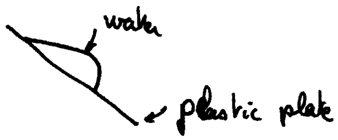
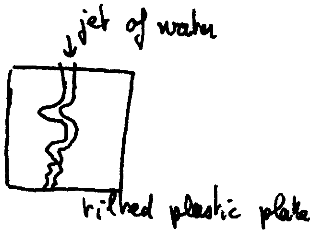
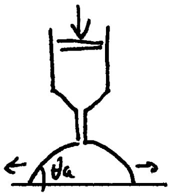
④ Actual surfaces

demo :

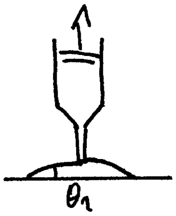




4.1 Contact angle hysteresis



advancing



receding

hysteresis $\boxed{\Delta\theta = \theta_a - \theta_r.}$

"good" surface : $\Delta\theta < 10°$.

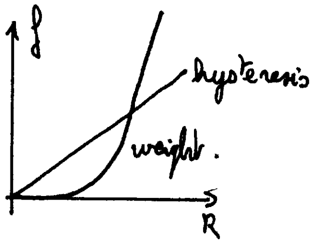
$$\boxed{\theta_a > \theta_{eq} > \theta_r}$$

Young relation

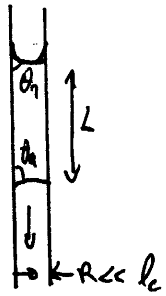
$f_{hyst} \sim 2\pi R \sigma (\cos\theta_r - \cos\theta_a)$.

weight $\sim \rho g R^3 f(\theta)$

⇒ small droplets get stuck.



index pinned in a straw:



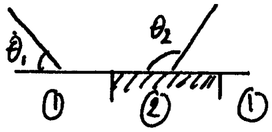
L_{min} for the index to move?

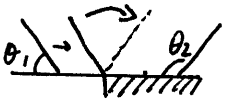
$$\frac{\sigma}{R}(\cos\theta_r - \cos\theta_a) \simeq L\rho g$$

$$\Rightarrow L_{min} = \frac{\sigma}{\rho g R}(\cos\theta_r - \cos\theta_a) = \frac{l_c^2}{R}(\cos\theta_r - \cos\theta_a).$$

Origin of hysteresis: → heterogeneity of the surface.

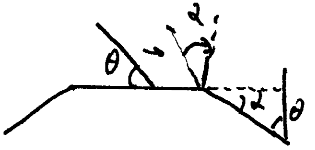
→ chemistry: → localy "good" θ.



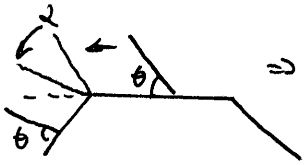


$$\Rightarrow \begin{cases} \theta_a = \theta_2 \\ \theta_r = \theta_1 \end{cases}$$

→ geometry:



$\Rightarrow \theta_a = \theta + \alpha$



$\Rightarrow \theta_r = \theta - \alpha$

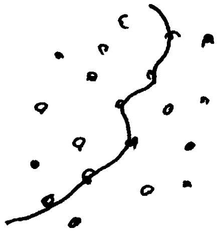
bump on the surface

$$\begin{cases} \theta_a = \theta + \alpha & (\text{or } \pi) \\ \theta_r = \theta - \alpha & (\text{or } 0). \end{cases}$$

↳ sometimes called cantotaxy

→ glass overfilled.

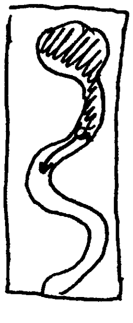
↳ in reallity not all the defects are in the same time on the contact line



⇒ jumpy motion of the contact line

↳ general case: pinning force and hysteresis difficult to describe.

→ using hysteresis: → microfluidic devices (open microchannels)



microscope slide → chanel made with hydrophobic treatment for car windows under a mask of tape.

4.2 Rough surfaces

demo :  lycopodium petri dish.

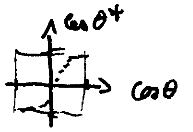
slide : experiment Johnson & Dettre.

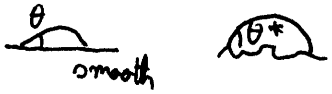
↳ huge effect of the roughness.

slide : japanise hydrophobic surface.

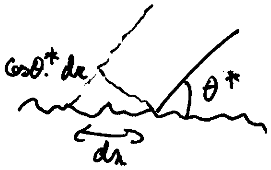
↪ modelize ? → compare with wetting on the same material but flat.

slide





4.2.1 Wenzel model: → if time enough.



roughness factor: $r = \frac{\text{Actual surface}}{\text{apparent surface}}$ $(r \geq 1)$

$$dE_s = r(\sigma_{SL} - \sigma_{SV}) + \sigma_{LV} \cos\theta^* \, dx.$$

$$\left. dE_s \right/_{eq} = 0 \Rightarrow \boxed{\cos\theta^* = r \, \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} = r \cdot \cos\theta.}$$

$\Rightarrow \theta^*$ amplified $\begin{cases} \theta < 90° \rightarrow \theta^* < \theta \\ \theta > 90° \rightarrow \theta^* > \theta. \end{cases}$

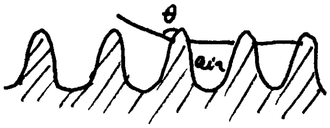
limits: $\begin{cases} \theta^* = 0 \quad \text{for} \quad \cos\theta = 1/r \\ \theta^* = 180° \quad \text{for} \quad \cos\theta = -1/r \end{cases}$ → not observed.

4.2.2 Composite surfaces (Cassie & Baxter)

$\theta > 90°$

low amplitude

↳ contact line can adapt

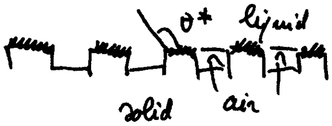


high amplitude

↳ contact line doesn't explore the roughness

⇒ air trapped.

simple model: crenelated surface



→ $\phi_s = \frac{\text{top of the roughness}}{\text{apparent area}} \neq 1.$

↳ effective solid : ϕ_s solid, $(1-\phi_s)$ air

$$\begin{cases} \sigma^*_{SL} = \sigma_S \, \sigma_{SL} + (1-\phi_s)\sigma_{LV} \\ \sigma^*_{SV} = \phi_s \sigma_{SV} + 0 \end{cases}$$

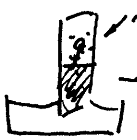
$$\Rightarrow \cos\theta^* = \frac{\phi_s(\sigma_{SV}-\sigma_{SL}) - (1-\phi_s)\sigma_{LV}}{\sigma_{LV}}$$

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

jump for $\theta > 90°$.

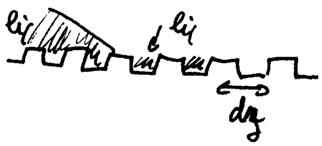
4.2.3 The hydrophilic side (if time enough)

demo :



→ impregnation of the roughness.

⇝ condition for impregnation:



$$dE_S/l = (r-\phi_S)\underbrace{(\sigma_{SL}-\sigma_{SV})}_{-\sigma_{LV}\cos\theta}\,dz + (1-\phi_S)\,\sigma_{LV}\,dz$$

imbibition if $dE_S<0$ $\Rightarrow$ $\boxed{\cos\theta > \frac{1-\phi_S}{r-\phi_S}}$

$$\begin{cases} r\to\infty : \text{3D porous (or capillary tube), impregnation for } \theta<90^\circ \\ r=1 : \text{flat surface, impregnation (precursor) for } \theta=0 \end{cases}$$

effective contact angle on an impregnated surface:

effective surface:
ϕ_S surface, $(1-\phi_S)$ liquid

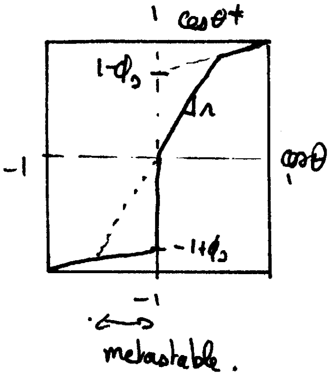
$$\Rightarrow \begin{cases} \sigma_{SL}^* = \phi_S\,\sigma_{SL} \\ \sigma_{SV}^* = \phi_S\,\sigma_{SV} + (1-\phi_S)\,\sigma_{LV} \end{cases}$$

$$\cos\theta^* = \frac{\phi_S(\sigma_{SV}-\sigma_{SL}) + (1-\phi_S)\sigma_{LV}}{\sigma_{LV}}$$

$$\boxed{\cos\theta^* = 1 + \phi_S(\cos\theta - 1).}$$

how to check these relations? → textured surface microfabricated.

→ slide : surface Margolin.

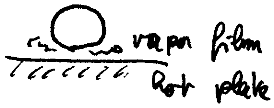


4.3 Pearl drops:

→ type 1 :

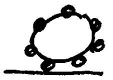
fakir carpet

→ type 2 :



calefaction

→ type 3:



coated droplets.

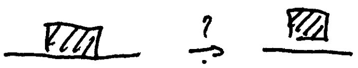
↳ demo : liquid marbles.

→ slide : aphids marbles.

↳ condition to get them :

$\theta > 90°$ → particles doesn't get wet

adhesion?



$$\Delta E/S = \sigma_{SV} + \sigma_{LV} - \sigma_{SL}$$

$$\Delta E/S = \sigma_{LV}(1+\cos\theta) > 0$$ ⇒ always some adhesion

↳ dynamics: slide

peanut

torus.

centrifuge forces / surface tension: → $B_o = \frac{\rho R^3 \omega^2}{\sigma}$

$\rho R\omega^2 R$ ↳ acceleration

σ/R

$B_o \ll 1$ ⇒ sphere $B_o \sim 1$ shape

$B_o \gg 1$ break up.