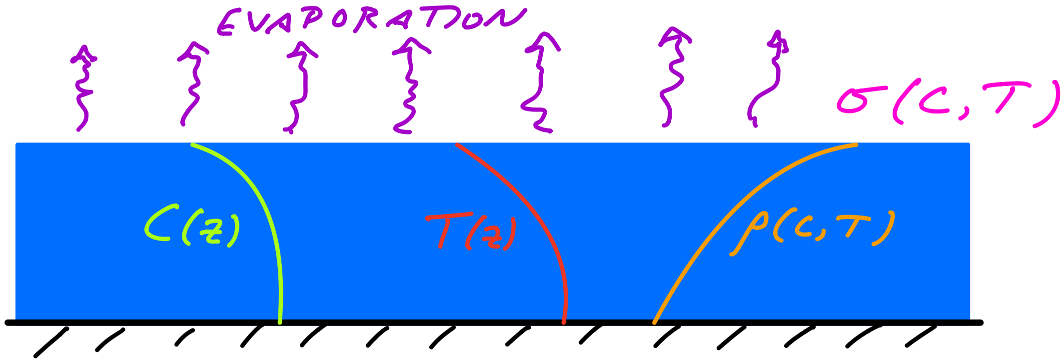
Lecture 9. Marangoni flows II

Eg. 5 Evaporatively-driven convection

e.g. alcohol-water solution with alcohol concentration c



For alcohol-water:

$$\frac{d\rho}{dT} < 0, \quad \frac{d\rho}{dc} < 0, \quad \frac{d\sigma}{dT} < 0, \quad \frac{d\sigma}{dc} < 0$$

Surface cooling due to loss of latent heat

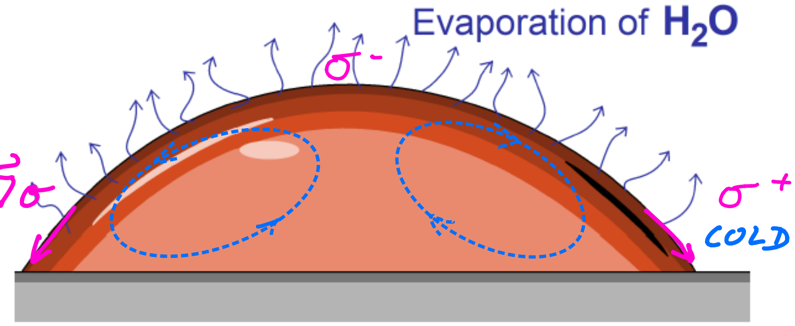
- may render the layer unstable to thermal convection
- either Ra-B or Marangoni since $\rho(T)$, $\sigma(T)$

Depletion of alcohol at the surface

- may render layer unstable to compositional convection
- either Ra-B or Marangoni since $\rho(c)$, $\sigma(c)$

⇒ 4 possible modes of convection

Eg. 6 Coffee drop ⇒ ring



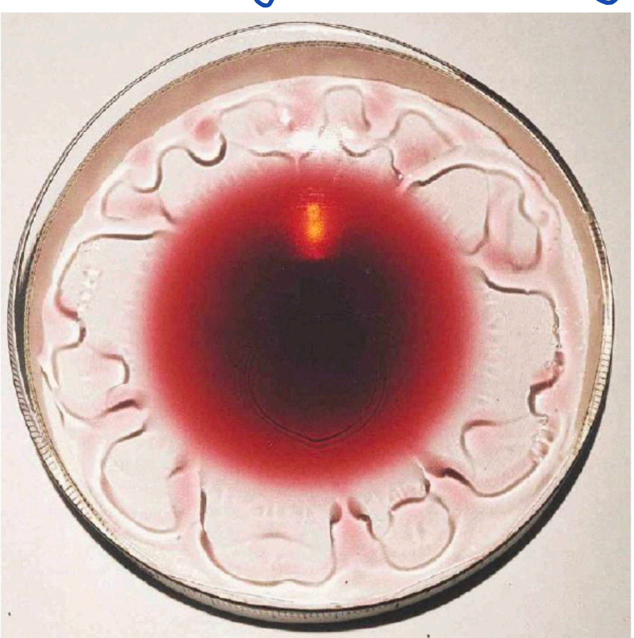
- coffee grains tend to stick to surface
- evaporation leads to surface cooling

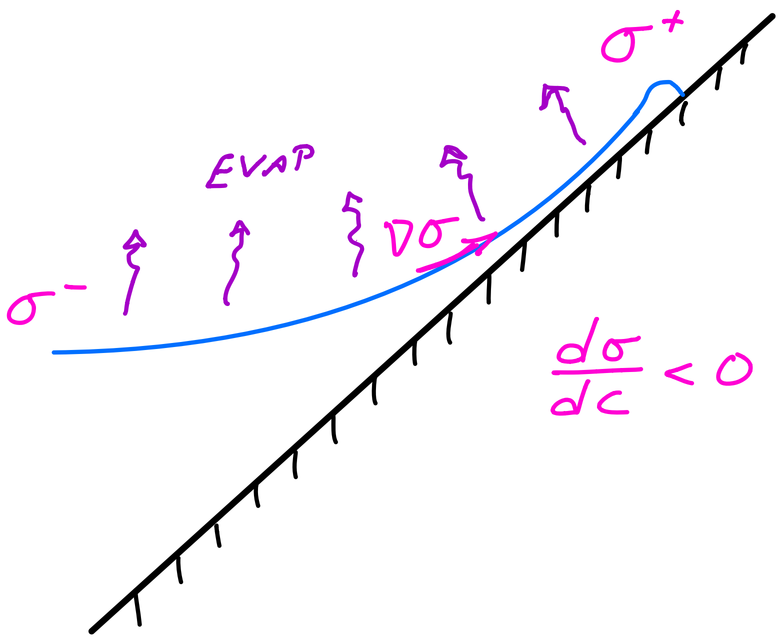
⇒ most pronounced near edges, where surface area-to-volume ratio is highest

⇒ resulting thermal Marangoni stresses drive radial outflow on surface ⇒ RING

Eg. 7 The tears of wine

- driven by evaporation of alcohol
- thin film becomes depleted in alcohol relative to the bulk ⇒ $\vec{\nabla}\sigma(c)$ drives flow up the film
- fluid accumulates in a band until going unstable due to g, releasing the tears of wine





- for certain liquors (e.g. port), the climbing film, a Marangoni shear layer, goes unstable to streamwise vortices and an associated radial corrugation

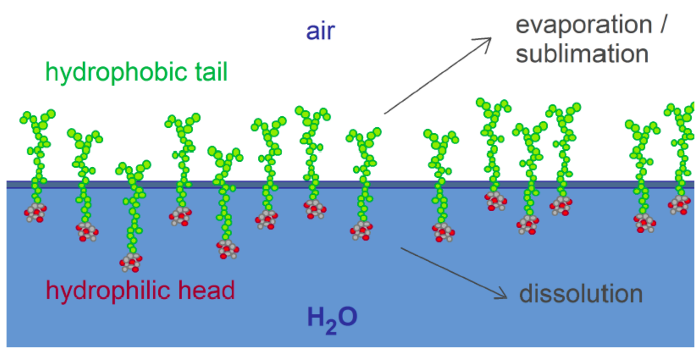
  $\Rightarrow$ the "Tear Ducts of Wine"

Surfactants : "surface active reagents"

- molecules that find it energetically favourable to reside at an interface

  e.g. commercial detergents

Γ



- generally act to reduce σ locally $\Rightarrow$ effects?

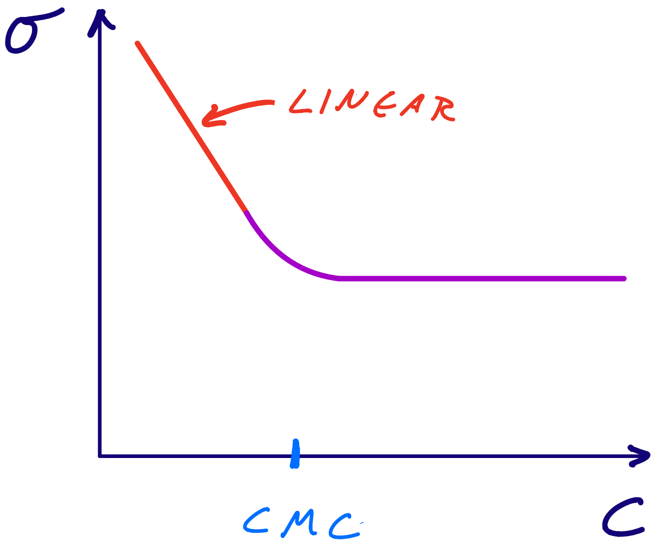
  (1.) reduce curvature pressure $\sigma \underline{\nabla} \cdot \underline{n}$

  (2.) denoting surface concentration of surfactant by Γ $\Rightarrow$ $\frac{d\sigma}{d\Gamma} < 0$

  $\therefore$ $\vec{\nabla} \Gamma$ will induce $\vec{\nabla} \sigma$

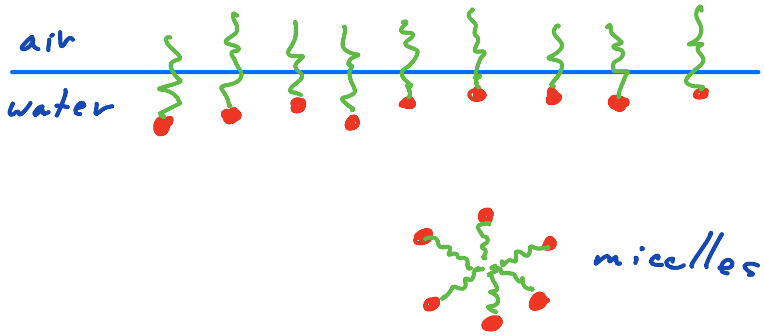
  $\Longrightarrow$ Marangoni flows

Dependence of σ on bulk concentration C



$\Rightarrow$ beyond CMC, $\frac{d\sigma}{dC} = 0$.

Why?



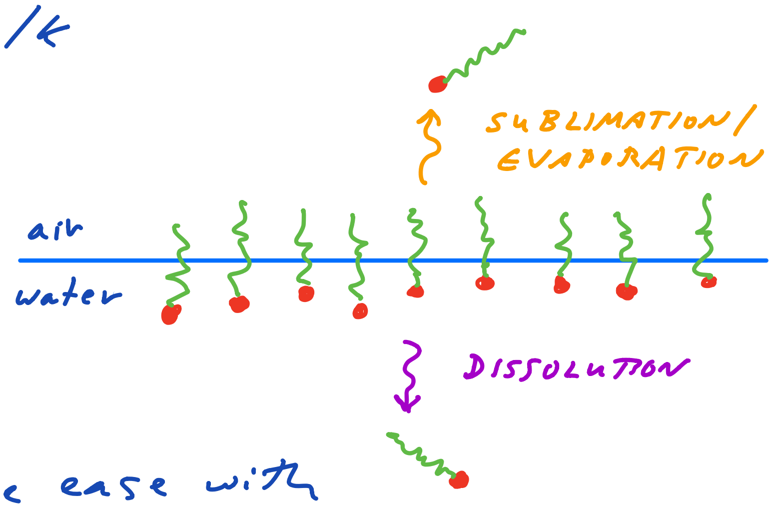
- micelles shed by saturated interface desorbed into bulk

Surfactant Properties

Diffusivity: prescribes rate of diffusion D_s of Γ on surface
D_b of $C(\Gamma)$ in bulk

Solubility: prescribes ease with which Γ passes from surface to bulk

- an insoluble surfactant cannot dissolve into bulk, must remain on the surface



Volatility: prescribes the ease with which surfactant sublimates/evaporates from the free surface

Theoretical Approach

: NS eqns coupled to surfactant evolution eqns through BCs since $\sigma(\Gamma)$

In bulk, $\frac{\partial c}{\partial t} + \underline{u} \cdot \underline{\nabla} c = D_b \nabla^2 c$

where c = surfactant conc. in bulk

D_b = bulk diffusivity

On surface,

VANISHES FOR INSOLUBLE SURFACTANTS

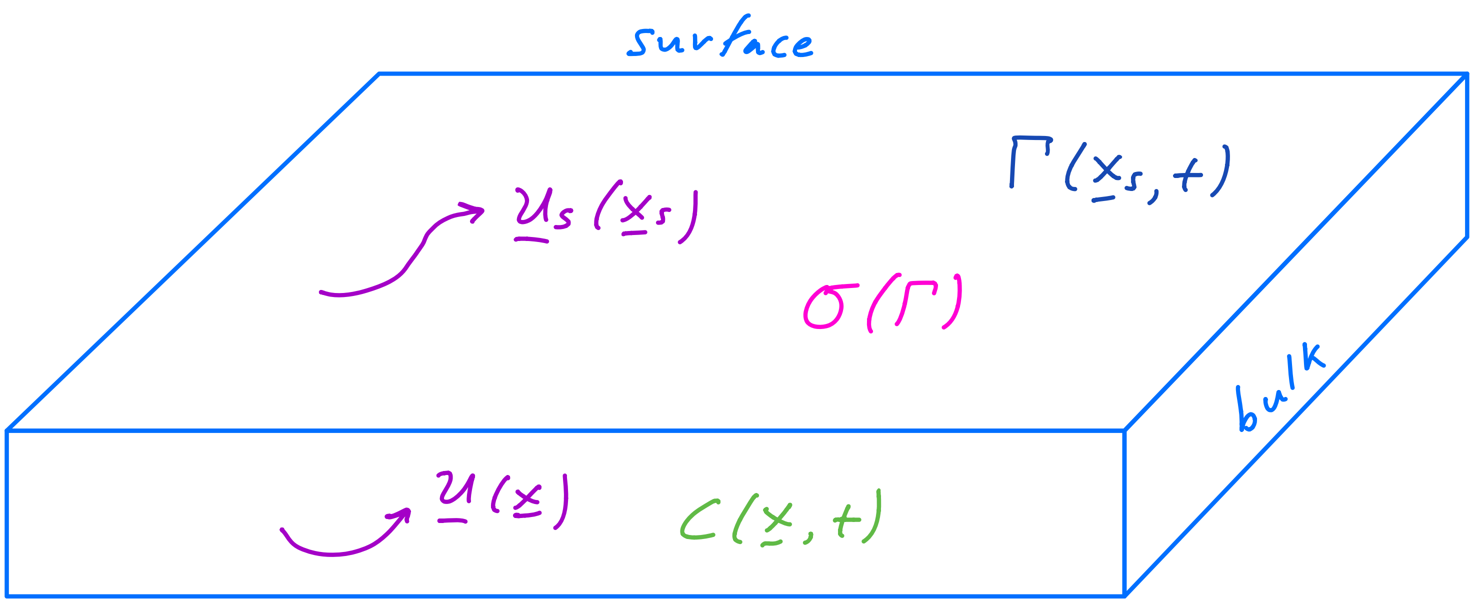
$$\underbrace{\frac{\partial \Gamma}{\partial t} + \underline{\nabla}_s \cdot (\Gamma \underline{u}_s)}_{\text{ADVECTION}} + \underbrace{\Gamma (\underline{\nabla}_s \cdot \underline{n})(\underline{u} \cdot \underline{n})}_{\text{SURFACE EXPANSION}} = \underbrace{J(\Gamma, c)}_{\text{EXCHANGE W/ AMBIENT VIA DISSOLUTION OR EVAPORATION}} + \underbrace{D_s \nabla_s^2 \Gamma}_{\text{SURFACE DIFFUSION}}$$

SYSTEM BECOMES TRACTABLE IF THESE VANISH

where Γ = surfactant conc. on surface

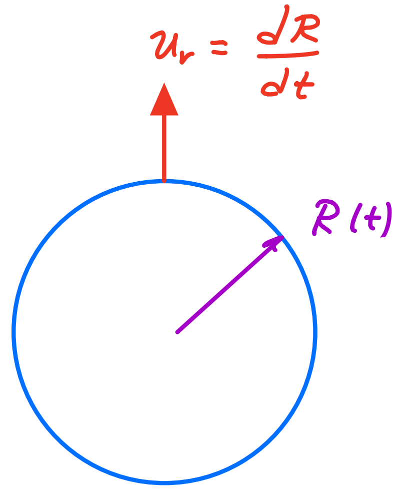
$\underline{u}_s$ = surface velocity

D_s = surface diffusivity



Consider surface expansion term.

Special Case: expansion of a spherical bubble



$$\frac{d\Gamma}{dt} + \Gamma(\nabla_s \cdot n)\, u_r = 0$$

Here $\nabla_s \cdot n = \frac{2}{R}$, $u_r = \frac{dR}{dt}$

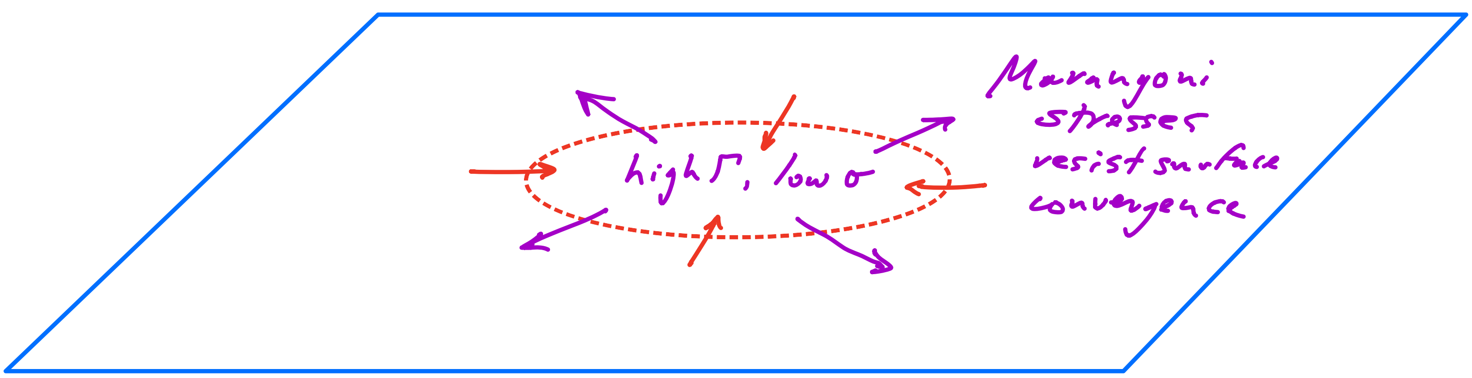
$$\Rightarrow \frac{d\Gamma}{dt} + \Gamma \frac{2}{R}\frac{dR}{dt} = 0$$

$$\Rightarrow \frac{d\Gamma}{\Gamma} = -\frac{2}{R}\frac{dR}{R} \Rightarrow \Gamma = c R^{-2}$$

$$\Rightarrow \Gamma \cdot 4\pi R^2 = \text{const} \Rightarrow \text{Conservation of surfactant}$$

Marangoni Elasticity

- surfactants impart an effective elasticity to contaminated interfaces through resisting flows with non-zero surface divergence



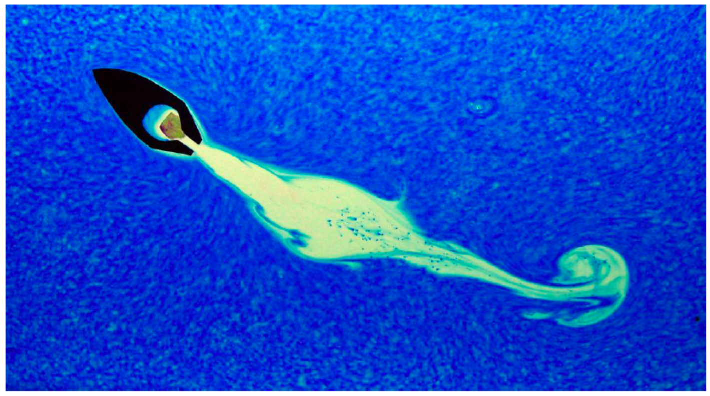
Heuristic Picture

- clean interface ≃ slippery trampoline
- contaminated interface ≃ trampoline

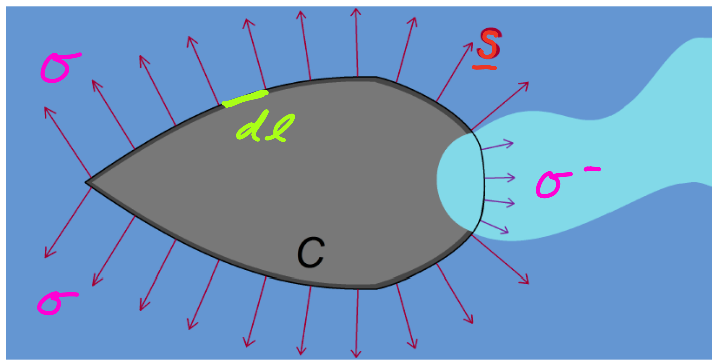
Some examples of Surfactant-Driven Marangoni Flows

(1.) Marangoni Propulsion :

- employed by water-walking insects, pine needles, soap boat



$$\underset{\sim}{F} = \int_C \sigma \, \underset{\sim}{s} \, dl$$

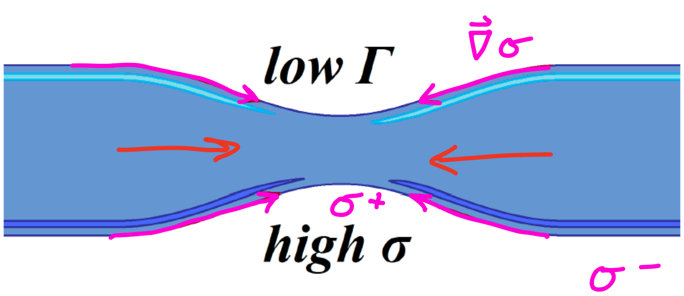


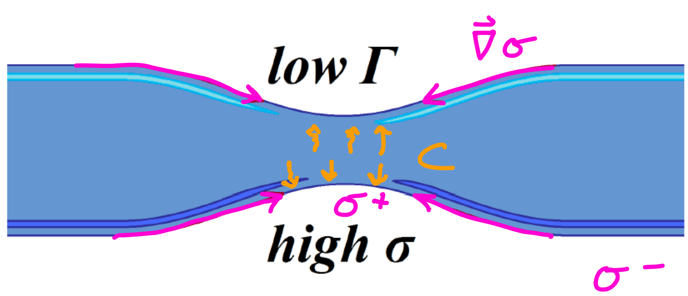
Observation :

- water films are unstable, soap films stable.

Why?

(2.) Soap Film Stability





- pinch film ⇒ increase area, decrease Γ, increase σ
  ⇒ fluid drawn in

⇒ film is stabilized by Marangoni or Gibbs elasticity

Marangoni Elasticity

- for insoluble Γ
- Γ stuck to surface
- increase A → $\downarrow \Gamma$
  → $\uparrow \sigma$

MOST COMMON

Gibbs Elasticity

- for soluble Γ
- Γ diffuses rapidly from bulk
- Γ in equilib with C in bulk
- pinched region soon becomes depleted in Γ, since its reservoir of C is smaller

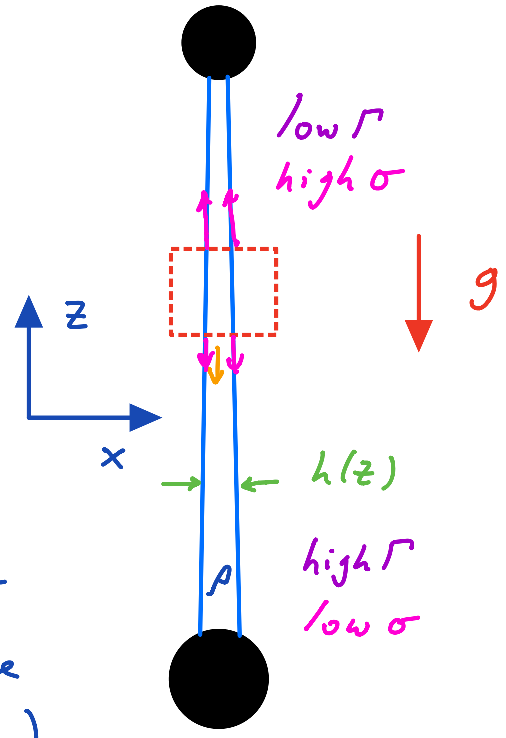
⇒ $\uparrow \sigma$

RELATIVELY RARE

- arises when timescale of diffusion from bulk is short

③ Vertical Soap Film

- weight of film supported by Marangoni stress

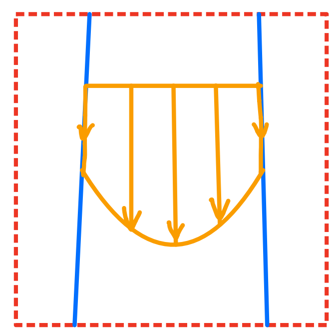


Force balance:

$$\rho g h(z) = 2 \frac{d\sigma}{dz} = 2 \frac{d\sigma}{d\Gamma} \frac{d\Gamma}{dz}$$

Internal dynamics

- soap film is DYNAMIC, as are all Marangoni flows. (If it were static, its MAX height would be l_c).
  ↑ CAP LENGTH



On surface:

$$\frac{d\sigma}{dz} \sim \mu \frac{du}{dx}$$ Marangoni–Viscous

Inside:

$$\rho g \sim \mu \frac{d^2 u}{dx^2}$$ Gravity – Viscous

⟹ soap film thins via drainage

⟹ black film