15. Contact angle hysteresis, Wetting of textured solids

`Recall`: In Lecture 3, we defined the equilibrium contact angle θ_e, which is prescribed by Young's Law: $\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma$ as deduced from the horizontal force balance at the contact line.
Work done by a contact line moving a distance dx:

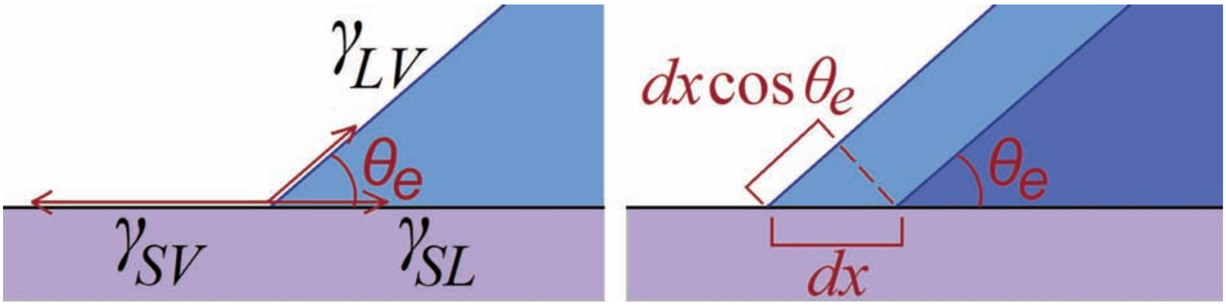

Figure 15.1: Calculating the work done by moving a contact line a distance dx.

$$dW = \underbrace{(\gamma_{SV} - \gamma_{SL})\,dx}_{contact\ line\ motion} - \underbrace{\gamma\cos\theta_e dx}_{from\ creating\ new\ interface} \tag{15.1}$$

In equilibrium: d$W = 0$, which yields Young's Law. It would be convenient if wetting could be simply characterized in terms of this single number θ_e. Alas, there is:

15.1 Contact Angle Hysteresis

For a given solid wetting a given liquid, there is a range of possible contact angles: $\theta_r < \theta < \theta_a$, i.e. the contact angle lies between the retreating and advancing contact angles; θ_r and θ_a, respectively. That is, many θ values may arise, depending on surface, liquid, roughness and history.

Filling a drop

- begin with a drop in equilibrium with $\theta = \theta_e$
- fill drop slowly with a syringe
- θ increases progressively until attaining θ_a, at which point the contact line advances

Draining a drop

- begin with a drop in equilibrium with $\theta = \theta_e$
- drain drop slowly with a syringe
- θ decreases progressively until attaining θ_r, at which point the contact line retreats

Origins: Contact line pinning results from surface heterogeneities (either chemical or textural), that present an energetic impediment to contact line motion.
The pinning of a contact line on impurities leads to increased interfacial area, and so is energetically costly. Contact line motion is thus resisted.

Contact Line Pinning at Corners
A finite range of contact angles can arise at a corner $\theta_1 < \theta < \pi - \phi + \theta_1$; thus, an advancing contact line will generally be pinned at corners. Hence surface texture increases contact angle hysteresis.

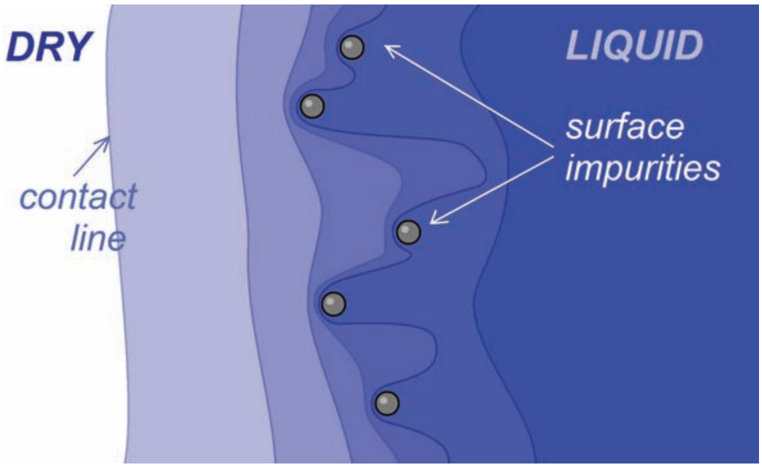

Figure 15.2: Pinning of a contact line retreating from left to right due to surface impurities.

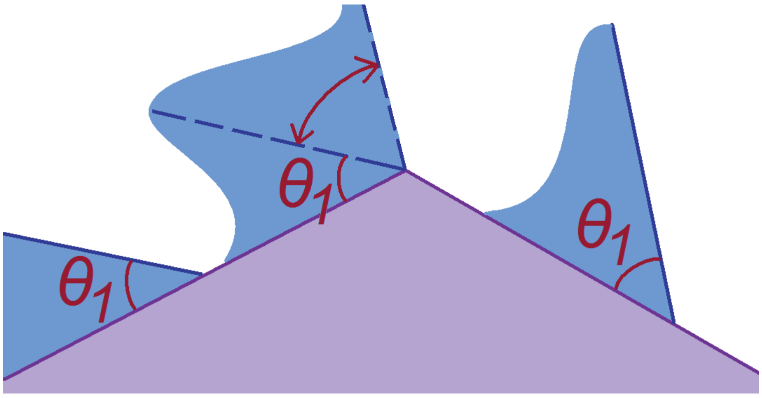

Figure 15.3: A range of contact angles is possible at a corner.

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 the weight of the slug.

$$\underbrace{2\pi R\sigma(\cos\theta_1 - \cos\theta_2)}_{\text{max contact force}} = \underbrace{\rho g\pi R^2 H}_{\text{weight}} \tag{15.2}$$

Force balance requires:

$$\frac{2\sigma}{R}\left(\cos\theta_1 - \cos\theta_2\right) = \rho g H \tag{15.3}$$

Thus, an equilibrium is possible only if $\frac{2\sigma}{R}\left(\cos\theta_r - \cos\theta_a\right) > \rho g H$.

`Note`: if $\theta_a = \theta_r$ (no hysteresis), there can be no equilibrium.

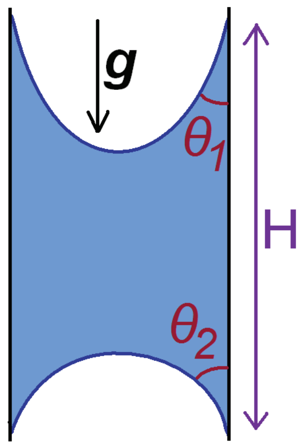

Figure 15.4: A heavy liquid column may be trapped in a capillary tube despite the effects of gravity.

II. Raindrops on window panes *(Dussan+Chow 1985)*

If $\theta_1 = \theta_2$ then the drop will fall due to unbalanced gravitational force. θ_2 can be as large as θ_a, θ_1 as small as θ_r. Thus, the drop weight may be supported by the capillary force associated with the contact angle hysteresis.

Note: $F_g \sim \rho R^3 g$, $F_c \sim 2\pi R\sigma(\cos\theta_1 - \cos\theta_2)$ which implies that $\frac{F_G}{F_C} \sim \frac{\rho g R^2}{\sigma} \equiv \mathcal{B}o$. In general, drops on a window pane will increase in size by accretion until $\mathcal{B}o > 1$ and will then roll downwards.

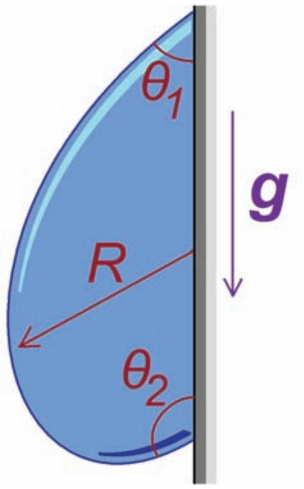

Figure 15.5: A raindrop may be pinned on a window pane.

15.2 Wetting of a Rough Surface

Consider a fluid placed on a rough surface.
Define: roughness parameters

$$r = \frac{\text{Total Surface Area}}{\text{Projected Surf. Area}} > 1 \qquad \phi_S = \frac{\text{Area of islands}}{\text{Projected Area}} < 1 \tag{15.4}$$

The change in surface energy associated with the fluid front advancing a distance dz:

$$dE = (\gamma_{SL} - \gamma_{SV})(r - \phi_S)dz + \gamma(1-\phi_S)ds \tag{15.5}$$

Spontaneous Wetting (demi-wicking) arises when $dE < 0$
i.e. $\cos\theta_e = \frac{\gamma_{SV}-\gamma_{SL}}{\gamma} > \frac{1-\phi_S}{r-\phi_S} \equiv \cos\theta_c$, i.e. when $\theta_e < \theta_C$. Note:

1. can control θ_e with chemistry, r and ϕ_S with geometry, so can prescribe wettability of a solid.
2. if $r \gg 1$, $\theta_C = \frac{\pi}{2}$, so one expects spontaneous wicking when $\theta_e < \pi/2$
3. for a flat surface, $r \sim 1$, $\theta_c = 0$: wicking requires $\cos\theta_e > 1$ which never happens.
4. most solids are rough (except for glass which is smooth down to $\sim 5\mathring{A}$).

Wetting of Rough Solids with Drops
Consider a drop placed on a rough solid. Define: Effective contact angle θ^* is the contact angle apparent on a rough solid, which need not correspond to θ_e. Observation:
$\theta^* < \theta_e$ when $\theta_e < \pi/2$ (hydrophilic)
$\theta^* > \theta_e$ when $\theta_e > \pi/2$ (hydrophobic).
The intrinsic hydrophobicity or hydrophilicity of a solid, as prescribed by θ_e, is **enhanced** by surface roughening.

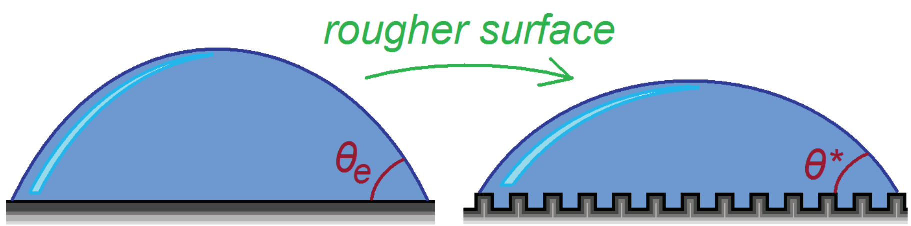

Figure 15.6: A drop wetting a rough solid has an effective contact angle θ^* that is generally different from its equilibrium value θ_e.

15.3 Wenzel State (1936)

A Wenzel state arises when the fluid impregnates the rough solid. The change in wetting energy associated with a fluid front advancing a distance dx (see Fig. 15.7) is

$$dE_W = r(\gamma_{SL} - \gamma_{SV})dx + \gamma \cos\theta^* dx \tag{15.6}$$

If $r = 1$ (smooth surface), Young's Law emerges.
If $r > 1$: $\cos\theta^* = r\cos\theta_e$

Note:

1. wetting tendencies are amplified by roughening, e.g. for hydrophobic solid ($\theta_e > \pi/2$, $\cos\theta_e < 0 \Rightarrow \theta_e \gg \pi/2$ for large r)
2. for $\theta_e < \theta_c$ (depends on surface texture) $\Rightarrow$ demi-wicking / complete wetting
3. Wenzel state breaks down at large $r \Rightarrow$ air trapped within the surface roughness $\Rightarrow$ *Cassie State*

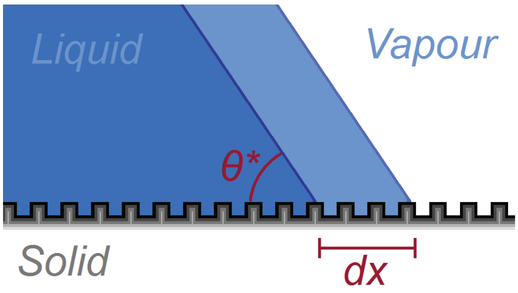

Figure 15.7: The wetting of a rough solid in a Wenzel state.

15.4 Cassie-Baxter State

In a Cassie state, the fluid does not impregnate the rough solid, leaving a trapped vapour layer. A fluid placed on the rough surface thus sits on roughness elements (e.g. pillars or islands), and the change of energy associated with its front advancing a distance dx is

$$dE_c = \phi_S(\gamma_{SL} - \gamma_{SV})dx + (1-\phi_S)\gamma dx + \gamma\cos\theta^* dx \tag{15.7}$$

For equilibrium ($dE_c/dx = 0$), we require:

$$\cos\theta^* = -1 + \phi_S + \phi_S\cos\theta_e \tag{15.8}$$

Note:

1. as pillar density $\phi_S \to 0$, $\cos\theta^* \to -1$, i.e. $\theta^* \to \pi$
2. drops in a Cassie State are said to be in a "fakir state".
3. contact angle hysteresis is greatly increased in the Wenzel state, decreased in the Cassie.
4. the maintenance of a Cassie state is key to water repellency.

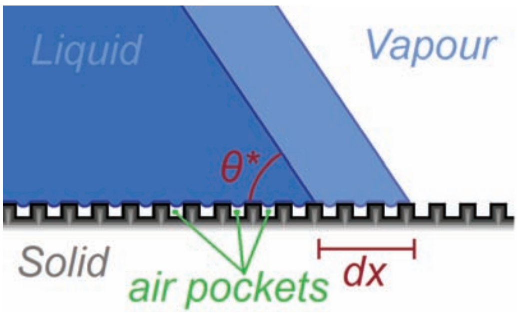

Figure 15.8: The wetting of a rough solid in a Cassie-Baxter state.

Crossover between Wenzel and Cassie states:

For $dE_W > dE_c$, we require $-r\cos\theta_e + \cos\theta^* > -\phi_s\cos\theta_e + (1-\phi_s) + \cos\theta^*$, i.e. $\cos\theta_e < \frac{-1+\phi_S}{r-\phi_S} = \cos\theta_c$, i.e. one expects a Cassie state to emerge for $\cos\theta_e > \cos\theta_c$. Therefore, the criterion for a Wenzel State giving way to a Cassie state is identical to that for spontaneous wicking.

Summary:

Hydrophilic: Wenzel's Law ceases to apply at small θ_e when demi-wicking sets in, and the Cassie state emerges.

Hydrophobic: Discontinuous jump in θ^* as θ_e exceeds $\pi/2 \Rightarrow$ Cassie state. Jump is the largest for large roughness (small ϕ_S)

`Historical note:`

1. early studies of wetting motivated by insecticides
2. chemists have since been trying to design superhydrophobic (or oliophobic) surfaces using combinations of chemistry and texture
3. recent advances in microfabrication have achieved $\theta^* \sim \pi$, $\Delta\theta \sim 0$ (e.g. Lichen surface *McCarthy*)

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Fall 2010