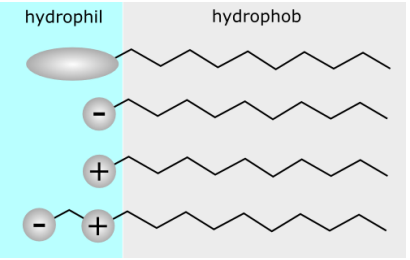
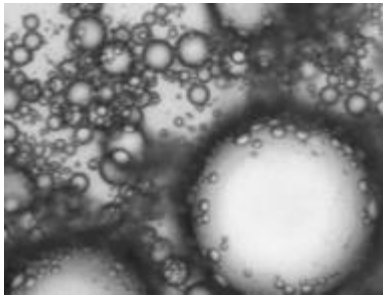
- Surface tension and wetting
- Introduction to surfactants
- Emulsions
- Foams





Surface tension phenomena in daily life

images: http://en.wikipedia.org

Surface tension phenomena in daily life

Refer to the pictures on slide #2 and discuss in groups

1. Sketch the shapes of water drops on:
   - a lotus leaf
   - water-repellent fabric
   - a windshield

2. What causes the difference between the drop shapes?

3. Why can an insect walk on the surface of a pond?

Surface tension phenomena on the International Space Station

Watch the video:
http://www.youtube.com/watch?v=lMtXfwk7PXg
and discuss in groups

1. Sketch the shape of a water drop on Earth and a water drop on the ISS.

2. What is the Bond number on the ISS?

3. Why does the washcloth absorb water even if you are in space?

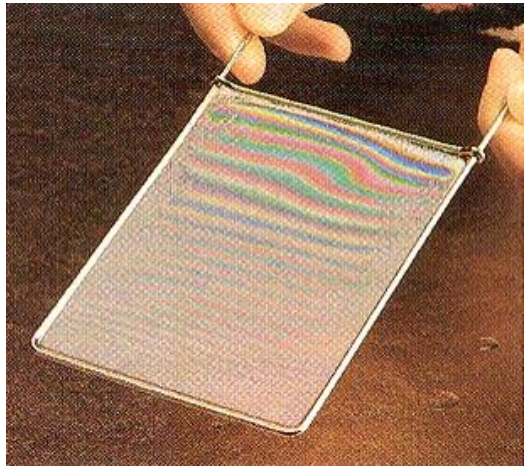
Surface tension and wetting

- thermodynamic definition of surface tension
- molecular origin of surface tension
- wetting of a liquid by a liquid
- intermolecular interactions and surface tension
- measuring surface tension
- wetting of a solid by a liquid
- contact angle and Young’s law
- measuring contact angle
- contact angle hysteresis
- superhydrophobic surfaces
- capillarity and porous media

Surface tension causes fluid interfaces to contract

OBSERVATION:

- wire loop with a movable slide
- form a liquid film
- slide retracts so as to decrease surface area of film



- need to do work dW to increase area of film by dA
- $dW = \gamma\, dA$
- γ surface tension

- reversible work => change in Gibbs free energy $(dG)_{T,P} = \gamma\, dA$
- surface tension: increase in Gibbs free energy per unit increment of surface area

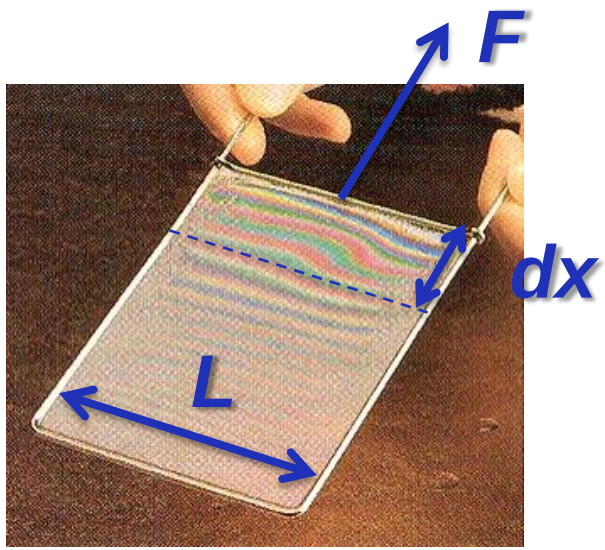
$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

Stokes & Evans, *Fundamentals of Interfacial Engineering* (Wiley-VCH 1997)

Surface tension is the key concept in characterizing fluid interfaces

Units of surface tension: energy per unit area (Joule/m^2)

or: force per unit length (N/m)



- need to do work *dW* to increase area of film by *dA = 2Ldx*
- force applied: *F*
- displacement: *dx*
- $dW = Fdx = \gamma\, dA = \gamma\, 2Ldx$
- $\gamma = F/(2L)$

Stokes & Evans, *Fundamentals of Interfacial Engineering* (Wiley-VCH 1997)

Surface tension of common liquids

Liquid			γ (mN/m) at 20°C
n-Perfluoro-Pentane			10.3
n-Pentane			16.1
n-Octane			21.8
n-Hexadecane			27.5
Glycol			48
Glycerol			63
Water			73

Israelachvili, *Intermolecular and Surface Forces 3rd Ed* (Academic Press 2011)

Origin of surface tension: intermolecular interactions

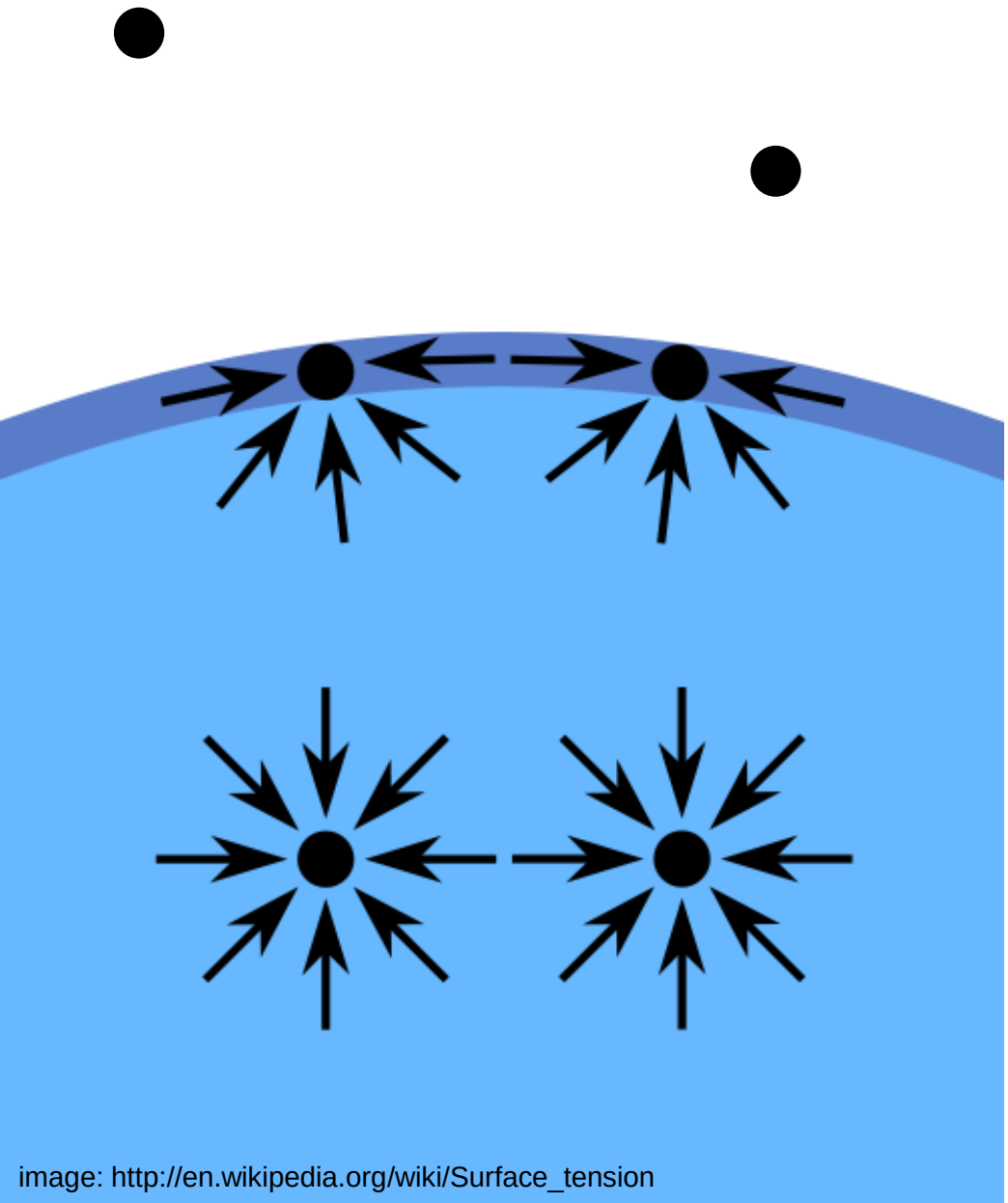


image: http://en.wikipedia.org/wiki/Surface_tension

Vapour

Liquid/Vapour Interface

cohesive forces towards the liquid bulk are not balanced

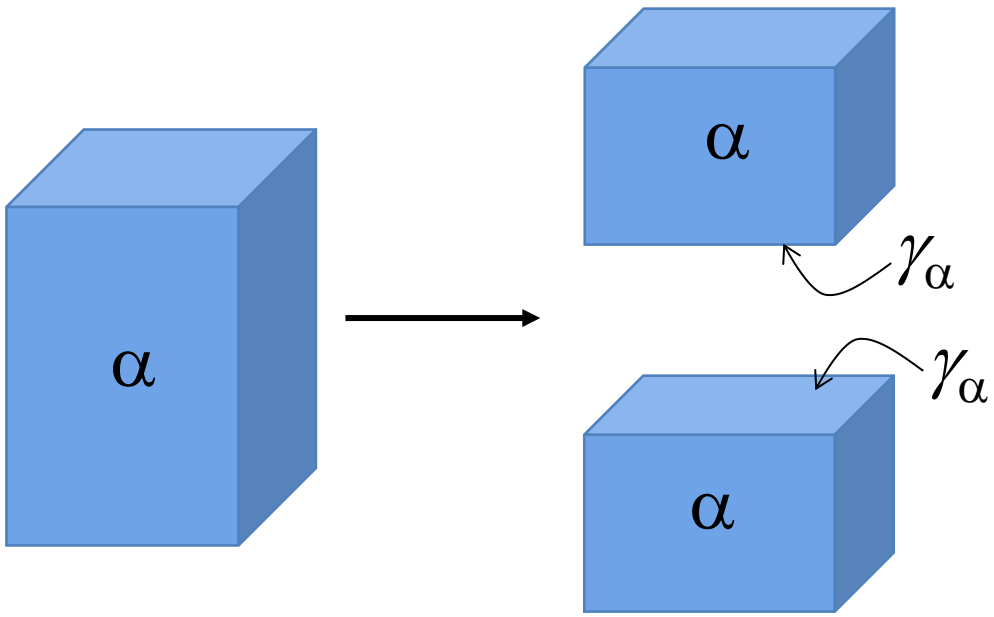
the molecules are attracted inwards

Bulk liquid

cohesive forces are balanced in all directions

the molecules do not experience any net force

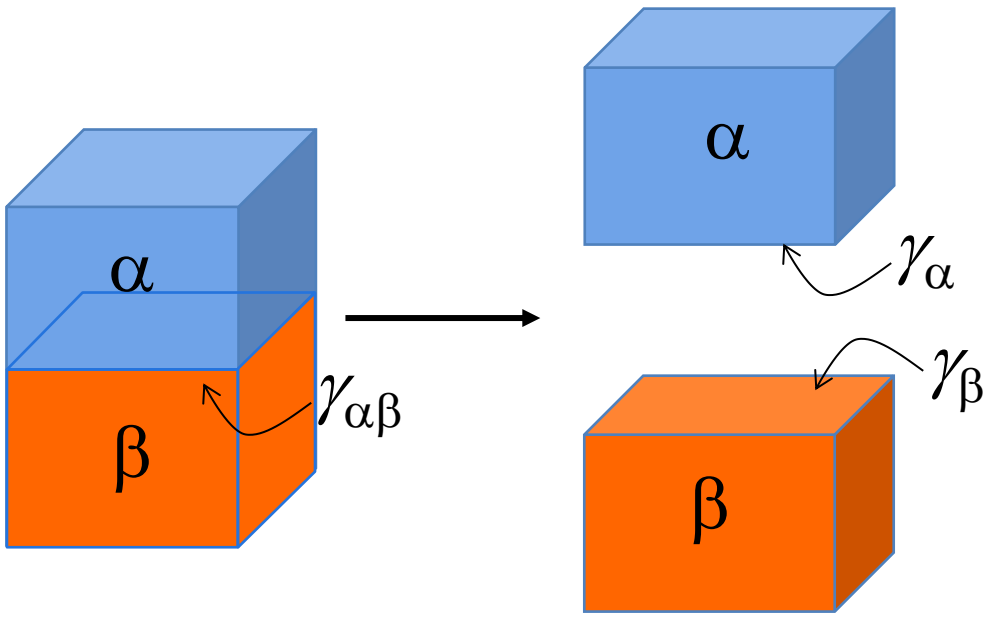
Relation between surface tension and work of **cohesion**



- Liquid phase (α)
- Work of **cohesion**: work required to pull apart a volume of unit cross sectional area (A=1)
- two new surfaces of area A=1 are created
- Work done $W_{\text{cohesion}} = 2\gamma_\alpha$
- $\gamma_\alpha = W_{\text{cohesion}}/2$ is surface energy per unit area (or **surface tension**)

Stokes & Evans, *Fundamentals of Interfacial Engineering* (Wiley-VCH 1997)

Work of **adhesion** between different materials



- Phases α and β: liquid or solid
- Work of **adhesion**: work required to separate a unit area of interface between two phases (α and β) to form a new surface of each phase
- $W_{\text{adhesion }\alpha\beta} = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta}$
- $\gamma_{\alpha\beta}$ is interfacial energy per unit area (or **interfacial tension**)

Work of adhesion affects **spreading** of liquid upon another liquid

What determines whether a liquid spreads to cover the surface of another liquid or remains as an isolated droplet?

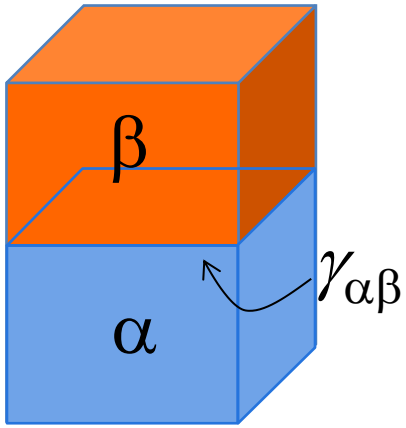
olive oil on water:
no spreading

- If oil spreads on water, area of oil-water interface increases; area of water-vapor interface decreases
- Change in free energy $dG \sim (\gamma_{ov} + \gamma_{ow} - \gamma_{wv})dA$
- Spreading is **spontaneous** if $dG < 0$, i.e. if $\gamma_{ov} + \gamma_{ow} - \gamma_{wv} < 0$
- **Spreading coefficient $S = \gamma_{wv} - (\gamma_{ov} + \gamma_{ow}) > 0$** spontaneous spreading
- $S = W_{\text{adhesion oil-water}} - W_{\text{cohesion oil}} > 0$ spontaneous spreading
- spontaneous spreading would mean that the oil adheres to the water more strongly than it coheres to itself

Stokes & Evans, *Fundamentals of Interfacial Engineering* (Wiley-VCH 1997)

Fluid β spreading over fluid α

Show that: $S = W_{\text{adhesion } \alpha\beta} - W_{\text{cohesion } \beta}$



spreading coefficient $S = \gamma_\alpha - (\gamma_\beta + \gamma_{\alpha\beta})$

$W_{\text{adhesion } \alpha\beta}$ =

$W_{\text{cohesion } \beta}$ =

S =

Origin of surface tension: intermolecular interactions

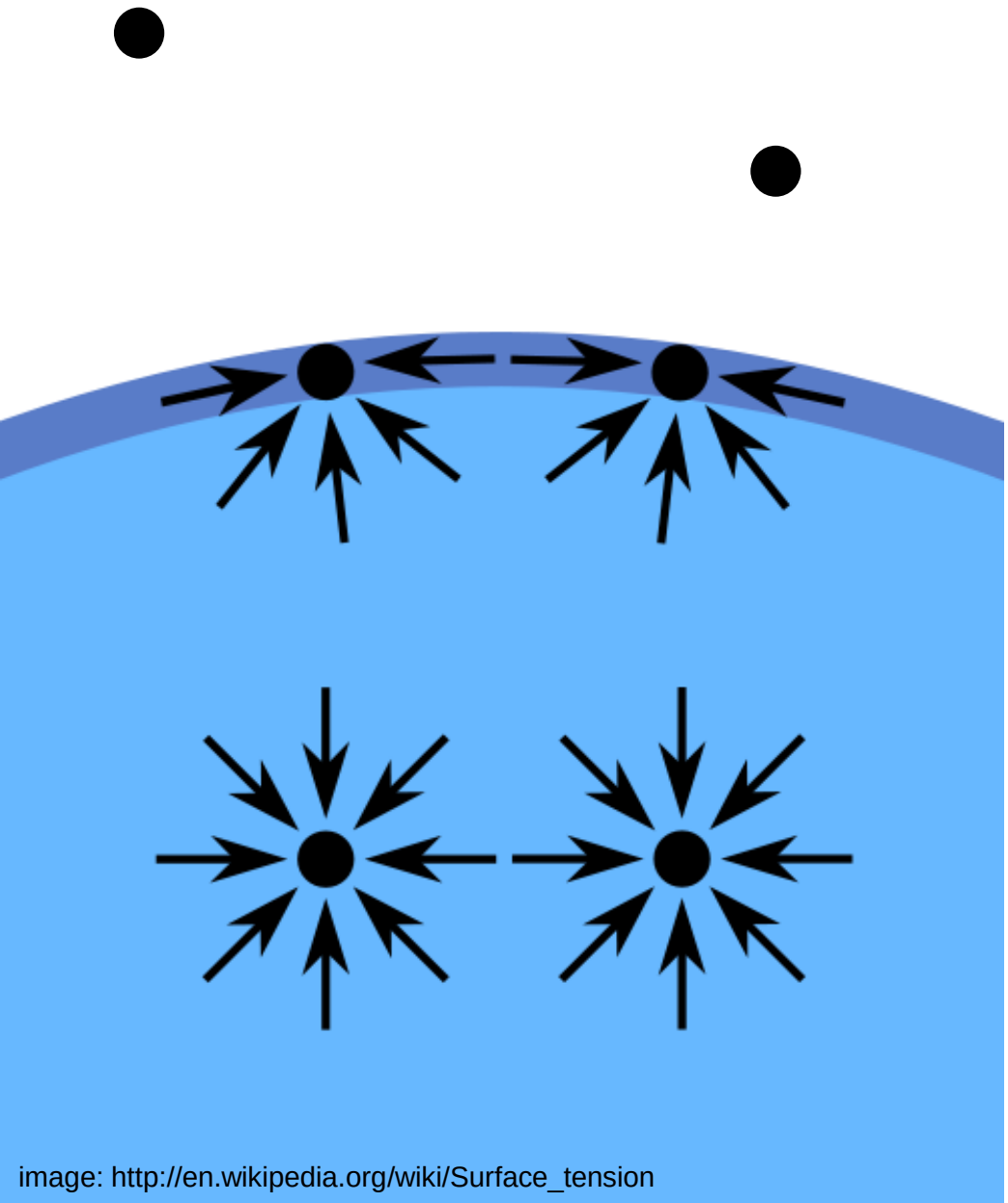


image: http://en.wikipedia.org/wiki/Surface_tension

Vapour

Liquid/Vapour Interface

cohesive forces towards the liquid bulk are not balanced

the molecules are attracted inwards

Bulk liquid

cohesive forces are balanced in all directions

the molecules do not experience any net force

Origin of surface tension: intermolecular interactions

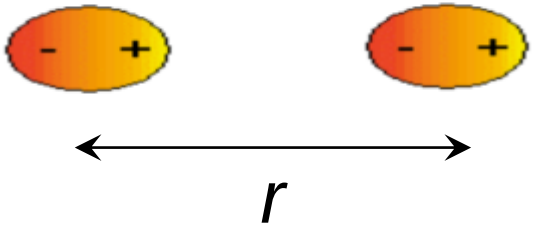
- **Cohesive** forces in a fluid:
  - van der Waals interactions:
    1. between polar molecules: permanent dipole-permanent dipole (Keesom or **orientation** interaction)
    2. between a polar and a non-polar molecule: permanent dipole-induced dipole (Debye or **induction** interaction)
    3. between ALL molecules: fluctuating dipole-induced dipole (London or **dispersion** interaction)
  - polar; metallic (e.g. mercury); hydrogen bonding; etc
- Each interaction contributes (approx. independently of each other) to total surface tension:

$$\gamma^{\text{total}} = \underbrace{\gamma^{\text{d}}}_{\text{dispersion interactions: always present}} + \underbrace{\cdots + \gamma^{\text{H}} + \cdots}_{\text{all other interactions specific to liquid under consideration}}$$

Dispersion forces: interaction energy

$$W(r) = -\frac{3}{4}\frac{\alpha^2 I}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

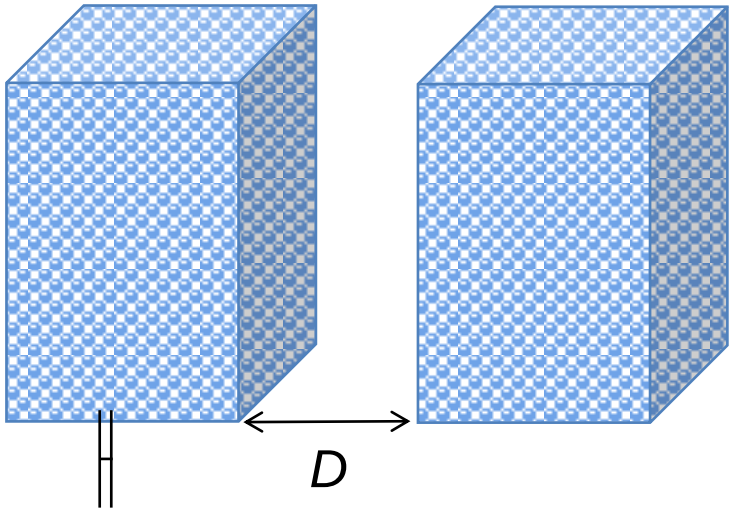
attractive interaction



- α is molecular polarisability
- I is ionisation potential
- ε_0 is permittivity of free space

See: lecture on van der Waals interactions

Dispersion forces: relationship between Hamaker constant and surface tension



- Summation over all the atoms of one medium with all the atoms of the other medium gives **interaction energy** between two planar surfaces:

$$W(D) = -A/12\,D^2$$

A: **Hamaker constant** (bulk property of material)

- If we also sum over all the atoms **in the same medium** we get:
  - From atoms in bulk: work of cohesion
  - From atoms near interface: **surface energy**
- Surface energy per unit area: $\gamma = A/24\pi D_0^2$ (energy needed to separate two flat surfaces from contact to infinity)
- It is found that D_0 ~ 0.165 nm gives predicted values of surface tension in good agreement with experiment

Israelachvili, *Intermolecular and Surface Forces 3rd Ed* (Academic Press 2011)

Surface tension of common liquids - Continued

Liquid	A (10^{-20} J)	$\gamma = A/24\pi D_0^2$	γ (mN/m) at 20°C
n-Perfluoro-Pentane	2.59	12.6	10.3
n-Pentane	3.75	18.3	16.1
n-Octane	4.5	21.9	21.8
n-Hexadecane	5.2	24.4	27.5
Glycol	5.6	**28**	48
Glycerol	6.7	**33**	63
Water	3.7	**18**	73
	Hamaker constant	simple theory (D_0 = 0.165 nm)	experiment

simple theory fails for polar substances because dispersion interactions are not the dominant interactions

Israelachvili, *Intermolecular and Surface Forces 3rd Ed* (Academic Press 2011)

Combining relations: interfacial tension

- What is the relationship between γ_{α}, γ_{β}, and $\gamma_{\alpha\beta}$?
- **Fowkes equation**, based on assumption that cross-interaction term across interface (work of adhesion) is due exclusively to dispersion forces:

$$\gamma_{\alpha\beta}^{\text{total}} = \gamma_{\alpha}^{\text{total}} + \gamma_{\beta}^{\text{total}} - 2\sqrt{\gamma_{\alpha}^{\text{d}}\gamma_{\beta}^{\text{d}}}$$

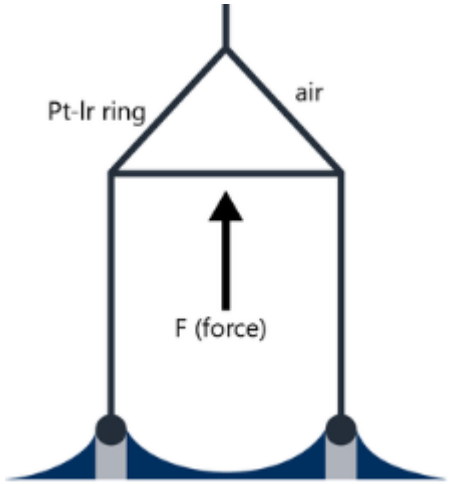
- Hydrocarbons only have dispersion interactions, hence: $\gamma_{\text{hc}}^{\text{d}} = \gamma_{\text{hc}}^{\text{total}}$
- Assuming that water interacts with hydrocarbons mainly via dispersion forces, we can apply Fowkes equation.
- **EXAMPLE: water-hexane interface**.
  - For water: $\gamma_{\text{water}}^{\text{d}} = 21.8$ mN/m and $\gamma_{\text{water}}^{\text{total}} = 72.8$ mN/m.
  - For hexane: $\gamma_{\text{hexane}}^{\text{total}} = 18.4$ mN/m.
  - $\gamma_{\text{water-hexane}}^{\text{total}} = \gamma_{\text{water}}^{\text{total}} + \gamma_{\text{hexane}}^{\text{total}} - 2\sqrt{\gamma_{\text{water}}^{\text{d}}\gamma_{\text{hexane}}^{\text{d}}} = 51.4$ mN/m
  - measured value: 51.1 mN/m.

Liquid Surface Tension Measurements

Du Noüy ring method

- Ring is pulled through liquid surface or liquid-liquid interface until rupture
- **Maximum force** exerted on the ring, F_{max}, is measured using a force sensor
- Ring is made of material (e.g. Pt-Ir) that is well wetted by liquid, so that $\cos\theta \approx 1$
- *L* is wetted length of the ring (inner + outer circumference)

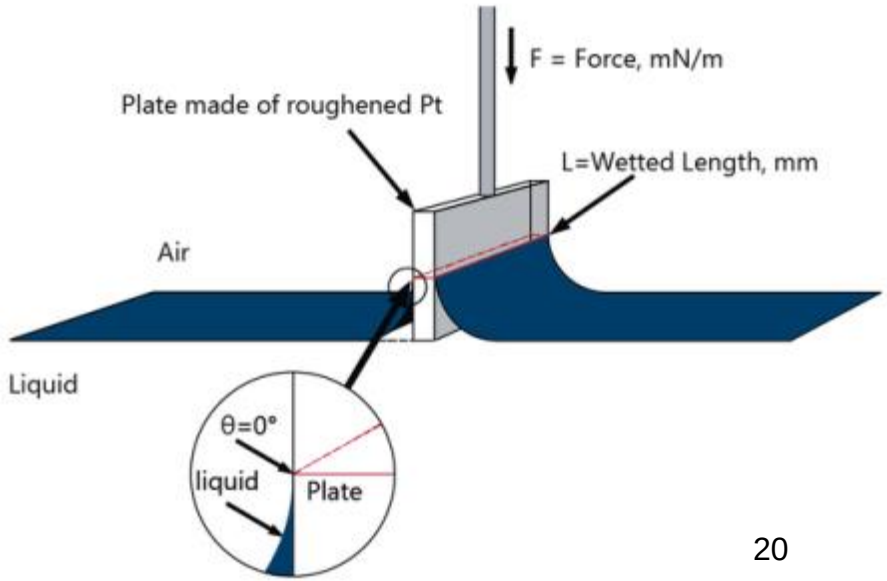
$$\gamma = \frac{F_{\max}}{L\cos\theta}$$



Wilhelmy plate method

- The force acting on a vertically immersed plate is measured using a force sensor
- Plate is made of material (e.g. Pt) with $\cos\theta \approx 1$
- *L* is wetted perimeter on the plate
- Method is suitable to measure interfacial tension as a function of time (interface is not ruptured)

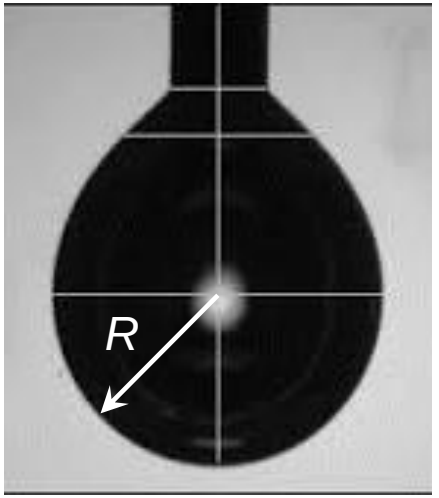
$$\gamma = \frac{F}{L\cos\theta}$$



images: www.kruss.de

Liquid Surface Tension Measurements

Pendant drop method



- A drop of the heavier fluid is formed into the lighter fluid (density difference $\Delta\rho$)
- Shape is determined by balance between weight of drop and surface tension forces, described by the **Bond number**:

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

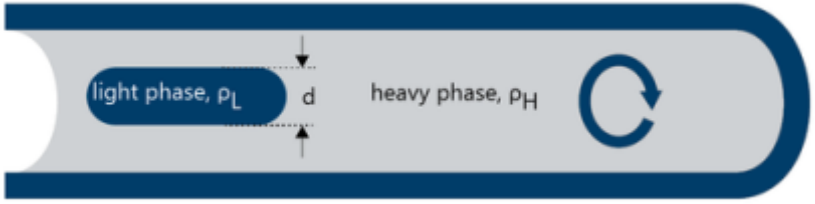
- Numerical fit of shape returns surface tension
- If *Bo* is too large, drop can detach (e.g. very low surface tension)

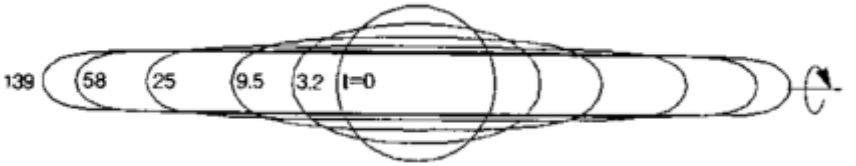
Spinning drop method

- Drop of lighter fluid is formed into heavier fluid (density difference $\Delta\rho$)
- During rotation with velocity ω, drop shape evolves to form long cylinder of radius $R = d/2$
- Interfacial tension is calculated from Vonnegut's equation:

$$\gamma = \frac{\Delta\rho\, R^3 \omega^2}{4}$$

- Method for very low surface tension ($\gamma < 0.1$ mM/m)

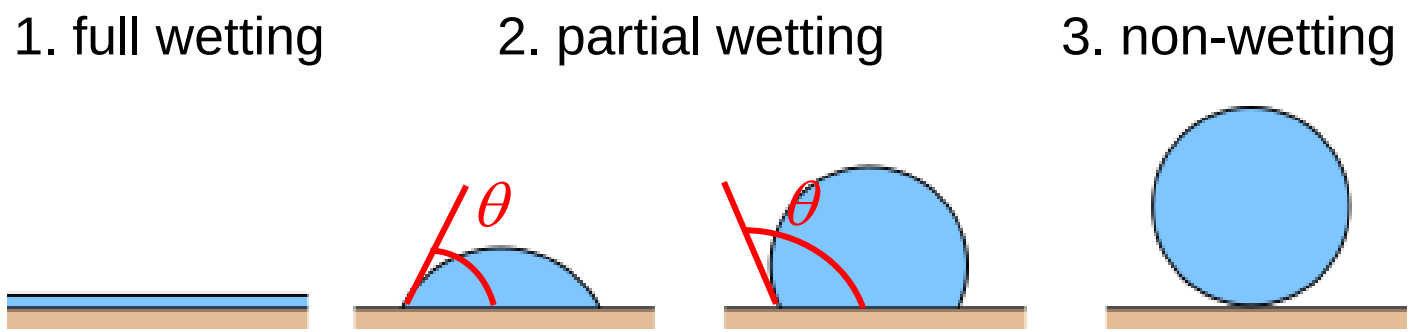




images: www.kruss.de

Wetting of a solid by a liquid

A liquid on a solid surface can take one of three configurations:



contact angle:

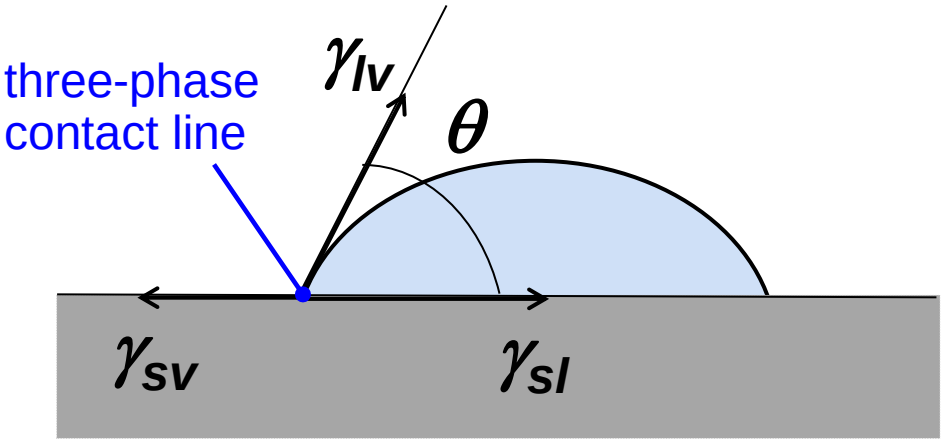
$\theta = 0^\circ$ $0^\circ < \theta < 90^\circ$ $90^\circ < \theta < 180^\circ$ $\theta = 180^\circ$

if liquid is **water**: hydrophilic hydrophobic

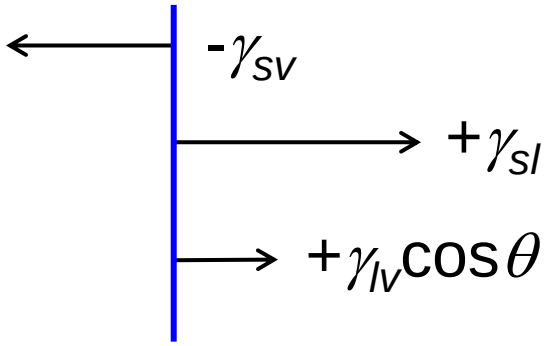
Superhydrophobic

if liquid is **oil**: oleophilic oleophobic

Contact Angle θ



Force balance on contact line
(per unit length):



Equilibrium:

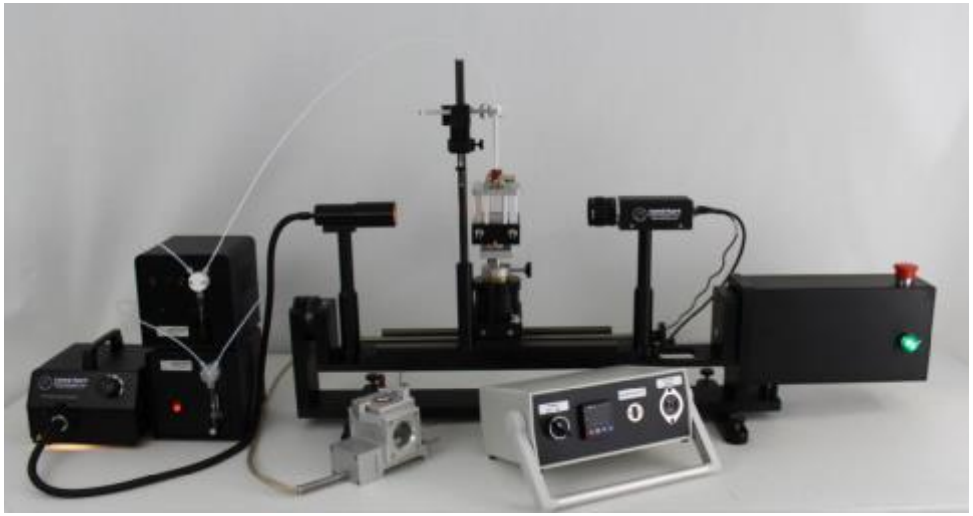
$$-g_{sv}+g_{sl}+g_{lv}\cos q=0$$

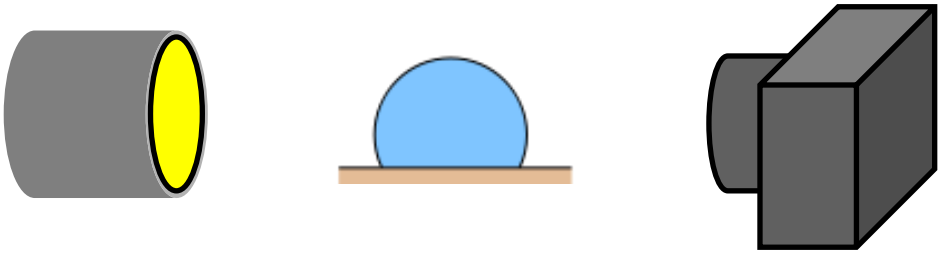
$$g_{lv}\cos q=g_{sv}-g_{sl}$$

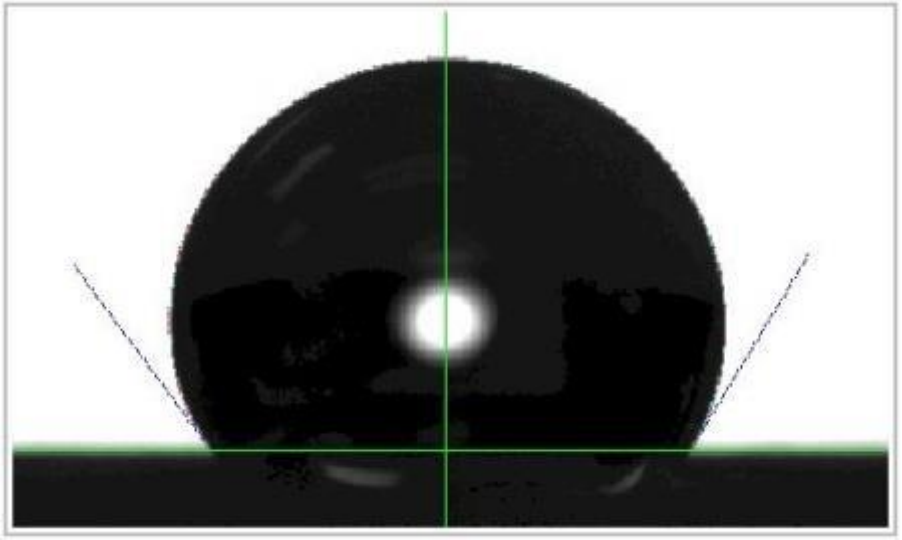
Young's equation:

$$\cos q=\frac{g_{sv}-g_{sl}}{g_{lv}}$$

Contact angle measurements: sessile drop





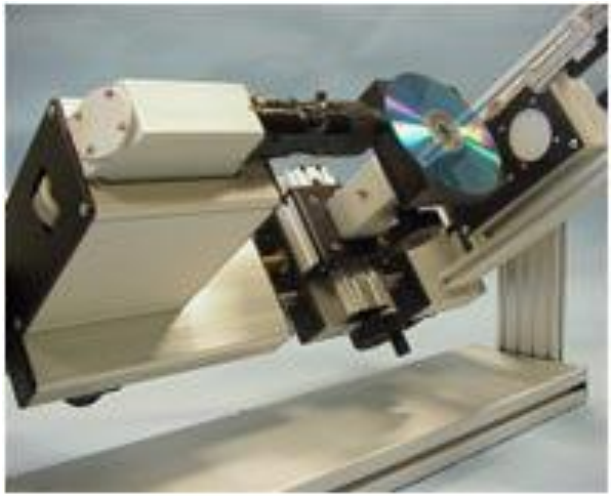


Advancing and receding contact angle

Static (advancing) contact angle

Dynamic contact angle: advancing and receding

Sliding of drop for tilting angle of substrate α



Force (per unit length) needed to make a drop slide over a solid surface:

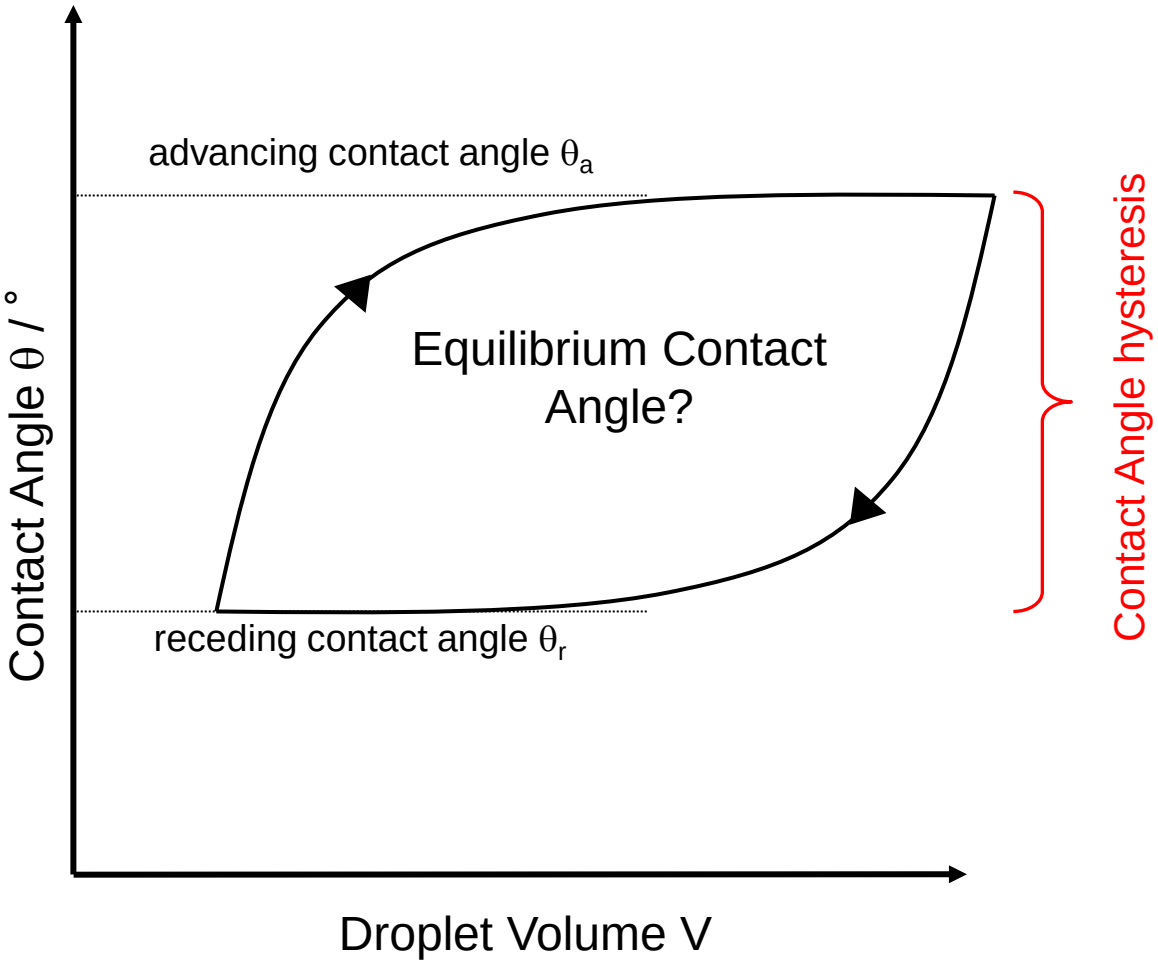
$$f = \frac{\gamma_{lv}(\cos\theta_r - \cos\theta_a)}{2}$$

At angle α, a liquid drop with perimeter *L* and mass *m* slides on a smooth surface. Sliding constant:

$$k_\alpha = mg\sin\frac{\alpha}{L}$$

Wolfram, E.; Faust, R. Liquid Drops on a Tilted Plate, Contact Angle Hysteresis and the Young Contact Angle. In *Wetting, Spreading and Adhesion*, Padday, J. F., Ed., Academic Press, London, **1978; 213 - 222.**

Contact Angle Hysteresis



Increasing droplet volume → approaching maximum (advancing) contact angle

Decreasing droplet volume → approaching minimum (receding) contact angle

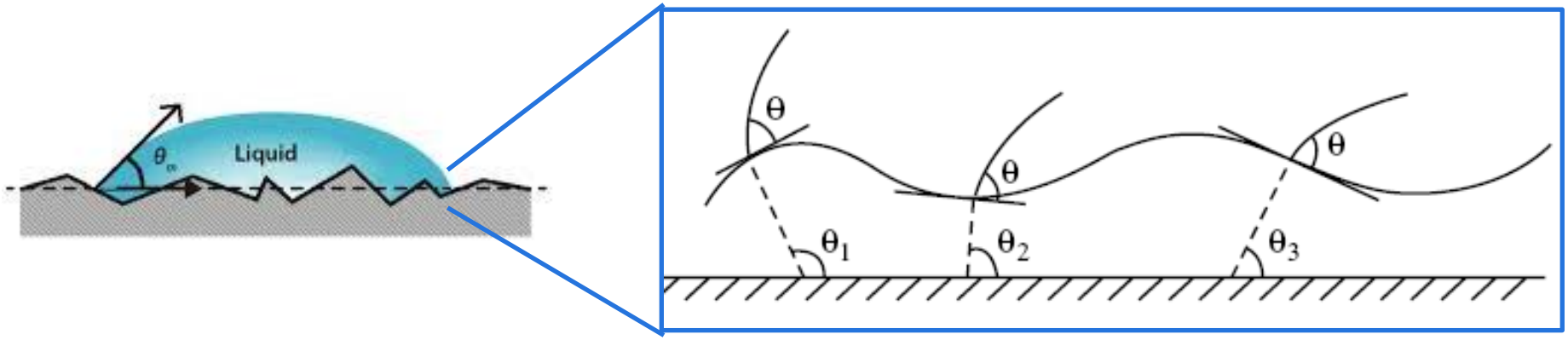
Contact angle hysteresis:

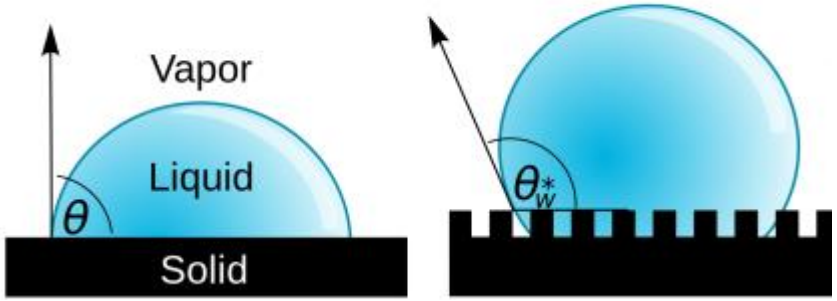
$$\Delta\theta = \theta_a - \theta_r$$

is caused by non-ideal surfaces (roughness, chemical heterogeneity)

Effect of surface roughness

different (apparent) values of θ on rough surfaces:





drop in
Wenzel state

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$ Young's contact angle

$$R_{\mathrm{W}} = \frac{A_{\mathrm{true}}}{A_{\mathrm{apparent}}}$$ roughness factor

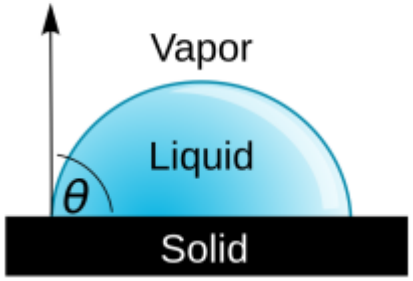
Wenzel Equation:

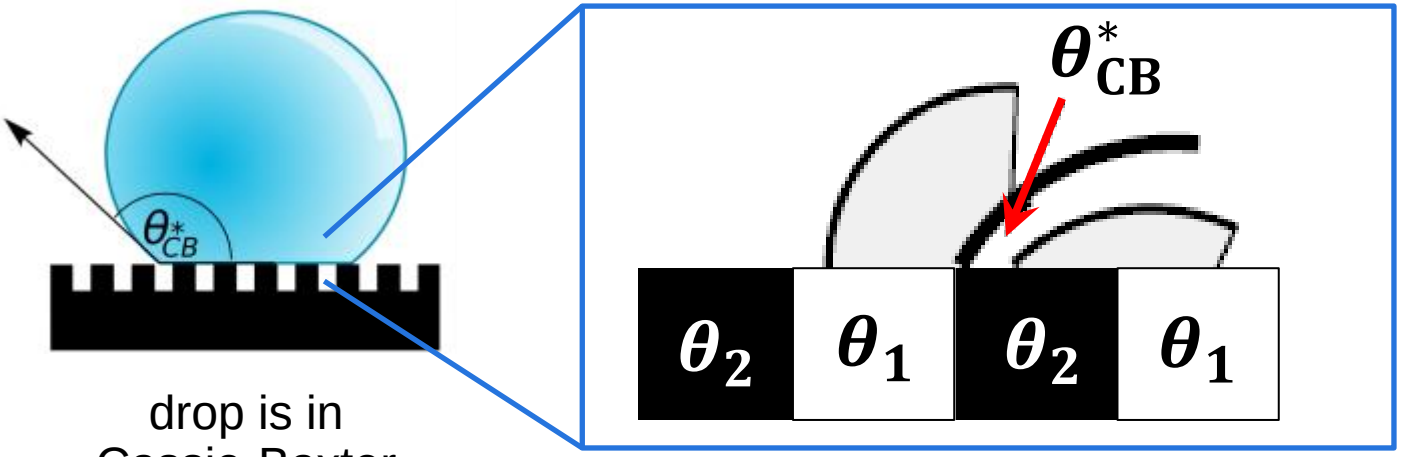
$$\cos\theta^{*}_{\mathrm{W}} = R_{\mathrm{W}}\cos\theta$$ θ^{*}_{W}: apparent contact angle

images: Wikipedia

Effect of chemical heterogeneity

Contact angle is different on different parts of surface





drop is in Cassie-Baxter state

$$\cos\theta_1 = \frac{\gamma_{1v} - \gamma_{1l}}{\gamma_{lv}}$$

Young's contact angle on solid surface 1

$$\cos\theta_2 = \frac{\gamma_{2v} - \gamma_{2l}}{\gamma_{lv}}$$

Young's contact angle on solid or fluid surface 2

Cassie-Baxter-Equation:

θ^*_{CB}: apparent contact angle

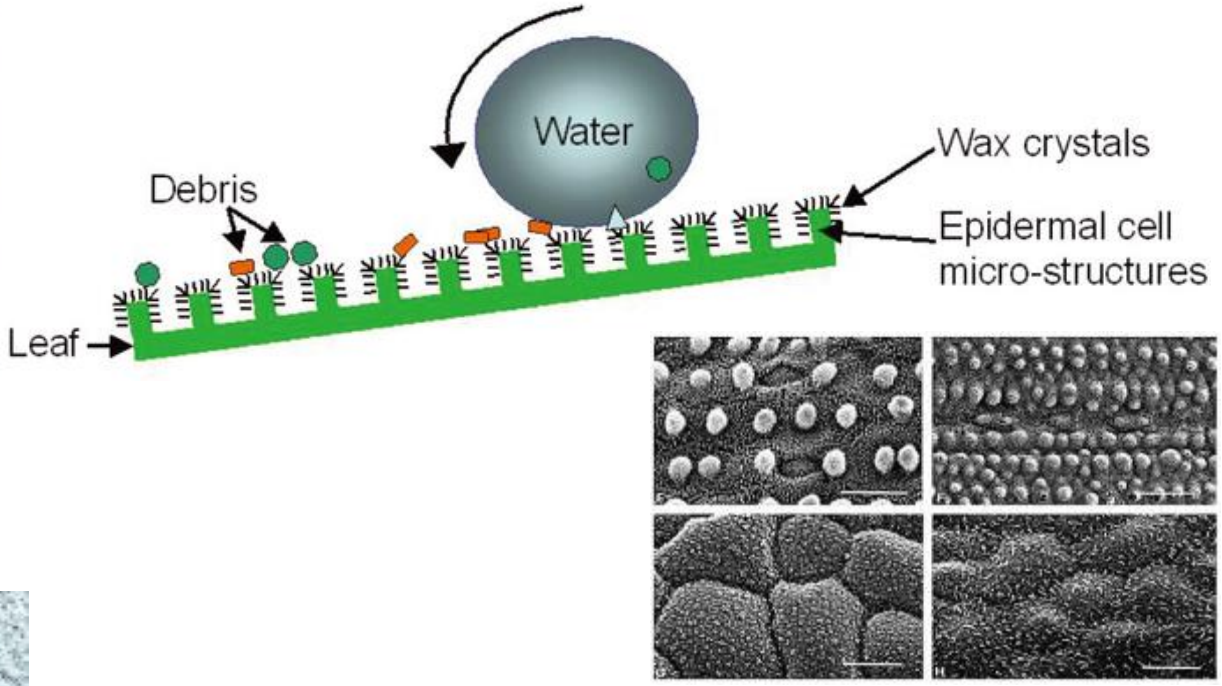
$$\cos\theta^*_{\mathrm{CB}} = f_1 \cos\theta_1 + f_2 \cos\theta_2$$

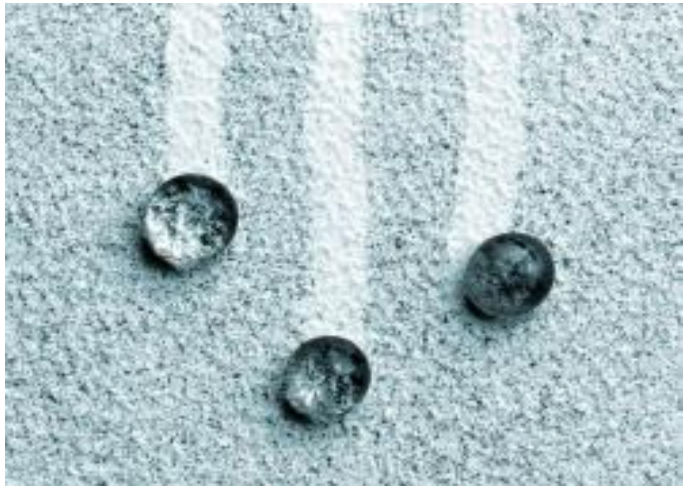
$$f_1 = 1 - f_2$$

f_i: surface fractions (i = 1,2)

images: Wikipedia

Superhydrophobicity and the Lotus effect





Link between roughness and self-cleaning:

(a) On smooth surfaces, dirt particles are redistributed by water

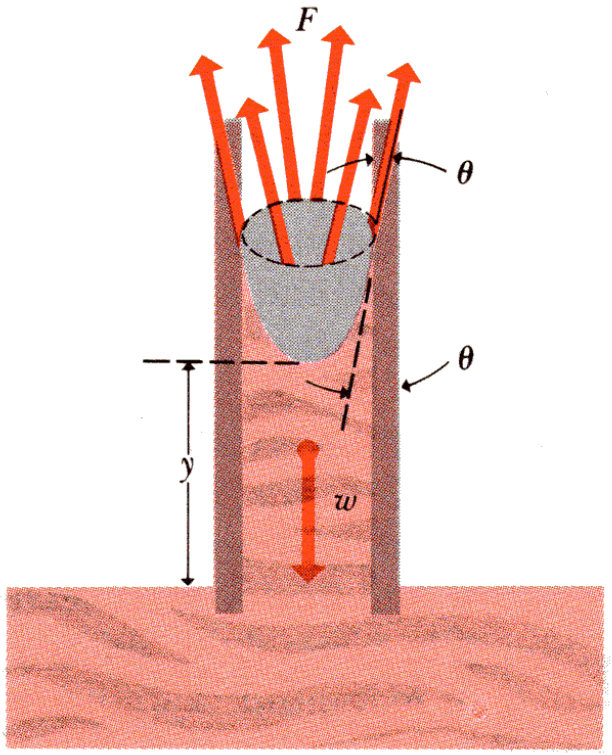
(b) On rough surfaces, dirt adheres to drop and is removed from leaves when droplets roll off

Neinhuis & Barthlott, Characterization and distribution of water-repellent, self-cleaning plant surfaces." *Ann. Bot.* **79** (1997) 667–677

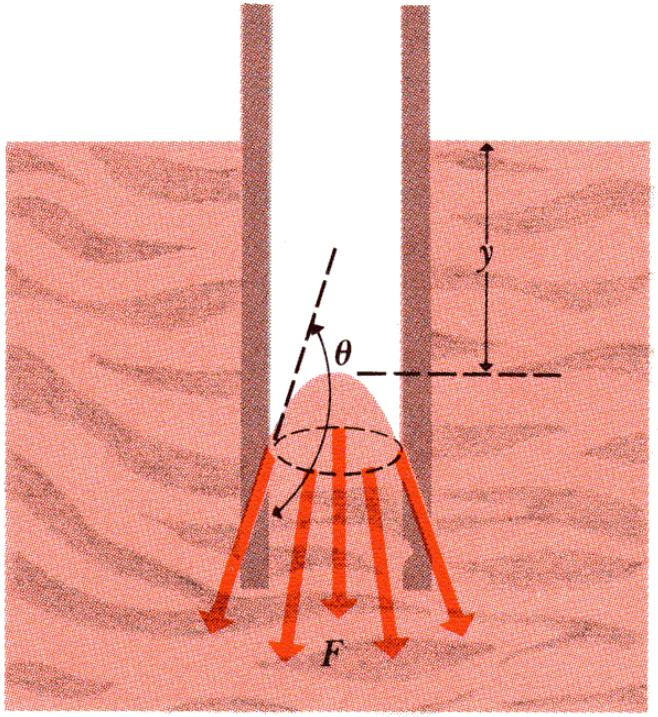
Self-cleaning coatings

Videos: https://youtu.be/UwoGsCAKsxU?t=7s
https://youtu.be/BvTkefJHfC0?t=3m18s

Capillary Action



(a)



(b)

$\theta < 90^o$, small surface tension liquid on a high energy surface, water on clean glass

→ <u>adhesive forces are greater than the cohesive forces</u>

$\theta > 90^o$, large surface tension liquids (such as Hg)

→ <u>Adhesive forces are less than cohesive forces</u>

source: http://local.phys.strath.ac.uk/12-142/lectures/Fluids3.html

Capillary Action

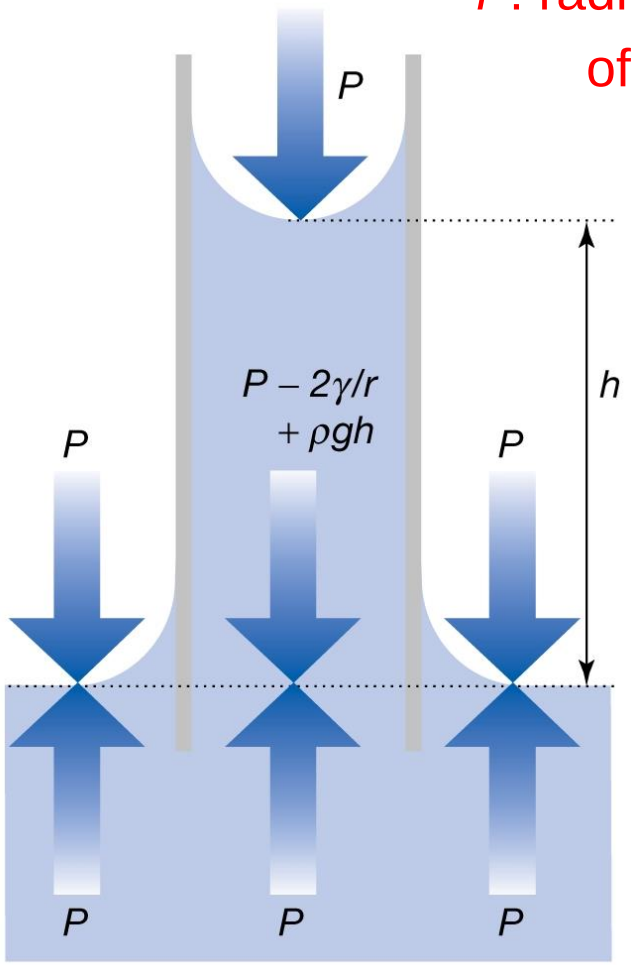
Laplace pressure

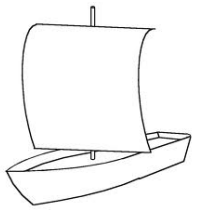
$2\gamma/r$

r : radius of curvature of meniscus

- Pressure under meniscus in capillary is less than atmospheric pressure P: pressure just below curved surface is $P–2\gamma/r$
- liquid rises until weight of column balances surface tension forces (hydrostatic pressure ρgh)
- equilibrium height:

$$h = \frac{2g\cos q}{r\,gR}$$

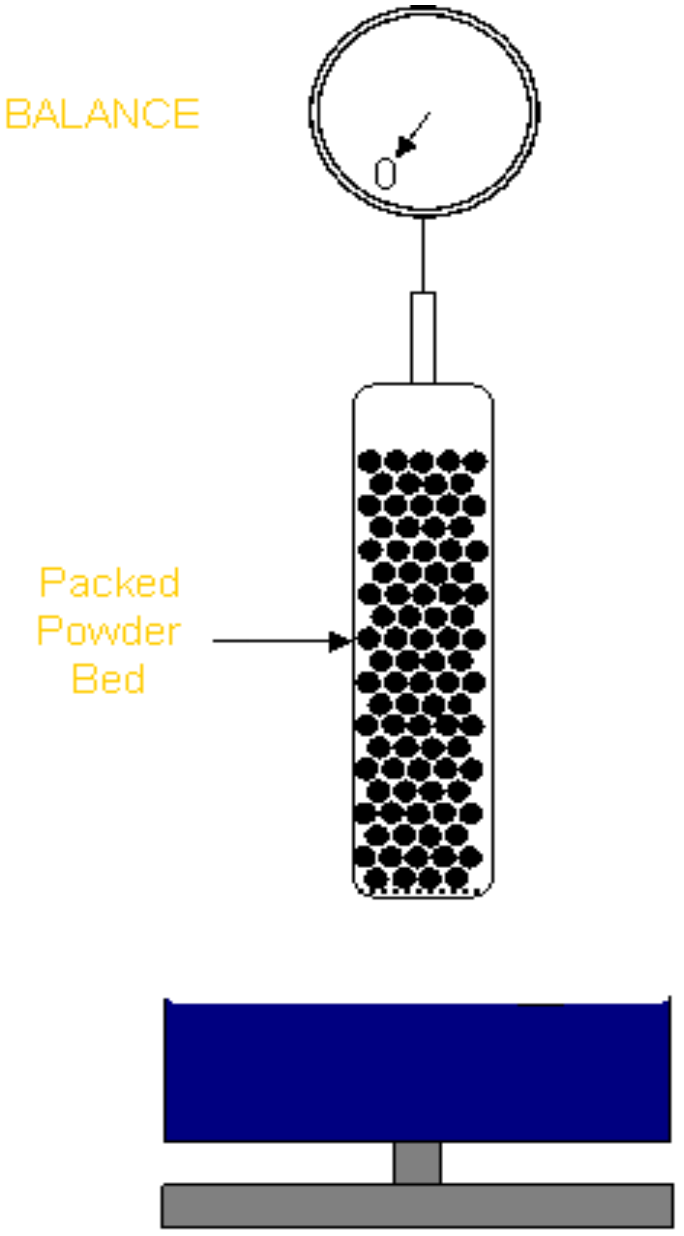




R: radius of capillary

Capillary rise in porous medium

- packed bed (porous medium = foam, fibre bed or textile, powder bed) is brought in contact with liquid phase
- if solid is wetted by liquid, liquid rises due to capillary action in small pores/interstices
- Height (mass) is measured over time *t*
- Contact angle of porous material can be obtained:



Washburn equation:

$$h^2 = \frac{r\gamma_{LV}\cos\theta}{2\eta} \times t$$

r – effective interstitial pore radius

η – liquid viscosity

γ_{lv} – liquid/vapor surface tension

Surface tension and wetting

- recall: definition of surface tension
- apply: spreading coefficient
- understand: molecular origin of surface tension
- understand: surface tension components
- apply: Fowkes equation
- apply: equations used in liquid surface tension measurements
- understand: wetting of solids by liquids
- derive and apply: Young’s law of contact angle
- recall: contact angle hysteresis
- understand: effect of surface roughness and heterogeneity
- recall: superhydrophobicity
- apply: Wenzel equation and Cassie-Baxter equation
- understand: Laplace pressure and capillary action
- apply: equation for equilibrium height of liquid column in capillary
- apply: Washburn equation for capillary rise method