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

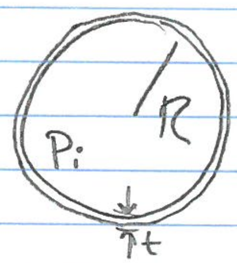
see image I.1

Blowing a Bubble vs Inflating a Balloon

↓ fluid ↓ solid

→ thin shells, deformed by pressure

Pressurized Shell



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

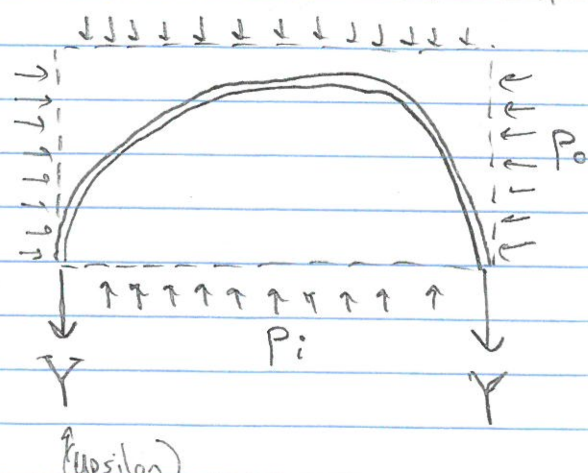
spherical shell of radius, R
and thickness, t
with $t \ll R$

mechanical equilibrium

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

for system and any sub system

cut shell in half:



- γ: tension due to thin shell, in plane

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

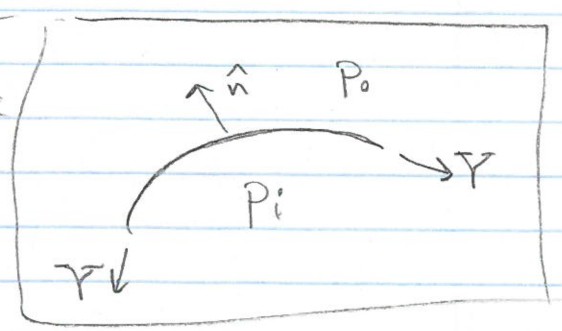
- $\sum \vec{F} = 0 \Rightarrow \pi R^2 (p_i - p_o) - 2\pi R \gamma = 0$

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

- more generally

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

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



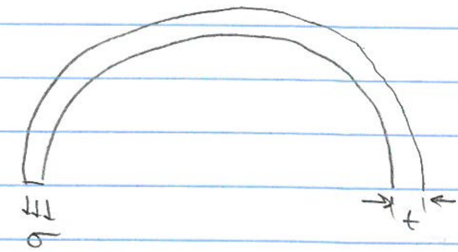
κ: total curvature

(kappa)

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

when $K_{ij} = \frac{\partial n_i}{\partial x_j}$ ← derivatives in place

solid shell



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

$\downarrow$

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

  $\Downarrow$

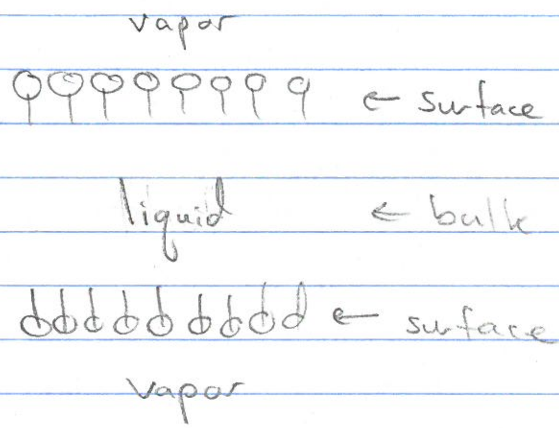
  tension only depends on current shape

- can ignore the bulk of the film provided:

  $t \ll R$

  $t \gg$ scale of intermolecular forces

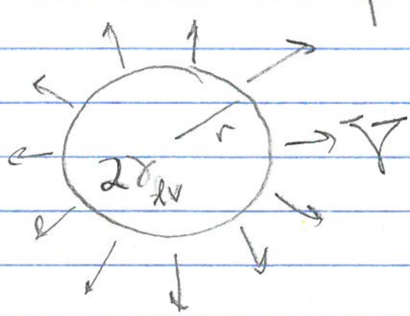
- Υ comes from the free energy of the fluid vapor interfaces, γ_{lv} (gamma)



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

- 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 $\approx \dfrac{\text{H-bond}}{\text{molecular area}}$

oil ≈ 0.02 J/m^2 $\hat{\approx}$ vdW / molecular area

mercury 0.4 J/m^2 $\hat{\approx} \dfrac{\text{metallic bond}}{\text{molecular area}}$

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 $\vec{\nabla} p = -\underset{\text{density}}{\rho} g \hat{z}$

gravity will perturb an initially spherical droplet when:

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

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

"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

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

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

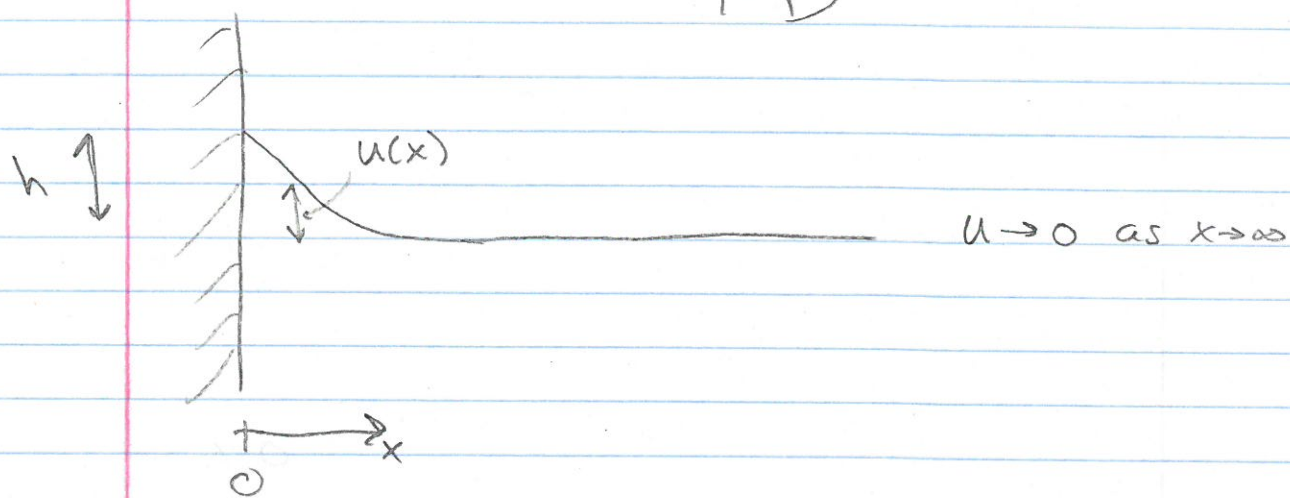
$$g \approx 10 \ m/s^2$$

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

*Image I.3

Meniscus

1-D



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

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

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

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

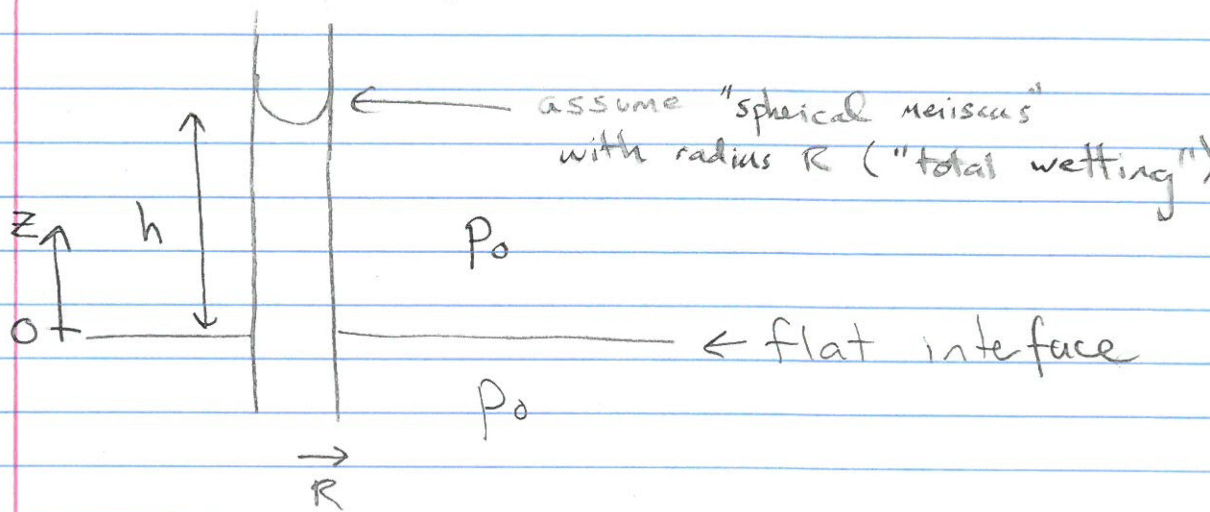
generally $u(x) = A e^{x/L_{cap}} + B e^{-x/L_{cap}}$

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

h will be determined by furthe B.C.'s discussed late

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 @ $z=h$

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

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

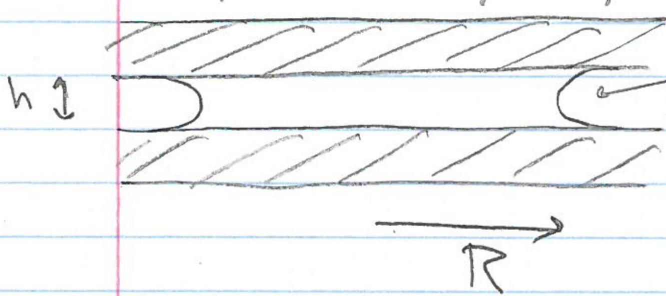
for water $L_{cap} \approx 3mm$

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

See image I.5

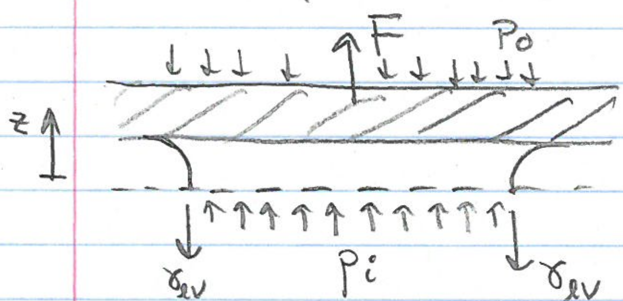
Capillary Adhesion (of rigid plates)

cylindrical symmetry



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

free-body of top half



$$\Sigma F_z = 0$$

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

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

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

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

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

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

for fixed liquid volume

$$V = \pi R^2 h \quad (R \gg h)$$

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

for 1 μL of water and $h = 5 \mu m$

($R \approx 1 cm$)

$F = 10 N$

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

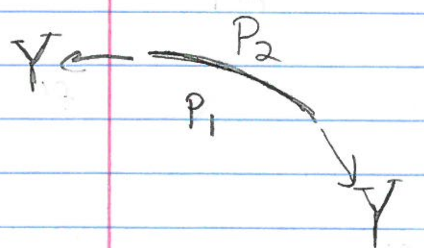
Soap Films

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

See Image I.6,7

Last Time

Young-LaPlace



$$\boxed{p_1 - p_2 = \Delta p = \gamma \kappa}$$

total curvature

- local relation
- requires 1 and 2 to be fluid
- the tension, γ, needs to be isotropic
- $[\gamma] = [F]/[L]$
- the interface can be solid, but only in special cases, see discussion problem too (solid shell needs to be spherical.(?))
- $\gamma = \gamma_{12}$ for a fluid interface

  $\gamma = 2\gamma_{12}$ for a fluid film

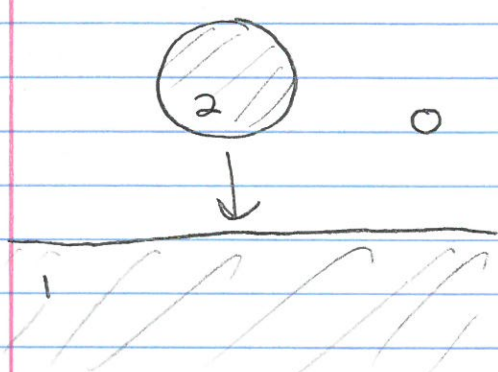
  $\gamma = \sigma t$ for a solid shell

Contact Lines

Contact between two immiscible fluids

bring together a puddle of liquid 1
$R \gg L_{cap}$

with a droplet of liquid 2
$R \ll L_{cap}$



if surface tension is the only significant factor, what is the equilibrium shape?

relevant surface tensions:

γ_{20}, γ_{10}, γ_{12}. the surrounding fluid is '0'

Method I: minimize surface energy with volume constraint

"first principles"

Method II

impose mechanical equilibrium on bulk + interfaces

Bulk: $\vec{\nabla} p_0 = \vec{\nabla} p_1 = \vec{\nabla} p_2 = 0$

Interfaces:

- $p_1 - p_0 = K_{10} \gamma_{10}$

  total curvature of 10 interface (no components)

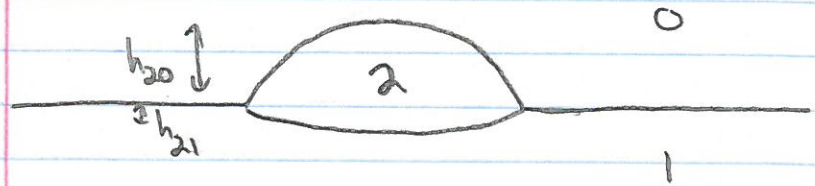
  but $K_{10} = 0$ by construction

  $\Rightarrow p_1 = p_0$

- $p_2 - p_1 = K_{21} \gamma_{21} = p_2 - p_0$
- $p_2 - p_0 = K_{20} \gamma_{20}$

  $$\Longrightarrow K_{21} \gamma_{21} = K_{20} \gamma_{20} \quad (*)$$

$\Rightarrow$ 2,1 and 2,0 are spheical caps whose radii depend on the interfacial enegres so the equilibrium shape looks something like this



"lenticular shape"

how many degrees of freedom does this shape have?

$$R_{21},\ R_{20},\ h_{20},\ h_{21}$$

we have 1 constraint $(\star)$

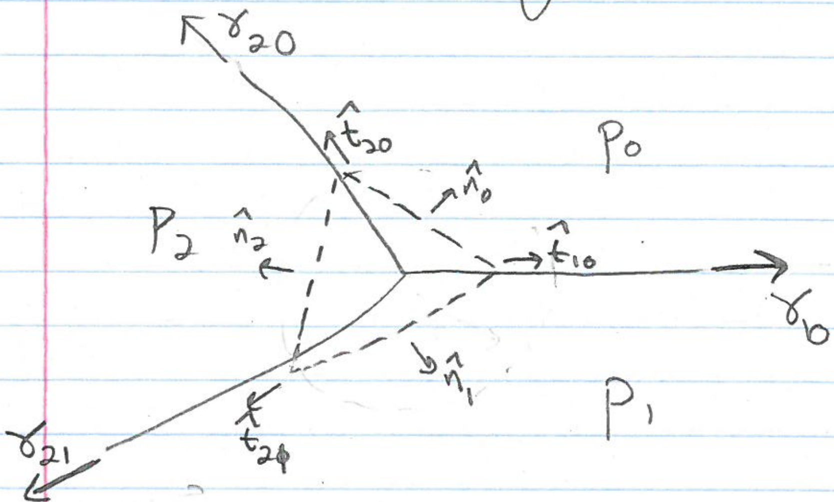
also volume conservation

$\Rightarrow$ need two more!

We enforced mechanical equilibrium in the bulk and @ interfaces

... but what about the "contact line" where all three phases meet?

Mechanical Equilibrium @ Contact Line



control volume: thin prism as shown

$$\sum \vec{F} = 0 = -A_0 p_0 \hat{n}_0 - A_1 p_1 \hat{n}_1 - A_2 p_2 \hat{n}_2 + \ldots$$

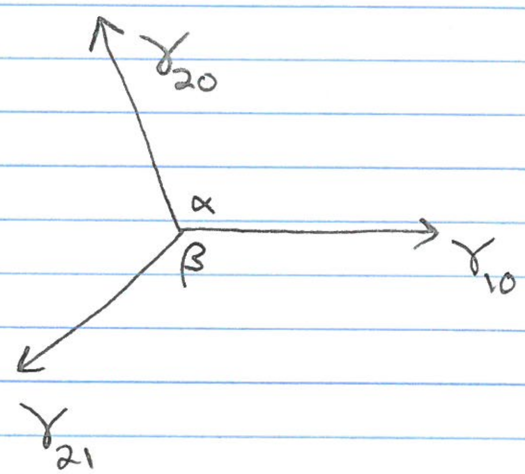
$$\ldots + \gamma_{10} \hat{t}_{10} + \gamma_{21} \hat{t}_{21} + \gamma_{20} \hat{t}_{20}$$

- now, scale volume by factor λ
- in $\lim_{\lambda \to 0}$:

$$\sum \vec{F} = 0 = \gamma_{10} \hat{t}_{10} + \gamma_{21} \hat{t}_{21} + \gamma_{20} \hat{t}_{20}$$

interpretation:

- surface tensions must balance at contact line



- for given values of γ's, there are unique values of α, β

$\Longrightarrow$ angles between interfaces are fixed

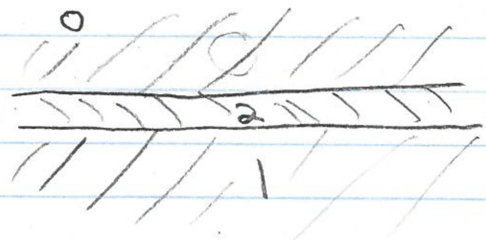
important lesson:

☆ the contact line is singular

its structure depends only on "local physics" and doesn't care about any far-field B.C.'s ☆

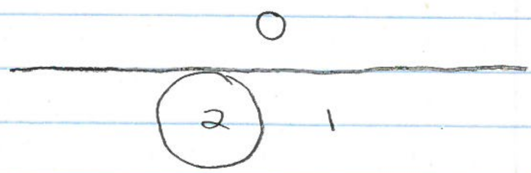
Limiting Scenarios

- $\gamma_{10} > \gamma_{20} + \gamma_{21}$ "complete spreading" or "total wetting"

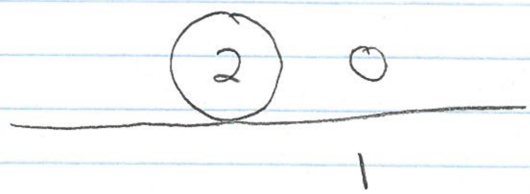


film thickness limited by available area or molecular-scale physics

- $\gamma_{20} > \gamma_{21} + \gamma_{10}$

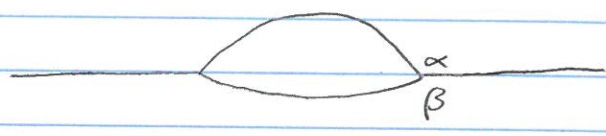


- $\gamma_{21} > \gamma_{20} + \gamma_{10}$



Effect of Gravity

for $R \ll L_{cap}$

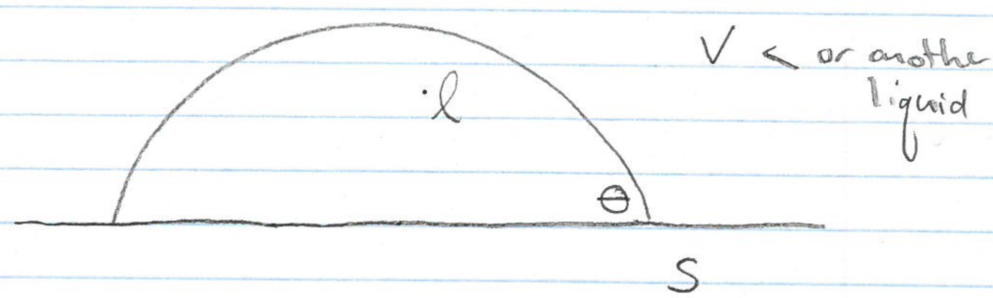


for $R \gg L_{cap}$

$$\rho_2 \lesssim \rho_1$$

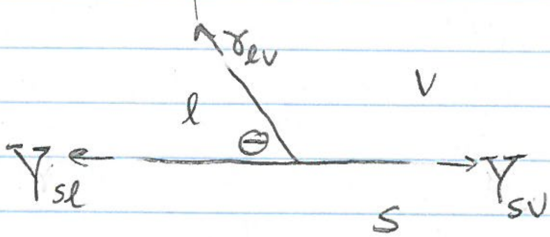
Contact Between a Liquid Droplet on a Rigid Solid

- equilibrium of bulk and fluid interface require a spherical cap



- free parameters θ, R
- volume conservation takes care of one
- equilibrium of contact line?

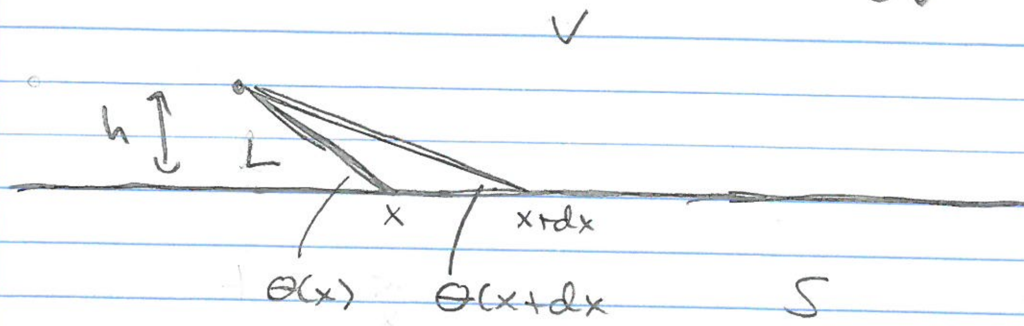
expect to be singular



can we balance forces?

NO

at least not with surface tensions alone so let's minimize the energy...



pin LV boundary at some height h far from contact line, with a reservoir of liquid

since C.L. is singular, we can apply any convenient far field B.C.

let's minimize interfacial energies w.r.t. x

$$\frac{dE}{dx} = d\left[\gamma_{sv}\frac{dl_{sv}}{dx} + \gamma_{sl}\frac{dl_{sl}}{dx} + \gamma_{lv}\frac{dl_{lv}}{dx}\right]$$

depth out of plane

$$\frac{dl_{sl}}{dx} = 1 \quad ; \quad \frac{dl_{sv}}{dx} = -1$$

$$l_{lv}^2 = h^2 + x^2 \Rightarrow 2 l_{lv}\frac{dl_{lv}}{dx} = 2x$$

$$\Rightarrow \frac{dl_{lv}}{dx} = \frac{x}{l} = \cos\theta$$

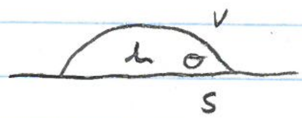
so

$$\frac{dE}{dx} = 0 \Rightarrow \quad -\gamma_{sv} + \gamma_{sl} + \gamma_{lv}\cos\theta = 0$$

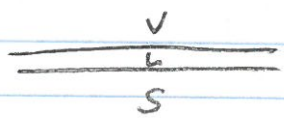
or $$\boxed{\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}}$$ Young-Dupré

three regimes

- $-1 < \dfrac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} < 1$ "partial wetting"

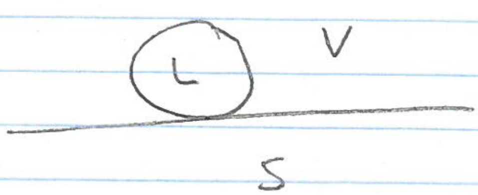


- $\dfrac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} > 1$ "total wetting"
"0° contact angle"
thickness determined by available area or molecular scale physics

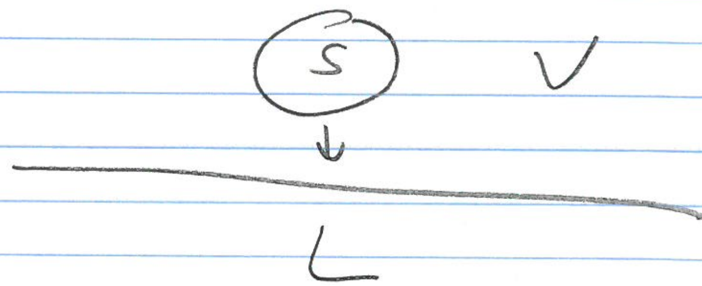


- $\dfrac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} < -1$

"super-fluid-phobic"
minimal contact between drop and substrate
"180° contact angle"



Rigid Particle on a Fluid Interface

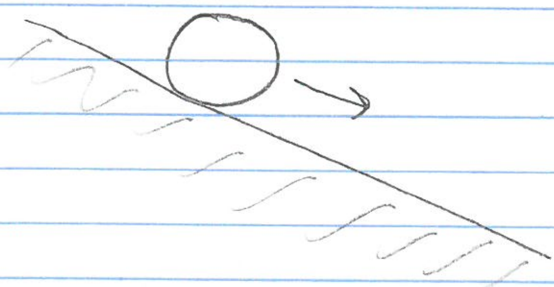


?

far field B.C.'s don't matter,
liquid must meet solid with contact angle Θ

$$\gamma_{LV} \cos\Theta = \gamma_{SV} - \gamma_{SL}$$

Droplet Motion



when $\Theta = 180°$

droplets roll dow substate

→ surface roughess essential to achieve $\Theta = 180°$

- when $0 < \Theta < 180$

droplets slide

- contact angle driven out of equilibrium

- lots of viscous dissipation, esp at contact line

if droplet translates at velocity V, the free surface moves at V, while the base has V=0 (no-slip condition)

$\Rightarrow \dot{\gamma} \approx V/t$ ← local thickness of droplet

$\dot{\gamma}$ diverges at contact line!!

for a newtonian liquid $\underset{\text{shear stress}}{\sigma} = \rho\nu\dot{\gamma} = \underset{\text{dynamic viscosity}}{\mu}\dot{\gamma}$

☆ "YouTube Hydrobead-See the Magic"
2:49 partial wetting 2:20 superhydrophobic

if time remains do capillary
adhesion from last time