Determining Contact Angles by Wilhelmy Method and Critical Surface Tension by Zisman Plot

Teng-Jui Lin
Department of Chemical Engineering, University of Washington
Surface and Colloid Science

Surface tension can be measured by partial immersion (Wilhelmy) method

- Partial immersion method (Wilhelmy slide)
  - Force required to maintain the position of a solid which penetrates a fluid interface
- Force balance
  - Down = Weight - Buoyancy + Surf. Tension

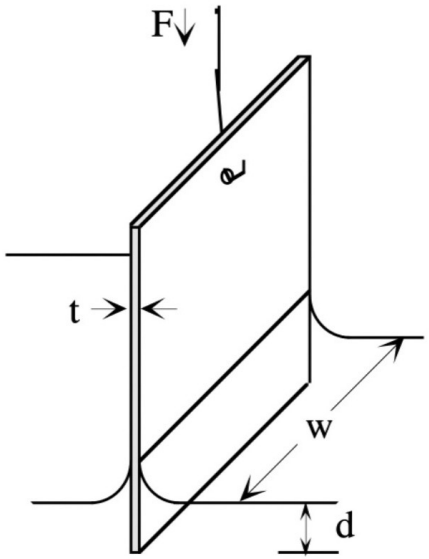
$$F_{\downarrow} = F_g - F_b + F_\sigma$$

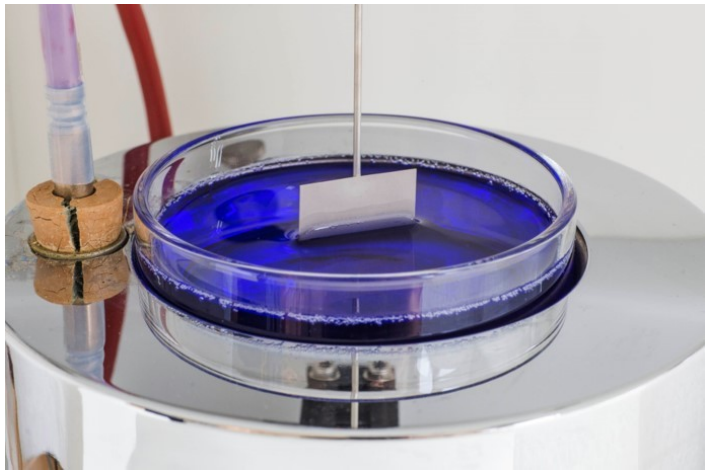
$$F_{\downarrow} = mg - \rho g V_{\text{disp}} + P\sigma$$

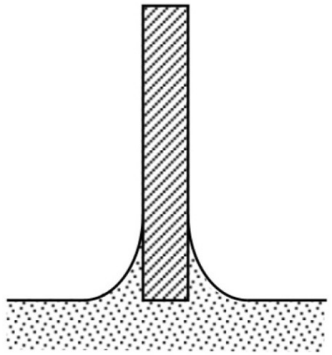
Assumes: uniform σ, fully wetted $\theta = 0$

$$\sigma = \frac{F_{\downarrow} - mg - \rho g V_{disp}}{P}$$

Wilhelmy slide







Contact angle can also be measured by partial immersion (Wilhelmy) method

- Force balance
  - Down = Weight - Buoyancy + Surf. Tension

$$F_{\downarrow} = F_g - F_b + F_\sigma$$

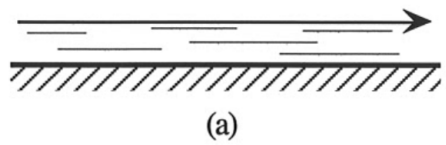
$$F_{\downarrow} = mg - \rho g V_{\text{disp}} + P\sigma$$

Assumes: uniform σ, ~~fully wetted~~ ~~$\theta = 0$~~

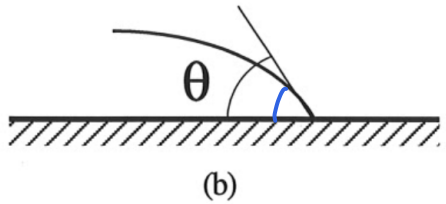
- Relax contact angle assumption
  - Contact angle as contribution to surface tension

$$F_{\downarrow} = mg - \rho g V_{\text{disp}} + P\sigma \cos\theta$$

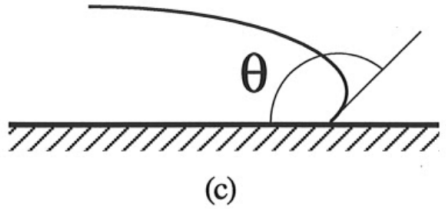
- $P\sigma \cos\theta$
  - Know any two terms
  - Solve the other one



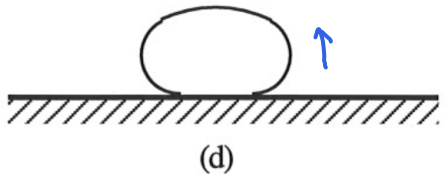
θ = 0°
"wetting out"



0° < θ < 90°
"partial wetting"



90° < θ < 180°
"partial non-wetting"



θ = 180°
"total non-wetting"

Contact angle of solid-liquid interactions is defined by pair-wise surface tensions

- Horizontal force balance

$$\theta \in (0, \pi] = (0, 180]\,\text{deg} \quad \Rightarrow \quad \cos\theta \in (1, -1]$$

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg}\cos\theta$$

$$\cos\theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}}$$

- **Young's equation**

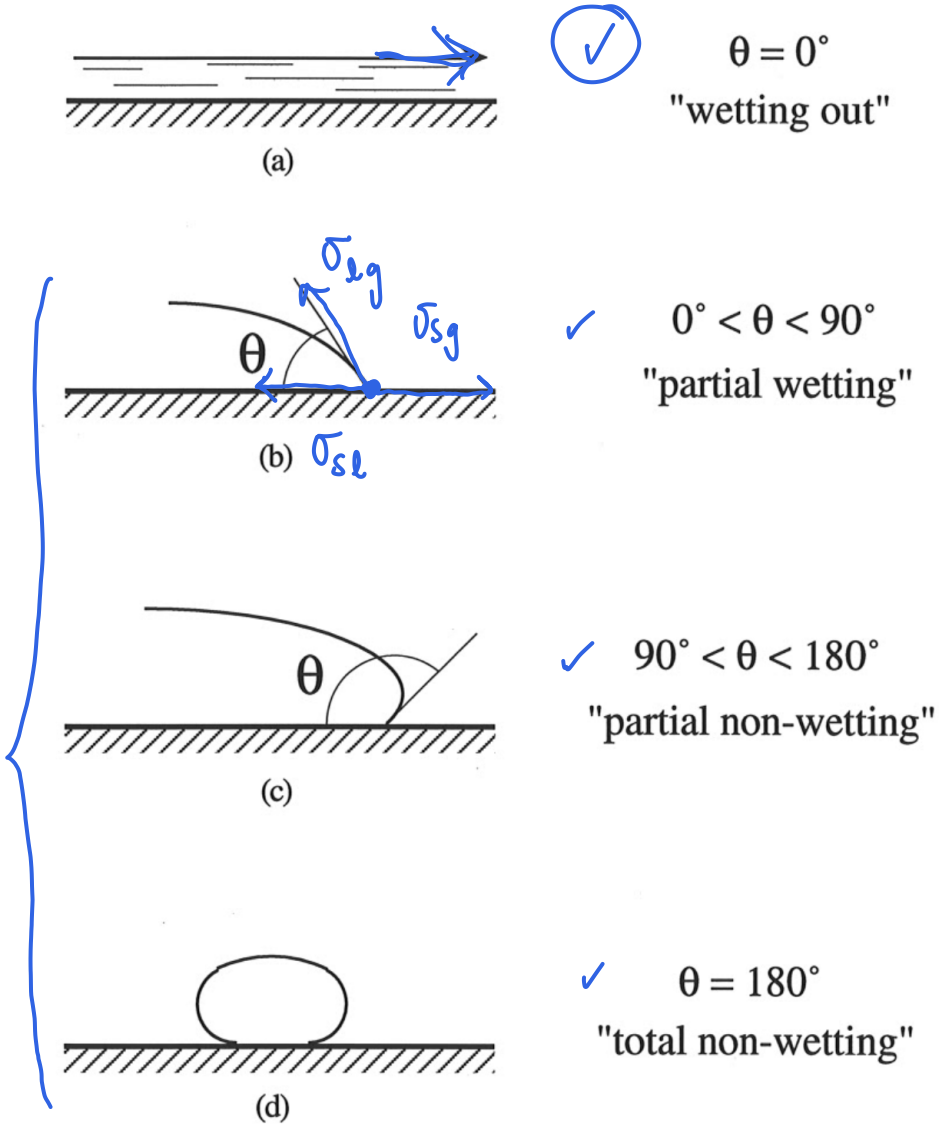
$$\boxed{\cos\theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}}}$$

  - Low energy surfaces - does not wet out by most liquids
    - Plastics, polymers

$$(\sigma_{sg} - \sigma_{sl}) < \sigma_{lg}$$

  - High energy surfaces - wet out by most liquids
    - Clean metals, mineral oxides

$$(\sigma_{sg} - \sigma_{sl}) > \sigma_{lg}$$



Zisman plot gives critical surface tension of low-energy solids using contact angles

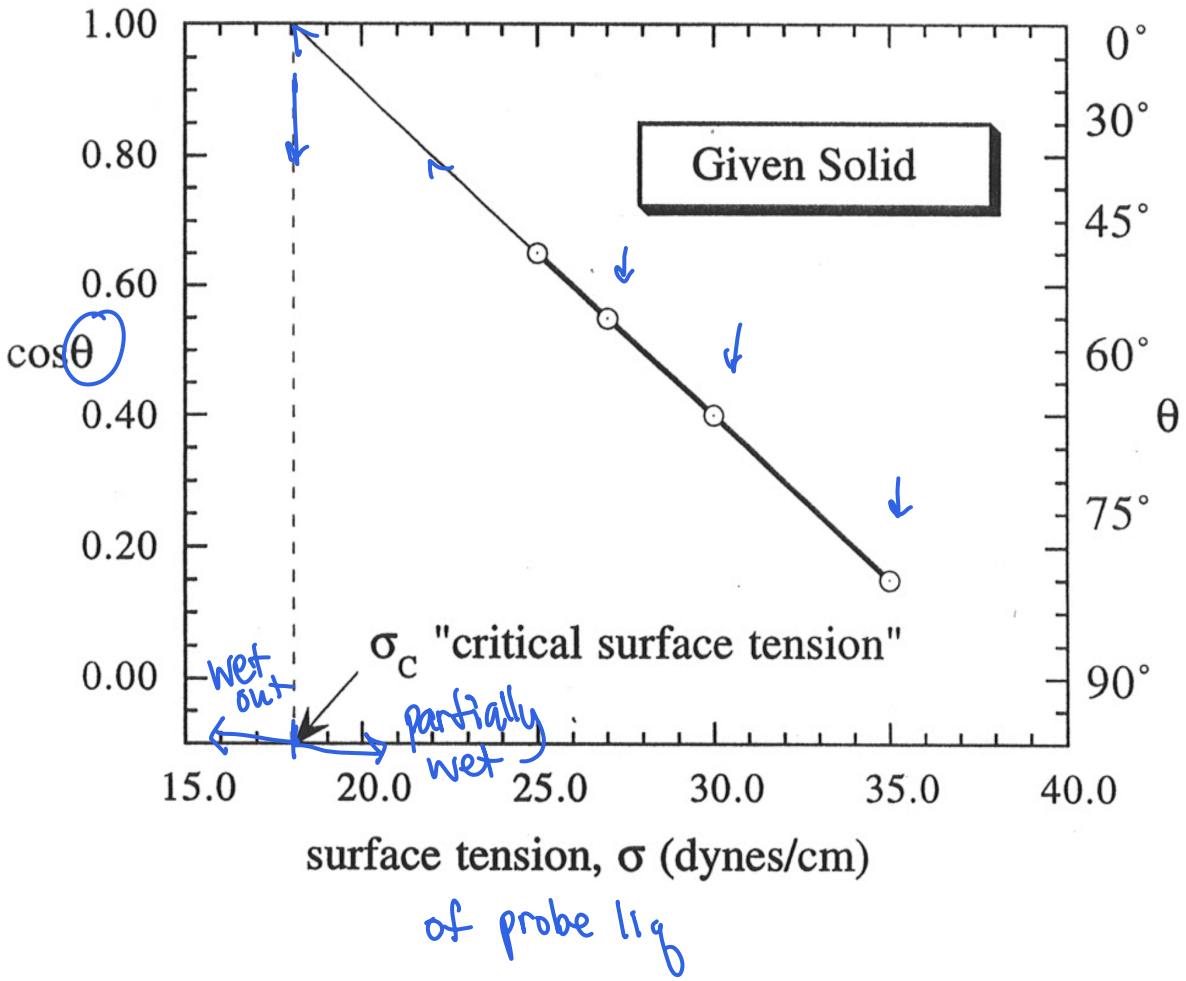
- $P\sigma\cos\theta$

  Know σ and P, solve for $\cos\theta$

- **Critical surface tension σ_c of a solid** - surface tension at or below which solid can be totally wet out

  $\sigma \leq \sigma_c \quad \Rightarrow \cos\theta = 1 \quad \Rightarrow$ wet out

- Teflon has $\sigma_c = 19\ \mathrm{mN/m}$
  - Can't be wetted by almost any liquid at room temperature
  - Water: σ = 72 mN/m
  - Oil: σ = 30 mN/m



- Assumes:
  - Liquid does not dissolve or swell solid
  - Liquid does not interact specifically with solid (no H-bond, acid-base)
  - Liquid vapor does not adsorb on solid

Force method allows calculation of any variable in $P\sigma\cos\theta$ given the other two

- $F_{\downarrow} = mg - \rho g V_{\text{disp}} + P\sigma\cos\theta$
  - Measure perimeter P

    Given σ, ~~$\cos\theta$~~ 1
  - Measure surface tension σ

    Given P, ~~$\cos\theta$~~ 1
  - Measure contact angle θ

    Given P, σ
  - Measure critical surface tension σ_c

    Given Zisman plot ($\cos\theta$ vs. σ)

    given