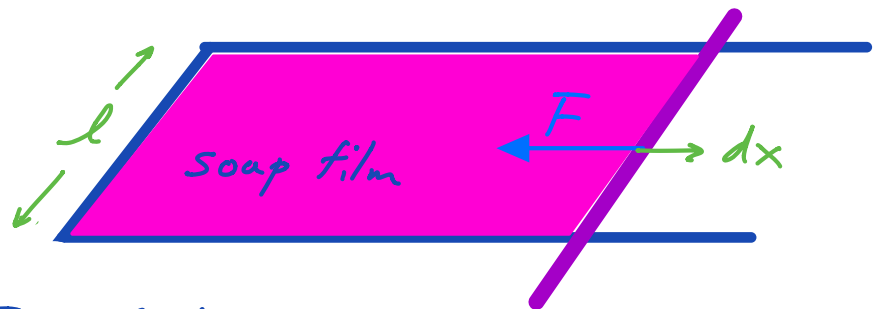


Capillary Forces

Consider a soap film on a rail

Work done by rod retraction:

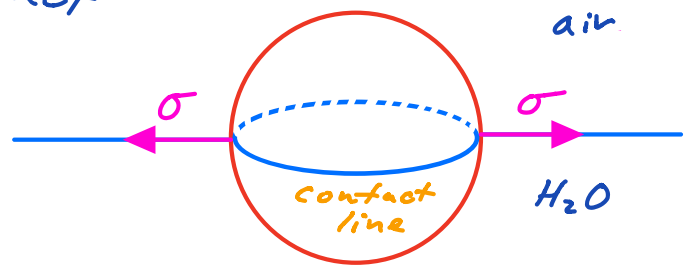


$$\delta W = F dx = 2\sigma l dx$$

↑ since film has 2 sides

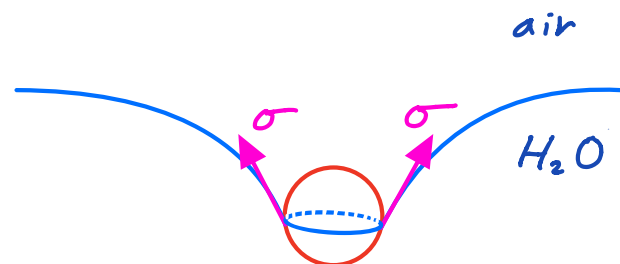
⇒ $F = 2\sigma l$ is the force acting on the rod.

More generally, for a body partially submerged in a liquid, σ is the interfacial force per unit length applied on its contact line tangent to the interface.



Note: if the body is heavy w.r.t. water, then σ will contribute to weight support

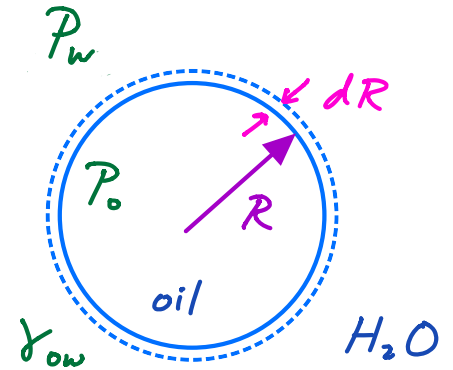
e.g. water-walking insects, floating paper clip



Laplace Pressure

Consider an oil drop in H_2O , bound by interfacial tension σ_{ow} , of radius R .

Work required to increase radius by dR :



$$\delta W = \underbrace{-P_o dV_o - P_w dV_w}_{\text{mechanical energy}} + \underbrace{\sigma_{ow} dA}_{\text{surface energy}}$$

$$\text{where } dV_o = 4\pi R^2 dR = -dV_w$$

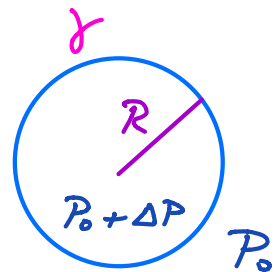
$$dA = 8\pi R dR$$

For mechanical equilibrium, $\delta W = 0$

$$\Rightarrow 0 = (-P_o + P_w) 4\pi R^2 dR + \sigma_{ow} 8\pi R dR$$

$$\Rightarrow \Delta P = P_o - P_w = \frac{2\sigma_{ow}}{R}$$

Note: 1. Pressure inside a drop/bubble is higher than that outside by an amount $\sim 2\sigma/R$

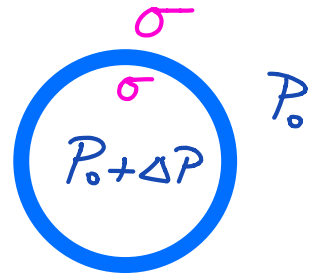


\Rightarrow smaller bubbles have higher Laplace pressure

\Rightarrow champagne is louder than beer

2. for a soap bubble, which has 2 interfaces

$$\Delta p = \frac{4\sigma}{R}$$



Some numbers:

i.) for an aerosol drop ($R \sim 1 \mu\text{m}$),
 $\Delta p \sim 1 \text{ atm}$

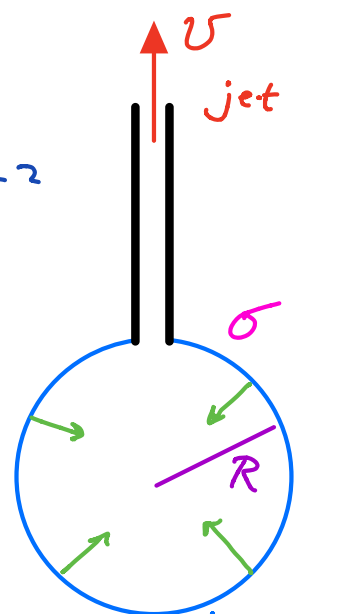
ii.) for soap bubbles ($R \sim 5 \text{ cm}$, $\sigma \sim 35 \frac{\text{dynes}}{\text{cm}}$)
 $\Rightarrow \Delta p \sim 3 \text{ Pa} \sim 3 \times 10^{-5} \text{ atm}$

iii.) for champagne bubbles: $R \sim 0.2 \text{ mm}$,
 $\sigma \sim 50 \frac{\text{dynes}}{\text{cm}}$
 $\Rightarrow \Delta p \sim 10^3 \text{ Pa} \sim 10^{-2} \text{ atm}$

Soap bubble jet: exit speed?

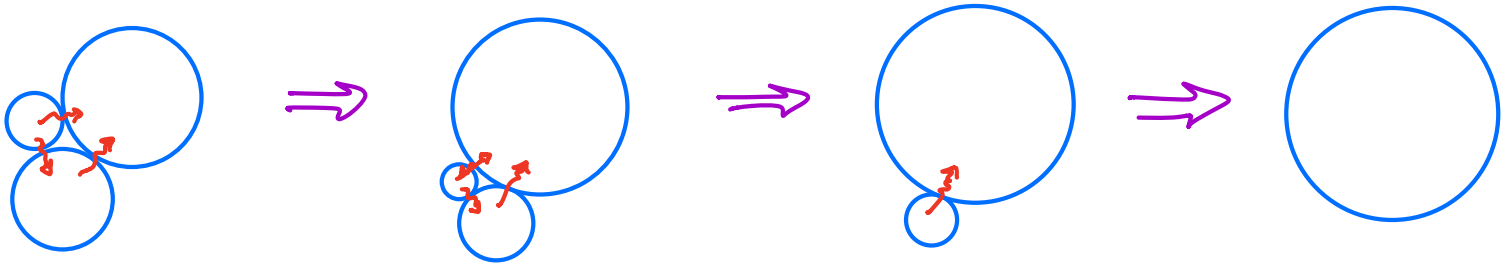
Force balance: $\Delta p = \frac{4\sigma}{R} \sim \rho_{\text{air}} v^2$

$$\Rightarrow v \sim \left(\frac{4\sigma}{\rho_{\text{air}} R} \right)^{\frac{1}{2}} \sim \left(\frac{4 \cdot 30 \frac{\text{dynes}}{\text{cm}}}{.001 \text{ g/cc} \cdot 3 \text{ cm}} \right)^{\frac{1}{2}} \sim 200 \text{ cm/s}$$



\Rightarrow high ejection speeds also arise when a drop coalesces with a bath, and a vortex is ejected.

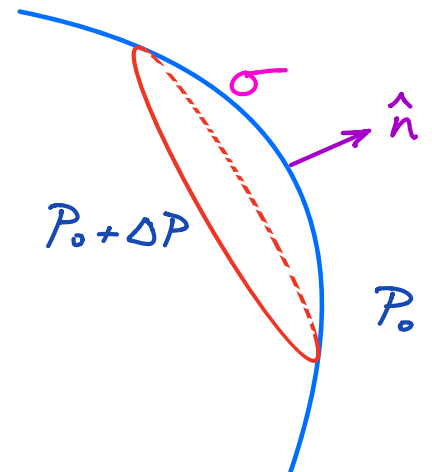
Ostwald Ripening : the coarsening of foams (or emulsions) owing to diffusion of gas across interfaces, from small to large bubbles.



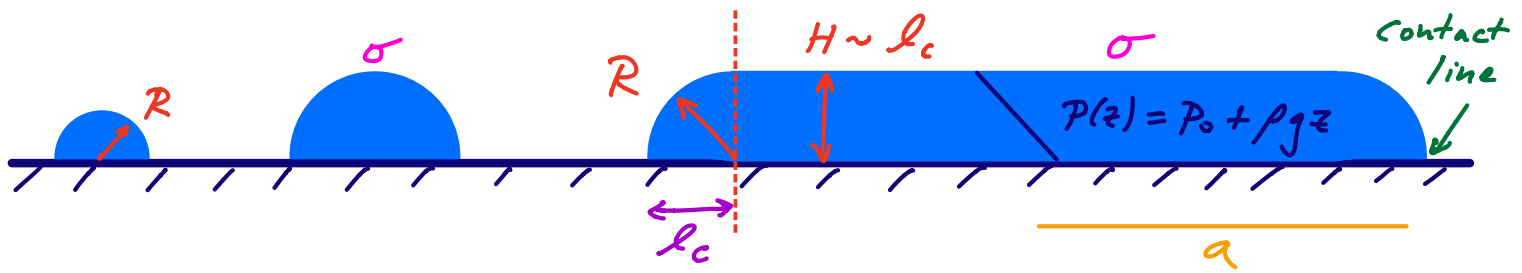
More generally, we shall see that there is a pressure jump across any curved interface :

Laplace / Curvature Pressure

$$\Delta P = \sigma \underbrace{\vec{\nabla} \cdot \hat{n}}_{\text{curvature}}$$



Puddles : what sets their size?



Laplace / Curvature pressure balances g if

$$\sigma/R > \rho g H \quad \text{but} \quad R \sim H \quad \text{for a puddle}$$

$$\Rightarrow R < l_c = \sqrt{\sigma/\rho g} = \text{capillary length}$$

\therefore Drops with $R < l_c$ remain nearly spherical

Large drops spread to a depth $H \sim l_c$, so that there is a balance at the puddle's edge between curvature and hydrostatic pressure.

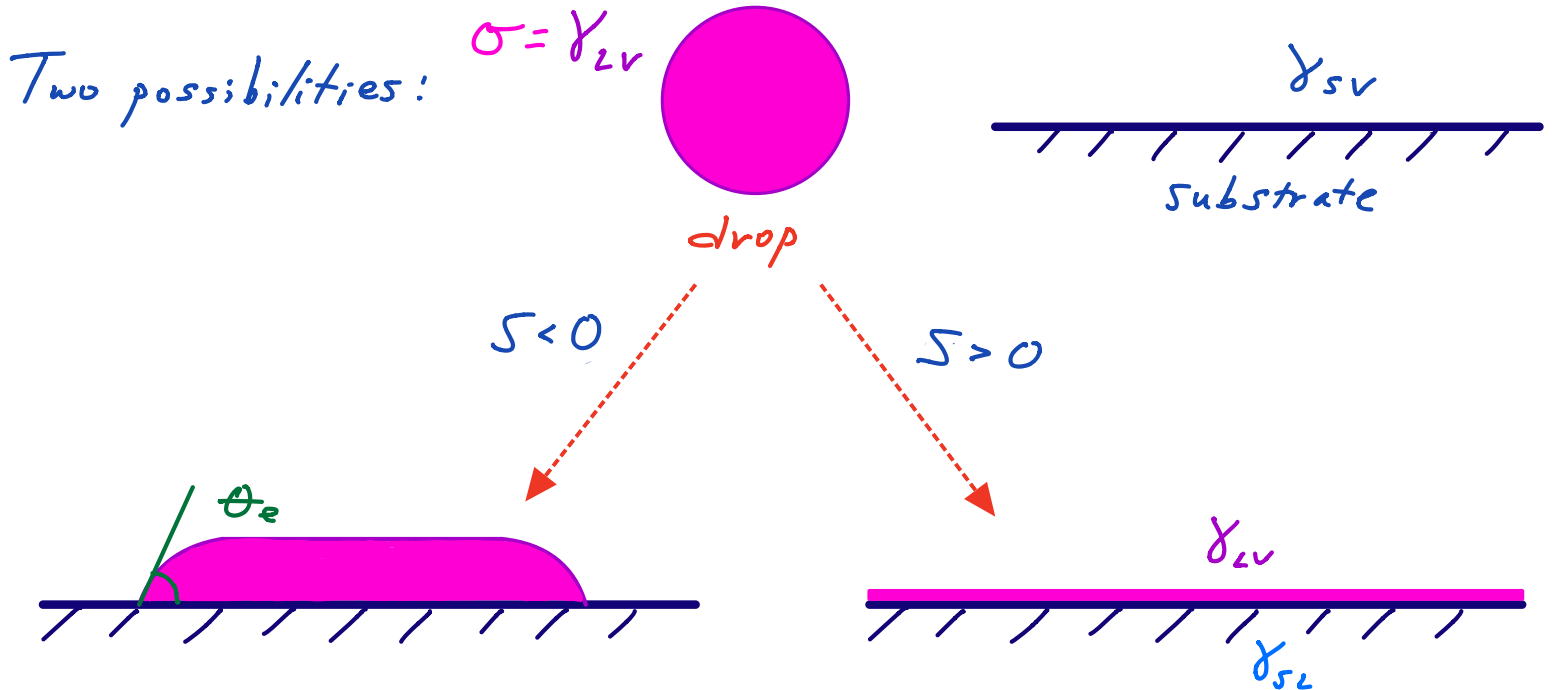
\Rightarrow for a puddle of volume V , radius a :

$$\pi a^2 l_c = V \Rightarrow a = \left(\frac{V}{\pi l_c} \right)^{\frac{1}{2}}$$

Note : this is the case for H_2O on most surfaces, where a CONTACT LINE exists.

And in general? Surface chemistry can dominate : one need not have a contact line.

Wetting: fluid-solid contact



- depends on the surface energies of the 3 interfaces:

$$\gamma_{lv} \equiv \sigma, \gamma_{sv}, \gamma_{sl}$$

- just as $\sigma = \gamma_{lv}$ represents a surface energy/area or a tensile force/length at a liquid-vapour surface, γ_{sl} and γ_{sv} represent the same at solid-liquid and solid-vapour interfaces.

Degree of wetting determined by SPREADING PARAMETER:

$$\begin{aligned} S &= [E_{\text{substrate}}]_{\text{dry}} - [E_{\text{substrate}}]_{\text{wet}} \\ &= \underbrace{\gamma_{sv} - \gamma_{sl}}_{\text{NOT EASILY MEASURED}} - \gamma_{lv} \end{aligned}$$

Total Wetting : $\mathcal{F}^* > 0$

- liquid spreads completely to minimize its surface energy ($\theta_e = 0$)

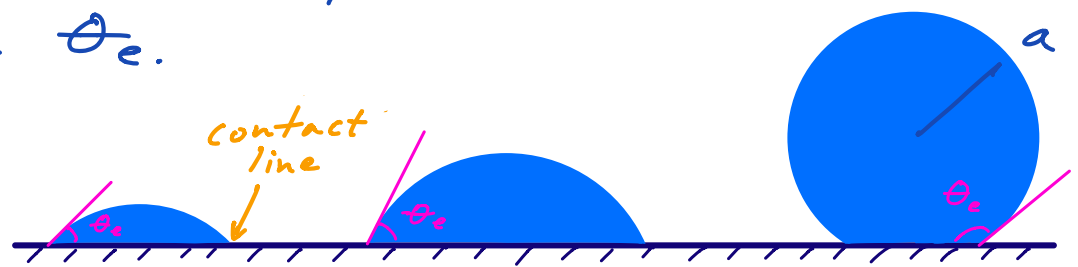
e.g. Si oil on glass. H_2O on very clean glass.

Note: Si oil spreads more rapidly than H_2O since
 $\sigma_w \sim 70$ dynes/cm, $\sigma_{Si} \sim 20$ dynes/cm

- final result: a film of nanoscopic thickness resulting from competition between molecular + capillary forces

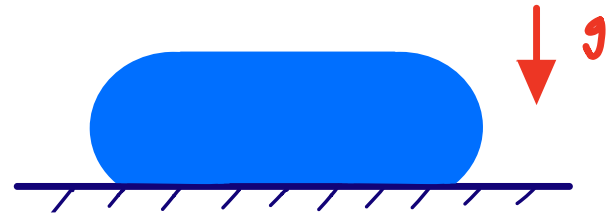
Partial Wetting : $\mathcal{F}^* < 0$

- in absence of g (or for drop size $a \ll l_c$), drop forms a spherical cap that meets surface at contact line at the equilibrium contact angle θ_e .



- a liquid is "wetting" on a particular solid when $\theta_e < \frac{\pi}{2}$
"non-wetting" " " " $\theta_e > \frac{\pi}{2}$
- for water, a surface is HYDROPHILIC if $\theta_e < \frac{\pi}{2}$,
HYDROPHOBIC if $\theta_e > \frac{\pi}{2}$, and SUPERHYDROPHIC if $\theta_e > 150^\circ$.

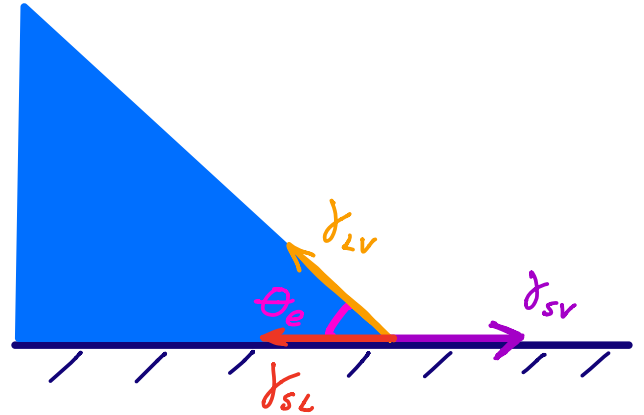
Note: if $a \gtrsim l_c$, then drop will be flattened by gravity



Young's Law: what is θ_e ?

Horizontal force balance at contact line:

$$\gamma_{LV} \cos \theta_e = \gamma_{SV} - \gamma_{SL}$$



Young's Law (1805):

$$\cos \theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = 1 + \frac{S}{\gamma_{LV}}$$

Note: 1. when $S \geq 0$, $\cos \theta_e \geq 1$

$\Rightarrow \theta_e$ undefined \Rightarrow spreading unbounded

2. VERTICAL force balance not satisfied

\Rightarrow dimpling of soft surfaces

e.g. bubbles in drying paint leave a rim.

