# Wetting and adhesion

Dispersions in liquids: suspensions, emulsions, and foams

*ACS National Meeting*

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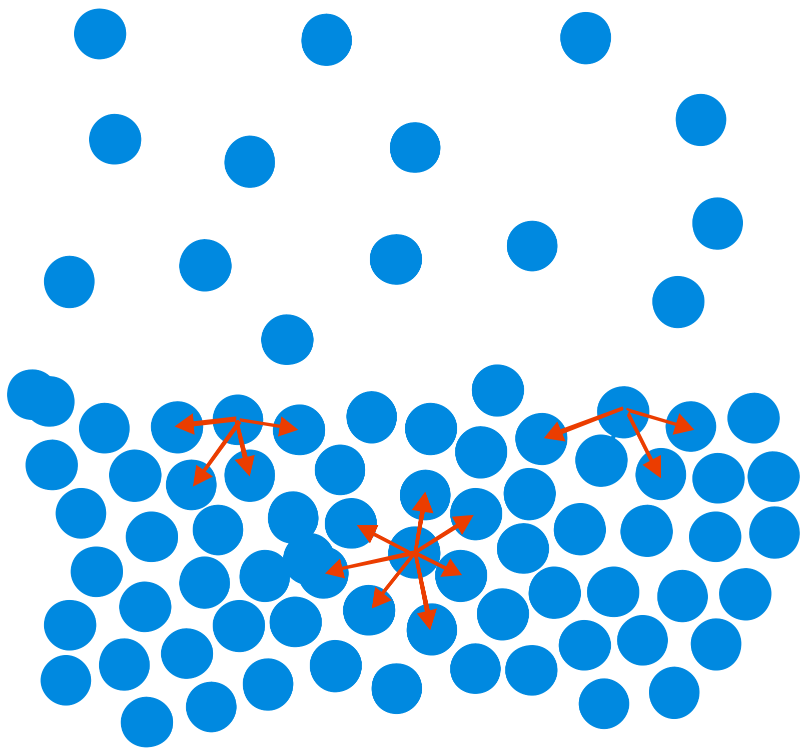
# The molecular origin of surface tension



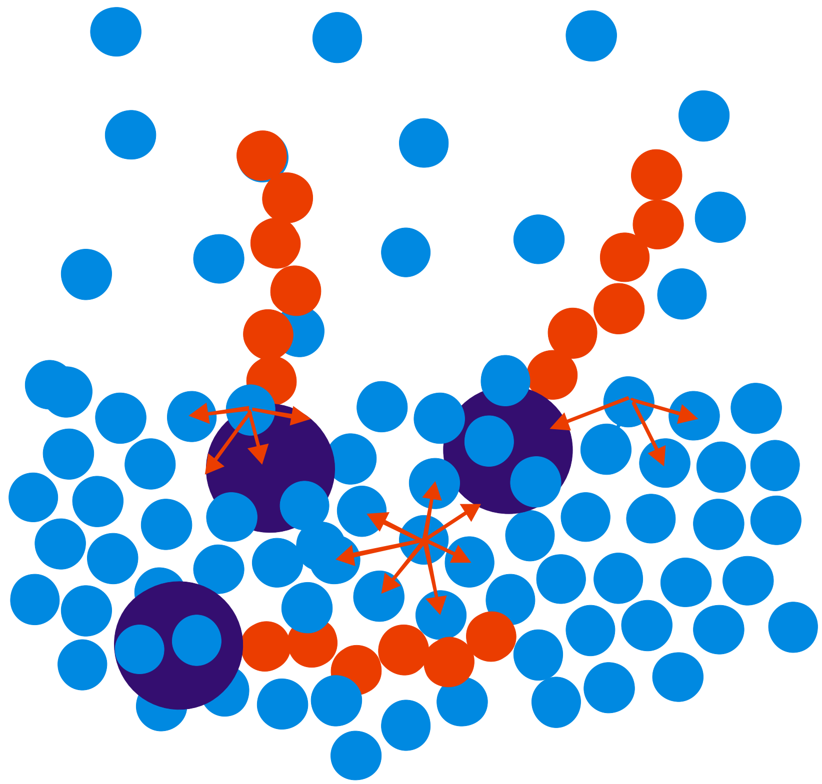
The free energy to stretch a surface is:

$$\Delta F = \sigma_L \Delta A$$

Where $\sigma_L$ is the surface tension.

To increase surface area, molecules must be pulled from the bulk. This increase requires work.

# Reduction of surface tension by adsorption



The free energy to stretch this surface is also:

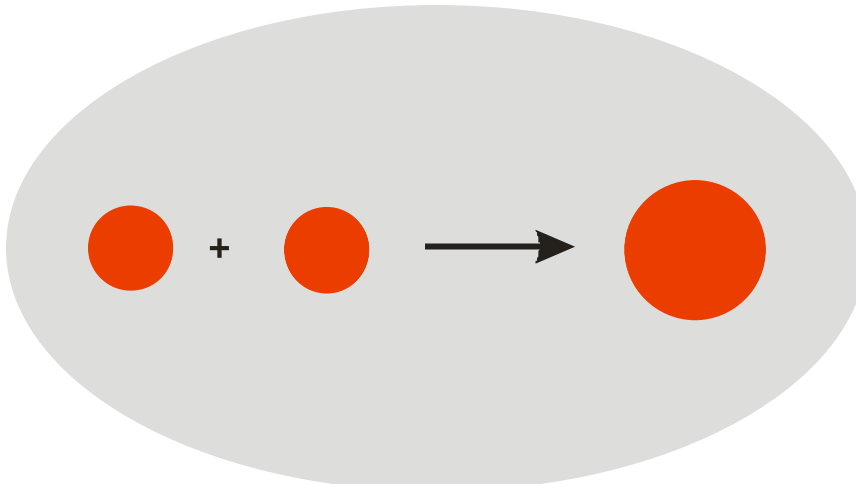
$$\Delta F = \sigma_L \Delta A$$

But $\sigma_L$ is the surface tension reduced by the adsorption of surfactant.

To increase surface area, molecules must be pulled from the bulk. This increase requires work. Because surfactants go to the surface spontaneously, the work is less.

# Surface tension is a pull

# Coalescence of droplets



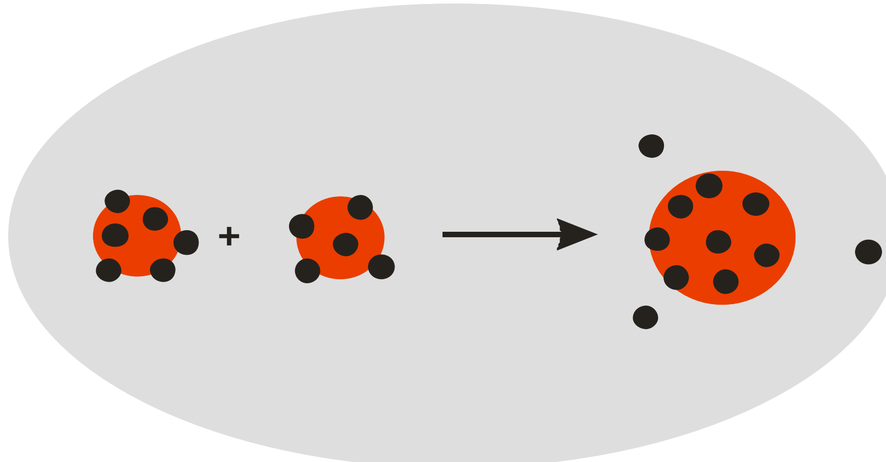

The change in energy is:

$$
\begin{aligned}
\Delta F &= F_{final} - F_{initial} \\
&= \sigma(A_{final} - A_{initial}) \\
&= \sigma\Delta A \\
&< 0
\end{aligned}
$$

Therefore the drops coalesce spontaneously.

# Coalescence of droplets with emulsifier

When droplets covered with emulsifier coalesce, some emulsifier must be desorbed. This requires work.




$$\Delta F = \sigma \Delta A + \text{ work of desorption}$$

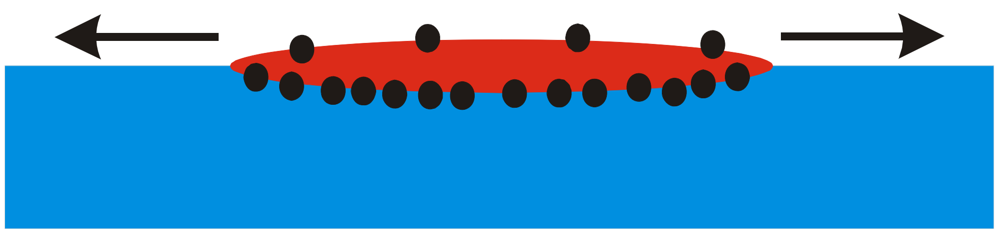
If the emulsifier is strongly adsorbed, the work to remove it is large, and the drops do not coalesce.

# Spreading on a substrate

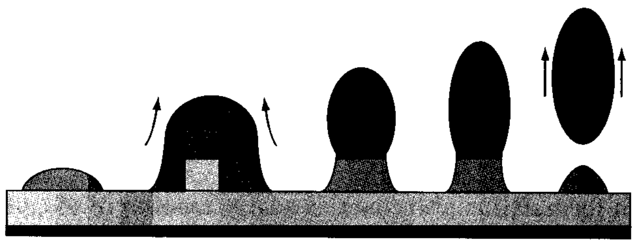
The energy change per unit area for liquid 2 (top) to spread across the surface 1 (bottom) is:

$$\Delta \overline{F} = (\sigma_2 + \sigma_{12} - \sigma_1)$$

Surfactants reduce the two terms positive terms allowing the drop to spread.

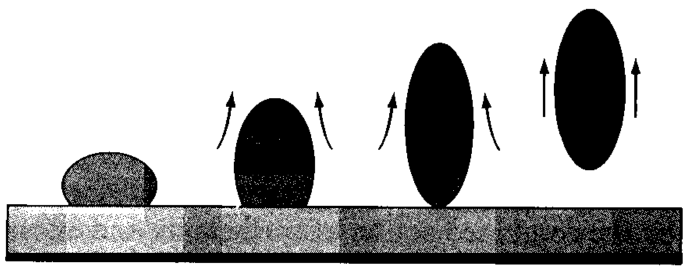


# Detergency – more than one mechanism!



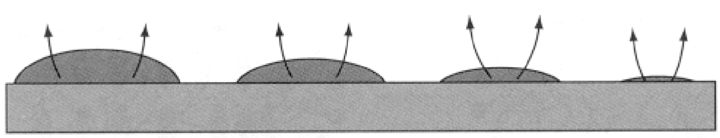
The emulsification mechanism of removal of oily soil from a solid surface

Requires only that the energy of surfactant adsorption is greater than the energy of the new liquid surface created.



The roll-up mechanism of removal of oily soil from a solid surface

Requires that the surfactant lower the new solid/liquid interface to be less than the previous solid/oil interface.

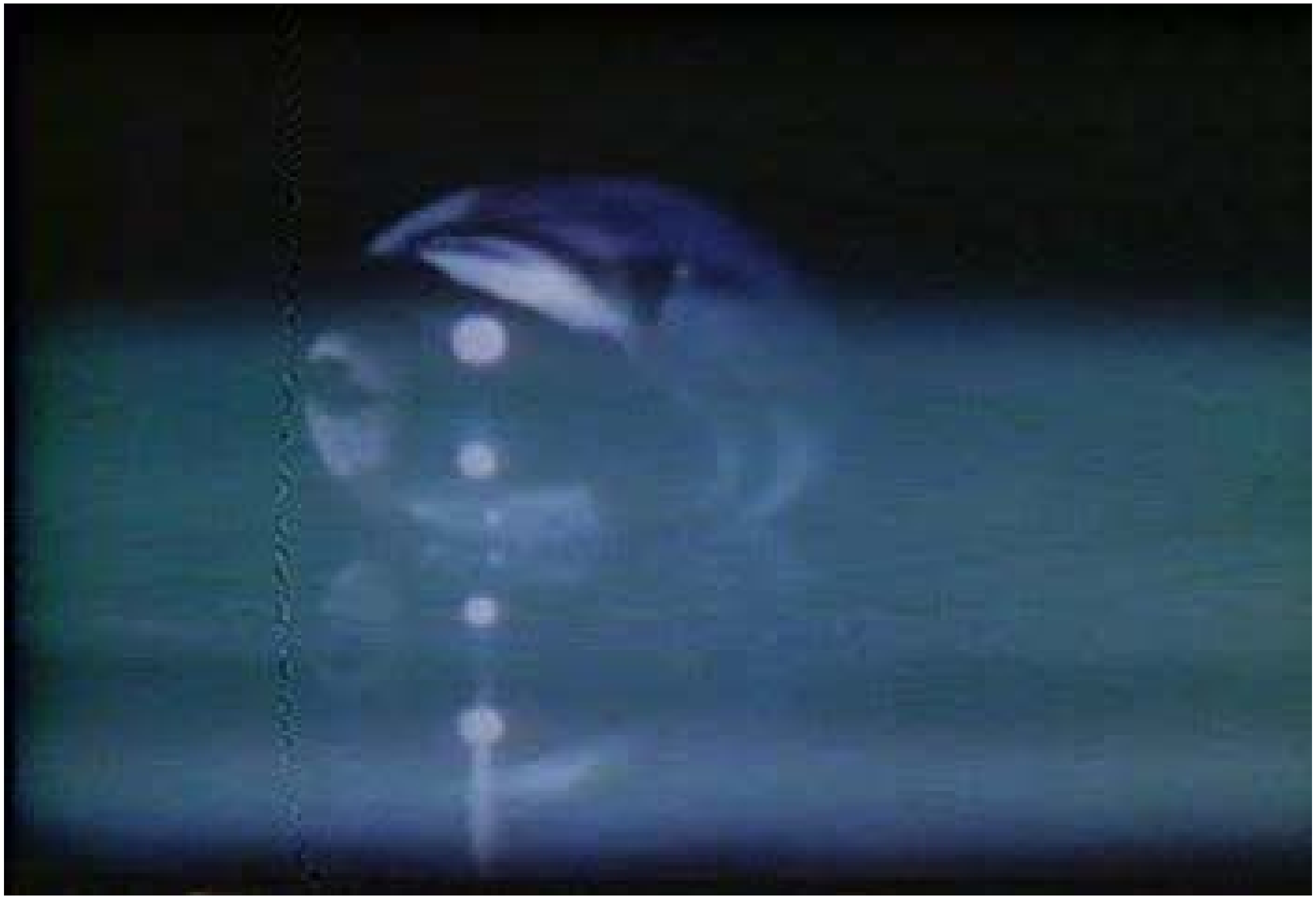


The solubilization mechanism of removal of oily soil from a solid surface

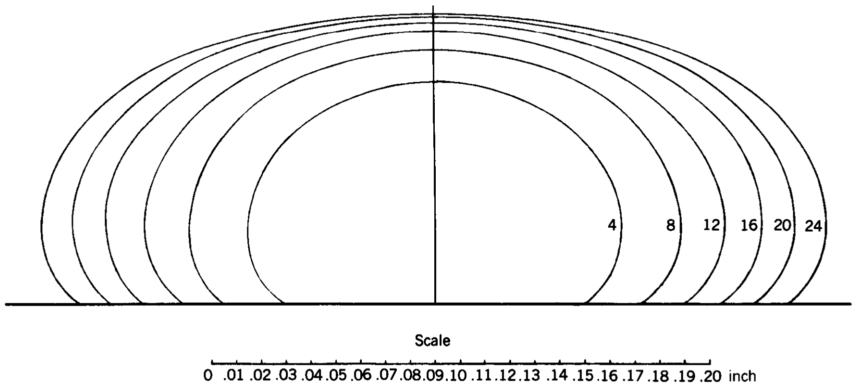
Requires spontaneous absorption of oil into micelles.

Holmberg et al. pp 474-5.

# Different contact angles on different solids



# Contact angles – independent of shape




Mercury drops on glass.*

Drops vary in size from 4 to 24 grains (1 grain = 64.8 mg)

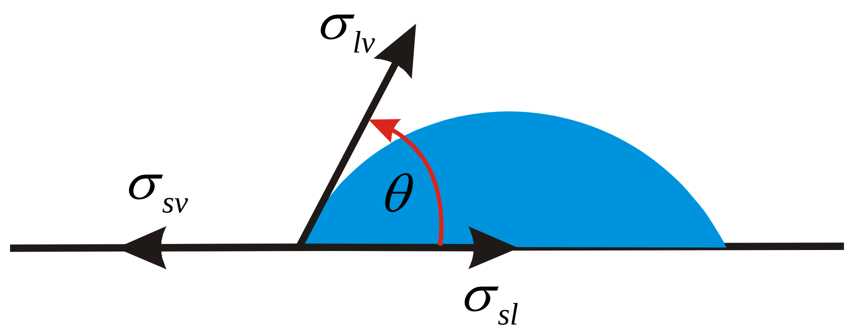
The contact angle of 140º is the same for each drop, independent of drop size.

The observation is that the contact angle depends on the materials but not the particular geometry.

* Bashforth and Adams, 1883.

# Contact angles reflect solid-liquid interactions

Young and Dupré (independently) assert this simple idea:




That three tensions balance;

$$\sigma_{sv} = \sigma_{lv}\cos\theta + \sigma_{sl}$$

Or similarly,

or

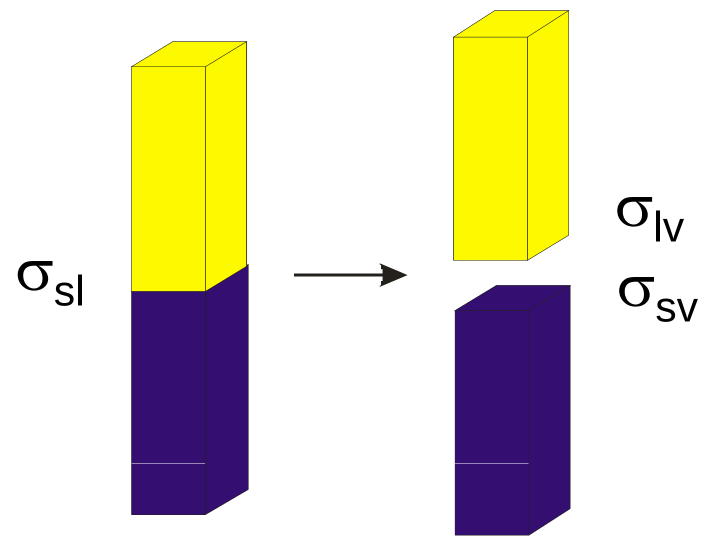
That three energies balance.

$$\sigma_{sv} - \sigma_{sl} = \sigma_{lv}\cos\theta$$

# The Young-Dupre' applied to adhesion

The work of adhesion is the separation to create two new surfaces from one interface:

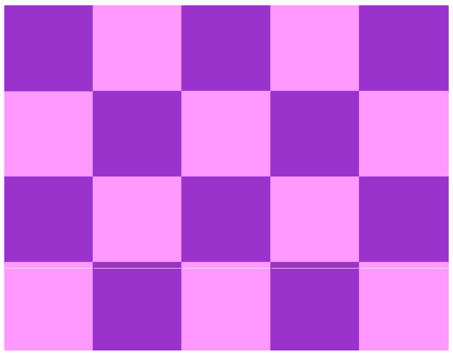
$$W^{adh} = \sigma_{sv} + \sigma_{lv} - \sigma_{sl}$$




Inserting the Young-Dupré idea gives:

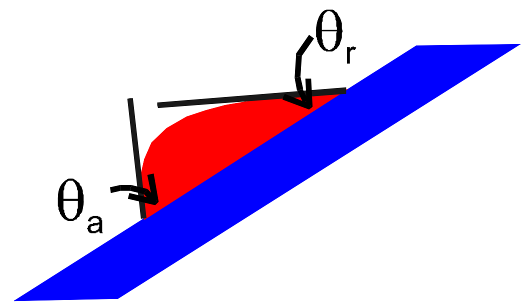
$$W^{adh} = \sigma_{lv} \cos\theta + \sigma_{lv}$$

# Contact angle hysteresis



High energy spots – low contact angles.

Low energy spots – high contact angles.




Advancing liquids are held up by low energy spots and show high contact angles.

Receding liquids are held by high energy spots and show low contact angles.

# Motion of liquids due to surface energies

Capillary flow –

Motion as a consequence of shape.

Key idea: pressure drop across a curved surface

Marangoni flow –

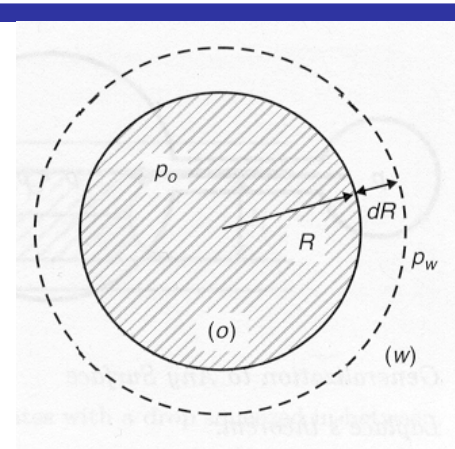
Motion as a consequence of variation in surface tension.

# Laplace pressure - 1

*Pierre Simon, Marquis de Laplace*

(www.swlearning.com)

Overpressure inside a drop of oil “o” in water “w”.




de Gennes, 2004, Fig. 1.5

If the surface is perturbed from a sphere:

$$\delta W = -p_o dV_o - p_w dV_w + \sigma_{o/w} dA$$

For a sphere:

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

$$dA = 8\pi R dR$$

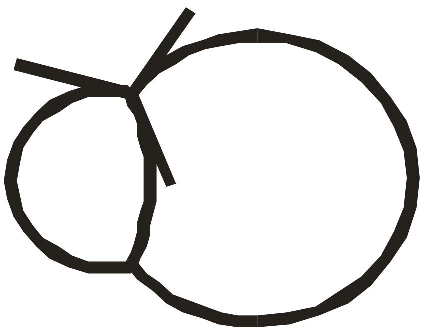
At equilibrium: $\delta W = 0$

$$p_o - p_w = \Delta p = \frac{2\sigma_{o/w}}{R}$$

# Laplace pressure - 2

For oil/water $\Delta p = \frac{2\sigma_{o/w}}{R} \approx \frac{2 \cdot 30 \cdot 10^{-3}\, N/m}{R}$

For a 1μm drop: $\Delta p \approx \frac{6 \cdot 10^{-2}\, N/m}{10^{-6}\, m} \approx 6 \cdot 10^{4}\, Pa \approx 0.6 \text{ atm}$



For drops (or bubbles) of different sizes, the internal pressures will be different.

The smaller is at a higher pressure and so molecules inside it will diffuse into the larger.

An effect called Ostwald ripening.

A more general form of the Laplace equation is $\Delta p = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$

Where $R_1$ and $R_2$ are the principle radii of curvature.

de Gennes, 2004, pp 6f

# The capillary length

The Laplace pressure can be written as:

$$\Delta p = \sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \kappa\sigma$$

where $\kappa^{-1}$ is a curvature.

Hydrostatic pressure can be written similarly:

$$\Delta p = \rho g \kappa^{-1}$$

where $\kappa^{-1}$ is a height.

The capillary length is defined when these two pressure are equal

$$\frac{\sigma}{\kappa^{-1}} = \rho g \kappa^{-1} \quad \text{or} \quad \kappa^{-1} = \sqrt{\sigma/\rho g}$$

Typically $\sigma \approx 30\times10^{-3}\ J/m^3$ $\rho \approx 1\ gm/cm^3 \approx 10^3\,\mathrm{kg}/m^3$ and $g = 9.8\ m/s^2$

So that $\kappa^{-1} \sim 1\ mm$

Gravity is generally neglected for sizes smaller than the capillary length.

de Gennes, 2004, p. 33f

# Capillary adhesion

The large radius of curvature, *R*, is in the plane of the plates. The smaller one is perpendicular and opposite in sign: $-H/(2\cos\theta_e)$

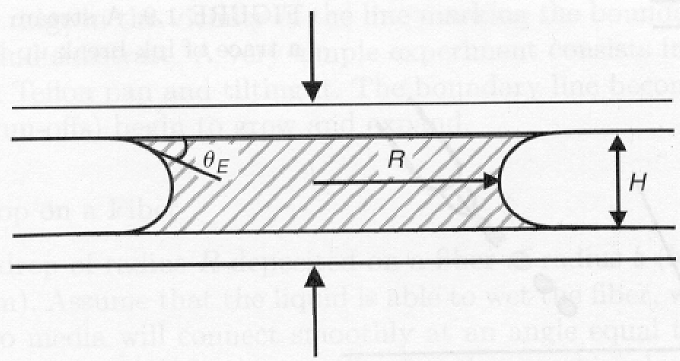



FIGURE 1.8. Capillary adhesion of two plates with a drop squeezed in-between.

The Laplace pressure is: $$\Delta p = \sigma\left(\frac{1}{R} - \frac{2\cos\theta_e}{H}\right) \sim -\frac{2\sigma\cos\theta_e}{H}$$

The force pushing the plates together is the drop area times Laplace pressure. $$F = \pi R^2 \frac{2\sigma\cos\theta_e}{H}$$

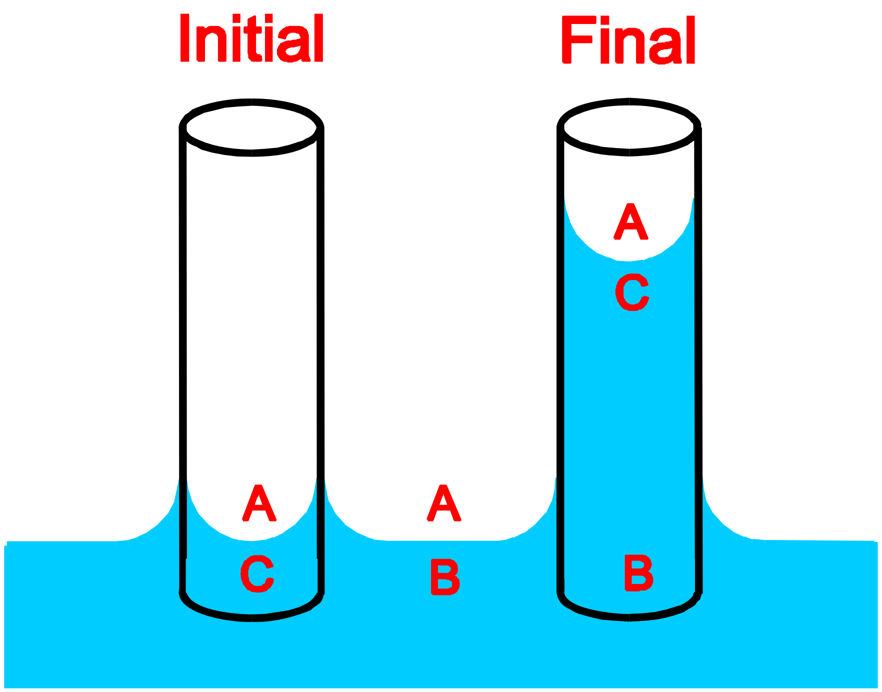
For $R = 1$ cm, $H = 5\mu$m, and $\theta = 0$ the pressure is about 1/3 atm and the force 10 N.

(What is the stable state? What are the dynamics?)

de Gennes, 2004.

# Capillary rise is an example of Laplace pressure

# Capillary rise – because of Laplace pressure




The curvature inside the tube depends on the radius and the contact angle:

$$\frac{2\cos\theta}{R}$$

The pressure is lower! inside the liquid.

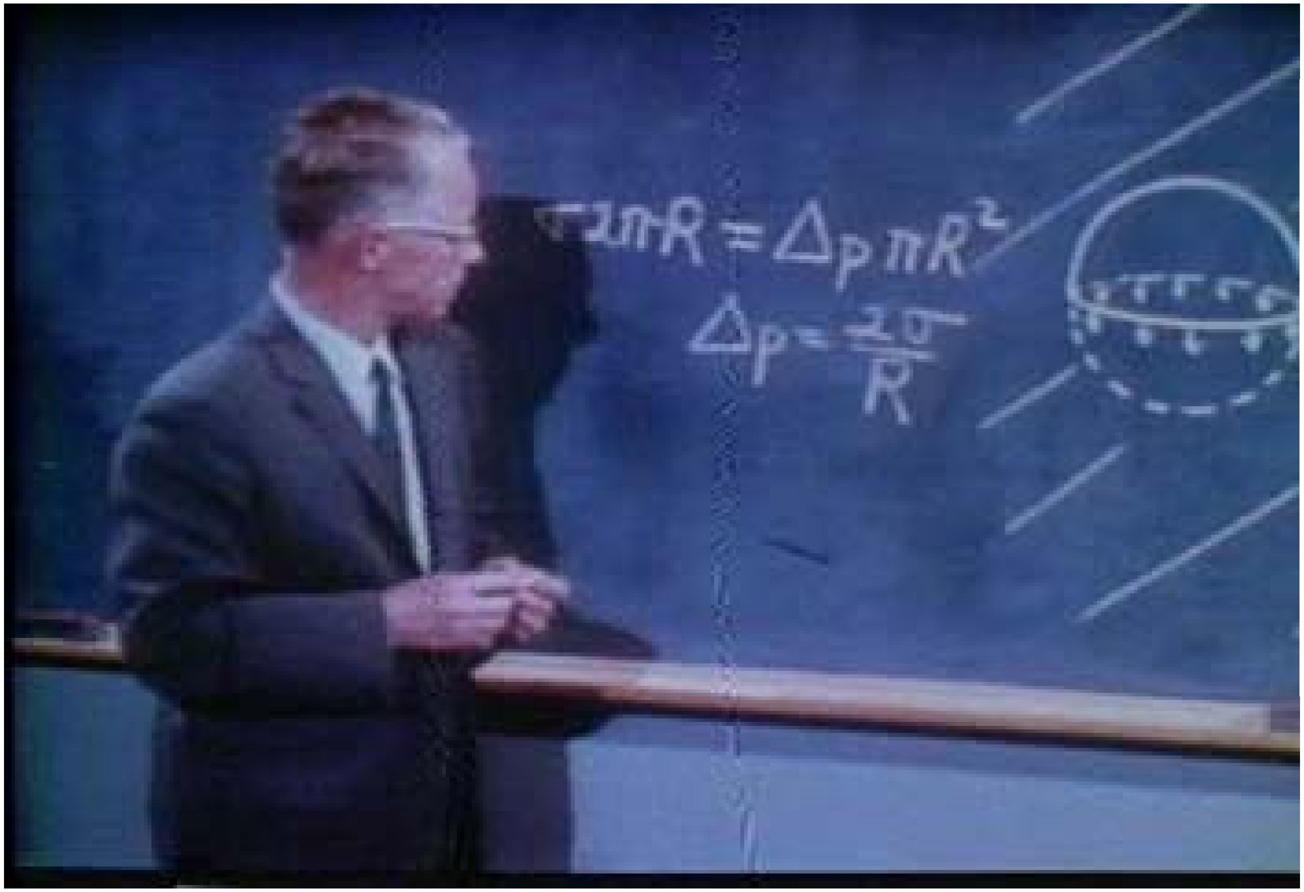
The balance is the capillary rise:

$$\frac{2\sigma_L \cos\theta}{R} = \rho g h$$

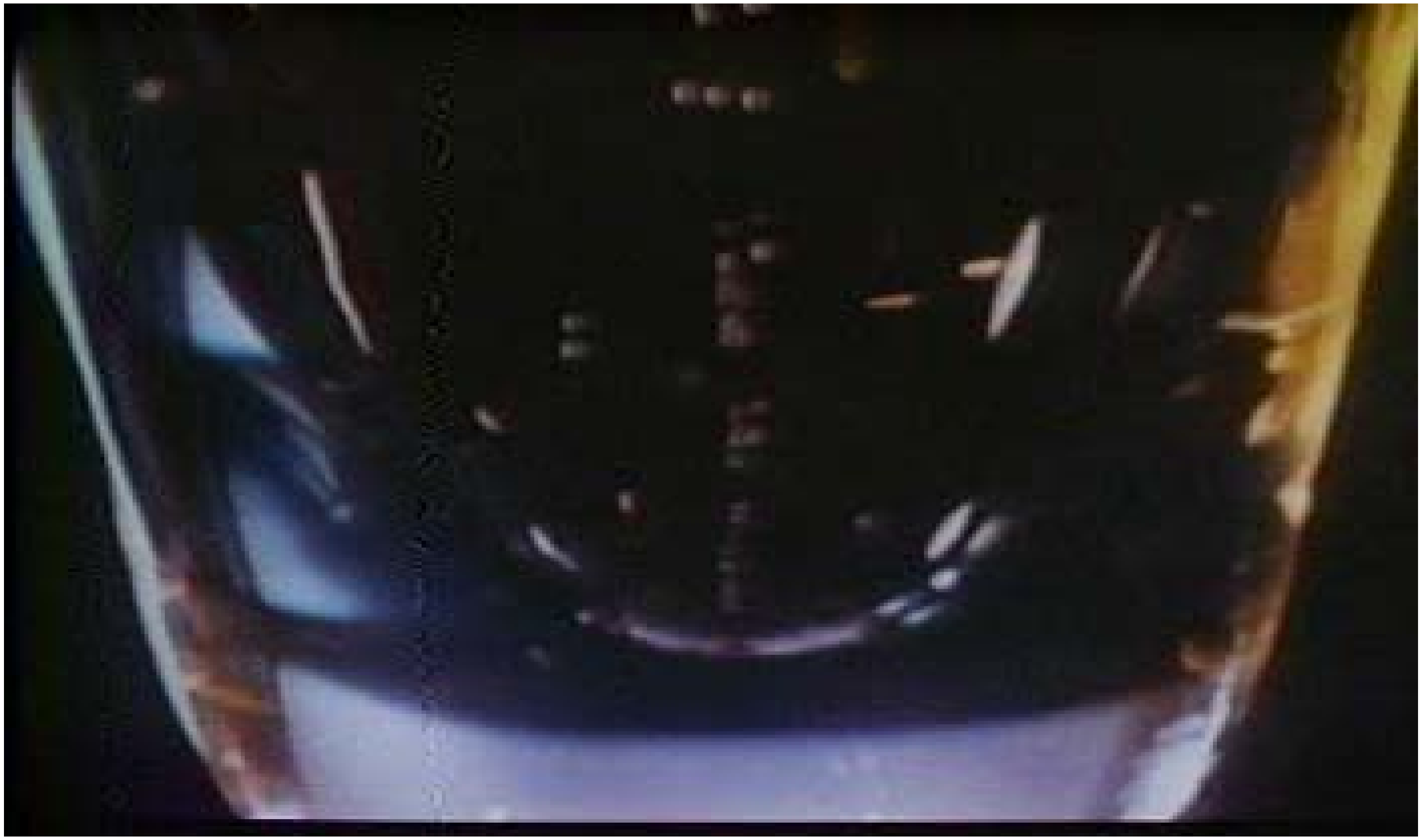
# The break-up of a jet is also:

Mathilde Reyssat, Harvard 2007

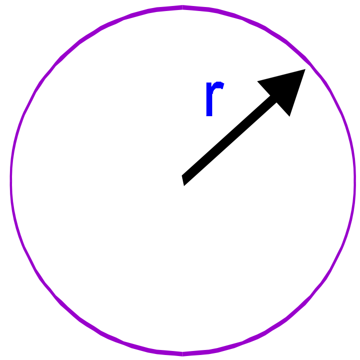
# Capillary pressure determines nucleation



# “Controlled” nucleation of bubbles



# Laplace pressure creates Ostwald ripening




The pressure inside > pressure outside

$$\Delta p = \frac{2\sigma}{r}$$

This equation implies that in an emulsion with a range of drop sizes or a foam with a range of bubble sizes, material diffuses from small drops to large drops.

Also, this equation implies that bubbles are difficult to nucleate.

# Small particles also “ripen”

$$\ln\left(\frac{P}{P_o}\right) = \frac{2\sigma V_m}{rRT}$$

If the particles have any solubility, small particles become smaller and the large particles become larger. The effect is described by the Kelvin equation.

$$\ln\left(\frac{c}{c_0}\right) = \frac{2\sigma V_m}{rRT}$$

# Marangoni flow

Marangoni flow –

flow resulting from local differences in surface tension.

Causes of Variation in Surface Tension –

Local temperature differences.

Local differences in composition due to differential evaporation.

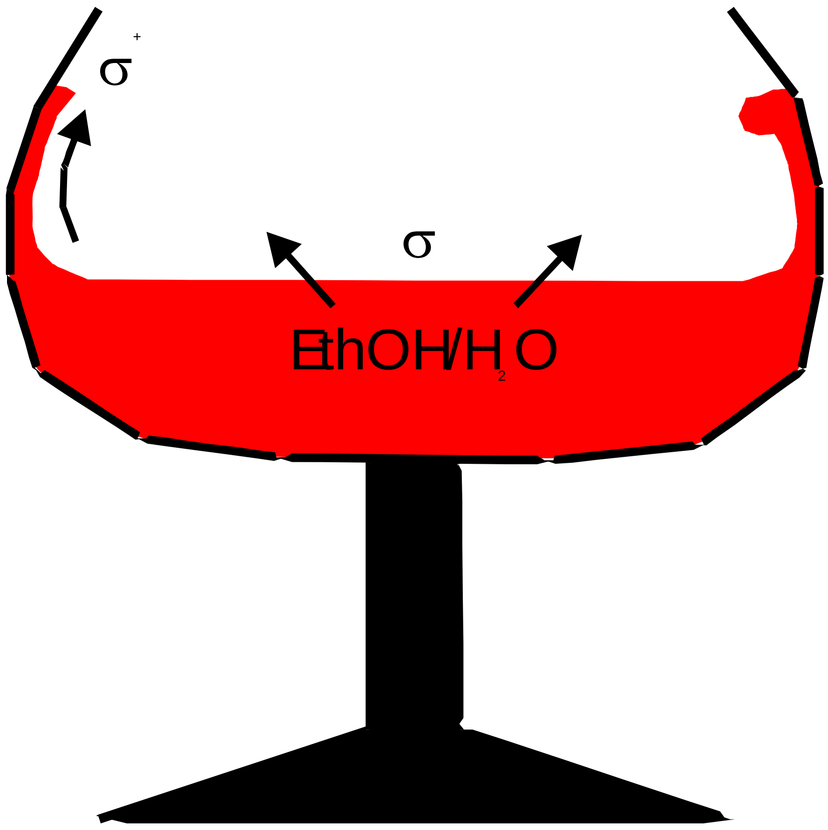
Electric charges at surfaces.

Local compression or dilatation of adsorbed films.

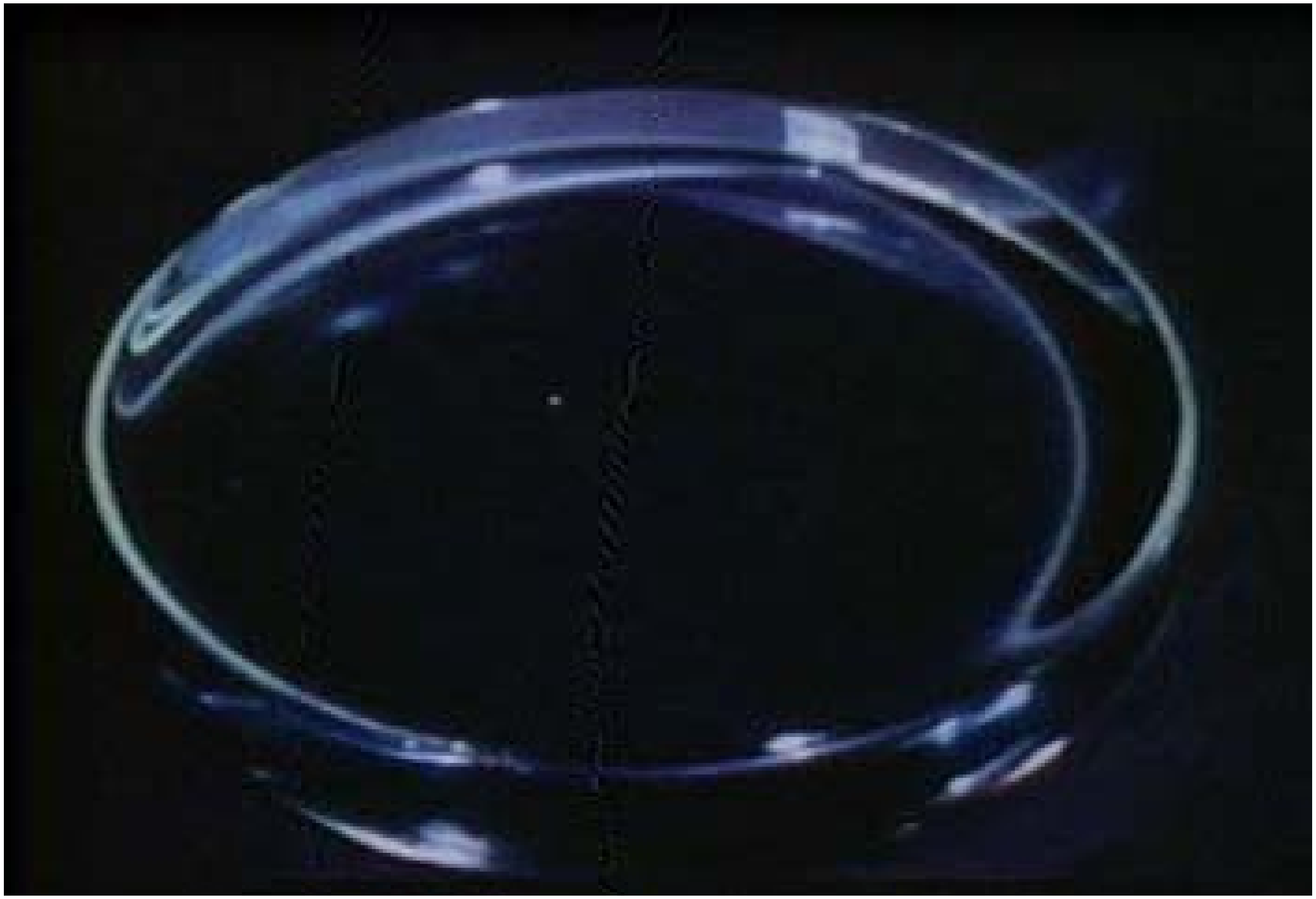
# Liquid flows from a low surface tension region

# Liquid flows to a high surface tension region.

# "Tears of Wine"



# Flow due to surface tension differences



# Liquid flows away from a hot spot

# Liquid flows to a cold spot