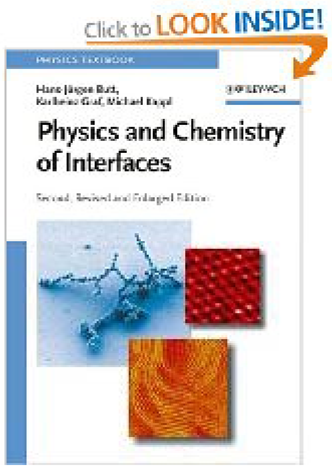
Reaction at the Interfaces

Lecture 1

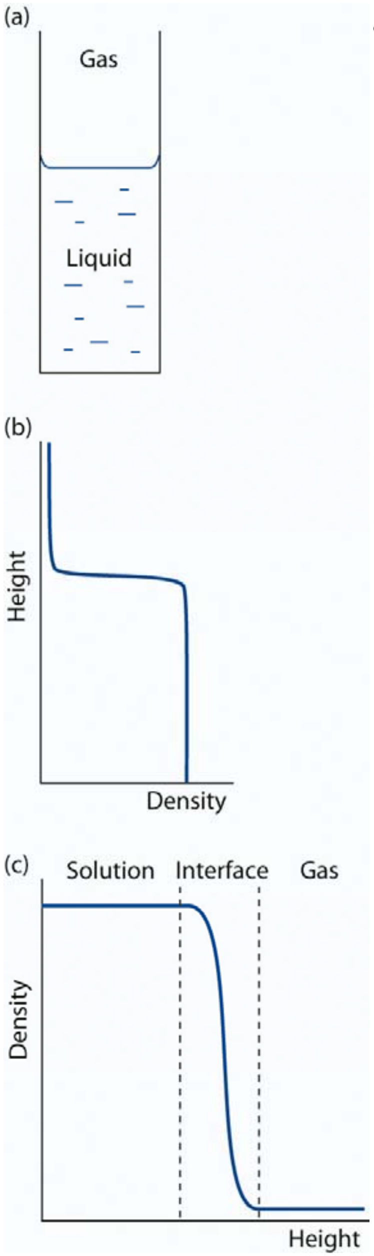
On the course



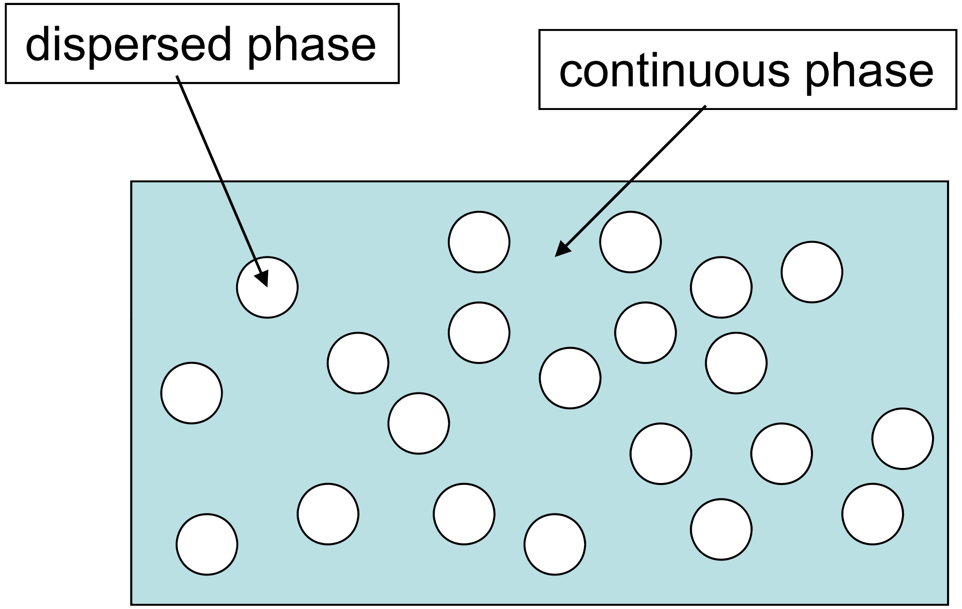
Physics and Chemistry of Interfaces
by HansJürgen Butt, Karlheinz Graf, and
Michael Kappl
Wiley VCH; 2nd edition (2006)

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



- in some cases dispersed and continuous phases can be difficult to distinguish (intervowen phases)

Types of interfaces

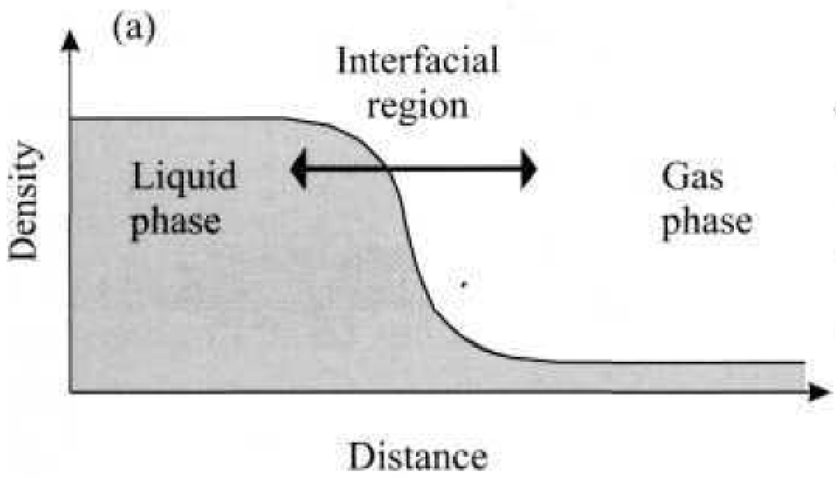
- it's possible to classify interfaces based on the nature of bulk phase.
- Gases intermix completely, so there are no gas-gas interface

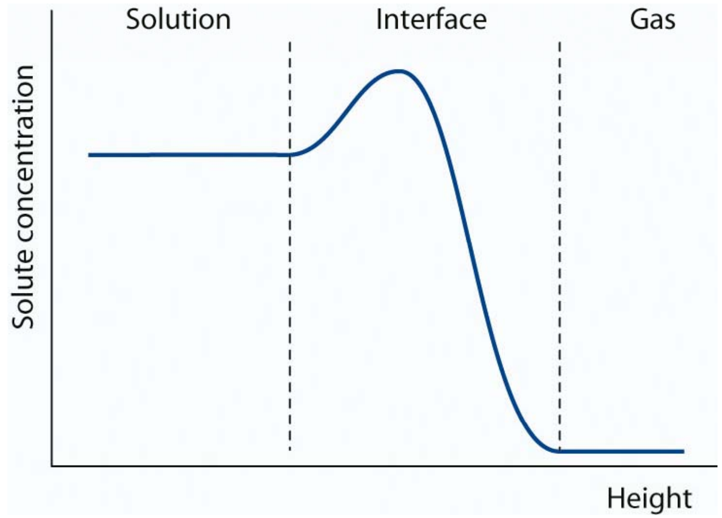
$$\text{fluid interfaces}\begin{cases}\text{gas-liquid} & \text{G-L}\\ \text{liquid1-liquid2} & L_1\text{-}L_2\end{cases}$$

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

Key concepts

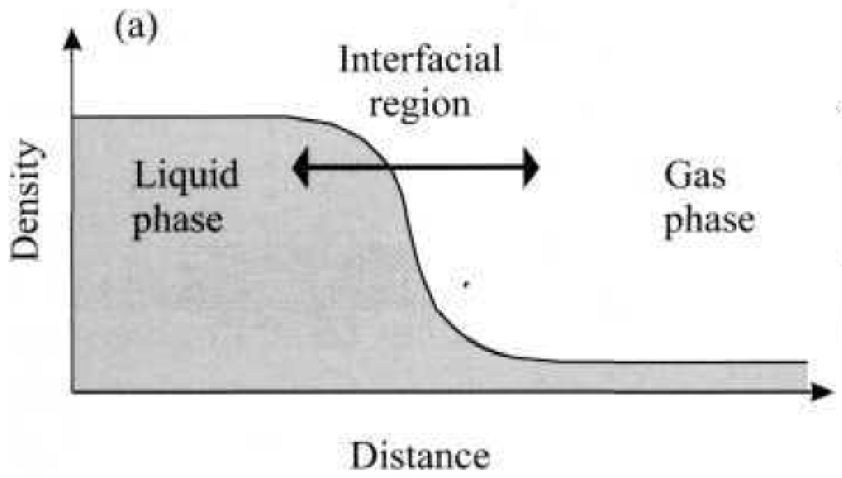
- Surface tension
- Wetting
- Adsorption
- Emulsions
- Colloids
- Membranes



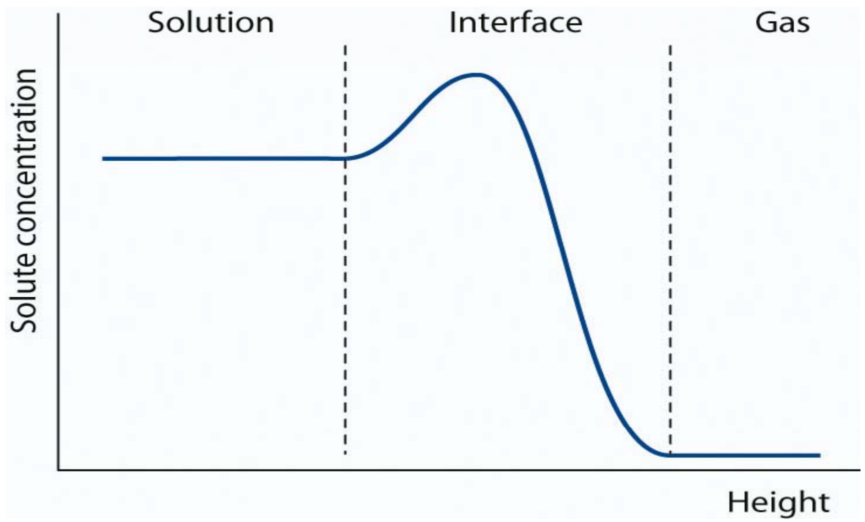


Why the surface is different

- Different density
- Different orientation of molecules (e.g. water)
- Different concentration of solutes (adsorption)



- The **thickness of the interface** will be different when defined from different viewpoints (e.g. thinner in terms density and larger in terms of adsorption)

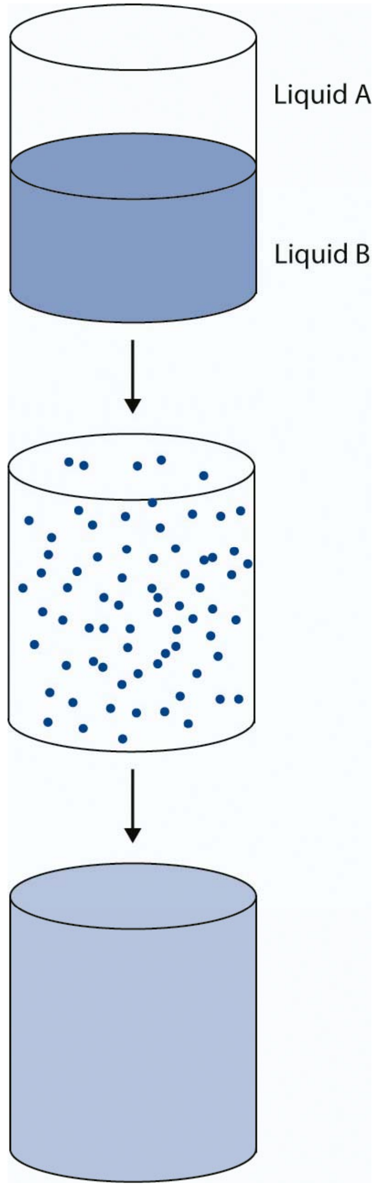


Stability of an interface

- interface can possess and extra energy, so

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

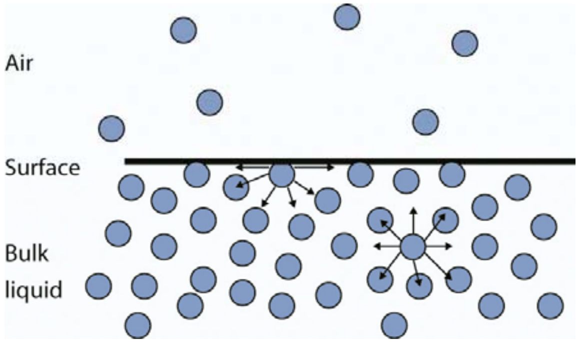
- surface tension should be positive otherwise the system is totally miscible



Surface tension

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

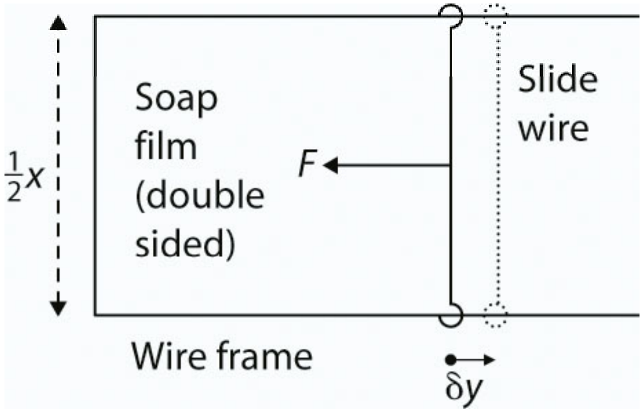
$$\gamma = \frac{F}{\delta x}$$



- Forces can be understood as a result of broken bonds when moved to a dissimilar phase.
  Rough estimate of a bond energy (Example 2.3) gives a reasonable values

- work of extension:

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

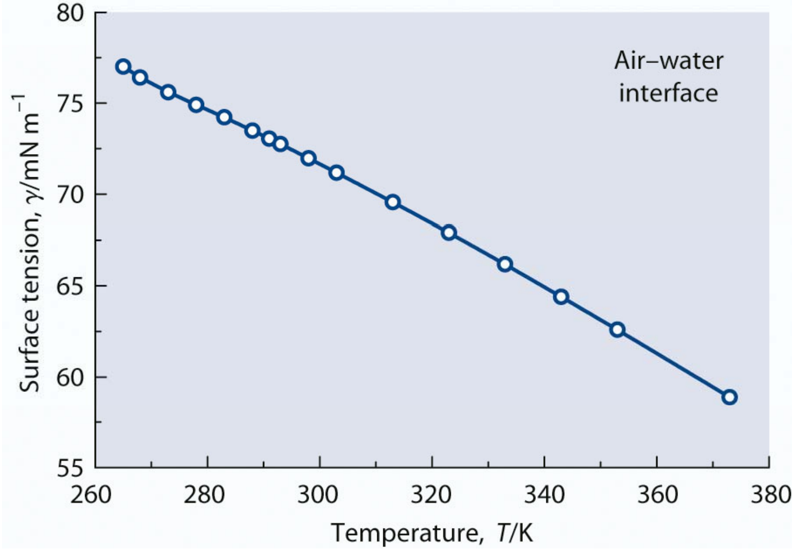


Effect of temperature on surface tension

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

- Eötvös equation:

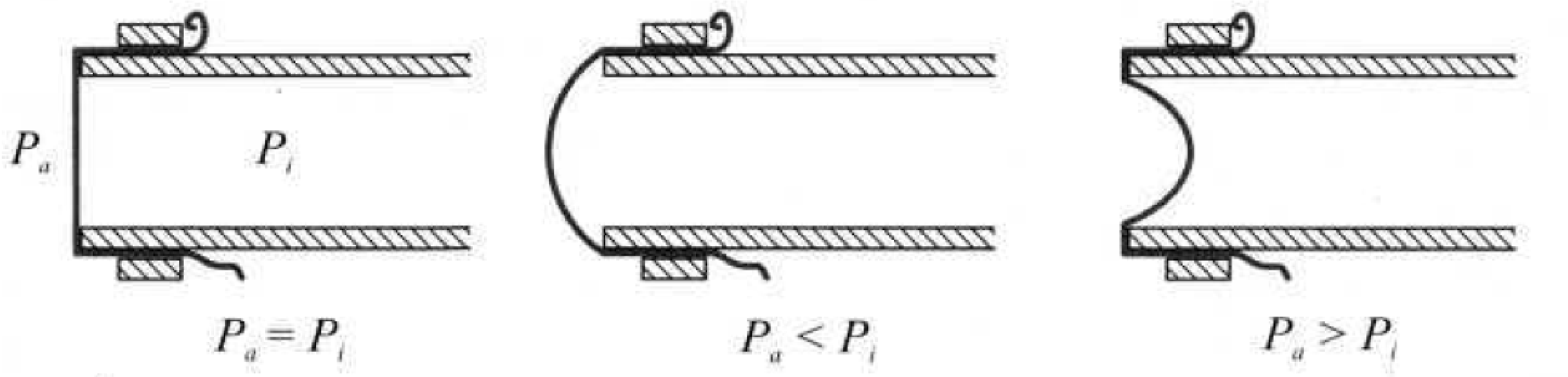
$$\frac{d\left(\gamma\left(M/\rho\right)^{2/3}\right)}{dT} = -2.12\times10^{-7}\ Jmol^{-2/3}K^{-1}$$



Young-Laplace equation

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

Example: Rubber membrane on a tube

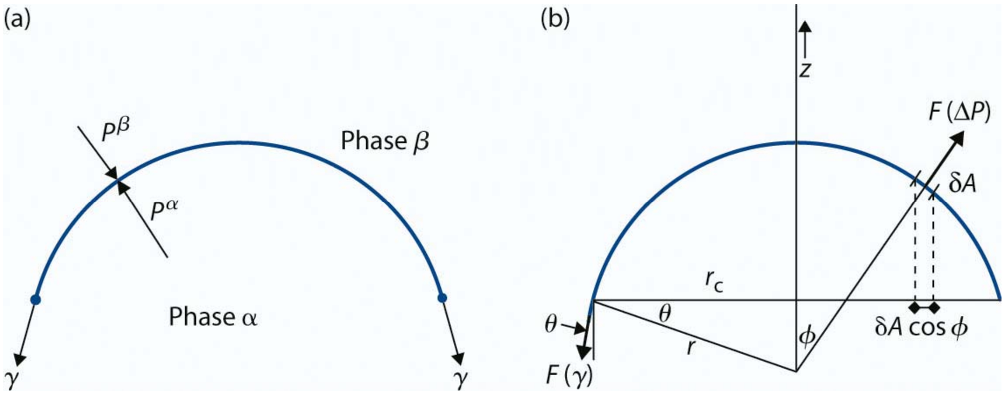


The Young-Laplace equation:

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

- If the shape of a surface is known the pressure difference can be found
- in the absence of external fields the pressure is the same everywhere so the curvature should be the constant as well
- If the pressure difference is known, the curvature can be calculated

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:

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

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

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

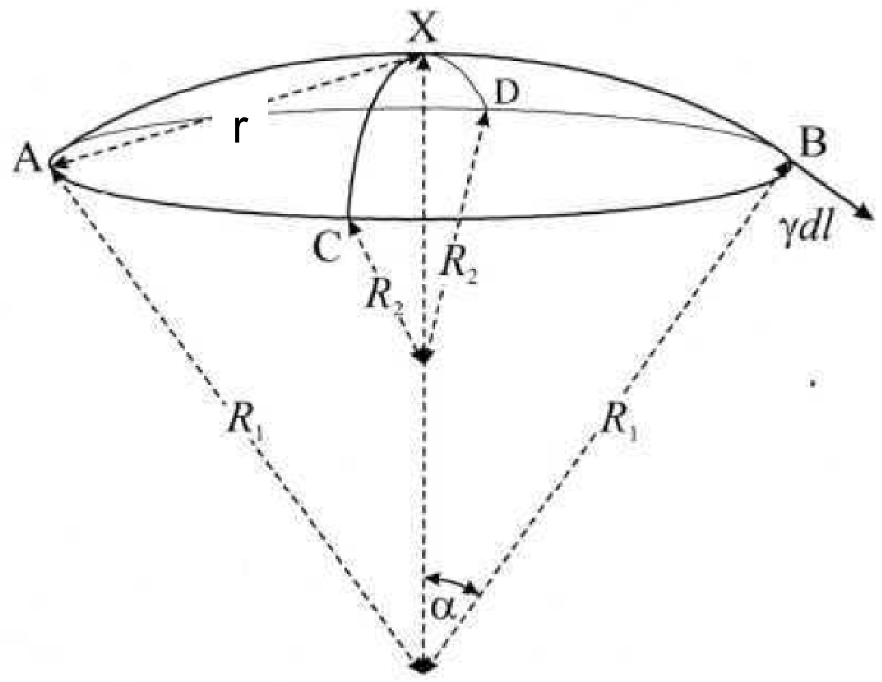
Laplace equation for spherical surface

The Laplace equation

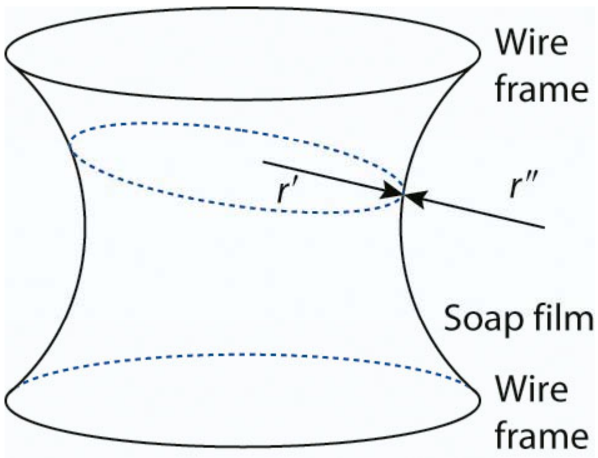
- in general case:

$$\left(P^{\alpha}-P^{\beta}\right)\pi r^{2}=\int_{0}^{\pi r/2}\gamma dl\left(\frac{2r}{R_1}+\frac{2r}{R_2}\right)$$

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



$P_1 = P_2$

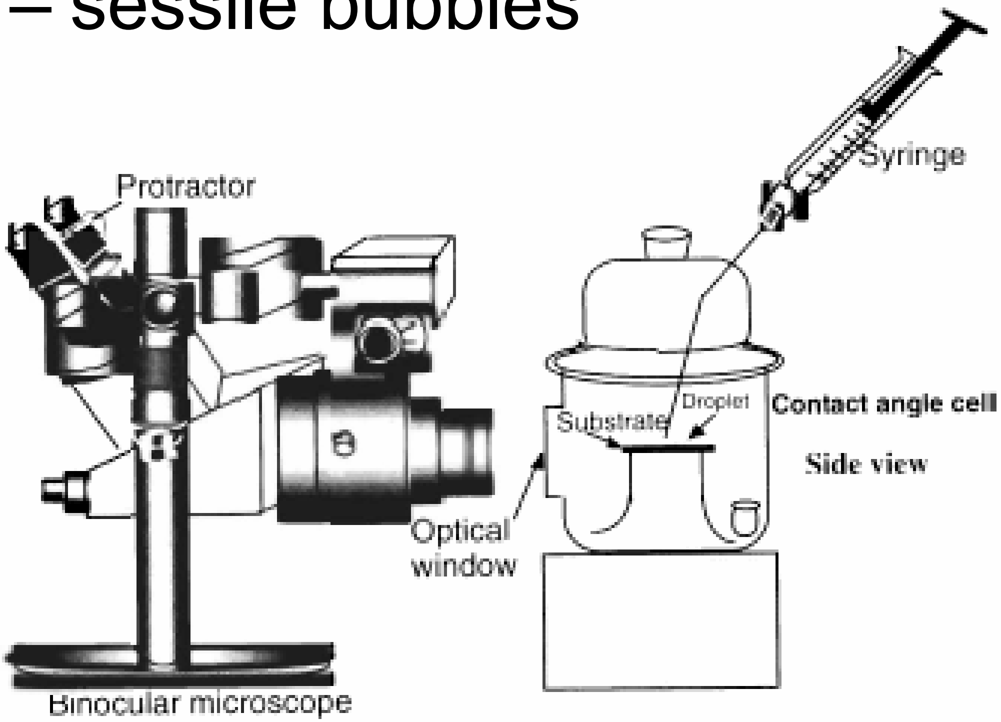


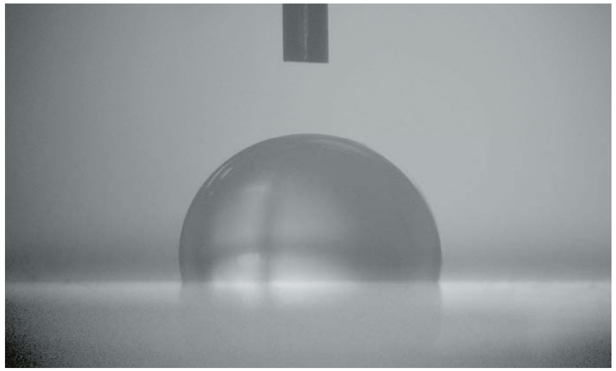
- for large structure, gravity should be taken into account:

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

Measurements of surface tension

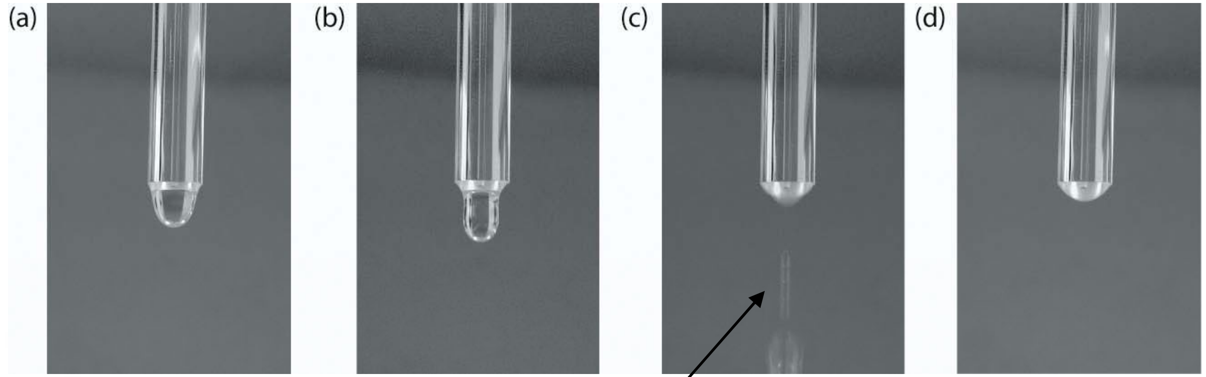
- From the shape (contour) measurements
  - – sessile drops
  - – pendent drops
  - – pendent bubbles
  - – sessile bubbles





Measurements of surface tension

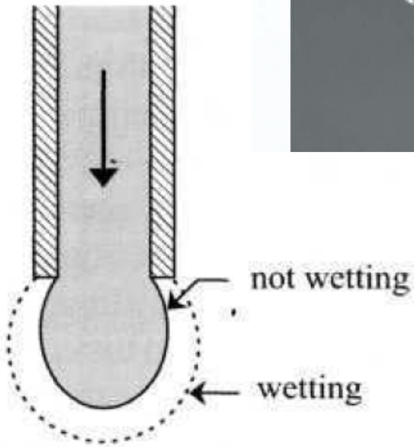
- Drop weight method

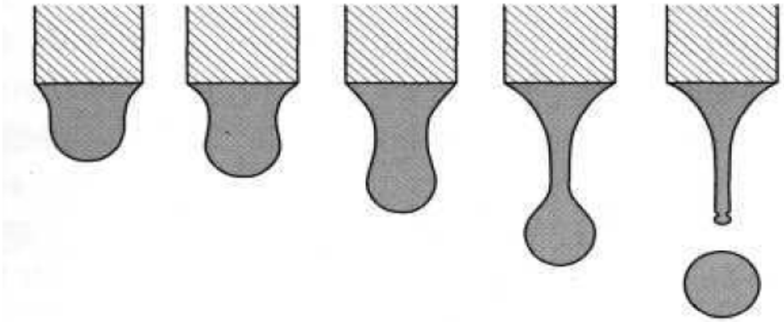


Neck formation

$$mg = 2\pi r_C \gamma$$

$$mg = 2\pi f r_C \gamma$$



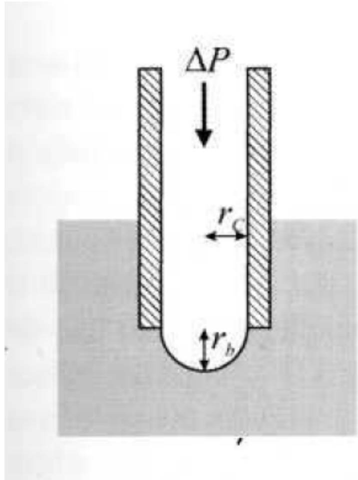


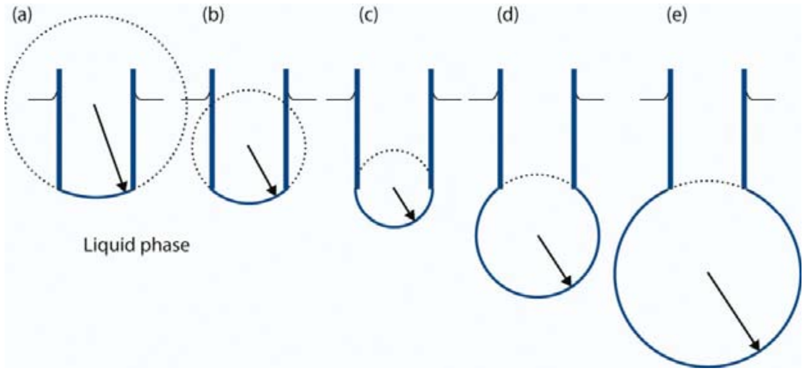
- in practice a correction factor is introduced to take inro account neck formation

Measurements of surface tension

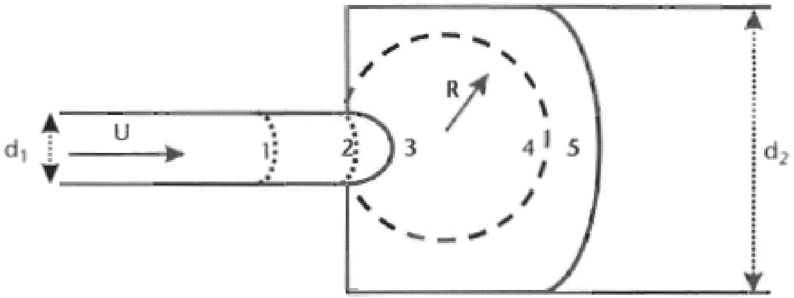
- Maximum bubble pressure

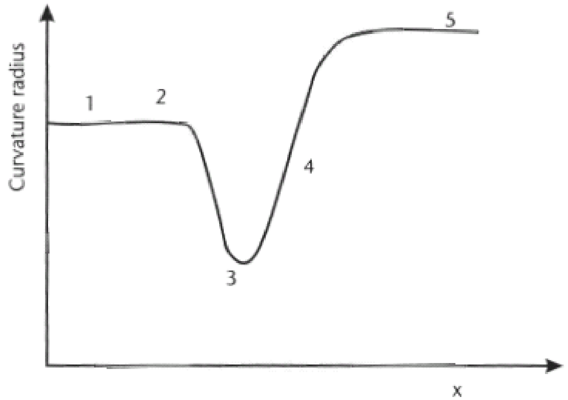
$$\gamma = r_c \Delta P / 2$$





- Valving effect in capillaries

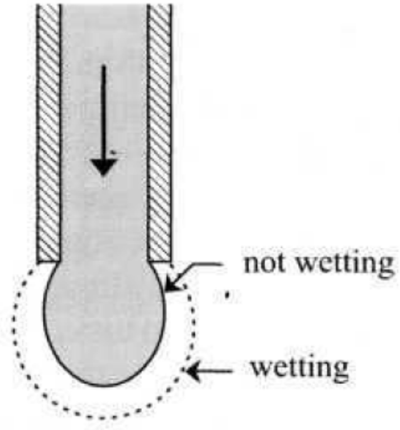




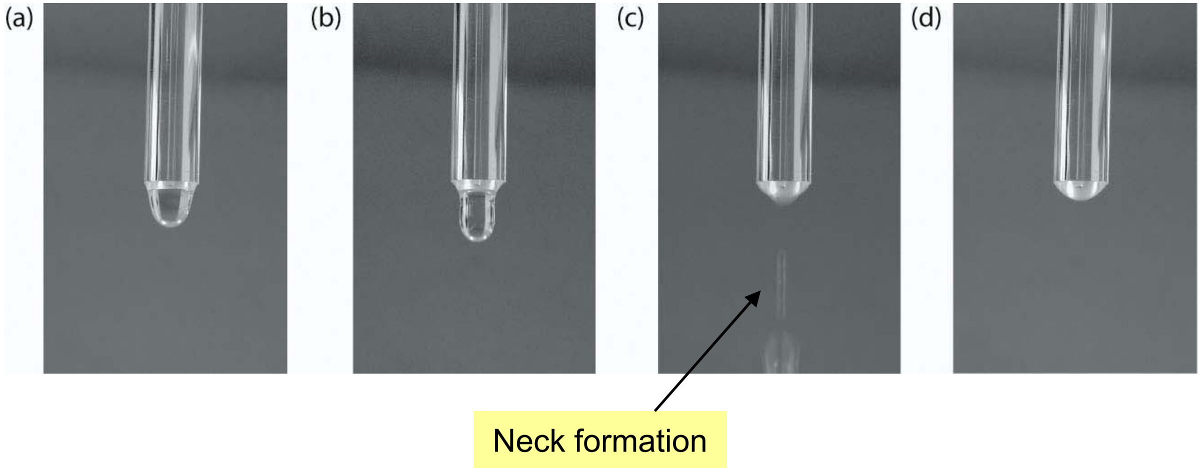
$$\Delta P_1 = \frac{-4\gamma \cos\theta}{d_1} \qquad \Delta P_1 = \frac{-4\gamma}{d_1} \qquad \Delta P_1 = \frac{-4\gamma \cos\theta}{d_2}$$

Measurements of surface tension

- Drop weight (pendent droplet)



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

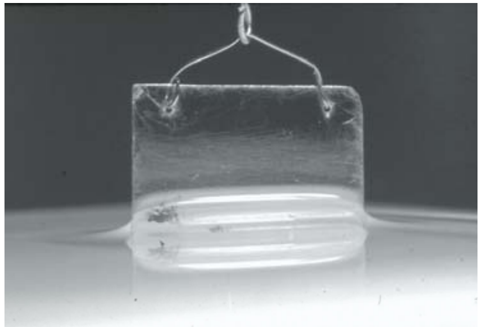


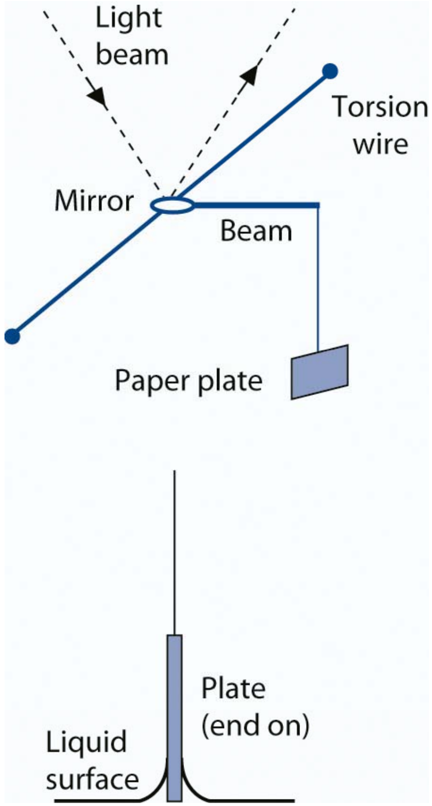
  - Correction factor required due to neck formation

Measurements of surface tension

- Wilhelmy plate:

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

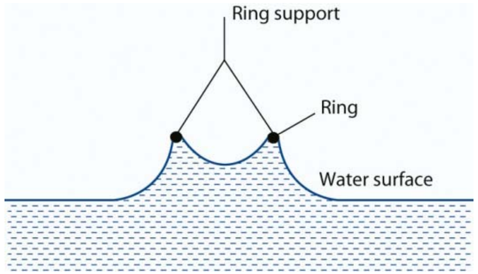


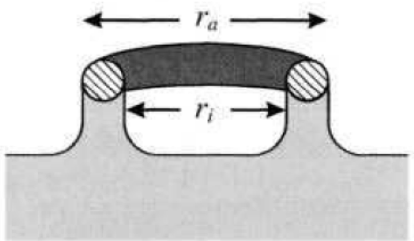


in the past was mainly measured on **roughened mica, etched glass** etc. Currently **paper plates** (i.e. filter paper) is the material of choice

- du Noüy ring:

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



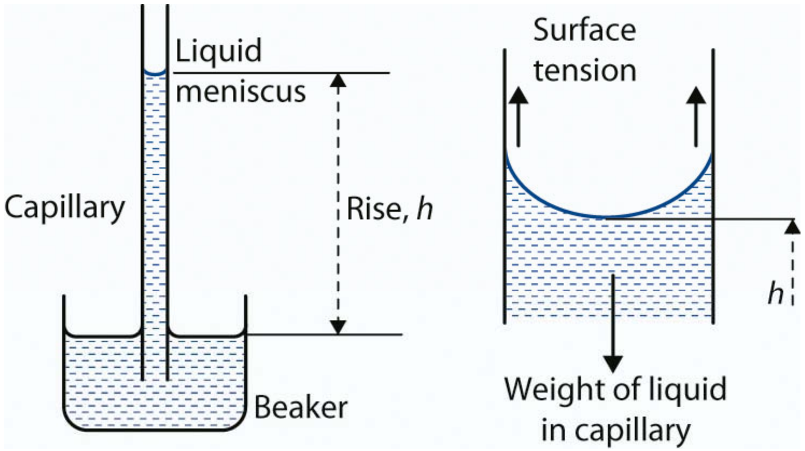


Measurements of surface tension

- 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

- Dynamic methods: relaxation of an elliptic liquid jet.

The Kelvin equation

- vapour pressure above a droplet

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

Kelvin equation

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

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

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

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

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

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

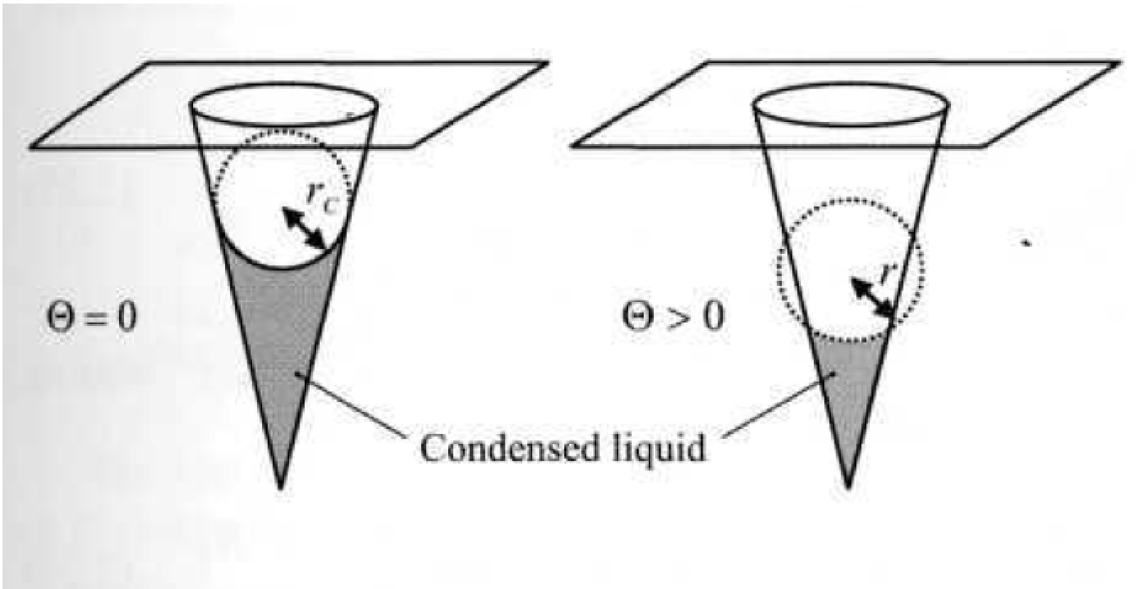
$$RT\ln\left(\frac{p^c}{p^\infty}\right) = \frac{\gamma \bar{V}^L}{RT}\frac{2}{r_m}$$

Consequences of Kelvin equation

- smaller droplets will have higher vapour pressure and therefore evaporate faster
- small droplets have higher chemical potential
- small bubbles have lower vapour pressure
- 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)**

Capillary condensation

- condensation in a capillary (e.g. in a porous materials) will happen below the dew point



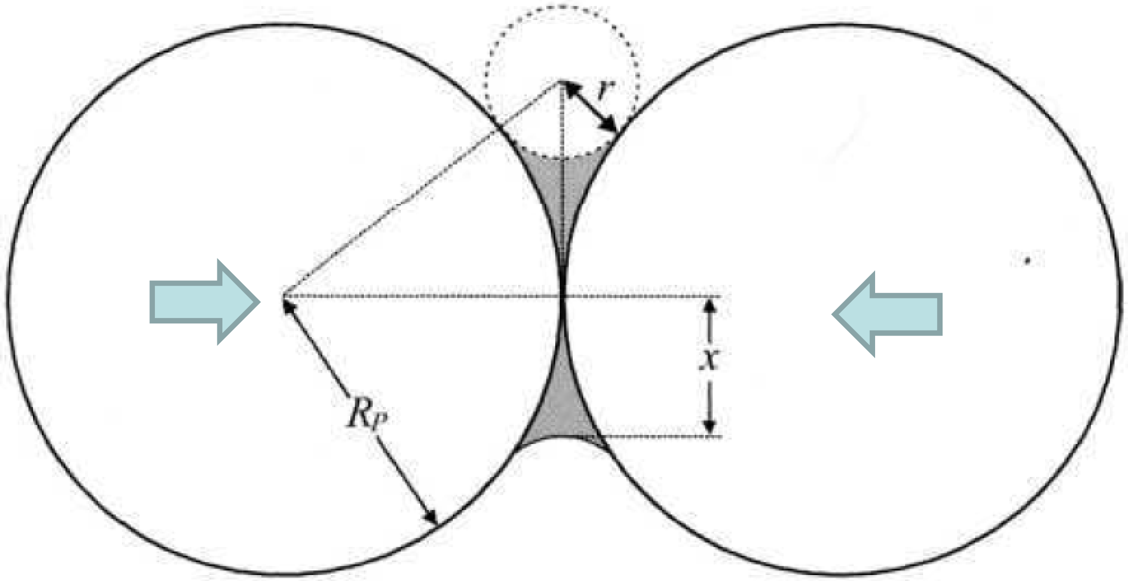
$$RT \ln\left(\frac{P_0^{\,k}}{P_0}\right) = -\frac{2\gamma V_m}{r_C}$$

in the case of contact angle Θ

$$r = r_C / \cos\Theta$$

Capillary adhesion of fine particles

- capillary condensation will cause adhesion between particles in a powder:



$$F = \pi x^2 \cdot \gamma \left(\frac{1}{x} - \frac{1}{r} \right) \approx -\pi x^2 \cdot \gamma \frac{1}{r}$$

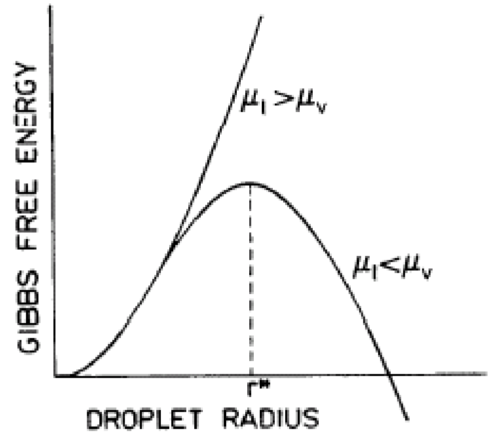
$$\left(R_p + r\right)^2 = \left(x + r\right)^2 + R_p{}^2; \;\; 2rR_p = x^2 + 2xr \approx x^2$$

$$\Rightarrow \quad F \approx -2\pi R_P \gamma$$

- the force is independent on the vapour pressure and curvature radius: their effect is mutually compensated!

Nucleation theory

- Homogeneous nucleation: nucleation in the absence of an external surface.
- As a phase transformation requires formation of an interface, the change of Gibbs free energy is:



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

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

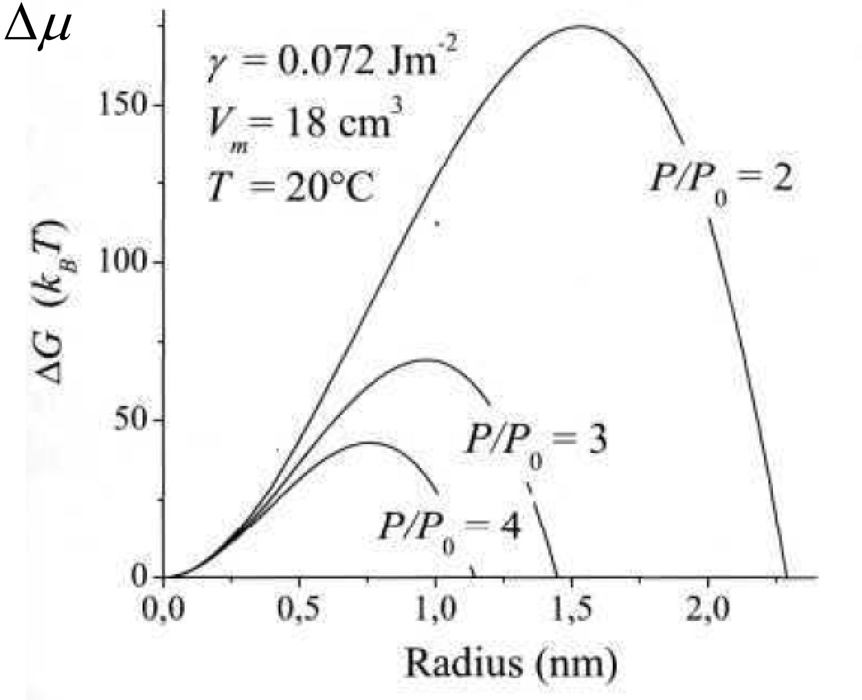
- In the case of vapour condensation:

$$\mu_V = \mu_0 + RT\ln P \qquad \mu_L = \mu_0 + RT\ln P_0^k$$

$$\Delta\mu = RT\ln\left(P_0^k/P\right)$$

$$\Delta G = -\frac{4\pi r^3}{3V_m}RT\ln\left(P_0^k/P\right) + 4\pi r^2\gamma$$

$$r^* = \frac{2\gamma V_m}{RT\ln\left(P_0^k/P\right)}$$



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