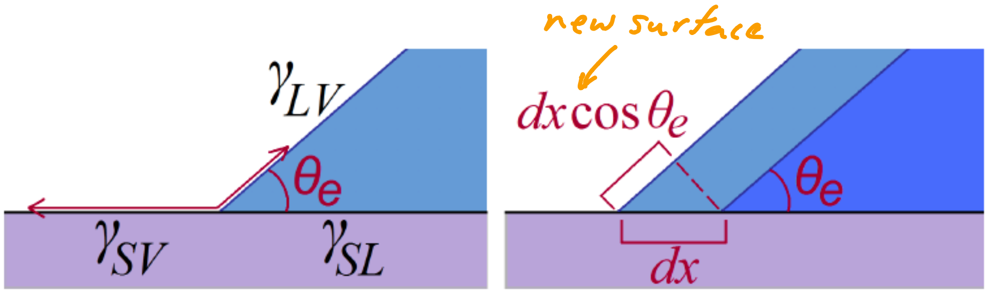
Lecture 15: Contact angle hysteresis, Wetting of rough solids

Recall from Lec. 3: we defined an EQUILIBRIUM CONTACT ANGLE θ_e to describe the wetting of a flat solid.



From a horizontal force balance at contact line...

Young's Law:

$$\boxed{\cos\theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}}$$

Alternatively, we can calculate the work done by moving the contact line a distance dx:

$$dW = \underbrace{(\gamma_{SV} - \gamma_{SL})\,dx}_{\text{from new wetted solid}} - \underbrace{\gamma\cos\theta_e\,dx}_{\text{from new interface}}$$

In equilibrium, $dW = 0$, which yields

It would be nice/simple if wetting could be simply characterized in terms of this single number θ_e. Alas, there is...

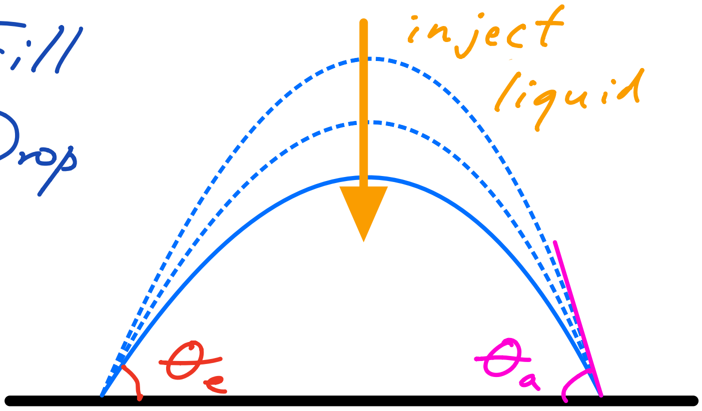
Contact Angle Hysteresis

- for a given solid, liquid, there is a range of possible contact angles $\theta_r < \theta < \theta_a$

RETREATING ADVANCING

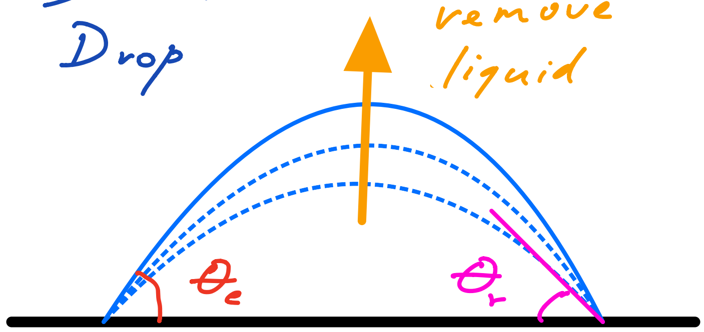
- many θ values may coexist, depending on surface, liquid, gas, roughness and history

Fill Drop



- begin with $\theta = \theta_e$
- θ increases until attaining $\theta_a \Rightarrow$ contact line advances

Drain Drop

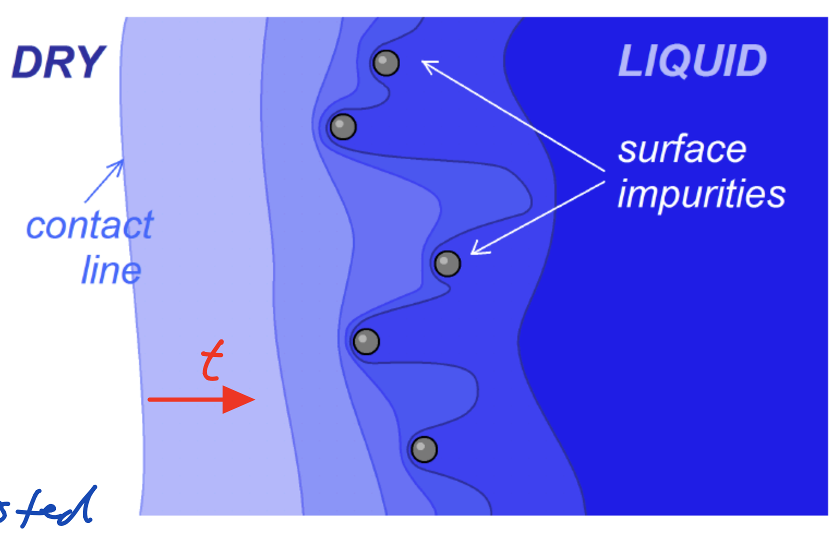


- θ decreases until reaching $\theta_r \Rightarrow$ contact line retreats

Origins of Contact Angle Hysteresis

- contact line pinning results from surface heterogeneities (either chemical or textural)

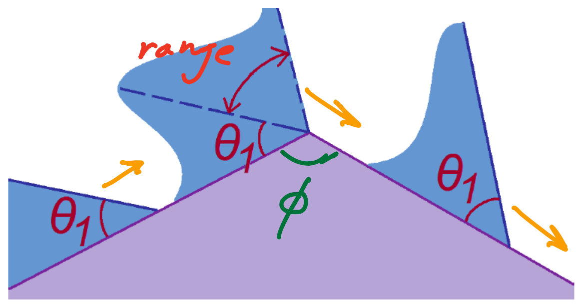
- pinning of contact line on impurities leads to increasing surface area and so surface energy
$\Rightarrow$ energetically costly
$\Rightarrow$ contact line motion resisted



Contact Line Pinning at Corners

- a finite range of contact angles can arise at a corner:

$$\theta_1 < \theta < \pi - \phi + \theta_1$$



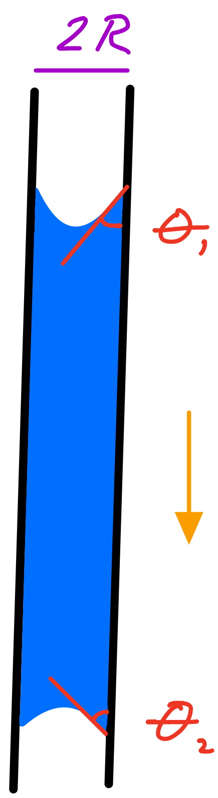
$\Rightarrow$ an advancing contact line will be pinned at corners

$\therefore$ surface texture increases contact angle hysteresis

Manifestations of Contact Angle Hysteresis

I. Liquid Column Trapped in a Capillary Tube

- θ_2 can be as large as θ_a
- θ_1 can be as small as θ_r
- in general, $\theta_2 > \theta_1$, so there is a net capillary force available to support weight of the column:



$$\underbrace{2\pi R\sigma(\cos\theta_1 - \cos\theta_2)}_{\text{contact force}} = \underbrace{\rho g \pi R^2 H}_{\text{wt}}$$

$\Rightarrow$ Force balance : $\boxed{\dfrac{2\sigma}{R}(\cos\theta_1 - \cos\theta_2) = \rho g H}$

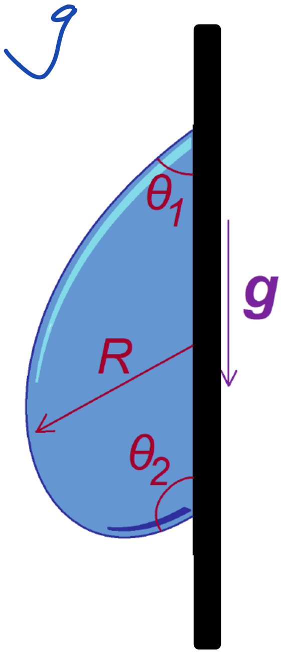
Equilibrium only possible if

$$\frac{2\sigma}{R}(\cos\theta_r - \cos\theta_a) > \rho g H$$

Note: if $\theta_a = \theta_r$ (no hysteresis) $\Rightarrow$ no equilibrium

II. Raindrop on a Window Pane

- if $\theta_1 = \theta_2 \Rightarrow$ drop will roll due to g
- θ_2 can be as large as θ_a
  θ_1 " " " small " θ_r
- drop's weight can be supported by contact force associated with contact angle hysteresis



Note: $F_g \sim \rho R^3 g$, $F_{contact} \sim 2\pi R(\cos\theta_1 - \cos\theta_2)\sigma$

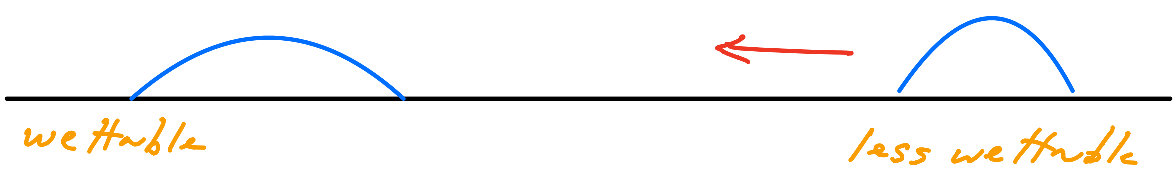
$$\Rightarrow \frac{F_g}{F_c} \sim \frac{\rho g R^2}{\sigma} \sim \mathcal{B}_o \quad \text{Bond number}$$

- drops will increase in size (by condensation or drop impact) until $Bo > 1$, and then they will roll downwards

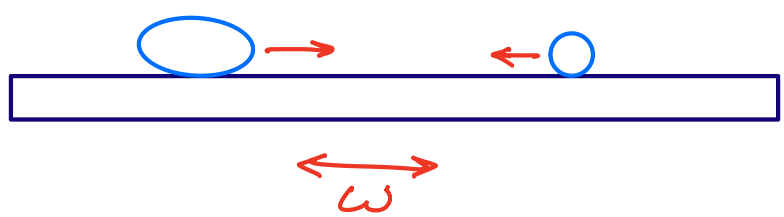
Other Ways to Overcome Contact Angle Hysteresis

In addition to gravity, one may free contact lines via

A. Wettability Gradients



B. Vibration-induced motion



- asymmetric vibration e.g. sawtooth first $\frac{1}{2}$-cycle, sinusoidal in 2nd

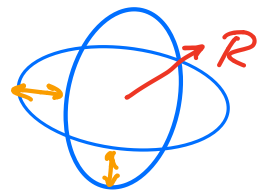
  $\Rightarrow$ asymmetry drive force

Note: different sized drops may move in different directions.

Why?

Drops have a natural frequency :

$\rho U^2 \sim \sigma / R$ where $U \sim \omega R$



$\Rightarrow \quad \omega \sim \left(\frac{\sigma}{\rho R^3}\right)^{\frac{1}{2}}$ that depends on drop size

- different sized drops will have different vibrational modes excited

  $\Rightarrow$ may move in opposite directions

Generally, contact angle hysteresis causes drops to stick to solids, and so is undesirable in many natural and industrial processes.

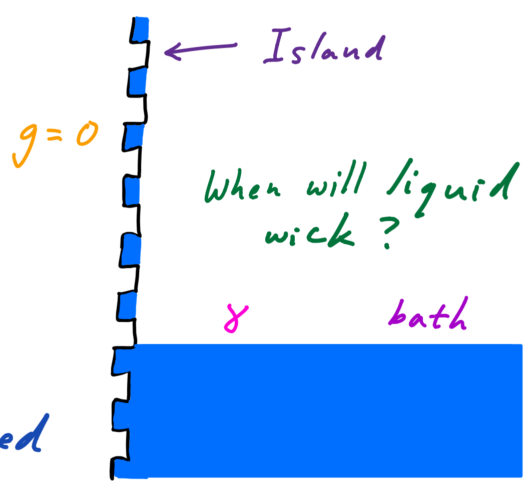
How can we minimize its effects?

Wetting of a Roughened Surface

Define : roughness parameters

$r = \frac{\text{TOTAL SURFACE AREA}}{\text{PROJECTED SURFACE AREA}} > 1$

$\phi_s = \frac{\text{AREA OF ISLANDS}}{\text{PROJECTED AREA}} < 1$



Change in surface energy associated with bath advancing a distance dz :

$$dE = \underbrace{(\gamma_{SL} - \gamma_{SV})(r - \phi_s)\, dz}_{\text{CHANGE IN WETTING S.E.}} + \underbrace{\gamma(1-\phi_s)\, dz}_{\text{NEW LV S.E.}}$$

Spontaneous wetting (demi-wicking) when $dE < 0$

i.e. $\underbrace{\cos\theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}}_{\text{CHEMISTRY}} > \underbrace{\frac{1-\phi_s}{r - \phi_s} \equiv \cos\theta_c}_{\text{GEOMETRY}}$

i.e. $\theta_e < \theta_c$

Note: 1. can control θ_e with chemistry, r and ϕ_s (and so θ_c) with geometry

$\Rightarrow$ can prescribe wettability

2. if $r \gg 1$, $\theta_c = \frac{\pi}{2}$ $\Rightarrow$ demi-wicking when $\cos\theta_e > 0$, i.e. $\theta_e < \frac{\pi}{2}$ $\Rightarrow$ whenever surface likes fluid

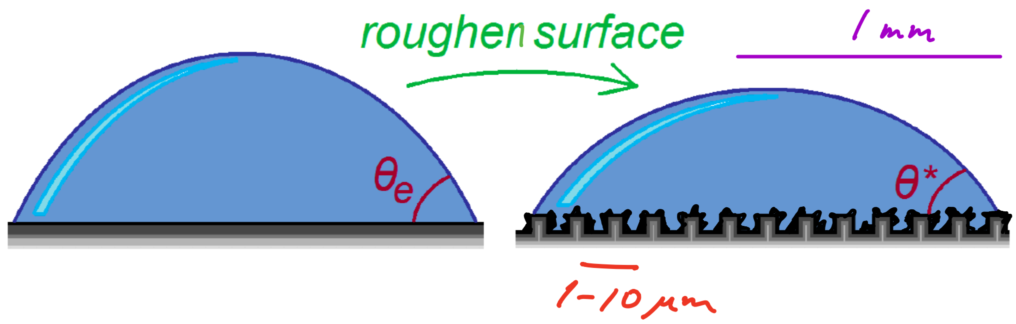
3. if surface is nearly flat, $r \sim 1$, $\theta_c = 0$.

$\Rightarrow$ demi-wicking when $\cos\theta_e > 1$ (NEVER)

4. most solids are rough (except glass $\rightarrow$ smooth down to ~ 5 Å)

Wetting of Textured Solids with Drops

Define: effective contact angle θ^*



Observation : $\theta^* < \theta_e$ when $\theta_e < \frac{\pi}{2}$

$\theta^* > \theta_e$ when $\theta_e > \frac{\pi}{2}$

$\Rightarrow$ surface roughening enhances intrinsic wettability of a substrate (as prescribed by chemistry and so θ_e)

$\Rightarrow$ roughening often causes hydrophobic surfaces to become superhydrophobic

e.g. the waxy integument of plants and insects