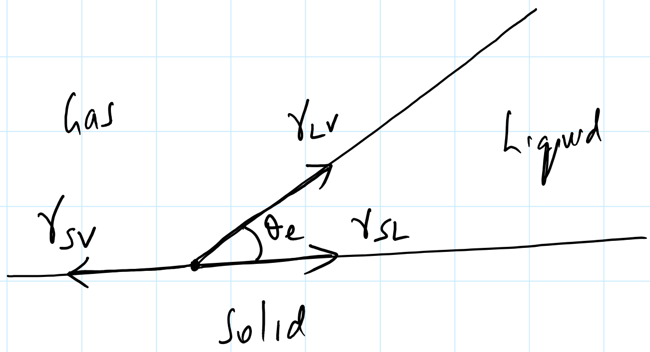
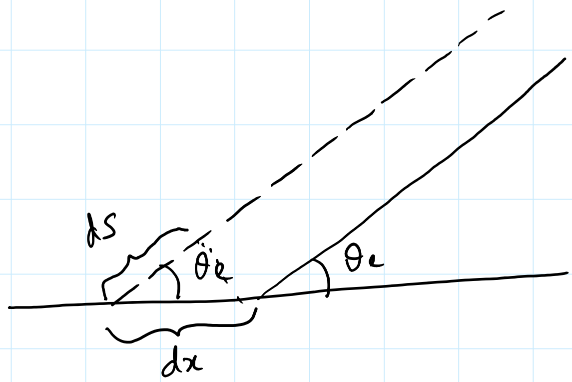
More on Wetting :-





$$ds = dx \cos\theta_e$$

Work done to move the contact line by a distance dx is given by :-

$$dW = \gamma_{SV}\,dx - \gamma_{SL}\,dx - \gamma_{LV}\,ds$$

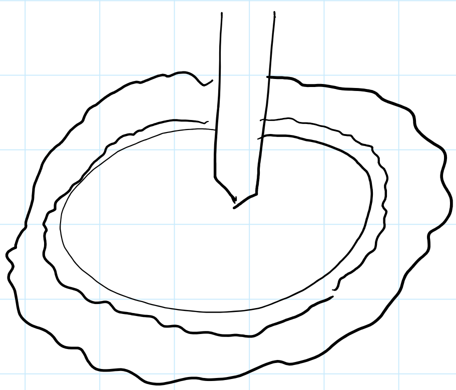
$$dW = (\gamma_{SV} - \gamma_{SL})\,dx - \gamma_{LV}\,dx\cos\theta_e$$

In equilibrium, $dW = 0$

$$\Rightarrow \gamma_{SV} - \gamma_{SL} - \gamma_{LV}\cos\theta_e = 0$$

$$\Rightarrow \boxed{(\gamma_{SV} - \gamma_{SL}) = \gamma_{LV}\cos\theta_e \quad : \text{Young's Law}}$$

Pinning of contact line :-



Drops spread preferentially depending on the angle they make.

Unfortunately for us, the equilibrium contact angle is not unique. Interfaces can support a range of contact angles called the contact angle hysteresis.

When not in equilibrium, a net force arises given by:

$$F(\theta_D) = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}\cos(\theta_D)$$

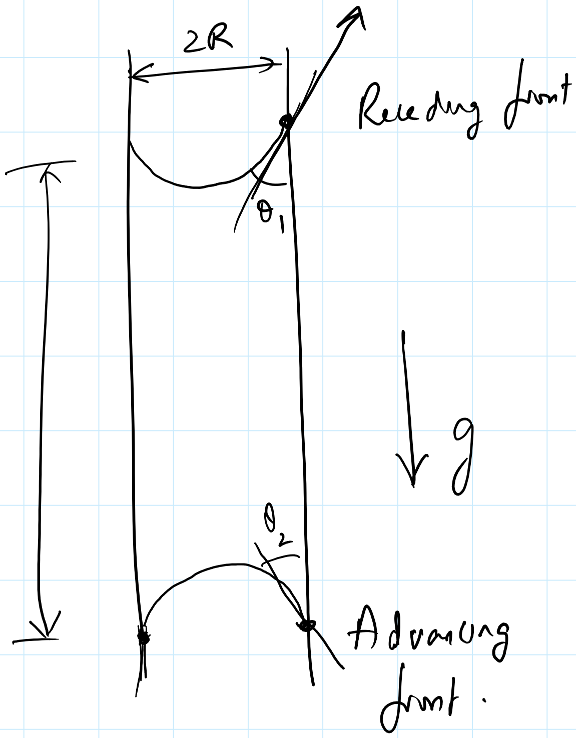
Note that when $\theta_D = \theta_e$, $F(\theta_e) = 0$: Young's Law.

θ_D in general is $\neq \theta_e$. : Contact angle hysteresis even in static scenario.

Manifestation of contact angle hysteresis:-

Plug in a capillary tube:-

Net force of gravity $\approx \rho \cdot \pi R^2 \cdot H \cdot g$



Net force of surface tension

$$= 2\pi R \cdot \sigma \cos\theta_1 - 2\pi R \cdot \sigma \cdot \cos\theta_2$$

For equilibrium,

$$2\pi R\sigma(\cos\theta_1 - \cos\theta_2) = \rho \cdot \pi R^2 H g$$

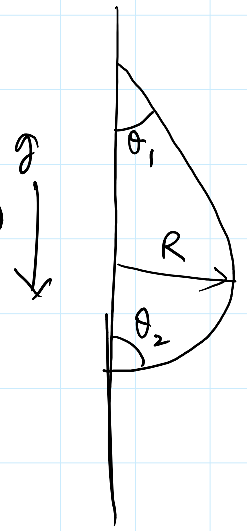
θ_2 can be as large as θ_a (advancing contact angle)

θ_1 can be as small as θ_r (receding contact angle)

Almost always, $\theta_a > \theta_e$

& $\theta_r < \theta_e$

<u>Drop on a window pane</u>:-



Gravity $\approx \rho R^3 g$

Surface tension force $\approx 2\pi R\sigma(\cos\theta_1 - \cos\theta_2)$

<u>Force balance</u>:

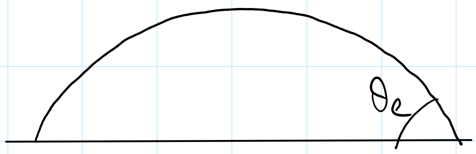
$$2\pi \cancel{R}\,\sigma(\cos\theta_1 - \cos\theta_2) \approx \rho R^{\cancel{3}\,2} g$$

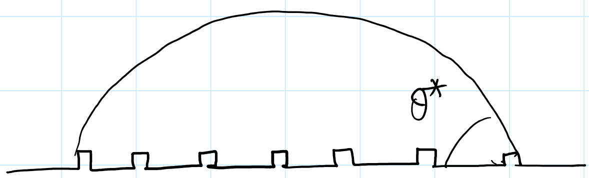
$$\frac{F_G}{F_\sigma} \approx \frac{\rho R^2 g}{\sigma} \approx B_0 \quad \text{(Bond numbers)}$$

Large drops have $B_0 \gg 1 \implies$ They slide down

Small drop have $B_0 \ll 1$ & they tend to stay on the surface.

<u>Wetting</u> on <u>rough surfaces</u>:-





<u>Define</u>: Roughness parameters:-

$$r = \frac{\text{Total surface area}}{\ldots} > 1$$

Projected surface area

$$\phi_s = \frac{\text{Area of Islands}}{\text{Projected area}} < 1$$

The change in surface energy associated with a contact line motion travelling a distance dx:-

$$dE = (\gamma_{SL} - \gamma_{SV})(r - \phi_s)\,dx + \gamma_{LV}(1-\phi_s)\,ds$$

If $r = 1$ & $\phi_s = 0$, we recover the Youngs Law.

Here $ds = dx \cos\theta^*$

At equilibrium $dE = 0 \Rightarrow (\gamma_{SL} - \gamma_{SV})(r-\phi_s)\,dx + \gamma_{LV}(1-\phi_s)\,dx\cos\theta^* = 0$

$$\Rightarrow -\gamma_{LV}\cos\theta_e\,(r-\phi_s) + \gamma_{LV}(1-\phi_s)\cos\theta^* = 0$$

$$\boxed{\cos\theta^* = \frac{(r-\phi_s)}{(1-\phi_s)}\cos\theta_e}$$

If $dE < 0$, then there is a tendency for the liquid to completely wet the surface. $\Longrightarrow$ demi-wicking.

$$dE<0 \Rightarrow -\cancel{\gamma_{LV}}\cos\theta_e(r-\phi_s) + \cancel{\gamma_{LV}}(1-\phi_s)\cos\theta^* < 0$$

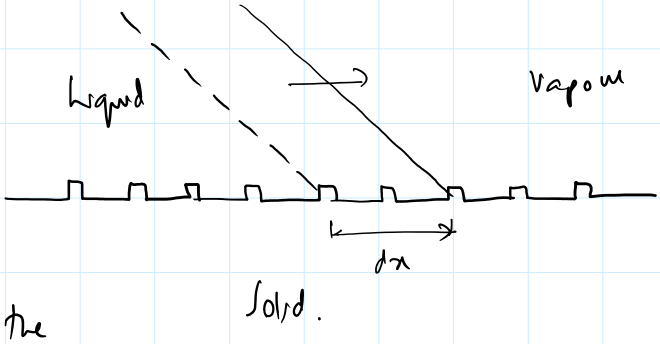
$$(1-\phi_s)\cos\theta^* < (r-\phi_s)\cos\theta_e$$

$$\cos\theta^* < \left(\frac{r-\phi_s}{1-\phi_s}\right)\cos\theta_e$$

<u>Two states</u> <u>for a drop on</u> a <u>rough surface</u>:-

Two states for a drop on a rough surface:-

(i) Wenzel State:-



In this state, the drop completely wets the surface i.e; it impregnates the surface

$$dE = r(\gamma_{SL} - \gamma_{SV})\,dx + \gamma \cos\theta^* \,dx$$

(we get this by setting $\phi_s = 0$)

If $r = 1$ (smooth surface) : Youngs equation

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

Hydrophilic surface ($\theta_e < \frac{\pi}{2}$) become more hydrophilic as $r >> 1$

i.e; $\theta^* << \theta_e$ if $\theta_e < \pi/2$

Similarly, Hydrophobic surfaces ($\theta_e > \pi/2$) become much more hydrophobic as $r >> 1$

i.e; $\theta^* >> \theta_e$ if $\theta_e > \pi/2$

(ii) Cassie-Baxter State:-