Ville Jokinen, 12.1.2021

Background material on contact angles and wetting for CHEM-E8135 Lecture 2.

On this course the focus, relating to wettability will be on capillary filling microchannels. But everyone should have a basic background understanding of contact angle as a parameter, it will not be extensively covered on Lecture 2.

If you have not encountered contact angle on your previous studies or want to refresh your understanding, you can study this material.

(Material is adapted from CHEM-E5150 Surfaces and Films Lecture on Wetting and Superhydrophobicity)

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:

$$\gamma = \delta W / \delta A \quad [\, J / m^2]$$
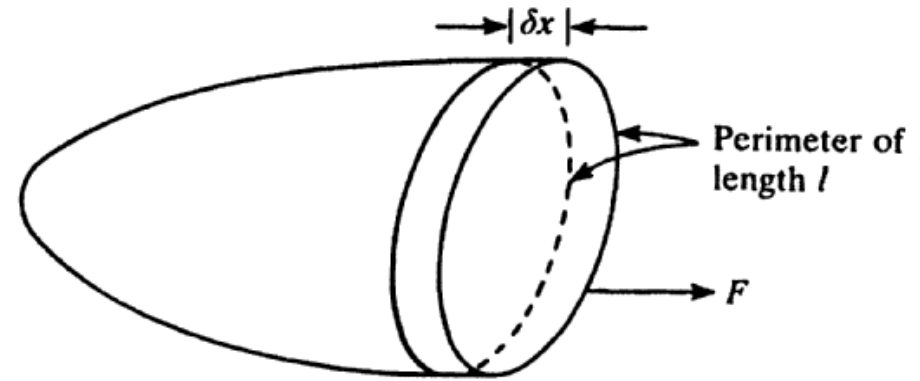
Surface energy is also known as surface tension:

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

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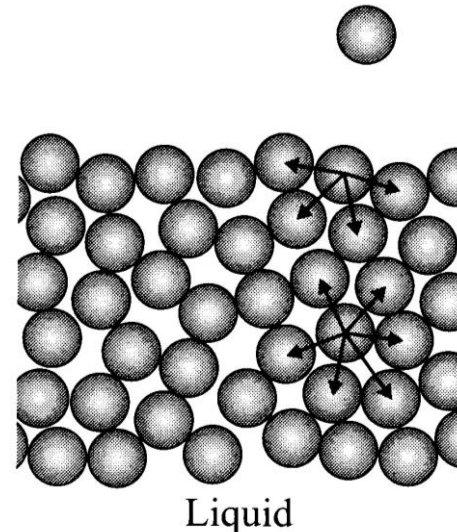solid-solid, solid-liquid, liquid-liquid, solid-gas, liquid-gas

Interfaces   *Surfaces*

Hunter: Introduction to Modern Colloid Science, p.134

Vapor

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

Liquid

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

UNITS: mN/m = mJ/m²

Liquid	σ (10⁻³ N/m)	Liquid	σ (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

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°C, 59 mN/m at 100°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.**

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
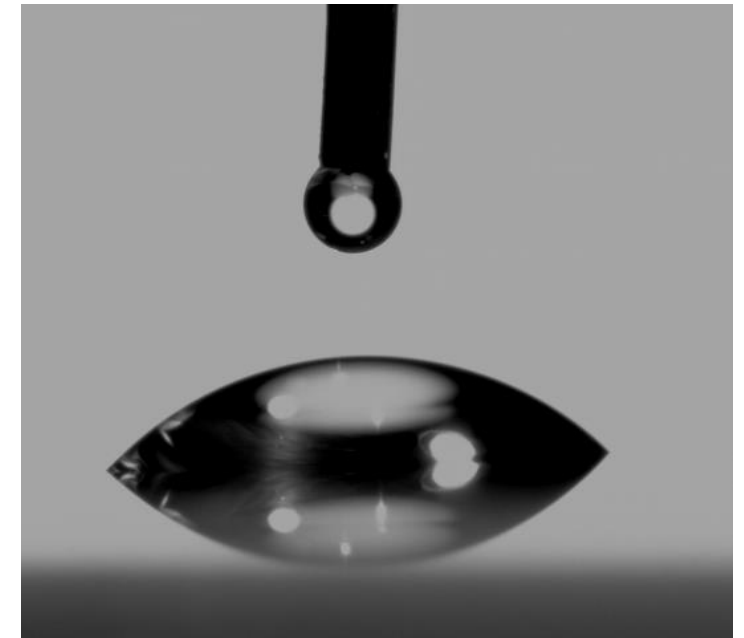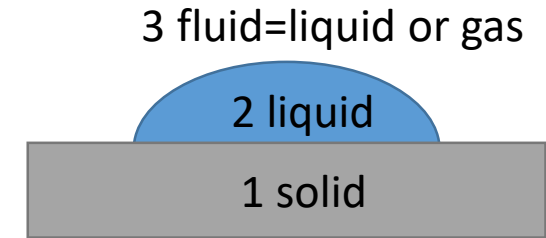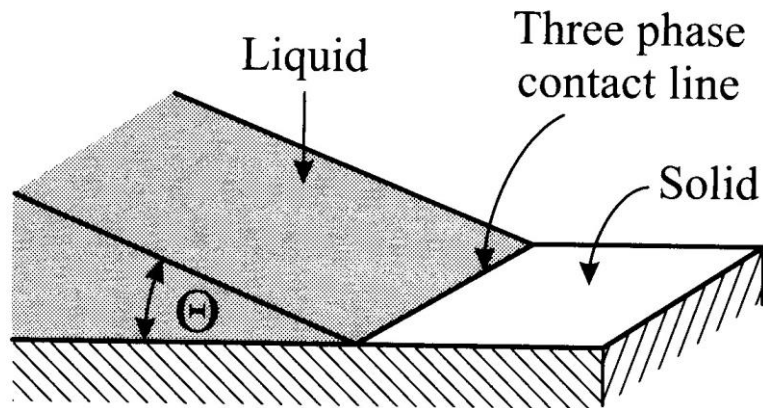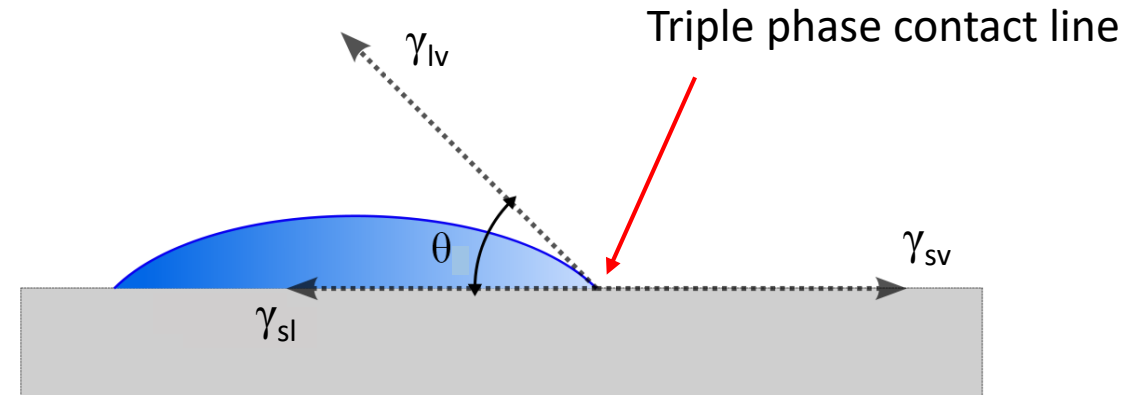
3 fluid=liquid or gas

2 liquid

1 solid

Image: wikipedia

Contact angle, theoretical

Young's equation:

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

Triple phase contact line

θ Thermodynamic, or Young's, **contact angle**

γ_{lv} Liquid-vapor surface energy ("liquid surface tension")   (sometimes just γ_l)

γ_{sv} Solid-vapor surface energy ("solid surface energy")   (sometimes just γ_s)

γ_{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, γ_{lv}, γ_{sv} and γ_{sl} so that the triple phase contact line does not move horizontally?
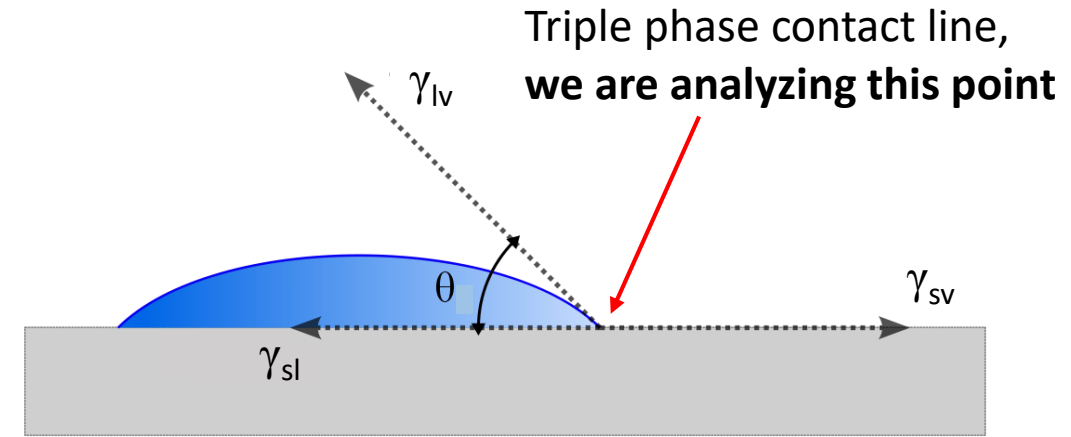
Force pulling 3-phase contact line left: γ_{sv}

Forces pulling 3-phase contact line right: γ_{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.

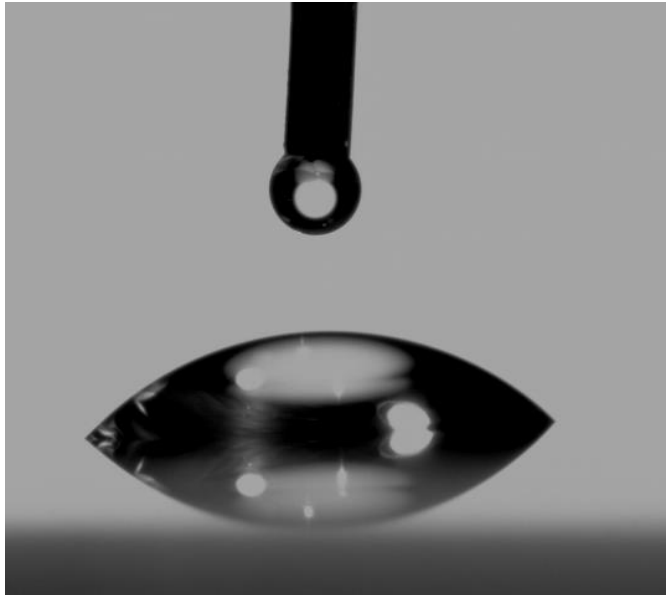(The 3-phase contact line is not free to move in the vertical direction)

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

γ_{lv}

γ_{sv}

θ

γ_{sl}

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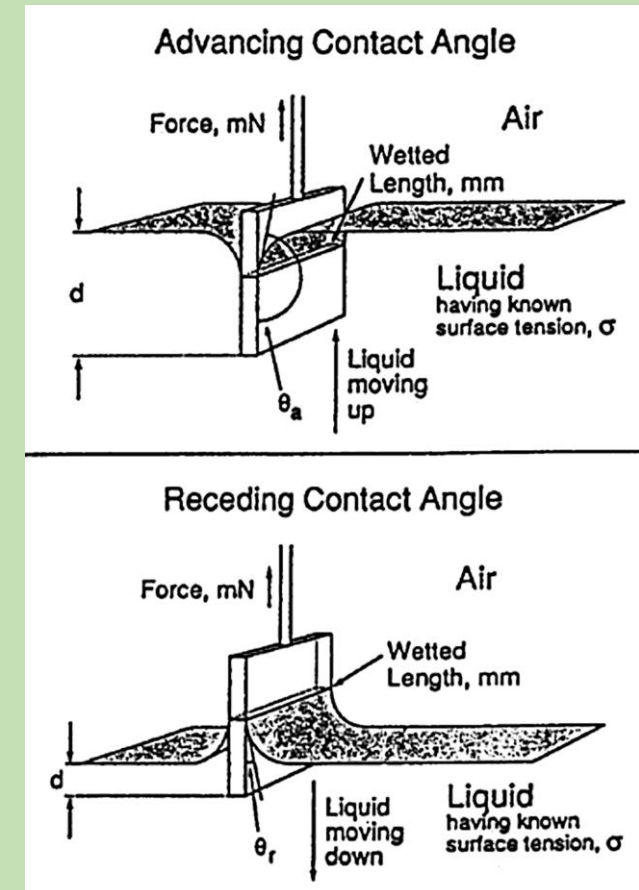
Contact angle measurement

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).

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 θ_{adv} ,**
and a lower bound, called the **receding contact angle θ_{rec}**

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

θ_{rec} = Receding contact angle
θ_{eq} = Equilibrium/static contact angle
θ_{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.

Contact angle hysteresis 2

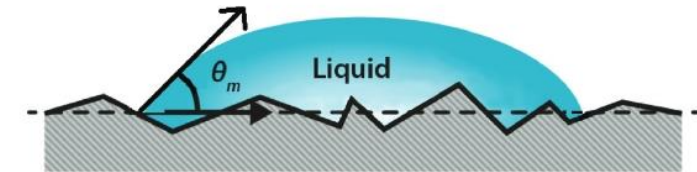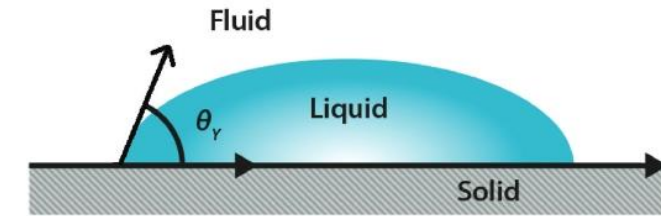**Reasons for contact angle hysteresis:**
1. Surface roughness
2. Chemical inhomogeneities

(less fundamental reasons: adsorption or desorption on the surface, or reactions between the liquid and the solid.)
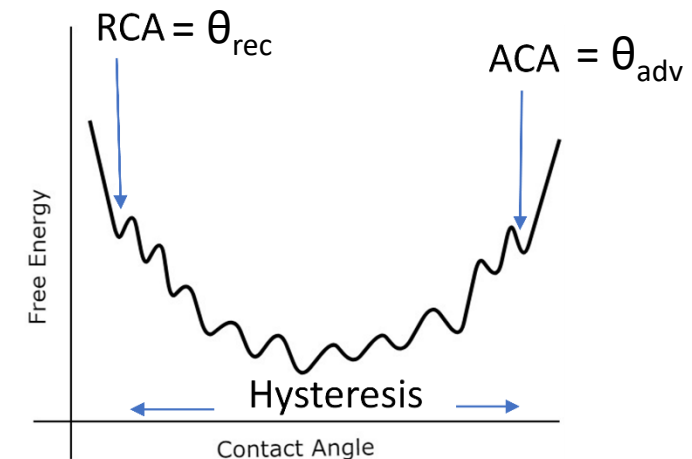
Microscopically at the triple phase contact line, these two surfaces have the same contact angle. But measured macroscopically, they do not.

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

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

θ_{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. θ_{adv}
2. $(\theta_{adv} + \theta_{rec}) / 2$
3. $acos((\cos\theta_{adv} + \cos\theta_{rec})/2)$
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, θ_{adv} and θ_{rec}
2. For calculations, if we are calculating an advancing case, θ_{adv} is used, and if we are calculating a receding case, θ_{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.

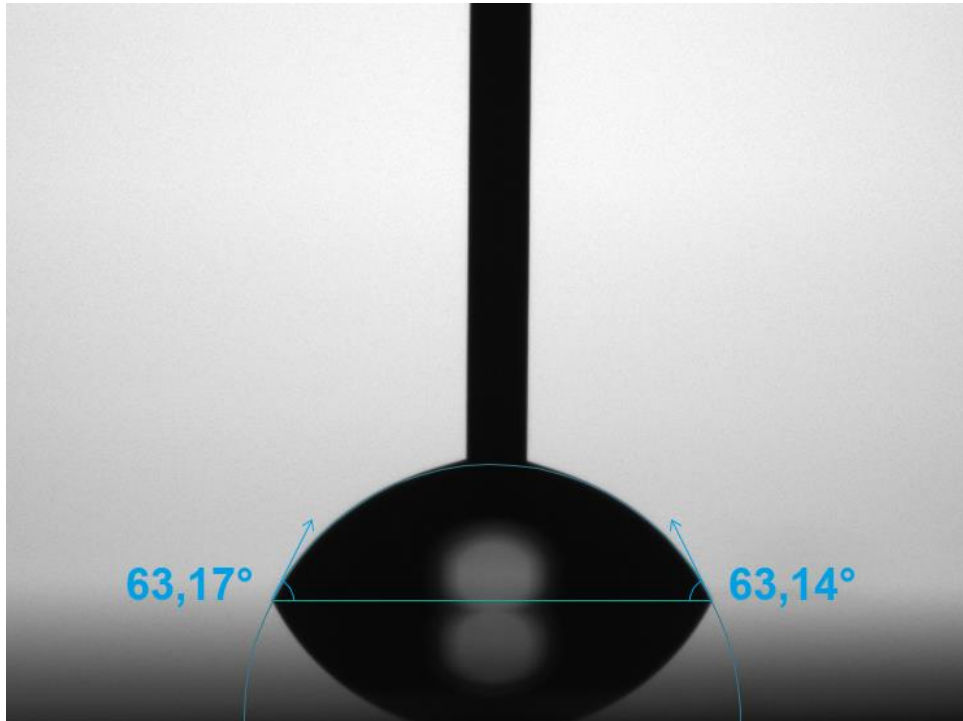Liquid: Deionized water = very clean water

Fluid: air

Measurement technique: "needle-in" sessile droplet goniometry.
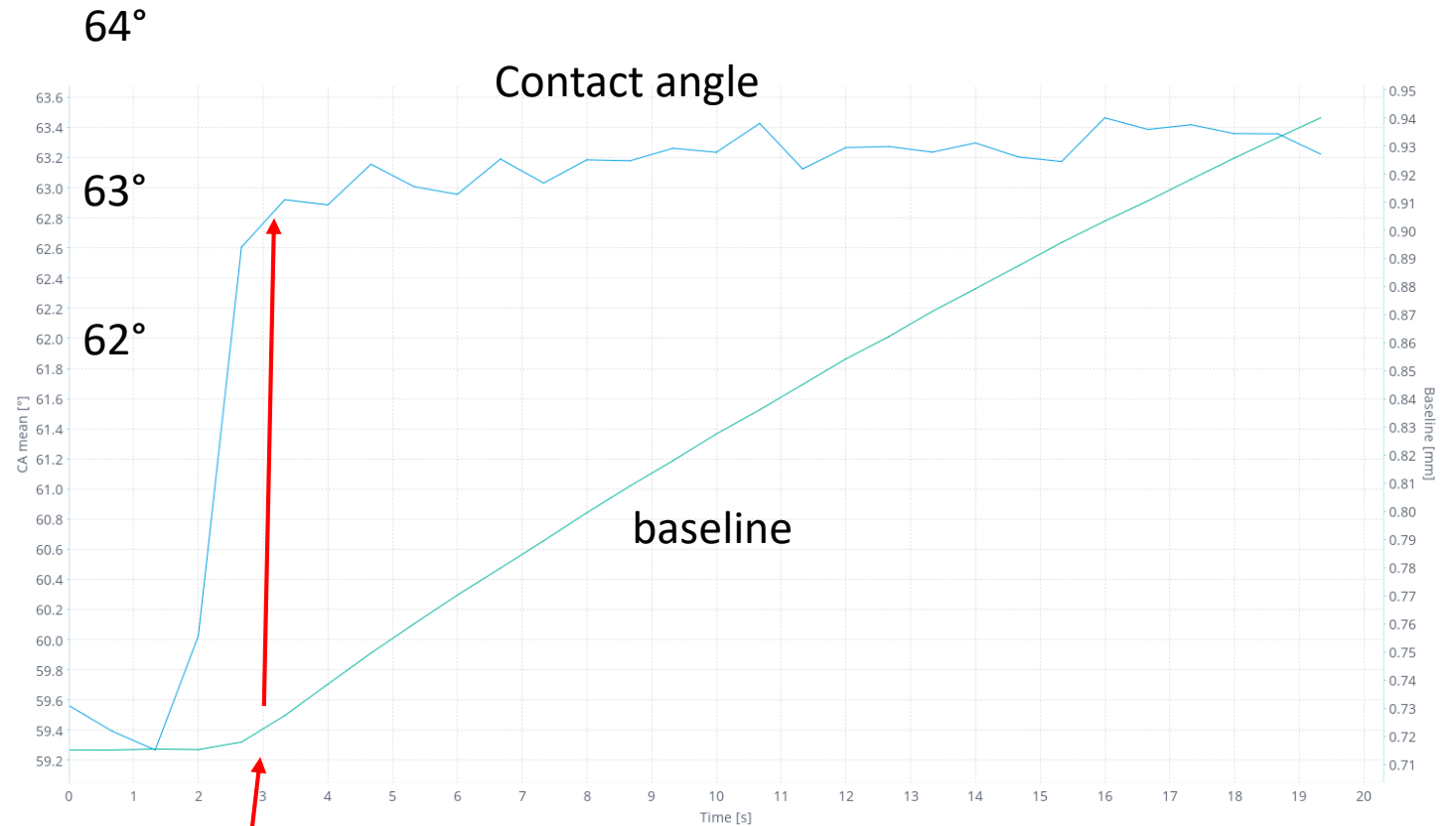
Starting droplet size 1.5 µl

Droplet size increased and decreased with rate 0.1 µl/s

Advancing contact angle

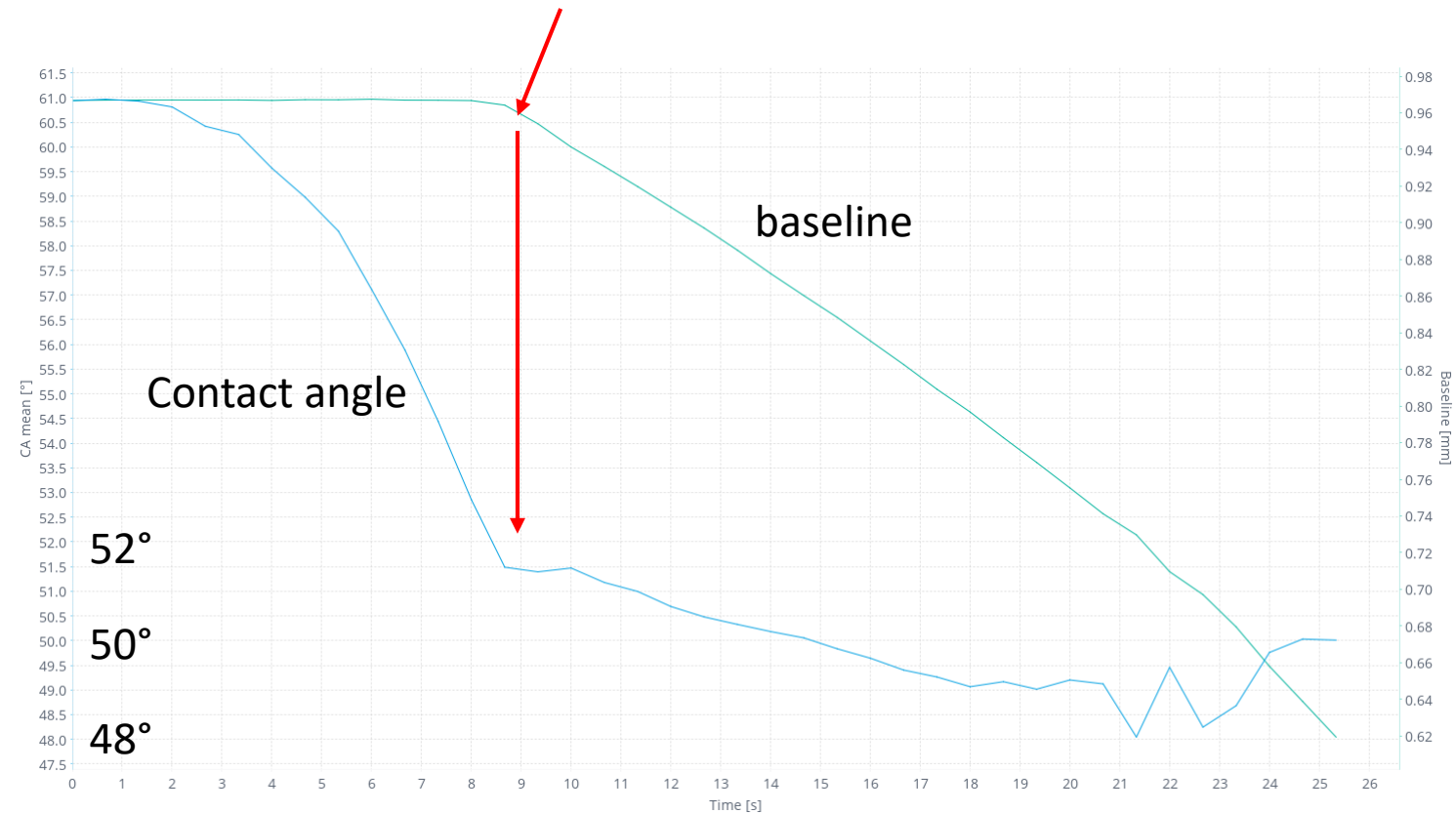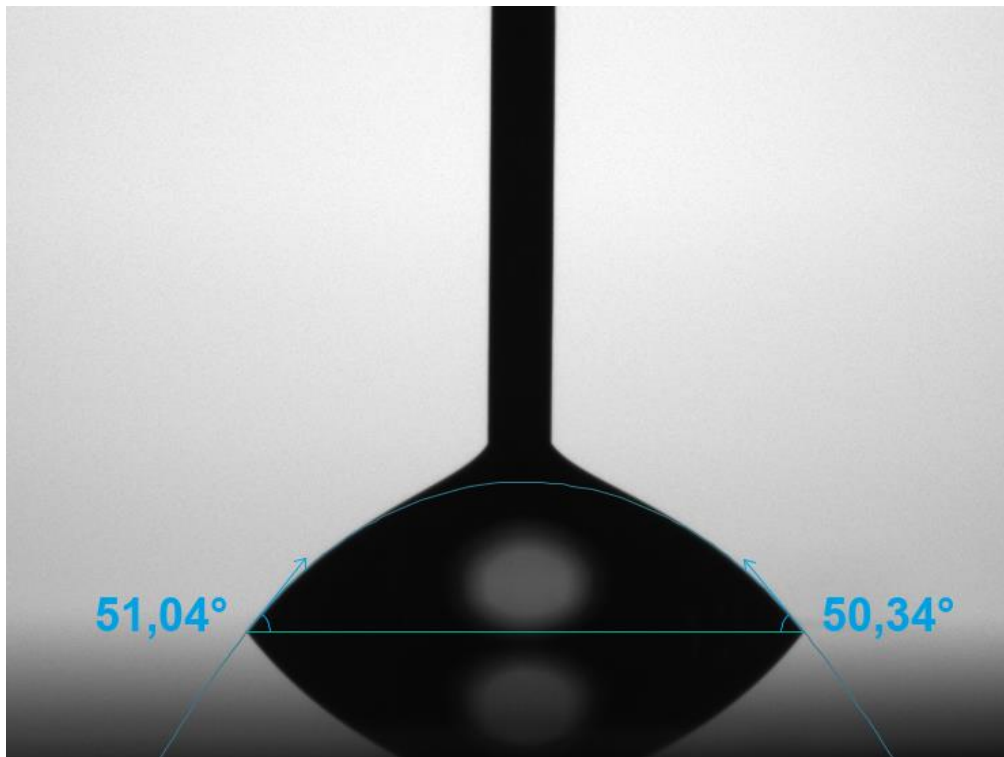Baseline is the width of the droplet, when baseline changes, the droplet is advancing or receding

Baseline and contact angle vs time

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

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: 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.
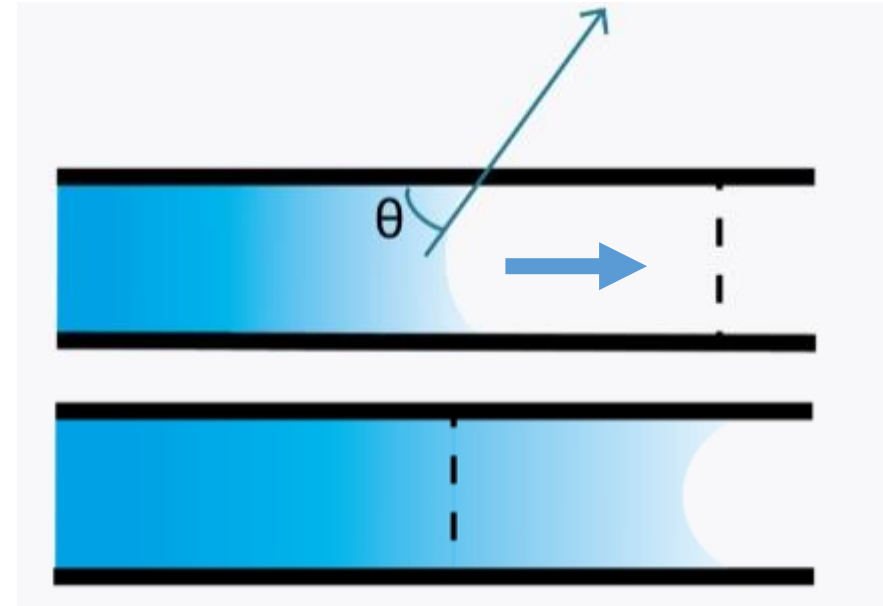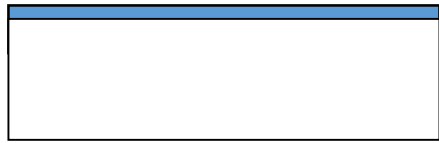
Lateral flow home diagnostic test

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°
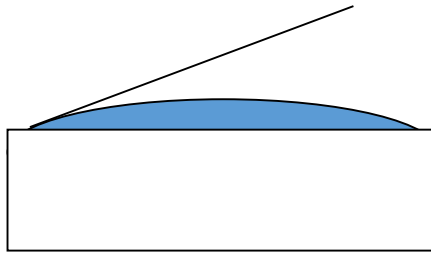Completely wetting

WCA = 20°
Wetting/hydrophilic

WCA = 70°
Wetting/hydrophilic

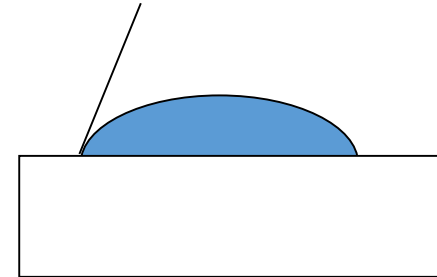Clean metals, strongly polar surfaces, strongly charged surfaces.

Roughened hydrophilic surfaces.

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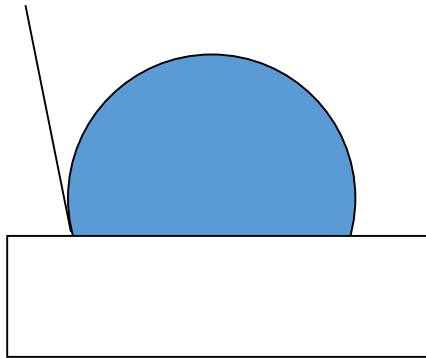
Case 2:
If WCA >90°, the material is said to be *nonwetting* (by water), or *hydrophobic*.

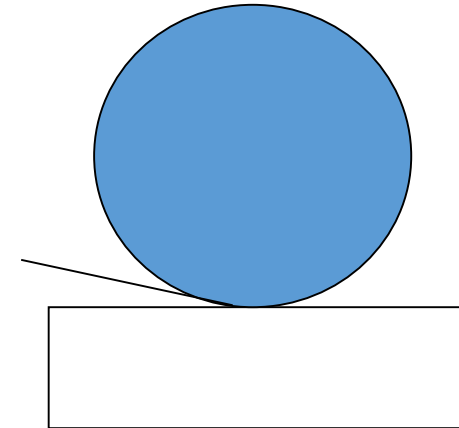The term *superhydrophobic* we define in 2nd half of lecture.

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).