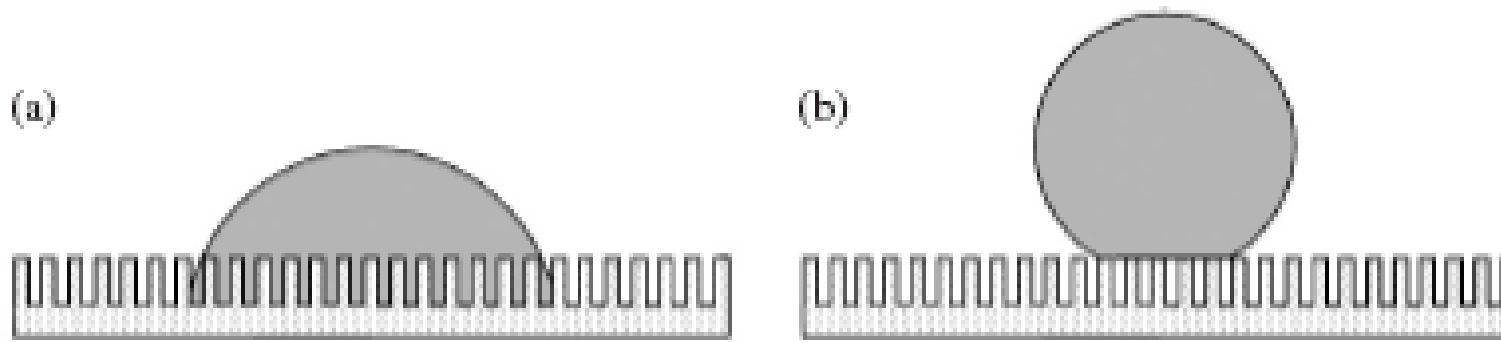
For $\theta_Y > 90°$, a completely different liquid morphology is possible (Fig. b).

A_{sl} is dramatically reduced and much of the apparent solid–liquid interface is in fact a liquid–vapor interface.

This reduction in A_{sl} *gives rise to a very high mobility with* extremely small contact angle hysteresis.

In this state, the contact angle is given by the **Cassie–Baxter equation**,
cos $\theta = -1 + f \cdot (1 + \cos \theta_Y)$, *where f is the fractional surface area of the* pillar tops and θ_2 (on air) $= 180°$

The range of stability for both morphologies depends on the aspect ratio, the spacing between the pillars, and the contact angle

$$\cos \theta_W = r \cos \theta \qquad\qquad \cos \theta_C = f \cos \theta + (1 - f) \cos \theta_0$$
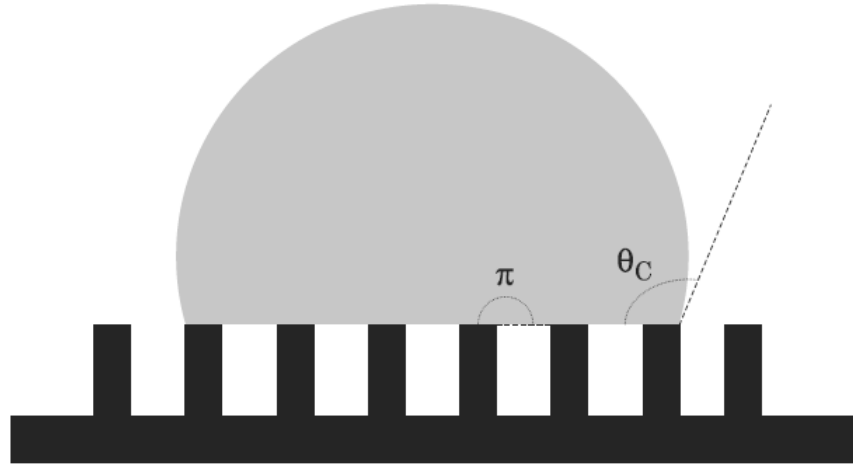
Sketch of a Cassie drop (fakir effect). The interface between the pillars is roughly horizontal.

If the pillars are not too far from each other, the value of θ_0 is roughly $\theta_0 = \pi$

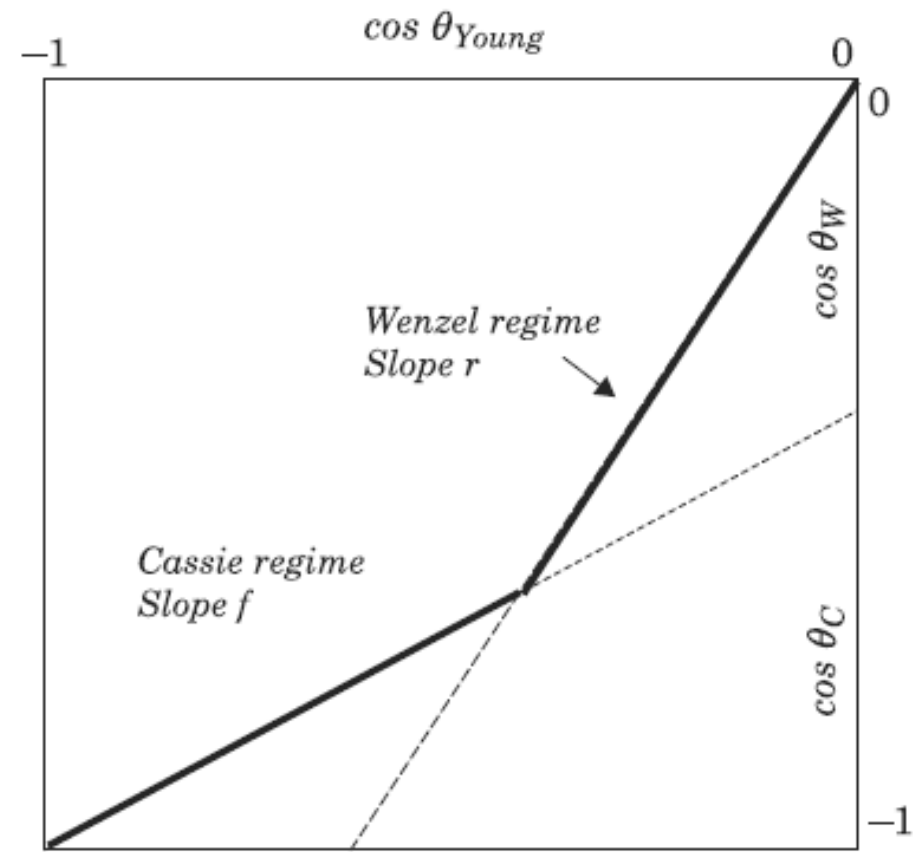$$\cos \theta_C = -1 + f\,(1 + \cos \theta)$$

Plot the Wenzel and
Cassie Laws

$$\cos \theta_W = r \cos \theta$$

$$\cos \theta_C = -1 + f (1 + \cos \theta)$$

$$r = \frac{S_{\text{total}}}{S_{\text{horizontal}}} > f = \frac{S_{\text{top}}}{S_{\text{horizontal}}}$$
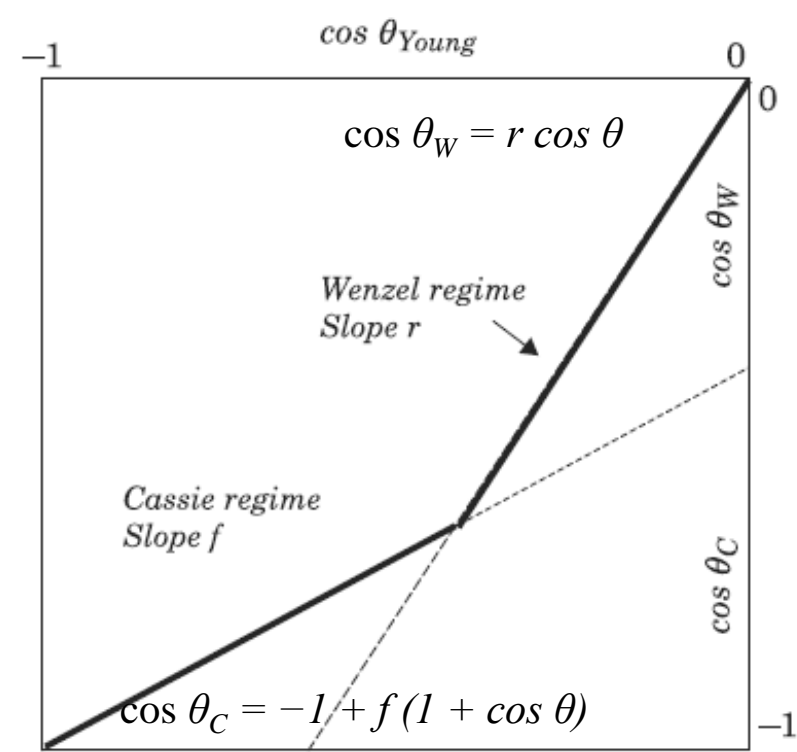
Plot of the Wenzel and Cassie laws for a sessile droplet sitting on a surface textured with micro-pillars.

The two lines intersect at a Young contact angle θ_i defined by $\theta_C = \theta_W$, so that

$$\cos \theta_i = \frac{f - 1}{r - f}$$

In the diagram, for a given Young angle, there are two contact angles

From energy considerations—for example using Laplace's law—it can be deduced that the real contact angle is the smaller one.

$\cos \theta_{Young}$

-1 0

0

$\cos \theta_W = r \cos \theta$

$\cos \theta_W$

Wenzel regime
Slope r

Cassie regime
Slope f

$\cos \theta_C$

$\cos \theta_C = -1 + f(1 + \cos \theta)$

-1

So when the Young contact angle is not very hydrophobic ($\theta < \theta_i$), the contact corresponds to a Wenzel regime and the drop wets the whole surface.

When the Young contact angle is more hydrophobic ($\theta > \theta_i$), the drop is in a Cassie regime and sits on top of the pillars.

General rule, exceptions are common, droplets are sometimes at metastable regimes.
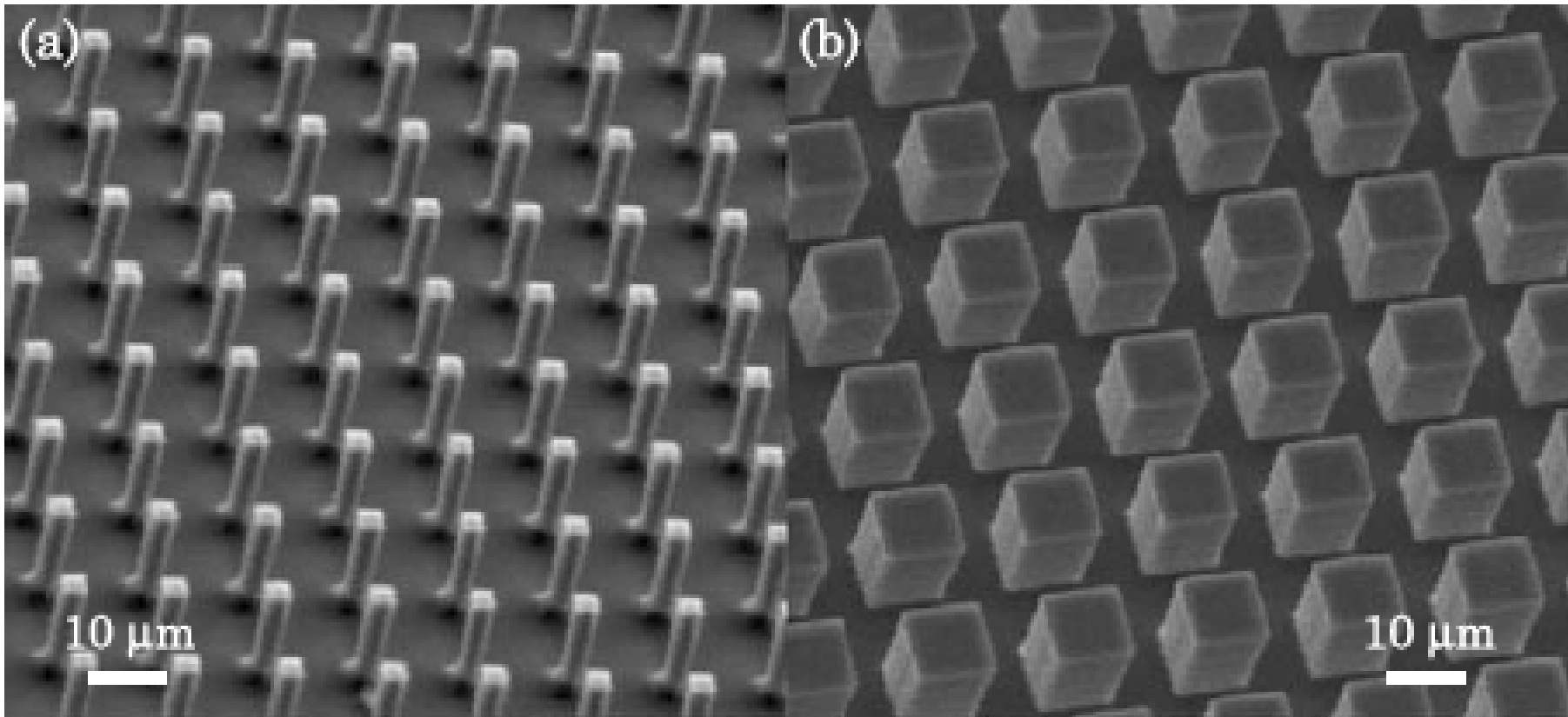
Microfabricated pillars of silicon.

Transition from a Cassie droplet to a Wenzel droplet by electrowetting actuation.
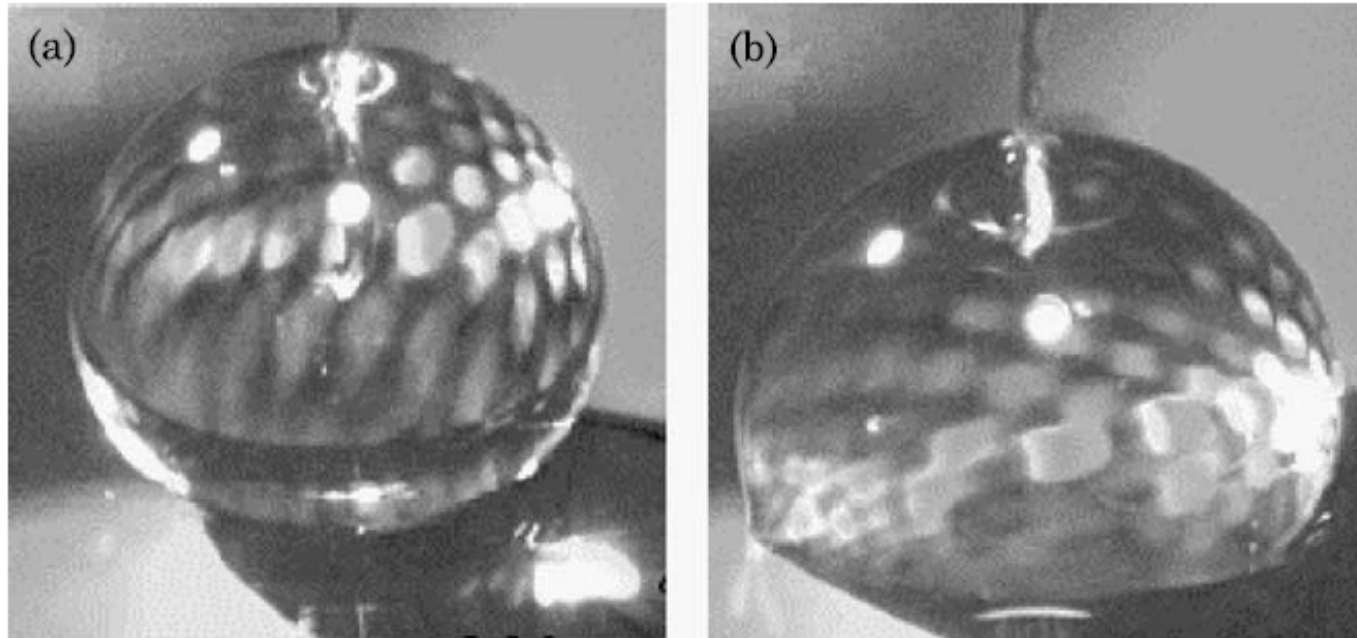
(a)When no electric actuation, the drop sits on top of the pillars, b)electrode actuated with 22V electric potential: the droplet wets the flat part of the substrate. The wire at the top is the zero potential electrode.

Example of a Square Lattice
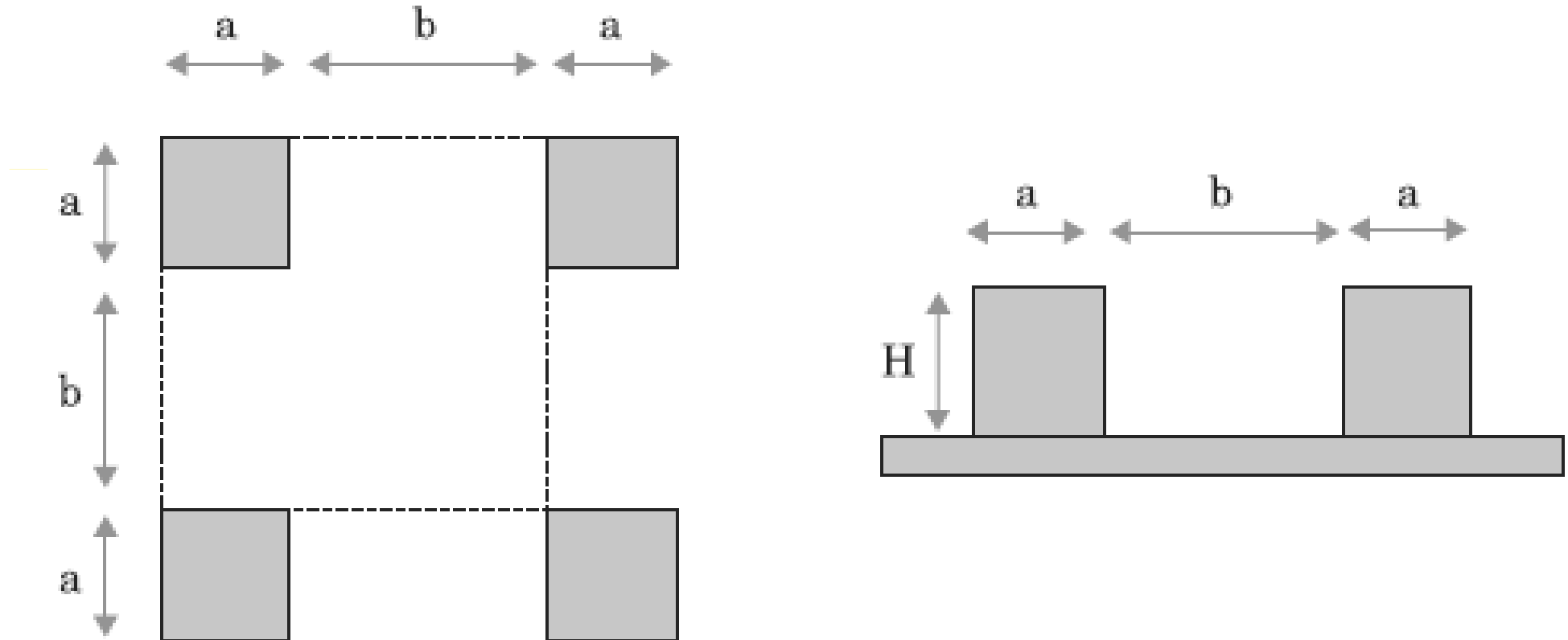
Square pillars along a square grid

Square pillars of size a×a, height H and spacing b
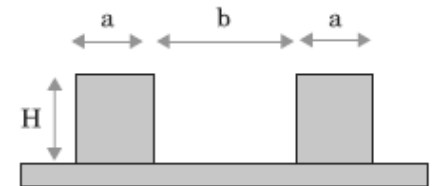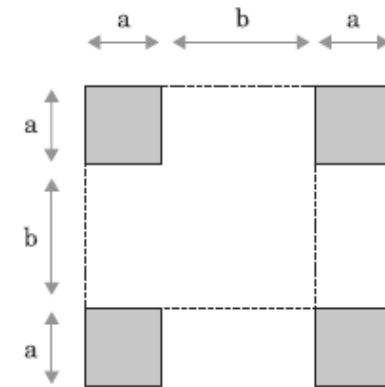
The roughness "r" is determined by

$$r = \frac{S_{\text{total}}}{S_{\text{horizontal}}} = \frac{(a+b)^2 + 4aH}{(a+b)^2} = 1 + \frac{4A}{(a/H)}$$

Where,

$$A = \left(\frac{a}{a+b}\right)^2$$

The Cassie coefficient is given by -

$$f = \frac{S_{\text{top}}}{S_{\text{horizontal}}} = \frac{a^2}{(a+b)^2} = A$$

Substitution of these into the Wenzel and Cassie formulas leads to the following relations for square pillars

$$\cos \theta_W = r \cos \theta$$

$$\cos \theta_W = \left[1 + \frac{4\,A}{(a/H)}\right] \cos \theta$$

$$\cos \theta_C = -1 + f\,(1 + \cos\theta)$$

$$\cos \theta_C = -1 + A\,(1 + \cos\theta)$$

Using these relations the shift from Wenzel to Cassie state occurs when

$$\cos \theta_i = \frac{-1}{1 + 4\frac{aH}{b^2}}$$

Super-Hydrophobicity

A surface is said to be super-hydrophobic when the contact angle of aqueous liquid is close to 180°. In nature, some tree leaves in wet regions of the globe have super-hydrophobic surfaces in order to force water droplets to roll off the leaves, preventing rotting of the leaves.

Super-hydrophobicity requires either a super-hydrophobic Young contact angle or a Cassie regime. Super-hydrophobicity corresponds to $\theta_{real} = \pi$ and $\cos\theta_{real} = -1$.

Super-Hydrophobicity

It can only be approached in a Cassie regime when the value of "f" is very small

$$f = \frac{S_{\text{top}}}{S_{\text{horizontal}}} = \frac{a^2}{(a+b)^2} = A$$

"f" is small when b/a >> 1. In such a case, the pillars are very thin and the contact area of the droplet with the solid substrate is very small.

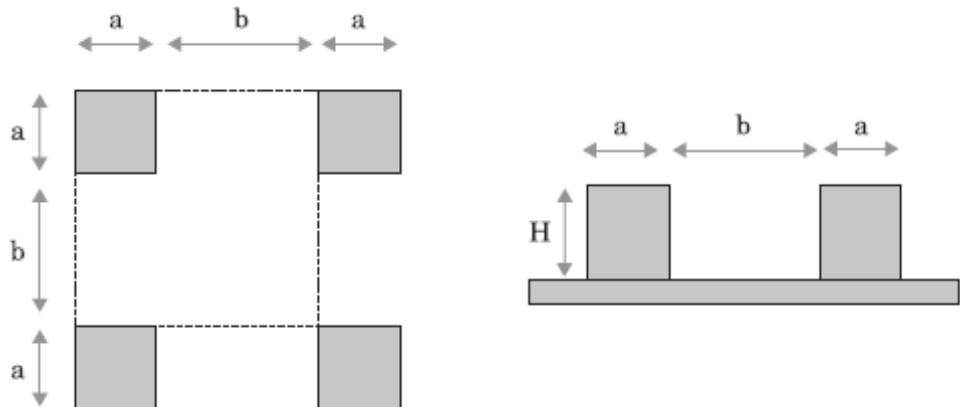$$f = \frac{a^2}{(a+b)^2} = \frac{1}{(1+\frac{b}{a})^2}$$

The best situation for super-hydrophobicity for a geometrically textured surface is "f" as small as possible and "r" as large as possible.

$$r = \frac{S_{\text{total}}}{S_{\text{horizontal}}} = \frac{(a+b)^2 + 4aH}{(a+b)^2} = 1 + \frac{4A}{(a/H)}$$

If H is sufficiently high, "r" will be large

# Fabricated Surfaces: The Transition Between the Wenzel and Cassie Laws

PDMS, Teflon, SU8, glass, silicon, gold. Plastics are generally hydrophobic whereas glass and metals are hydrophilic and silicon neutral.
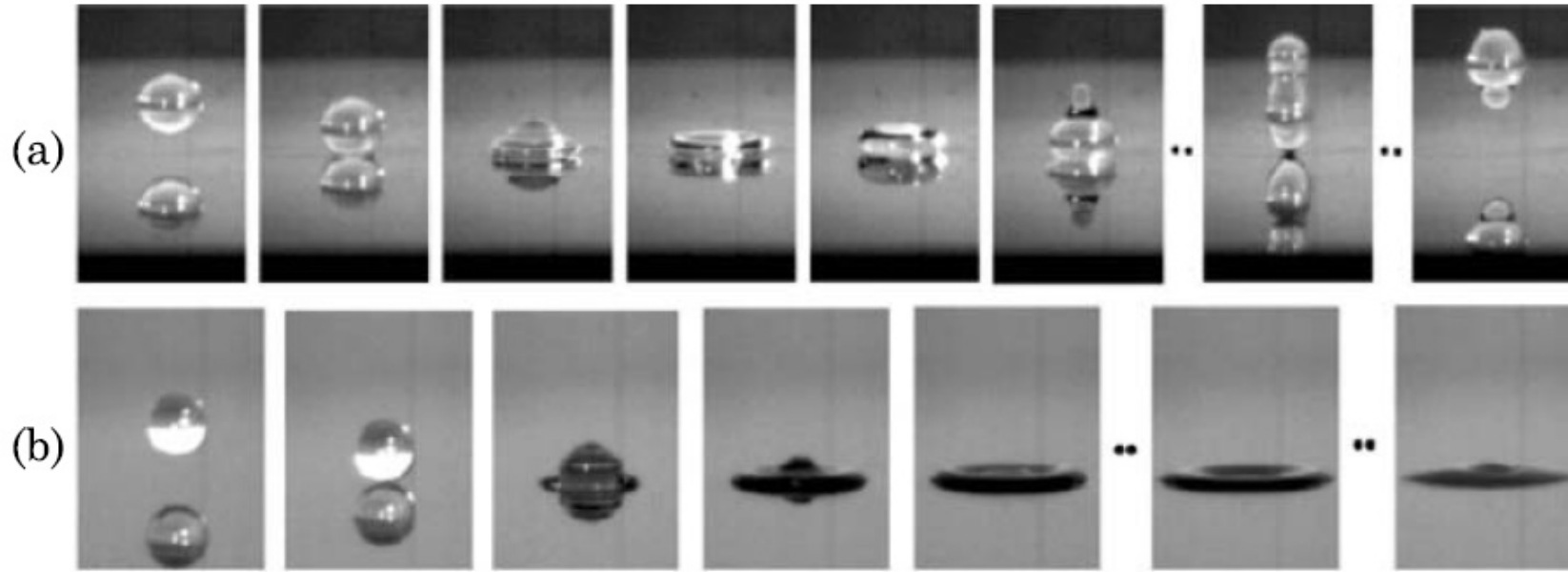

Chemical deposition of a hydrophobic/hydrophilic coating on top of the substrate. A flat gold plate with CF_4–H_2–He plasma deposition becomes very hydrophobic.

(a) A water droplet bounces back from the surface treated with CF_4–H_2–He plasma deposition, (b) whereas it spreads on the original gold surface

Partial Rebound of Droplets on Unidirectionally Structured Hydrophobic Surfaces
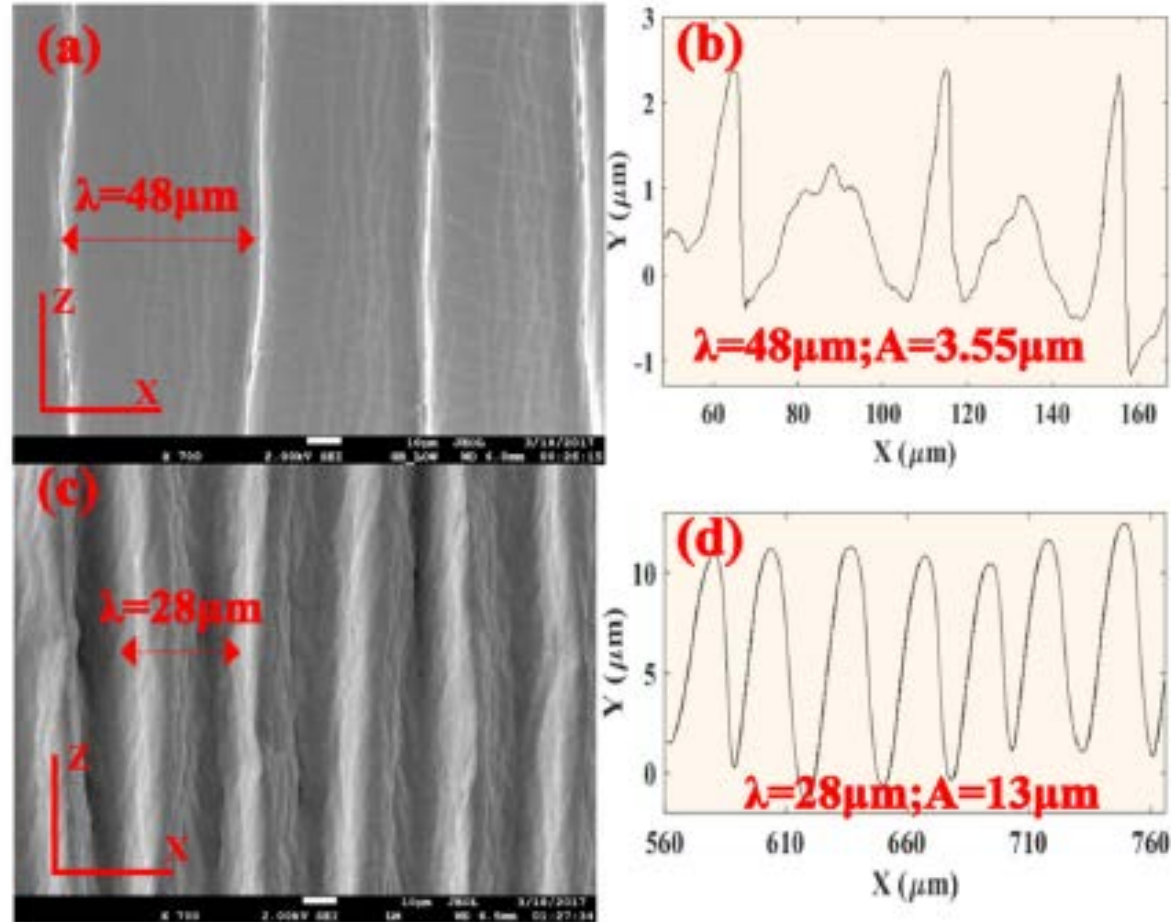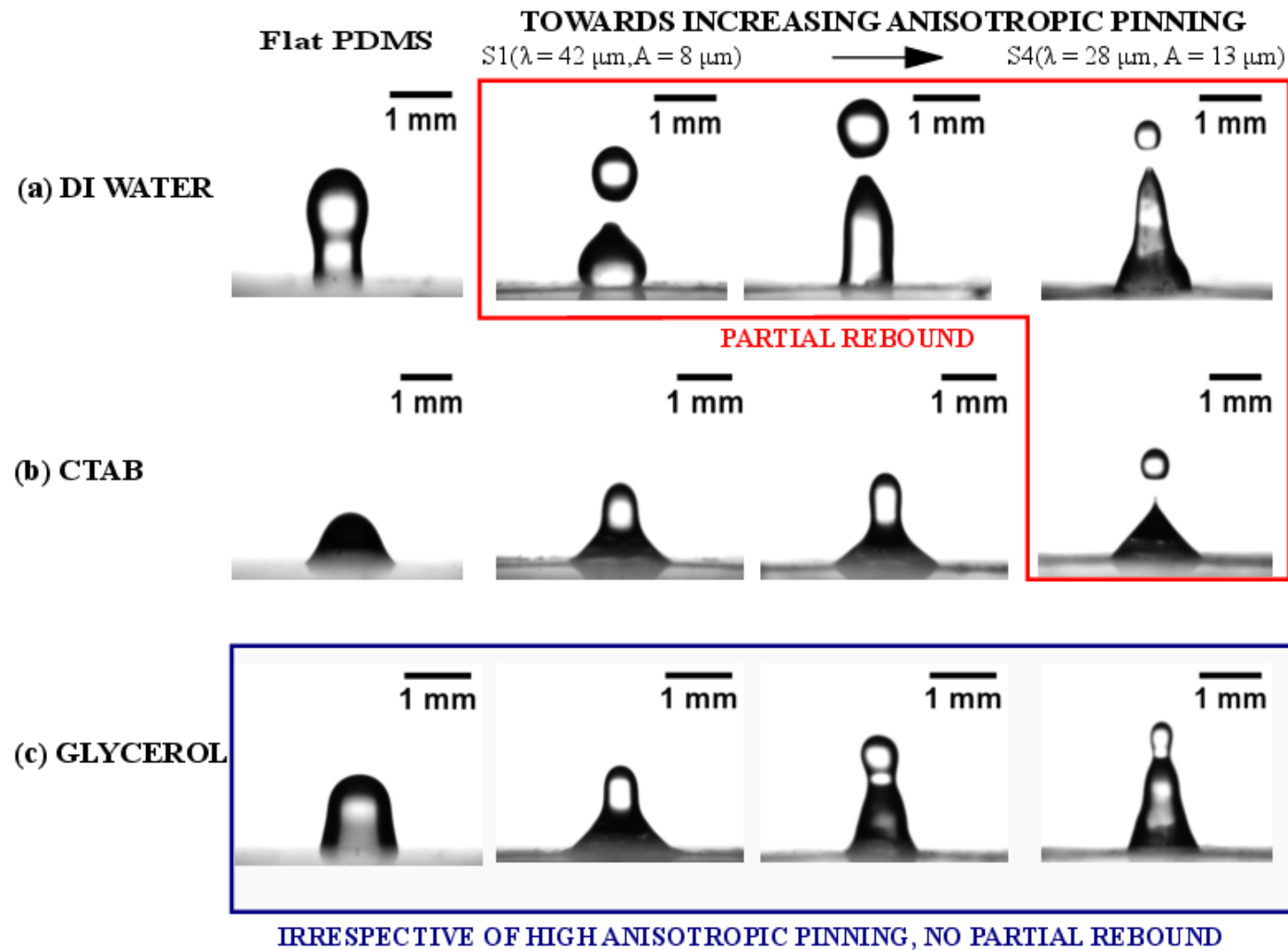
Partial rebound over flat as well as wrinkled PDMS surfaces with varying topography. Partial rebound is observed for DI water even for moderately wrinkled surfaces (S1), whereas for CTAB it is experienced for narrow wrinkles (S4) only. No partial rebound is seen for Glycerol for even highly wrinkled surfaces.

Water drops stay on ordinary lenses

Water drops roll off Titan Advantage

Super Hydrophobic
Water droplets roll off.

Dust Repellant
Does not attract dust due to anti-static property.

**Smudge Resistant**
Easy to clean fingerprints and dirt.

Water repellent treatment to make the viewing surface hydrophobic

Drops Moving by Capillarity

At the microscopic scale there are other forces to move fluids that are not efficient at the macroscopic scale. These forces are electro-osmosis and capillarity. In particular capillarity is widely used for actuating droplets.

1. Drop Moving Over a Transition of Wettability

Resulting force directed towards the hydrophilic region

Droplet at equilibrium
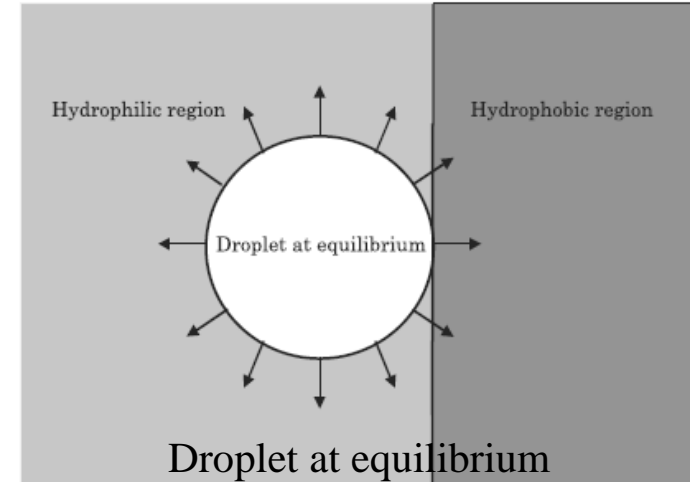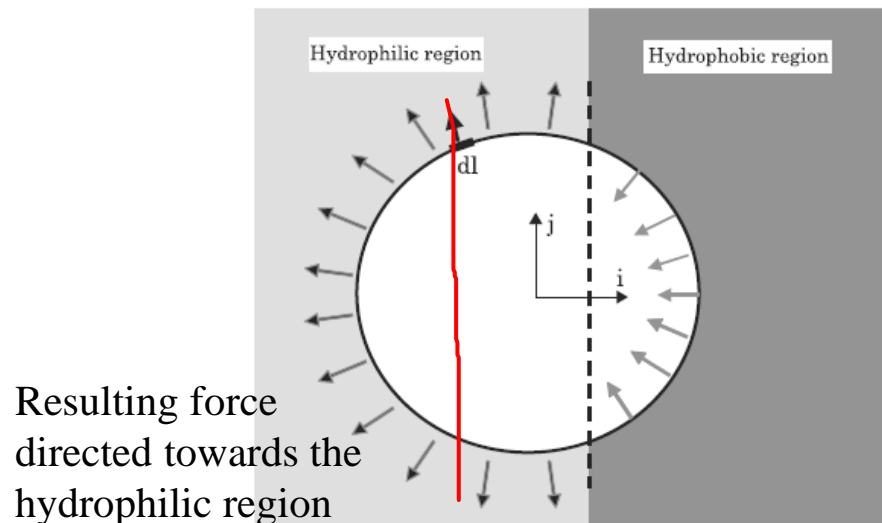
If L_1 and L_2 are the contact lines in the hydrophilic and hydrophobic planes, and θ_1 and θ_2 the contact angles, the force acting on the drop is

$$F_x = \int_{L_1} (\gamma_{SG} - \gamma_{SL})_1 \, (\vec{i}.\vec{dl}) - \int_{L_1} (\gamma_{SG} - \gamma_{SL})_2 \, (\vec{i}.\vec{dl})$$

$$= \int_{L_1} \gamma_{LG} \cos\theta_1 (\vec{i}.\vec{dl}) - \int_{L_2} \gamma_{LG} \cos\theta_2 (\vec{i}.\vec{dl}) < 0.$$

2. Drop Moving Uphill

Capillary forces may be sufficient to make micro-drops move upwards on an inclined plane.

M.K. Chaudhury and G.M. Whitesides, "How to make water run uphill," *Science, Vol.* 256, pp. 1539–1541, 1992.
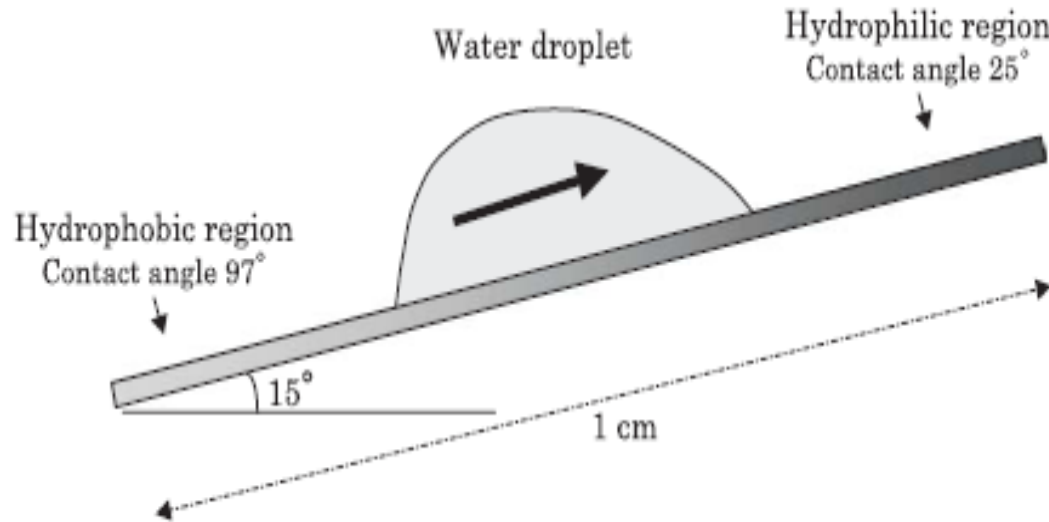
The required gradient in surface free energy was generated on a polished silicon wafer by exposing it to the diffusing front of a vapor of decyltrichlorosilane,

The average velocity is approximately 1 to 2 mm/s

A drop moves uphill towards the more hydrophilic region.

3. Drop Moving up a Step

A micro-drop of water is initially located on a step at the boundary of a hydrophilic region (on top of the step) and a hydrophobic region (at the base of the step). The drop progressively moves towards the hydrophilic region, even if this region is located at a higher level (simulation result)
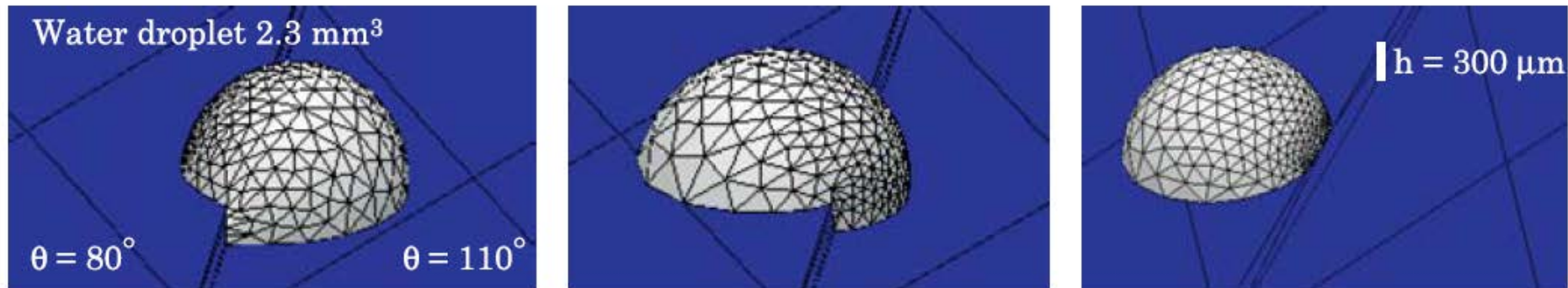

Motion of a drop up a step towards the hydrophilic plane (simulation)

4. Drop Moving Over a Gradient of Surface Concentration of Surfactant

Chemical reactions between the liquid of the droplet and the substrate can create droplet motion. A droplet of n-alkanes containing silane molecules is placed on a hydrophilic surface. Silane molecules form dense grafted monolayers on silicon or glass, rendering the surface hydrophobic.

If such a droplet is deposited on a glass surface and pushed with a pipette, then the droplet continues to move on the substrate. It moves in nearly linear segments and changes its direction each time it encounters a hydrophobic barrier. The droplet cannot cross its own tracks.

Direction of droplet motion
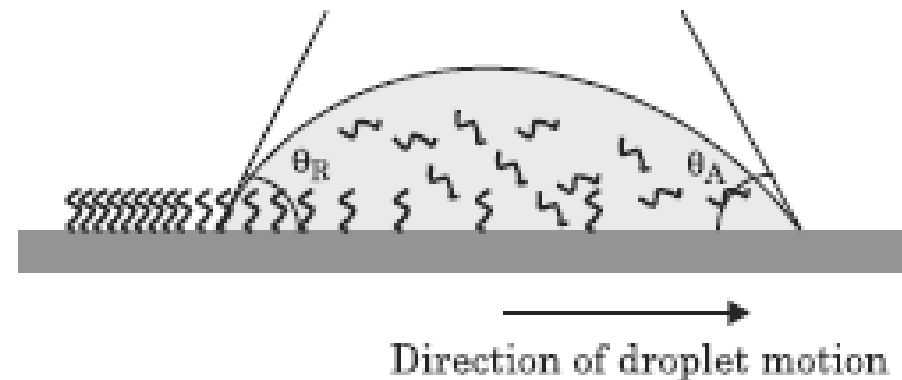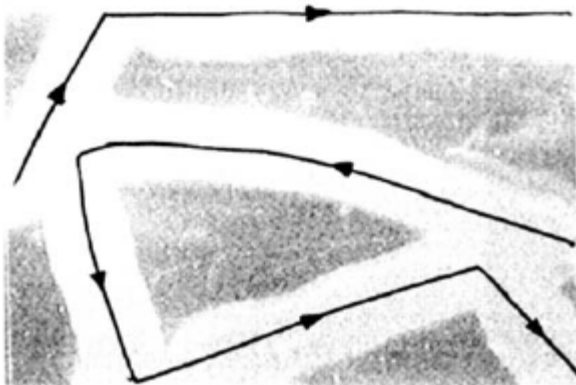
The advancing contact line has a hydrophilic Young contact angle. Molecules of silane concentrate at the vicinity of the receding contact line and form a hydrophobic layer.