COMMONWEALTH OF AUSTRALIA

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Surface Wetting

Lecture 32

Surface tension



Lecture 34

Adhesion and friction

Spreading parameter

What happens when a liquid droplet is placed on a solid substrate? The outcome is determined by the **spreading parameter** which is simply the difference in surface energy (per unit area) between the dry solid and a liquid film which entirely covers the surface:

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma)$$

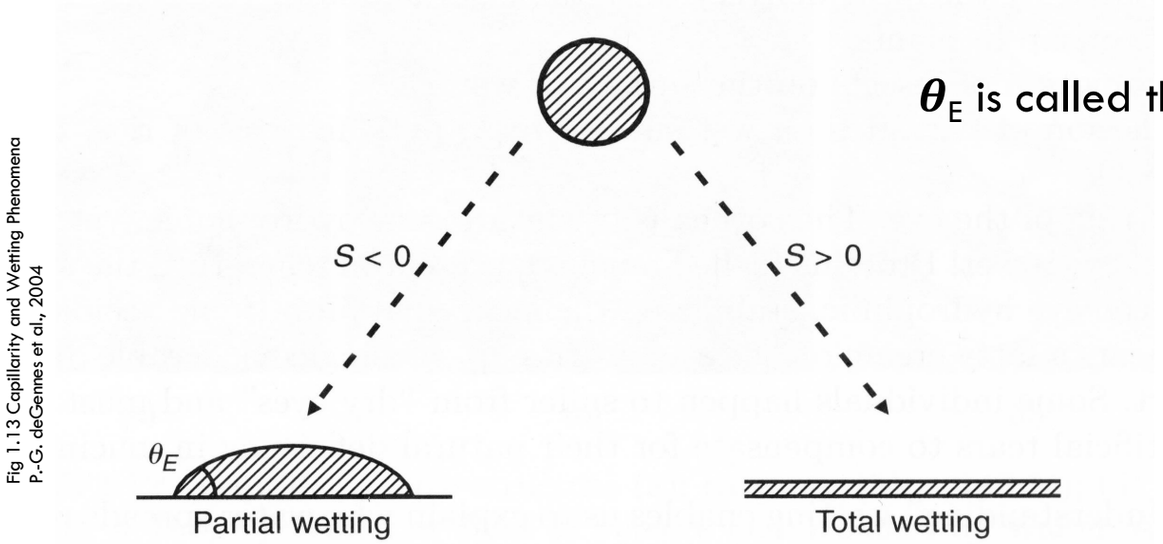


Fig 1.13 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004

θ_E is called the "equilibrium contact angle"

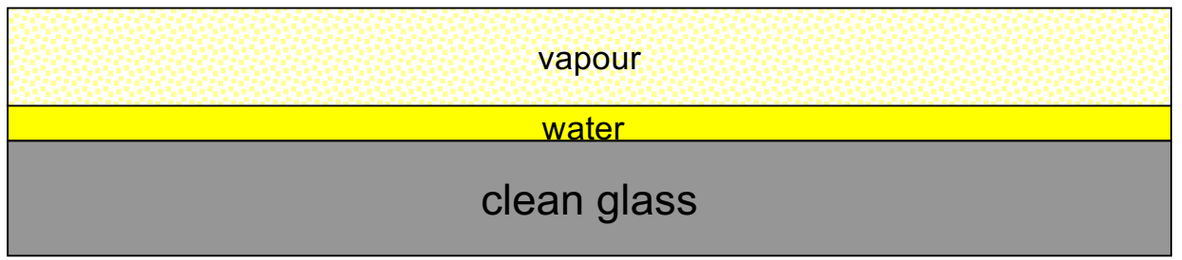
High-energy surfaces

Q1

- "High-energy surfaces" have high γ_{sv} ~ 500 – 5000 mN/m

  These include ionic, covalent and metallic materials

- High-energy surfaces are wetted by most liquids, because this reduces the total energy
- For example, glass is a fairly high-energy surface



Water spreads totally, into a thin film
Contact angle $\theta = 0°$

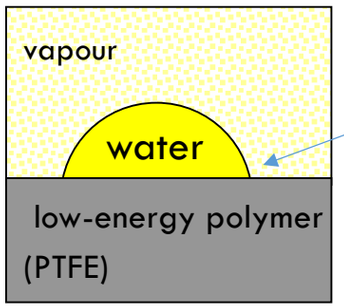
of Commonly Encountered Solids

Material	Surface Energy (mJ m^{-2})
Lead iodide (PbI_2)	130
Silica	462
Lead fluoride (PbF_2)	900
Iron	1360
Gold	1500
Mica	4500

- The energy of the system is reduced the water spreads

Low-energy surfaces

- "Low-energy surfaces" have low $\gamma_{sv} \sim 10 - 60$ mN/m
- Low-energy surfaces are wetted by few liquids, because this increases the total energy
- Liquids do not spread on surfaces that have lower surface energy than them



Water does not spread, forms a droplet
Contact angle $\theta >> 0°$

- Examples: molecular crystals, plastics, teflon

TABLE 7.1. Reported Surface Energies

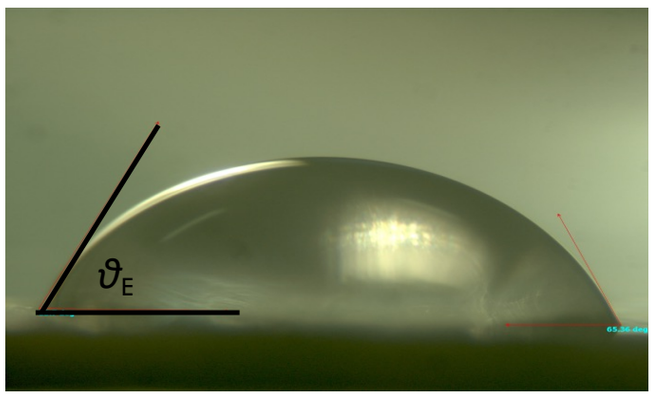
Material	Surface Energy (mJ m^{-2})
Teflon	20
Paraffin wax	26
Polypropylene	28
Polyethylene	36
Polystyrene	44
Ice	82

Contact angle and Young's equation

Q2

In the case of partial wetting ($S < 0$) the shape of the droplet depends on the interfacial forces. The **equilibrium contact angle** ϑ_E is given by **Young's equation:**

$$\gamma_{SV} = \gamma_{SL} + \gamma \cos\theta_E$$



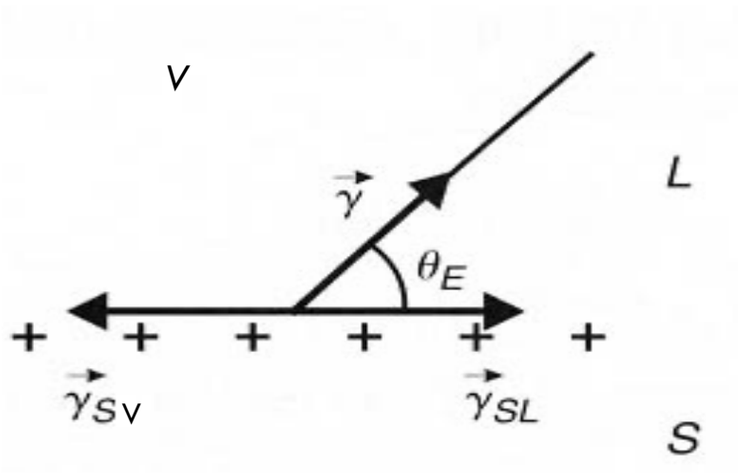


Fig 1.14 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004

Demonstation using a force argument: at equilibrium, force pointing to the left must equal force to the right.

Spreading parameter and contact angle

The **spreading parameter** $S = \gamma_{SV} - (\gamma_{SL} + \gamma)$

can be rewritten using Young's equation $\gamma_{SV} = \gamma_{SL} + \gamma \cos\theta_E$

$$S = \gamma_{SL} + \gamma\cos\theta_E - (\gamma_{SL} + \gamma) = \gamma(\cos\theta_E - 1)$$

into the Young - Dupré equation $S = \gamma(\cos\theta_E - 1)$

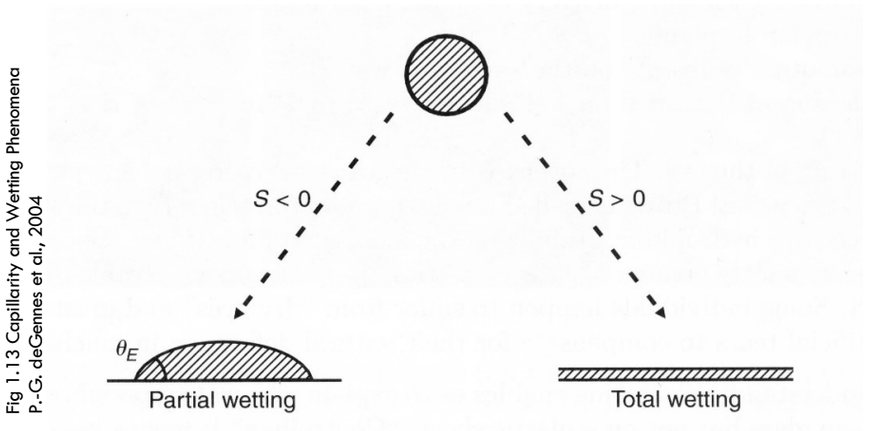


Fig 1.13 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004

Hysteresis

Real surfaces contain defects that pin the three-phase line, preventing us from measuring the equilibrium value θ_E.

If the three-phase line is advancing, one observes the 'advancing contact angle' θ_A.

When the three-phase line is receding, one observes the 'receding contact angle' θ_R.

The **contact angle hysteresis** is given by $\Delta\theta = \theta_A - \theta_R$. Often, $\Delta\theta \sim \theta_E$ which can be frustrating!

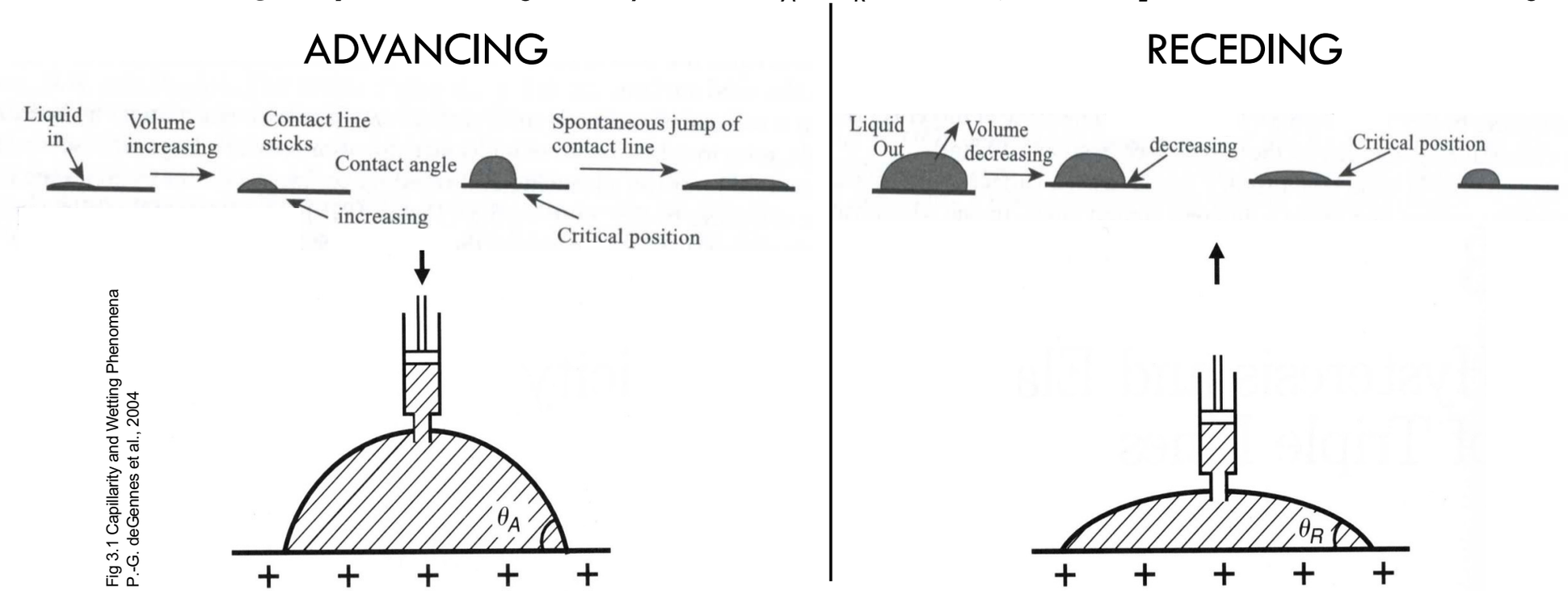
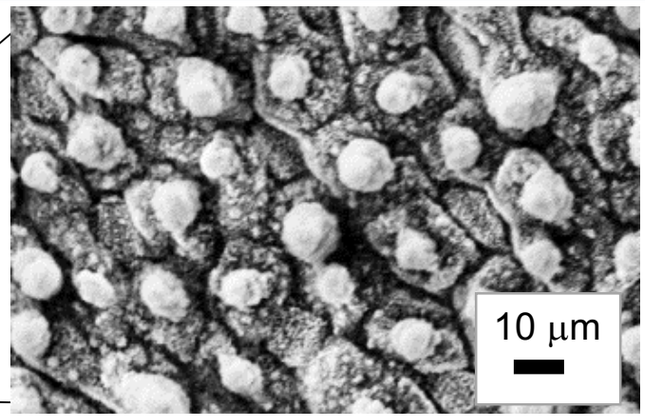


Fig 3.1 Capillarity and Wetting Phenomena
P.-G. deGennes et al., 2004

The ‘superhydrophobic’ self-cleaning lotus leaf



High $\theta_E \geq 150^\circ$
Low $\Delta\theta$

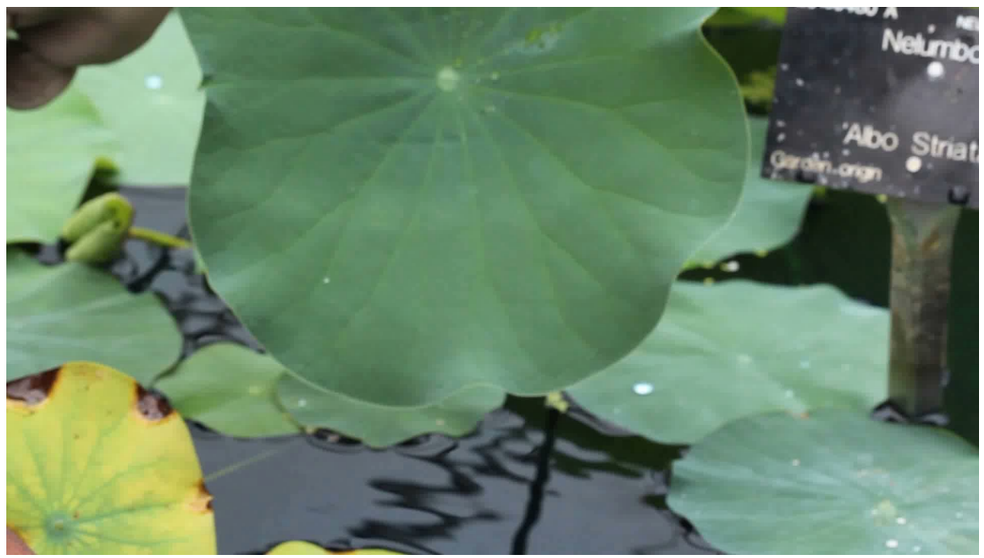


Very low contact area ~ 1%

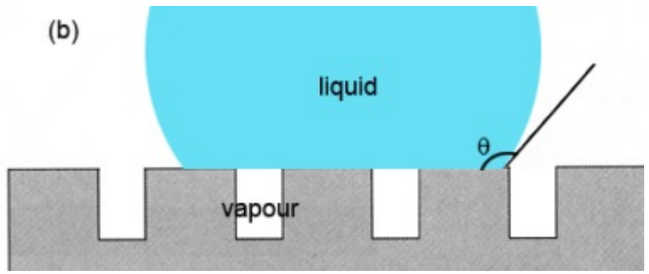
Double-scale roughness



The Sacred Lotus (Sydney Botanical Gardens)

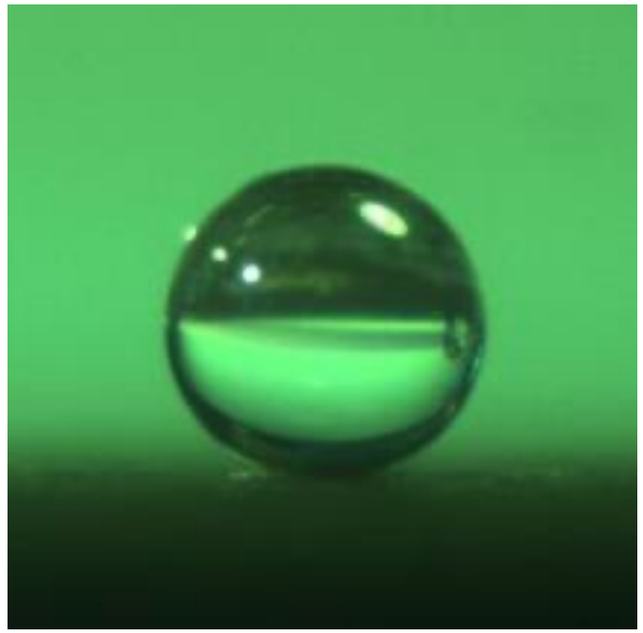


Artificial superhydrophobicity

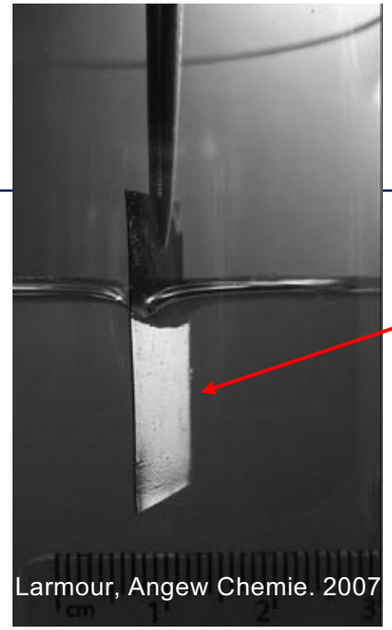


Double-scale roughness traps air

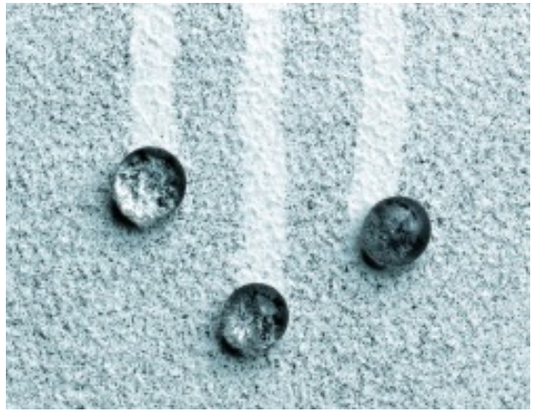
Contact angle ≥ 150˚
Very low hysteresis
Very low roll-off angle



Water droplets on superhydrophobic teflon



Self-cleaning surfaces

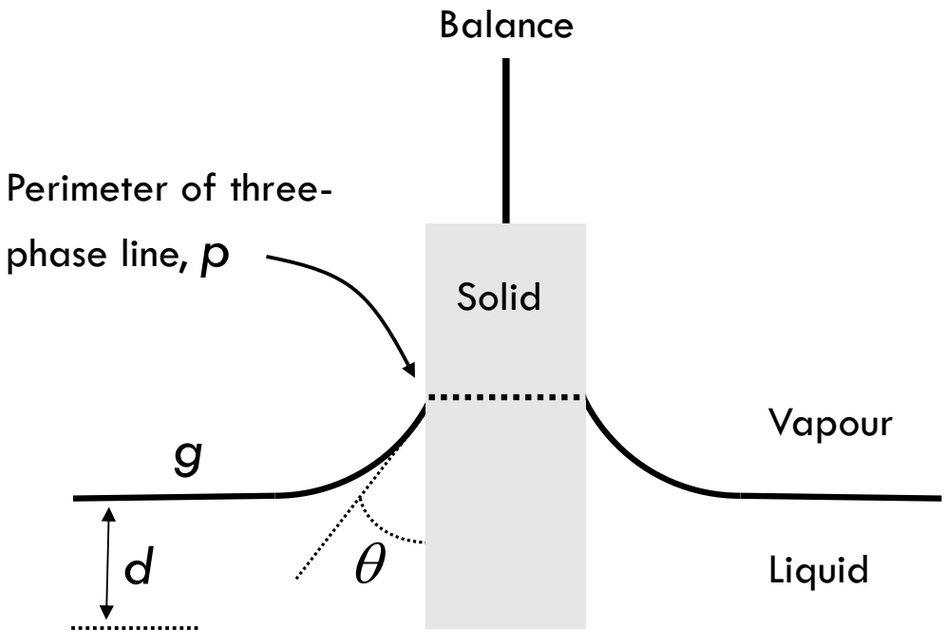


www.lotus-effekt.de

Wilhelmy method to measure surface tension

Measure force on a partially submerged object (commonly a plate or a fibre):
the total force on the object = weight + buoyancy force + surface tension force.

We know the weight, can measure the perimeter of the object, can make the buoyancy force = 0 (by making $d = 0$), and so can determine the surface tension force (and hence one of γ and θ).



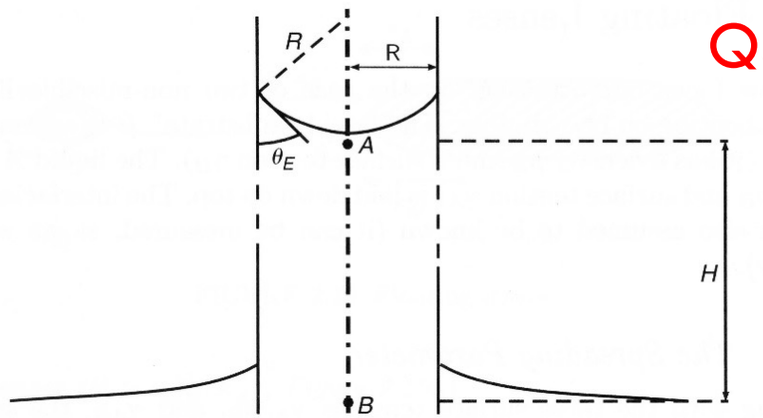
Surface tension force = $p\gamma\cos\theta$

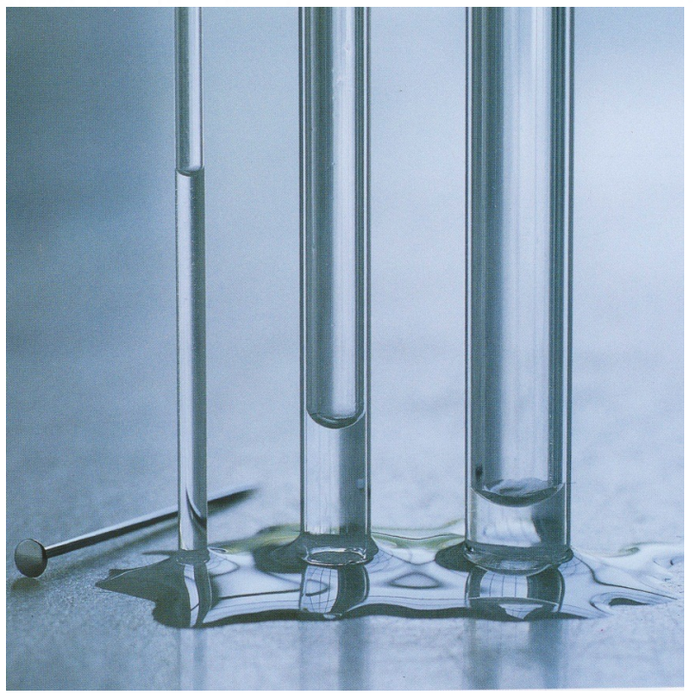
p = perimeter of the contact line
γ = surface tension (N/m)
θ = equilibrium contact angle of liquid

Capillary rise

Q3

$$\Rightarrow H = \frac{2\gamma \cos\theta_E}{\rho g \mathrm{R}}$$





Wick, W. *A drop of Water, A book of science and wonder; Scholastic Press: Singapore, 1997.*

H	height of the liquid in the capillary (m)
γ	surface tension (N/m)
θ_E	equilibrium contact angle of liquid on capillary
ϱ	density of liquid (kg/m^3)
g	gravitational acceleration is approximately 9.8 m/s^2
R	radius of the capillary (m)

See the extra reading for a derivation of this equation

Learning outcomes

After this lecture you should be able to:

- Define spreading and relate it to contact angle and interfacial energies
- Define the equilibrium contact angle and derive Young's Equation
- Understand the origin of superhydrophobicity and the lotus leaf effect
- Explain how dipping-probe and capillary-rise methods can determine γ of a liquid

This week's reading

- Pages 146 - 150 of Atkins "*Physical Chemistry*", Oxford University Press
  on surface tension and capillary rise

- Pages 1 - 11 and 49-53 of *P.-G. de Gennes et al* "*Capillarity and Wetting Phenomena*", *Springer, 2004*
  on surface tension, spreading, contact angle, Laplace pressure

- Pages 209 -241 of Hiemenz "Principles of Colloid and Surface Chemistry" Marcel Dekker Inc.: New York, 1997; on surface tension, spreading, contact angle, Laplace pressure