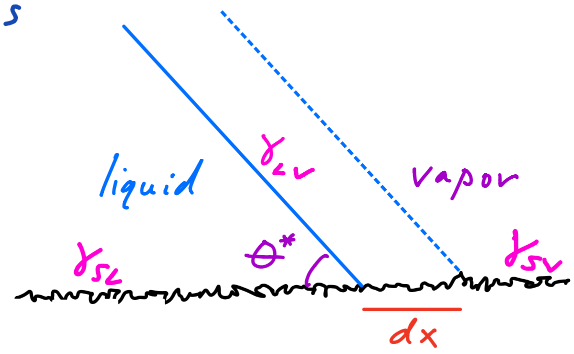
Lecture 16. Wetting of rough solids; coating flows

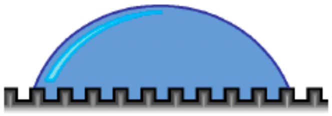
Effective contact angle θ^* depends on both chemistry (which sets θ_e) and roughness parameters

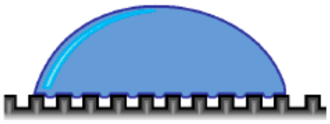


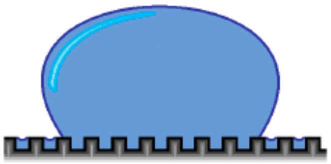
$$r = \frac{\text{TOTAL SURFACE AREA}}{\text{PROJECTED AREA}}$$

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

For drops on rough solids, there are 3 possible states:


Wenzel state

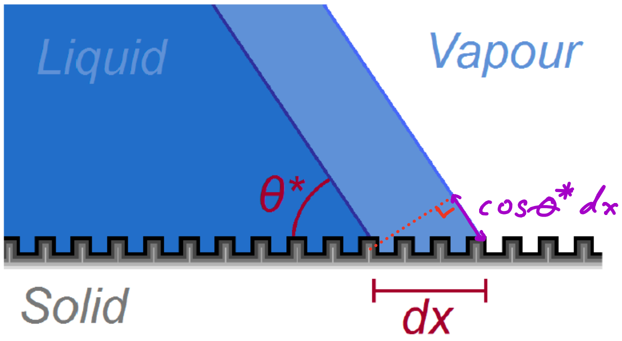

Fakir Cassie state


Wet Cassie state

Wenzel Model (1936)

Change in wetting energy :

$$dE_w = \overset{\text{NEW WET SOLID}}{r(\gamma_{SL} - \gamma_{SV})\,dx} \\ + \underset{\text{NEW INTERFACE}}{\gamma \cos\theta^*\,dx}$$



If $r = 1$ (smooth surface): $\Rightarrow$ retain Young's Law

If $r > 1$: $\boxed{\cos\theta^* = r\cos\theta_e}$

$\Rightarrow$ wetting/nonwetting tendencies amplified by roughness

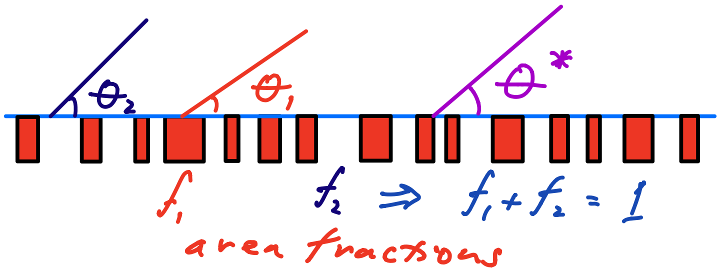
e.g. a hydrophobic surface may become superhydrophobic in respond to roughening

Note: for $\theta_e < \theta_c$ (depends on texture)
$\Rightarrow$ demi-wicking, complete wetting
$\Rightarrow$ Wet Cassie state

Restriction of Wenzel Model: for $\theta_e > \frac{\pi}{2}$, breaks down at large r, when air is trapped in inclusions

Cassie – Baxter Model : applies to wetting on a planar but chemically heterogeneous surface.

Consider surface with 2 species, one with area fraction f_1 and equilibrium contact angle θ_1, the other with f_2, θ_2.



Energy Variation

$$dE = f_1(\gamma_{SL} - \gamma_{SV})_1 dx + f_2(\gamma_{SL} - \gamma_{SV})_2 dx + \gamma \cos\theta^* dx$$

Equilibrium when $dE = 0$:

$$\boxed{\cos\theta^* = f_1 \cos\theta_1 + f_2 \cos\theta_2}$$

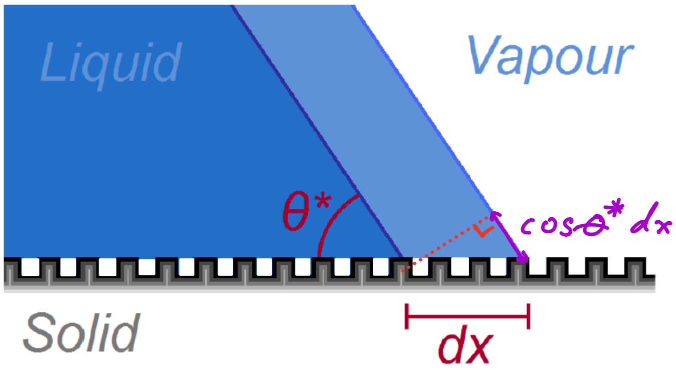
Cassie – Baxter ★

Consider 2 special cases ...

I. Hydrophobic ($\theta_e > \frac{\pi}{2}$, $\cos\theta_e < 0$)

$\Rightarrow$ Dry Cassie State

- the 2 phases are the solid ($\theta_1 = \theta_e$; $f_1 = \phi_s$) and air ($\theta_2 = \pi$, $f_2 = 1 - \phi_s$), so we have :

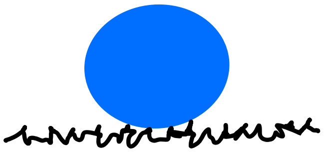


$$\boxed{\cos\theta^* = \phi_s \cos\theta_e - 1 + \phi_s}$$

Note : 1. as pillar density $\phi_s \to 0$,

$\cos\theta^* \to -1$, $\theta^* \to \pi$

2. drops in the dry Cassie state are said to be in the "Fakir state"



3. contact angle hysteresis greatly increased in Wenzel state, decreased in Cassie

4. maintenance of Cassie state is key for water repellency

5. Cross-over between Wenzel and Dry Cassie States

Wenzel state preferable when

$$dE_W < dE_C$$

i.e. $-r\cos\theta_e + \cancel{\cos\theta^*} < -\phi_s\cos\theta_e + (1-\phi_s) + \cancel{\cos\theta^*}$

i.e. $$\boxed{\cos\theta_e > \frac{-1+\phi_s}{r-\phi_s}} = \cos\theta_c^*$$

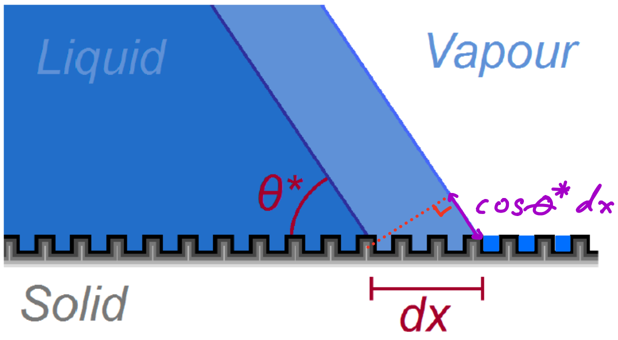
$$= -\cos\theta_c$$

II. Hydrophilic Case ($\theta_e < \theta_c$) : Wet Cassie

- here, the Cassie state corresponds to a tiled surface with 2 phases, the solid ($\theta_1 = \theta_e$, $f_1 = \phi_s$) and the liquid ($\theta_2 = 0$, $f_2 = 1-\phi_s$)

Subing into ☆ :

$$\boxed{\cos\theta^* = 1-\phi_s+\phi_s\cos\theta_e}$$



The critical transition value of θ_e between Wenzel and Wet Cassie states may be deduced by equating energies in these 2 states :

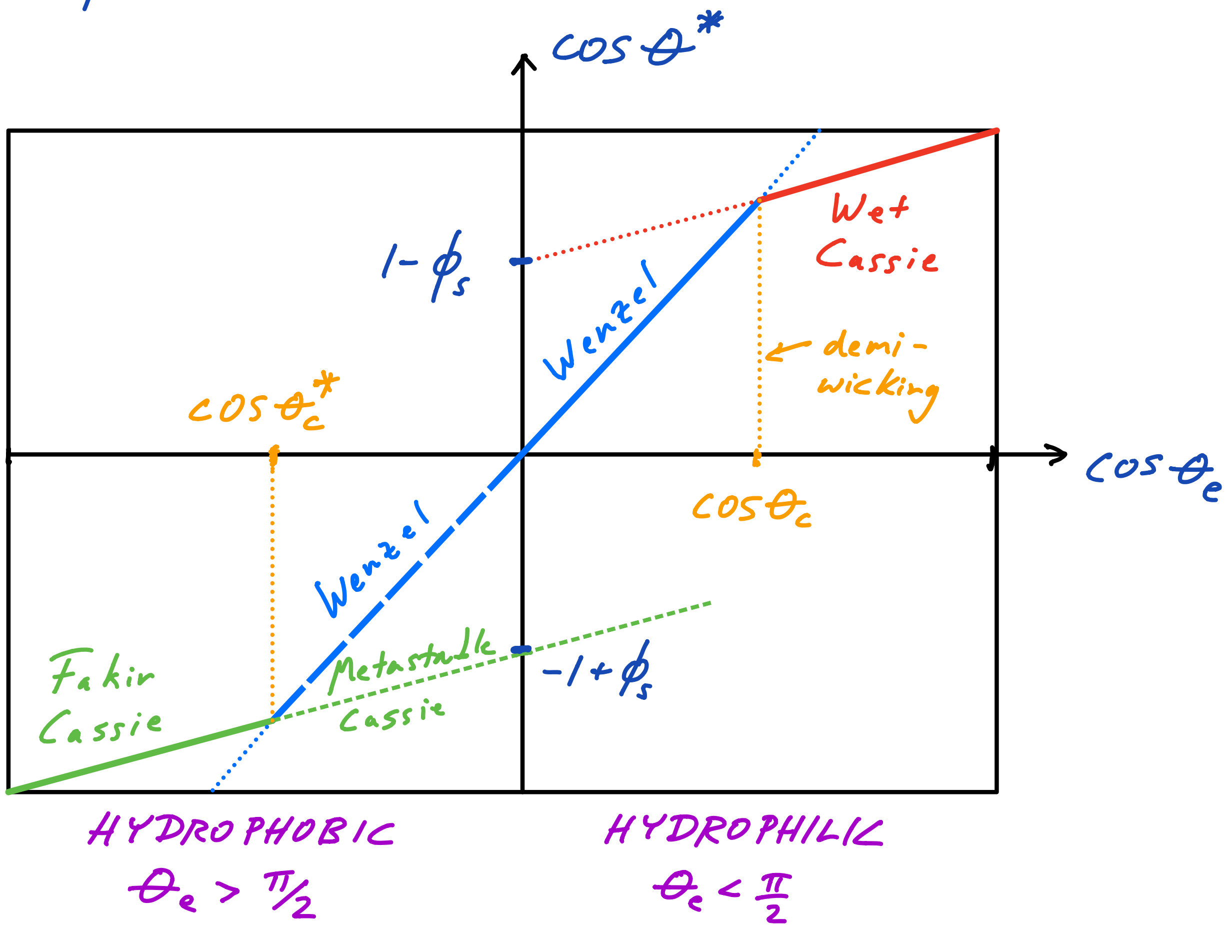
$$r\cos\theta_e = 1-\phi_s+\phi_s\cos\theta_e \Rightarrow \theta_e = \theta_c$$

and corresponds to condition for demi-wicking

$\Rightarrow$ when $\frac{\pi}{2} > \theta_e > \theta_c$, solid remains dry ahead of the drop $\Rightarrow$ Wenzel

$\Rightarrow$ when $\theta_e < \theta_c$ $\Rightarrow$ liquid penetrates texture
$\Rightarrow$ Wet Cassie

Summary



Note differences between hydrophobic + hydrophilic regimes.

Hydrophilic : Wenzel's Law ceases to apply at small θ_e, when demi-wicking sets in

$\Rightarrow$ Wet Cassie states

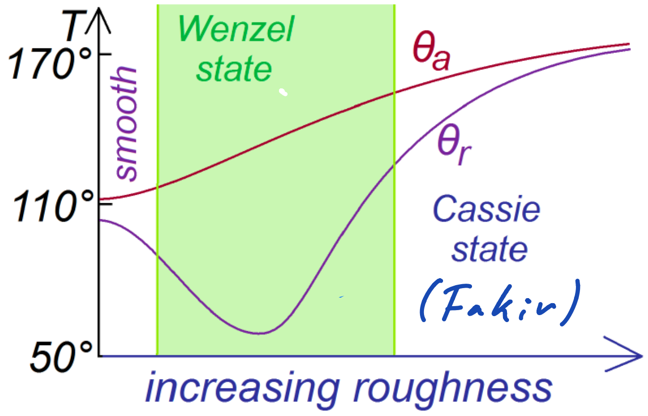
Hydrophobic : one may see a discontinuous jump in θ^* as θ_e increases due to hysteresis, the existence of a metastable Cassie state

- jump largest for large roughness (small ϕ_s)

Historical Notes

1. Early studies of wetting motivated by insecticides
2. Chemists have since been trying to design hydrophobic (or oleophobic) surfaces using a combination of chemistry + texture
3. recent advances in micro-fabrication have achieved

   $\theta^* \sim \pi$, $\Delta\theta = 0$.



4. Johnson + Dettre (1964)
   - examined water drops on wax, whose roughness was controlled with temperature

   ⇒ showed increase, then decrease of $\Delta\theta = \theta_a - \theta_r$ as roughness increased: smooth → Wenzel → Cassie

Water-repellency

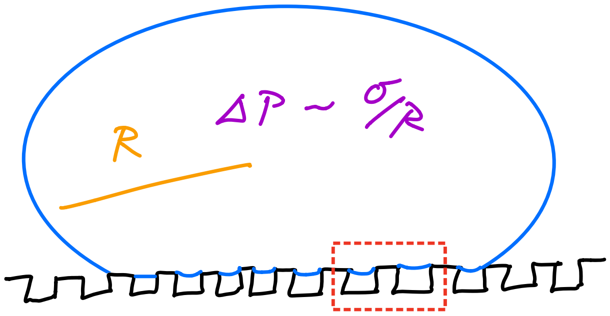
- requires the maintenance of a Dry Cassie state

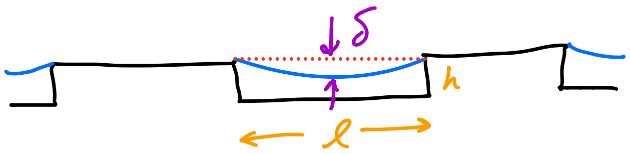
  i.e. impregnation pressure must be exceeded by Laplace pressure induced by roughness

Eg. 1 Static drop

Pressure jump across its surface: $\frac{\sigma}{R} \simeq \sigma \frac{\delta}{\ell^2}$

Interface will touch down if $\delta > h$.



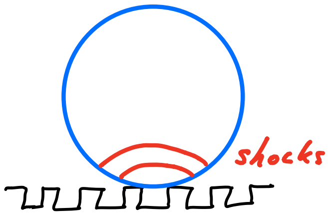


i.e. $R < \frac{\ell^2}{h}$ ⇒ longer pillars are more hydrophobic

Eg. 2 Impacting Drop

$$\Delta P \sim \rho v^2 \text{ or } \rho v c$$

speed of sound



Eg. 3 Submerged surface

e.g. on side of boat or diving insect

Impregnation pressure

$$\Delta P = \rho g z$$