# Wetting and Superhydrophobicity

30.9.2020

Ville Jokinen

# Expected learning outcomes

1st half: Wetting, theory and measurement:

-the fundamentals of wetting, both the thermodynamics (Young’s equation) and in practice (contact angle hysteresis).

- Wetting characterization by contact angles

2nd half: Superhydrophobicity, theory and applications:

-What properties define a superhydrophobic surface?

-What type of structures and surface chemistries are needed?

-How is superhydrophobicity characterized?

-Applications, challenges and current trends.

# Surface tension & Surface energy

Work required to create new surface =
surface energy x area created

$$\delta W = \gamma\, \delta A = \gamma\, L\delta x$$

Fundamental definition of surface energy:

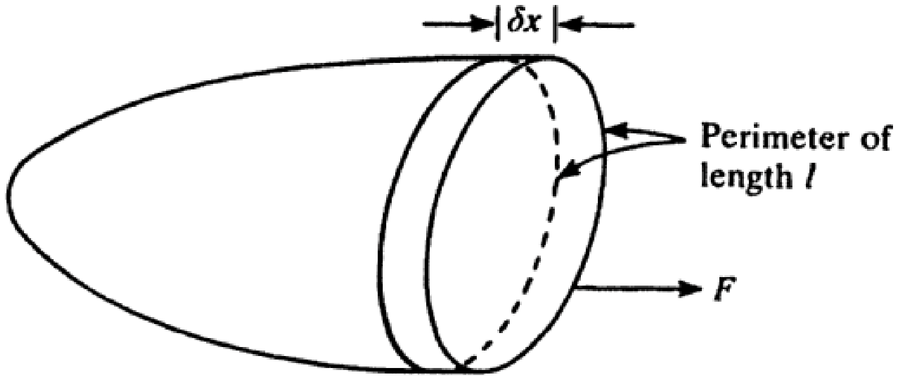
$$\gamma = \delta W / \delta A \quad [\, J / m^2 ]$$

Surface energy is also known as surface tension:

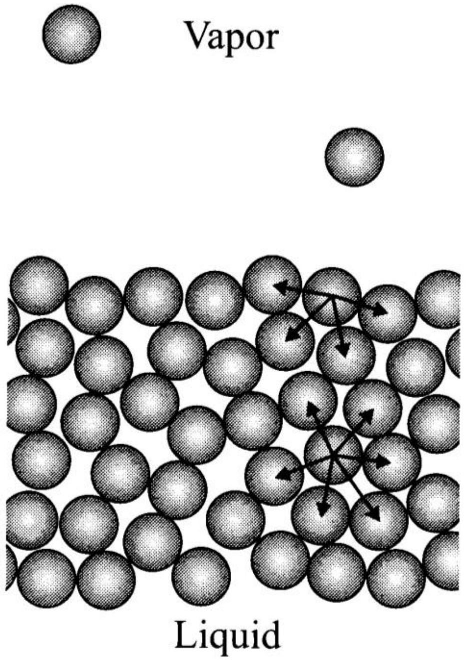
$$\gamma = \delta F / \delta x \quad [\, N / m ]$$

Concept applicable to all surfaces and interfaces:
solid-solid, solid-liquid, liquid-liquid, solid-gas, liquid-gas

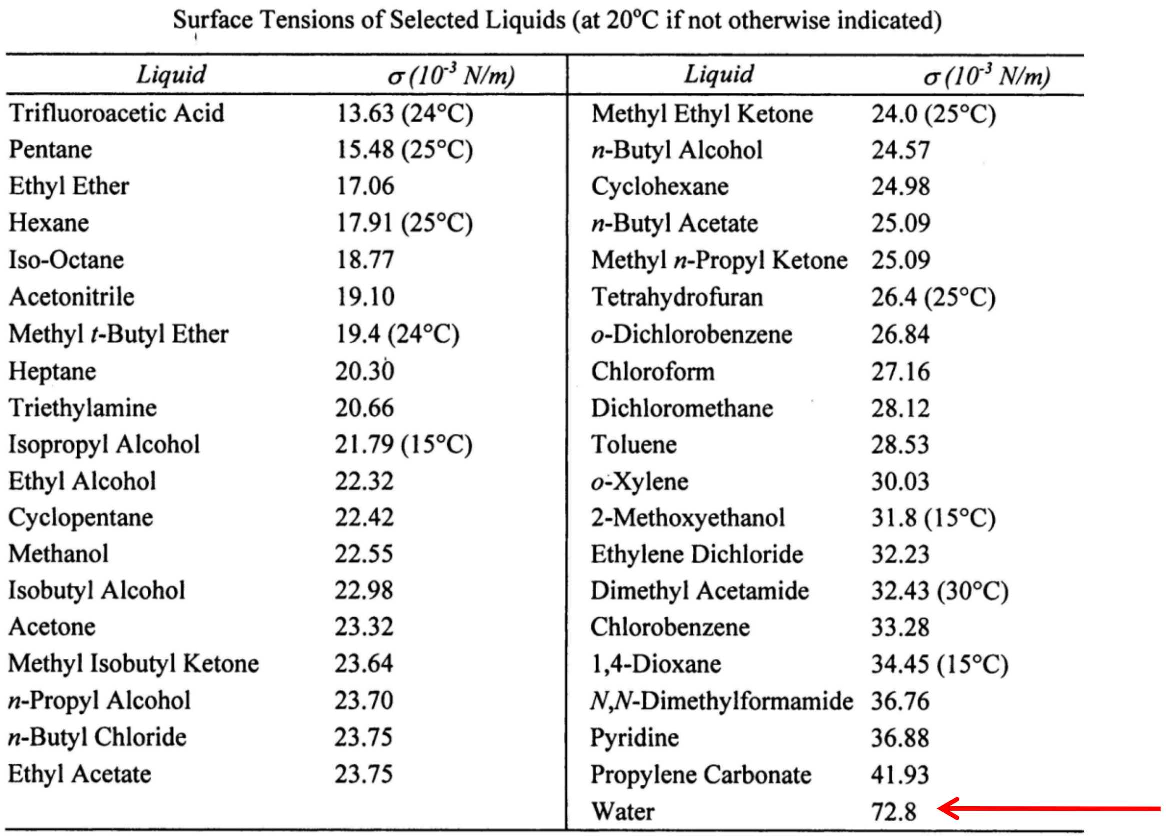
*Interfaces* *Surfaces*



Hunter: Introduction to Modern Colloid Science, p.134



Reminder:
The cause of surface energy, in liquids and solids alike, is the diminished number of bonds of atoms/molecules on the surface



Surface Tensions of Selected Liquids (at 20°C if not otherwise indicated)

| *Liquid* | *$\sigma$ ($10^{-3}$ N/m)* | *Liquid* | *$\sigma$ ($10^{-3}$ N/m)* |
|---|---|---|---|
| Trifluoroacetic Acid | 13.63 (24°C) | Methyl Ethyl Ketone | 24.0 (25°C) |
| Pentane | 15.48 (25°C) | *n*-Butyl Alcohol | 24.57 |
| Ethyl Ether | 17.06 | Cyclohexane | 24.98 |
| Hexane | 17.91 (25°C) | *n*-Butyl Acetate | 25.09 |
| Iso-Octane | 18.77 | Methyl *n*-Propyl Ketone | 25.09 |
| Acetonitrile | 19.10 | Tetrahydrofuran | 26.4 (25°C) |
| Methyl *t*-Butyl Ether | 19.4 (24°C) | *o*-Dichlorobenzene | 26.84 |
| Heptane | 20.30 | Chloroform | 27.16 |
| Triethylamine | 20.66 | Dichloromethane | 28.12 |
| Isopropyl Alcohol | 21.79 (15°C) | Toluene | 28.53 |
| Ethyl Alcohol | 22.32 | *o*-Xylene | 30.03 |
| Cyclopentane | 22.42 | 2-Methoxyethanol | 31.8 (15°C) |
| Methanol | 22.55 | Ethylene Dichloride | 32.23 |
| Isobutyl Alcohol | 22.98 | Dimethyl Acetamide | 32.43 (30°C) |
| Acetone | 23.32 | Chlorobenzene | 33.28 |
| Methyl Isobutyl Ketone | 23.64 | 1,4-Dioxane | 34.45 (15°C) |
| *n*-Propyl Alcohol | 23.70 | *N,N*-Dimethylformamide | 36.76 |
| *n*-Butyl Chloride | 23.75 | Pyridine | 36.88 |
| Ethyl Acetate | 23.75 | Propylene Carbonate | 41.93 |
|  |  | Water | 72.8 |

**UNITS: mN/m = mJ/m$^2$**

Water has a very high surface energy because of strong intermolecular bonds, ≈ 72 mN/m at room temperature

The lowest surface energies of liquids are around 10 mN/m. Fluorinated solvents. E.g. perfluorohexane 11-12 mN/m

Liquid metals have can have higher surface tension than water, 100s of mN/m.
Solid materials even more so, commonly 100s or 1000s of mN/m.

Temperature dependence: water: 72 mN/m at RT, 68 mN/m at 50$^{o}$C, 59 mN/m at 100$^{o}$C

# Wetting

Wetting means how much a liquid spread or beads up on a surface.

If a liquid spreads over a large area, that *surface is wetted* by that liquid.
If the liquid beads up, then the surface is not wetted by that liquid.

Wetting is characterized primarily by **contact angles.**

**Which parameters determine wettability?**
**Which parameters affect how much a droplet spreads on the surface?**

**Answers in chat!**

Wetting (or the lack thereof) of water droplets on a lotus leaf. https://www.flickr.com/photos/jspark/9467891206/

Applications of wettings: paints, coatings, capillary filling, heterogeneous nucleation etc.

# Wetting

Wetting means how much a liquid spread or beads up on a surface.

If a liquid spreads over a large area, that *surface is wetted* by that liquid.
If the liquid beads up, then the surface is not wetted by that liquid.

Wetting is characterized primarily by **contact angles.**

Wettability is determined by:

1. The topography of the surface
2. The surface chemistry
3. The properties of the liquid (surface tension)

(4. the properties of the 3rd phase)

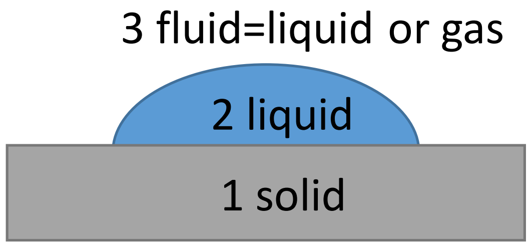
Wetting (or the lack thereof) of water droplets on a lotus leaf. https://www.flickr.com/photos/jspark/9467891206/

Applications of wettings: paints, coatings, capillary filling, heterogeneous nucleation etc.

# Contact angle, observational

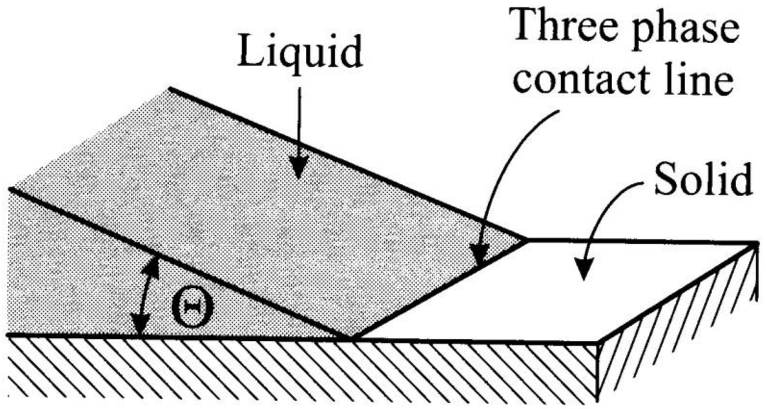
- A liquid droplet makes a certain *angle of contact* with a solid surface
- This angle at the *three phase contact line* is the apparent **contact angle θ**

- **Contact angle is a property of a solid-liquid-fluid three phase system!**
- *For a fixed liquid and fluid*, contact angle is characteristic parameter of a surface/material


3 fluid=liquid or gas

2 liquid

1 solid



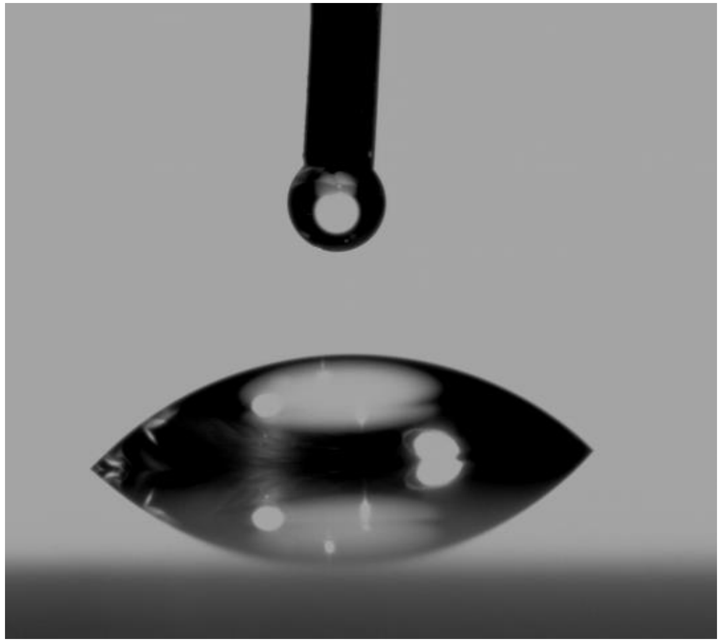
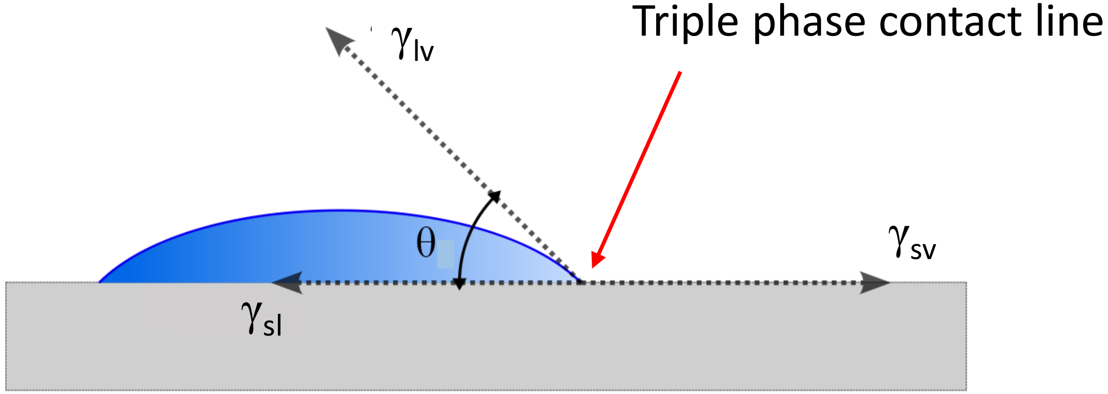


Image: wikipedia

# Contact angle, theoretical

Young’s equation:

$$\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{sl}$$



$\theta$ Thermodynamic, or Young’s, **contact angle**

$\gamma_{lv}$ Liquid-vapor surface energy (“liquid surface tension”) (sometimes just $\gamma_l$)

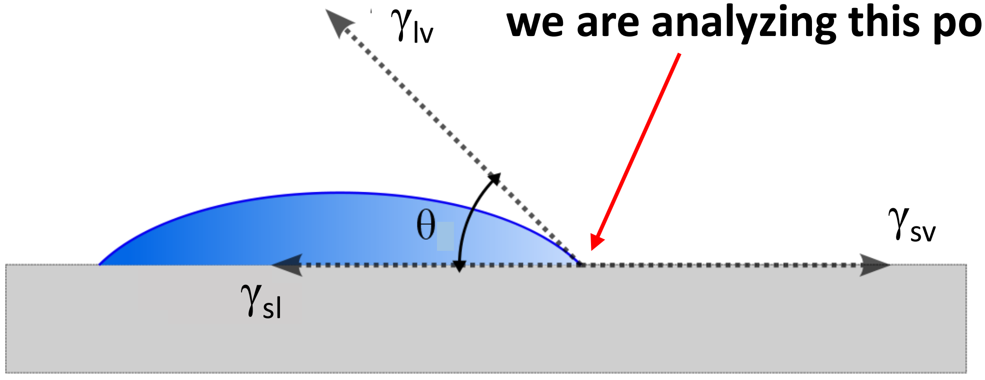
$\gamma_{sv}$ Solid-vapor surface energy (“solid surface energy”) (sometimes just $\gamma_s$)

$\gamma_{sl}$ Solid-liquid surface energy (“solid-liquid interfacial energy”)

In upcoming slides we will discuss if and when the observational contact angle and the Young’s theoretical contact angle are the same.

# Derivation of Young's equation

Mechanical equilibrium: what are the conditions for θ, $\gamma_{lv}$ , $\gamma_{sv}$ and $\gamma_{sl}$ so that the triple phase contact line does not move horizontally?



Triple phase contact line,
**we are analyzing this point**

$$\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{sl}$$

Force pulling 3-phase contact line left: $\gamma_{sv}$

Forces pulling 3-phase contact line right: $\gamma_{sl}$ , $\gamma_{lv} \cos(\theta)$

Forces are balanced if: $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos(\theta)$

If he forces are not balanced, the 3-phase contact line will move (to either direction) until they are.

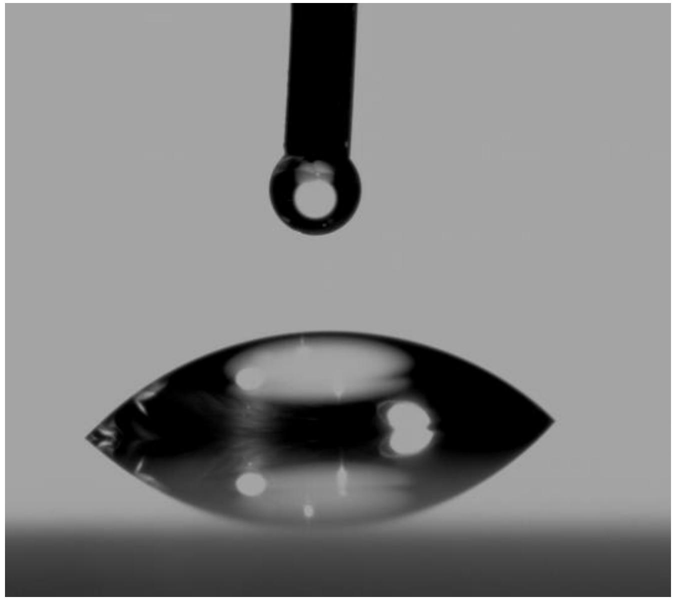
(The 3-phase contact line is not free to move in the vertical direction)

# Contact angle measurement

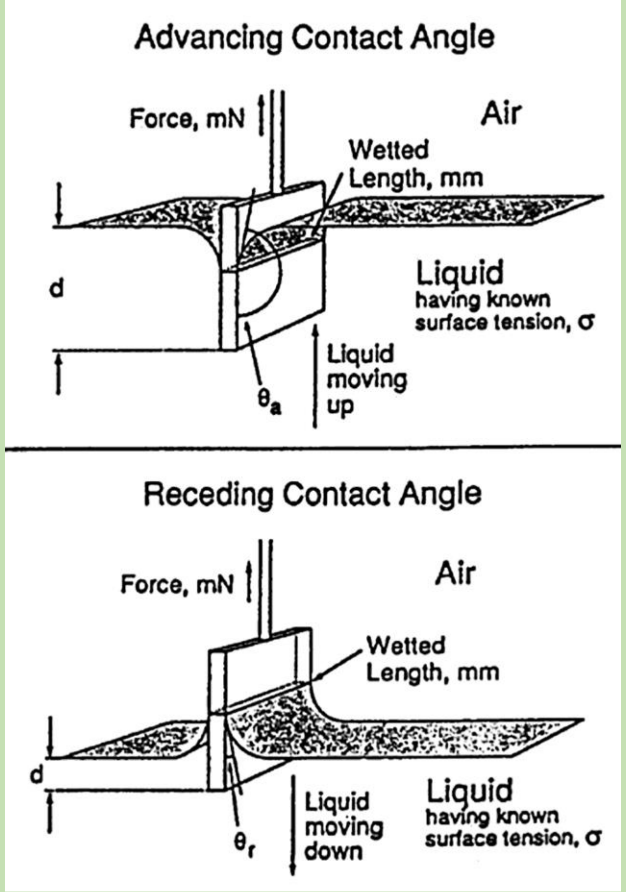
Contact angles are measured by the same principles as surface tensions: based on either forces or optical image analysis.

Optical goniometry (contact angle goniometry):

1. Droplet is placed on a surface
2. A fitting algorithm identifies the droplet and the surface and fits a curve the droplet edge
3. The contact angle is extracted from the fitted curve



There are also force based contact angle measurement methods (e.g. Wilhelmy plate method), but we do not discuss them further.



# Contact angle hysteresis 1

**Now comes the curveball…** 3 phase systems in the real world have **multiple stable contact angles!**
**This is a problem because:**

1. Contact angle was supposed to be a characteristic parameter of the surface (3 phase system)
2. We need to know the contact angle to calculate several real effects (examples upcoming)

All of the stable contact angles fall between an upper bound, called the **advancing contact angle $\theta_{adv}$**, and a lower bound, called the **receding contact angle $\theta_{rec}$**

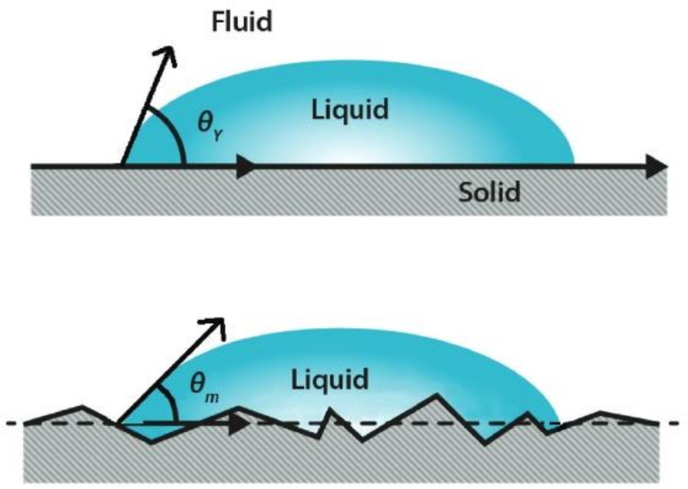
On real surfaces: $\theta_{rec} < \theta_{eq} < \theta_{adv}$

$\theta_{rec}$ = Receding contact angle
$\theta_{eq}$ = Equilibrium/static contact angle
$\theta_{adv}$ = Advancing contact angle

We define contact angle hysteresis: $\theta_{adv} – \theta_{rec}$
Hysteresis have any positive values between 0° and 180°, on most surfaces it is at least 10°)
On an ideal surface $\theta_{adv} – \theta_{rec} = 0°$ and we again have a singly defined contact angle.

Figure: Biolin Scientific tech note: Influence of surface roughness on contact angle and wettability

# Contact angle hysteresis 2



**Reasons for contact angle hysteresis:**

1. Surface roughness
2. Chemical inhomogeneities

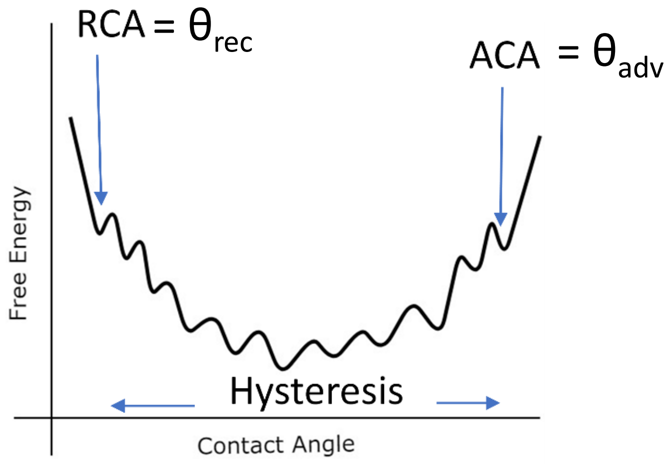
(less fundamental reasons: adsorption or desorption on the surface, or reactions between the liquid and the solid.)

Microscopically at the triple phase contact line, these two surfaces have the same contact angle. But measured macroscopically, they do not.

Real surfaces are filled with local energy barriers when the 3 phase contact line attempts to move.

$\theta_{adv}$ corresponds to the ability to bypass all local energy barriers when the droplet is advancing (spreading)

$\theta_{rec}$ corresponds to the ability to bypass all local energy barriers when the droplet is receding (beading-up)



# Contact angle hysteresis 3

**Hysteresis is a problem since:**

1. Contact angle was supposed to be a characteristic parameter of the surface (3 phase system)
2. We need to know the contact angle to calculate several real effects (examples upcoming)

Which experimental contact angle is the one appearing in Young's equation?
**Unresolved,** but some suggestions that have been made in the literature:

1. $\theta_{adv}$
2. $(\theta_{adv} + \theta_{rec})/2$
3. $\mathrm{acos}((\cos\theta_{adv} + \cos\theta_{rec})/2)$
4. the most stable θ (obtained after ultrasonic vibrations)

**However:**
The real answers to the problem is that:

1. For real surfaces, 3 phase system is characterized by 2 values instead of 1, $\theta_{adv}$ and $\theta_{rec}$
2. For calculations, if we are calculating an advancing case, $\theta_{adv}$ is used, and if we are calculating a receding case, $\theta_{rec}$ is used.

# Let’s see measurement in practice

Solid: (100) silicon wafer that has been in a closed box inside a cleanroom for >1 month. On the surface there is the native silicon oxide and many things adsorbed from the atmosphere.

Liquid: Deionized water = very clean water

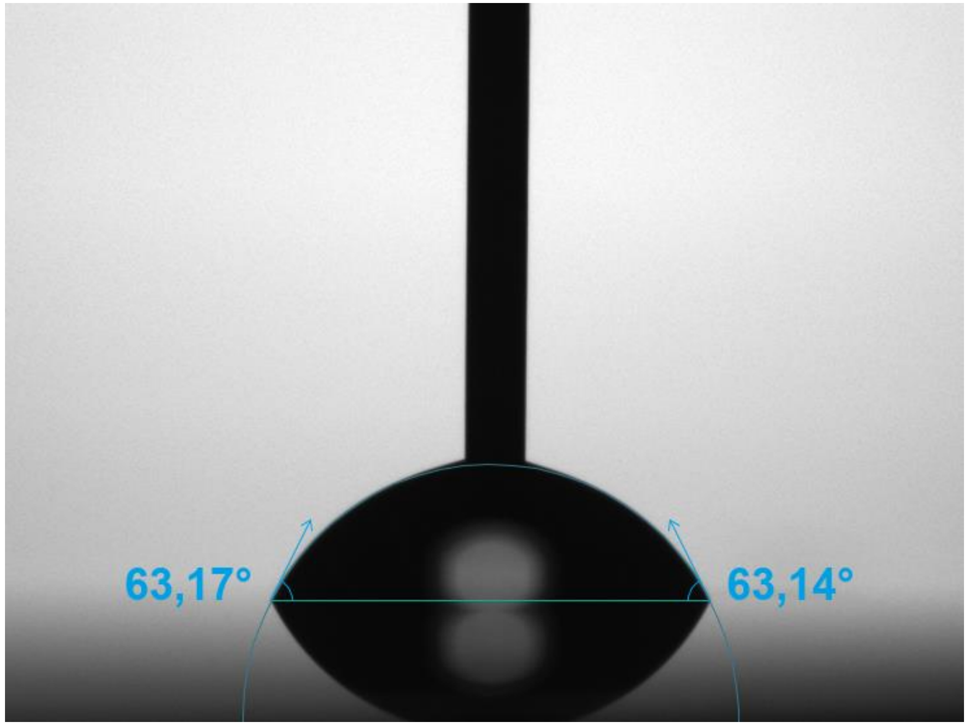
Fluid: air

Measurement technique: “needle-in” sessile droplet goniometry.

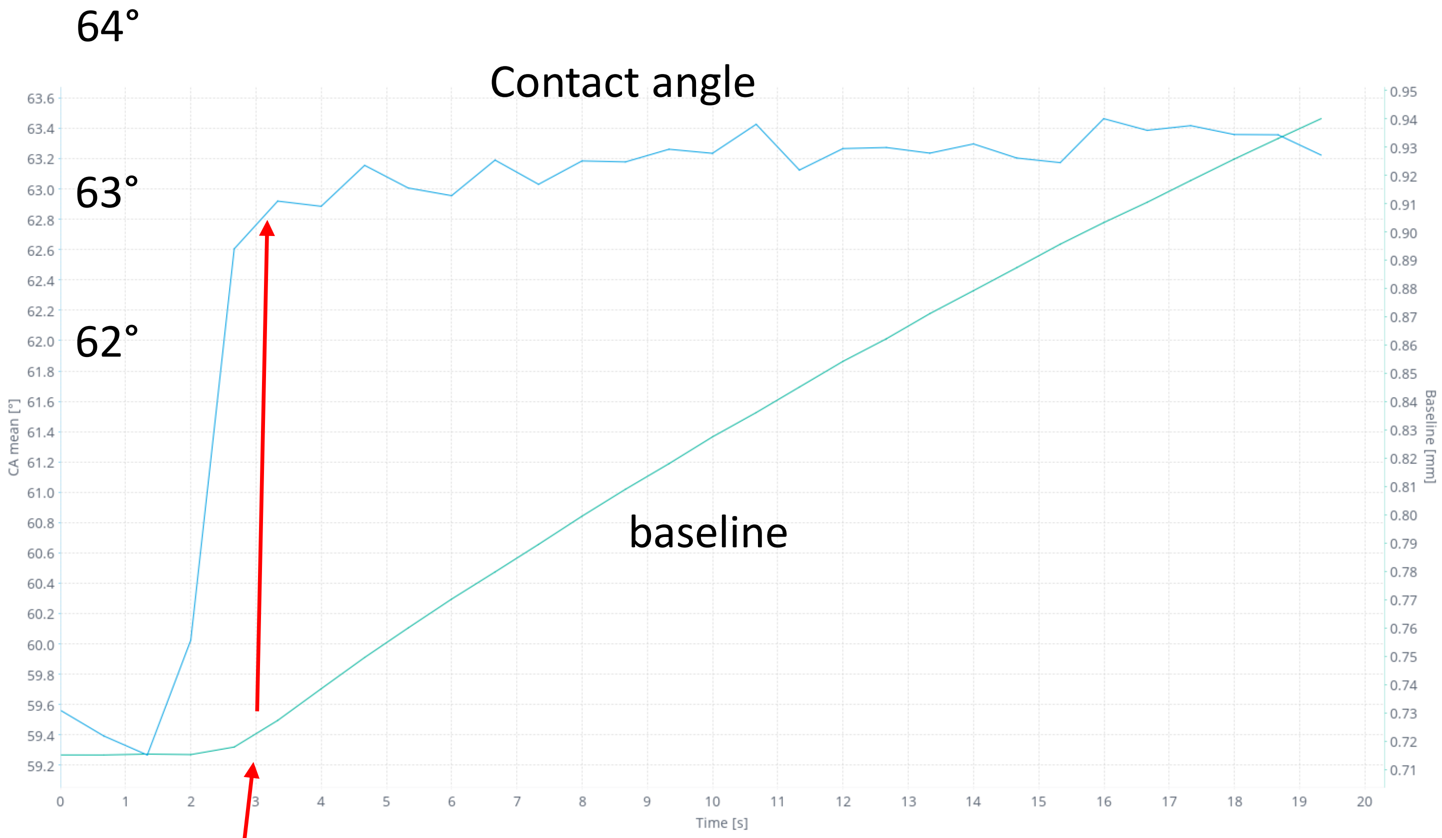
Starting droplet size 1.5 µl

Droplet size increased and decreased with rate 0.1 µl/s

# Advancing contact angle



Baseline and contact angle vs time

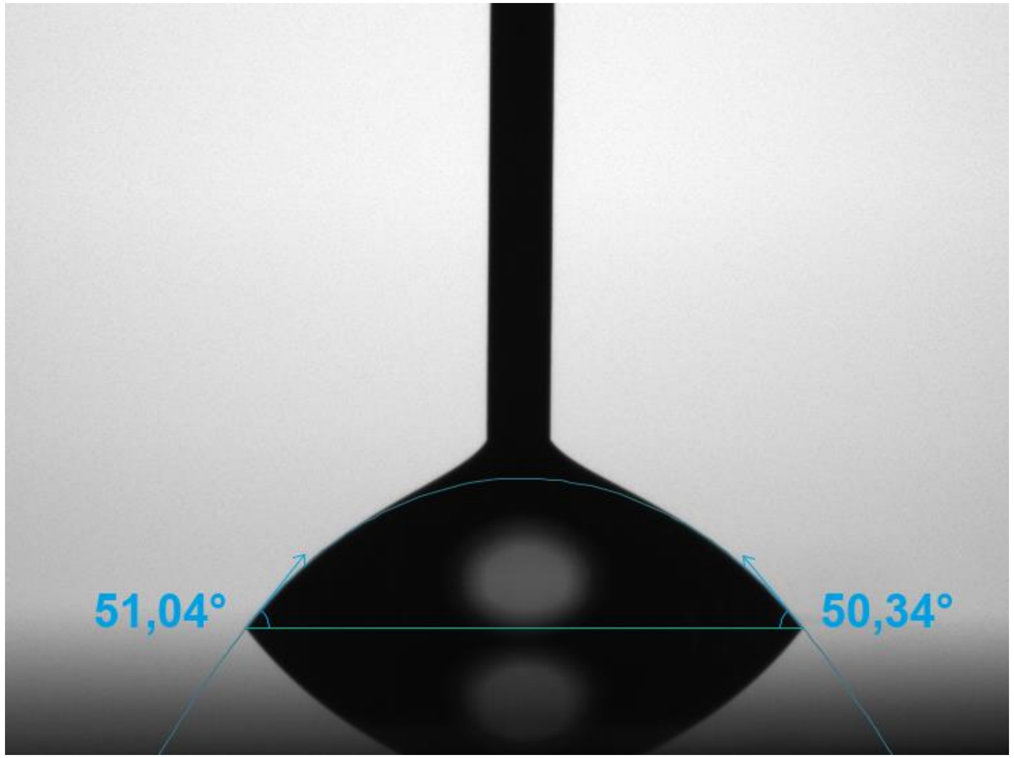


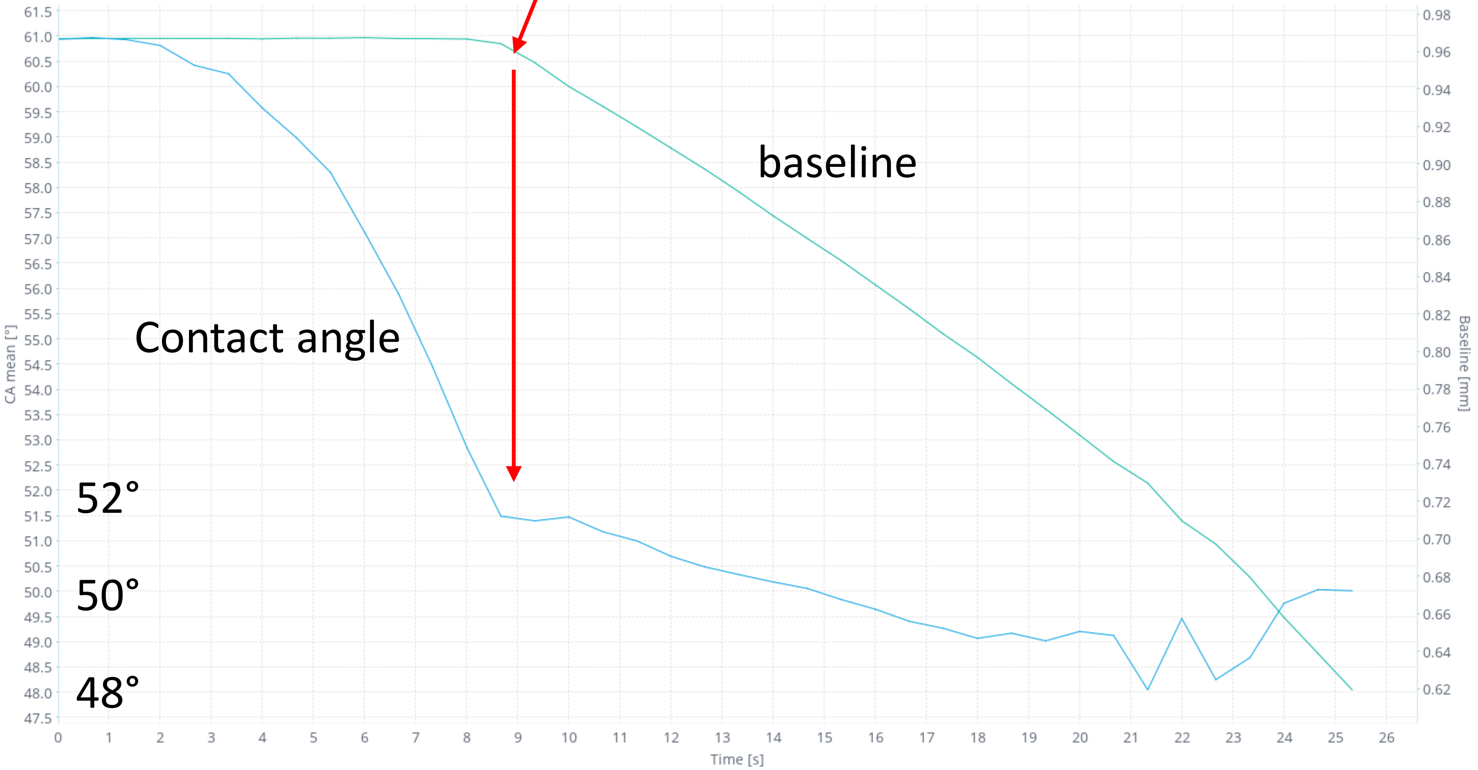
Baseline is the width of the droplet, when baseline changes, the droplet is advancing or receding

Here baseline starts to increase
At the same timepoint contact angle reaches a steady value, the advancing contact angle

# Receding contact angle

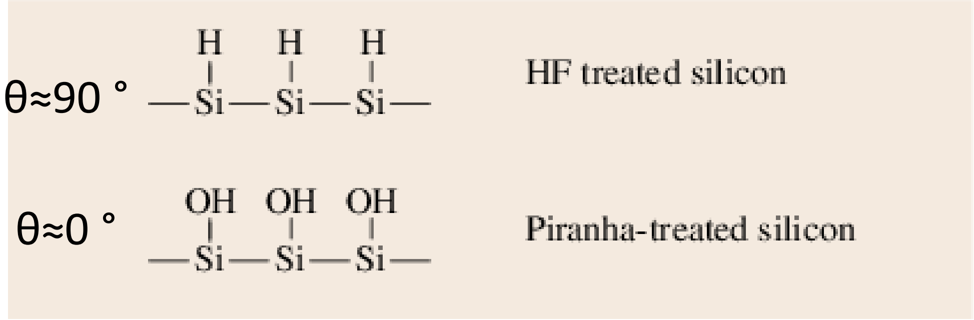
Here baseline starts to decrease
Receding contact angle in theory should also stabilize completely, but in practice it retains a small downward trend. The receding contact angle is this value where depinning of the 3 phase line happens.





# Results of measurement

Examples why silicon does not have a single contact angle



Bhushan: Self-Assembled Monolayers for Nanotribology and Surface Protection

Advancing contact angle: 63°

Receding contact angle: 51°

Contact angle hysteresis: 12°

Accuracy of any single measurement is 1°-2°, repeat measurements are always necessary.

Contact angle between water and silicon wafer can be anything between 0° up to 90+°.

High energy surfaces only have well defined contact angles after a carefully standardized surface preparation step.

Otherwise the measurement is measuring also atmospheric adsorbates etc. and not just the surface.

# Example of application/calculation

**Capillary pressure:**

A small hydrophilic capillary (circular cross section, radius r) fills spontaneously by capillary pressure. This pressure is given by the formula:

$$P_{cap} = \frac{2\gamma_{lv}\cos(\theta)}{r}$$

*which contact angle to use???*

**Answer to the poll!**

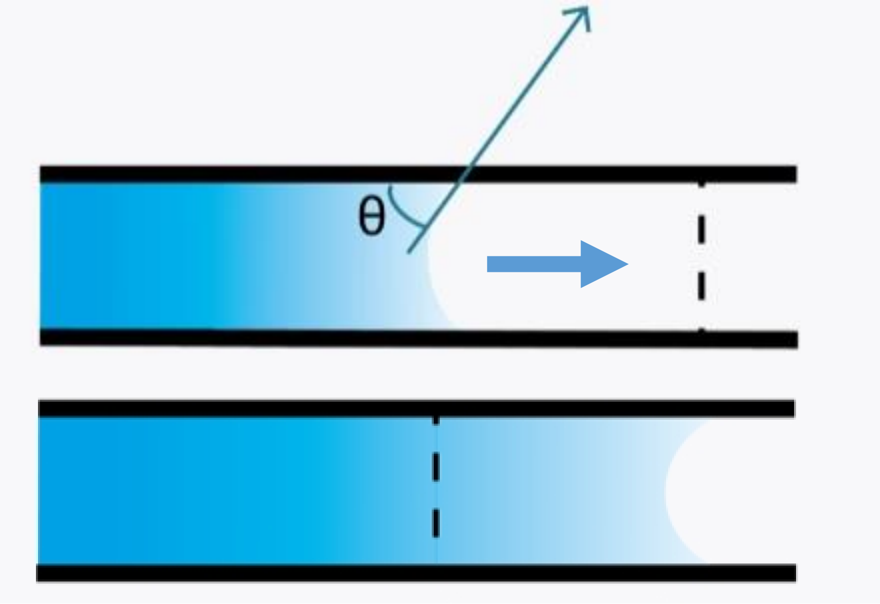


Figure: Biolin scientific blog Capillary action – how contact angle and surface tension are related?

Application of capillary flow: Home diagnostics, e.g. pregnancy test, some infectious disease tests.

(more on that kind of stuff on my other Masters level course CHEM-E8135 Microfluidics & BioMEMS, periods III and IV)

Lateral flow home diagnostic test

# Example of application/calculation

**Capillary pressure:**

A small hydrophilic capillary (circular cross section, radius r) fills spontaneously by capillary pressure. This pressure is given by the formula:

$$P_{cap} = \frac{2\gamma_{lv}\cos(\theta)}{r}$$

*which contact angle to use???*

**Answer**: capillary pressure of a **filling** capillary is determined by the **advancing** contact angle.

Application of capillary flow: Home diagnostics, e.g. pregnancy test, some infectious disease tests.

(more on that kind of stuff on my other Masters level course CHEM-E8135 Microfluidics & BioMEMS, periods III and IV)

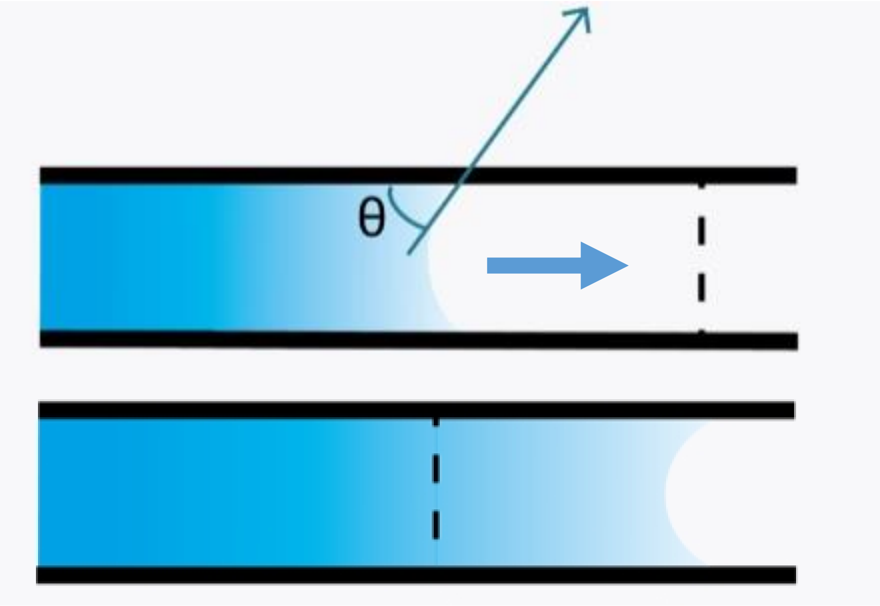


Figure: Biolin scientific blog Capillary action – how contact angle and surface tension are related?

Lateral flow home diagnostic test

# Water contact angles of materials

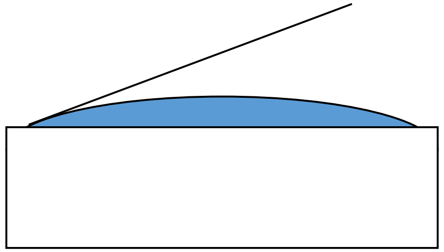
**Water contact angle (WCA) of material X:** The contact angle when the liquid is water, the solid is X and the fluid is air or other inert gas

**Case 1:**
If WCA < 90°, the material is said to be *wetting* (by water), or *hydrophilic*. If WCA = 0°, the material is said to be *completely wetting*.
There is also the term *superhydrophilic*, but it is not clearly defined, WCA is very low.

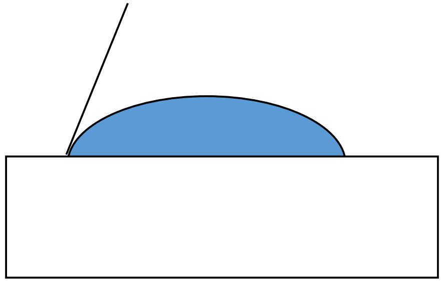
WCA = 0°
Completely wetting

Clean metals, strongly polar surfaces, strongly charged surfaces.

*Roughened hydrophilic surfaces.*



WCA = 20°
Wetting/hydrophilic



WCA = 70°
Wetting/hydrophilic

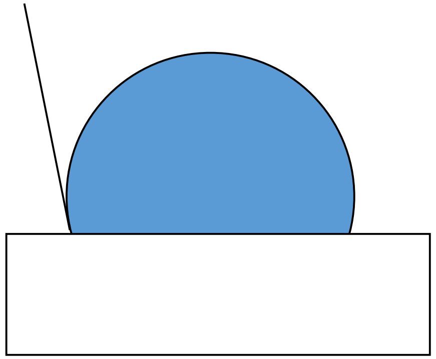
Typical wetting surfaces in the lower WCA end are ceramics and glasses.

Typical wetting surfaces in the higher WCA end are polymers. High energy surfaces contaminated by atmospheric contaminants tend to also be in this range

**Case 2:**
If WCA >90°, the material is said to be *nonwetting* (by water), or *hydrophobic*.

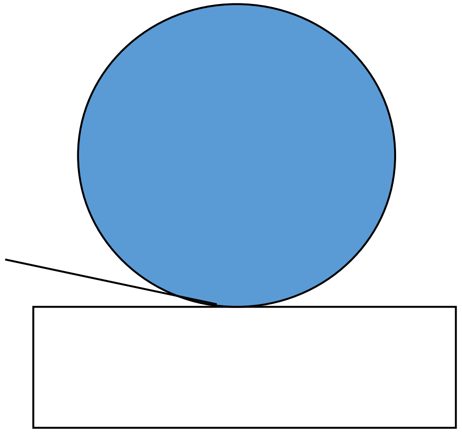
The term *superhydrophobic* we define in 2nd half of lecture.

Definitions of hydrophilic and hydrophobic, which contact angle to use?
Answer: *unclear currently.* If I had to choose I would go with RCA (https://doi.org/10.1021/jz402762h)



WCA = 90°-120°
Nonwetting, hydrophobic

Uncharged and relatively nonpolar surfaces. E.g. fluoropolymers, some other polymers, silicones, waxes.



WCA > 120°
Nonwetting, hydrophobic, superhydrophobic?

**No material has WCA > 120° <u>on a smooth surface</u>.**

*Roughness and hydrophobic chemistry.*

# Terminology

Until now I have tried to use the really cumbersome (but precise) language that contact angle and wetting are properties of a 3 phase system. However:

1: In the common language of the field, if the fluid phase is not specified it is an inert gas (usually air).

2: The liquid can be specified by using terms like hydro, or if it is not specified water can be assumed by default or else the liquid is clear from the context.

Now we can finally simplify and make statements like:

*"Glass is a hydrophilic material"* = The contact angle of a glass, water, air 3 phase system is less than 90°

*"Teflon has a contact angle of 120°"* = The contact angle of a teflon, water, air 3 phase system is 120° (notice that the water in the statement on the left was silent)

*So in this way, wettability can be said to be a surface property.*

# Hydrophilic, Hydrophobic, Young’s equation

Young’s equation: $\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{sl}$

**Hydrophilic materials:**
$\theta < 90°$
$\cos(\theta) > 0$
$\gamma_{sv} - \gamma_{sl} > 0$
$\gamma_{sv} > \gamma_{sl}$

This means that the surface energy of the dry surface is higher than the surface energy of the wetted surface

**There is a free energy drive for the dry surface to be coated by water.**

**Hydrophobic materials:**
$\theta > 90°$
$\cos(\theta) < 0$
$\gamma_{sv} - \gamma_{sl} < 0$
$\gamma_{sv} < \gamma_{sl}$

This means that the surface energy of the wetted surface is higher than the dry surface.

**There is a free energy drive for the wetted surface to be de-wetted (dried).**

# Part 2: Superhydrophobicity

# Definitions of Superhydrophobicity

**Superhydrophobic surface = surface where water droplets adhere extremely poorly.**

Superhydrophobic (SHB) surfaces are *commonly* characterized by:

- High advancing and receding contact angles

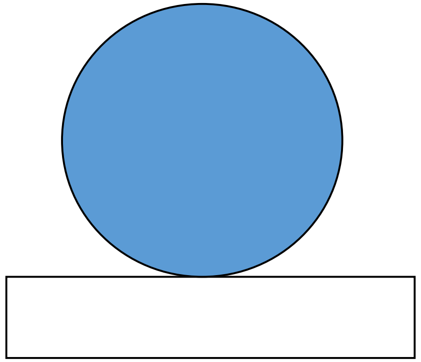
- Low contact angle hysteresis

- Low sliding angles (definition coming soon)

Sometimes sources attempt to define superhydrophobic surfaces by these parameters

For example: contact angle > 150°, sliding angle < 5°.

Lets return to these criteria later.



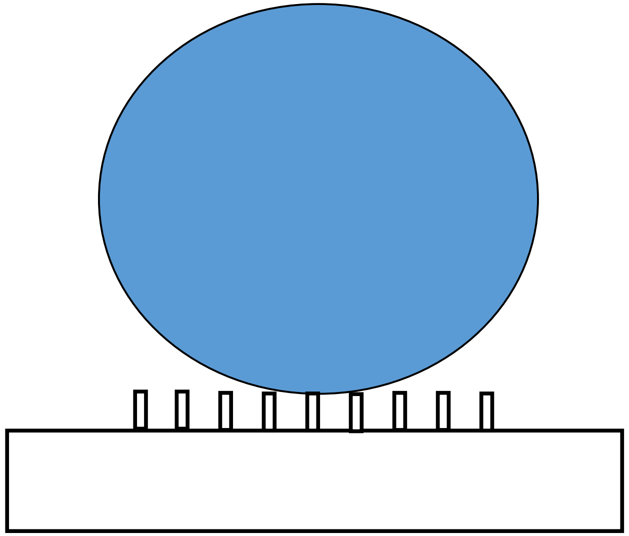
# Superhydrophobic surfaces are mostly air

If the best material has WCA 120°, how can we get any higher?

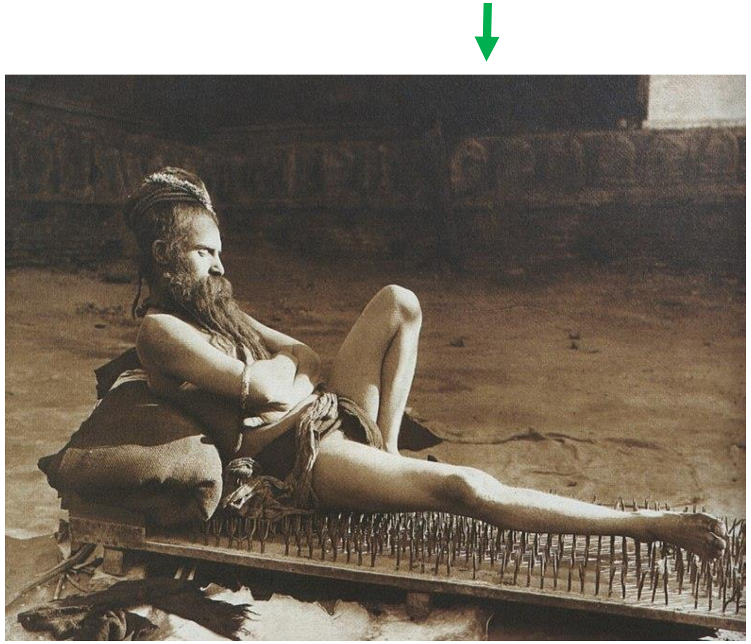
There is a material which actually has a WCA of 180°… air! (or other inert gas).

However…some solid is needed since the droplet does not levitate.

The trick is to have only a small fraction of the surface to solid, and the rest air. How low can the fraction go? 20%, 10%, 5%, 1%? *Hint: what limits the fakir case?*



Droplet on SHB surfaces rests mostly on air



Fakir rests mostly on air (figure: wikipedia)

# Cassie-Baxter state

The superhydrophobic state is called the Cassie-Baxter state (sometimes just Cassie state).

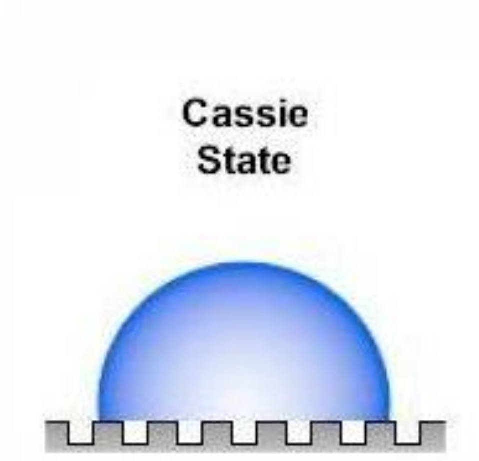
The key feature is the air pocket, called plastron.

In the Cassie state the, the contact angle $\theta_C$ is enhanced by the surface topography and it is given by the Cassie-Baxter equation:

$$\cos(\theta_C) = f * \cos(\theta_{solid}) + (1 - f) * \cos(\theta_{air})$$

$$\cos(\theta_C) = f * \cos(\theta_{solid}) + (1 - f) * \cos(180)$$

$$\cos(\theta_C) = f * \cos(\theta_{solid}) - 1 + f \longleftarrow \text{Usual form}$$



f is the solid fraction = the fraction of the surface that the liquid contacts that is solid material

Note: to treat air as 180° is mathematical shorthand. Air, as a gas, has neither surface energy nor contact angle as such.

# Wenzel state

There is another wetting mode which can produce high contact angles.

The Wenzel state is characterized by **the lack of the air pocket**, the liquid fills or cavities underneath it.

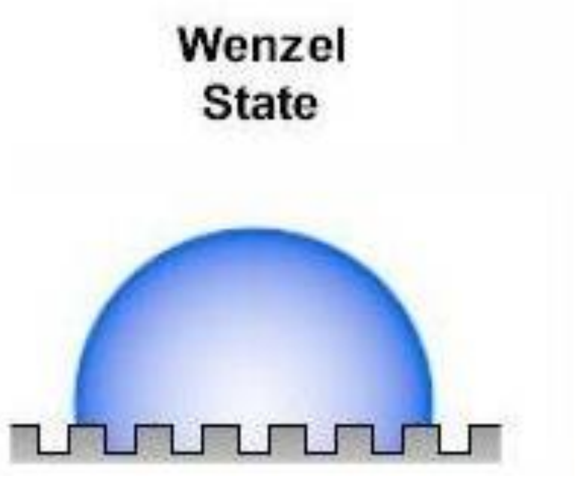
These surfaces are NOT superhydrophobic and have high adhesion to water. This is sometimes called the petal effect (compared to lotus effect)

Wenzel equation can be used for designing superhydrophilic surfaces.

In the Wenzel state the contact angle $\theta_W$ is given by:

$$\cos(\theta_w) = r\cos(\theta)$$

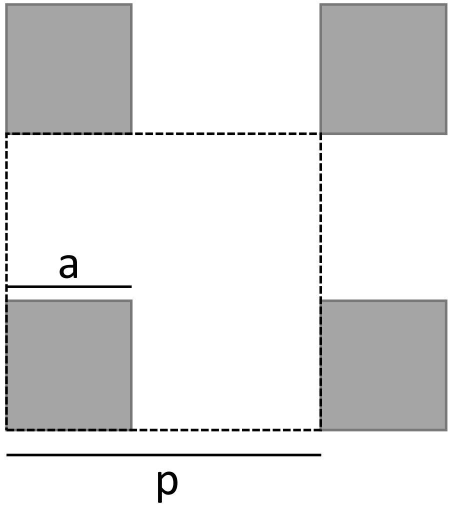
, where r is the roughness factor that tells how much more liquid solid contact area there is on the rough surface compared to smooth.



# Stability of the Cassie state

As a model surface, lets take square shaped micropillars with side a are in a regular square lattice with pitch p. The advancing WCA is $\theta_{adv}$. What is the maximum pressure the Cassie state can sustain?

Top:



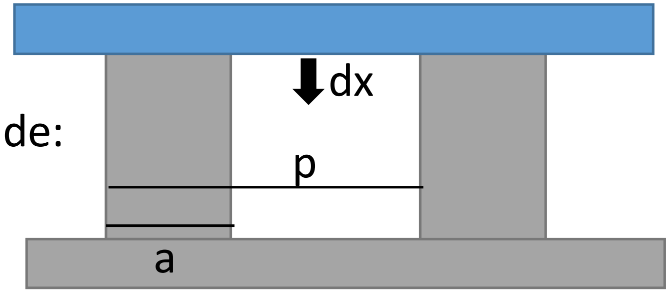
$$dV = (p^2 - a^2)dx$$

$$dE = dA * (\gamma_{sl} - \gamma_{sv}) = -4a * dx * \gamma_{sv}\cos(\theta_{adv})$$

$$P_{breakthrough} = \frac{dE}{dV} = \frac{-4a\gamma_{sv}\cos(\theta_{adv})}{(p^2 - a^2)}$$

Note: this $\theta_{adv}$ is the advancing angle of the material (smooth), not the Cassie angle

Side:



If $\theta_{adv}$<90°, breakthrough pressure is negative and the plastron wets by capillary forces (exactly the same situation as with the capillary filling example).

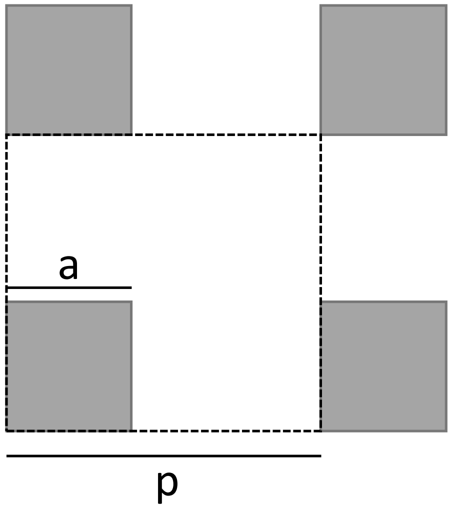
Therefore: To have a stable plastron, we need $\theta_{adv}$>90°

# Examples

This tells us how stable the superhydrophobic state is

This tells us how good the Superhydrophobicity is

| $a$ | $p$ | $\theta_{adv}$ | $P_{breakthrough}$ | $f_{Cassie}$ | $\theta_{Cassie}$ |
|---|---|---|---|---|---|
| 10µm | 20µm | 120° | ≈4.8 kPa | 0.25 | ≈151° |
| 10µm | 20µm | 95° | ≈0.84 kPa | 0.25 | ≈141° |
| 10µm | 40µm | 120° | ≈0.96 kPa | 0.0625 | ≈166° |
| 100nm | 200nm | 120° | ≈480 kPa | 0.25 | ≈151° |
| 100nm | 400nm | 120° | ≈96 kPa | 0.0625 | ≈166° |



We see that:

Increasing $\theta_{adv}$, increases the stability and the superhydrophobicity

Increasing the pitch, lowers the stability but increases the superhydrophobicity

Downscaling, increases the stability without affecting superhydrophobicity

↑ ↑ Limited by materials

↓ ↑ Not limited

↑ → Limited by fabrication complexity

# Surface chemistries for superhydrophobicity

If the structures are made of high surface energy solids, a low surface energy coating is needed.

All kinds of coating methods are suitable: vacuum, gas and liquid phase deposited have all been used.

Self-assembled monolayers are (perhaps) the gold standard

Methylated SAM coating ≈ 15-20 mN/m

Fluorinated SAM coating ≈ 5-10 mN/m

Langmuir 2003,19,3288-3296

Or: if the substrate is already of low surface energy, maybe a coating is not needed?

Some polymers might qualify:

Polyethylene: ≈30 mN/m

Polytetrafluoroethylene (Teflon): ≈20 mN/m

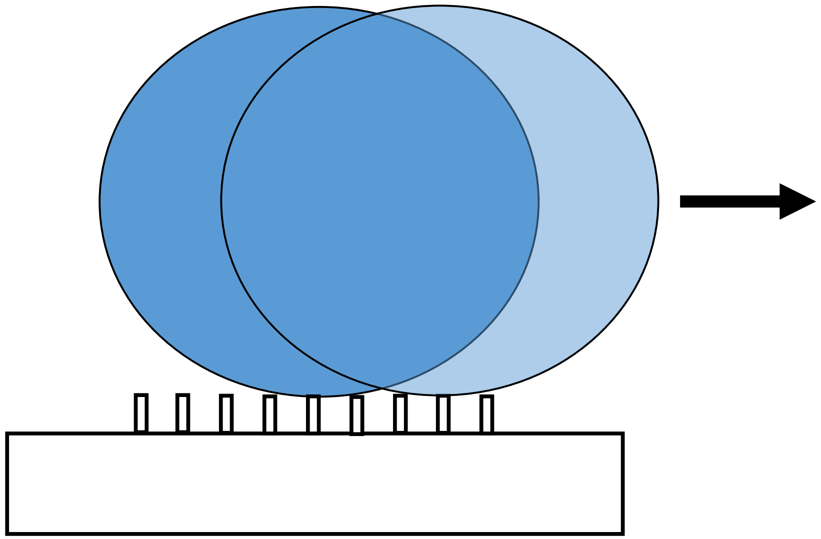
For water, fully methylated surfaces $\theta_{adv}\approx 110°$ and fluorinated surfaces $\theta_{adv}\approx 120°$

# Two types of adhesion

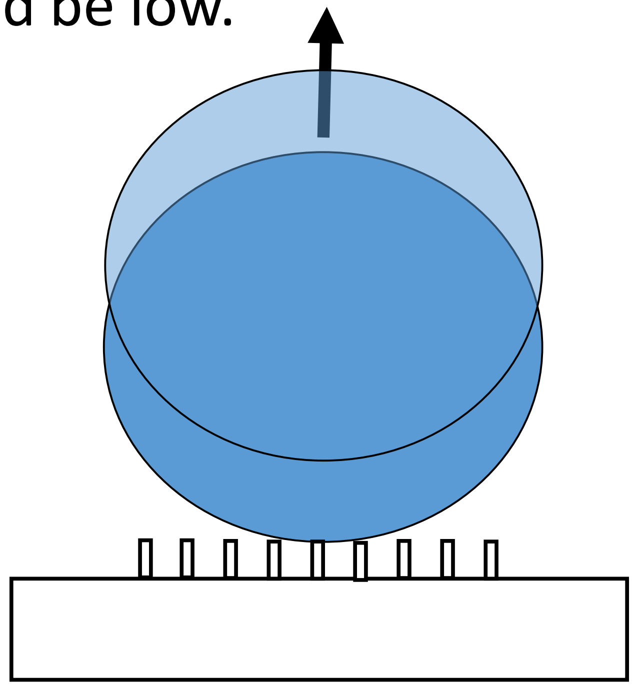
Superhydrophobicity = lack of adhesion of water droplets

But this means two different things!

Lateral (shear) and vertical (tensile) adhesion, both should be low.



Lateral: droplets rolls/slides on surface
Right side of droplet: 3 phase line advances
Left side of droplet: 3 phase line recedes



Vertical: droplet is lifted from the surface
Both sides: 3 phase line recedes

# Lateral adhesion, Sliding angle

The lateral adhesion force for a droplet is given by: $F_{lateral} = \frac{24}{\pi^3} \gamma_{lv} D[\cos(\theta_{rec}) - \cos(\theta_{adv})]$

,where D is the diameter of the contact line.

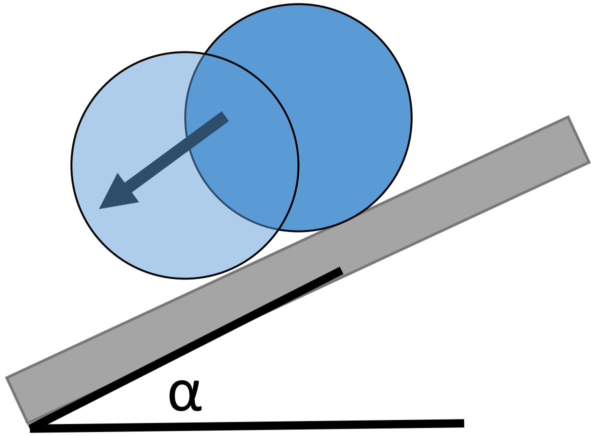
Note: depends on both $\theta_{adv}$ and $\theta_{rec}$ (so depends on hysteresis)

*Sliding angle* (SA): For a droplet with size V, what is the lowest tilting angle of the surface where the droplet will roll of due to gravity?

**SA is an excellent parameter to demonstrate SHB**

Just remember to always specify the volume.

The bigger the droplet the easier it rolls.



$F_{gravity} = mgsin(\alpha)$

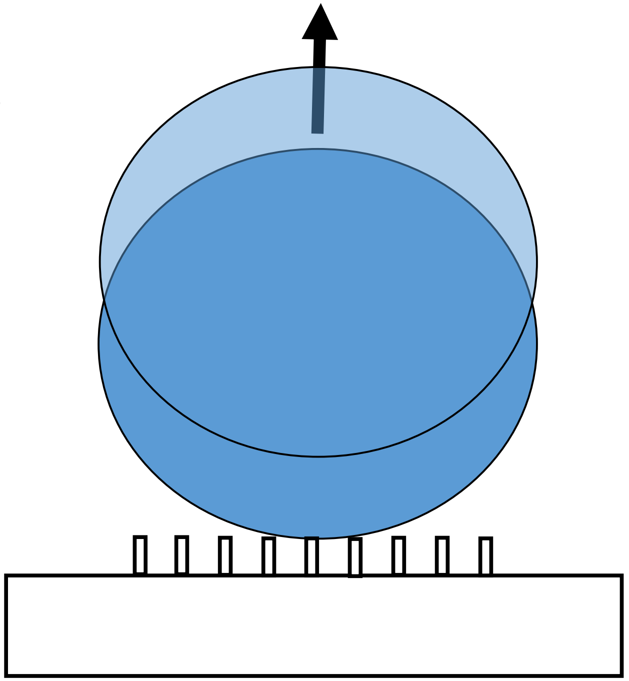
# Vertical adhesion

The adhesion energy (per unit area) of a droplet on a surface is given by the Young-Dupre equation:

$$W_{adhesion} = \gamma_{lv}(1 + \cos(\theta_{rec}))$$

Since this is a receding case, the receding angle should be used.

**We see that if the $\theta_{rec}$ = 180°, then the work of adhesion is 0!**



# Superhydrophobicity demonstration

Pyramid shaped silicon nanopillars (black silicon), coated by a fluoropolymer coating.

Adhesion-wise, a very high end superhydrophobic surface

**$\theta_{adv} \approx 170^\circ, \theta_{rec} \approx 170^\circ$**

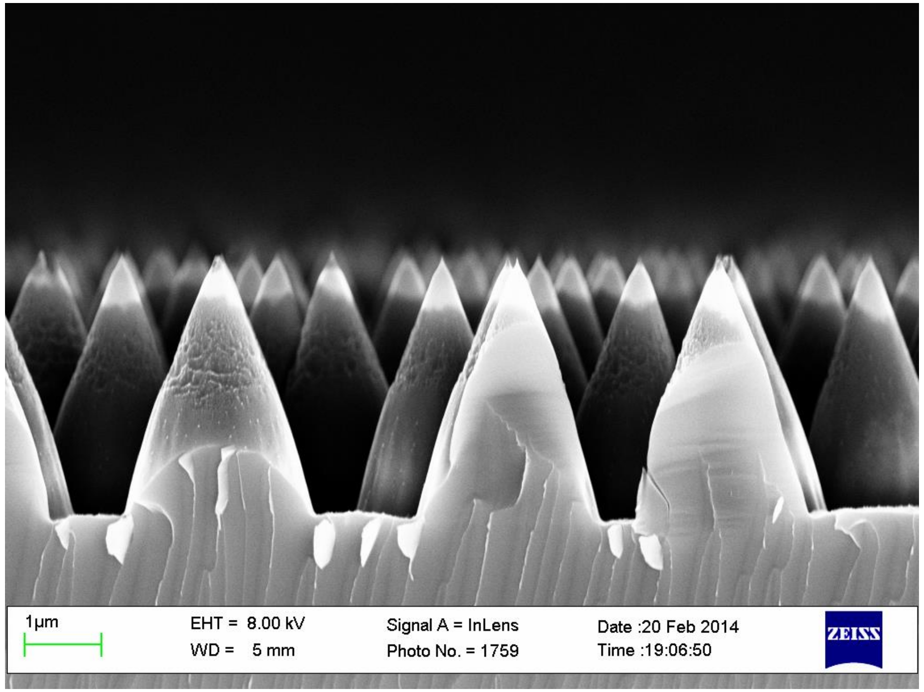
Lateral adhesion force **1-5 nN** for µL sized droplets

(Backholm et al. 2020, ttps://doi.org/10.1038/s43246-020-00065-3)

Vertical pull off forces ≈ **200 nN** for µl sized droplets

(Liimatainen et al, 2017, DOI: 10.1038/s41467-017-01510-7)

<1µm scale and pyramidal shape



# Superhydrophobicity characterization

Lateral adhesion:

$$F_{lateral} = \frac{24}{\pi^3}\gamma_{lv}D[\cos(\theta_{rec}) - \cos(\theta_{adv})]$$

Vertical adhesion:

$$W_{adhesion} = \gamma_{lv}(1 + \cos(\theta_{rec}))$$

The most important parameter to minimize both types of adhesion: $\theta_{rec}$

$\theta_{adv}$ appears on lateral adhesion but the dependency is quite weak.

Therefore: *SHB surfaces have low adhesion to water, which is characterized primarily by high receding contact angles and low sliding angles.*

High receding angle alone is (almost) enough to define superhydrophobicity.

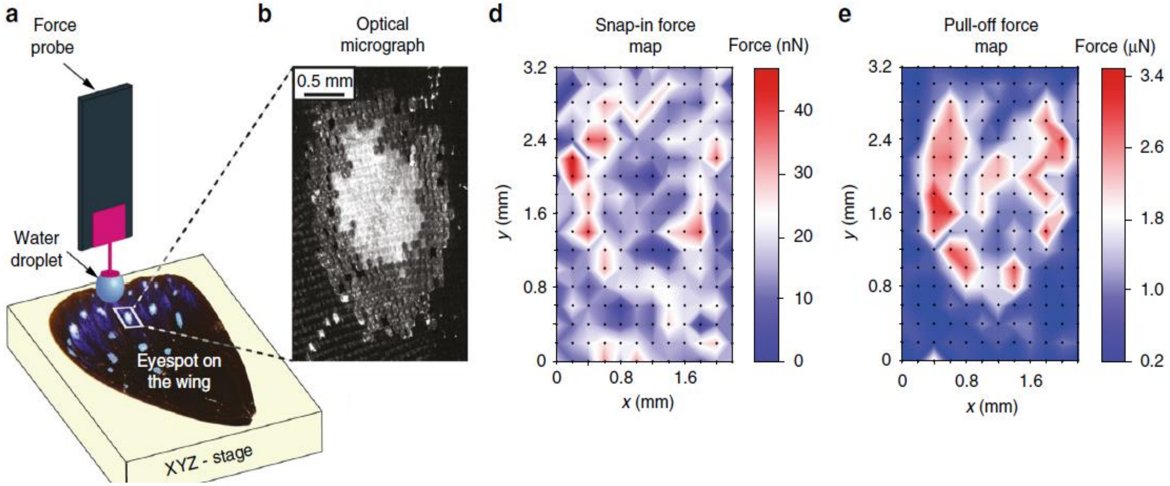
**In practice, to demonstrate SHB, one or both:**

1. Advancing and receding contact angles (by e.g. goniometry)
2. Sliding angle for a known droplet size

# Quiz time!

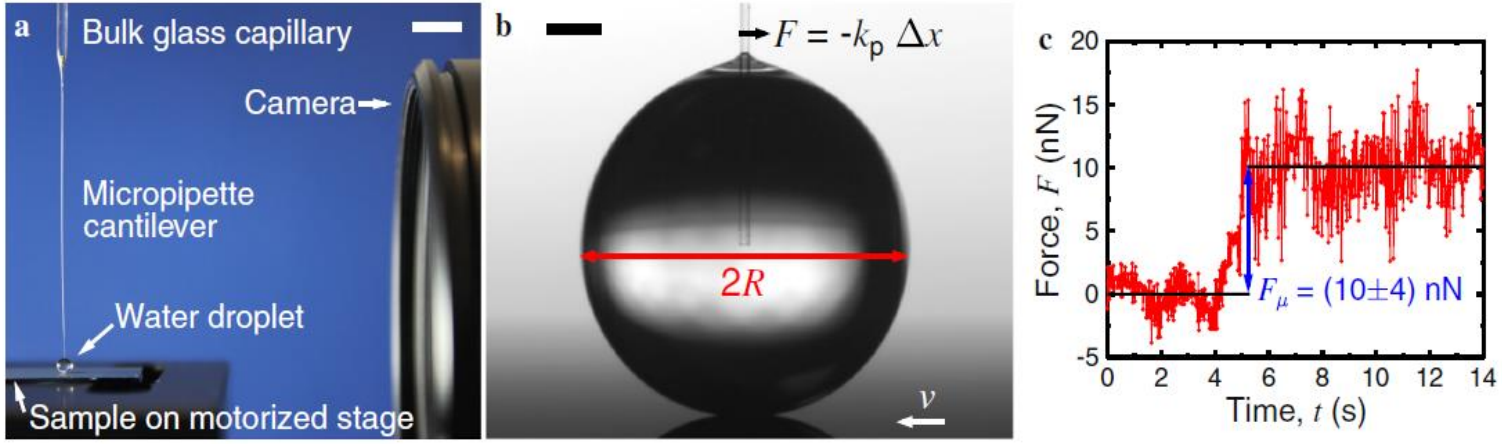
# More advanced SHB characterization

Vertical pull off forces by scanning droplet adhesion force microscope:



(Liimatainen et al, 2017, DOI: 10.1038/s41467-017-01510-7)

Lateral adhesion forces by micropipette cantilevers:



(Backholm et al. 2020, ttps://doi.org/10.1038/s43246-020-00065-3)

# OLEOPHOBICITY

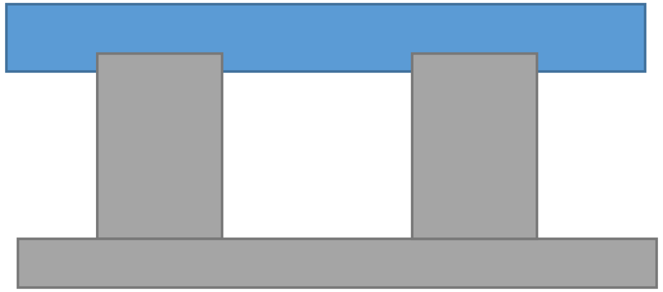
The maximum WCA that exists for water is ≈120°.

The lower the surface tension, the lower the contact angles, and for many oils the maximum CA of any material can be <90°

Since the stability of the Cassie state required >90°, these cannot be repelled?

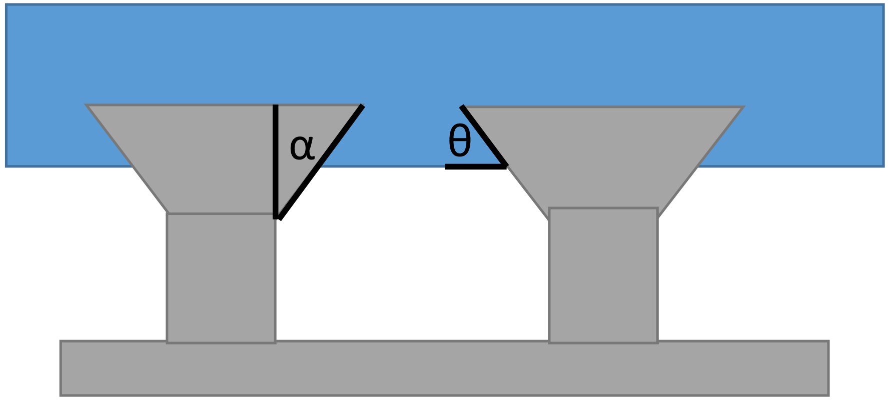
**There is a trick!** Re-entrant (overhanging) geometries enable stable Cassie states.

Liquid penetrating downwards would need to create new liquid-air interface.



Old condition: $\theta>90^\circ$ ($\alpha=0^\circ$)

=≈



New condition: $\alpha+\theta>90^\circ$, If $\alpha=45^\circ$, then $\theta>45^\circ$

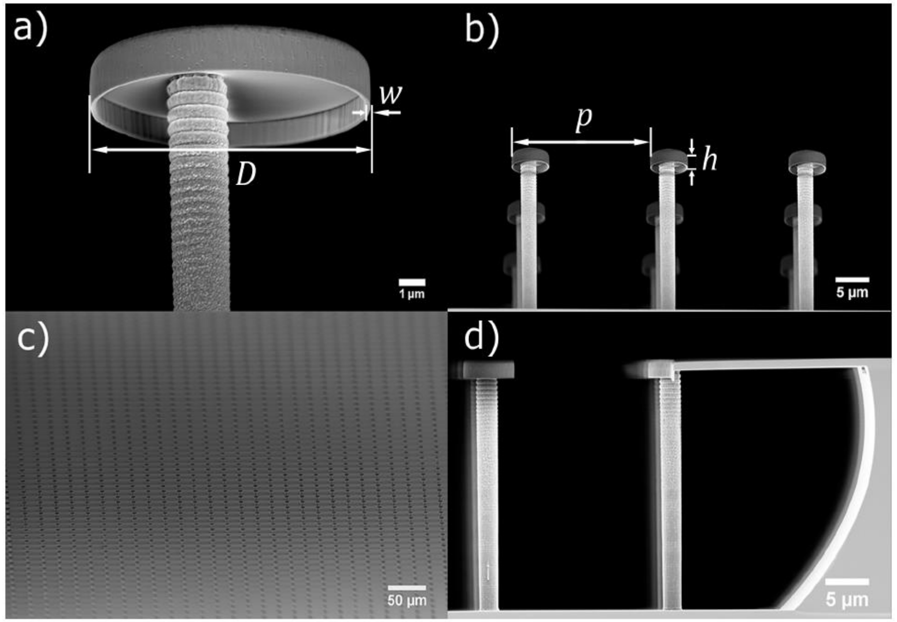
# Liquid repellency

**For water:** hydrophilic/hydrophobic, superhydrophilic/superhydrophobic
**For oils:** oleophilic/oleophobic
**For a liquid in general:** hygrophilic/hygrophobic,
**For all liquids simultaneously:** omniphilic/omniphobic

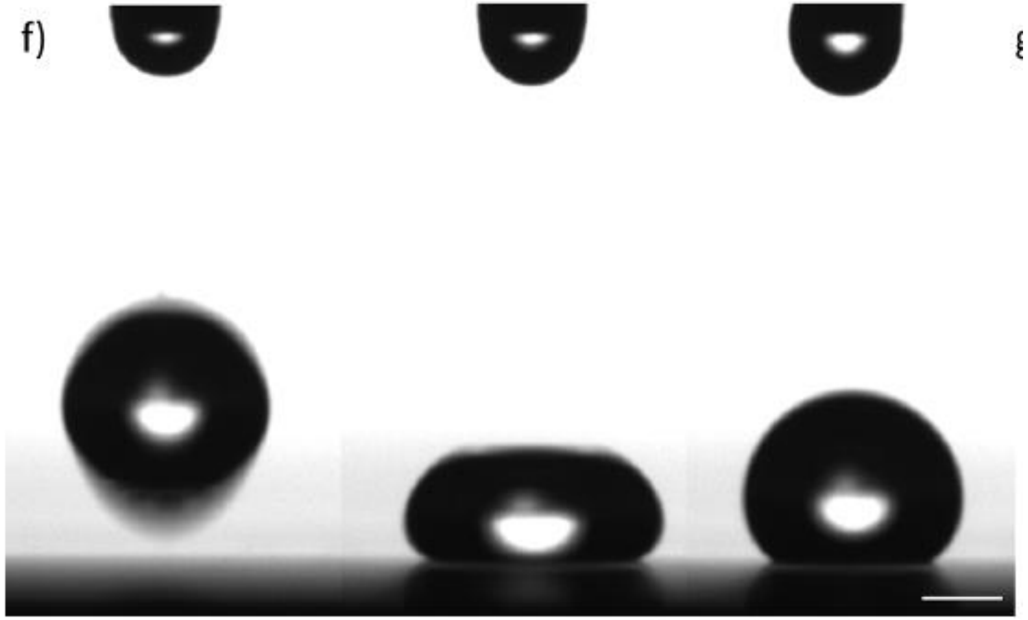
# Omniphobic surface

Doubly re-entrant silicon dioxide pillars.
Able to repel even perfluorohexane, $\gamma_{lv} \approx 12$ mN/m, among the lowest of all liquids.

Doubly re-entrant surfaces with no surface tension limitations can be called omniphobic.



Omniphobic micropillars



1.6 µl perfluorohexane droplet dropped on the surface

Rontu, Jokinen, Franssila 2020, https://ieeexplore.ieee.org/abstract/document/8896921

# Applications of superhydrophobicity

SHB surfaces can be used in applications where, for example:

1. Things need to be kept dry. E.g. windows of sensors outdoors.
2. Things need to be kept clean (self cleaning)
3. When friction between liquid and solid needs to be reduced (e.g. high-tech swimming gear, ships, tubes/pipes)

There are also related applications in anti-icing and repelling biological fluids but these need something extra on top of superhydrophobiity.

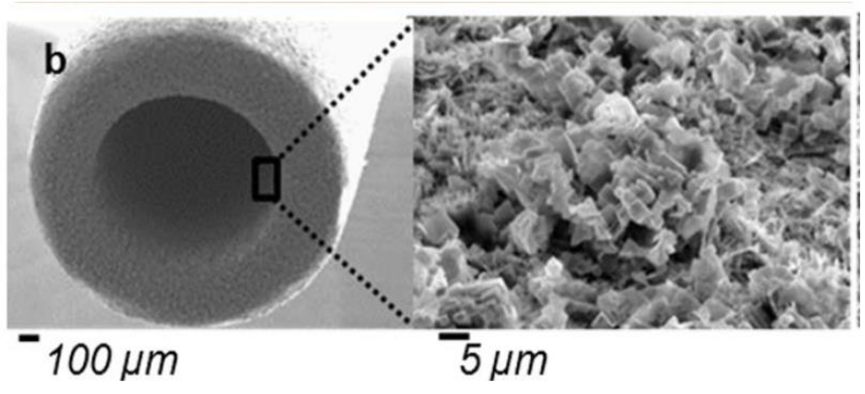
# Pipe/tube friction reduction

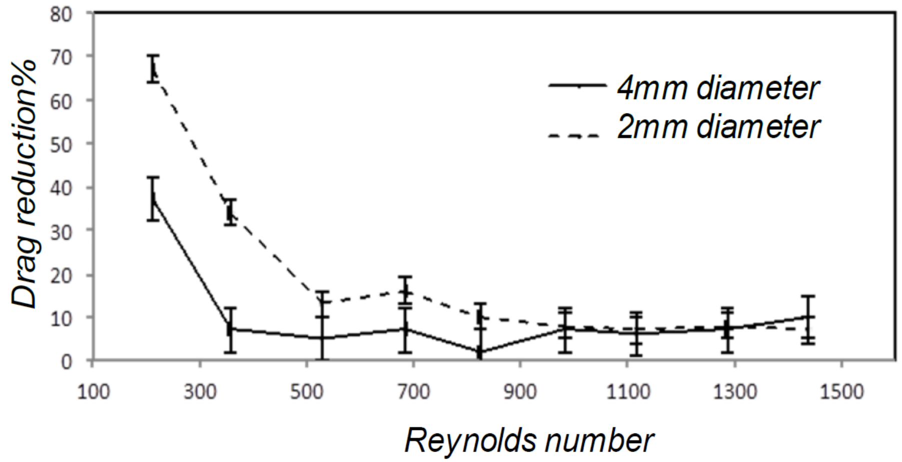
Liquid flowing in a normal tube: velocity at the walls is 0.

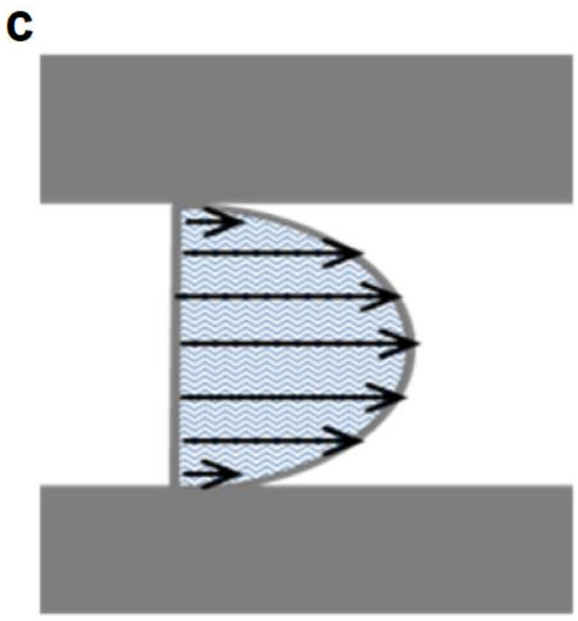
Liquid flowing in a SHB tube: velocity at the walls is >0.

Velocity gradients cause viscous energy losses, so SHB pipes/tubes save in energy costs.

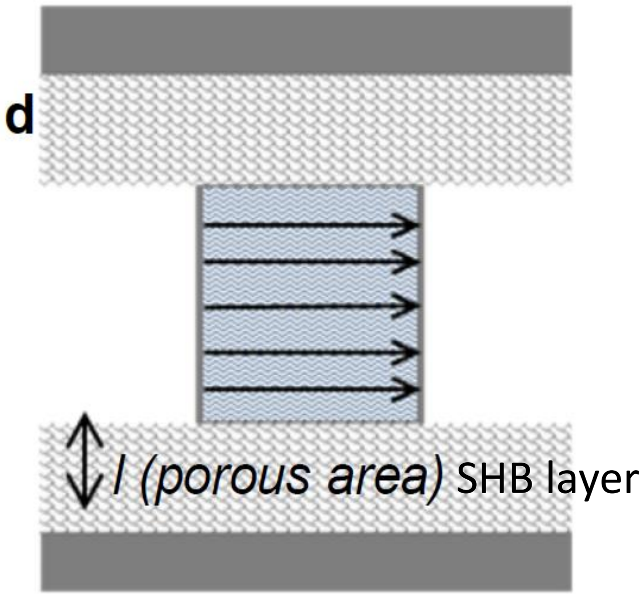
Hoshian et al. 2017
https://www.nature.com/articles/s41598-017-16369-3







Water flow profile in normal tube



Water flow profile in SHB tube (effect is exaggerated)

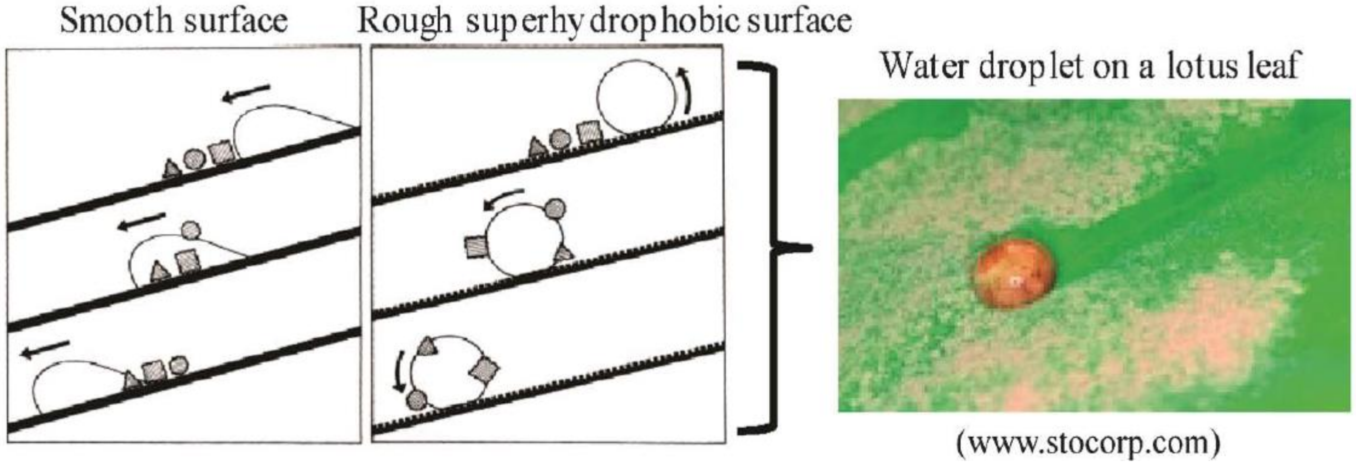
# Self cleaning

Superhydrophobic surfaces tend to stay clean since water droplets do not deposit on them.

They are also *self cleaning*, meaning that if there is some dirt on the SHB surface it easily comes off when droplets roll-off the surface.

Droplet sliding on a non-SHB surface do not clean the surface because:

1. Velocity near the surface is low
2. There is no vertical component to the velocity field



RSC Advances, 2013, 3, 671

# Next:

There is no homework for this week!

Next week, 12:15-13:00 we will have the lab project kick-off session.

The lab work will be about SHB surfaces

The labs themselves are on weeks 43-45 (19.10-6.11)

# Bonus slide: Young's equation, adhesion and number of independent parameters:

Nice to know slide, not covered in class.

$$Adhesion = \gamma_{lv} + \gamma_{sv} - \gamma_{sl}$$

$$\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl}$$

On first sight, these two equations contain 4 parameters each.

However, since the solid surface is unable to deform, $\gamma_{sv} + \gamma_{sl}$ = constant. In wetting phenomena, we are only interested in changes, which is why the 2 solid surface energy terms only ever appear in the term ($\gamma_{sv}$ - $\gamma_{sl}$) and not independently. So in reality, both wetting related equations have only 3 independent terms.

This is good news since both $\gamma_{lv}$ and cos(θ) are easily measurable, and measuring 2/3 of independent parameters is enough to know everything about the system.

Inserting Young's equation into the work of adhesion equation we get:

$$Adhesion = \gamma_{lv} + \gamma_{lv} * \cos(\theta) = \gamma_{lv}(1 + \cos(\theta))$$

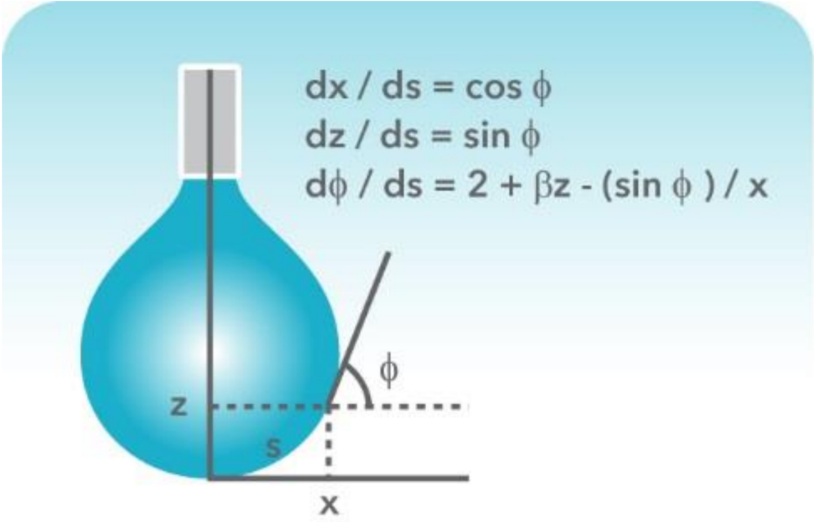
This is called the Young-Dupré equation, and it relates the work of adhesion to the surface tension and contact angle.

You can test what happens to adhesion when θ=0, 90 or 180 degrees.
Compare the results to the equation for the work of cohesion (Cohesion = $2*\gamma_{lv}$)

# Liquid surface tension measurement:

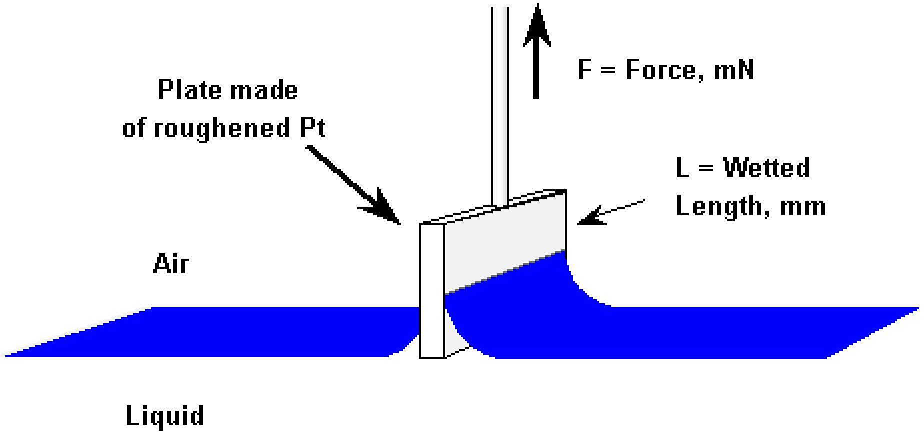
Nice to know slide,
not covered in class

**Optical tensiometry**:
- Surface tension measured from the shape of a hanging droplet
- Shape determined by the balance of gravity (hydrostatic pressure) and surface tension (laplace pressure).



**Force tensiometry:**
The force a liquid exerts on a plate is measured
- $F = 2 L \gamma$
- No correction factor needed
- Good method also in practice

Surface Tension Measurement - Wilhelmy Plate Method



# Solid surface energy measurement

Nice to know slide,
not covered in class

Surface energies of solids typically cannot be measured directly.
Fundamental reason is that bulk bonds in solids are too strong compared to surface forces.

Instead, contact angle measurements are made with multiple liquids and there are several theories how to derive the solid surface energy from these.

- Critical surface tension (Zisman method)
- Good and Girifalco
- Owens-Wendt
- Van Oss et al.

As far as I know, solid-liquid interfacial energies also cannot be directly measured and are instead derived from contact angle measurements and the above theories.