

Surfaces and Interfaces

Lecture 2

Thermodynamics for Interfacial Systems

Work must be done to increase surface area just as work must be done to compress a gas.

At constant temperature (T), volume (V) and composition (n), the energy, ΔF , necessary to increase the surface area by an amount, ΔA , is:

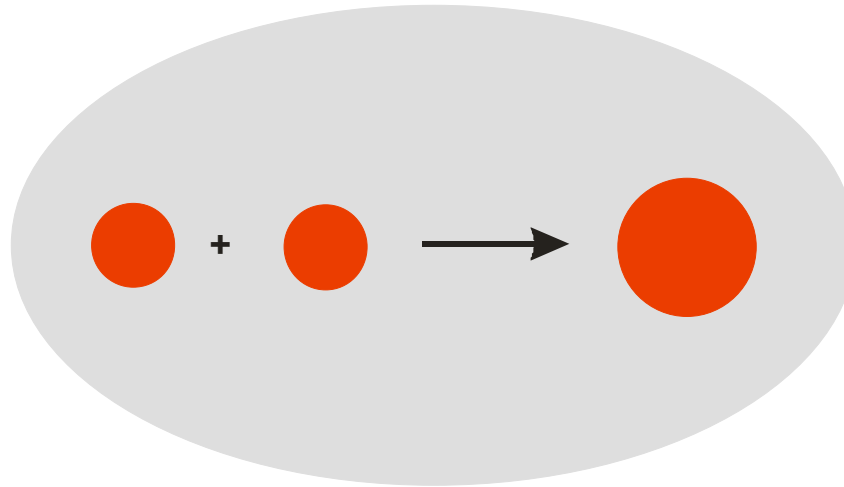
$$\Delta F = \sigma \Delta A$$

Where σ is the surface tension.

When ΔF is negative, the process is spontaneous.

When ΔF is positive, the process reverses.

Coalescence of Droplets



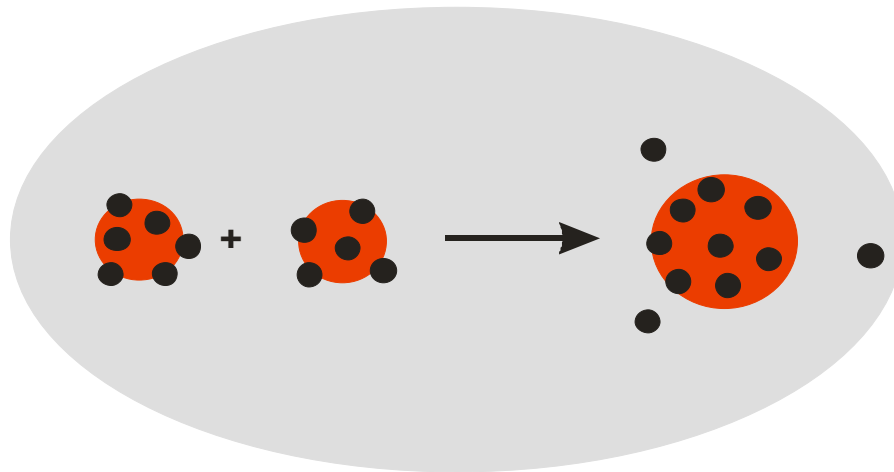
The change in energy is:

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

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 of One Liquid on Another



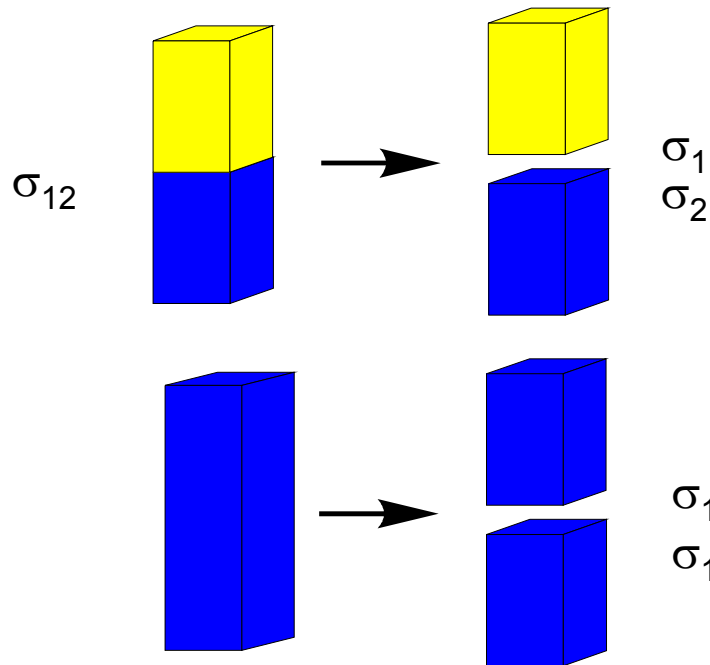
The energy change per unit area for liquid 2 (top) to spread across the surface of liquid 1 (bottom) is:

$$\begin{aligned}\Delta \bar{F} &= \bar{F}_{final} - \bar{F}_{initial} \\ &= (\sigma_2 + \sigma_{12} - \sigma_1)\end{aligned}$$

The top liquid will spread when: $\sigma_1 > \sigma_2 + \sigma_{12}$

This is not the common assertion.

Works of Cohesion and Adhesion



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

$$W^{adh} = \sigma_1 + \sigma_2 - \sigma_{12}$$

The work of cohesion is the separation to create two new surfaces.

$$W^{coh} = 2\sigma_1$$

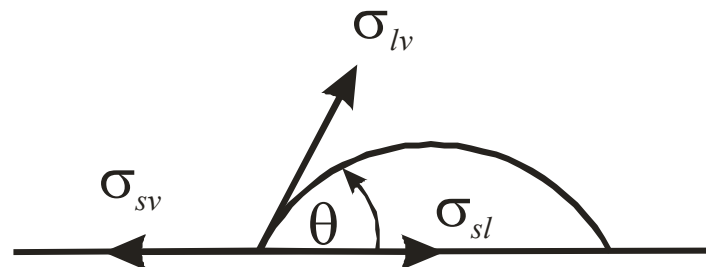
Liquids have different contact angles on different solids



The interaction of a liquid and a solid

The Young-Dupré introduces the idea of a solid surface/vapor surface tension, σ_{sv} and a solid/liquid interfacial tension, σ_{sl} .

A sessile liquid drop on a solid:

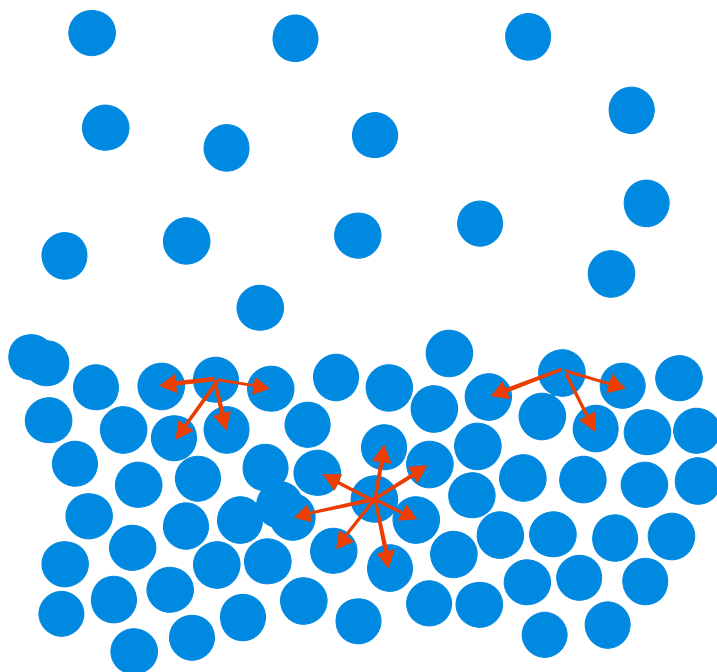


The contact angle is θ and is assumed to be independent of the geometry.

The idea is that the three tensions are balanced:

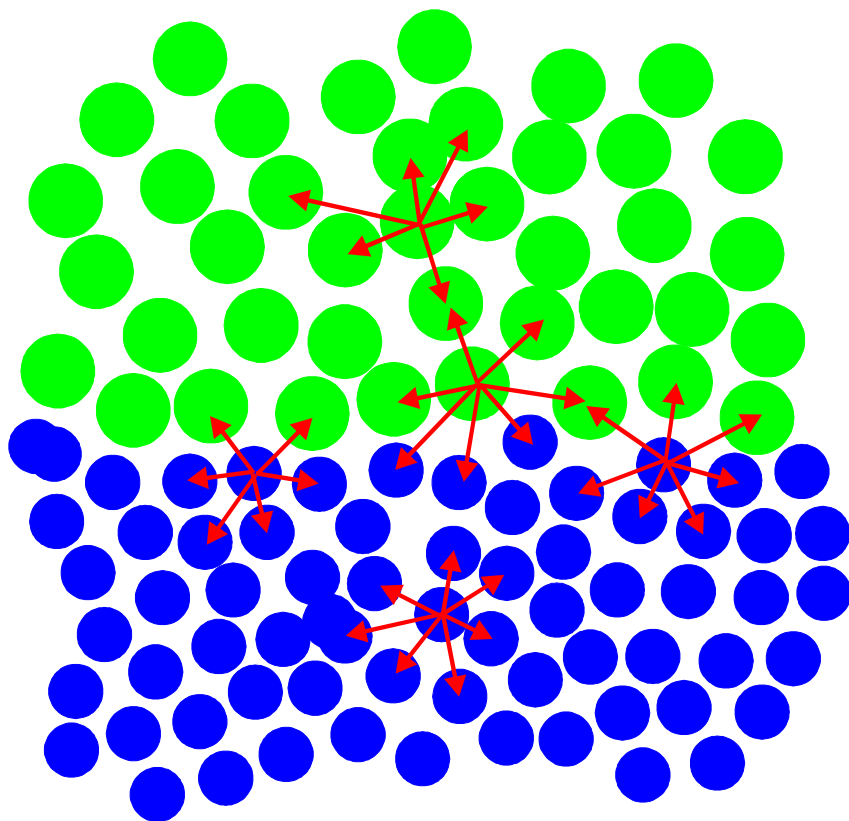
$$\sigma_{sv} = \sigma_{lv} \cos \theta + \sigma_{sl}$$

The Molecular Origin of Surface Tension



The molecules at the liquid surface are pulled towards the bulk liquid. To expand the surface requires work. The work is the surface tension times the change in area.

The Molecular Origin of Interfacial Tension

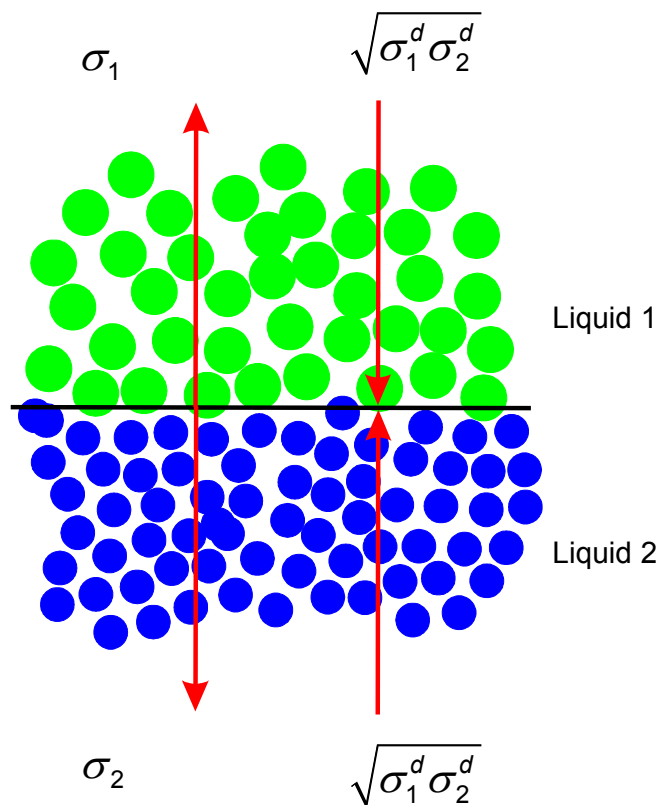


The stronger the interfacial interactions, the lower the interfacial tension!

But the greater the work of adhesion:

$$W^{adh} = \sigma_1 + \sigma_2 - \sigma_{12}$$

A theory for interfacial tensions



The “adhesion” between the liquids is approximated by the root-mean-square of the surface tensions:

$$W^{adh} = 2\sqrt{\sigma_1^d \sigma_2^d}$$

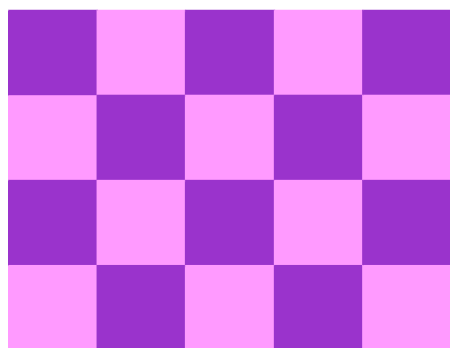
hence

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^d \sigma_2^d}$$

The superscript “*d*” refers to the “dispersion” or van der Waals types of attraction.

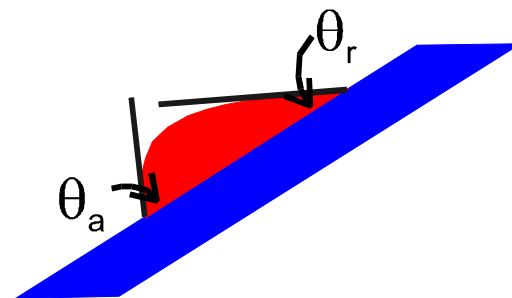
Fowkes, in Ross, ed. 1965, p. x

Large surface heterogeneities - 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 –

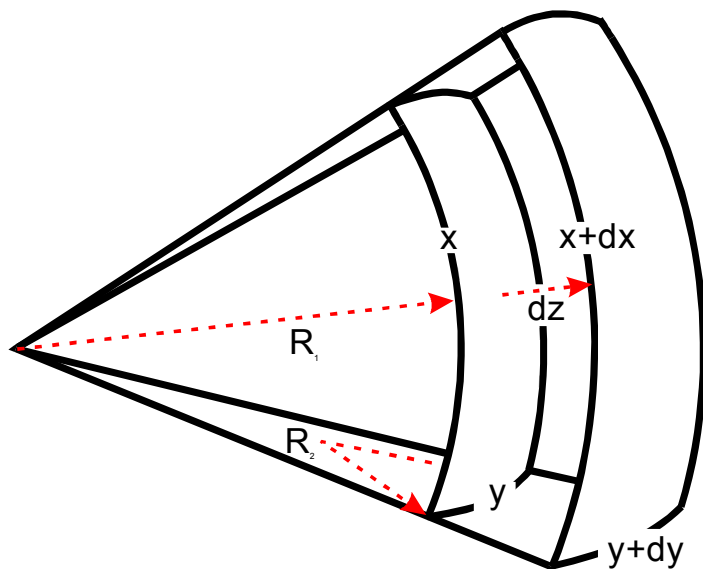
Motion as a consequence of shape.

Key idea: pressure drop across a curved surface

Marangoni flow –

Motion as a consequence of variation in surface tension.

Pressure drops across a curved surface



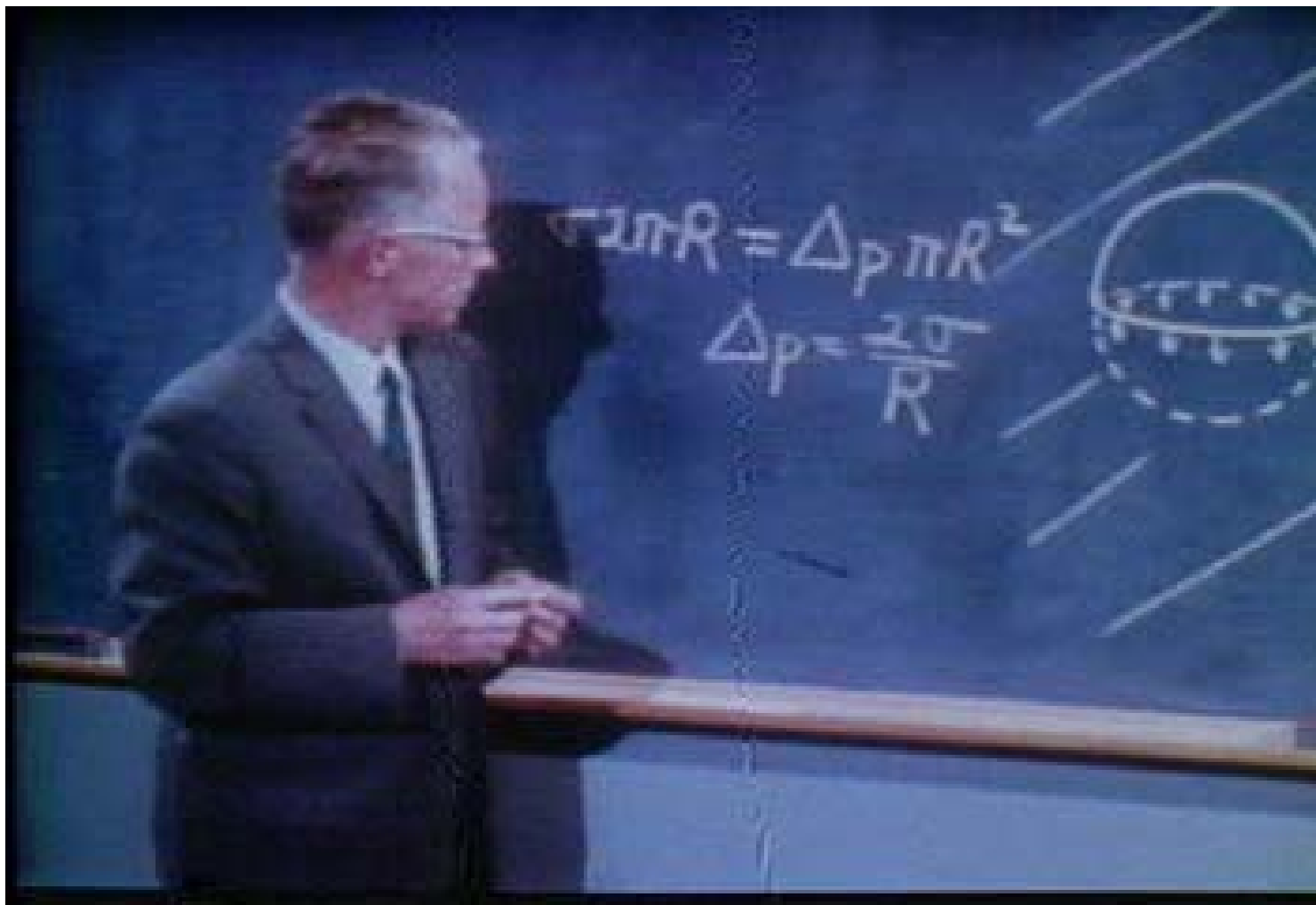
The Laplace equation:

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

R_1 and R_2 are the radii of curvature.

The pressure is larger on the concave (inside) of the curved surface.

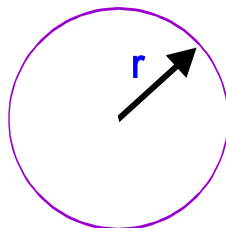
Bubbles are difficult to nucleate



“Controlled” nucleation of bubbles



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.

The Kelvin Equation

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

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

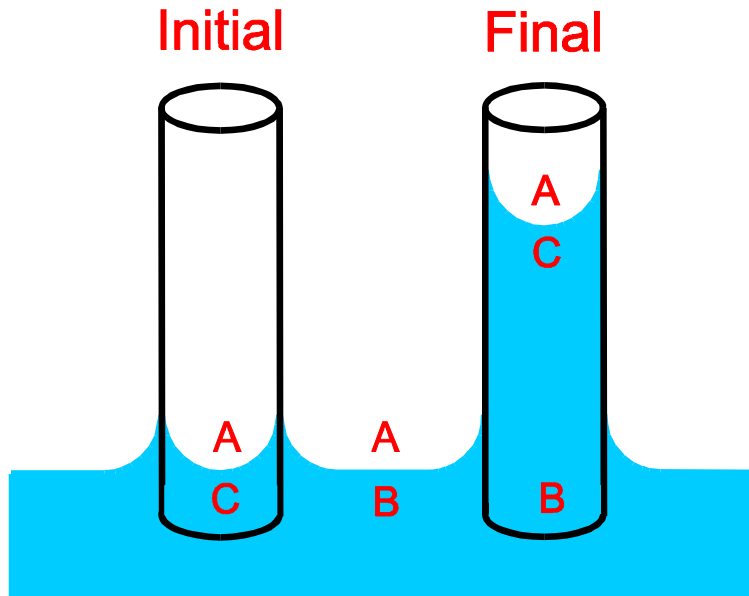
$$\ln\left(\frac{c}{c_0}\right) = \frac{2\sigma V_m}{rRT}$$

All these processes are called **Ostwald ripening**.

Capillary rise is another example of Laplace pressure



Capillary rise



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

The final position is determined by 2 principles:

- (1) The pressure drops across curved interfaces.
- (2) The pressure in the liquid must be the same at the same depth.

In the final state the pressure drop across the AC interface equals the hydrostatic pressure from C to B.

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.

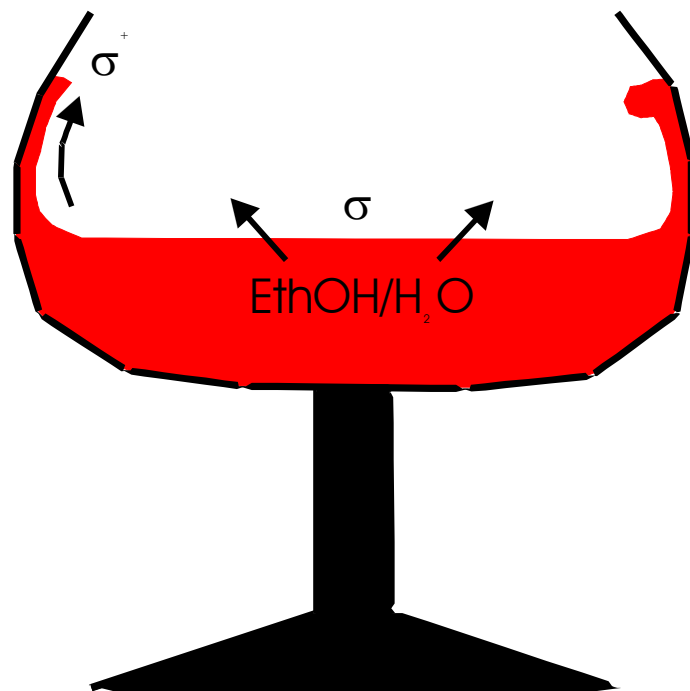
Liquid will flow away from a low surface tension region



Liquid flows to the higher surface tension



“Tears of Wine”



Flow due to surface tension differences



Liquid flows away from a hot spot



Liquid flows to a cold spot



Equations of Capillarity

Surface Free Energy

$$\left(\frac{\partial F}{\partial A}\right)_{T,V,n_i} = \sigma$$

Young-Dupré Equation

$$\sigma_{SV} = \sigma_{LV} \cos \theta + \sigma_{SL}$$

LaPlace Equation

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

Marangoni Flow

$$\mathit{grad}(\sigma) = \tau_\alpha + \tau_\beta$$