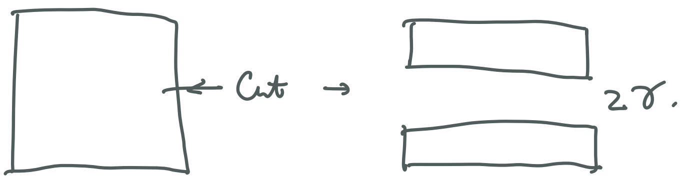
# Surface energy

The surface energy $\gamma$ of a solid (or liquid) in the presence of a gaseous phase is defined as the work $\gamma dA$ needed to create reversibly and isothermally an elemental area $dA$ of new surface in equilibrium with the medium.

Dimension [=] force / Length or Energy / area.

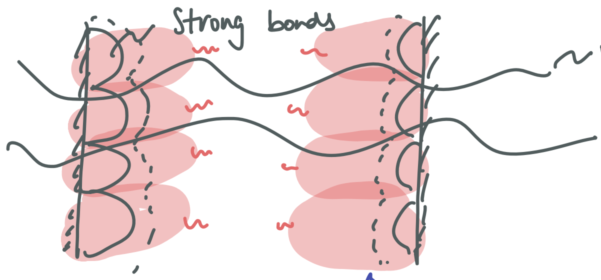



- Some typical values of surface energy

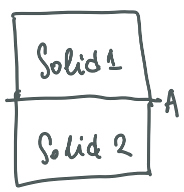
| Liquid-Vapor | $\gamma$ (mJ/m²) |
|---|---|
| water | 72.5 |
| typical organics | 20-30 |
| liquid metal | 1000-2000 |
| Liquid-Liquid | |
| water-organics | 35-50 |
| Solid-Vapor | |
| ploymers | 35-50 |
| metals | 1000-4000 |

A reflection of the nature of bonds between atoms which constitute it. → Ionic, covalent or metallic bonds are strong and short-ranged. VdW bonds are weak but "relatively" long-ranged.

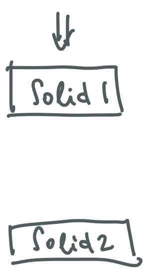
Why a metallic surface in air has a VERY low surface energy, ~ (vdW)?




## • Cohesion & Adhesion




$U = U_0 + \gamma_{12} A$ . $\gamma_{12}$ is interfacial enery




$U = U_0 + (\gamma_1 + \gamma_2) A$

To separate them reversibly & isothermally, one has to furnish the work

$$\boxed{w = \gamma_1 + \gamma_2 - \gamma_{12}} .$$

also termed Dupré's enery of adhesion (1869).

① When 1 and 2 form the same material, $\gamma_{12}=0$, $\omega=2\gamma$.

② 1, 2 are 2 grains of polycryster, interface enery $\gamma_G$ is a function of misorientation of grains. $\gamma_G \sim \frac{1}{3}\gamma_s$, $\gamma_{Twin\text{-}G} \sim \frac{1}{5}\gamma_s$.

## • Surface energy of a Lennard-Jones Solid

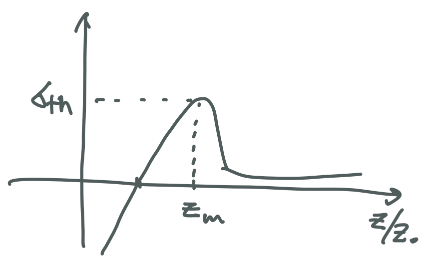
We have obtained the interaction between two L-J solids in homework 1.

$$\sigma(z) = \frac{A}{6\pi z^3} - \frac{B}{z^9}.$$

where $A = \pi^2 n^2 C$ is Hamaker constant of the solid.

Using $\sigma = 0$ at $z_0$, we have

$$\sigma(z) = \frac{A}{6\pi z_0^3}\left[\left(\frac{z_0}{z}\right)^3 - \left(\frac{z_0}{z}\right)^9\right].$$




$$\left.\frac{\partial\sigma}{\partial z}\right|_{z_m} = 0 \Rightarrow -\frac{3z_0^3}{z_m^4} + \frac{9z_0^3}{z_m^{10}} = 0 \rightarrow z_m = 3^{1/6} z_0.$$

$$\sigma_{th} = \sigma(z = 3^{1/6} z_0) = \frac{A}{6\pi z_0^3}\left(\frac{1}{\sqrt{3}} - \frac{1}{3\sqrt{3}}\right) = \frac{A}{6\pi z_0^3}\cdot\frac{2}{3\sqrt{3}}$$

We then have $\boxed{\sigma(z) = \frac{3\sqrt{3}}{2}\sigma_{th}\left[\left(\frac{z_0}{z}\right)^3 - \left(\frac{z_0}{z}\right)^9\right]}$.

Potential energy reads:

$$U(z) = \int_{\infty}^{z} \sigma(z)\,dz$$

$$= \underbrace{-\frac{A}{12\pi z_0}}_{\to -\frac{8}{3}\gamma} \left[ \left(\frac{z_0}{z}\right)^2 - \frac{1}{4}\left(\frac{z_0}{z}\right)^8 \right]$$

Surface energy by definition $\gamma = -\frac{1}{2} U(z \to z_0) = \frac{3}{8} \cdot \frac{A}{12\pi z_0} = \frac{A}{32\pi z_0}$

- $A \sim 10^{-19}$ J, $z_0 \sim 2\times10^{-10}$ m, $\gamma \sim 25\,mJ/m^2$, is of the correct order of magnitude.

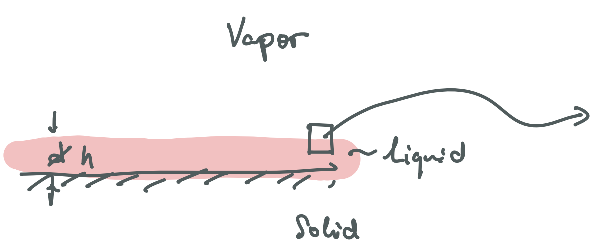
- Young's modulus.

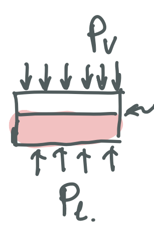
$$E = \frac{\sigma}{\varepsilon}\Big|_{z=z_0} = z_0 \frac{d\sigma}{dz}\Big|_{z=z_0} = 9\sqrt{3}\,\sigma_{th} \cdot \to \sigma_{th} \sim \frac{1}{10} E.$$

| | E (GPa) | $\sigma_{th}$ (MPa) |
|---|---|---|
| Al | 69 | 110 |
| Epoxy | 3-2 | 26~85 |
| Glass | 50-90 | 50 |
| Polystyrene PS | 3-3.5 | 30-100 |
| Steel | 200 | 400 |

why $\sigma_{th} \sim \frac{E}{100}$ or $\frac{E}{1000}$ in experiments?

## · Wetting and de-wetting of films.




$$F = \frac{A_{SLV}}{6\pi d^3}$$

$$\Delta P = P_L - P_V = \frac{A_{SLV}}{6\pi h^3}$$

(Disjoining pressure $\Pi = -\Delta P = -F$)

If $A_{SLV} < 0$, $h$ grows by absorbing liquid molecules from vapor till an equilibrium with chemical pressure/potential is established.

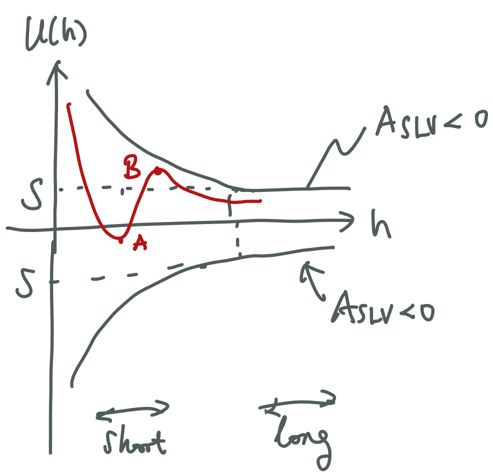
$$U(h) = -\frac{A_{SLV}}{12\pi h^2} \quad \text{for } h \geq h_0$$

May naturally define surface energies $\gamma_{SL} + \gamma_L - \gamma_{SV} = \frac{A_{SLV}}{12\pi h_0^2}$, Or.

$$\boxed{S = \gamma_{SV} - (\gamma_{SL} + \gamma_L) = -\frac{A_{SLV}}{12\pi h_0^2}}$$

, $A_{SLV}$ given by Lifshitz.

Spreading parameter by Marangoni in 1865, Cooper and Nuttal in 1915, measuring the difference between surface energy (per unit area) of the substrate when DRY and WET. Also see A. Pahlavan PRL (2015), D. Peschka PNAS (2019) for intermediate states.

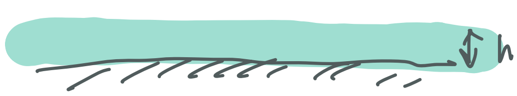



- $A_{SLV} < 0$, $S > 0$, Complete wetting → thin film
- Non-monotonic $A_{SLV}$ → Stable/unstable films.
- $A_{SLV} > 0$, $S < 0$, Non-wetting, Partially wetting.

Qs: ① What is $h_c$?

② What is $\theta$?

$A_{SLV} > 0$



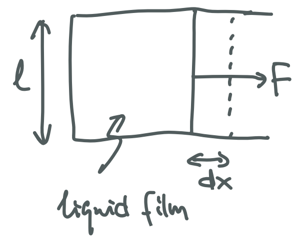

$h < h_c \Rightarrow$

# Surface tension

As erery system has a tendency to reduce it potential enery (including surface energy), the surface of liquid tends to minimize and thus to contract.

It is as if the surface of a liquid was stretched, "like" a rubber membrane.

Example:




$dW = F dx = \gamma dA = 2\gamma l dx$

$\rightarrow F = 2l\gamma$ = "Constant" [Differing from membrane tension]

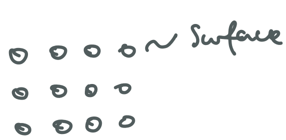
Surface tension is considered no more than a methematical abstraction of surface energy. [$\sigma \equiv \gamma$ for liquids]

Young (1805): Tension, Gauss (1830): Energy, Rayleigh (1890): "Tension" = "Energy" (numerically)

## · Several notes

### · From the point of energy

Boundary molecules are missing neighbors and therefor have a higher energy.

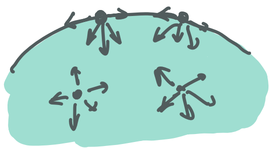



$$\gamma = \frac{E_s - E_b}{a_0}$$

Molecular interaction enery at surfaces (s) and bulk (b).

area/unit molecule

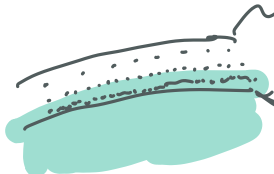
## • Perspective of cohesive forces (X)



A molecule in the bulk of a liquid undergoes from neighboring molecules attractive forces in all directions.

But a molecule at the surface are subject to force only directed toward the interior of the liquid and parallel to the surface

## • Perspective of desity gradient



High potential, low density of molecules

2-3 molecule layer

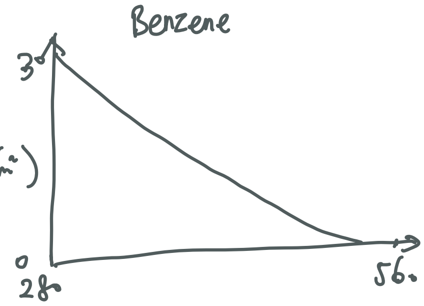
low potential, high density of molecules

"Boltzmann distribution"?

Net force is zero

## • Temperture effect.

Benzene




$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n, \quad n \simeq \frac{11}{9}.$$

Surface tension decreases with temperature and vanishes at critical point.

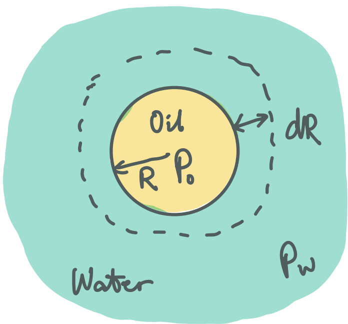
## • Pressure effect

Surface tension is relatively pressure insensitive – it varies only about 1.5% at 100 atm.

# · Laplace pressure (Laplace 1805)

## · A sphere

① Energy method.




A drop of oil in water.

· The drop adopts a spherical shape of radius R to lower its surface energy.

· If the o/w interface is displaced by a amount dR, the work by the pressure and Capillary force is

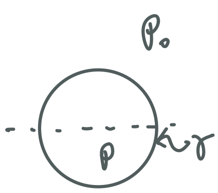
$$\delta W = -P_o dV_o - P_w dV_w + \gamma_{ow} dA$$

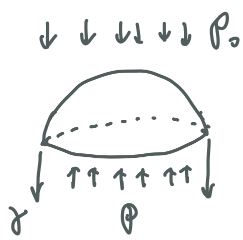
$$dV_o = 4\pi R^2 dR = -dV_w$$

$$dA = 8\pi R dR$$

$$\Rightarrow \boxed{\Delta P = P_o - P_w = \frac{2\gamma_{ow}}{R}}$$

② Force balance




$$(P - P_o) \times \pi R^2 = 2\pi R \times \gamma$$

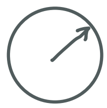
$$\Delta P = \frac{2\gamma}{R}$$

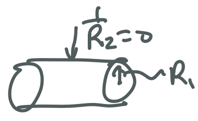
## · Any surface

Laplace's therom: The increase in hydrostatic pressure $\Delta P$ that occurs upon traversing the boundary between two fluids is equal to the product of surface tension $\gamma$ and the curvature of the surface $C = \frac{1}{R_1} + \frac{1}{R_2}$

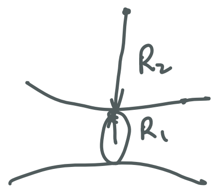
$$\boxed{\Delta p = \gamma \, \mathrm{Tr}(\underset{\sim}{\underset{\sim}{K}}) = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)}$$

Invariant.

① Sphere  $C = \frac{1}{R} + \frac{1}{R} = \frac{2}{R}$

② Cylinder 

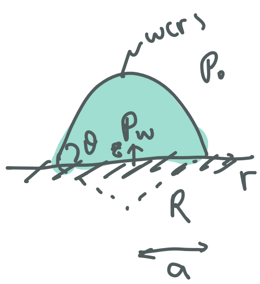
$C = \frac{1}{R_1}$

③ 

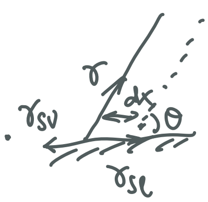
$C = \frac{1}{R_1} - \frac{1}{R_2}$

· Young's equation (Young 1805) : $\underbrace{\text{Young-Laplace equation}}_{\text{pressure}} + \underbrace{\text{Young-Dupré equation}}_{\text{contact angle.}}$

· A simple method (force balance)




$$\cdot \ \boxed{\Delta p = P_w - P_0 = \frac{2\gamma}{R} = \gamma \frac{-2w''}{(1+w'^2)^{3/2}}}$$

· 


$$(\gamma_{sv} - \gamma_{sl}) \cdot dx = \gamma \cos\theta \, dx$$

$$\rightarrow \boxed{\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma}}$$

$$\boxed{\begin{aligned} S &= \gamma_{sv} - (\gamma + \gamma_{sL}) \\ &= \gamma\cos\theta + \gamma_{sL} - \gamma = \gamma(\cos\theta - 1) \le 0 \quad (\text{Partially wetting}) \end{aligned}}$$

- A variational method.

Leibniz integral rule $\quad \frac{d}{dx}\int_{a(x)}^{b(x)} f(x,t)\,dt = \int_a^b \frac{\partial f}{\partial x}\,dt + f(x,b)\frac{d\,b(x)}{dx} - f(x,a)\frac{d\,a(x)}{dx}$

$$F = \gamma A - \Delta p V + (\gamma_{sl}-\gamma_{sv})\pi a^2$$

$$= \cancelto{\text{drop.}}{2\pi}\gamma\int_0^a \sqrt{1+w'^2}\, r\,dr - \Delta p\int_0^a \cancelto{\text{drop.}}{2\pi}\, w\, r\,dr + \cancelto{\text{drop}}{2\pi}(\gamma_{sl}-\gamma_{sv})\frac{1}{2}a^2$$

$$\delta F = \underbrace{\gamma\int_0^a \frac{w'\delta(w')}{\sqrt{1+w'^2}}\, r\,dr}_{①} - \Delta p\int_0^a \delta w\, r\,dr + \underbrace{\left(\gamma\sqrt{1+w'^2}\cdot a + \cancelto{0}{\Delta p w}\, a\right)\Big|_{r=a}\delta a}_{②}$$

$$+ (\gamma_{sl}-\gamma_{sv})\, a\,\delta a$$

$$① = \gamma\int_0^a \frac{w'}{\sqrt{1+w'^2}}\, r\, d(\delta w)$$

$$= \underbrace{\frac{\gamma w'}{\sqrt{1+w'^2}}\, r\,\delta w\Big|_0^a}_{③} - \int_0^a r\,\delta w\Bigg[\underbrace{\frac{w''}{\sqrt{1+w'^2}} - \frac{w'^2 w''}{(1+w'^2)^{3/2}}}_{\to \frac{w''}{(1+w'^2)^{3/2}}}\Bigg]dr - \int_0^a \frac{\gamma w'}{\sqrt{1+w'^2}}\,\delta w\,dr$$

$$② = \gamma\sqrt{1+\tan^2\theta}\cdot a\,\delta a = \frac{\gamma a}{\cos\theta}\,\delta a$$

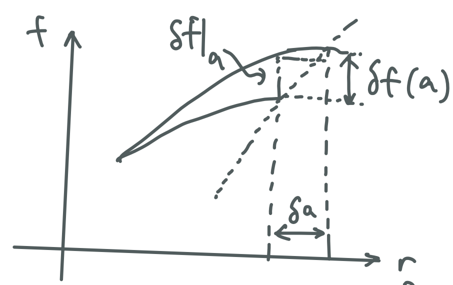
$$③ = \frac{\gamma w'}{\sqrt{1+w'^2}}\, r\,\delta w\Big|_a - \frac{\cancelto{0}{\gamma w'}}{\sqrt{1+w'^2}}\,\cancelto{0}{r}\,\delta w\Big|_0$$

$$= -\frac{\gamma w'^2(a)}{\sqrt{1+w'^2(a)}}\, a\,\delta a$$

$$= -\frac{\gamma\tan^2\theta}{\sqrt{1+\tan^2\theta}}\, a\,\delta a = -\frac{\gamma\sin^2\theta}{\cos\theta}\, a\,\delta a$$

$$\delta w(a) = \delta w\big|_a + w'(a)\,\delta a = 0$$

$$\to \delta w\big|_a = -w'(a)\,\delta a$$

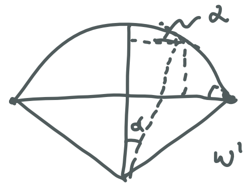



$$\delta f(a) = \delta f\big|_a + (f'(a) + \cancelto{0}{\epsilon})\,\delta a$$

What is this?

$$\delta F = -\int_0^a \left[ \frac{\gamma w''}{(1+w'^2)^{3/2}} + \frac{\gamma w'}{r(1+w'^2)^{1/2}} + \Delta p \right] r\, \delta w\, dr$$

$$+ \left( \frac{\gamma}{\cos\theta} - \frac{\gamma \sin^2\theta}{\cos\theta} + \gamma_{sl} - \gamma_{sv} \right) a\, \delta a$$




$w' = -\tan\alpha$

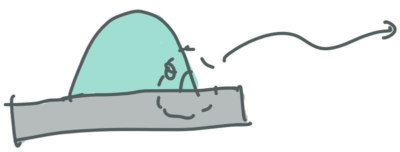
- $\frac{w'}{r(1+w'^2)^{1/2}} = -\frac{\sin\alpha}{r} = -\frac{1}{R}$

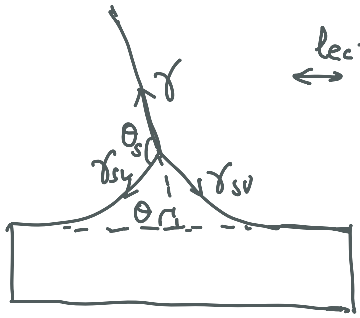
$w'' = -\frac{d\tan\alpha}{dr} = -\frac{1}{\cos^2\alpha}\frac{d\alpha}{dr}$

- $\frac{w''}{(1+w'^2)^{3/2}} = -\frac{d\sin\alpha}{dr} = \frac{-1}{R}$

Arbitrary $\delta w, \delta a \Rightarrow$ $\boxed{\Delta p = -\gamma\left[\frac{w''}{(1+w'^2)^{3/2}} + \frac{w'}{r(1+w'^2)^{1/2}}\right],\quad \cos\theta = \frac{\gamma_{sv}-\gamma_{sl}}{\gamma}}$

- Soft wetting



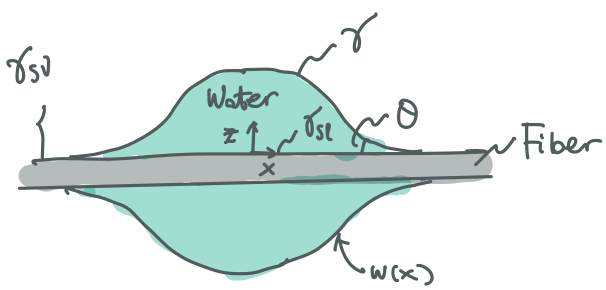




$l_{ec} \sim \frac{\gamma}{\mu} \sim 1\,\mu m$

$\gamma \sim 0.1\ N/m,\ \mu \sim 0.1\ MPa$

What determines $\theta_s$? Neumann's equation $\vec{\gamma} + \vec{\gamma}_{sv} + \vec{\gamma}_{sl} = 0$

- Drop on a fiber

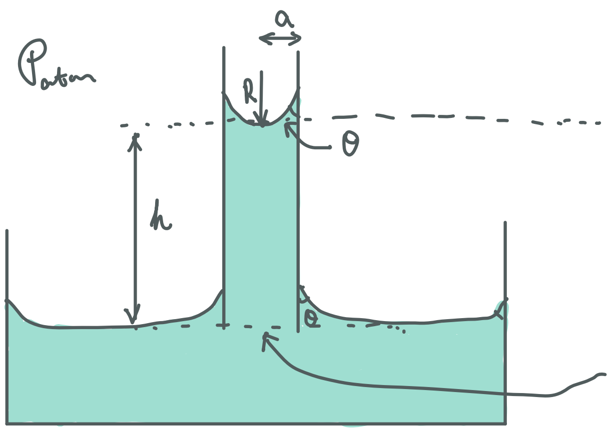



$$\boxed{\begin{aligned} \Delta p &= \gamma\left[\frac{-w''}{(1+w'^2)^{3/2}} + \frac{1}{w(1+w'^2)^{1/2}}\right] \\ \cos\theta &= \frac{\gamma_{sv}-\gamma_{sl}}{\gamma} \end{aligned}}$$

# Examples

## · Capillary rise

### ① By means of Laplace pressure




$$P_1 = P_{atm} - \frac{2\gamma}{R} \quad \leftarrow \quad R = \frac{a}{\cos\theta}$$

$$= P_{atm} - \frac{2\gamma\cos\theta}{a}$$

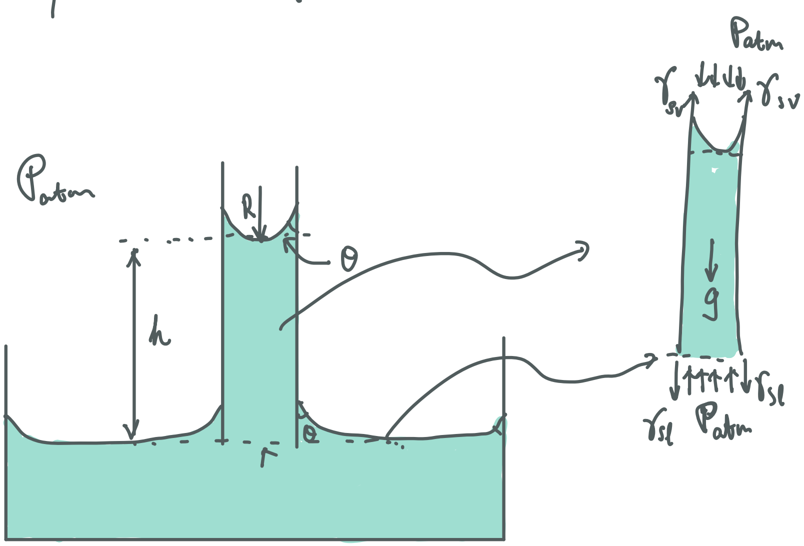
$$P_2 = P_{atm} = P_1 + \rho g h$$

$$\Rightarrow h = \frac{2\gamma\cos\theta}{\rho g a} = \frac{2 l_c^2 \cos\theta}{a}, \quad l_c = \left(\frac{\gamma}{\rho g}\right)^{1/2}$$

Capillary length.

$\gamma \sim 0.1\ J/m^2$, $\rho \sim 10^3\ kg/m^3$, $g \sim 10\ N/kg$ $\rightarrow$ $l_c \sim 3\ mm$

### ② By means of force balance



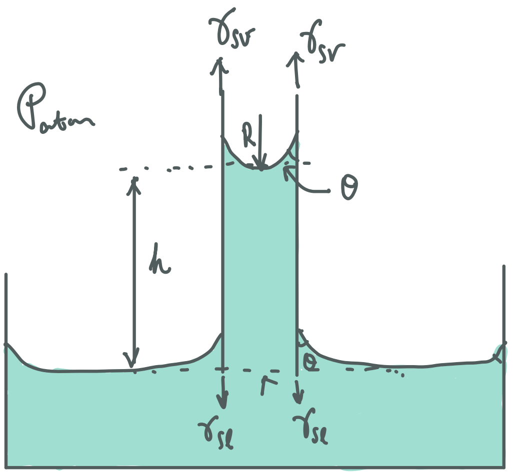

· Force balance along vertical direction.

$$2\pi a(\gamma_{sv} - \gamma_{sl}) = \rho g h \pi a^2$$

$$\gamma_{sv} = \gamma\cos\theta + \gamma_{sl}$$

$$\Rightarrow h = \frac{2\gamma\cos\theta}{\rho g h}$$

③ By means of energy argument




$$U(h) = -2\pi a(\gamma_{sv} - \gamma_{sl})h + \frac{1}{2}\rho g h^2 \pi a^2$$

$$= -2\pi a h \gamma \cos\theta + \frac{1}{2}\rho g h^2 \pi a^2$$

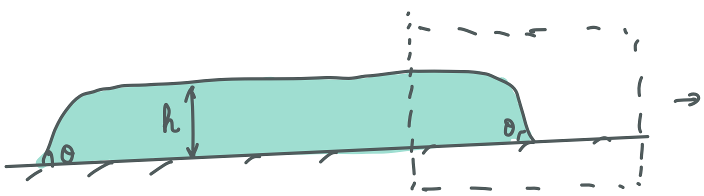
$$\frac{\partial U}{\partial h} = 0 = -2\pi a \gamma \cos\theta + \rho g h \pi a^2$$

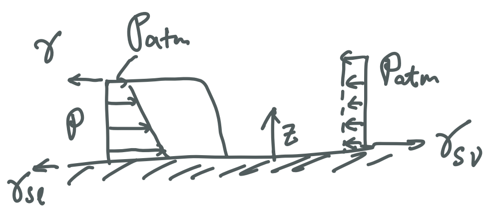
$$\Rightarrow h = \frac{2\gamma\cos\theta}{\rho g a}$$

· Thickness of a large drop on a surface

Consider a large drop that is flattened by gravitational forces.

How thick is it?



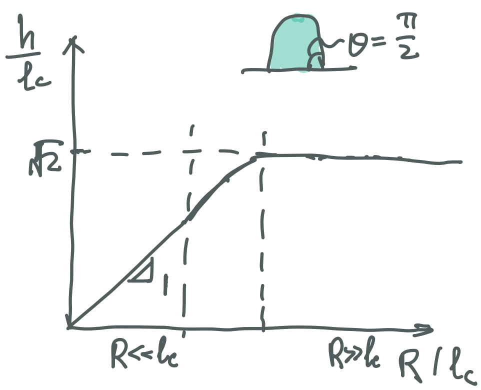




$$P = P_{atm} + \rho g(h - z)$$

$$\gamma + \gamma_{sl} + \int_0^h P\,dz = P_{atm} \times h + \gamma_{sv}$$

$$\gamma_{sv} = \gamma\cos\theta + \gamma_{sl}$$

$$\gamma(1-\cos\theta) = \frac{1}{2}\rho g h^2 \rightarrow \frac{h}{l_c} = \sqrt{2}(1-\cos\theta)^{1/2}$$



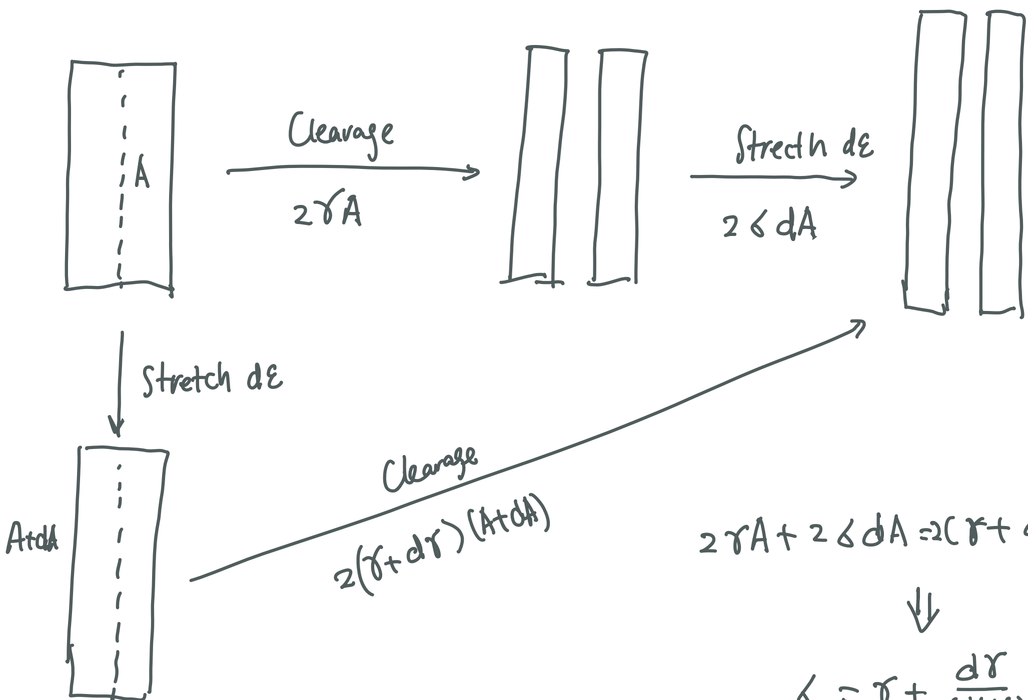
# Surface stress

The distinction for solids between the work $\gamma dA$ to create $\overbrace{\text{an elementary}}^{\frac{\text{atoms}}{\text{area}}\text{ not changed}}$ area of new surface and the work $\sigma dA$ to $\underbrace{\text{stretch a surface}}_{\frac{\text{atoms}}{\text{area}}\text{ changed}}$ elastically was established by Gibbs in 1876.

For liquids that can flow, surface energy = surface tension / surface stress $\rightarrow \gamma = \sigma$

For solids, surface energy $\neq$ surface stress $\rightarrow \gamma \neq \sigma$

Shuttleworth in 1950 established the relation between the two quantities $\sigma$ & $\gamma$.



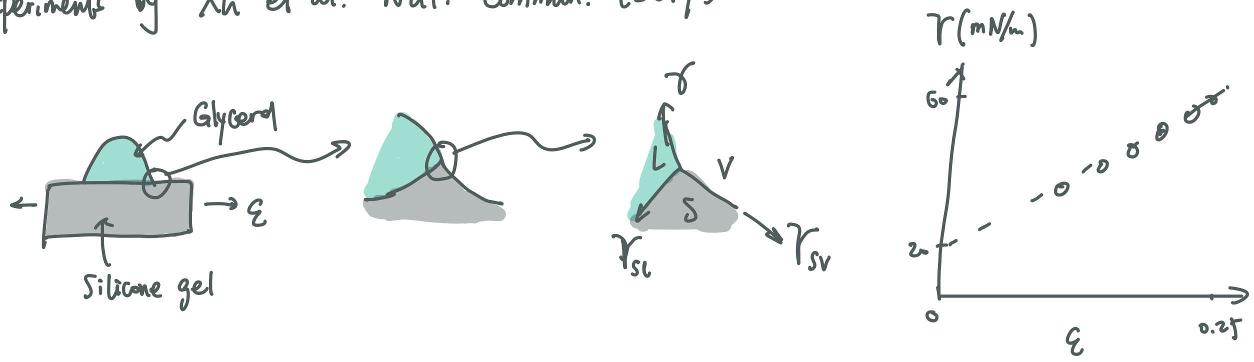

$$2\gamma A + 2\sigma dA = 2(\gamma + d\gamma)(A + dA)$$

$$\Downarrow$$

$$\sigma = \gamma + \frac{d\gamma}{(dA/A)} = \gamma + \frac{d\gamma}{d\varepsilon}$$

It is often written as $\Upsilon_{ij} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \varepsilon_{ij}}$ or $\underline{\underline{\Upsilon}} = \gamma \underline{\underline{I}} + \frac{\partial \gamma}{\partial \underline{\underline{\varepsilon}}}$

- Experiments by Xu et al. Nat. Commun. (2017)




- Also Schulman et al. Nat. Commun. (2018) for amorphous solids

- Strain-dependent surface energy remains controversial (Lagrangian & Eulerian, Linear & nonlinear laws, phase transition ....).