**Interfaces and interfacial energy**

kinds: l/g l/l s/g s/l s/s

mobile

**Example.** Estimate the percentage of water molecules on the surface of a fog droplet of diameter (i) 0.1 mm (naked eye visibility limit) (ii) 200 nm (optical microscope visibility limit)?

% I (i) % 0.002 (ii) % 0.02

The smaller particle, the more pronounced surface phenomena

**Interfacial energy**

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

liquids: interfacial energy = surface tension

\[ dG = dW_{\text{interface}} = \gamma dA \quad \text{for} \quad l/l, l/g \]

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 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: \( N_{\text{bulk}} \)

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

Vaporization internal energy: \( \Delta_{\text{vap}} U_m = N_{\text{bulk}} u N_A / 2 \)

Area per one surface molecule: \( A = r^2 \)

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

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

\[ \Rightarrow \gamma \approx \frac{\Delta_{\text{vap}} U_m (N_{\text{bulk}} - N_{\text{surf}})}{V_m^{2/3} N_A^{1/3} N_{\text{bulk}}} \] (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: $\Delta_{\text{vap}}H(T_c) = 0$, approx.:

$\Delta_{\text{vap}}H \propto T_c - T$

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

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

Empirical correction (Ramay and Shields)

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

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

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

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

$$\Delta p = p_{\text{inside}} - p_{\text{outside}} = \frac{2\gamma}{r}$$

generally $\gamma \left( \frac{1}{R_x} + \frac{1}{R_y} \right)$ where $R_x$ and $R_y$ are the main radii of curvature

**Soap bubble has two surfaces!**

Derivation 1 from the surface energy vs. volume dependence:

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

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

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

Derivation 2 from the force $F$ acting on the cross section area $A_\bigcirc$:

circumference $= l = 2\pi r$, $F = l\gamma$, $A_\bigcirc = \pi r^2$, $\Delta p = F/A_\bigcirc$
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 leaf)
Young equation and spreading

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:

Droplet: \( \gamma_{BC} < \gamma_{AB} + \gamma_{AC} \), spreading: \( \gamma_{BC} > \gamma_{AB} + \gamma_{AC} \)
**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 $\gamma = 72 \text{ mN m}^{-1}$. (Ignore osmotic pressure.)

$$d = 2.9 \text{ mm}$$

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

$$h = 3.8 \text{ mm}$$

“puddle” of spilled crude oil on water

[credit: http://hubpages.com/hub/Negative-Side-Of-Compact-Flourescent-Bulbs-CFLs] [credit: wikipedia [SEM image]]
Example. Estimate the typical size (volume) for which the surface forces are of the same order as gravitational forces.

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

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

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

Slowest surface: \( \lambda = 2\pi \sqrt{\frac{\gamma}{\rho g}} \)

\( l \) is called capillary length
Cohesion and adhesion work

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

\[ W_k = 2\gamma_{lg} \]

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

\[ W_a = \gamma_{sg} + \gamma_{lg} - \gamma_{ls} \]

the same for $s/s$

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

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

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

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

Harkins spreading coefficient:

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

\[ S_{l/s} > 0 \Rightarrow \text{energy is gained} \Rightarrow \text{liquid spreads} \]

NB sign: $W_a = \text{energy needed to unstick}$
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

\[
\Delta \mu = V_m \Delta p = V_m \frac{2\gamma}{r}
\]

Liquid is in equilibrium with vapor:

\[
\mu = \mu^\circ + RT \ln \frac{p^s_\infty}{p_{st}}
\]

\[
\mu + \Delta \mu = \mu^\circ + RT \ln \frac{p^s_r}{p_{st}}
\]

\( \Rightarrow \) Kelvin equation

\[
\ln \frac{p^s_r}{p^s_\infty} = -\frac{2\gamma V_m}{RT r}
\]

(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. \( \gamma_{\text{water}} = 72 \text{ mN m}^{-1} \).
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: \(S \approx 4\))
- heterogeneous on dirt, surface (wet air: \(S \approx 1.02\))
  on ions (wet air: \(S \approx 1.25\))

Homogeneous nucleation by the Kelvin equation (CNT, classical nucleation theory): A nucleus grows for \(p > p_\infty^S \Rightarrow \) 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.
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)
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 $\rightarrow$ drizzle

Measuring surface tension of liquids