

● types:  $\underbrace{l/g \quad l/l}_{\text{mobile}} \quad s/g \quad s/l \quad s/s$

$$\text{sphere surface} = 4\pi r^2$$

**Example.** Estimate the percentage of water molecules on the surface of a fog droplet of diameter 200 nm (optical microscope visibility limit)?

%  $\uparrow$

The smaller particle, the more pronounced surface phenomena

## Interfacial energy

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

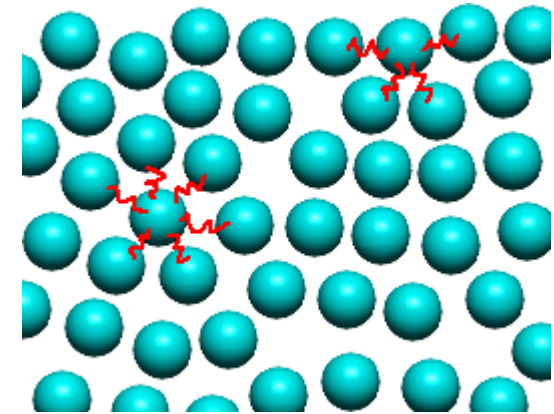
liquids: interfacial energy = surface tension

$$dG = dW_{\text{interface}} = \gamma d\mathcal{A} \stackrel{l/l, l/g}{=} \gamma l dx$$

Often denoted  $\sigma$ .

**Units:**  $\text{J m}^{-2} = \text{N m}^{-1}$ , CGS:  $\text{dyn cm}^{-1} = \text{mN m}^{-1}$

● Interfacial energy of a crystal depends on the direction (crystal plane)



surface molecules  
have higher energy

## Order-of-magnitude estimates:

Typical molecule–molecule separation =  $r = \left(\frac{V_m}{N_A}\right)^{1/3}$

Energy of neighboring molecules:  $u$

Number of neighbors in the bulk:  $N_{\text{bulk}}$

Number of neighbors at surface:  $N_{\text{surf}}$

Vaporization internal energy:  $\Delta_{\text{vap}}U_m = N_{\text{bulk}}uN_A/2$

Area per one surface molecule:  $\mathcal{A} = r^2$

Surface energy of one molecule:  $u_p = (N_{\text{bulk}} - N_{\text{surf}})u/2$

Surface tension:  $\gamma = u_p/\mathcal{A} = (N_{\text{bulk}} - N_{\text{surf}})u/(2\mathcal{A})$

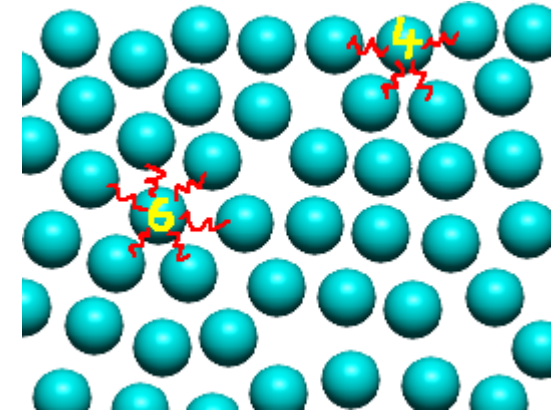
$$\Rightarrow \gamma \approx \frac{\Delta_{\text{vap}}U_m(N_{\text{bulk}} - N_{\text{surf}})}{V_m^{2/3} N_A^{1/3} N_{\text{bulk}}} \quad (\text{Stefan's rule})$$

**Example.** Water (25 °C):

$N_{\text{bulk}} \approx 4$ ,  $N_{\text{surf}} \approx 3$ ,  $\Delta_{\text{vap}}H_m = 40.65 \text{ kJ mol}^{-1}$ ,  $V_m = 18 \text{ cm}^3 \text{ mol}^{-1}$

$$\gamma \approx \frac{(40650 - 298 \times 8.314) \text{ J mol}^{-1} \times (4 - 3)}{(18 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})^{2/3} \times (6.022 \times 10^{23} \text{ mol}^{-1})^{1/3} \times 4} = 0.165 \text{ N m}^{-1}$$

Experiment:  $\gamma = 0.072 \text{ N m}^{-1}$



# Temperature dependence

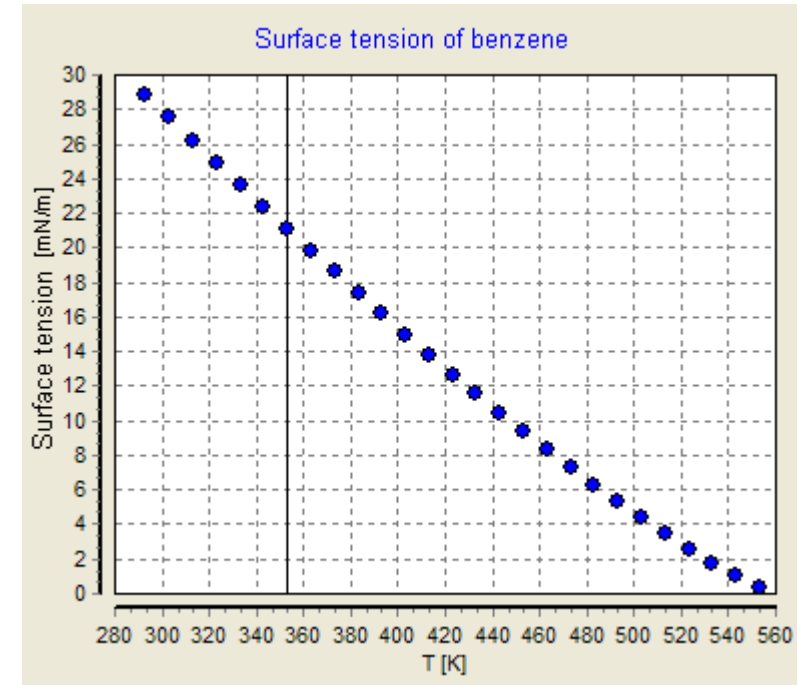
At saturated pressure, or (at lower  $T$ ) at constant pressure

In the critical point:  $\Delta_{\text{vap}}H(T_c) = \Delta_{\text{vap}}U(T_c) = 0$

If  $\Delta_{\text{vap}}H \propto T_c - T$  (inaccurate)

$$\Rightarrow \gamma = \text{const} \cdot \frac{T_c - T}{V_m^{2/3}} \quad (\text{Eötvös})$$

The surface tension decreases with increasing temperature. It limits to zero at the critical point.



credit: wikipedia

Empirical correction (Ramay and Shields)

$$\gamma = \text{const} \cdot \frac{T_c - 6 \text{ K} - T}{V_m^{2/3}}$$

Using the critical exponent (Guggenheim-Katayama, van der Waals)

$$\gamma = \text{const} \cdot (T - T_c)^{11/9}$$

**Pressure in a droplet** of radius  $r$  (Young–Laplace):

Soap bubble has two surfaces!

$$\Delta p = p_{\text{inside}} - p_{\text{outside}} = \frac{2\gamma}{r} \quad \text{generally } \gamma \left( \frac{1}{R_x} + \frac{1}{R_y} \right) \quad \text{where } R_x \text{ a } R_y \text{ are the main radii of curvature}$$

**Derivation 1** from the surface energy vs. volume dependence:

work needed to increase the surface by  $d\mathcal{A}$  is  $dW_{\text{surf}} = \gamma d\mathcal{A}$

work needed to swell the drop by  $dV$  is  $dW_{\text{vol}} = \Delta p dV$

$$dW_{\text{vol}} = dW_{\text{surf}} \Rightarrow \Delta p = \frac{\gamma d\mathcal{A}}{dV} = \frac{\gamma d(4\pi r^2)}{d(\frac{4}{3}\pi r^3)} = \frac{\gamma 8\pi r dr}{4\pi r^2 dr} = \frac{2\gamma}{r}$$

**Derivation 2** from the force  $F$  acting on the cross section area  $\mathcal{A}_\circ$ :

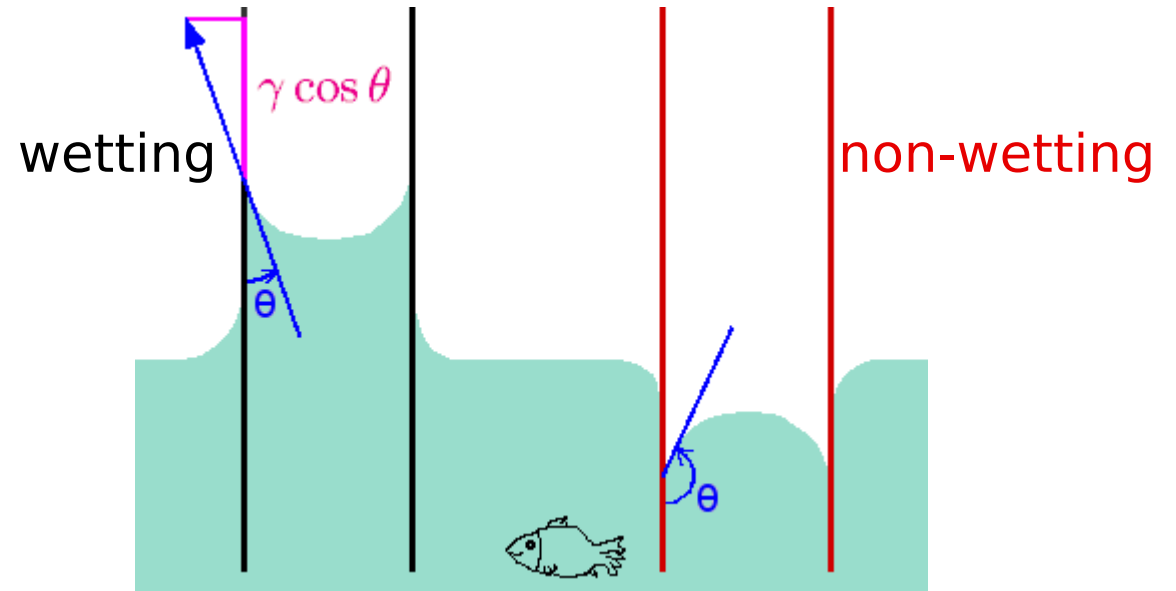
$$\text{circumference} = l = 2\pi r, \quad F = l\gamma, \quad \mathcal{A}_\circ = \pi r^2, \quad \Delta p = F/\mathcal{A}_\circ$$

## Capillary action

in a capillary of radius  $r$

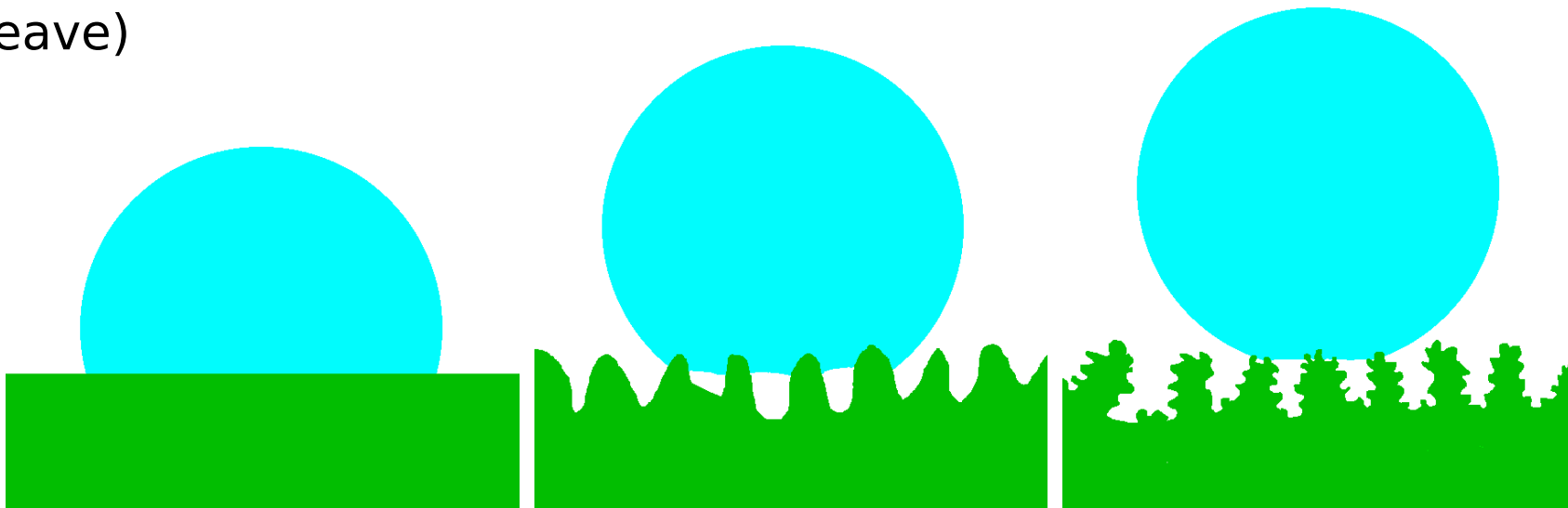
$$h = \frac{\cos \theta 2\pi r \gamma}{\pi r^2 \rho g} = \frac{2\gamma \cos \theta}{r \rho g}$$

$\theta =$  **contact angle**

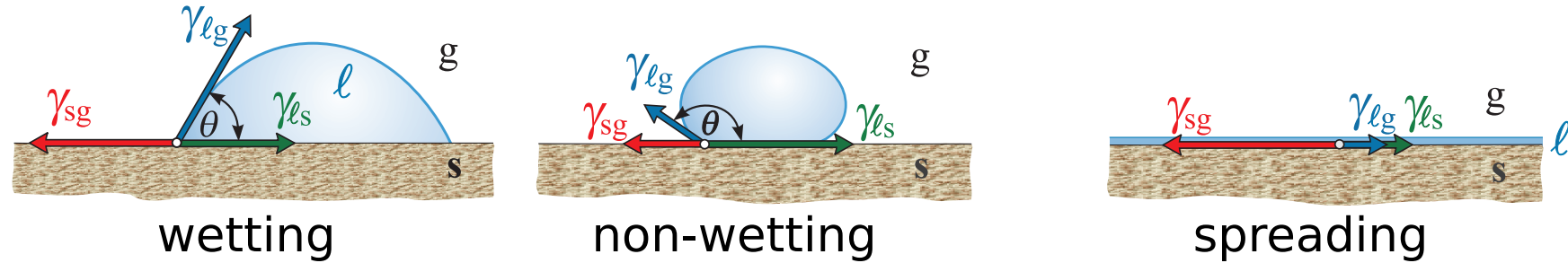


● hydrophilic (lyophilic) surface:  $\theta < 90^\circ$  (water–glass)

● hydrophobic (lyophobic) surface:  $\theta > 90^\circ$  (mercury–glass, water–teflon, water–lotus leave)



On a solid:

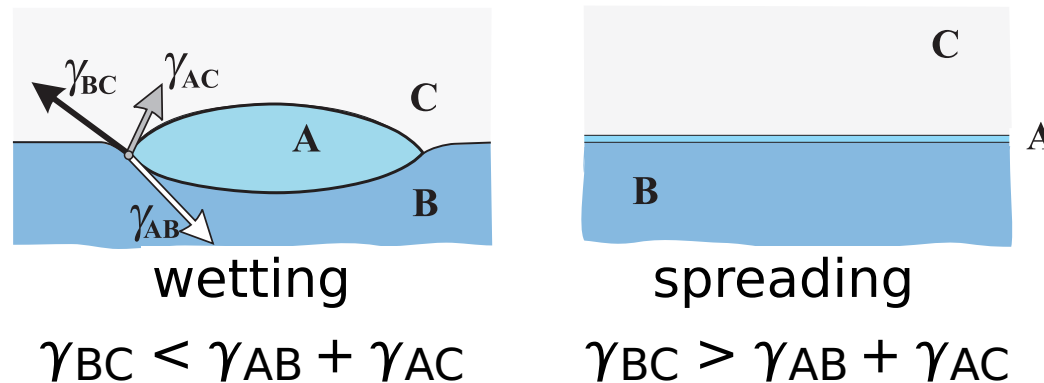


**Young equation:** vector sum of interfacial tensions = 0

$$\gamma_{sg} = \gamma_{ls} + \gamma_{lg} \cos \theta$$

**Spreading:**  $\gamma_{sg} > \gamma_{ls} + \gamma_{lg}$  ( $\gamma_{sg} - \gamma_{ls} - \gamma_{lg} > 0$ )

**Liquid droplet on liquid:**



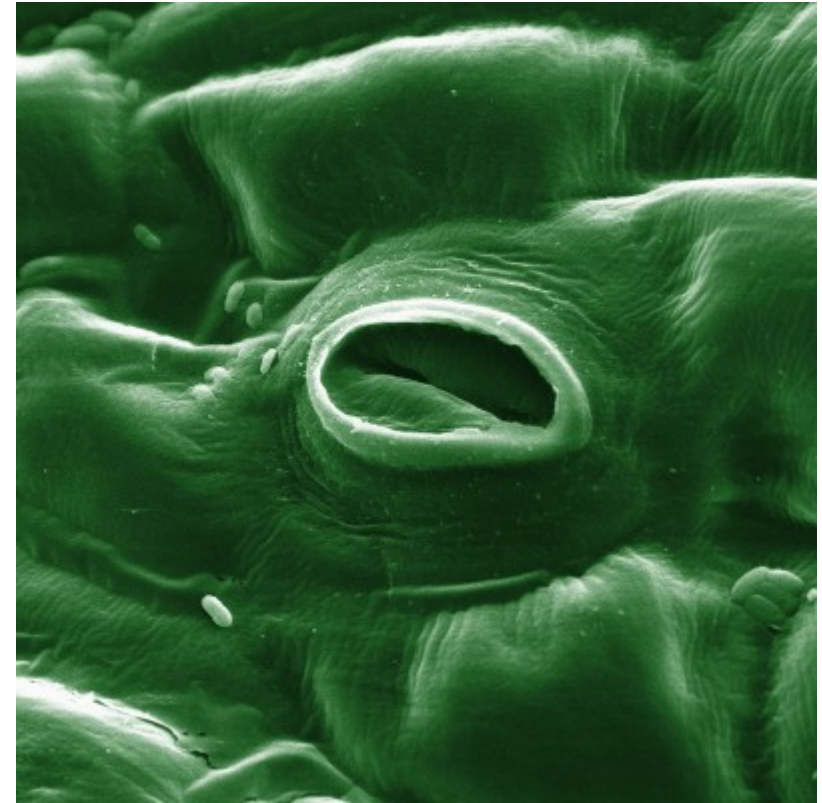
**Methods of calculation:** balance of forces, energy minimum

**Example.** Calculate the maximum size of pores (stomata, sg. stoma) in the leaves of 10 m high trees. Water surface tension is  $\gamma = 72 \text{ mN m}^{-1}$ . (Ignore osmotic pressure.)

$$\omega r l \gamma = \rho$$

**Example.** Calculate the thickness of a mercury puddle on a flat non-wetting surface.  $\gamma = 0.485 \text{ N m}^{-1}$ ,  $\rho = 13.6 \text{ g cm}^{-3}$ .

$$\omega \omega \gamma = \rho$$



credit: wikipedia [SEM image]



“puddle” of spilled crude oil on water



credit: <http://hubpages.com/hub/Negative-Side-Of-Compact-Flourescent-Bulbs-CFLs>



**Example.** Estimate the typical size (volume) for which the surface forces are of the same order as gravitational forces.

$$[\rho] = \text{kg m}^{-3}, [\gamma] = \text{N m}^{-1} = \text{kg s}^{-2}, [g] = \text{m s}^{-2}$$

$$m = \sqrt{\frac{\text{kg s}^{-2}}{\text{m s}^{-2} \cdot \text{kg m}^{-3}}} \Rightarrow l \sim \sqrt{\frac{\gamma}{g\rho}}, V \sim \left(\frac{\gamma}{g\rho}\right)^{3/2}$$

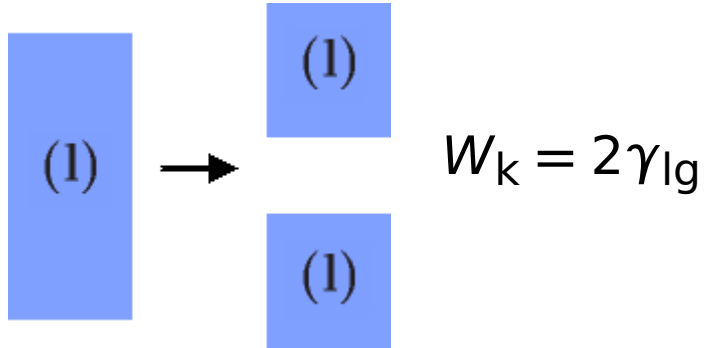
for water  $V \approx 0.02 \text{ cm}^3 \approx$  droplet volume (0.02–0.05  $\text{cm}^3$ )

Slowest surface waves:  $\lambda = 2\pi\sqrt{\frac{\gamma}{g\rho}}$

$l$  is called capillary length

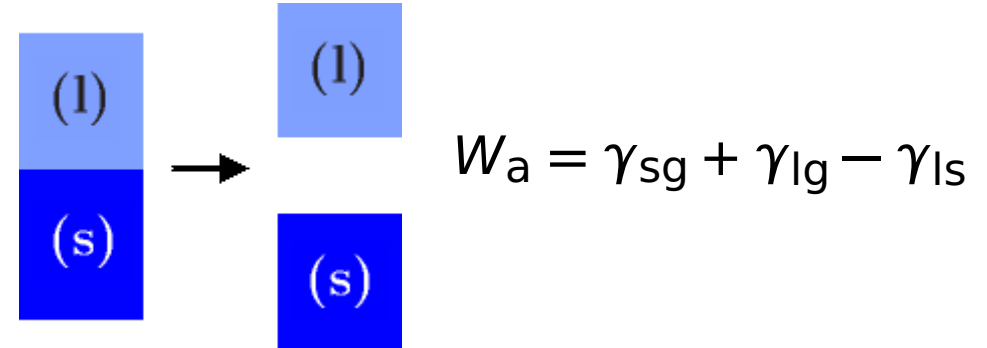


Cohesion work (energy)  $W_k$  (per unit area of the interface, here  $l/l$ )



the same for  $s/s$

Adhesion work (energy)  $W_a$  (per unit area of the interface, here  $l/s$ )



the same for  $l_1/l_2$ ,  $s_1/s_2$

**Spreading:** interface  $s/l$  created at the expense of  $l/l$ :

Cohesion work  $l/l = W_k = 2\gamma_{lg} \ominus$

Adhesion work  $s/l = W_a = \gamma_{sg} + \gamma_{lg} - \gamma_{ls} \oplus$



**Harkins spreading coefficient:**

$$S_{l/s} = W_a - W_k = \gamma_{sg} - \gamma_{ls} - \gamma_{lg}$$

$S_{l/s} > 0 \Rightarrow$  energy is gained  $\Rightarrow$  liquid spreads

NB sign:  $W_a =$  energy needed to unstick

# Chemical potential of a droplet

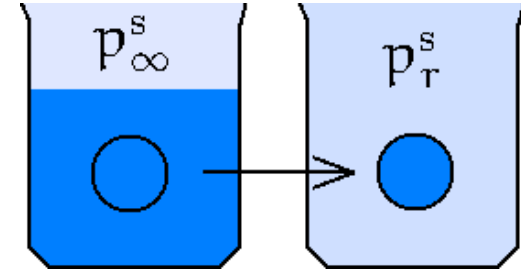
Transfer (1 mol) of liquid from the bulk (below a flat interface,  $r = \infty$ ) to droplets of diameter  $r$ . Pressure increases by  $\Delta p = 2\gamma/r$  and the chemical potential by

$$\Delta\mu = \mu_r^{(l)} - \mu_\infty^{(l)} = V_m^{(l)}\Delta p = V_m^{(l)}\frac{2\gamma}{r}$$

Liquid is in equilibrium with vapor ( $\mu_\infty^{(l)} = \mu^\circ$ ):

$$\mu_\infty^{(l)} = \mu^{(g)}(p_\infty^s) = \mu^\circ + RT \ln \frac{p_\infty^s}{p^{st}}$$

$$\mu_r^{(l)} = \mu_\infty^{(l)} + \Delta\mu = \mu^{(g)}(p_r^s) = \mu^\circ + RT \ln \frac{p_r^s}{p^{st}}$$



$$\left(\frac{\partial\mu}{\partial p}\right)_T = V_m^{(l)}$$

$\Rightarrow$  **Kelvin equation**  $\ln \frac{p_r^s}{p_\infty^s} = \frac{2\gamma V_m^{(l)}}{RT r}$  (also Gibbs–Thomson or Ostwald–Freundlich)

$\Rightarrow$  saturated vapor pressure **higher above a droplet / lower in a cavity**

**Example.** Saturated vapor pressure of water at 25 °C is 3.15 kPa. Calculate the partial pressure of water above a membrane of pore diameters 100 nm.  $\gamma_{\text{water}} = 72 \text{ mN m}^{-1}$ .

complete wetting: 3.08 kPa, non-wetting: 3.22 kPa

# Nucleation

Supersaturated vapor ( $p > p_{\infty}^S$  or  $T < T_{\text{boil}}$ ), supersaturated solution ( $c > c_{\infty}^S$ ), superheated liquid ( $T > T_{\text{boil}}$ ), etc., are **metastable**, beyond the spinodal **unstable** (cf. spinodal decomposition)

**Nucleation** = creation of nuclei of a new (stable) phase in a metastable region. A Gibbs energy barrier must be crossed.

Mechanism of nucleation:

- homogeneous (wet air:  $S \gtrsim 4$ )
- heterogeneous on dirt, surface (wet air:  $S \gtrsim 1.02$ )  
on ions (wet air:  $S \gtrsim 1.25$ )

Saturation  
 $S = p/p_{\infty}^S$

Homogeneous nucleation by the Kelvin equation (CNT, classical nucleation theory):  
 A nucleus grows for  $p > p_r^S \Rightarrow$  minimum radius of the nucleus:

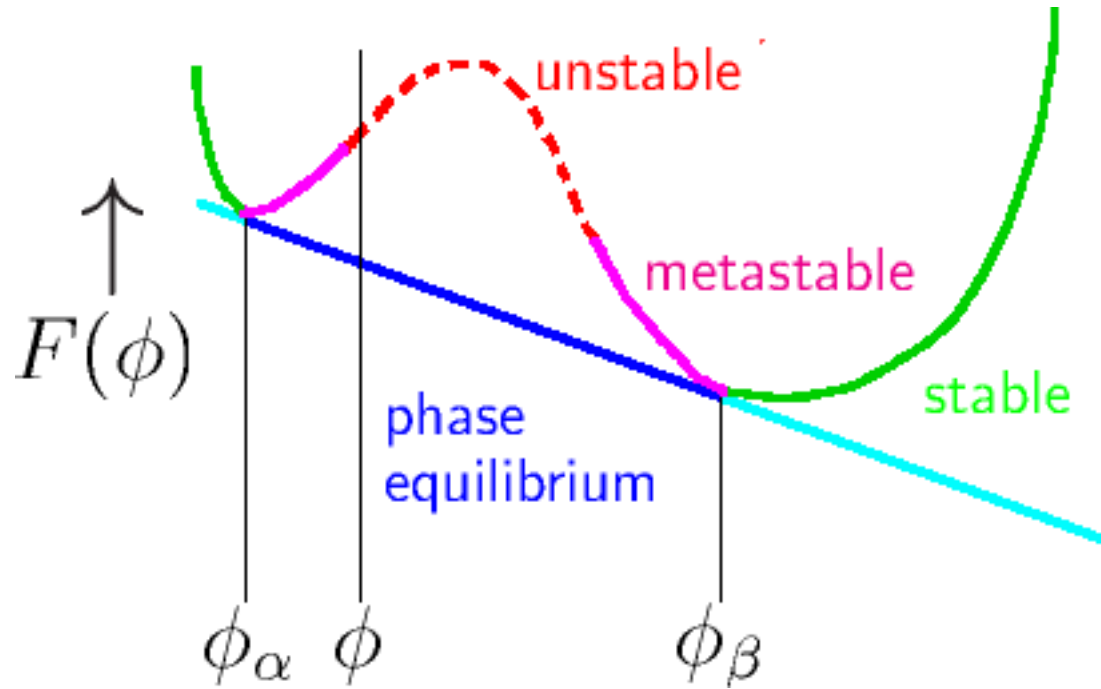
$$r^* = \frac{2\gamma V_m}{RT \ln S}$$

- distillation – boiling chips (stones) to prevent overheating
- bubble chambers to detect ionized radiation (obsolete)

# Spinodal decomposition

= spontaneous split of an unstable phase into two phases. There is no barrier.

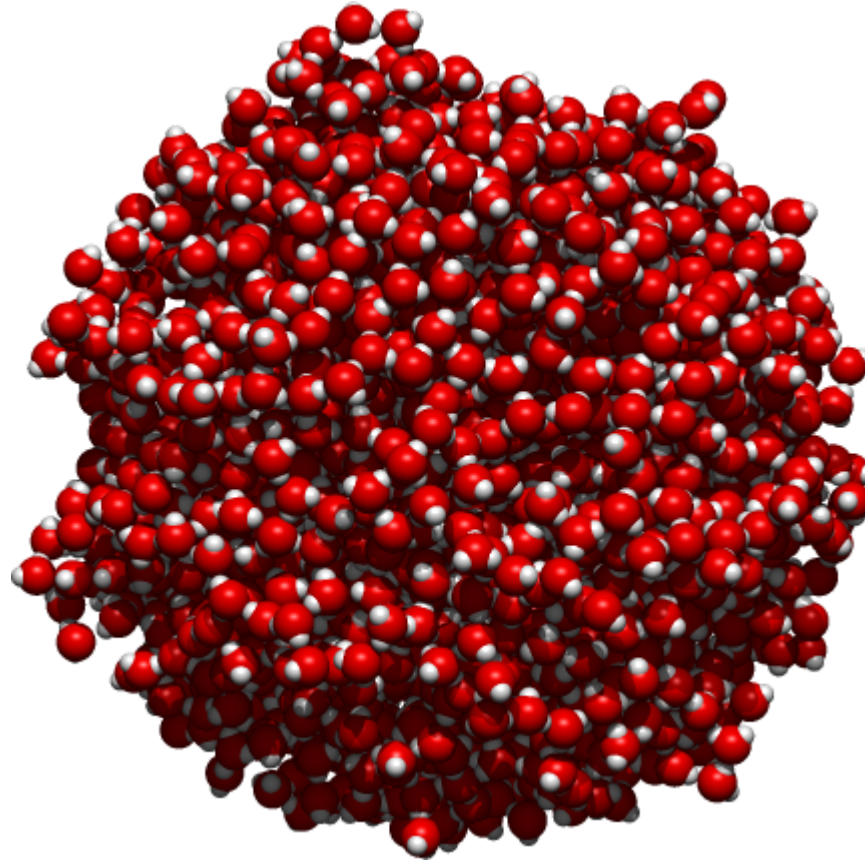
Helmholtz energy or Gibbs energy as a function of composition:



## Example: critical nucleus size

Calculate the critical nucleus size for humid (150% rel. humidity) air at 25°C.  $\gamma = 72 \text{ mN m}^{-1}$ .

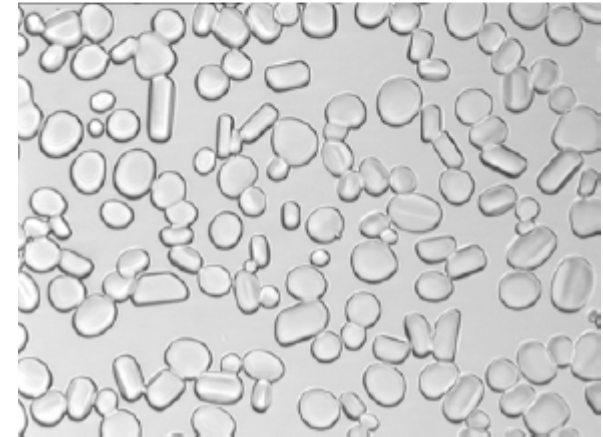
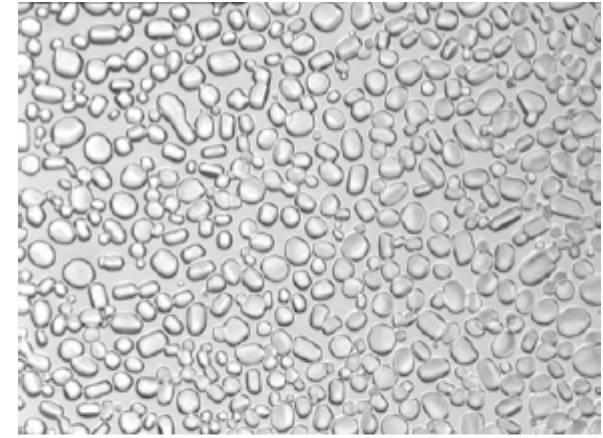
$$r_* = 2.6 \times 10^{-9} \text{ m (2400 molecules)}$$



Higher saturated pressure above small droplets  $\Rightarrow$  small droplets evaporate, big ones grow.

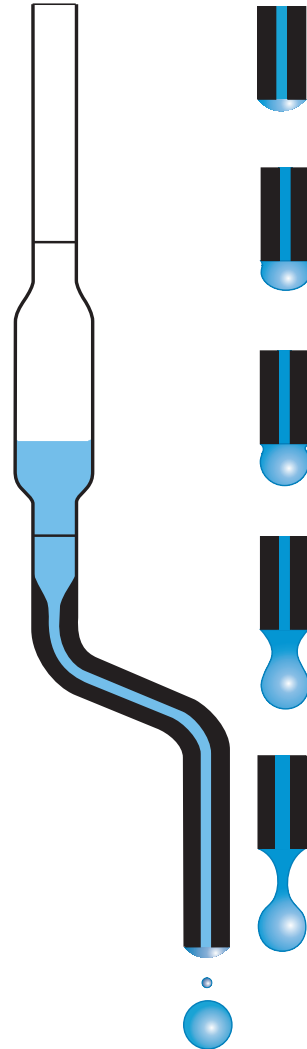
Higher concentration above small crystals  $\Rightarrow$  small crystals dissolve, large crystals grow.

- precipitate ageing (digestion)  $\Rightarrow$  bigger crystals  $\Rightarrow$  can be filtered
- snow quality change
- ice cream becomes crunchy
- fog  $\rightarrow$  drizzle

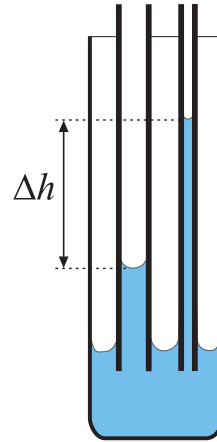


credit: [http://soft-matter.seas.harvard.edu/index.php/Ostwald\\_ripening](http://soft-matter.seas.harvard.edu/index.php/Ostwald_ripening), Clarke(2003)

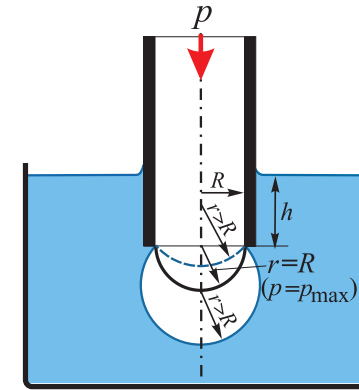
stalagmometrická metoda



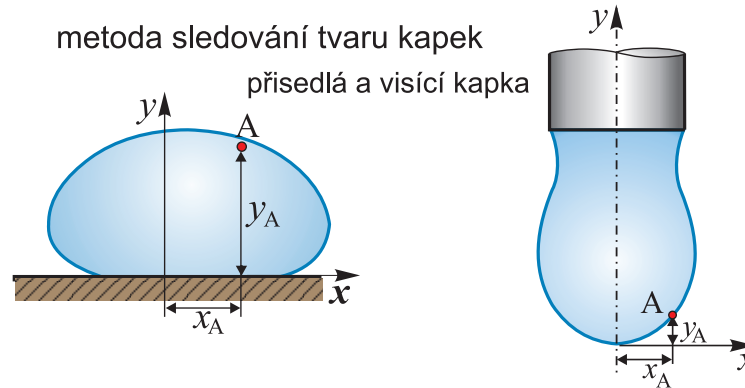
kapilární metoda



metoda maximálního tlaku v bublině v bublině



metoda sledování tvaru kapek  
přisedlá a visící kapka



metoda odtrhování prstence

