Interfaces and interfacial energy

● types: l/g l/l s/g s/l s/s
  └ mobile

sphere surface $= 4\pi r^2$

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

1 %

The smaller particle, the more pronounced surface phenomena

Interfacial energy

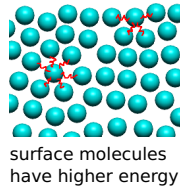$$\gamma = \left(\frac{\partial G}{\partial \mathcal{A}}\right)_{T,p}$$

liquids: interfacial energy = surface tension

$$dG = đW_{interface} = \gamma d\mathcal{A} \overset{l/l, l/g}{=} \gamma \ell dx$$

Often denoted σ.

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

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

surface molecules have higher energy

Surface energy and vaporization enthalpy

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_{bulk}
Number of neighbors at surface: N_{surf}

Vaporization internal energy: $\Delta_{vap}U_m = N_{bulk}uN_A/2$
Area per one surface molecule: $\mathcal{A} = r^2$
Surface energy of one molecule: $u_p = (N_{bulk} - N_{surf})u/2$
Surface tension: $\gamma = u_p/\mathcal{A} = (N_{bulk} - N_{surf})u/(2\mathcal{A})$

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

Example. Water (25 °C):
$N_{bulk} \approx 4$, $N_{surf} \approx 3$, $\Delta_{vap}H_m = 40.65\, kJ\, mol^{-1}$, $V_m = 18\, cm^3\, mol^{-1}$

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

Experiment: $\gamma = 0.072\, N\, m^{-1}$
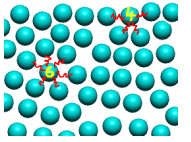
Temperature dependence
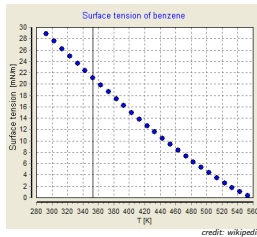
At saturated pressure, or (at lower T) at constant pressure

In the critical point: $\Delta_{vap}H(T_c) = \Delta_{vap}U(T_c) = 0$
If $\Delta_{vap}H \propto T_c - T$ (inaccurate)

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

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

Empirical correction (Ramay and Shields)

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

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

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

Surface tension of benzene

credit: wikipedia

Laplace pressure

Soap bubble has two surfaces!

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

$$\Delta p = p_{inside} - p_{outside} = \frac{2\gamma}{r} \overset{generally}{=} \gamma\left(\frac{1}{R_x} + \frac{1}{R_y}\right)$$ where R_x a R_y 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 $đW_{surf} = \gamma d\mathcal{A}$
work needed to swell the drop by dV is $đW_{vol} = \Delta p dV$

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

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

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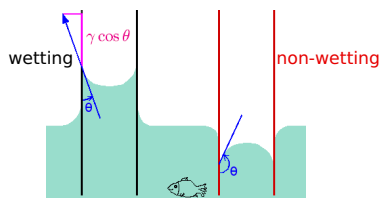
Capillary action

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**

wetting $\qquad$ $\gamma\cos\theta$ $\qquad$ non-wetting

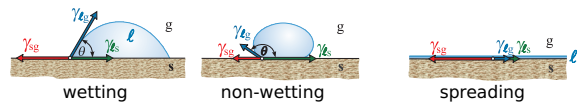● hydrophilic (lyophilic) surface: $\theta < 90°$ (water–glass)

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

Young equation and spreading

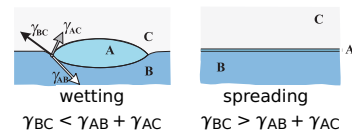On a solid:

wetting $\qquad$ non-wetting $\qquad$ spreading

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:

wetting $\qquad$ spreading
$\gamma_{BC} < \gamma_{AB} + \gamma_{AC}$ $\qquad$ $\gamma_{BC} > \gamma_{AB} + \gamma_{AC}$
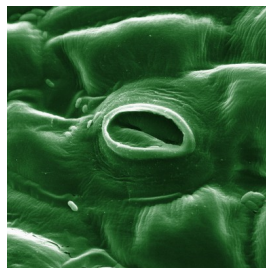
Surface tension

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 $\gamma = 72\, mN\, m^{-1}$. (Ignore osmotic pressure.)

$d = 2.9\ \mu m$

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

3.8 mm

"puddle" of spilled crude oil on water

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

credit: wikipedia [SEM image]

Using units

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

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

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

for water $V \approx 0.02\, cm^3 \approx$ droplet volume (0.02–0.05 cm^3)
Slowest surface waves: $\lambda = 2\pi\sqrt{\frac{\gamma}{g\rho}}$

l is called capillary length

Cohesion and adhesion work

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

$W_k = 2\gamma_{lg}$

the same for s/s

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

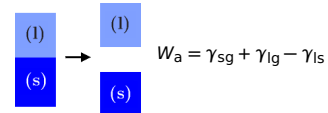$W_a = \gamma_{sg} + \gamma_{lg} - \gamma_{ls}$

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 = $W_k = 2\gamma_{lg}$ ⊖
Adhesion work s/l = $W_a = \gamma_{sg} + \gamma_{lg} - \gamma_{ls}$ ⊕

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

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

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

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

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

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

$\Rightarrow$ **Kelvin equation** $\boxed{\ln\frac{p_r^s}{p_\infty^s} = \pm\frac{2\gamma V_m^{(l)}}{RTr}}$ (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. $\gamma_{water} = 72$ mN m^{-1}.

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

Nucleation

Supersaturated vapor ($p > p_\infty^s$ or $T < T_{boil}$), supersaturated solution ($c > c_\infty^s$), superheated liquid ($T > T_{boil}$), 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:

$$r^* = \frac{2\gamma V_m}{RT}\frac{1}{\ln S}$$

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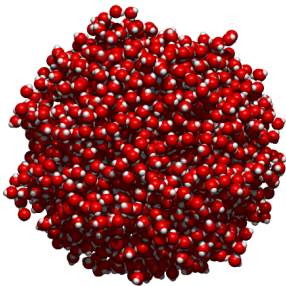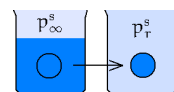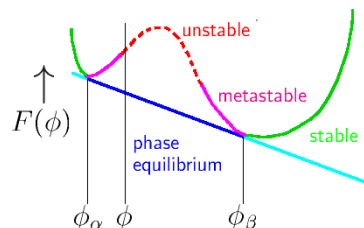
⬤ bubble chambers to detect ionized radiation (obsolete)

Spinodal decomposition

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

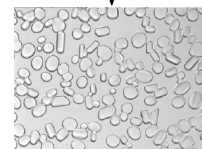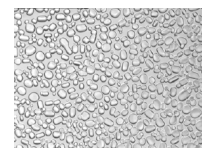Helmholtz energy or Gibbs energy as a function of composition:

Example: critical nucleus size

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

$r^* = 2.6\times10^{-9}$ m (2400 molecules)

Ostwald ripening

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

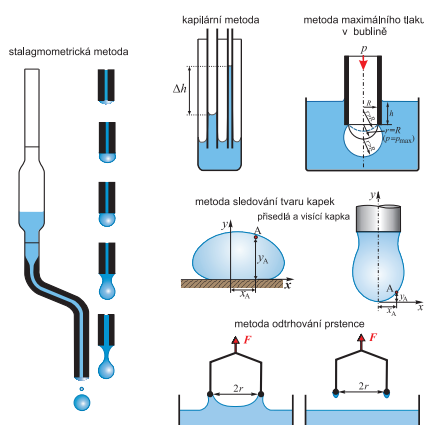Higher concentration above small crystals $\Rightarrow$ small crystals dissolve, large crystals grow.

⬤ precipitate ageing (digestion) $\Rightarrow$ bigger crystals $\Rightarrow$ can be filtered

⬤ snow quality change

⬤ ice cream becomes crunchy

⬤ fog → drizzle

credit: http://soft-matter.seas.harvard.edu/
index.php/Ostwald_ripening, Clarke(2003)

Measuring surface tension of liquids

stalagmometrická metoda
kapilární metoda
metoda maximálního tlaku v bublině
metoda sledování tvaru kapek
přisedlá a visící kapka
metoda odtrhování prstence

credit: L. Bartovská