16. More forced wetting

Some clarification notes on **Wetting**.

Figure 16.1: Three different wetting states.

Last class, we discussed the Cassie state only in the context of drops in a Fakir state, i.e. suspended partially on a bed of air. There is also a "wet Cassie" state. More generally, the Cassie-Baxter model applies to wetting on a planar but chemically heterogeneous surfaces.
Consider a surface with 2 species, one with area fraction f_1 and equilibrium contact angle θ_1, another with area fraction f_2 and angle θ_2. Energy variation associated with the front advancing a distance $\mathrm{d}x$:
$\mathrm{d}E = f_1(\gamma_{SL} - \gamma_{SV})_1 \mathrm{d}x + f_2(\gamma_{SL} - \gamma_{SV})_2 \mathrm{d}x + \gamma \cos\theta^* \mathrm{d}x$.
Thus, $\mathrm{d}E = 0$ when

$$\cos\theta^* = f_1 \cos\theta_1 + f_2 \cos\theta_2 \qquad \text{(Cassie-Baxter relation)} \quad (16.1)$$

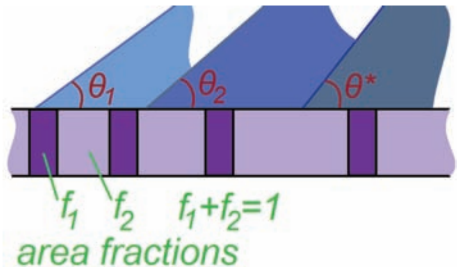

Figure 16.2: Wetting of a tiled (chemically heterogeneous) surface.

`Special Case`: in the Fakir state, the two phases are the solid ($\theta_1 = \theta_e$ and $f_1 = \theta_S$) and air ($\theta_2 = \pi$, $f_2 = 1 - \theta_S$) so we have

$$\cos\theta^* = \theta_S \cos\theta_e - 1 + \theta_S \qquad (16.2)$$

as previously. As before, in this hydrophobic case, the Wenzel state is energetically favourable when $\mathrm{d}E_W < \mathrm{d}E_C$, i.e. $\cos\theta_C < \cos\theta_e < 0$
where $\cos\theta_C = (\theta_S - 1)/(r - \theta_S)$, i.e. θ_E is between $\pi/2$ and θ_C.
However, experiments indicate that even in this regime, air may remain trapped, so that a *metastable Cassie* state emerges.

16.1 Hydrophobic Case: $\theta_e > \pi/2$, $\cos\theta_e < 0$

In the Fakir state, the two phases are the solid ($\theta = \theta_e$, $f_1 = \phi$) and vapour ($\theta_2 = \pi$, $f_2 = 1 - \phi_s$).
Cassie-Baxter:

$$\cos\theta^* = \pi_S \cos\theta_e - 1 + \phi_s \qquad (16.3)$$

as deduced previously. As previously, the Wenzel state is energetically favourable when $dE_W < dE_L$, i.e. $\cos\theta_C < \cos\theta_e < 0$ where $\cos\theta_C = \frac{\phi_S - 1}{r - \phi_S}$. Experiments indicate that even in this region, air may remain trapped, leading to a meta-stable Fakir state.

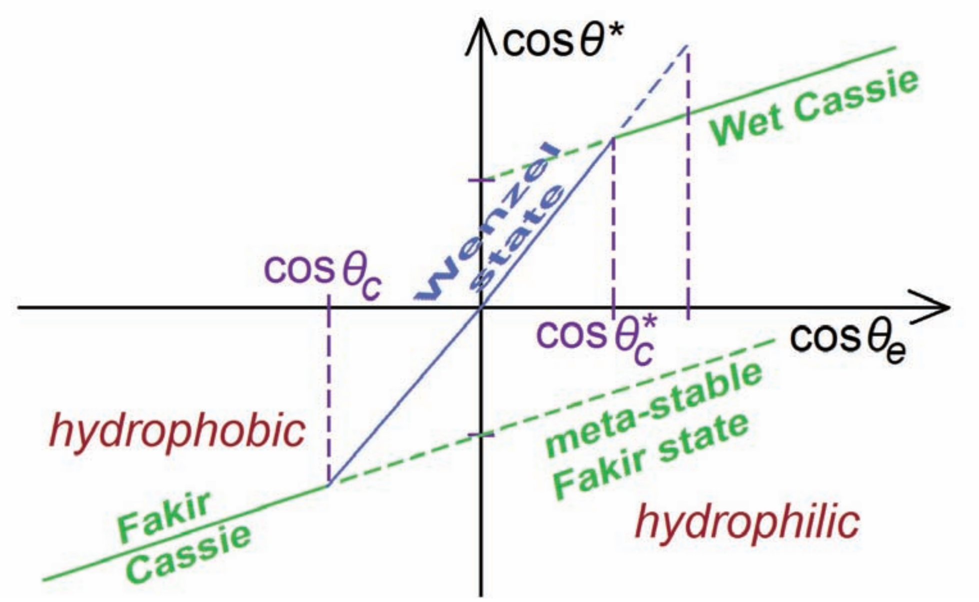

Figure 16.3: Relationship between $\cos\theta^*$ and $\cos\theta_e$ for different wetting states.

16.2 Hydrophilic Case: $\theta_e < \pi/2$

Here, the Cassie state corresponds to a tiled surface with 2 phases corresponding to the solid ($\theta_1 = \theta_e$, $f_1 = \phi_S$) and the fluid ($\theta_2 = 0$, $f_2 = 1 - \phi_S$).
Cassie-Baxter $\Rightarrow$ $\cos\theta^* = 1 - \phi_S + \phi_S \cos\theta_e$, which describes a "Wet Cassie" state. Energy variation: $\mathrm{d}E = (r - \phi_S)(\gamma_{SL} - \gamma_{SV})\mathrm{d}x + (1 - \phi_S)\gamma\mathrm{d}x$.

$$\Rightarrow \mathrm{d}E = 0 \text{ if } \qquad \cos\theta_e = \frac{\gamma_{SL} - \gamma_{SV}}{\gamma} > \frac{1 - \phi_S}{r - \phi_S} \equiv \cos\theta_c^* \tag{16.4}$$

For $\theta_e < \theta_c$, a film will impregnate the rough solid. Criteria for this transition can also be deduced by equating energies in the Cassie and Wenzel states, i.e. $r\cos\theta_e = 1 - \phi_S + \phi_S\cos\theta_e \Rightarrow \theta_e = \theta_C$. Therefore, when $\pi/2 > \theta_e > \theta_C$, the solid remains dry ahead of the drop $\Rightarrow$ Wenzel applies $\Rightarrow$ when $\theta_e < \theta_C \Rightarrow$ film penetrates texture and system is described by "Wet Cassie" state.

Johnson + Dettre (1964) examined water drops on wax, whose roughness they varied by baking. They showed an increase and then decrease of $\Delta\theta = \theta_a - \theta_r$ as the roughness increased, and system went from smooth to Wenzel to Cassie states.
Water-repellency: important for corrosion-resistance, self-cleaning, drag-reducing surfaces. It requires the maintenance of a Cassie State. This means the required impregnation pressure must be exceeded by the curvature pressure induced by roughness.
`E.g.1` **Static Drop in a Fakir State**
The interface will touch down if $\delta > h$. Pressure balance: $\frac{\sigma}{R} \sim \sigma\frac{\delta}{l^2}$ so $\delta > h \Rightarrow \frac{l^2}{R} > h$ i.e. $R < \frac{l^2}{h}$.
Thus taller pillars maintain Fakir State. (see Fig. 16.5)

`E.g.2` **Impacting rain drop**: impregnation pressure $\Delta P \sim \rho U^2$ or $\rho U c$ where c is the speed of sound in water.

`E.g.3` **Submerged surface**, e.g. on a side of a boat. $\Delta P = \rho g z$ is impregnation pressure.

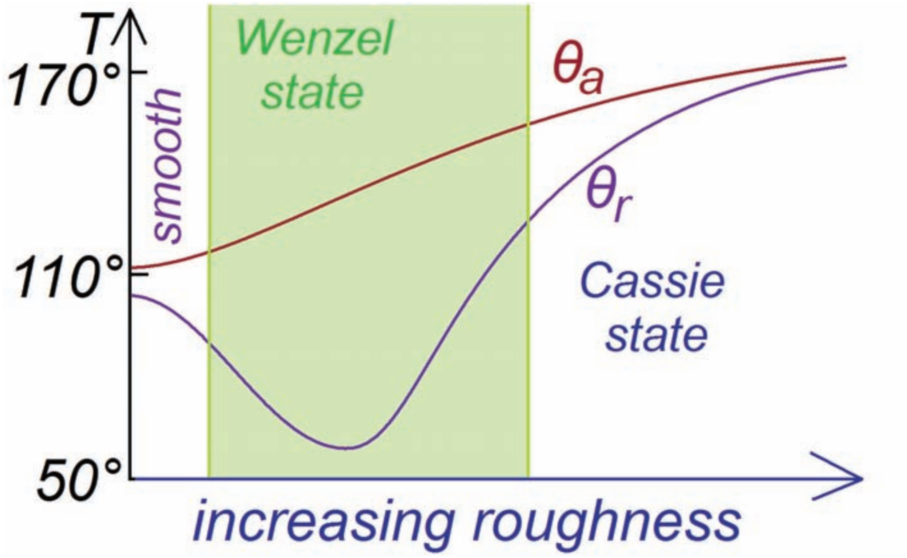

Figure 16.4: Contact angle as a function of surface roughness for water drops on wax.

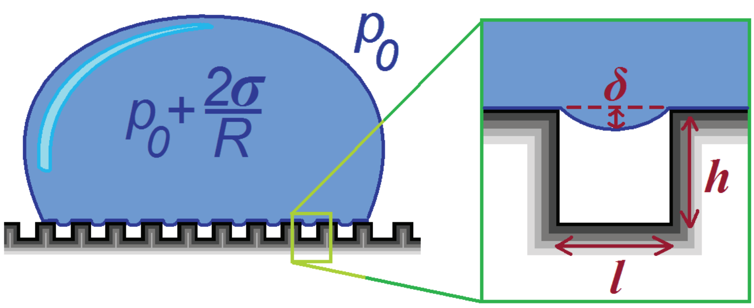

Figure 16.5: To remain in a Cassie state, the internal drop pressure $P_0 + 2\sigma/R$ must not exceed the curvature pressure induced by the roughness, roughly σ/ℓ.

16.3 Forced Wetting: the Landau-Levich-Derjaguin Problem

Withdraw a plate from a viscous fluid with constant speed. What is the thickness of the film that coats the plate? Consider a static meniscus.
For relatively thick films ($\mathcal{C}a \sim 1$), balancing viscous stresses and gravity: $\mu\frac{V}{h} \sim \rho g h \Rightarrow$

$$h \sim \left(\frac{\mu V}{\rho g}\right)^{1/2} \sim \ell_c \mathcal{C}a^{1/2} \qquad \text{(Derjaguin 1943)} \tag{16.5}$$

where $\ell_c = \sqrt{\frac{\sigma}{\rho g}}$ and $\mathcal{C}a = \frac{\mu V}{\sigma} = \frac{\text{viscous}}{\text{curvature}}$ is the Capillary number.

But this scaling is not observed at low $\mathcal{C}a$, where the coating is resisted principally by curvature pressure rather than gravity. Recall static meniscus (Lecture 6): $\eta(x) = \sqrt{2}\ell_c\,(1 - \sin\theta(x))$ and internal pressure: $p(x) = p_0 - \rho g \eta(x)$. As $x \to 0$, $\eta(x) \to \sqrt{2}\ell_c$ and $p(x) \to p_0 - \sqrt{2}\rho g \ell_c$. It is this capillary suction inside the meniscus that resists the rise of thin films.

Thin film wetting
We describe the flow in terms of two distinct regions:

Region I: Static meniscus. The balance is between gravity and curvature pressures: $\rho g\eta \sim \sigma\nabla\cdot\boldsymbol{n}$ so curvature $\nabla\cdot\boldsymbol{n} \sim 1/\ell_c$.
Region II: Dynamic meniscus (coating zone). The balance here is between viscous stresses and curvature pressure. Define this region as the zone over which film thickness decreases from $2h$ to h, whose vertical extent L to be specified by pressure matching. In region II, curvature $\nabla\cdot\boldsymbol{n} \sim h/L^2$. Matching pressure at point A: $p_0 - \frac{\sigma h}{L^2} \sim p_0 - \rho g\ell_c \Rightarrow L^2 \sim \frac{\sigma h}{\rho g\ell_c} \sim \ell_c h \Rightarrow L = \sqrt{\ell_c h}$ is the geometric mean of ℓ_c and h.
Force balance in Zone II: viscous stress vs. curvature pressure: $\mu\frac{V}{h^2} \sim \frac{\Delta P}{L} \sim \sigma\frac{h}{L^2}\frac{1}{L}$.

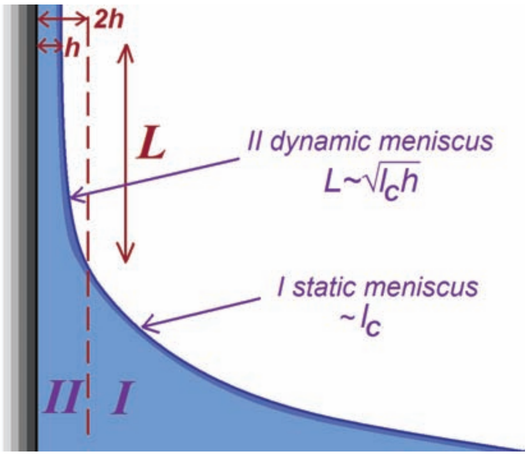

Figure 16.6: The two regions of the meniscus next to a moving wall.

Substitute in for $L \Rightarrow h^3 \sim \frac{\mu V}{\sigma}L^3 \sim \mathcal{C}a\ell_c^{3/2}h^{3/2} \Rightarrow h \sim \ell_c\mathcal{C}a^{2/3}$ where $\ell_c = \sqrt{\frac{\sigma}{\rho g}}$, $\mathcal{C}a = \frac{\mu V}{\sigma}$.
Implicit in above: $h \ll L$, $L \ll \ell_c$, $\rho g \ll \frac{\sigma h}{L^3}$, or equivalently $\mathcal{C}a^{1/3} \ll 1$. Matched asymptotics give $h \approx 0.94\ell_c\mathcal{C}a^{2/3}$.

`E.g.1` Jump out of pool at 1m/s: $\mathcal{C}a \sim 10^{-2}$ so $h \sim 0.1$mm $\Rightarrow \sim 300$g entrained.

`E.g.2` Drink water from a glass, $V \sim 1$cm/s $\Rightarrow \mathcal{C}a \sim 10^{-4}$.

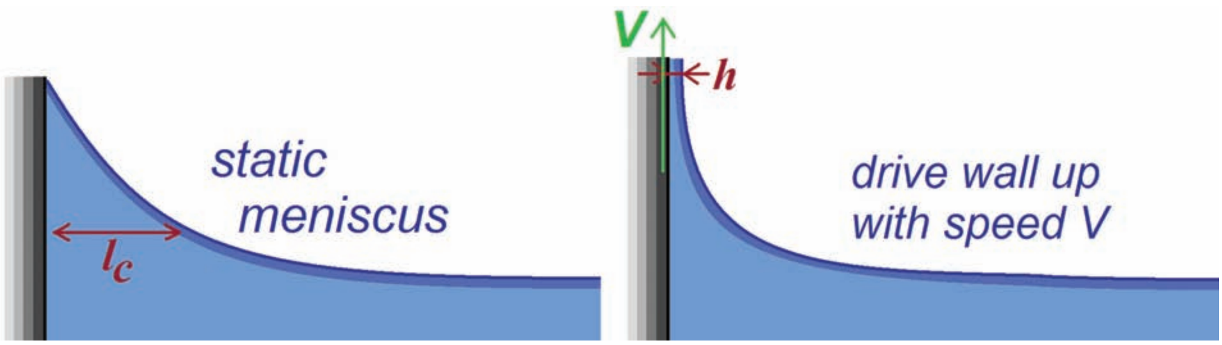

Figure 16.7: *Left*: A static meniscus. *Right*: Meniscus next to a wall moving upwards with speed V.

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