



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

## Capillarity and Wetting

Zhengmao Lu

Energy Transport Advances  
Laboratory

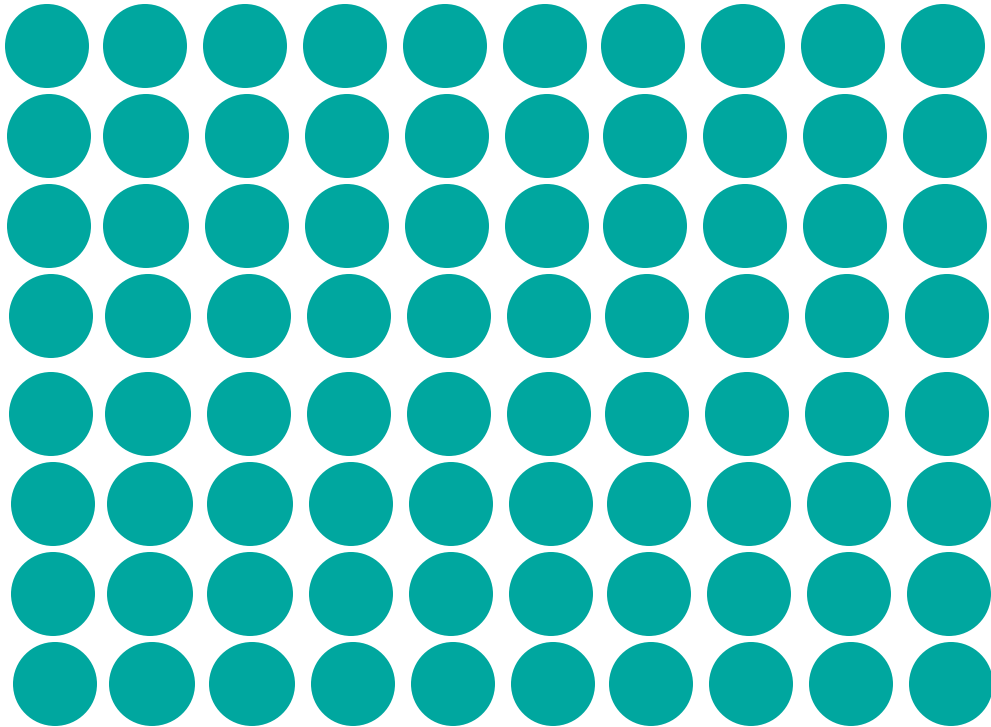
EPFL Mechanical Engineering

2025 Fall Semester

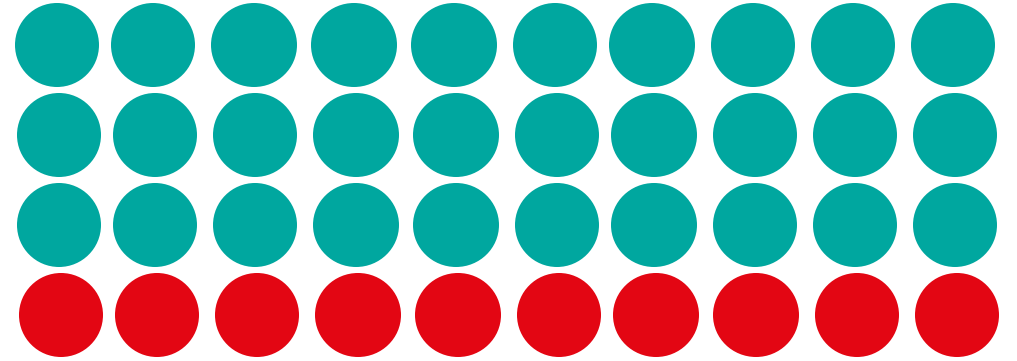
Photo Credit: Trougnouf

# Surface Energy ( $\text{J}/\text{m}^2$ )

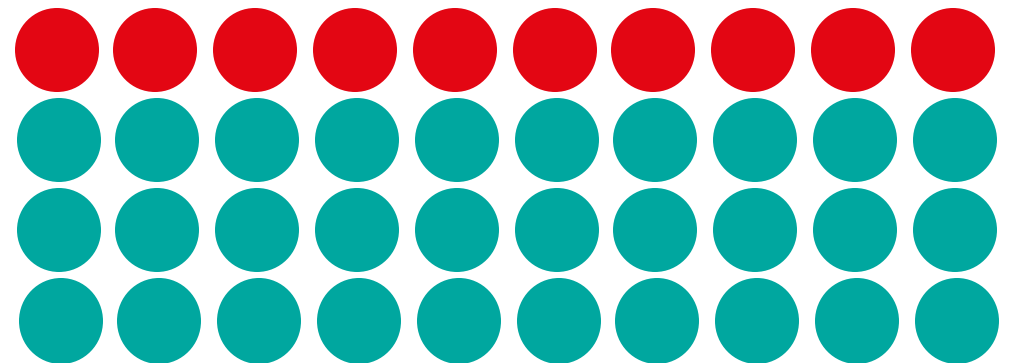
Lower energy state



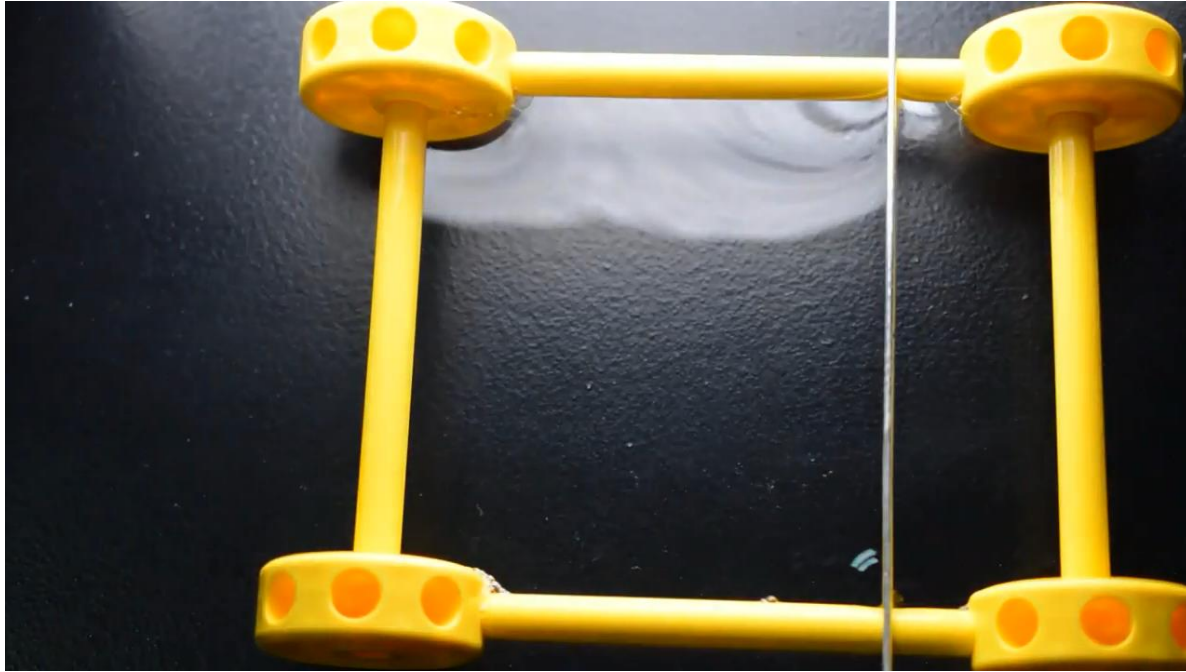
Work needed to create surfaces



High energy state (with 2 **surfaces**)



# Surface Tension (N/m)



PD, CC BY-SA 3.0

Surface exerting line forces on objects

# Young-Laplace Equation

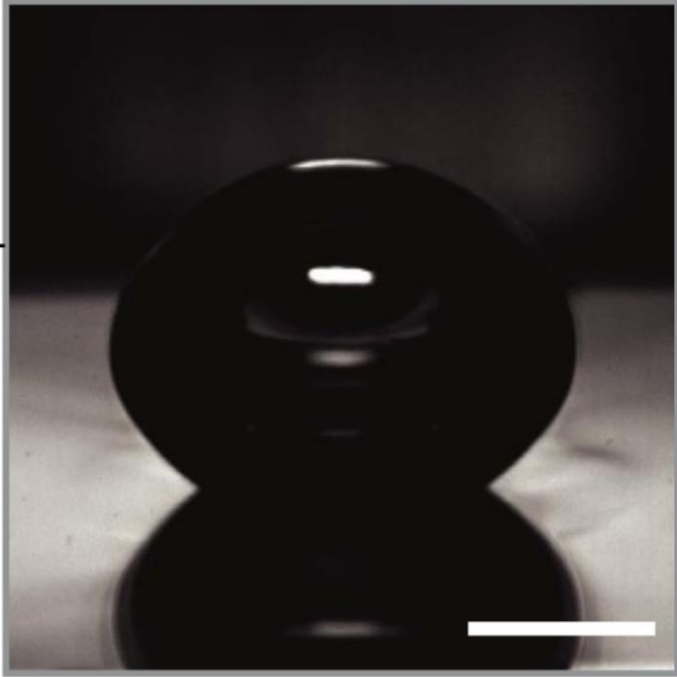
$$P_I - P_{II} = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

Young-Laplace Equation

- 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)

# Contact Angle: Force Balance Perspective

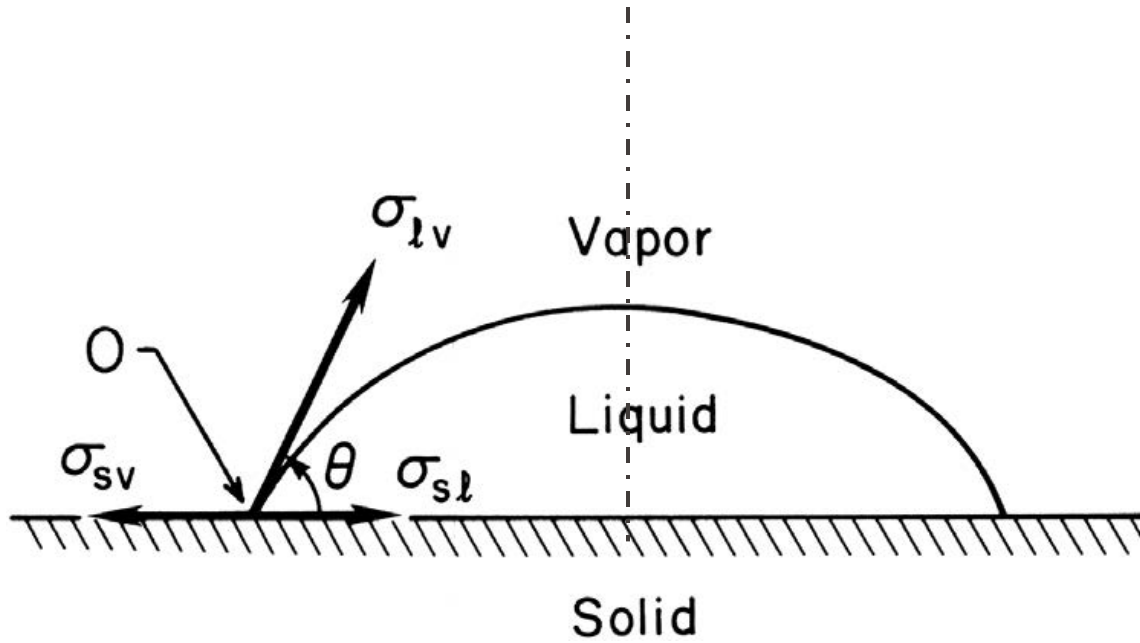


Figure 3.1 in Carey

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

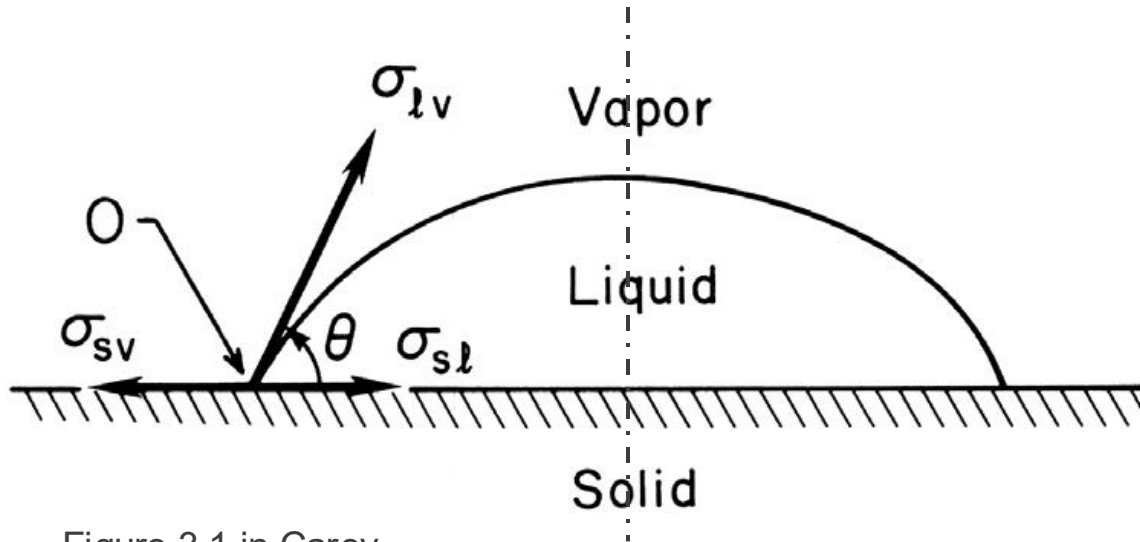


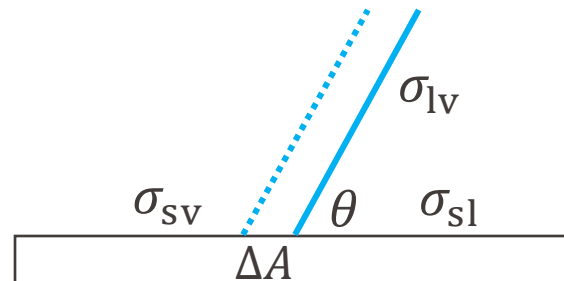
Figure 3.1 in Carey

Young's equation

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

Everything in [N/m] or [J/m<sup>2</sup>]

An energy perspective



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

- Hydrophilic surface (wetting)
  - $\theta$  between  $0^\circ$  and  $90^\circ$  when in contact with water
- Hydrophobic surface (non-wetting)
  - $\theta$  between  $90^\circ$  and  $180^\circ$  when in contact with water

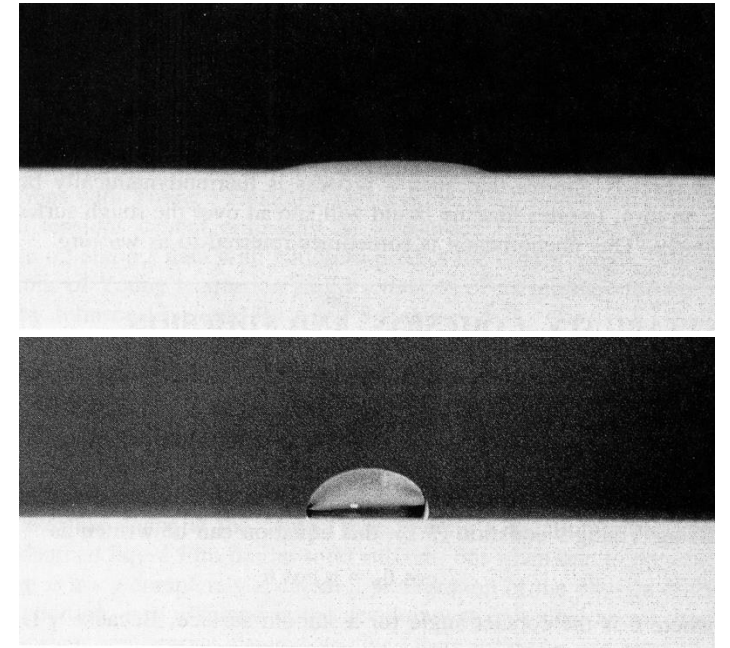


Figure 3.3 in Carey

# Capillary Rise/Fall

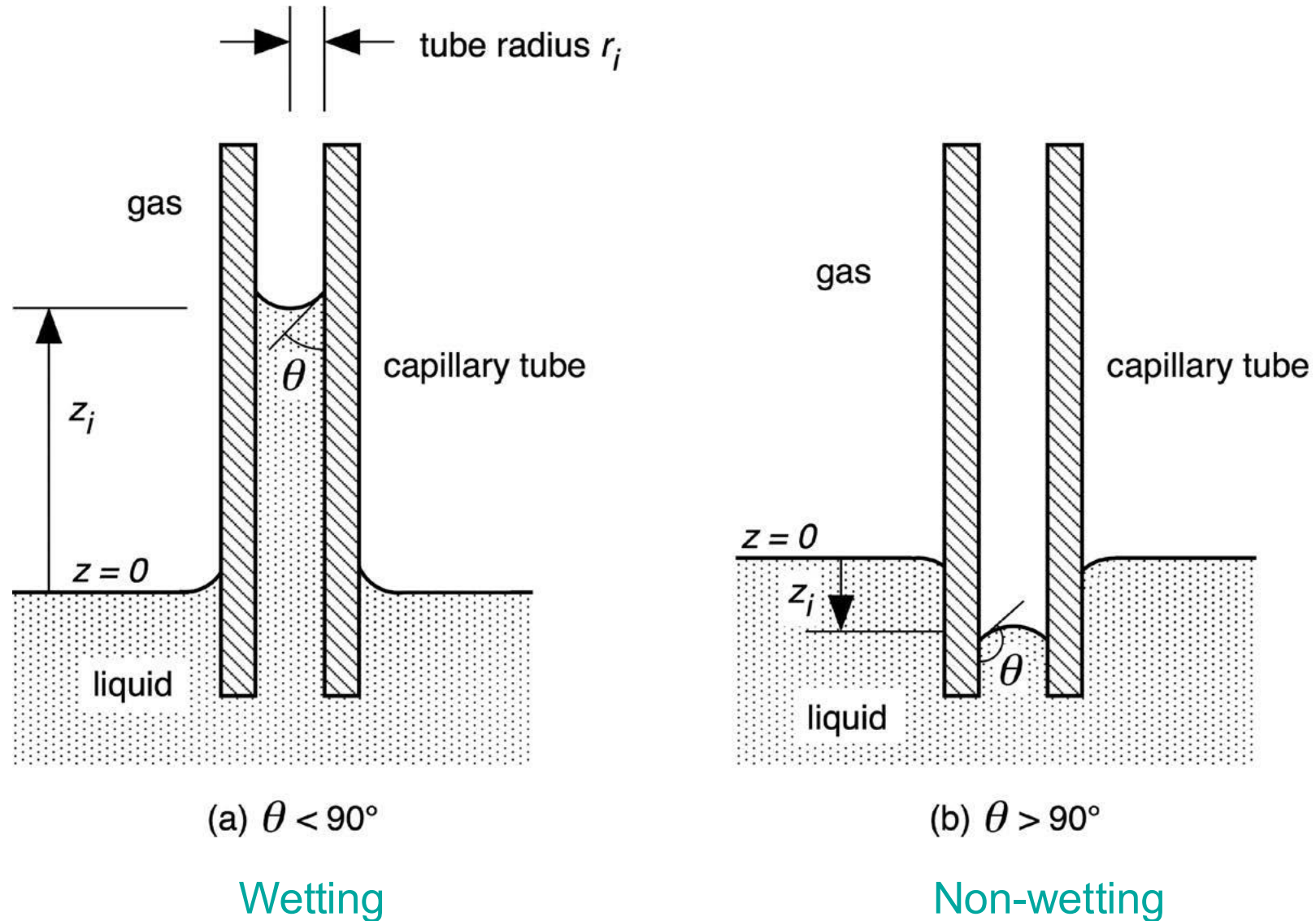
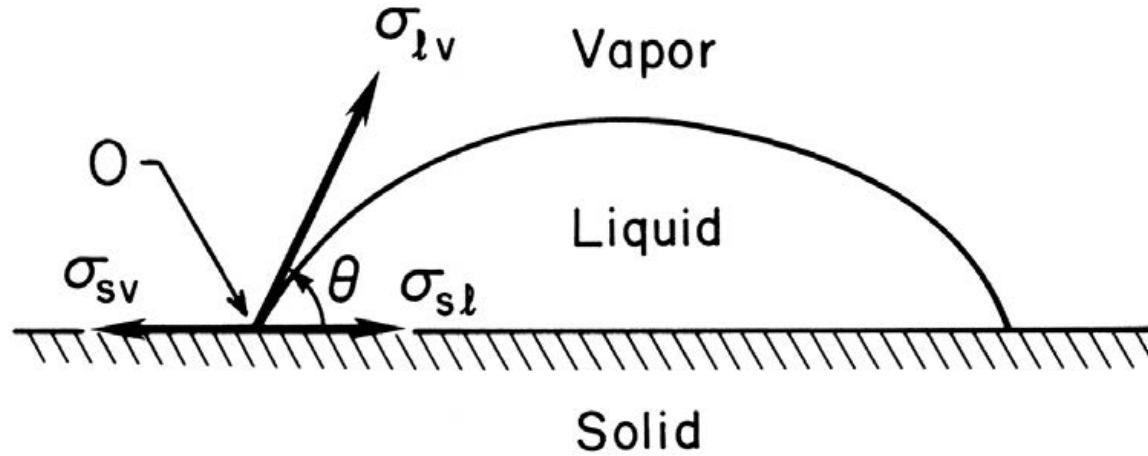


Figure 3.14 in Carey



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

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

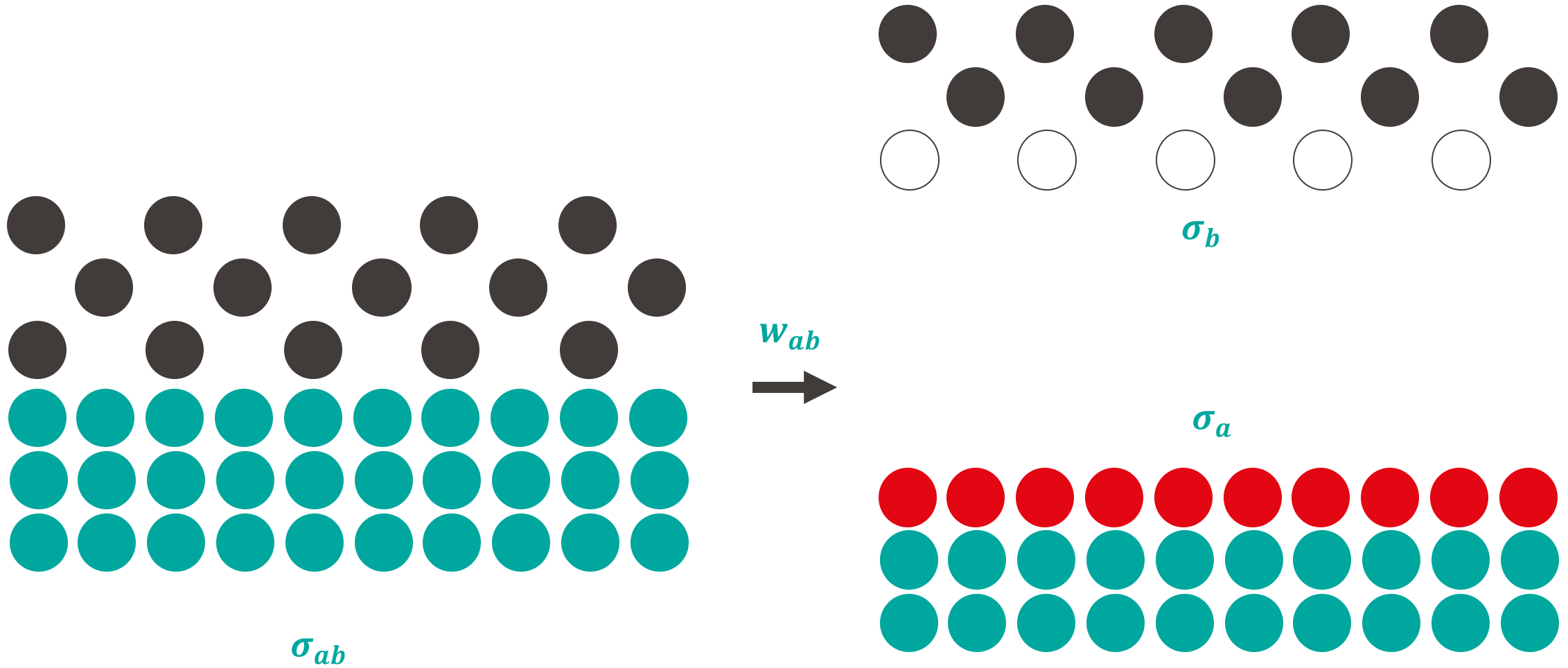
$\sigma_{sv}$ / Typical $\theta$ / $\sigma_{lv}$	Low (e.g., fluoropolymer)	Medium (e.g., nitride, oxide)	High (e.g., metal)
Low (e.g., alcohol, refrigerant)	< 90°	< 90°	< 90°
Medium (e.g., water)	> 90°	< 90°	< 90°
High (e.g., molten salt, liquid metal)	> 90°	> 90°	Mixed

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

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

Wilke *et al.*, PNAS 2021

# Interface Energy



$\sigma_{ab}$

$\sigma_b$

$W_{ab}$

$\sigma_a$

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

$W_{ab}$  depends on intermolecular interactions

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

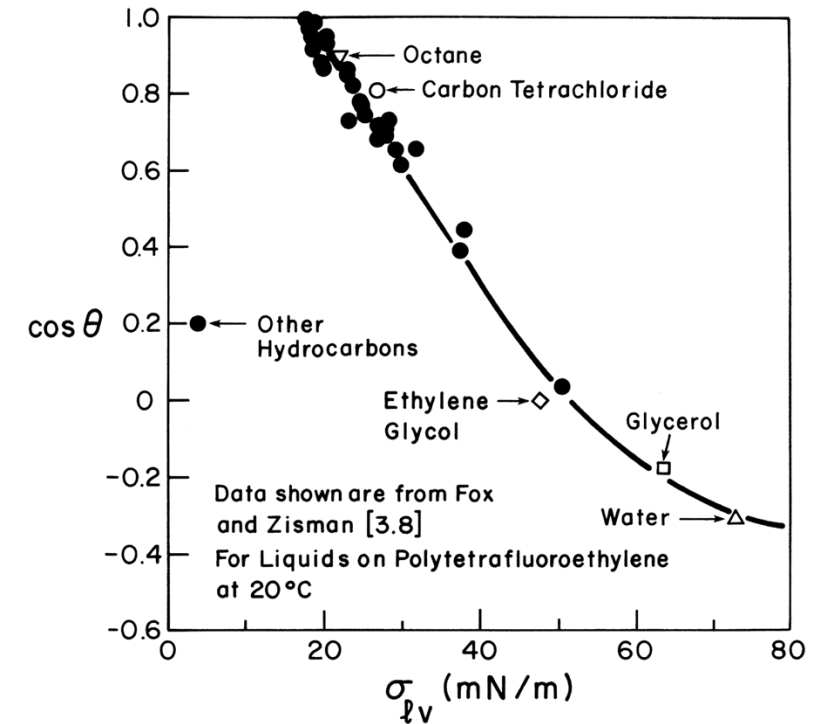
for nonpolar interactions

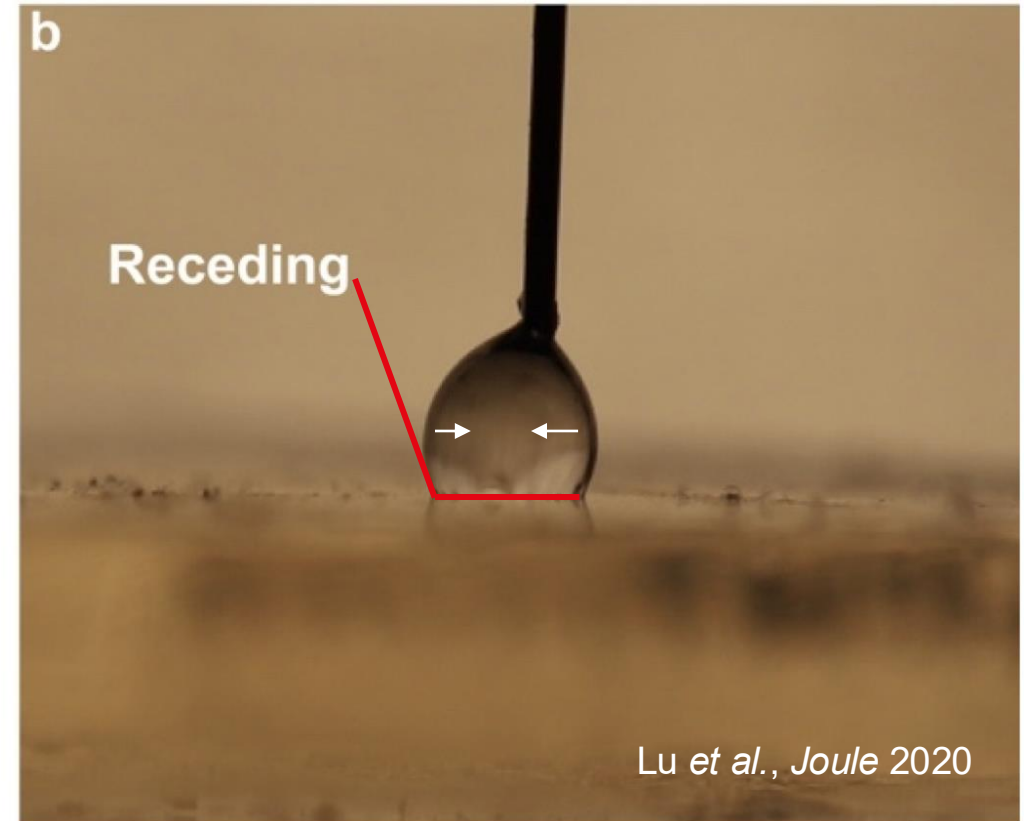
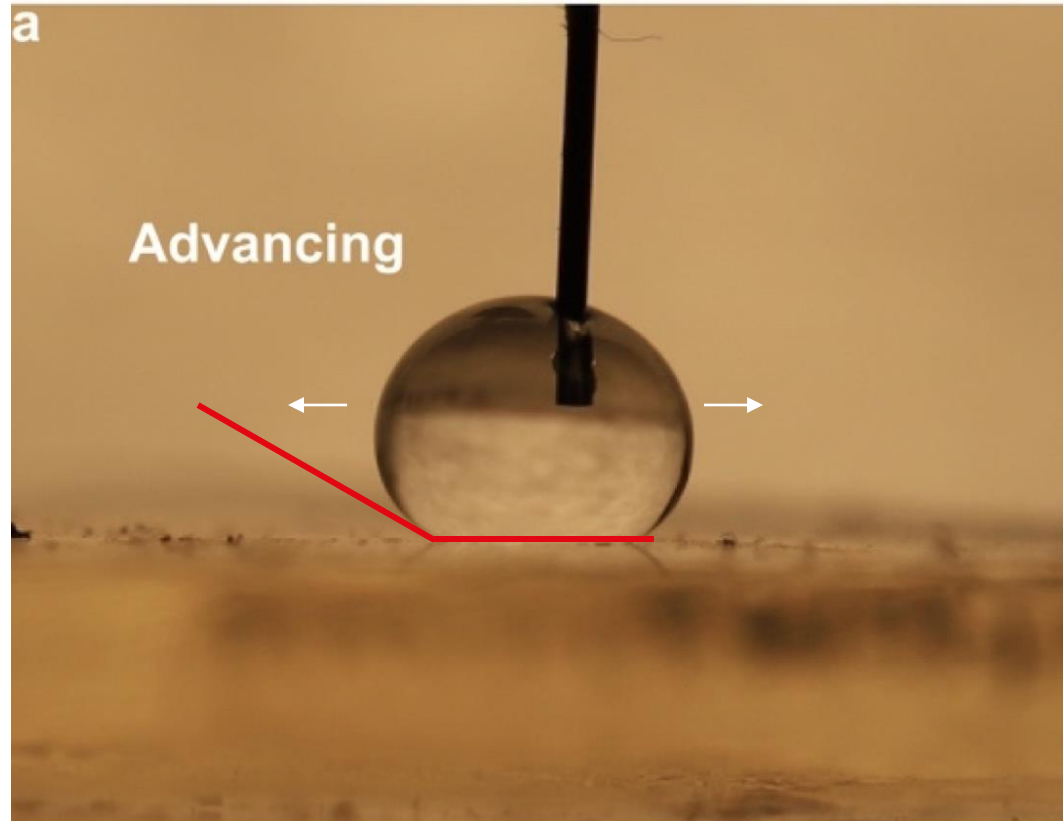
- Spreading coefficient (Eq. 3.20 in Carey)

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

- Critical surface tension (Chapter 3.3 in Carey)

the minimum surface tension at which a liquid will completely wet a solid surface





- 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

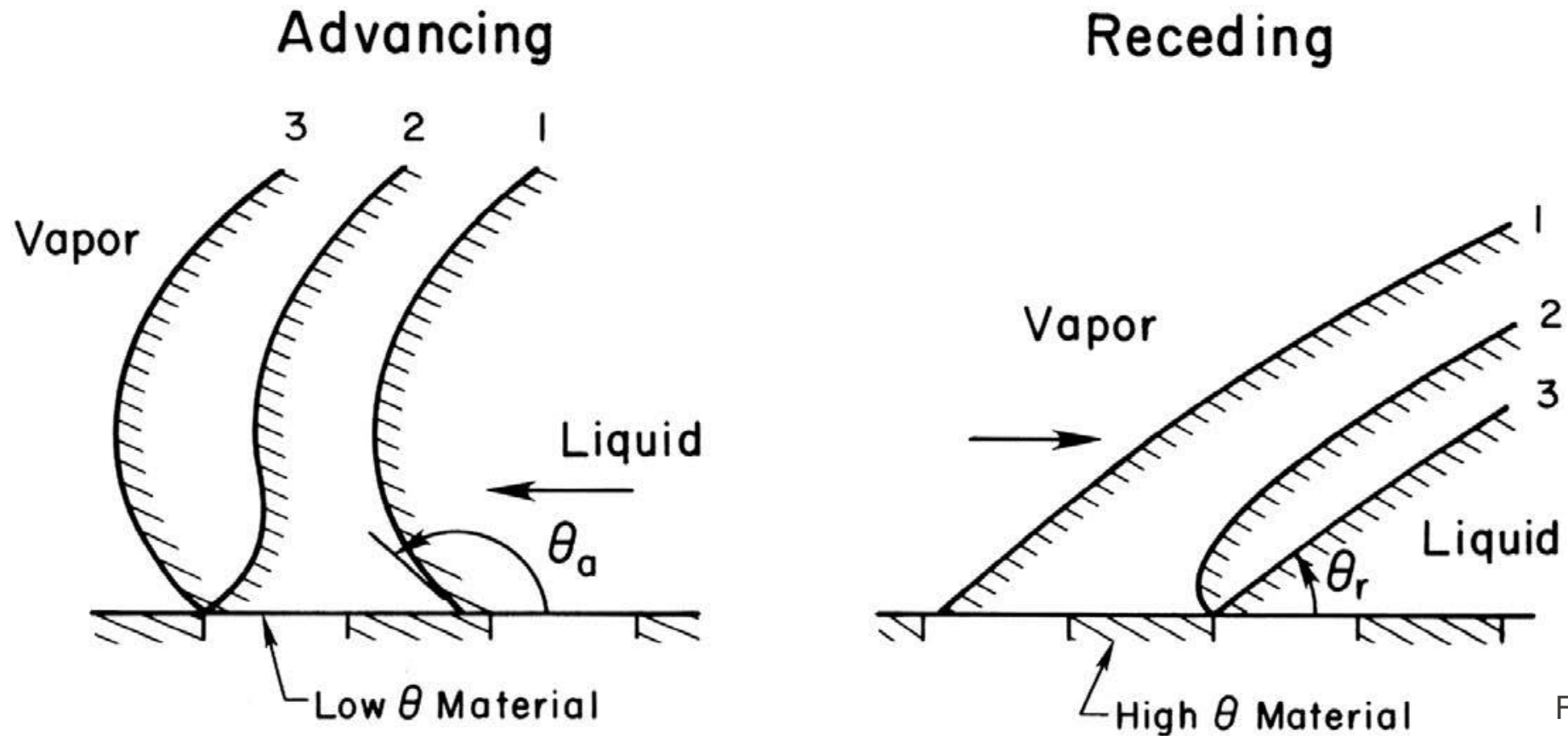


Figure 3.12a in Carey

- **Advancing** contact angle determined by the **high  $\theta$**  component
- **Receding** contact angle determined by the **low  $\theta$**  component

# Effect of Surface Inhomogeneity

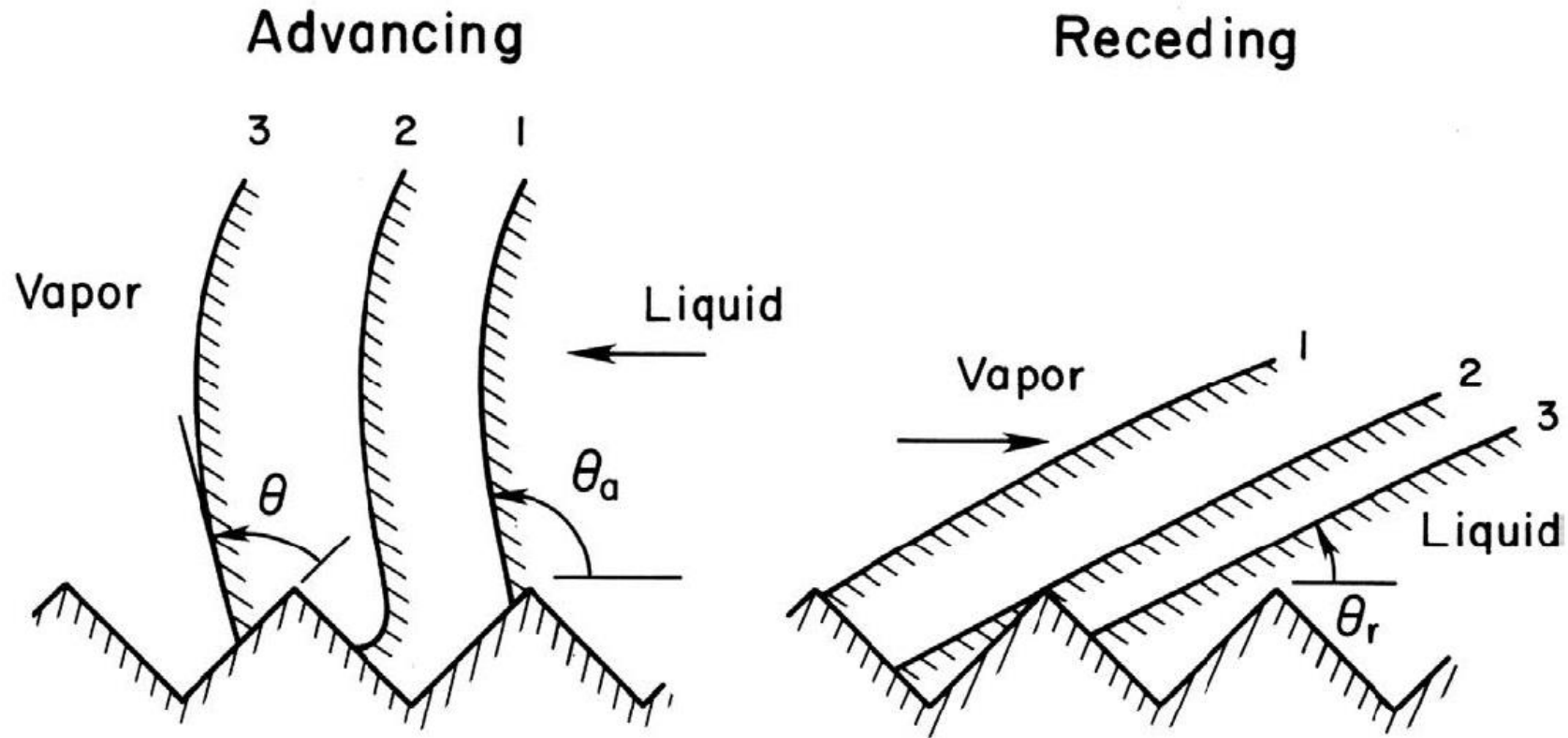


Figure 3.12b in Carey

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

# Contact Angle Hysteresis

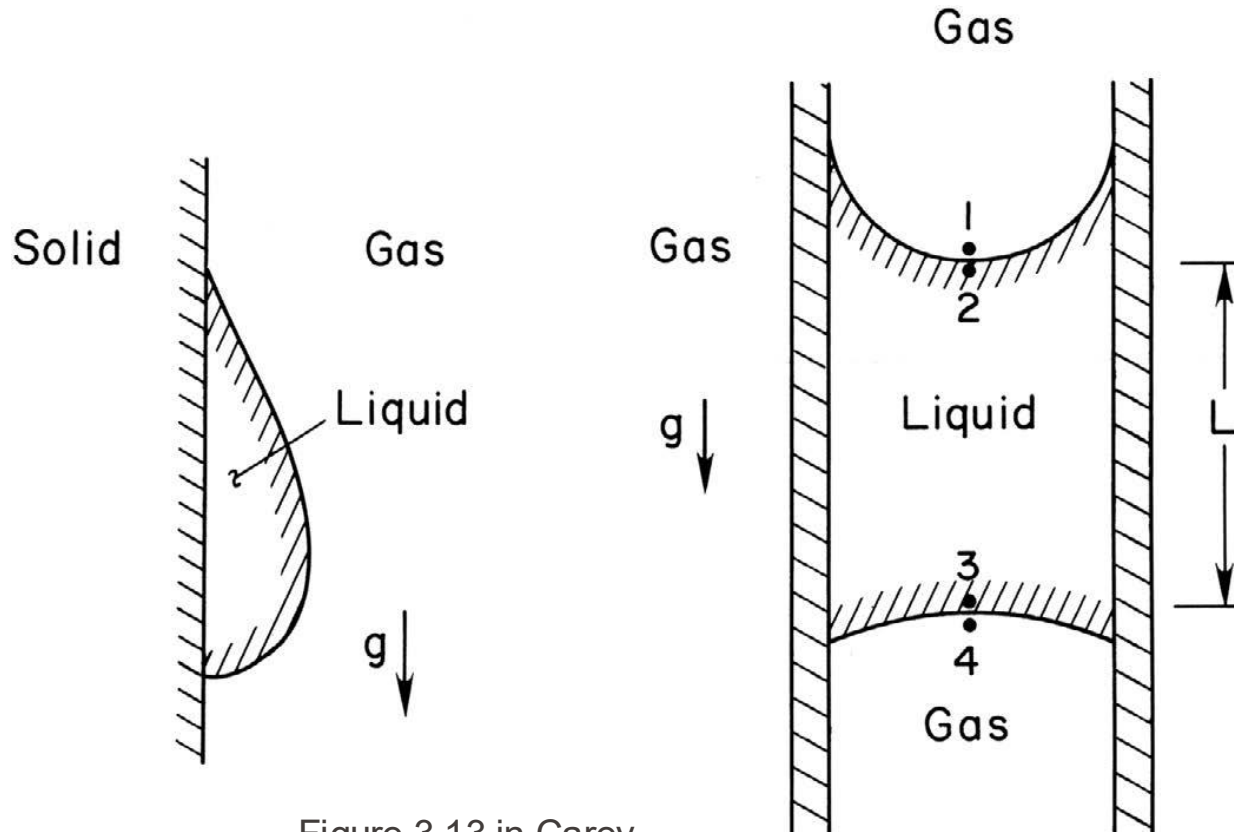


Figure 3.13 in Carey

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

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

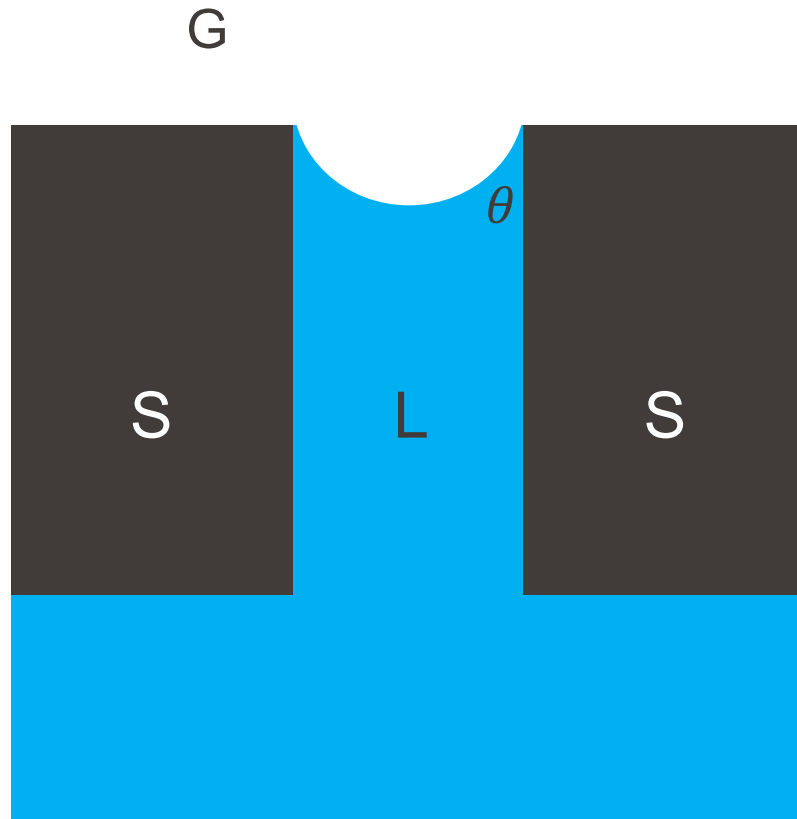
$$P_3 = P_2 + \rho_L g L$$

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

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

- Advancing CA > Equilibrium CA > Receding CA

# Contact Line Pinning



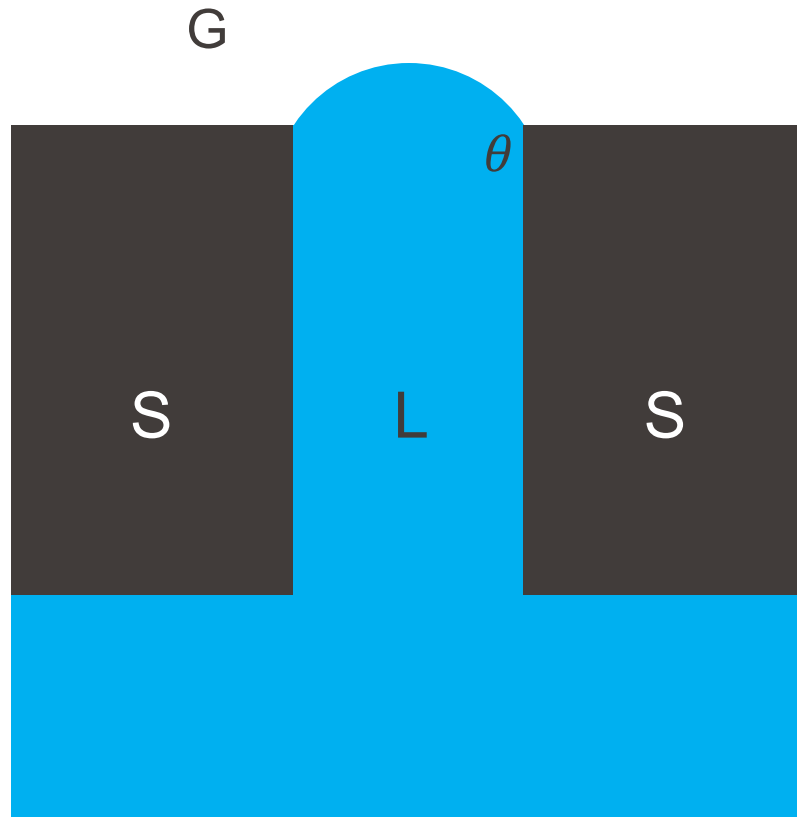
Cylindrical pore with radius  $r_p$

Initially  $P_L = P_G = P_0$ , interface flat

ACA =  $95^\circ$ , RCA =  $60^\circ$

Now, start increasing  $P_G$

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



Cylindrical pore with radius  $r_p$

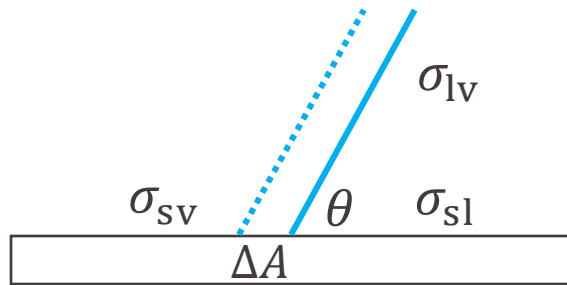
Initially  $P_L = P_G = P_0$ , interface flat

ACA =  $95^\circ$ , RCA =  $60^\circ$

If we instead increase  $P_L$

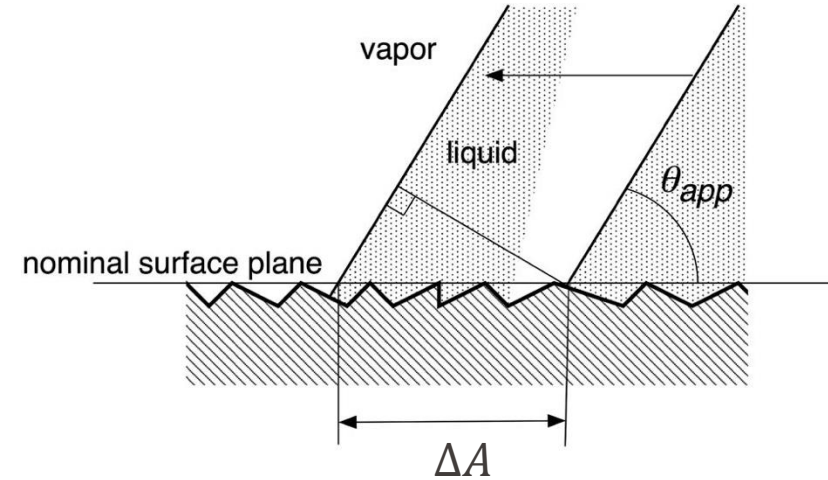
$$P_L - P_G = \frac{2\sigma \sin(\theta - 90^\circ)}{r_p}$$

Energy perspective of Young's Equation



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

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



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

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

$r$ : roughness ratio, actual surface area/projected area

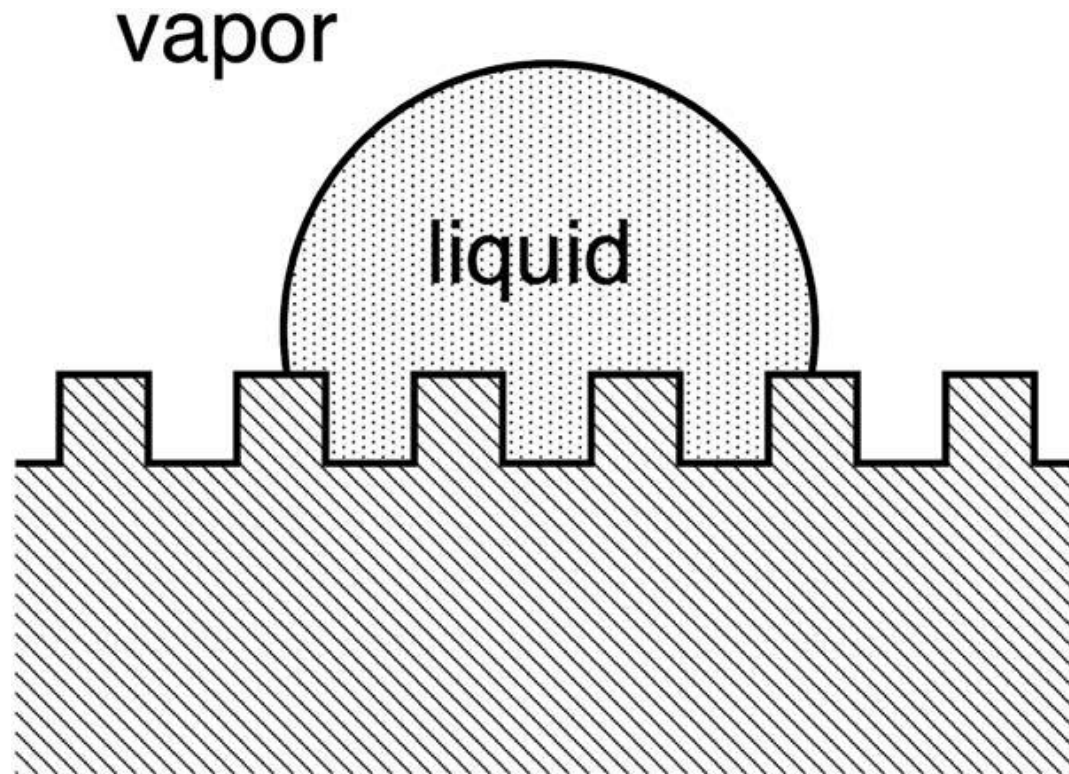


Figure 3.19 in Carey

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

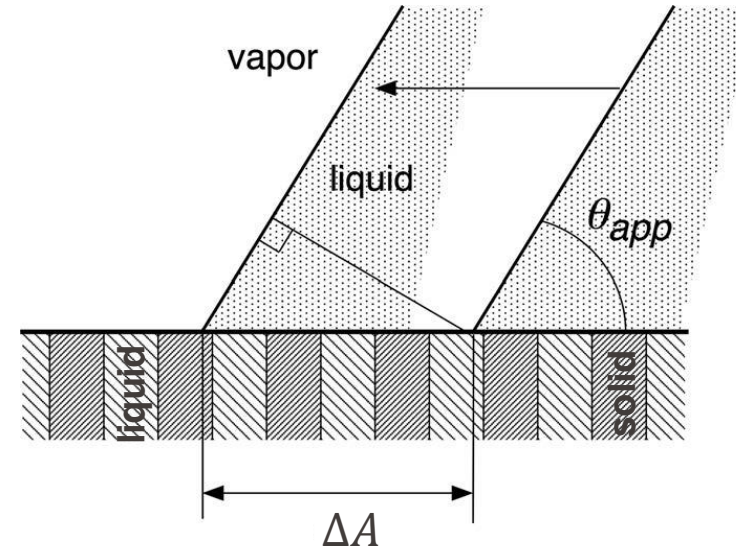
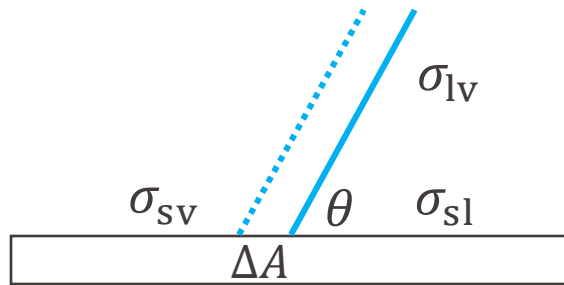
$$\cos \theta_{\text{app}} = r \frac{\sigma_{\text{sv}} - \sigma_{\text{sl}}}{\sigma_{\text{lv}}} = r \cos \theta_E$$

Since  $r \geq 1$  by definition

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

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

Energy perspective of Young's Equation



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

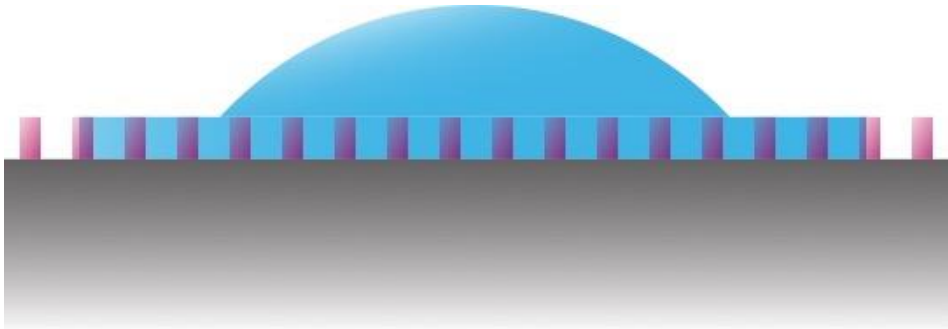
$$\sigma'_{sl} = \phi \sigma_{sl} \quad \sigma'_{sv} = \phi \sigma_{sv} + (1 - \phi) \sigma_{lv}$$

$\phi$ : 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

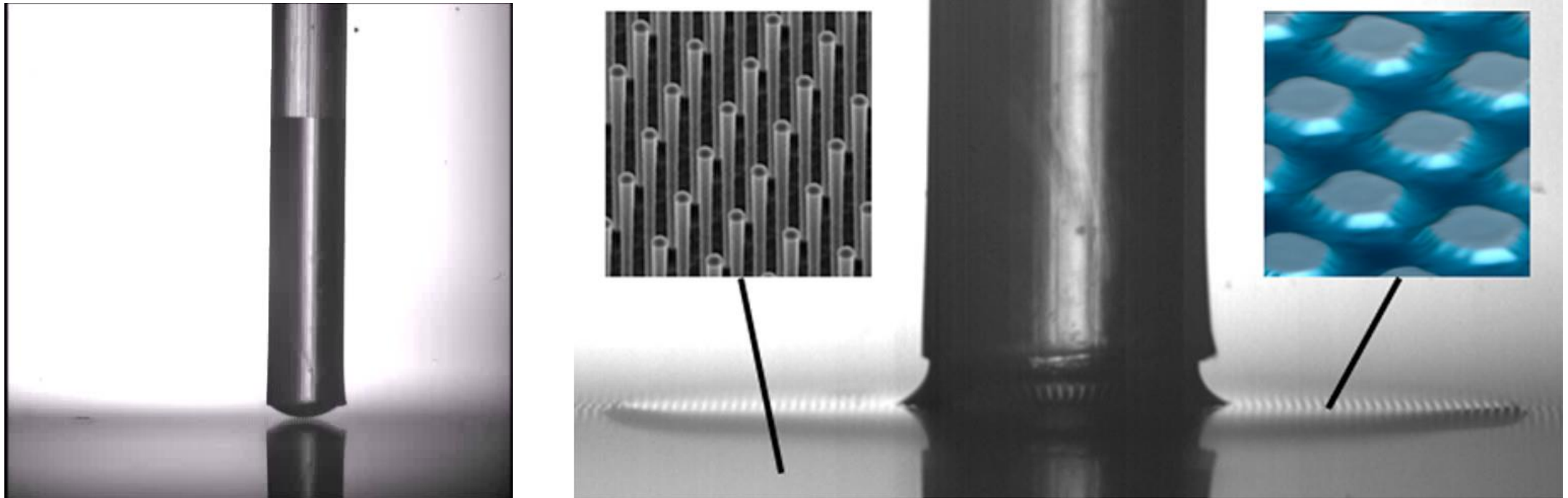


Liquid penetrates into surface structures ahead of macroscopic contact lines

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

$$\theta < 90^\circ \Rightarrow \theta_{\text{app}} \leq \theta \quad \phi \downarrow \Rightarrow \theta_{\text{app}} \downarrow$$

# Hemis-Spreading State



Allred *et al.*, *Langmuir* 2017

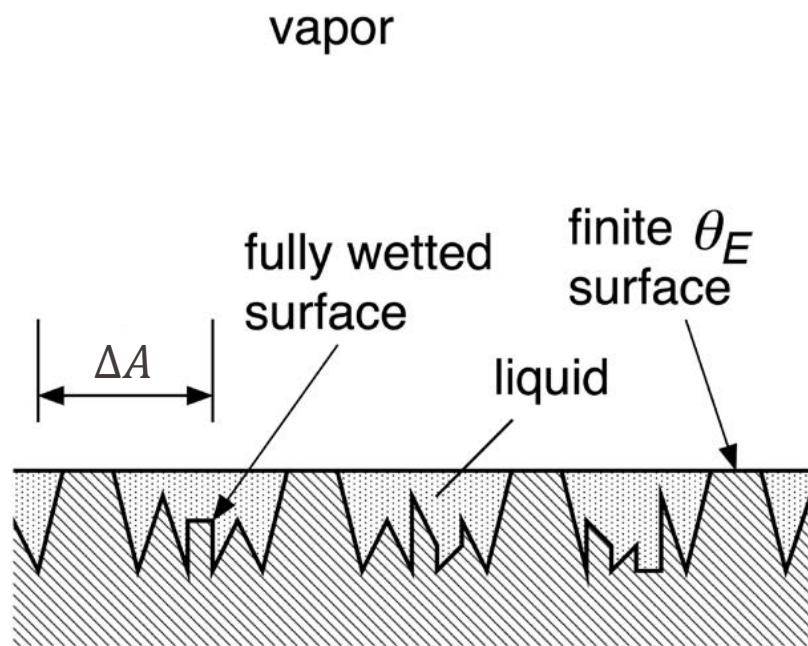


Figure 3.19 in Carey

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:

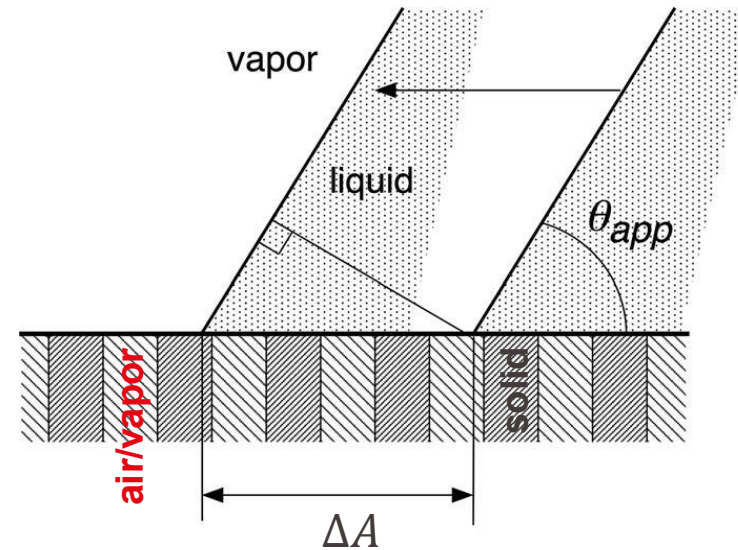
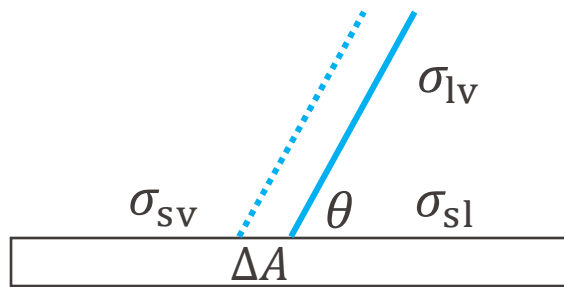
$$\sigma_{sv}r\Delta A > \sigma_{sv}\phi\Delta A + \sigma_{lv}(1 - \phi)\Delta A + \sigma_{sl}(r - \phi)\Delta A$$

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

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

$\theta$  needs to be smaller than the critical penetration contact angle  $\theta_c$  for hemi-spreading to happen

Energy perspective of Young's Equation



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

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

$\phi$ : top surface solid area fraction

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

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

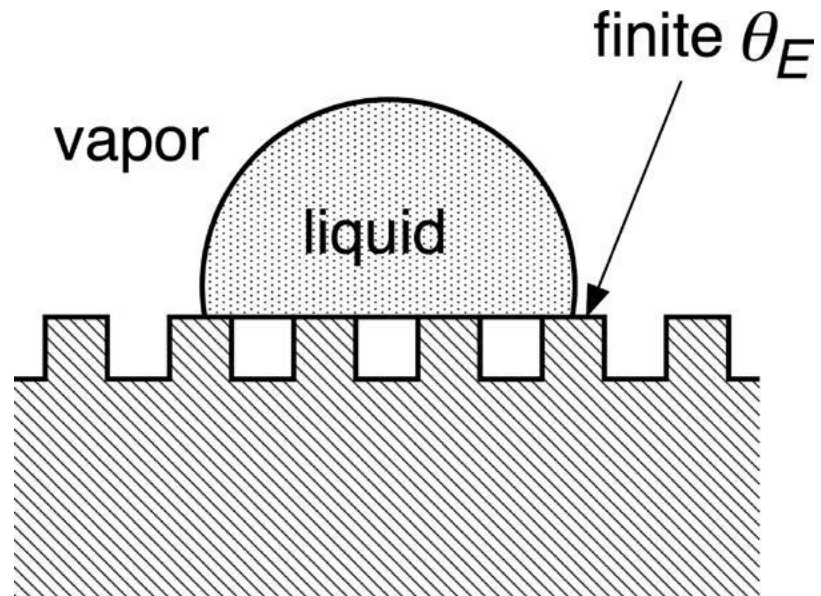


Figure 3.23 in Carey

Air/vapor trapped between the roughness elements underneath the droplet

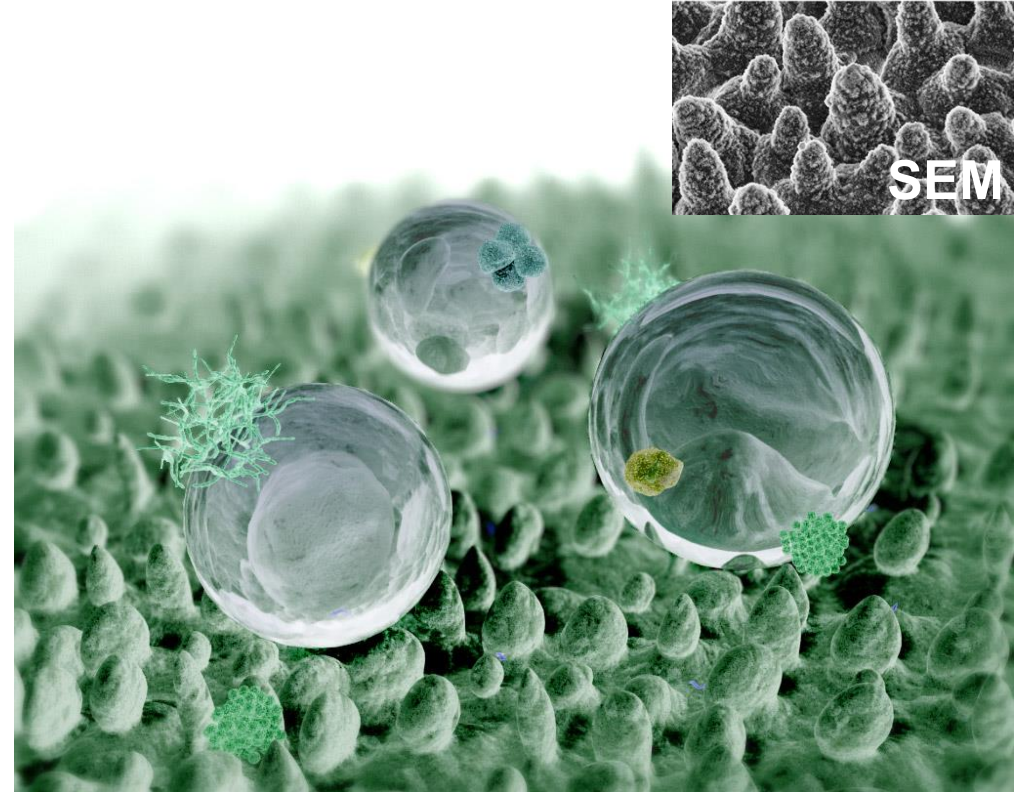
$$\cos \theta_{\text{app}} = \phi \cos \theta + \phi - 1$$

Since  $\phi \leq 1$  by definition

$$\theta > 90^\circ \Rightarrow \theta_{\text{app}} \geq \theta \quad \phi \downarrow \Rightarrow \theta_{\text{app}} \uparrow$$

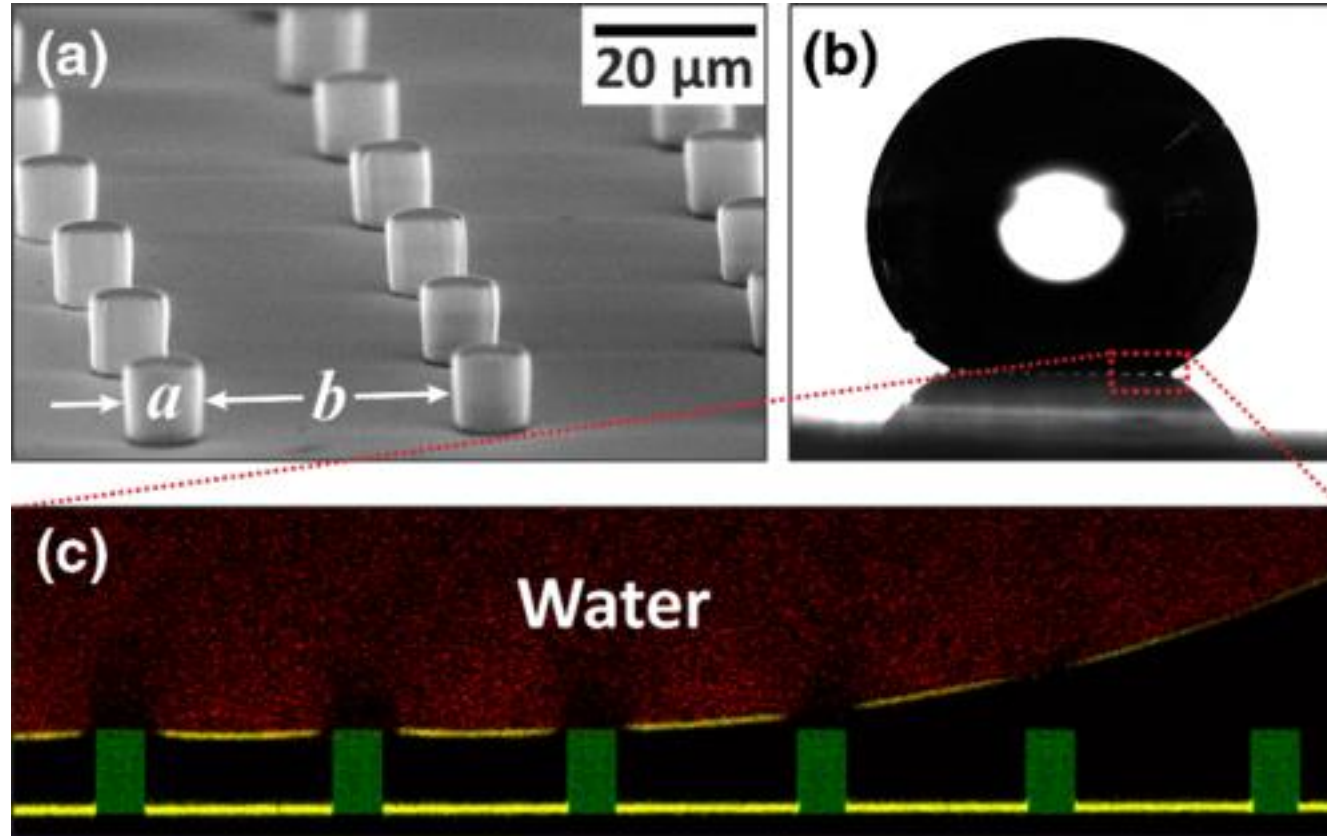


<http://davewirth.blogspot.com/2011/11/final-lotus-of-year.html>



Computer graphic of a lotus leaf surface,  
William Thielicke, CC BY-SA 4.0

# Conditions for Air Pocket Formation



Capillary pressure preventing liquid from entering surface structures

For pillar structure, this approximately means  
 $\theta > 90^\circ$

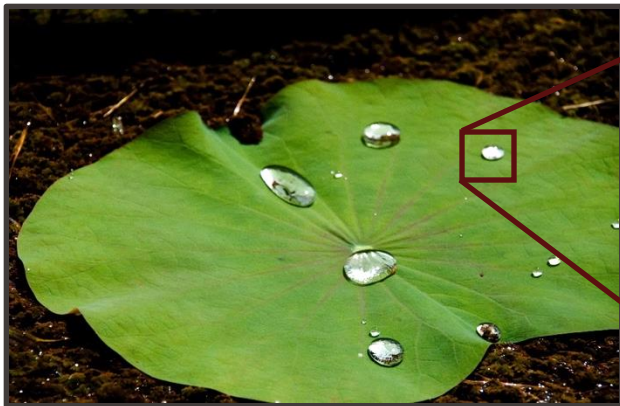
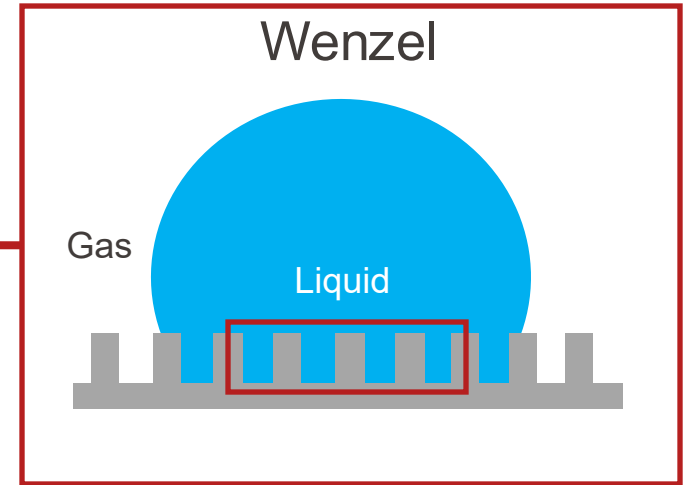
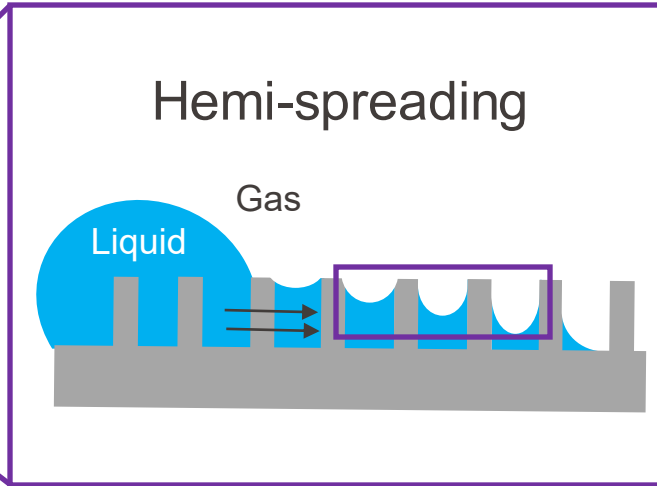
Schellenberger *et al.*, *Physical Review Letters* 2016

# Different Regimes



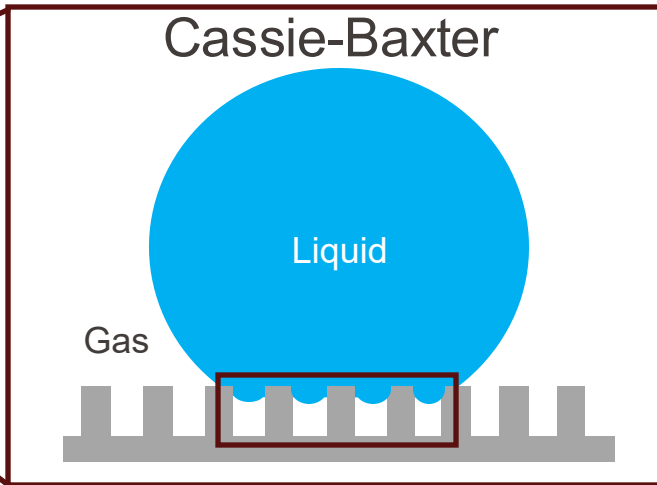
Texas horned lizard

Burton Robert, U.S. Fish and Wildlife Service



Lotus leaf

GJ Bulte (Own work) [CC BY-SA 3.0]



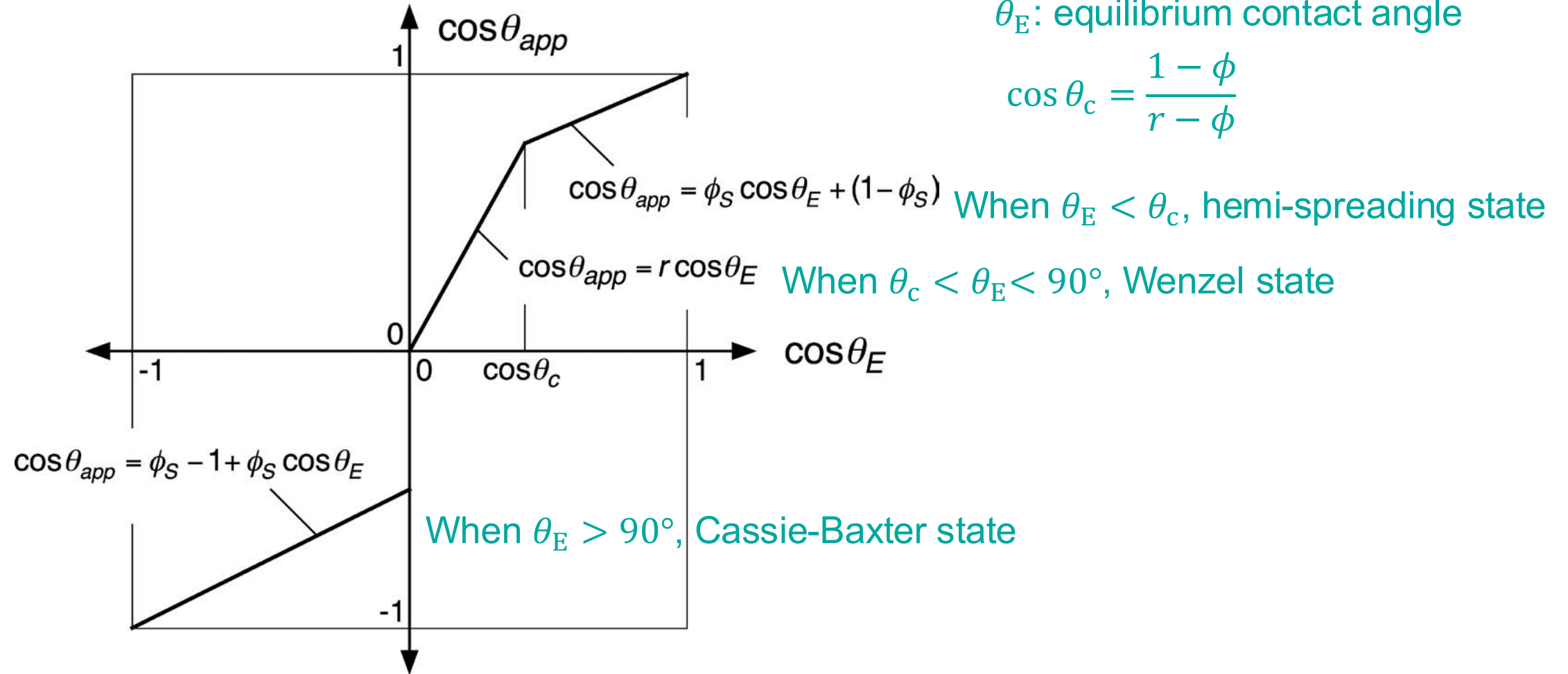
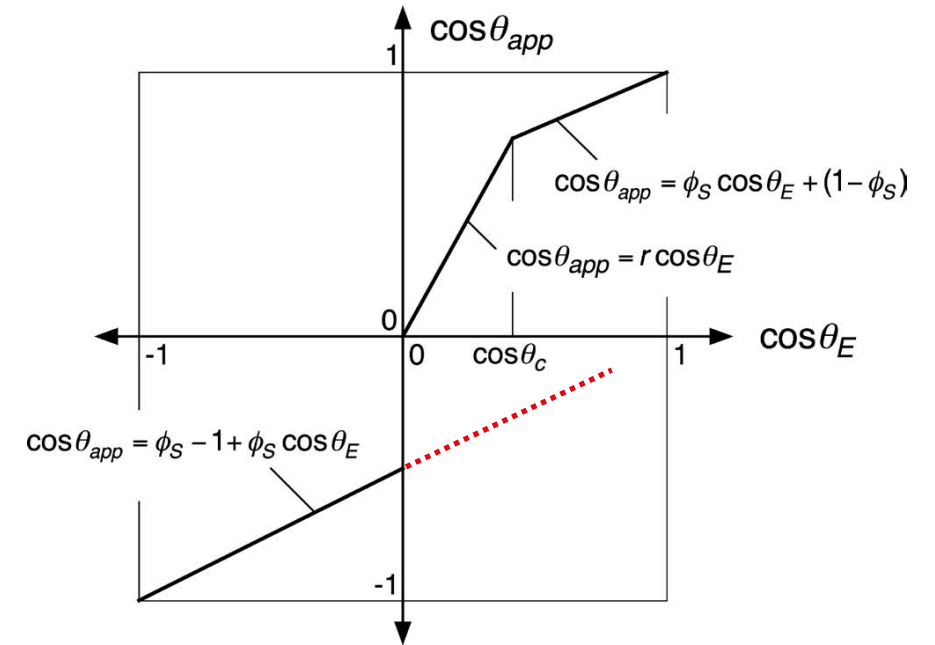


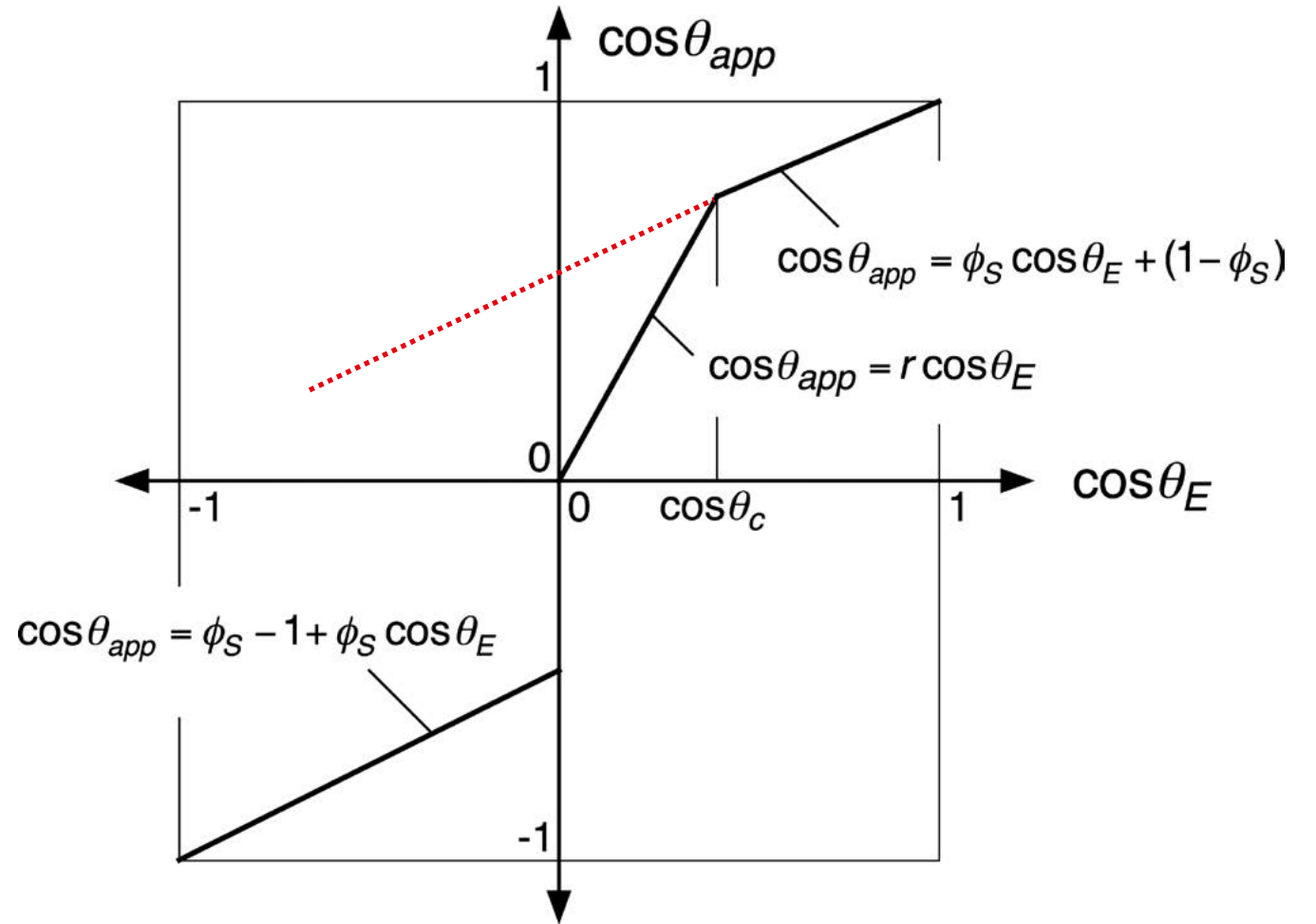
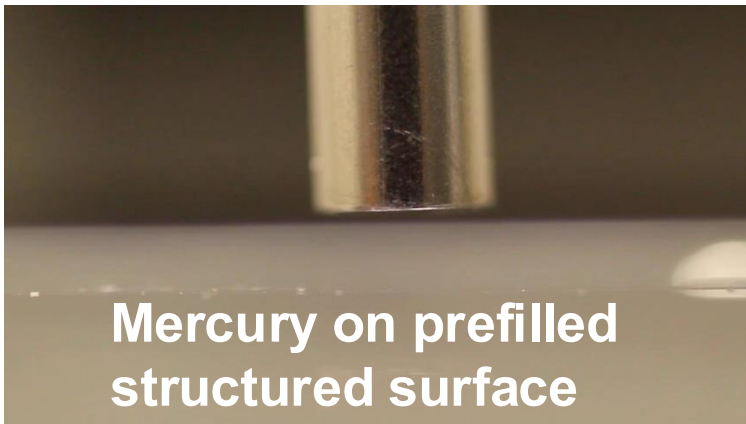
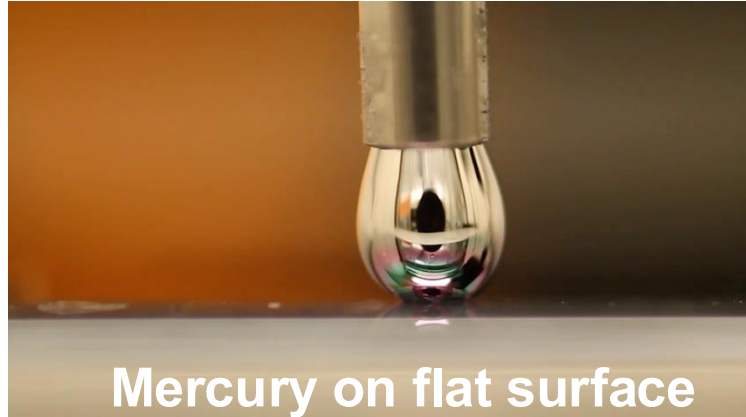
Figure 3.24 in Carey

# What We Have Learned Today

- What is **contact angle** and how it is generally affected by **surface tension/surface energy**?
- What is **contact angle hysteresis**?
- What is the effect of surface structures/roughness on contact angle? **Hemi-spreading, Wenzel, Cassie-Baxter**

Water (72 mN/m)





Wilke et al., PNAS 2021