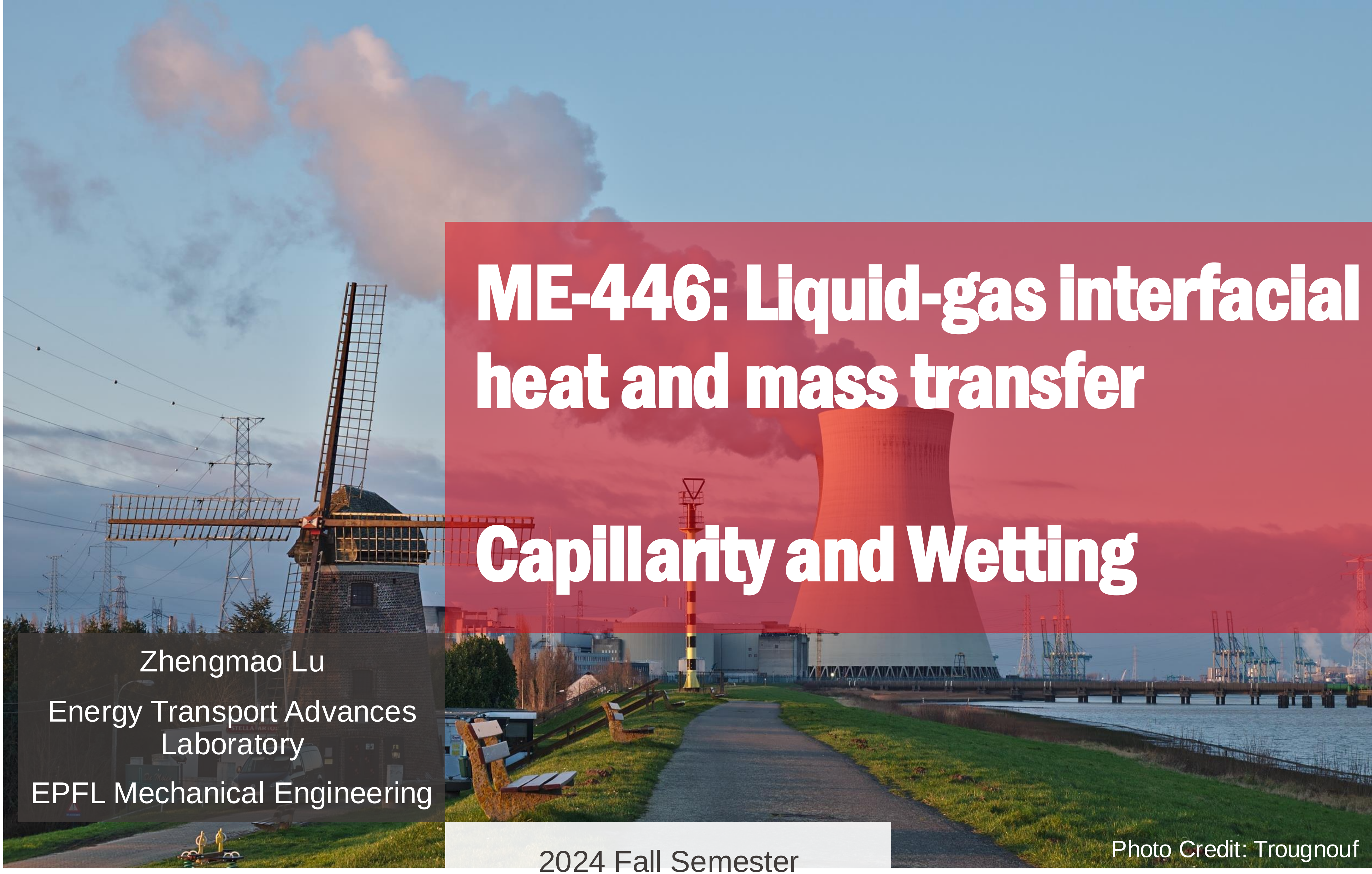


ETA-Lab
Energy Transport Advances

ME-446: Liquid-gas interfacial heat and mass transfer

Capillarity and Wetting

Zhengmao Lu

Energy Transport Advances Laboratory

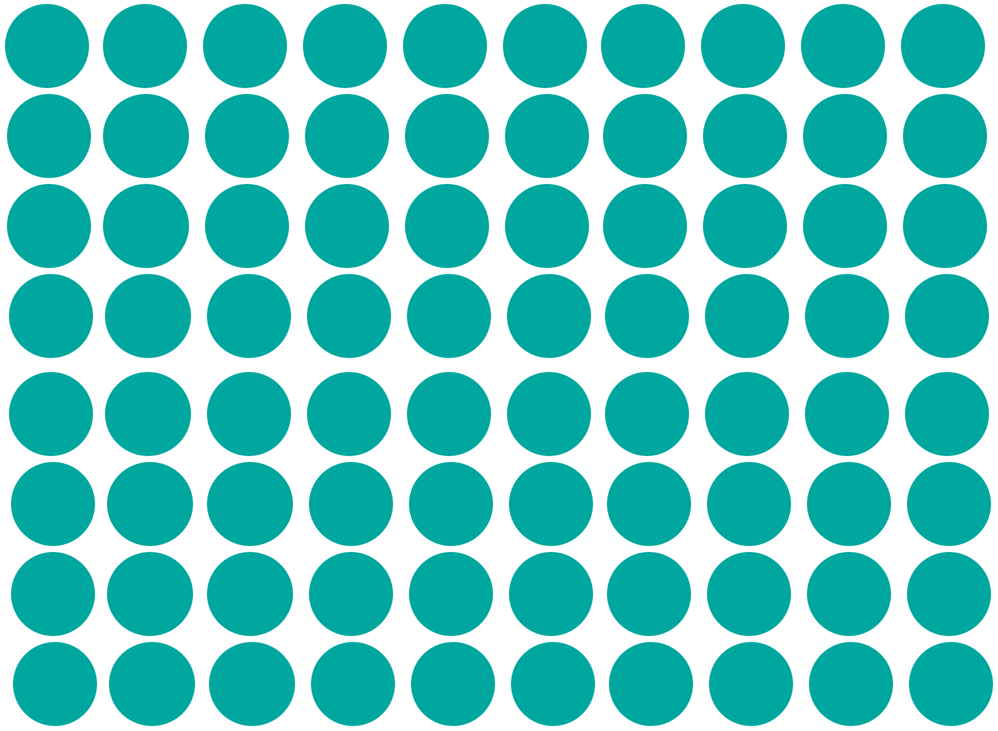
EPFL Mechanical Engineering

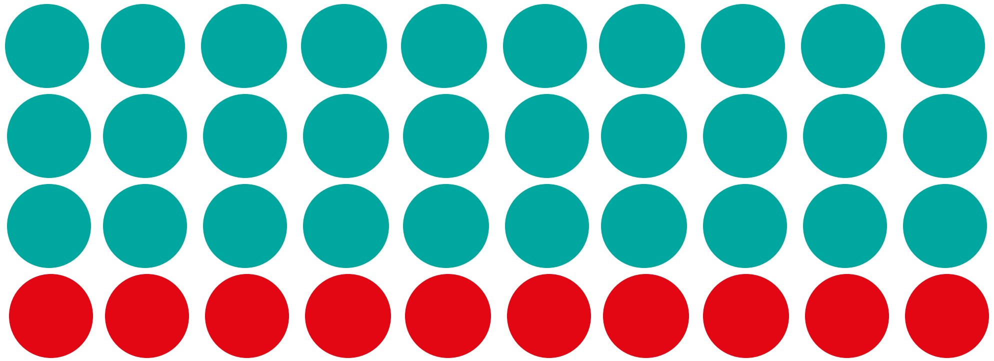
2024 Fall Semester

Photo Credit: Trougnouf

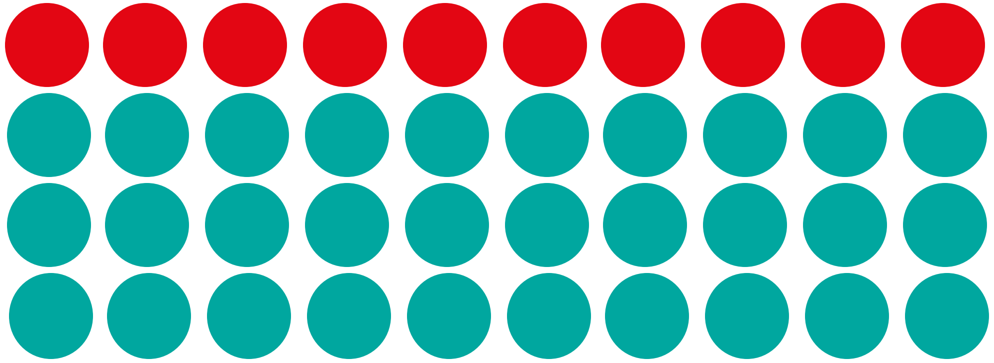
Surface Energy (J/m^2)

Lower energy state



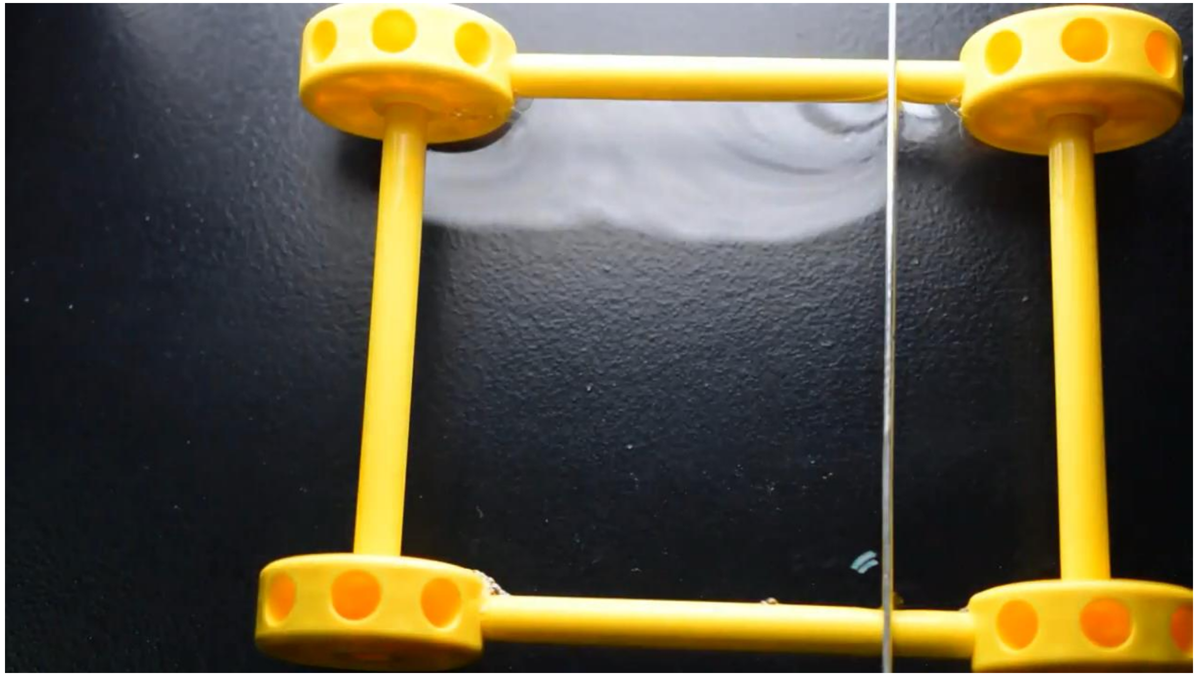


High energy state (with 2 surfaces)



Work needed to create surfaces

Surface Tension (N/m)

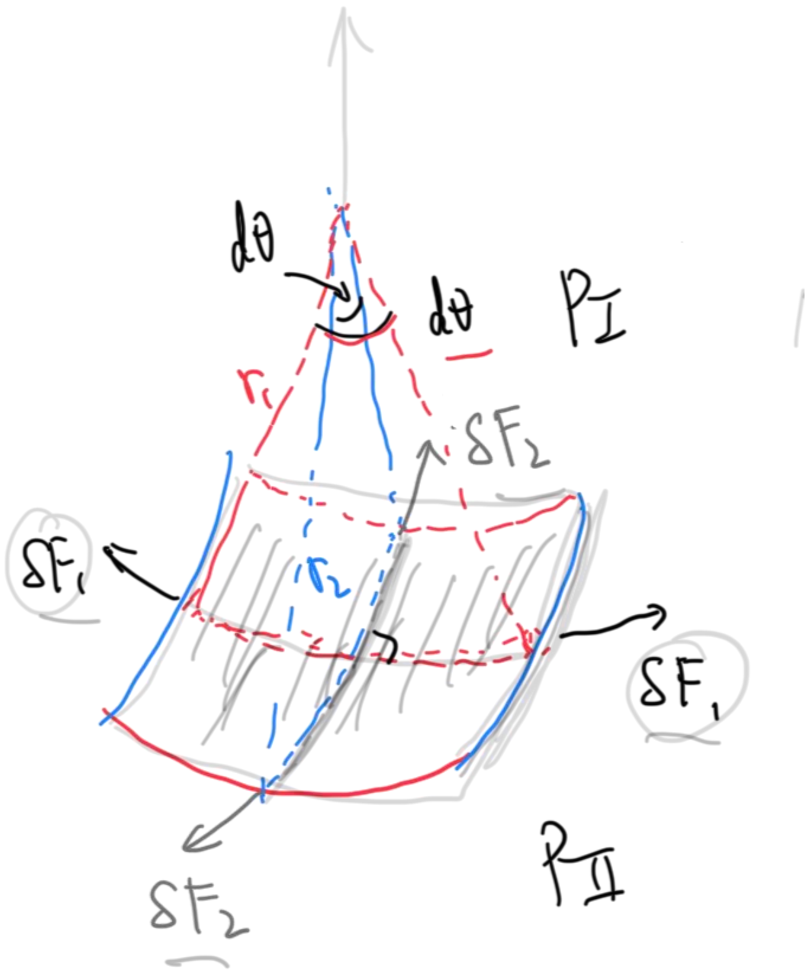


Surface exerting line forces on objects

Young-Laplace Equation

$$P_{\mathrm{I}} - P_{\mathrm{II}} = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Young-Laplace Equation

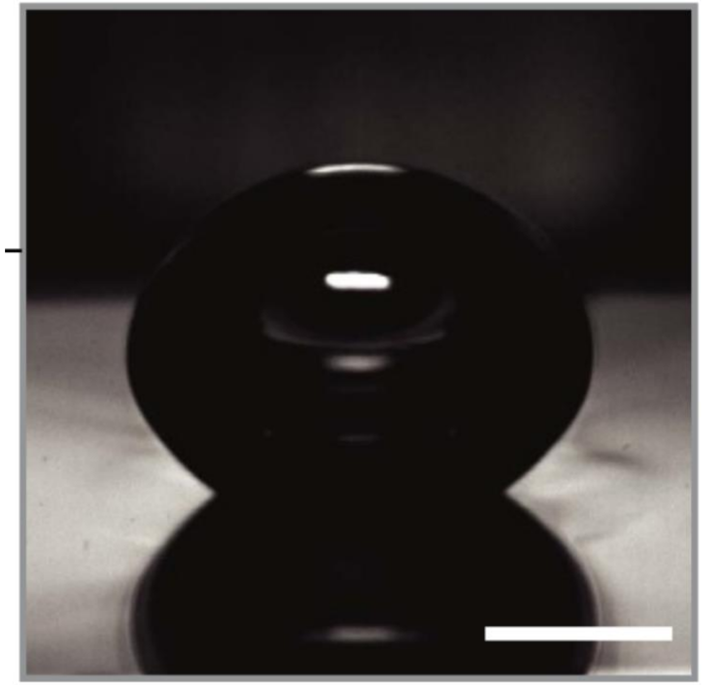


ILOs Today

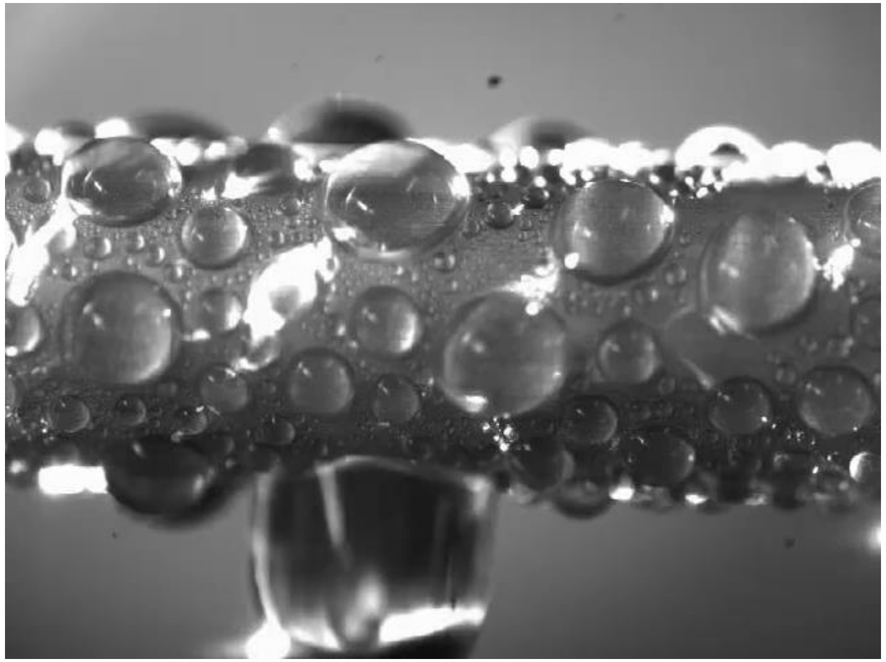
- Explain **the concept of contact angle**
- Evaluate **the effect of surface tension on contact angle**
- Explain **contact angle hysteresis**
- Analyze **wetting on rough surfaces**

Reading materials: **Carey** Chapter 3

Why We Care About Liquid-Solid Contact



Dhillon *et al.*, *Nat Commun* 2015



Miljkovic *et al.*, *Nano Lett.* (2013)

Force Balance

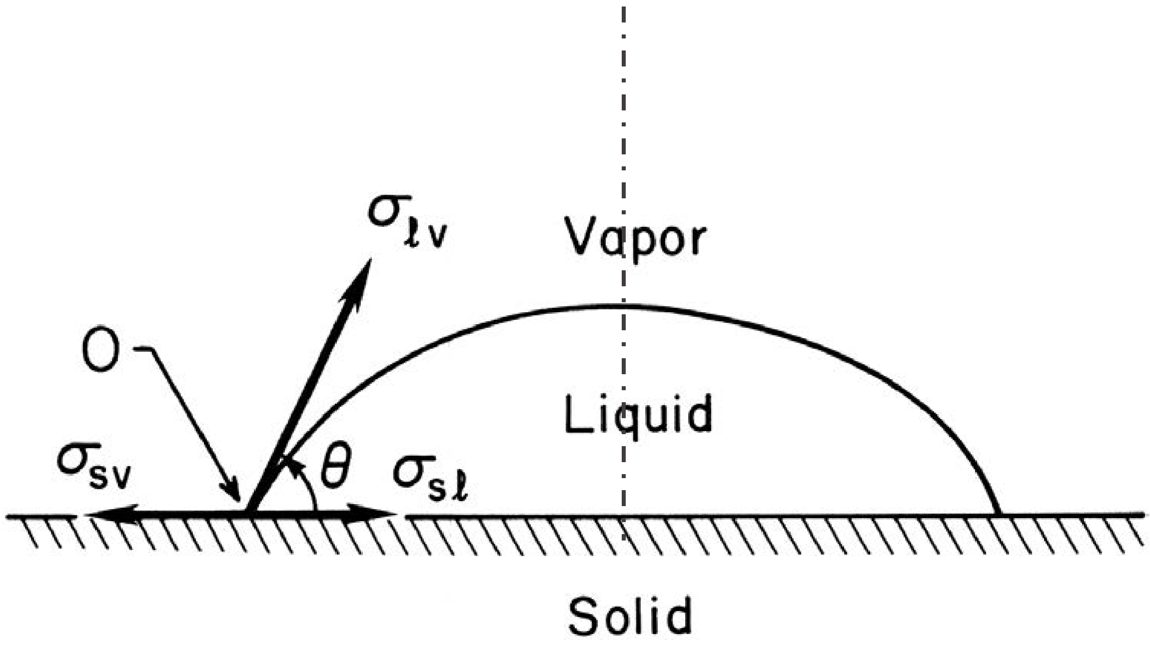


Figure 3.1 in Carey

Angle between **liquid-vapor interface** and **solid surface** measured at the **contact line**

Force Balance

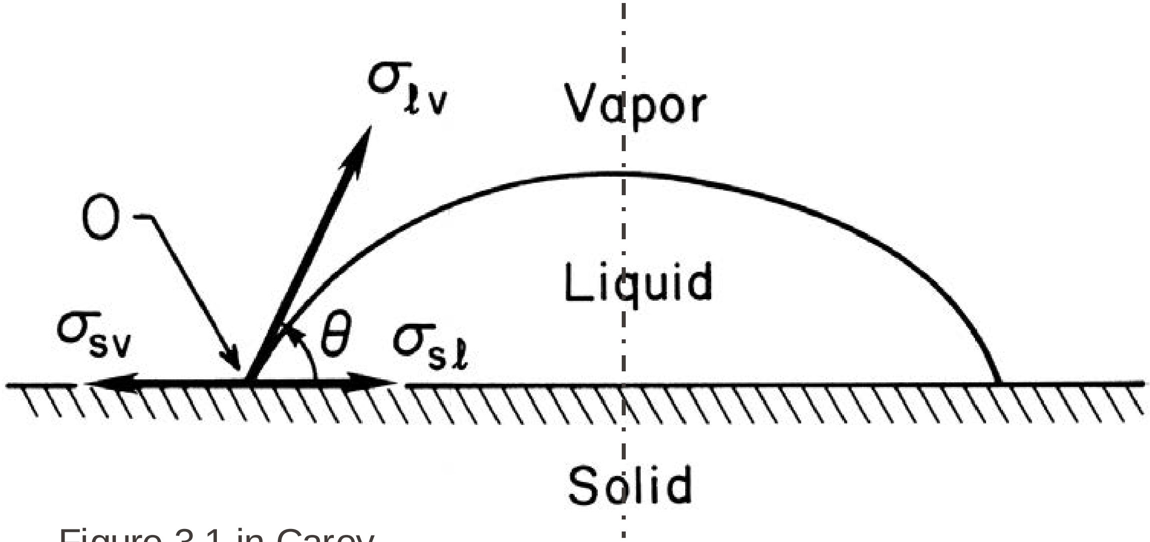
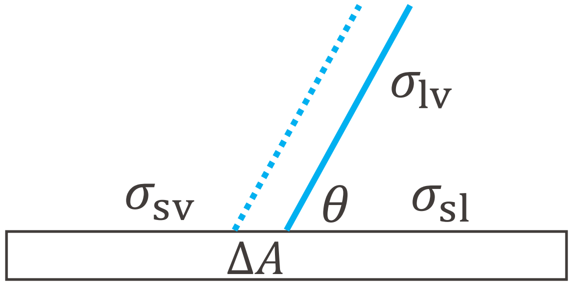


Figure 3.1 in Carey

Young's equation

$$\boldsymbol{\sigma_{sv} = \sigma_{lv}\cos\theta + \sigma_{sl}}$$

An energy perspective



$$-\sigma_{sv}\Delta A + \sigma_{sl}\Delta A + \sigma_{lv}\Delta A\cos\theta = 0$$

Wettability

- Hydrophilic surface (wetting)
  - θ between $0°$ and $90°$ when in contact with water
- Hydrophobic surface (non-wetting)
  - θ between $90°$ and $180°$ when in contact with water

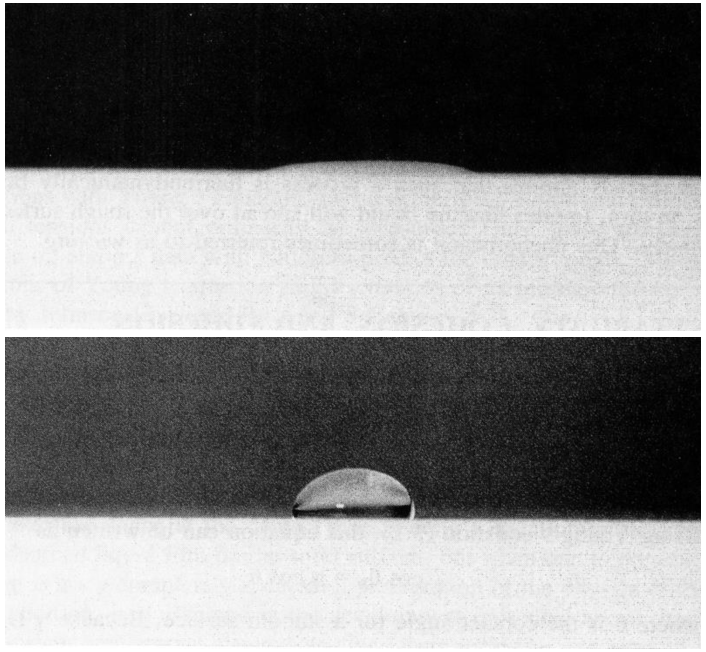


Figure 3.3 in Carey

Capillary Rise/Fall

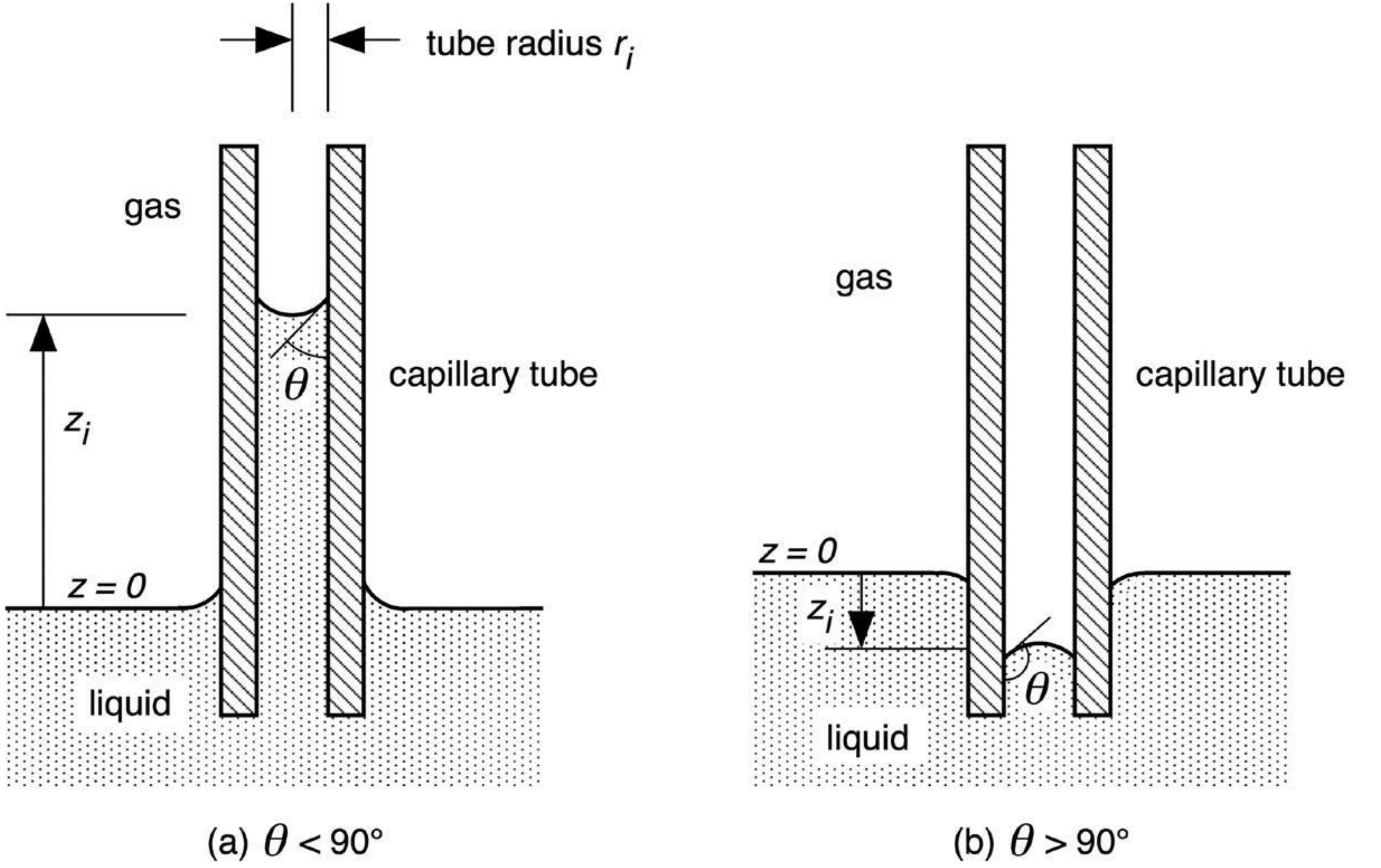
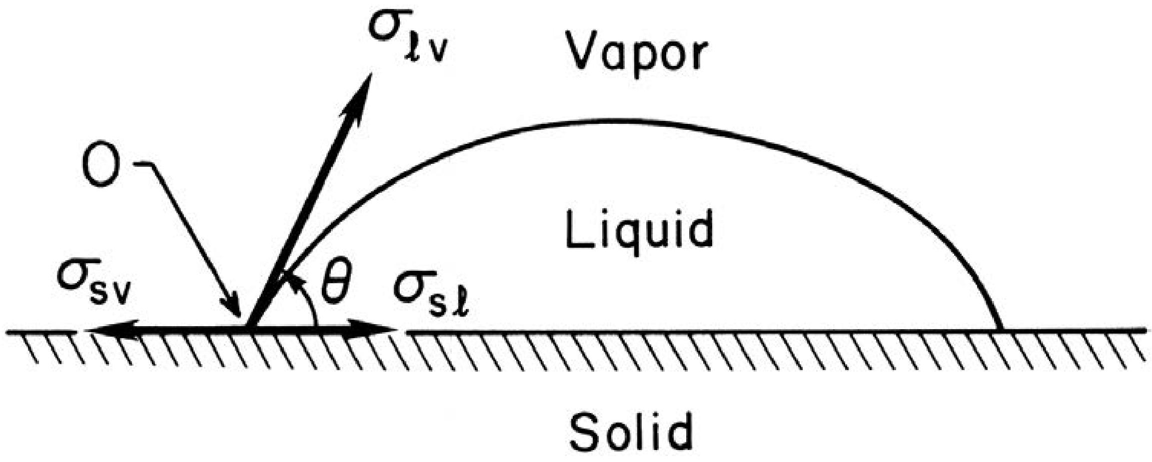


Figure 3.14 in Carey

Wetting

Non-wetting

Extreme Cases



$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}$$

What if $(\sigma_{sv} - \sigma_{sl})/\sigma_{lv} < -1$? Sphere

What if $(\sigma_{sv} - \sigma_{sl})/\sigma_{lv} > 1$? Film

Surface Energy and Contact Angle

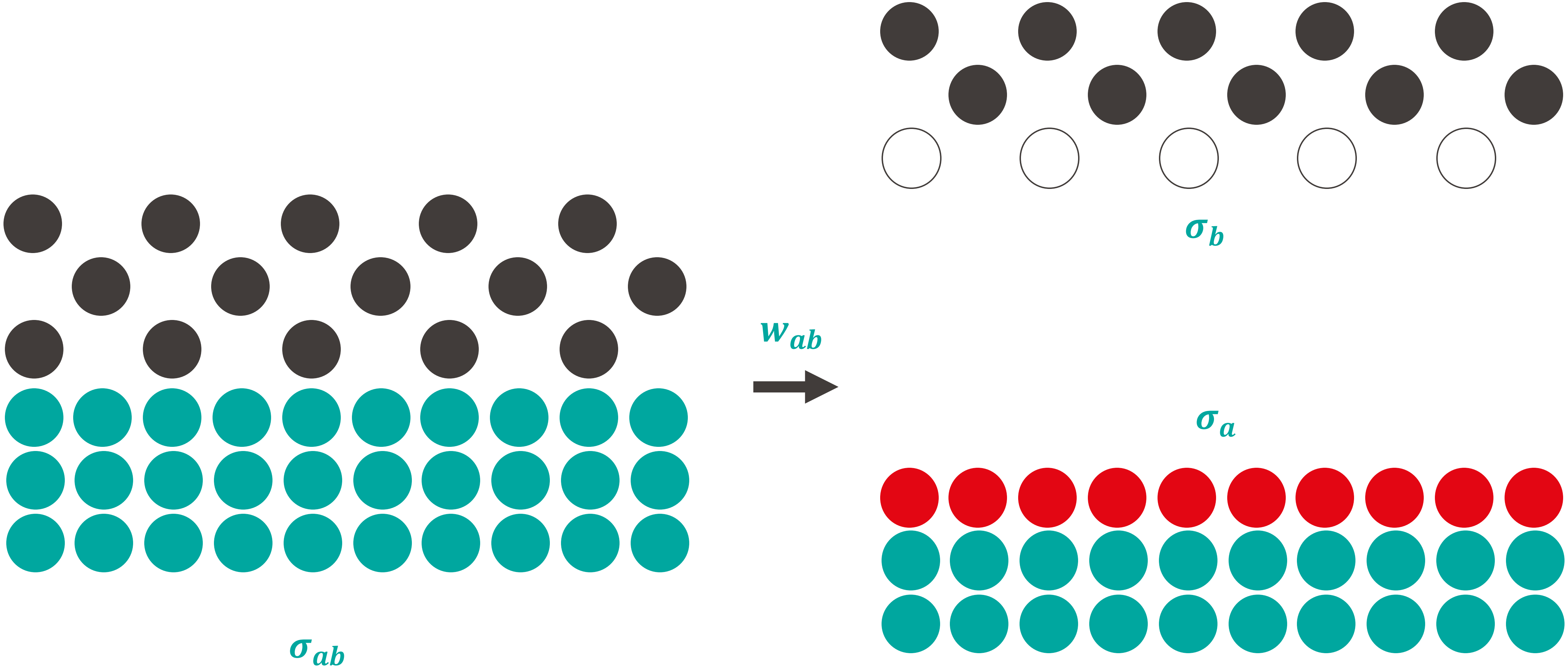
Typical θ (σ_{lv} \ σ_{sv})	Low (e.g., fluoropolymer)	Medium (e.g., nitride, oxide)	High (e.g., metal)
Low (e.g., alcohol, refrigerant)	< 90°	< 90°	< 90°
Medium (e.g., water)	> 90°	< 90°	< 90°
High (e.g., molten salt, liquid metal)	> 90°	> 90°	Mixed

Wilke *et al.*, *PNAS* 2021

$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}$$

In general, low surface tension liquids and high surface energy solids make wetting easier

Interface Energy



$$\sigma_{ab} = \sigma_a + \sigma_b - w_{ab}$$

w_{ab} depends on intermolecular interactions

$$w_{ab} = 2(\sigma_a \sigma_b)^{1/2}$$

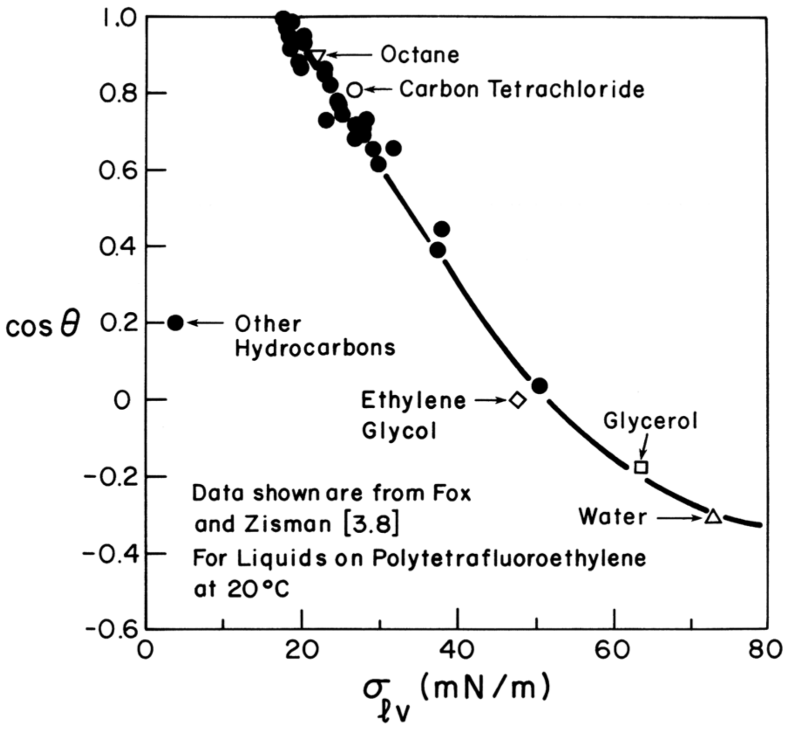
for nonpolar interactions

Additional Notes

- Spreading coefficient (Eq. 3.20 in Carey)

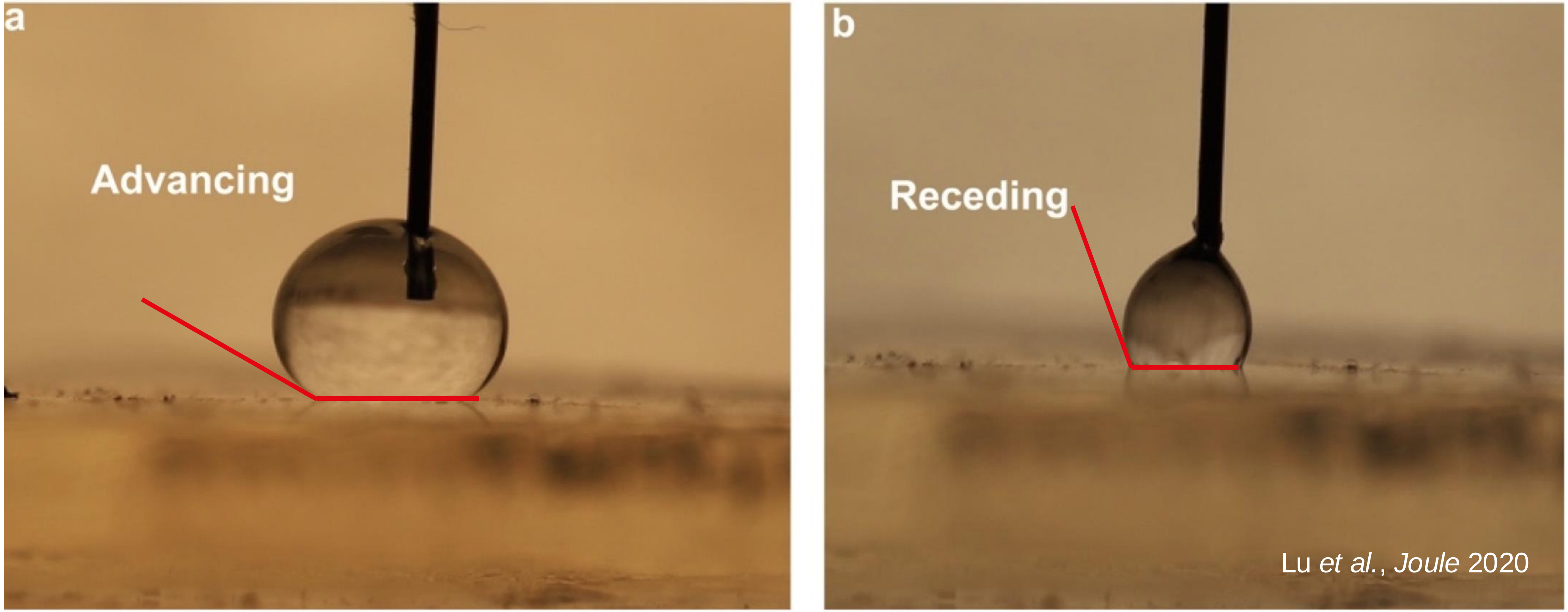
$$Sp_{ls} = \sigma_{sv} - \sigma_{lv} - \sigma_{sl}$$

- Critical surface tension (Chapter 3.3 in Carey)



Questions?

Contact Angle Hysterisis



Lu *et al.*, *Joule* 2020

- Equilibrium contact angle: a thermodynamic concept defined for smooth homogeneous surfaces
- Real surface wettability is characterized by advancing and receding contact angles, which are almost always different from each other

Effect of Surface Inhomogeneity

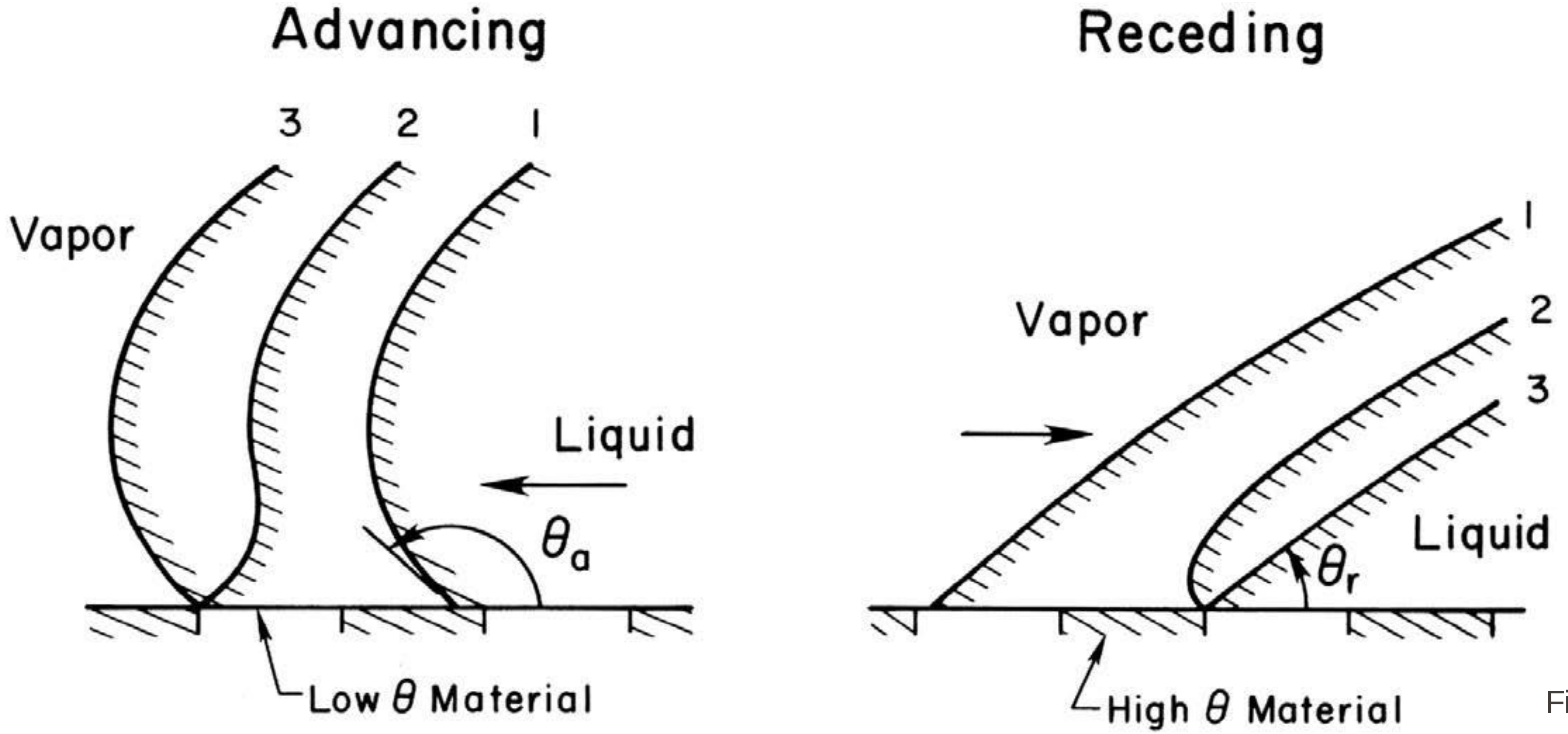


Figure 3.12a in Carey

- **Advancing** contact angle determined by the **high** θ component
- **Receding** contact angle determined by the **low** θ component

Effect of Surface Inhomogeneity

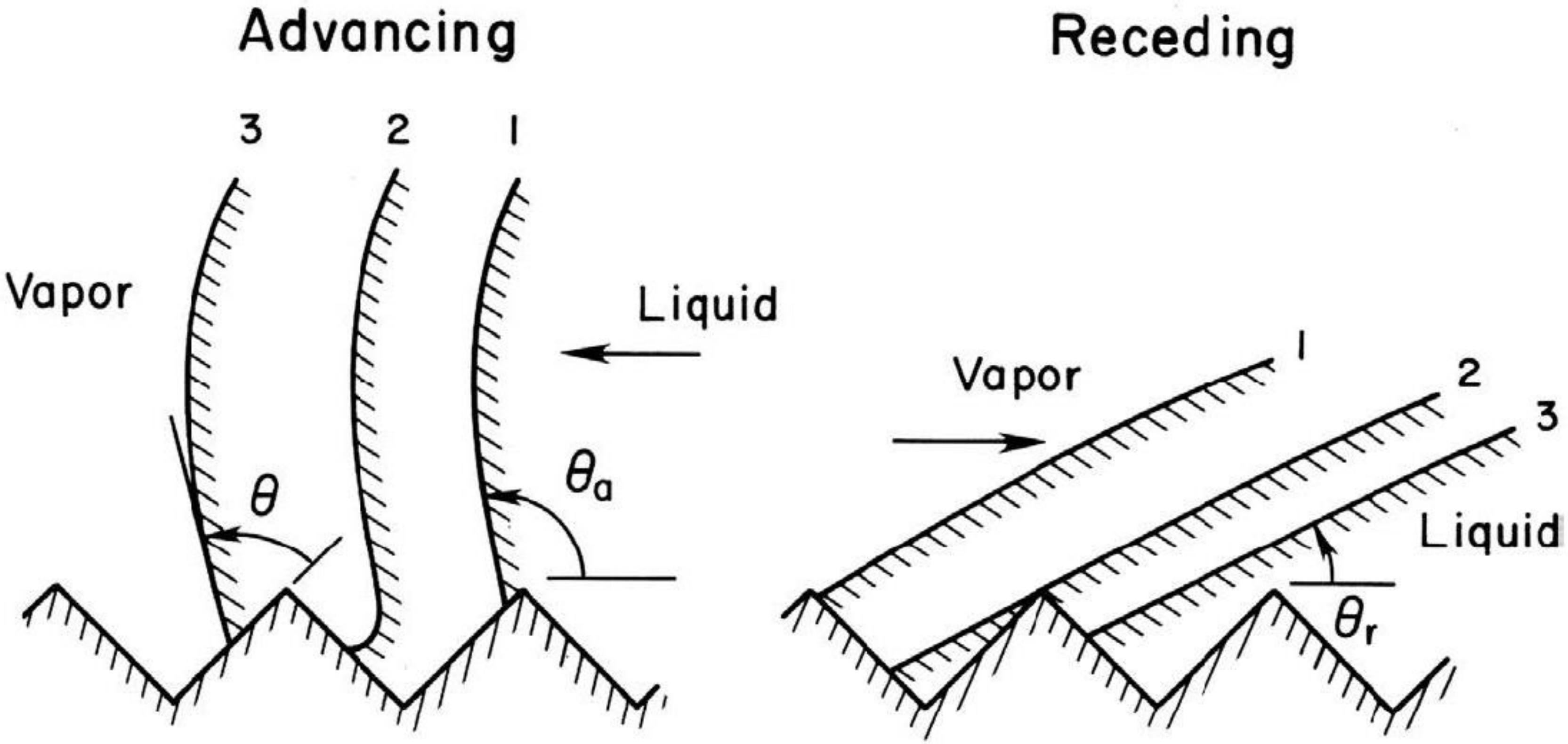


Figure 3.12b in Carey

- Contact angle hysteresis caused by asymmetric effects of surface structures during receding and advancing

Contact Angle Hysterisis

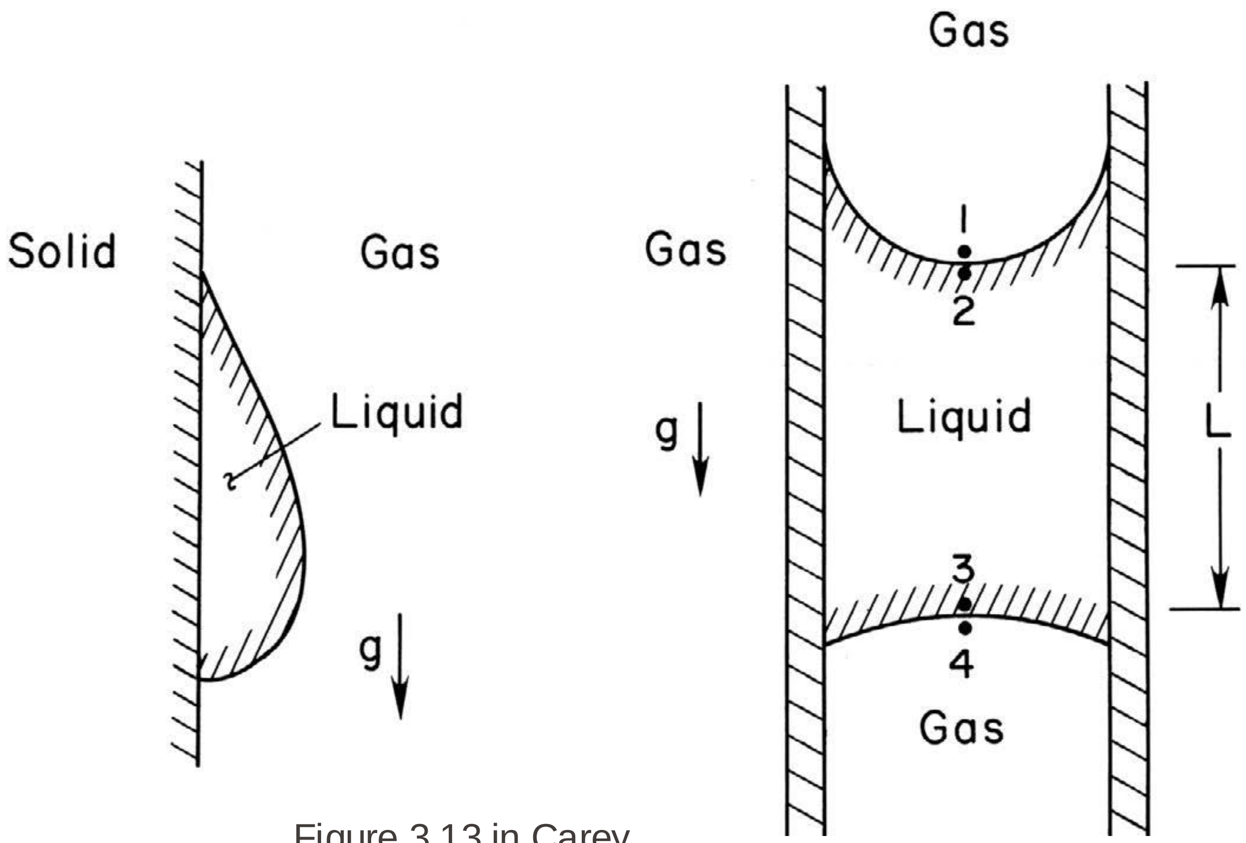


Figure 3.13 in Carey

$$P_1 - P_2 = \frac{2\sigma}{r_{12}}$$

$$P_4 - P_3 = \frac{2\sigma}{r_{34}}$$

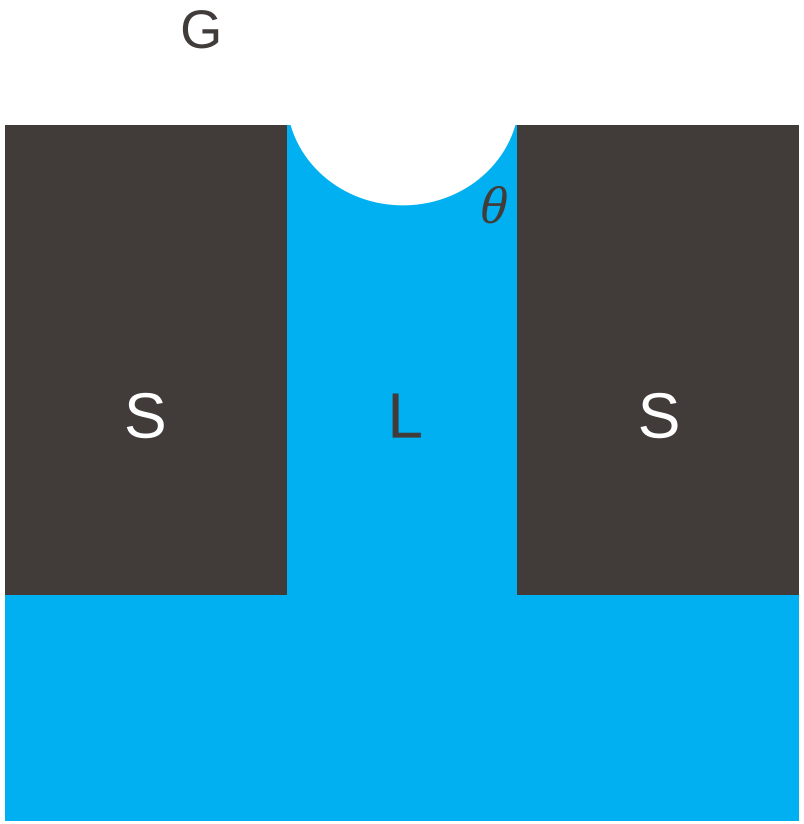
$$P_3 = P_2 + \rho_L g L$$

$$P_4 = P_1 + \rho_G g L$$

$$2\sigma\left(\frac{1}{r_{12}} - \frac{1}{r_{34}}\right) = (\rho_L - \rho_G) g L$$

- Advancing CA > Equilibrium CA > Receding CA

Contact Angle Pinning



Cylindrical pore with radius r_p

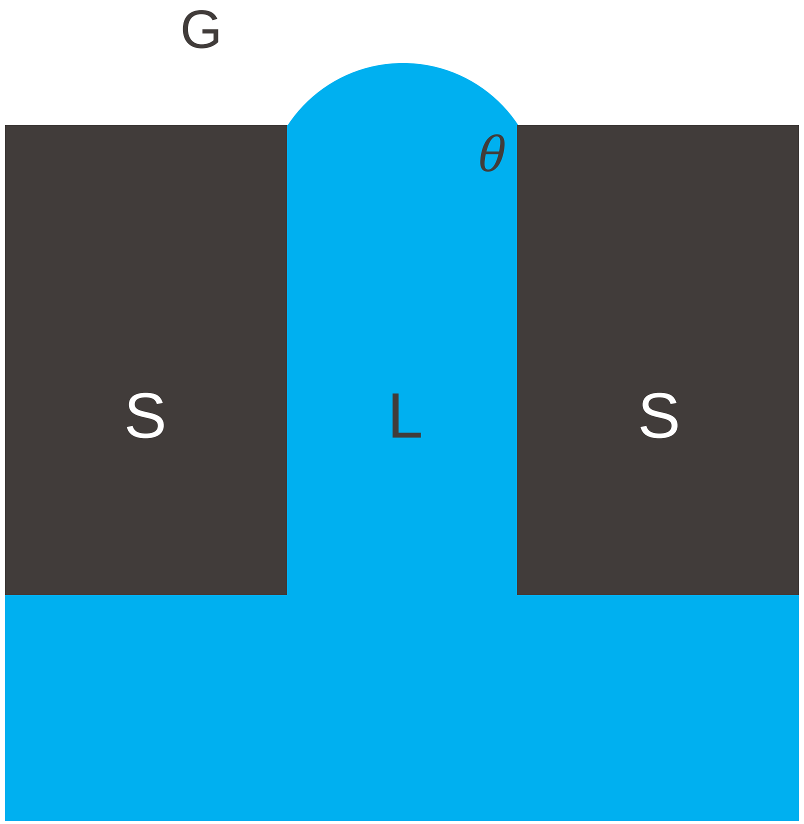
Initially $P_L = P_G = P_0$, interface flat

ACA = 95°, RCA = 60°

Now, start increasing P_G

$$P_G - P_L = \frac{2\sigma \cos\theta}{r_p}$$

Contact Angle Pinning



Cylindrical pore with radius r_{p}

Initially $P_{\mathrm{L}} = P_{\mathrm{G}} = P_0$, interface flat

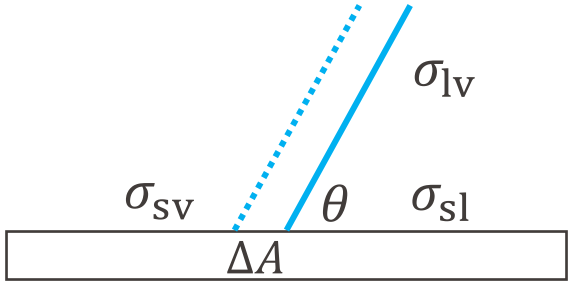
ACA = 95°, RCA = 60°

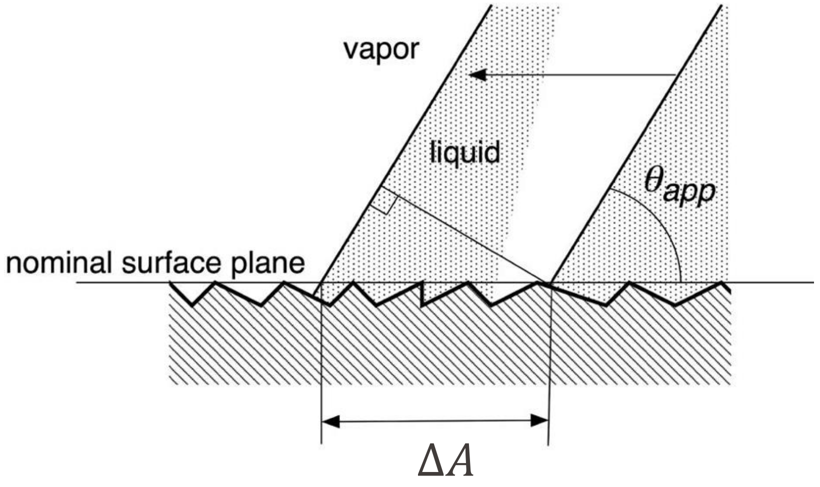
If we instead increase P_{L}

$$P_{\mathrm{L}} - P_G = \frac{2\sigma \sin(\theta - 90°)}{r_{\mathrm{p}}}$$

Wetting on a Structured Surfaces

Energy perspective of Young's Equation





$$-\sigma_{\mathrm{sv}}\Delta A + \sigma_{\mathrm{sl}}\Delta A + \sigma_{\mathrm{lv}}\Delta A\cos\theta = 0$$

$$-\sigma_{\mathrm{sv}} r\Delta A + \sigma_{\mathrm{sl}} r\Delta A + \sigma_{\mathrm{lv}}\Delta A\cos\theta_{\mathrm{app}} = 0$$

$$\cos\theta_E = \frac{\sigma_{\mathrm{sv}} - \sigma_{\mathrm{sl}}}{\sigma_{\mathrm{lv}}}$$

$$\cos\theta_{\mathrm{app}} = r\frac{\sigma_{\mathrm{sv}} - \sigma_{\mathrm{sl}}}{\sigma_{\mathrm{lv}}} = r\cos\theta_E$$

r: roughness ratio, actual surface area/projected area

Wenzel State

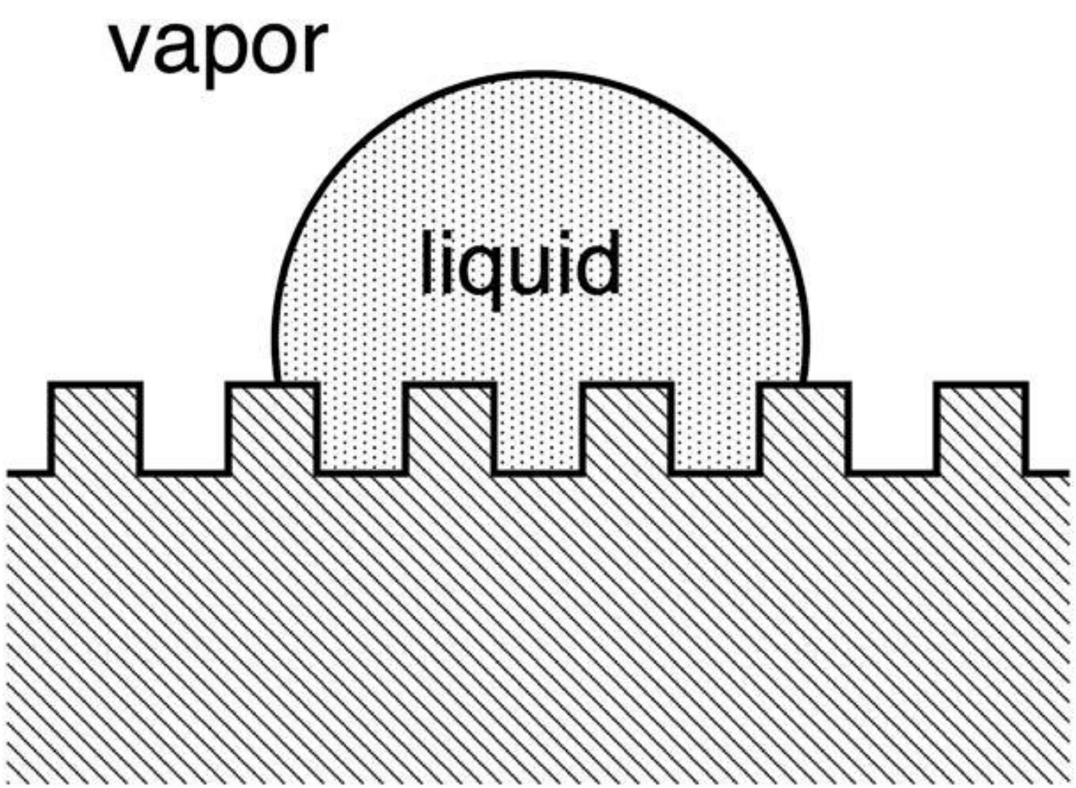


Figure 3.19 in Carey

Liquid penetrates through the surface structure underneath the droplet, yet not spreading further

$$\cos\theta_{\text{app}} = r\frac{\sigma_{\text{sv}} - \sigma_{\text{sl}}}{\sigma_{\text{lv}}} = r\cos\theta_E$$

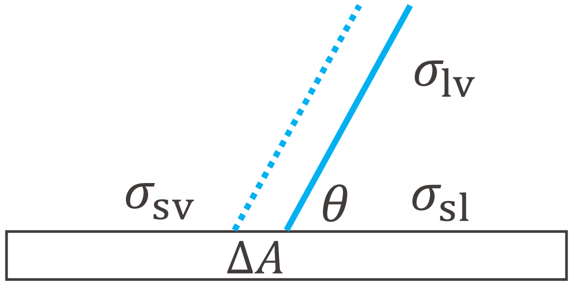
Since $r \geq 1$ by definition

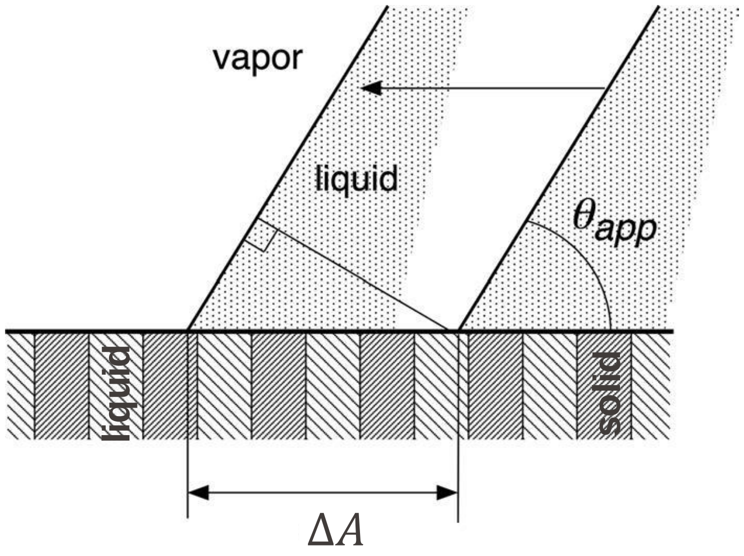
$\theta < 90° \Rightarrow \theta_{\text{app}} \leq \theta \quad r\uparrow \Rightarrow \theta_{\text{app}}\downarrow$

$\theta > 90° \Rightarrow \theta_{\text{app}} \geq \theta \quad r\uparrow \Rightarrow \theta_{\text{app}}\uparrow$

Hemi-Spreading State

Energy perspective of Young's Equation





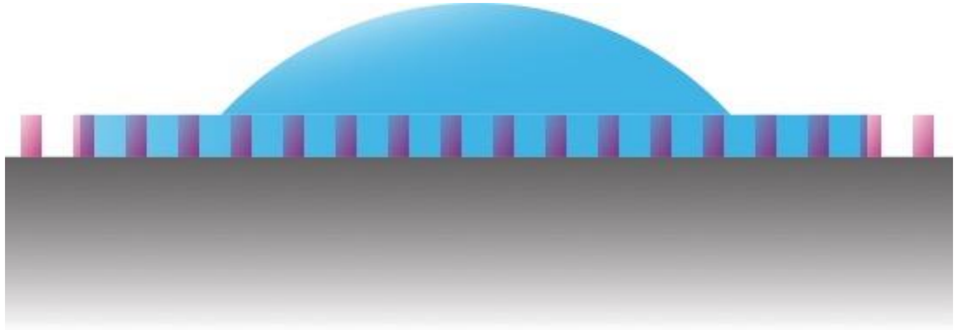
In the case that liquid infiltrates the surface structure beyond the original liquid footprint

$\sigma'_{sl} = \phi\sigma_{sl}$ $\sigma'_{sv} = \phi\sigma_{sv} + (1-\phi)\sigma_{lv}$ ϕ: top surface solid area fraction

$$-\sigma'_{sv}\Delta A + \sigma_{sl}'\Delta A + \sigma_{lv}\Delta A\cos\theta_{app} = 0$$

$$\cos\theta_{app} = \frac{\sigma'_{sv} - \sigma'_{sl}}{\sigma_{lv}} = \phi\cos\theta + (1-\phi)$$

Hemi-Spreading State

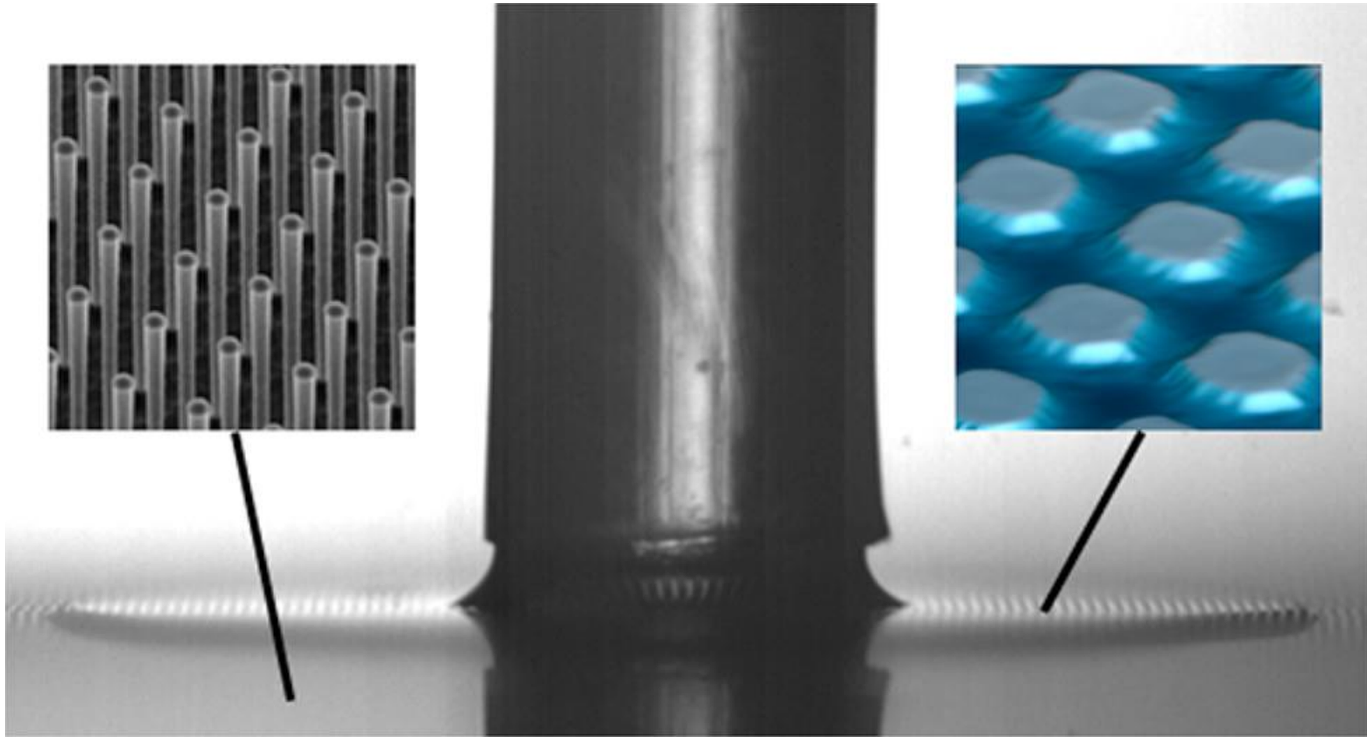


Liquid penetrates into surface structures ahead of macroscopic contact lines

$$\cos\theta_{\text{app}} = \phi\cos\theta + (1-\phi) = (\cos\theta - 1)\phi + 1$$

$$\theta < 90° \Rightarrow \theta_{\text{app}} \leq \theta \qquad \phi\downarrow \Rightarrow \theta_{\text{app}}\downarrow$$

Hemis-Spreading State



Allred *et al.*, *Langmuir* 2017

Spontaneous Hemi-Spreading Condition

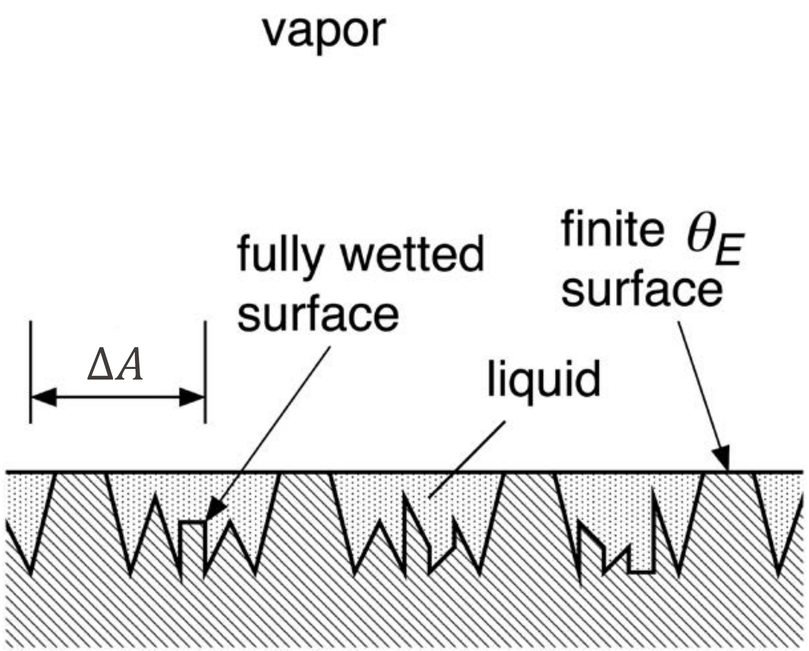


Figure 3.19 in Carey

Before liquid penetration

$$\sigma_{sv} r \Delta A$$

After liquid penetration

$$\sigma_{sv}\phi\Delta A + \sigma_{lv}(1-\phi)\Delta A + \sigma_{sl}(r-\phi)\Delta A$$

Liquid penetration condition:

$$\sigma_{sv} r \Delta A > \sigma_{sv}\phi\Delta A + \sigma_{lv}(1-\phi)\Delta A + \sigma_{sl}(r-\phi)\Delta A$$

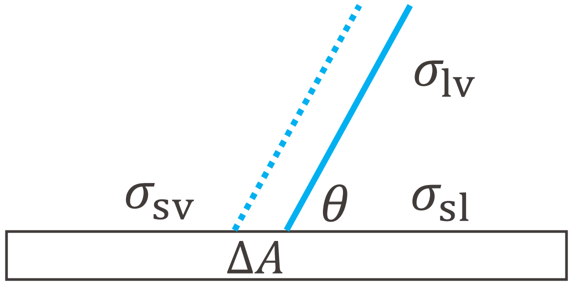
$$\sigma_{sv}(r-\phi) > \sigma_{lv}(1-\phi) + \sigma_{sl}(r-\phi)$$

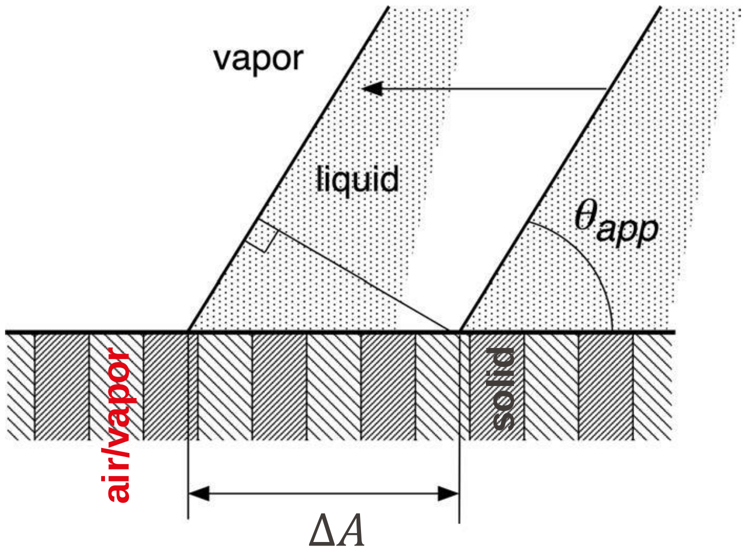
$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} > \frac{1-\phi}{r-\phi} = \cos\theta_c$$

θ needs to be smaller than the critical penetration contact angle θ_c for hemi-spreading to happen

Air Pocket Case

Energy perspective of Young's Equation





In the case that liquid cannot enter the interstitial space between the surface structure at all

$$\sigma_{sl}' = \phi\sigma_{sl} + (1-\phi)\sigma_{lv} \qquad \sigma_{sv}' = \phi\sigma_{sv}$$

ϕ: top surface solid area fraction

$$-\sigma_{sv}'\Delta A + \sigma_{sl}'\Delta A + \sigma_{lv}\Delta A\cos\theta_{app} = 0$$

$$\cos\theta_{app} = \frac{\sigma_{sv}' - \sigma_{sl}'}{\sigma_{lv}} = \phi\cos\theta + \phi - 1$$

Cassie-Baxter State

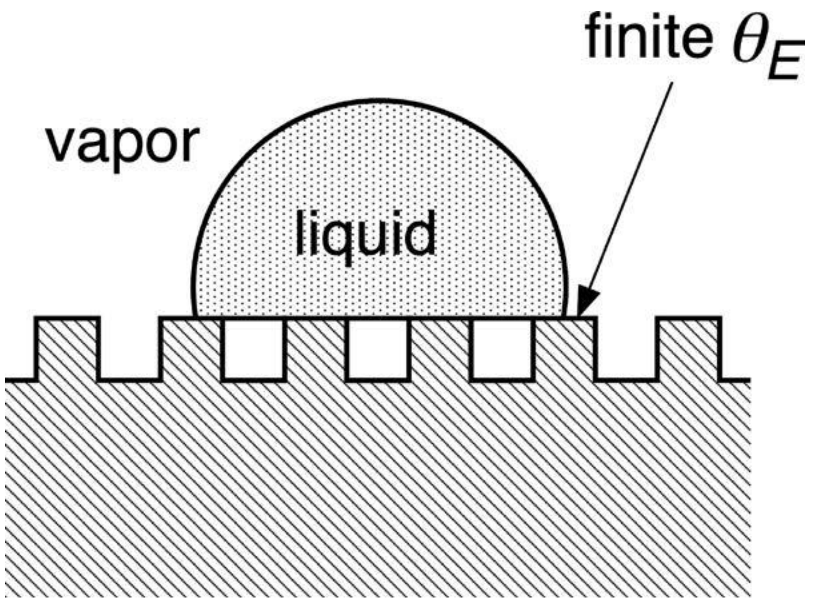


Figure 3.23 in Carey

Air/vapor trapped between the roughness elements underneath the droplet

$$\cos\theta_{app} = \phi\cos\theta + \phi - 1$$

Since $\phi \leq 1$ by definition

$\theta > 90° \Rightarrow \theta_{app} \geq \theta \qquad \phi \downarrow \Rightarrow \theta_{app} \uparrow$