Recall from Lec. 3: we defined an equilibrium contact angle $\theta_e$ to describe the wetting of a flat solid.

From a horizontal force balance at contact line...

**Young's Law:**

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

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

$$dW = (\gamma_{SV} - \gamma_{SL}) \, dx - \gamma \cos \theta_e \, dx$$

From new wetted solid \hspace{1cm} From new interface

In equilibrium, $dW = 0$, which yields $\theta_e$.

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

**Contact Angle Hysteresis**

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

- Many $\theta$ values may coexist, depending on surface, liquid, gas, roughness, and history

- Begin with $\theta = \theta_e$
- $\theta$ increases until attaining $\theta_a \implies$ contact line advances
- $\theta$ decreases until reaching $\theta_r \implies$ 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 $\implies$ energetically costly $\implies$ contact line motion resisted
Contact Line Pinning at Corners

- a finite range of contact angles can arise at a corner:
  \[ \theta_1 < \theta < \pi - \phi + \theta, \]

\[ \Rightarrow \] an advancing contact line will be pinned at corners

- surface texture increases contact angle hysteresis

Manifestations of Contact Angle Hysteresis

I. Liquid Column Trapped in a Capillary Tube

- \( \theta_2 \) can be as large as \( \theta_1 \)
- \( \theta_1 \) can be as small as \( \theta_1 \)
- in general, \( \theta_2 > \theta_1 \), so there is a net capillary force available to support weight of the column:
2\pi R \sigma \left( \cos \theta_1 - \cos \theta_2 \right) = \rho g \pi R^2 h \quad \text{contact force}

\Rightarrow \text{Force balance: } \frac{2\sigma}{R} \left( \cos \theta_1 - \cos \theta_2 \right) = \rho g h

Equilibrium only possible if

\frac{2\sigma}{R} \left( \cos \theta_1 - \cos \theta_2 \right) > \rho g h

Note: if \( \theta_1 = \theta_2 \) (no hysteresis) \Rightarrow no equilibrium

II. Raindrop on a Window Pane

• if \( \theta_1 = \theta_2 \) \Rightarrow drop will roll due to \( g \)
• \( \theta_2 \) can be as large as \( \theta_a \)
• \( \theta_1 \) " " " small " \( \theta_v \)
• drop's weight can be supported by contact force associated with contact angle hysteresis

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

\Rightarrow \frac{F_g}{F_c} \sim \frac{\rho g R^2}{\sigma} \sim B_0 \quad \text{Bond number}
drops will increase in size (by condensation or drop impact) until $B_0 > 1$, 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

![Diagram showing wettable and less wettable regions with arrows indicating direction of movement](image)

B. Vibration-induced motion

![Diagram showing vibration with arrows](image)

- 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:

$$\rho U^2 \sim \frac{\sigma}{R} \text{ where } U \sim \omega R$$

$$\Rightarrow \omega \sim \left( \frac{\sigma}{\rho R^3} \right)^{\frac{1}{2}}$$

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 $$dZ$$:
\[ dE = (\Delta \gamma_{lv} - \Delta \gamma_{sv}) (\nu - \phi_s) \, d\zeta + \delta (1 - \phi_s) \, d\zeta \]

**Change in Wetting S.E.**  **New LV S.E.**

*Spontaneous wetting (demi-wicking) when* \( \Delta E < 0 \)

*\[ \cos \theta_e = \frac{\Delta \gamma_{lv}}{\delta} > \frac{1 - \phi_s}{1 - \phi_s} = \cos \theta_c \]

*Chemistry*  **Geometry**

*\[ \therefore \theta_e < \theta_c \]*

**Note:** 1. can control \( \theta_e \) with chemistry, \( \nu \) and \( \phi_s \)
   (and so \( \theta_c \)) with geometry
   \( \Rightarrow \) can prescribe wettability

2. if \( \nu \gg 1 \), \( \theta_c = \frac{\pi}{2} \Rightarrow \) 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, \( \nu \approx 1 \), \( \theta_c = 0 \)
   \( \Rightarrow \) demi-wicking when \( \cos \theta_e > 1 \) (NEVER)

4. most solids are rough (except glass \( \Rightarrow \) smooth
down to \( \sim 5 \AA \))

**Wetting of Textured Solids with Drops**

Define: effective contact angle \( \theta^* \)
Observation: $\theta^* < \theta_e$ when $\theta_e < \frac{\pi}{2}$

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

⇒ Surface roughening enhances intrinsic wettability of a substrate (as prescribed by chemistry and so $\theta_e$)

⇒ Roughening often causes hydrophobic surfaces to become superhydrophobic

e.g. the waxy integument of plants and insects