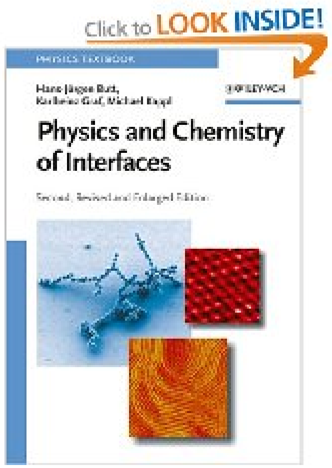
Reaction at the Interfaces

Lecture 1

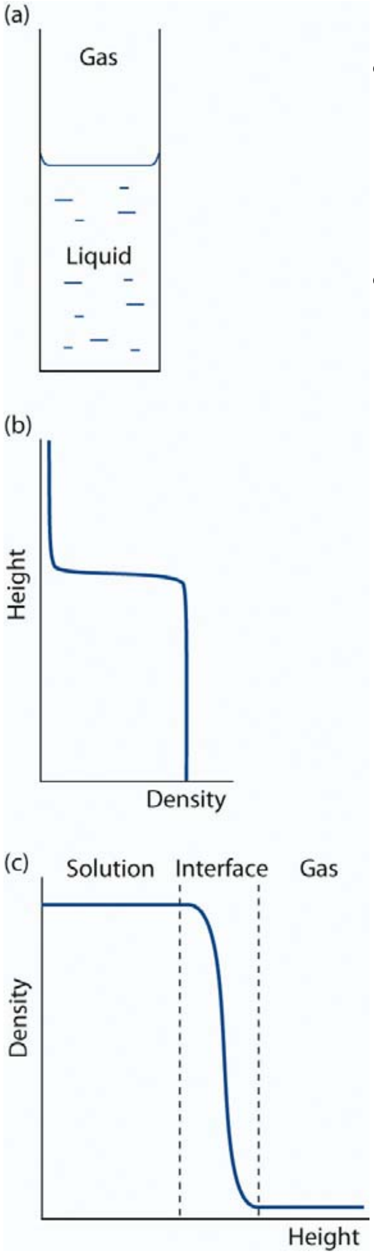
On the course



Physics and Chemistry of Interfaces
by HansJürgen Butt, Karlheinz Graf, and Michael Kappl
Wiley VCH; 2nd edition (2006)

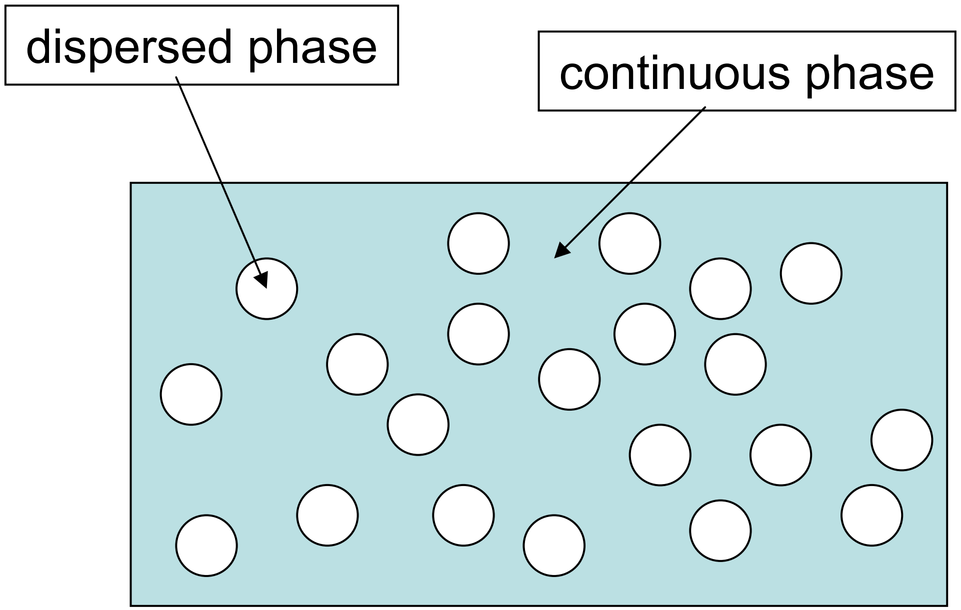
http://homes.nano.aau.dk/lg/Surface2009.htm

Interfaces



- interface – the region where properties change from one phase to another

- dispersed phase (colloid) – important case for interface science as the properties are large determined by interfaces



Types of interfaces

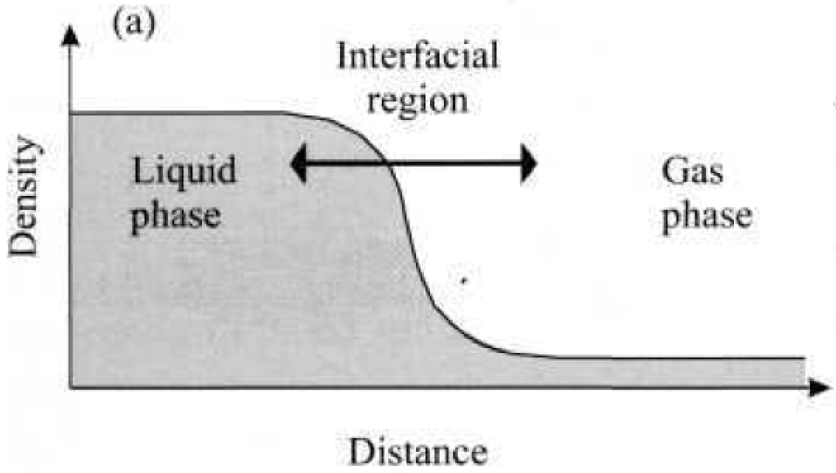
- it's possible to classify interfaces based on the nature of bulk phase.
- Gases intermix completely, so there are no gas-gas interface

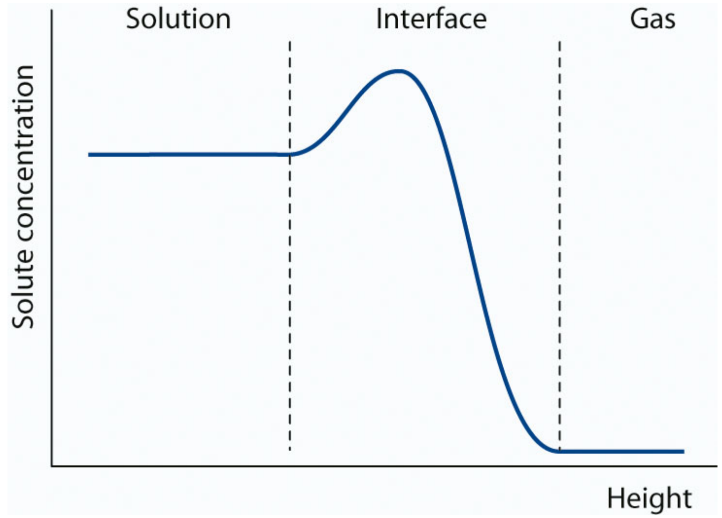
$$\text{fluid interfaces} \begin{cases} \text{gas-liquid} & \text{G-L} \\ \text{liquid1-liquid2} & L_1\text{-}L_2 \end{cases}$$

$$\text{solid interfaces} \begin{cases} \text{gas-solid} & \text{G-S} \\ \text{liquid-solid} & \text{L-S} \\ \text{solid-solid} & S_1\text{-}S_2 \end{cases}$$

Key concepts

- Surface tension
- Wetting
- Adsorption
- Emulsions
- Colloids
- Membranes



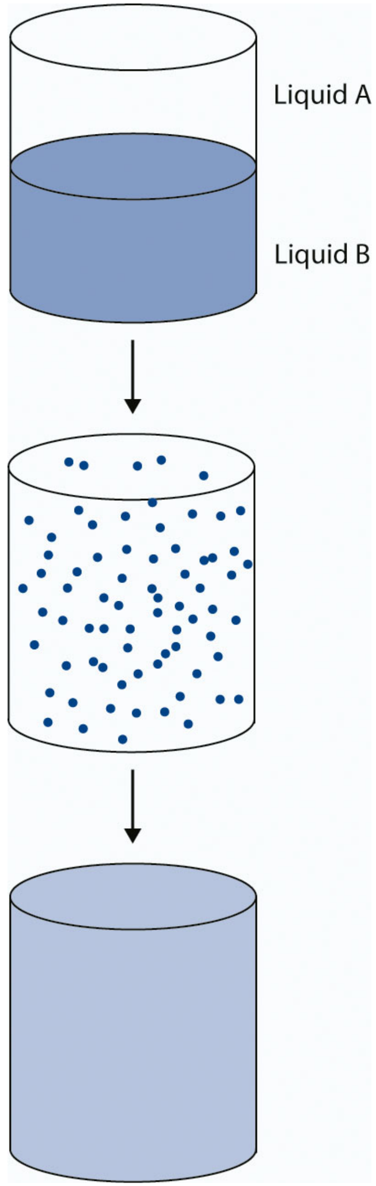


Stability of an interface

- interface can possess and extra energy, so

$$G = \gamma A + \text{other terms}$$

- surface tension should be positive otherwise the system is totally miscible

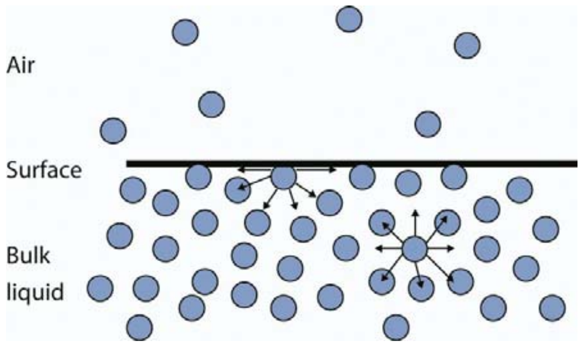


Surface tension

- Surface tension can be defined as a force per unit length acting on an interface

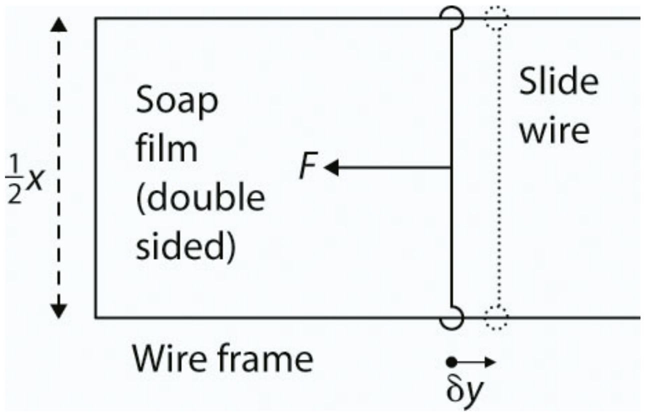
$$\gamma = \frac{F}{\delta x}$$

- Forces can be understood as a result of broken bonds when moved to a dissimilar phase



- work of extension:

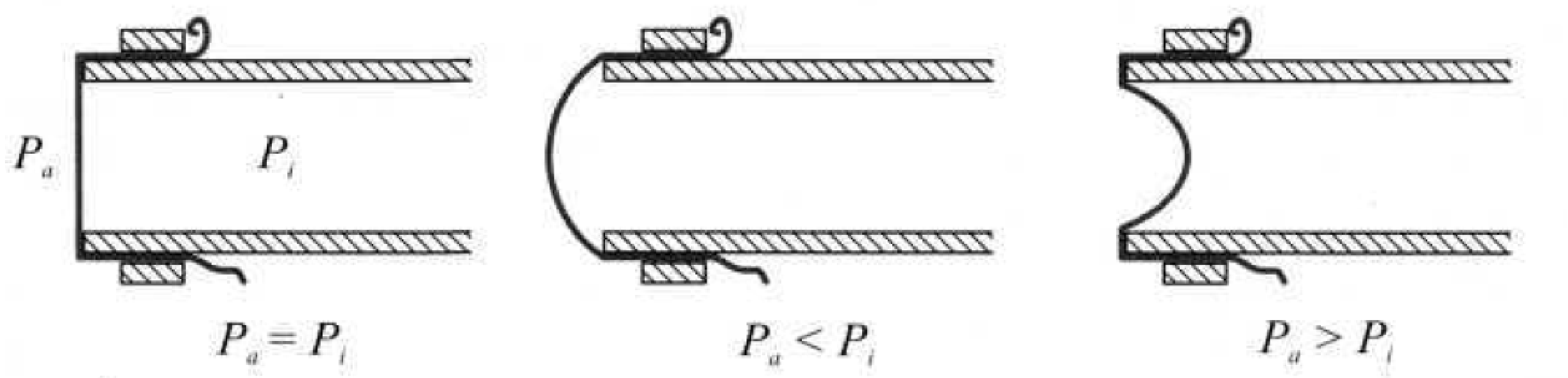
$$w_s = F\delta y = \gamma x \delta y = \gamma \delta A$$



Young-Laplace equation

- If the surface is curved in equilibrium, there should be a pressure difference across it

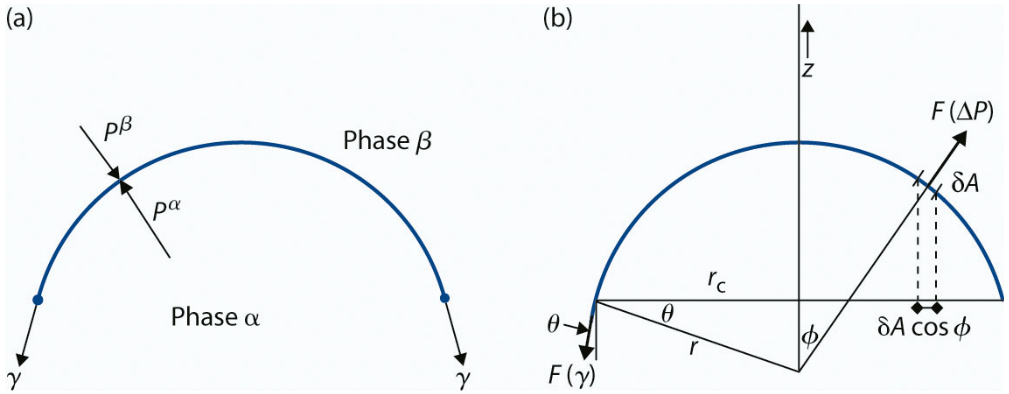
Example: Rubber membrane on a tube



The Young-Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

The Laplace equation



pressure forces:

$$\delta F = (P^\alpha - P^\beta)\delta A \cos\phi$$

$$F = (P^\alpha - P^\beta)\pi r_c^{\,2}$$

surface tension:

$$F_z^\gamma = -\gamma(2\pi r_c)\cos\theta = -\gamma(2\pi r_c) r_c / r$$

$$(P^\alpha - P^\beta)\pi r_c^{\,2} - \gamma(2\pi r_c) r_c / r = 0$$

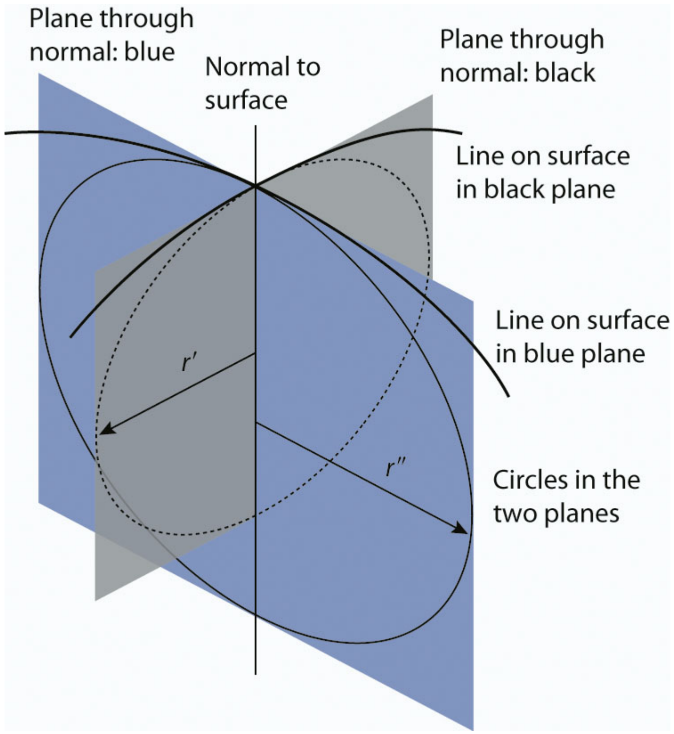
$$\boxed{P^\alpha - P^\beta = \frac{2\gamma}{r}}$$

Laplace equation for spherical surface

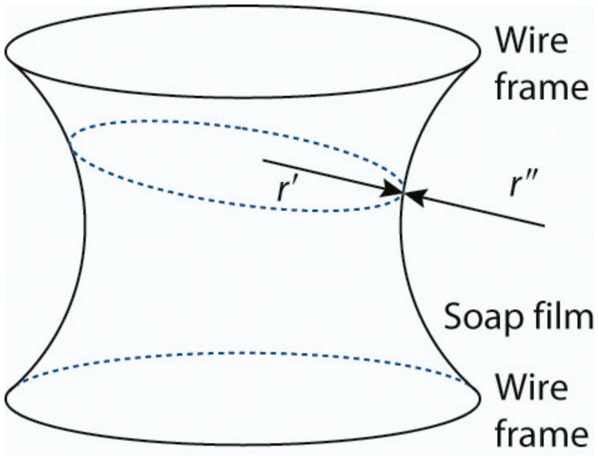
The Laplace equation

- in general case:

$$P^{\alpha} - P^{\beta} = \gamma\left(\frac{1}{r'} + \frac{1}{r''}\right) = \frac{2\gamma}{r_m}$$



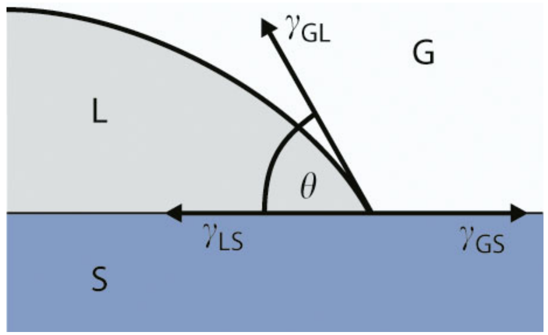
$P_1 = P_2$



Contact angle, wetting and spreading

- at equilibrium:

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos\theta$$



- before equilibrium is reached:

$$F_h = \gamma_{GS} - \gamma_{LS} - \gamma_{GL} \cos\theta'$$

- equilibrium shape is a result of balance between **cohesive** (inside the liquid) and **adhesive** (on the interface) forces.

Contact angle, wetting and spreading

- Wetting is determined by the equilibrium contact angle:
  - $\theta<90^o$ – liquid wets the sold,
  - $\theta>90^o$ – liquid doesn't wet the solid,
  - $\theta=0^o$ – complete or perfect wetting

partial wetting

total wetting

- Spreading coefficient:

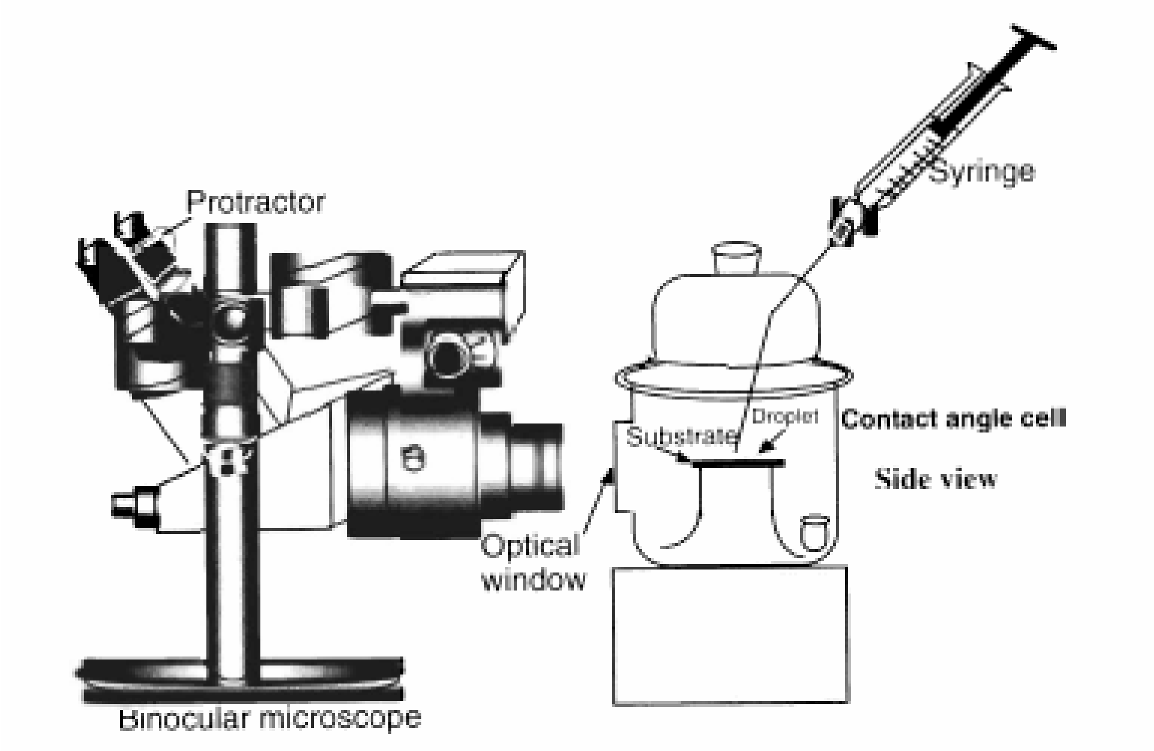
$$S_{LS} = \gamma_{GS} - \gamma_{LS} - \gamma_{GL}$$

if $S_{LS} > 0$ than the liquid spreads completely, otherwise equilibrium contact angle exists

compare: $F_h = \gamma_{GS} - \gamma_{LS} - \gamma_{GL} \cos\theta'$

Measurements of surface tension

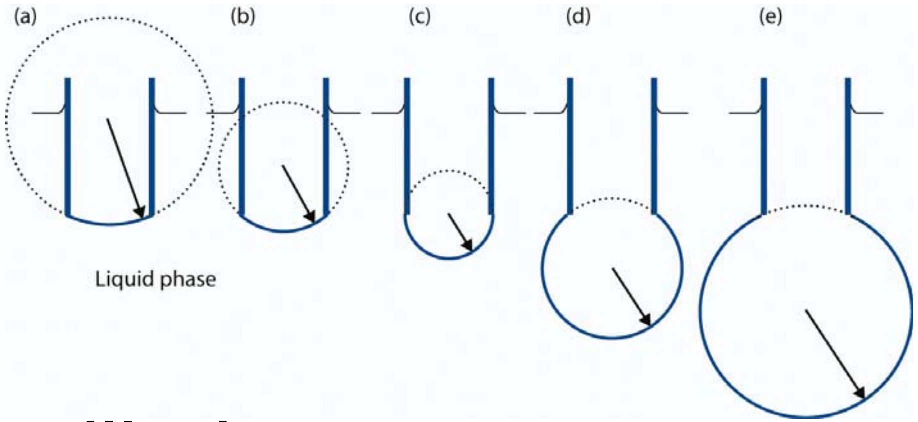
- Measuring contact angles: sessile droplet



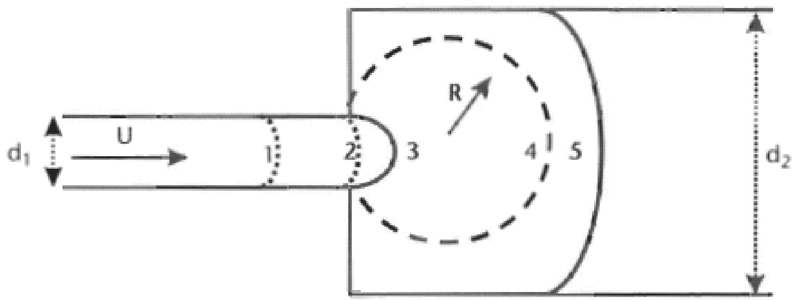
- Other possibilities:
  - pendant drops
  - pendent bubbles
  - sessile bubbles

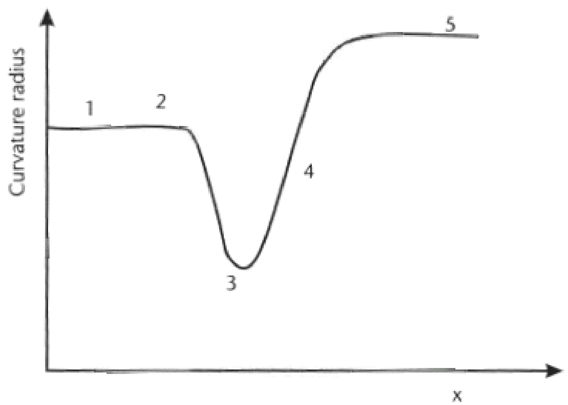
Measurements of surface tension

- Maximum bubble pressure



- Valving effect in capillaries

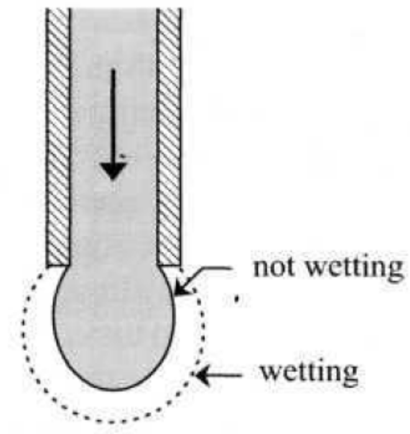




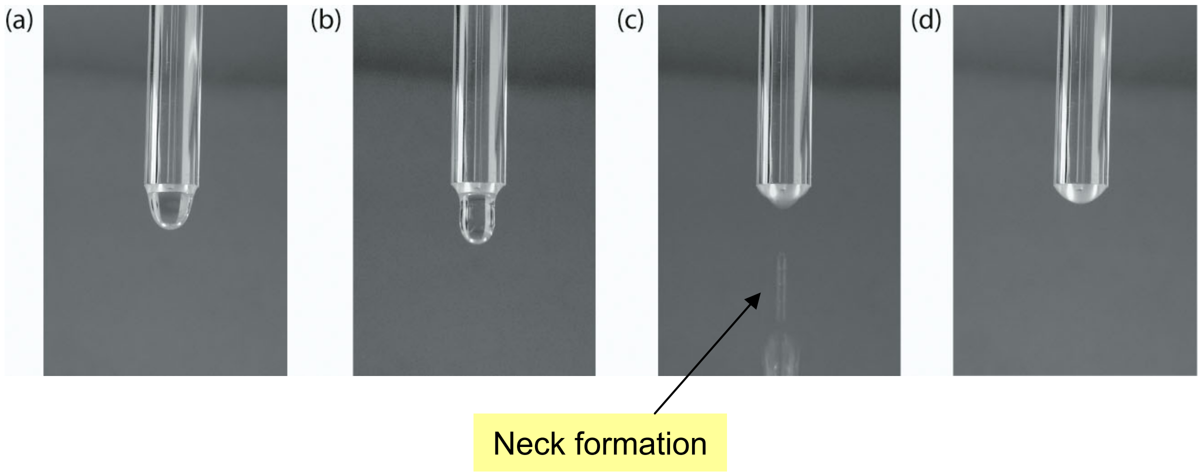
$$\Delta P_1 = \frac{-4\gamma\cos\theta}{d_1} \qquad \Delta P_3 = \frac{-4\gamma}{d_1} \qquad \Delta P_5 = \frac{-4\gamma\cos\theta}{d_2}$$

Measurements of surface tension

- Drop weight (pendent droplet)



$$mg = 2\pi r\gamma$$

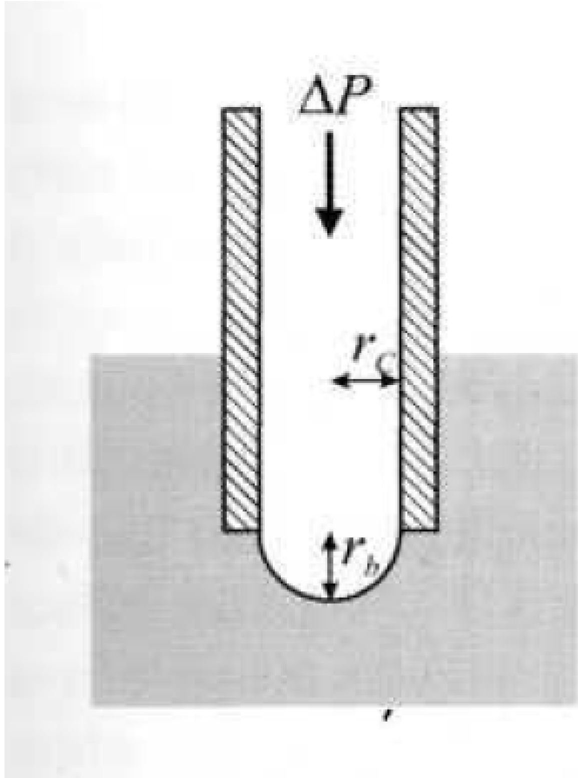


  – Correction factor required due to neck formation

Measurements of surface tension

Bubble pressure method

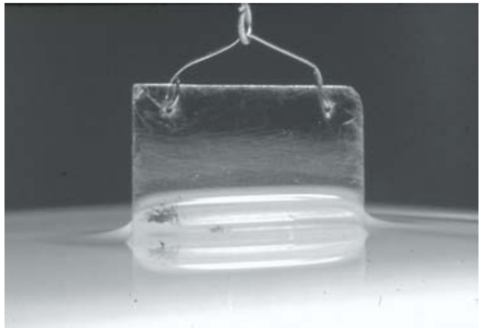
$$\gamma = r_c \Delta P / 2$$

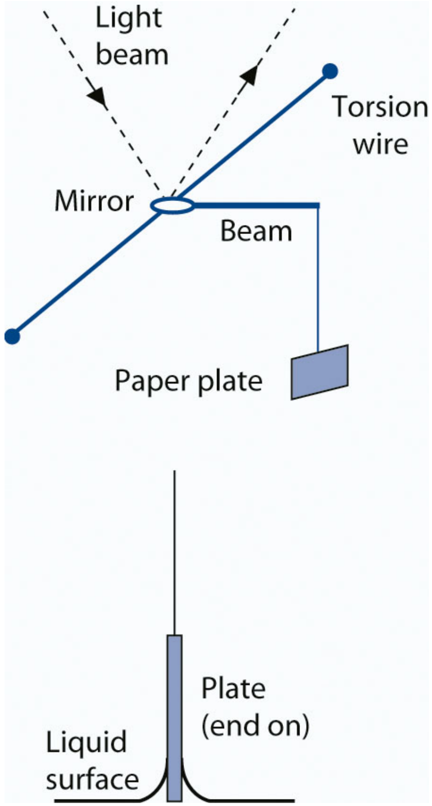


Measurements of surface tension

- Wilhelmy plate:

$$F = \gamma \cdot 2(x + y)$$

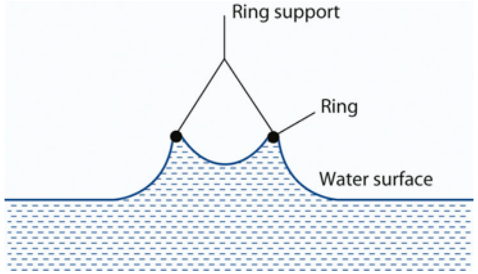


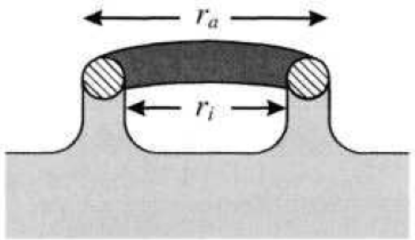


in the past was mainly measured on **roughened mica, etched glass** etc. Currently **paper plates** (i.e. filter paper) is the material of choice

- du Noüy ring:

$$F = 2\pi\gamma(r_i + r_a)$$



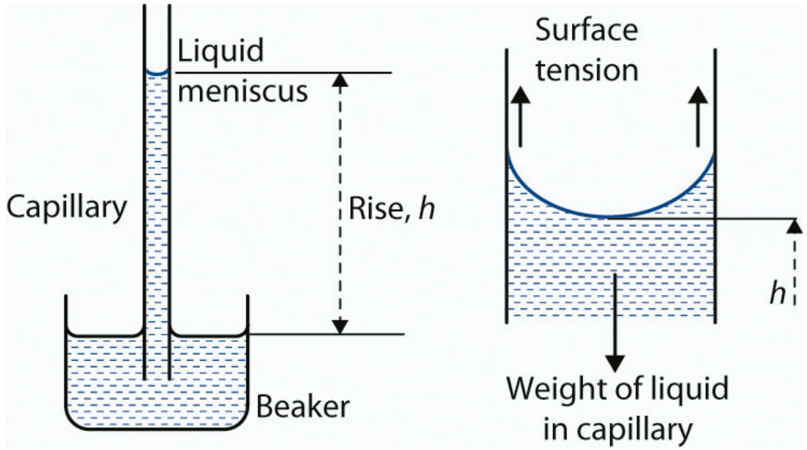


Measurements of surface tension

- Capillary rise

$$\gamma 2\pi r_c = \Delta\rho g h \pi r_c^{\,2}$$

$$\gamma = \frac{1}{2}\Delta\rho g h r_c$$



alternatively the difference between two capillaries of different diameter can be measured

The Kelvin equation

- vapour pressure above a droplet

$$\boxed{\ln\left(\frac{p^c}{p^\infty}\right) = \frac{\gamma \bar{V}^L}{RT}\frac{2}{r_m}}$$

Kelvin equation

$$dG = -SdT + Vdp,\ \mu = G_m \qquad \left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$\left.\begin{aligned} &\delta\mu^\alpha = \delta\mu^\beta \ \Rightarrow\ \bar{V}^\alpha \delta p^\alpha = \bar{V}^\beta \delta p^\beta \\ &\delta p^\alpha - \delta p^\beta = 2\gamma\delta(1/r_m) \end{aligned}\right\}$$

$$\delta p^\beta (\bar{V}^\beta - \bar{V}^\alpha)/\bar{V}^\alpha = 2\gamma\delta(1/r_m)$$

$$\text{if } \bar{V}^\beta \gg \bar{V}^\alpha,$$

$$\delta p^\beta \bar{V}^\beta / \bar{V}^\alpha = \delta\mu^\beta / \bar{V}^\alpha = 2\gamma\delta(1/r_m)$$

$$\mu^c - \mu^\infty = 2\gamma \bar{V}^L (1/r_m)$$

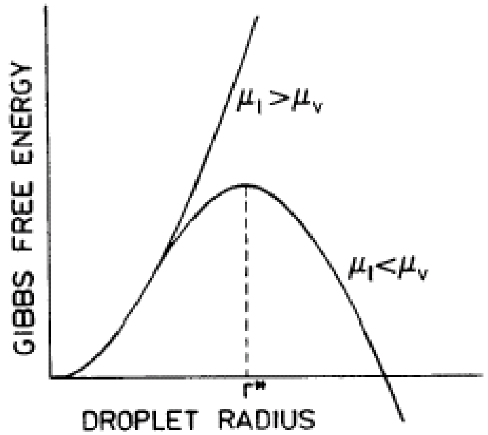
$$RT\ln\left(\frac{p^c}{p^\infty}\right) = \frac{\gamma \bar{V}^L}{RT}\frac{2}{r_m}$$

Consequences of Kelvin equation

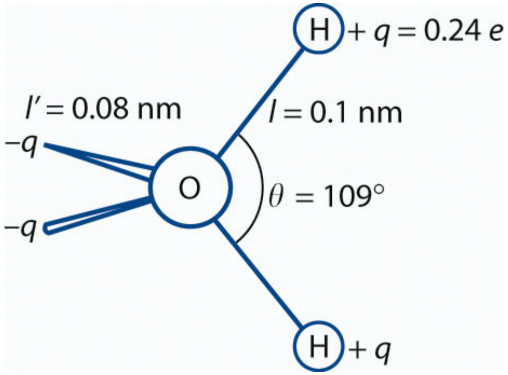
- smaller droplets will have higher vapour pressure and therefore evaporate faster
- small droplets have higher chemical potential
- condensation in a capillary
- at the phase transition only the nucleation center with **infinite** radius will grow. All finite nucleation center require finite overcooling/overheating (i.e. a **thermodynamic force)**

$$\Delta G = -\frac{4\pi r^3}{3V_m}\Delta\mu + 4\pi r^2 \gamma$$

$$\frac{\partial}{\partial r}\Delta G = -\frac{4\pi r^2}{V_m}\Delta\mu + 8\pi r\gamma \qquad r^* = \frac{2\gamma V_m}{\Delta\mu}$$



Hydrophilic-hydrophobic interaction



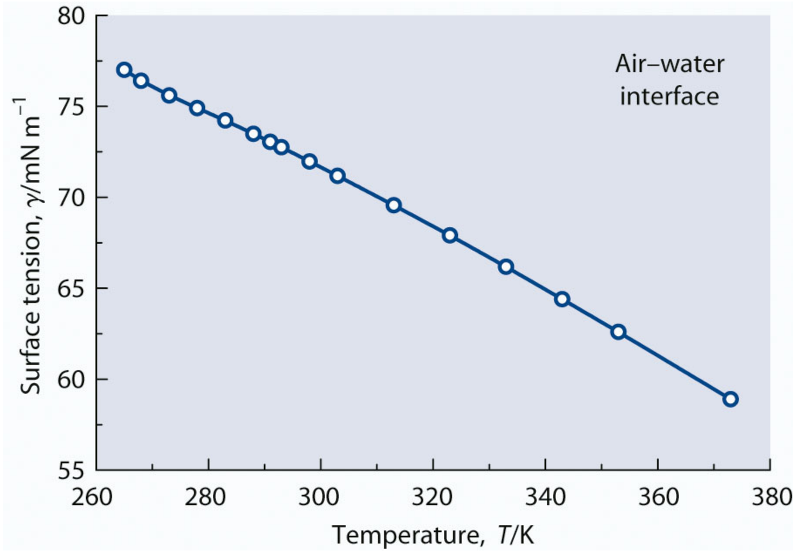
- water properties are governed by the presence of hydrogen bonds
- polar substances favour such type of arrangement and are therefore hydrophilic
- non-polar substances lead to clathrate formation and therefore increase free energy (via decrease in entropy)

Effect of temperature on surface tension

- experimentally, surface tension of pure liquids drops linearly with the temperature

- Eötvös equation:

$$\frac{d\left(\gamma\left(M/\rho\right)^{2/3}\right)}{dT} = -2.12\times10^{-7}\ Jmol^{-2/3}K^{-1}$$



Probelms

- **Problem 1** A jet aircraft is flying through a region where the air is 10% supersaturated with water vapour (*i.e.* the relative humidity is 110%). After cooling, the solid smoke particles emitted by the jet engines adsorb water vapour and can then be considered as minute spherical droplets. What is the minimum radius of these droplets if condensation is to occur on them and a “vapour trail” form?
  Data: $\gamma(H_2O)$ = 75.2 mN m^{-1}, $M(H_2O)$ = 0.018 kg mol^{-1}, $\rho(H_2O)$ = 1030 kg m^{-3}, T = 275 K.

- **Problem 2.** A hydrophilic sphere of radius R_p = 5 μm sits on a hydrophilic planar surface. Water from the surrounding atmosphere condenses into the gap. What is the circumference of the meniscus? Make a plot of radius of circumference x versus humidity. At equilibrium the humidity is equal to P_0^K/P_0