Surface Tension, Droplets + Contact Lines

I. Free Surfaces. (two phases)

II Contact Lines (three phases)

III Elasto-capillarity (surface vs bulk)

Reference:

Capillarity and Wetting Phenomena...
by de Gennes, Brochard-Wyart, Quéré

LaPlace Pressure

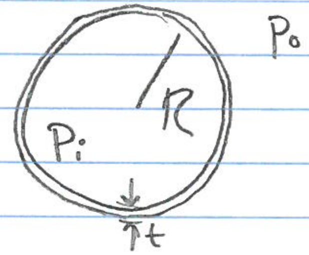
see image I.1

Blowing a Bubble vs Inflating a Balloon

$\downarrow$ fluid $\qquad\qquad$ $\downarrow$ solid

thin shells, deformed by pressure

Pressurized Shell



pressure difference: $\Delta p = p_i - p_o$

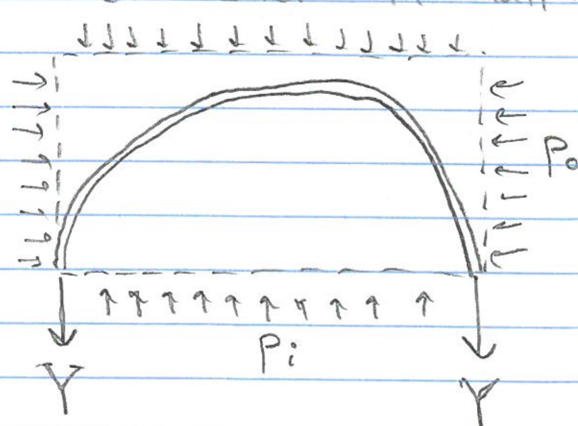
spherical shell of radius, R
and thickness, t
with $t \ll R$

mechanical equilibrium

$\Rightarrow \sum \vec{F} = 0$

for system and any sub system

cut shell in half:



(upsilon)

- γ: tension due to thin shell, in plane

  $[\gamma] = [\text{Force}]/[\text{Length}]$

- $\sum \vec{F} = 0 \Rightarrow \pi R^2 (p_i - p_o) - 2\pi R \gamma = 0$

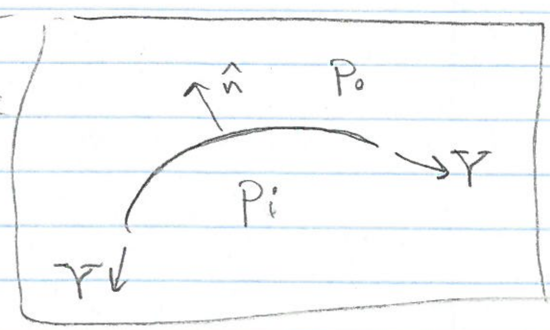
  or $\boxed{\Delta p = \dfrac{2\gamma}{R}}$ Laplace Law for Spheres

- more generally

  $\boxed{\Delta p = \gamma K}$ Laplace Law or Young-LaPlace

★ holds locally for any patch of surface bearing an isotropic tension γ with fluid on either side

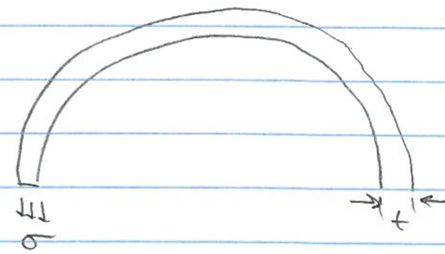
K: total curvature
(kappa)



$K = \vec{\nabla}_{\parallel} \cdot \hat{n} = \mathrm{Tr}\, K_{ij}$

where $K_{ij} = \dfrac{\partial n_i}{\partial x_j}$ ← derivatives in place

solid shell



in-plane tensile stress, $[\sigma] = [\text{Force}]/[\text{Length}^2]$

assume it to be isotropic and homogeneous (not general)

$$\Rightarrow \quad 2\pi R \Upsilon = 2\pi R t \sigma$$

$$\Rightarrow \quad \boxed{\Upsilon = \sigma t}$$

$\sigma = \sigma(\varepsilon)$, depends on strain relative to a zero-stress shape

fluid shell

- fluids have no memory

  $\Downarrow$

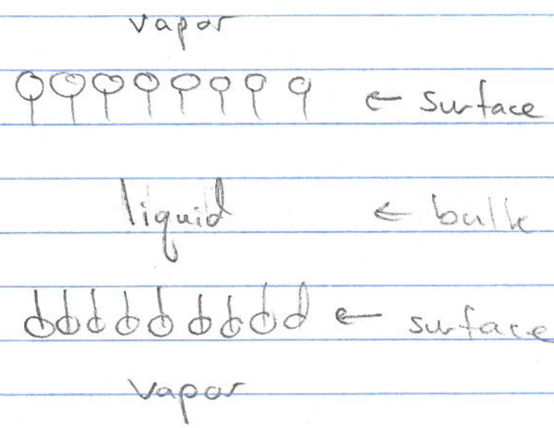
  tension only depends on current shape

- can ignore the bulk of the film provided:

  $t \ll R$

  $t \gg$ scale of intermolecular forces

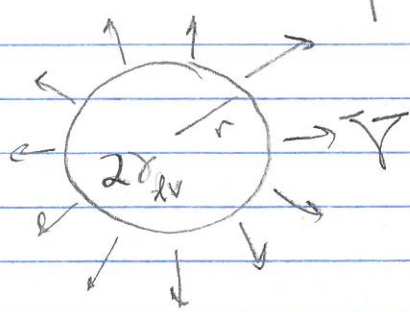
- Υ comes from the free energy of the fluid vapor interfaces, γ_{lv} (gamma)



$[\gamma_{lv}] = [\text{energy}]/[\text{Length}^2]$

- for liquids, γ_{lv} is isotropic and strain independent

- the film has two surfaces, so work to expand: $dW = 2\gamma_{lv}\, dA$



small patch radius r

but also

$$dW = 2\pi r \Upsilon\, dr$$

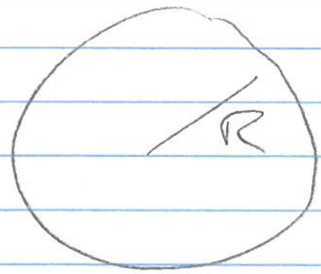
$$dA = 2\pi r\, dr$$

$$\Rightarrow 4\pi r \gamma_{lv} = 2\pi r \Upsilon$$

or $\boxed{\Upsilon = 2\gamma_{lv}}$

each side contributes γ_{lv} to tension

Liquid Droplets



as before, Laplace requires

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

homogeneous
isotropic
incompressible
fluid

single fluid interface

$$\Rightarrow \gamma = \gamma_{lv}$$

- equivalence of "surface tension" and interfacial energy (not true for solids)

- so Young-LaPlace for liquids becomes

$$\boxed{\Delta p = \gamma_{12} \kappa}$$

here γ_{12} is interfacial energy between any two fluids

- liquid surface energies:

water	0.07	J/m^2	$\approx \frac{\text{H-bond}}{\text{molecular area}}$
oil	≈ 0.02	J/m^2	$\hat{\approx}$ vdW/molecular area
mercury	0.4	J/m^2	$\hat{\approx} \frac{\text{metallic bond}}{\text{molecular area}}$

Droplet Shape

if surface tension is the only contribution, then you can find equilibrium by:

① minimize energy with volume constraint $\Rightarrow$ sphere

② demand that the fluid is in eq!.

$$\Rightarrow \vec{\nabla} p = 0 \quad \Rightarrow \vec{\nabla} \kappa = 0$$

$\Rightarrow$ surface of constant curvature with finite volume $\Rightarrow$ sphere

☆ SEE IMAGE I.2

with gravity, fluid equilibrium requires $\vec{\nabla} p = -\rho g \hat{z}$

density

gravity will perturb an initially spherical droplet when:

$$\rho g R \gtrsim \gamma_{lv} \kappa = \frac{2\gamma_{lv}}{R}$$

$$\Rightarrow R^2 \gtrsim \frac{\gamma_{lv}}{\rho g}$$

"Capillary Length"

$$L_{cap} \equiv \left(\gamma_{\ell v}/\rho g\right)^{1/2}$$

captures competition between gravity and surface tension

a droplet is only spherical when

$$R << L_{cap}$$

this length-scale comes up for any free-surface with gravity

for water

$$\gamma_{\ell v} \approx 10^{-1}\ J/m^2$$

$$\rho = 10^3\ kg/m^3$$

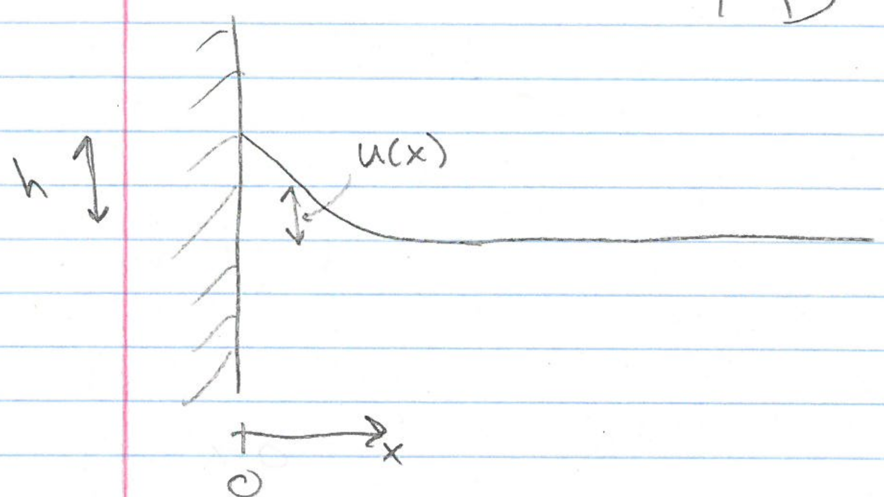
$$g \approx 10\ m/s^2$$

$$L_{cap} = \sqrt{\frac{10^{-1}}{10^4}} \approx 3\,mm$$

Meniscus

*Image I.3

1-D



$u \to 0$ as $x \to \infty$

Laplace $\Delta p = \gamma_{lv} \kappa$

for small deformations $\kappa = -u''$

hydrostatic $\Rightarrow$ $\Delta p = -\rho g u$

$\Rightarrow$ $\rho g u = \gamma_{lv} u''$ $\Rightarrow$ $\boxed{\dfrac{u''}{u} = \dfrac{1}{L_{cap}^2}}$

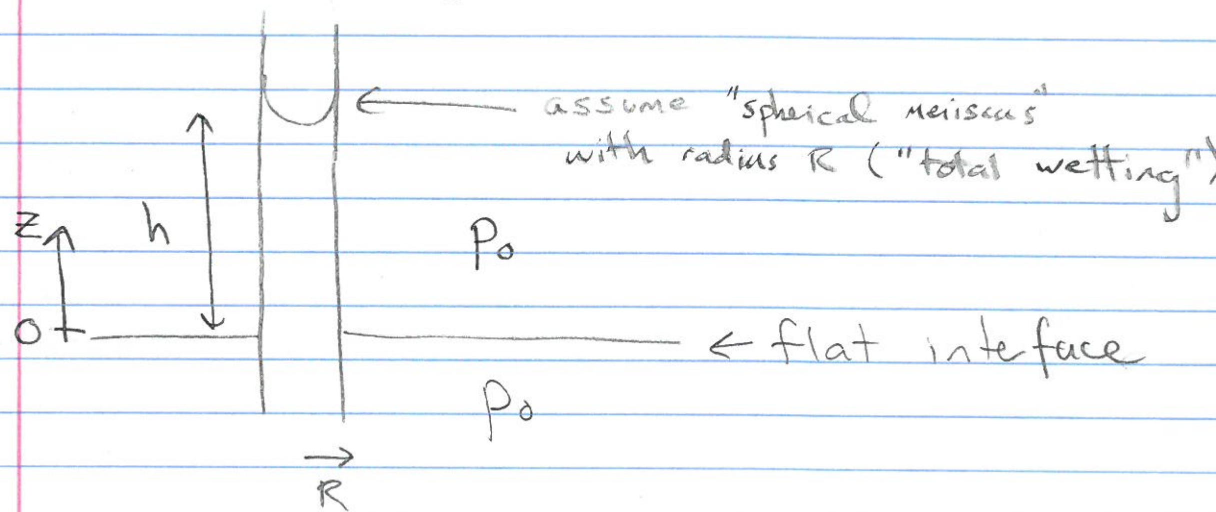
generally $u(x) = A e^{x/L_{cap}} + B e^{-x/L_{cap}}$

B.C. $\Rightarrow$ $\boxed{u(x) = h e^{-x/L_{cap}}}$

h will be determined by further B.C.'s discussed later

Capillary Rise

☆ See Image I.4



- LaPlace requires pressure at meniscus ($z=h$) to be $p_0 - \frac{2\gamma_{\ell v}}{R} = p(h)$

- Hydrostatic equilibrium requires pressure @ $z=h$

$$p(h) = p_0 - \rho g h$$

$$\Rightarrow \rho g h = 2\gamma_{\ell v}/R \Rightarrow h = \frac{2L_{cap}^2}{R}$$

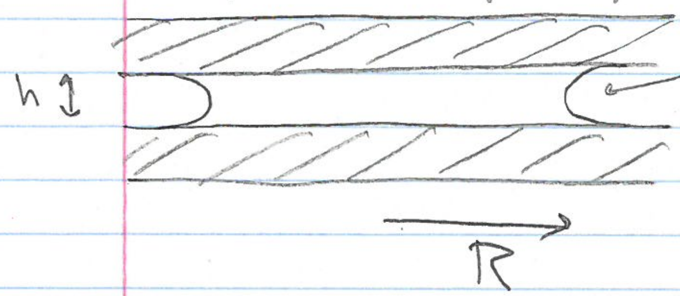
for water $L_{cap} \approx 3mm$

$$h(R=1mm) = 18mm$$
$$h(R=0.1mm) = 180mm$$

See image I.5

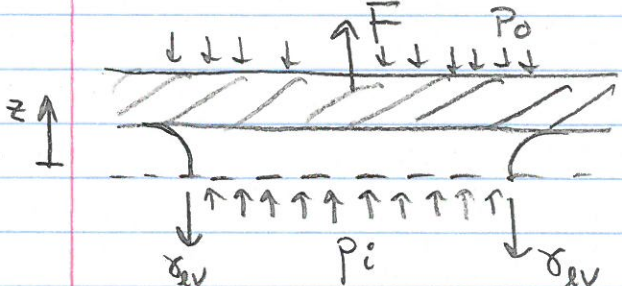
Capillary Adhesion (of rigid plates)

cylindrical symmetry



assume meniscus cross-section is circular with radius $h/2$ (total wetting)

free-body of top half



$$\Sigma F_z = 0$$

$$F + \pi R^2 p_i - \pi R^2 p_o - 2\pi R \gamma_{\ell v} = 0$$

$$\Rightarrow F = -\pi R^2 \Delta p + 2\pi R \gamma_{\ell v}$$

$$\Delta p = \gamma_{\ell v} \kappa = \gamma_{\ell v}\left(\frac{1}{R} - \frac{2}{h}\right)$$

$$\simeq \frac{-2\gamma_{\ell v}}{h} \text{ for } R \gg h$$

$$F = \frac{2\pi R^2 \gamma_{\ell v}}{h} + 2\pi R \gamma_{\ell v} = 2\pi R \gamma_{\ell v}\left(\frac{R}{h} + 1\right)$$

$$\Rightarrow F \approx \frac{2\pi R^2 \gamma_{\ell v}}{h} \text{ for } R \gg h$$

for fixed liquid volume

$$V = \pi R^2 h \qquad (R >> h)$$

$$\Rightarrow \quad F \approx \frac{2\gamma_{ev} V}{h^2}$$

for 1 μL of water and $h = 5\,\mu m$

($R \approx 1\,cm$)

$F = 10\,N$

(enough to support 1 L of water, 10^6 x it's weight!)

Soap Films

pressure same sides the same $\Rightarrow K=0$ "minimal surface"

☆ See Image I.6,7