Capillary Forces

Consider a soap film on a rail.

Work done by rod retraction:

\[ SW = F \, dx = 2\sigma \, l \, dx \]

\[ \Rightarrow F = 2\sigma l \text{ is the force acting on the rod.} \]

Move generally, for a body partially submerged in a liquid, \( \sigma \) 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 \( \sigma \) will contribute to weight support.

E.g. water-walking insects, floating paper clip.
Laplace Pressure

Consider an oil drop in H$_2$O, bound by interfacial tension $\gamma_{ow}$, of radius $R$.

Work required to increase radius by $dR$:

$$SW = -P_0 \, dV_o - P_w \, dV_w + \gamma_{ow} \, dA$$

where $dV_o = \frac{4}{3}\pi R^3 \, dR = -dV_w$

$$dA = 8\pi R \, dR$$

For mechanical equilibrium, $SW = 0$

$$0 = (-P_0 + P_w) \frac{4}{3}\pi R^2 \, dR + \gamma_{ow} 8\pi R \, dR$$

$$\Delta P = P_0 - P_w = \frac{2\gamma_{ow}}{R}$$

Note: In a drop/bubble, pressure inside is higher than that outside by an amount $\sim \frac{2\gamma}{R}$

Smaller bubbles have higher Laplace pressure

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 \((R \sim 1 \text{ mm})\),

\[ \Delta P \sim 1 \text{ atm} \]

ii) For soap bubbles \((R \sim 5 \text{ cm}, \sigma \sim 35 \text{ dynes/cm})\)

\[ \Rightarrow \Delta P \sim 3 \text{ Pa} \sim 3 \times 10^{-5} \text{ atm} \]

iii) For champagne bubbles: \(R \sim 0.1 \text{ mm}, \sigma \sim 50 \text{ dynes/cm}\)

\[ \Rightarrow \Delta P \sim 10^3 \text{ Pa} \sim 10^{-2} \text{ atm} \]

Soap bubble jet: exit speed?

Force balance: \(\Delta P = \frac{4 \sigma}{R} \sim \rho_{\text{air}} U^2\)

\[ \Rightarrow U \sim \left( \frac{4 \sigma}{\rho_{\text{air}} R} \right)^{\frac{1}{2}} \sim \left( \frac{4 \times 30 \text{ dynes/cm}}{0.001 \text{ g/cm} \cdot 3 \text{ cm}} \right)^{\frac{1}{2}} \sim 200 \text{ cm/s} \]

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

$$\Delta P = \sigma \nabla \cdot \hat{n}$$
Puddles: what sets their size?

Laplace / curvature pressure balances if

\[ \frac{\sigma}{R} > \rho g H \]  but \( R \approx H \) for a puddle

\[ \Rightarrow R < l_c = \sqrt{\frac{\sigma}{\rho g}} = \text{capillary length} \]

\[ \Rightarrow \text{drops with } R < l_c \text{ remain nearly spherical} \]

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

\[ \Rightarrow \text{for a puddle of volume } V, \text{ radius } a: \]

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

**Note:** this is the case for \( H_2O \) on most surfaces,
where a contact line exists.

And in general? Surface chemistry can dominate:
none need not have a contact line.
Wetting: fluid-solid contact

Two possibilities:

\[ \sigma = \gamma_{LV} \]

\[ \gamma_{SV} \]

\[ \gamma_{SL} \]

\[ S < 0 \]

\[ S > 0 \]

- 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/layer or a tensile force/length at a liquid-vapour surface, \( \gamma_{SL} \) and \( \gamma_{SV} \) represent the same at solid-liquid and solid-vapour interfaces.

Degree of wetting determined by SPREADING PARAMETER:

\[ S' = \left[ E_{\text{substrate}} \right]_{\text{dry}} - \left[ E_{\text{substrate}} \right]_{\text{wet}} \]

\[ = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \]

[\text{not easily measured}]
Total Wetting: $S > 0$

- Liquid spreads completely to minimize its surface energy ($\theta_e = 0$)
  
  * e.g., Si oil on glass, H$_2$O on very clean glass.

  **Note:** Si oil spreads more rapidly than H$_2$O 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: $S < 0$

- In absence of g (or for drop size $a << L_e$), drop forms a spherical cap that meets surface at contact line at the equilibrium contact angle $\theta_e$.

  ![Diagram of partial wetting](image)

- 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 SUPERHYDROPHOBIC if $\theta_e > 150^\circ$. 
Note: if $a > R_e$, then drop will be flattened by gravity.

Young’s Law: what is $\theta_e$?

Horizontal force balance at contact line:

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

Young’s Law (1805):

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

Note: 1. when $S = 0$, $\cos \theta_e = 1$  
\[ \Rightarrow \theta_e \text{ undefined } \Rightarrow \text{ spreading unbounded} \]

2. Vertical force balance not satisfied  
\[ \Rightarrow \text{dimpling of soft surfaces} \]
\[ \text{e.g. bubbles in drying paint leave a rim.} \]