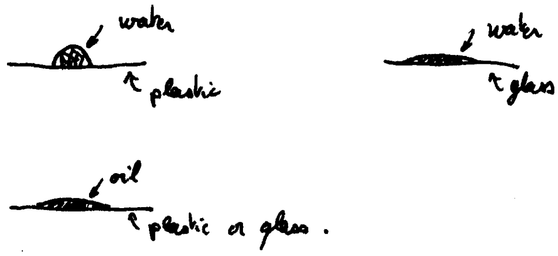
② Contact with a solid

experiments :



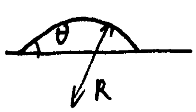
2.1 Wetting parameter

$$S = \sigma_{SV} - (\sigma_{LV} + \sigma_{SL})$$

$S > 0 \Rightarrow$ total wetting (film of liquid)

$S < 0 \Rightarrow$ partial wetting (droplet).

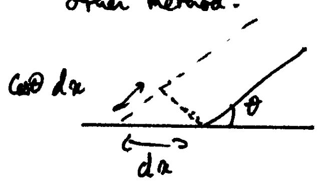
2.2 Partial wetting



θ (or R) to minimize E_s with constant V?

→ geometry argument works but long.

other method:



slight perturbation close to equilibrium

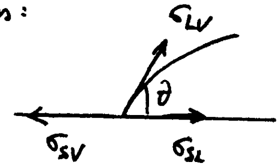
$$dE_s = (\sigma_{SL} - \sigma_{SV})\,dx + \sigma_{LV}\cos\theta\,dx$$

$dE_s = 0$ (equilibrium)

$$\boxed{\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}}$$ Young relation (1805)

↳ relation for theoreticians → only for perfect surface.

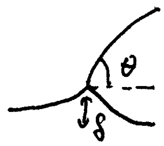
other derivation: forces:



→ projection on the horizontal ⇒ Young relation.

vertical? → pinching of the surface.

→ slide.



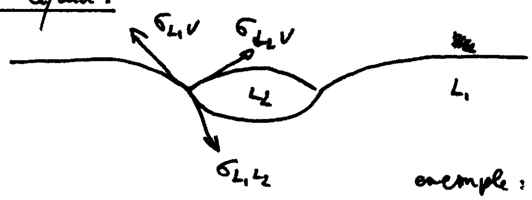
$\sigma_{LV} \sin\theta \sim E\delta$

↳ E: Young modulus (elastic)

$\delta \sim \frac{\sigma}{E}$ $\quad E \sim$ GPa ⇒ $\delta \sim 1$ nm.

↳ only visible for soft solids.

<u>case liquid/liquid:</u>

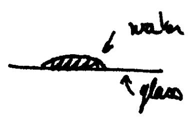


example: oil on water.

equilibrium: $\vec{\sigma}_{L_1V} + \vec{\sigma}_{L_2V} + \vec{\sigma}_{L_1L_2} = \vec{0}$.

<u>surface treatment</u>

experiment:



$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}$$

→ treatment ⇒ $\sigma_{SV} \searrow$, $\sigma_{SL} \nearrow$

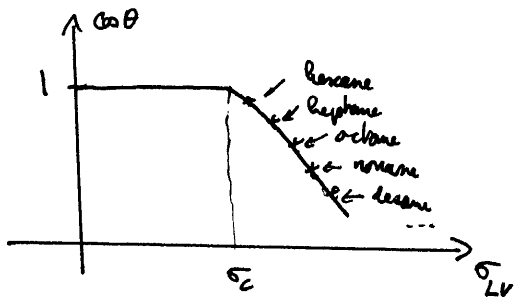
⇒ $\cos\theta \searrow$, $\theta \nearrow$

↳ pb: measures of σ_{SV}, σ_{SL} ?

2.3 Zisman criterium

surface tension of a solid? only $\sigma_{SV} - \sigma_{SL}$ (from σ_{LV} and θ)

Zisman method: $\cos\theta$ versus σ_{LV} (chemicals of the same family).



if $\sigma < \sigma_c \Rightarrow$ total wetting.

↳ semi-empirical: fine for non polar liquids

↳ slide.

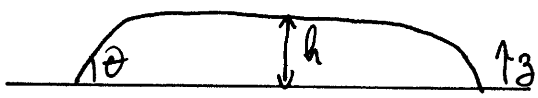
Typical values for σ_c:

material	Teflon	PE	PVC	Nylon
σ_c (mN/m)	~18	~30	~40	~50
	$-(CF_2)_n$	$-(CH_2)_n$	$-(CH_2-CH(Cl))_n$	$[(CH_2)_5-C(=O)NH]_n$

more polar $\Rightarrow \sigma_c \nearrow$.

2.4 From droplets to puddles

experiment:



thickness h? → gravity / surface tension

gravity: $dE_p = \rho g z \mathcal{A}\, dz \Rightarrow E_p = \frac{1}{2} \rho g h^2 \mathcal{A}$

surface energy: $E_s = (\sigma_{LV} + \sigma_{SL} - \sigma_{SV})\mathcal{A} = -S\mathcal{A}$. ($S<0$, partial wetting)

$$E = -S\mathcal{A} + \frac{1}{2}\rho g \mathcal{A} h^2$$

$V = \mathcal{A}h \Rightarrow$ constant.

$$E/V = -\frac{S}{h} + \frac{1}{2}\rho g h$$

$E/V)_{min} \rightarrow \frac{dE/V}{dh} = 0 \rightarrow \frac{S}{h^2} + \frac{1}{2}\rho g = 0$

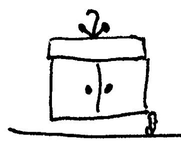
$$h = \sqrt{\frac{-2S}{\rho g}} = \sqrt{\frac{2\sigma_{LV}(1-\cos\theta)}{\rho g}}$$

$$\boxed{h = 2 \sin\theta/2 \cdot \sqrt{\frac{\sigma}{\rho g}}}.$$

↓ capillary lenght l_c (or κ^{-1}).

typical values: oil: $l_c \sim 2mm$.
water $l_c = 2.7mm$.

$h \nearrow$ if $\theta \nearrow$ – h_{max} for $\theta = \pi$ → water ~ 5mm.


shift height in bathroom furnitures.

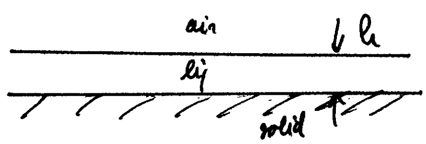
2.3 Total wetting

$S > 0$ → liquids with low σ (Zisman).

↳ how far can it spread?


→ final thickness?

Van der Waals interactions for a thin film:



} so close that the solid "feels" the upper interface.
typical cut-off: 100 nm

→ $E/A = \sigma_{SL} + \sigma_{SV} + \Sigma(h)$

$\Sigma(h) = \frac{H}{12\pi h^2}$ → Hamaker constant ~ contrast in the materials polarizabilities.

$H \sim 10^{-19} - 10^{-20} J$ usually > 0 (solid more polarizable)
< 0 (~teflon).

Final thickness of the pancake:

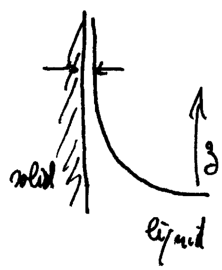
$$E/V = -\frac{S}{h} + \frac{H}{4\pi h^3}$$

$$E/V\Big)_{min} \to \frac{S}{h^2} = \frac{H}{4\pi h^4} \Rightarrow \boxed{h = \sqrt{\frac{H}{4\pi S}}}$$

→ slide : measures AM Cazabat.

Disjoining pressure

$$P_d = \frac{dE}{dh} = -\frac{H}{6\pi h^3}$$



Rollin films with liquid He (superfluid)

hydrostatics ↓, van der Waals ↓

$$\to -\rho g z = -\frac{H}{6\pi h^3}$$

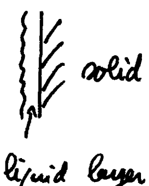
$$\boxed{h = \left(\frac{H}{6\pi \rho g z}\right)^{1/3}}$$

↳ Pb : filling a container with liquid He :

→ flows away.

↳ partial wetting on Cs.

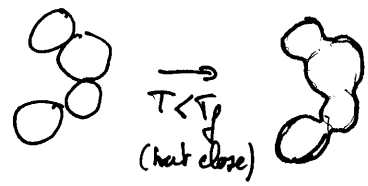
<u>Surface melting:</u>



$T < T_f$ => should not melt, but E ↘ if the solid is wetted by its own liquid => surface melting.

↳ thin film (molecular thickness) gets thick when $T \to T_f$.

In part responsible for sintering:



↳ question from Faraday: how making snow balls below 0°C?

↳ "adhesion" of ice cubes: