Surfaces and Interfaces

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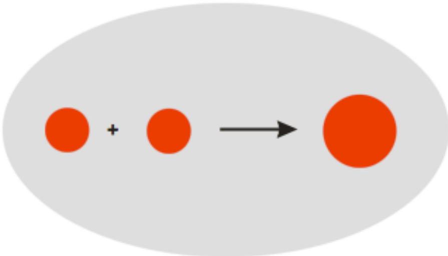
Thermodynamics for Interfacial Systems

- 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:

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

- Where σ is the surface tension.
- When ΔF is negative, the process is spontaneous
- When ΔF is positive, the process reverses.

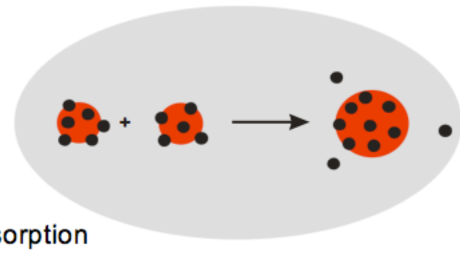
Coalescence of Droplets



- 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 coalescence, 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, 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:

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

- The top liquid will spread when:

$$\sigma_1 > \sigma_2 + \sigma_{12}$$

- This is not the common assertion.

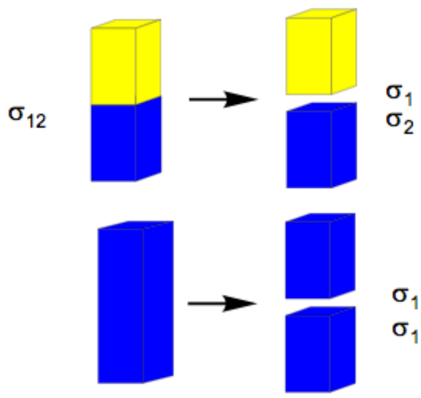
Works of Cohesion and Adhesion

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

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

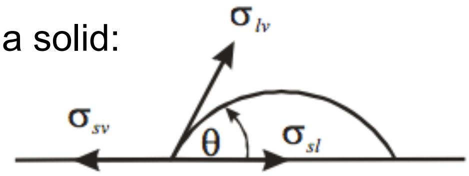
- The work of cohesion is the separation to create two new surfaces.

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



The interaction of a liquid and a solid

- The Young-Dupre interoduce 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:



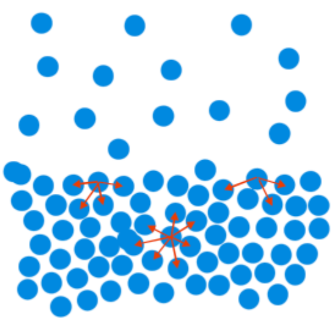
- The contact angle is θ and is assumed to be independent of the geometry.

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

- The idea is that the three tensions are balanced.

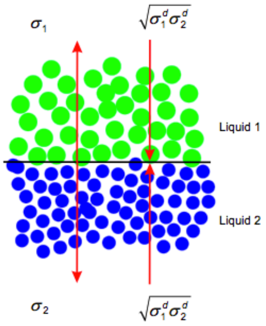
The Molecular Origin of Surface Tension

- 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.



Theory for interfacial tensions

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



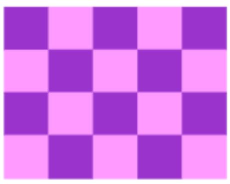
$$W^{adh} = 2\sqrt{\sigma_1^d \sigma_2^d}$$

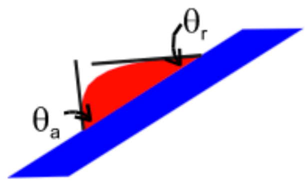
$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^d \sigma_2^d}$$

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

Large Surface Heterogeneities – Contact Angle Hysteresis

- High energy spots – low contact angles
- Low energy spots – high contact angles

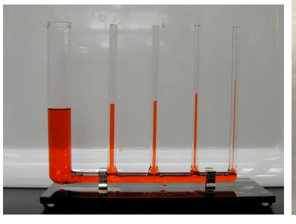




- Advancing liquids are held by low energy spots and show high contact angles.
- Receding liquids are held by high energy spots and show low contact angles.

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.

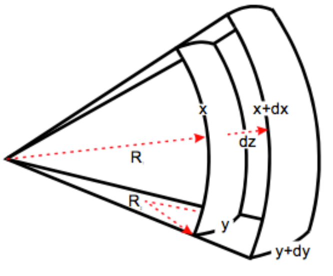


Pressure Drops across a Curved Surface

- The Young-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.



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.

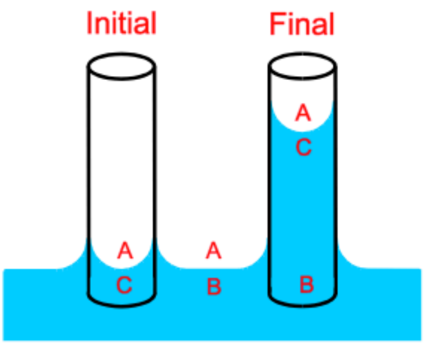
The Kelvin Equation

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

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

- All these processes are called *<u>Ostwald Ripening</u>*.

Capillary Rise



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.

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

Marangoni Flow

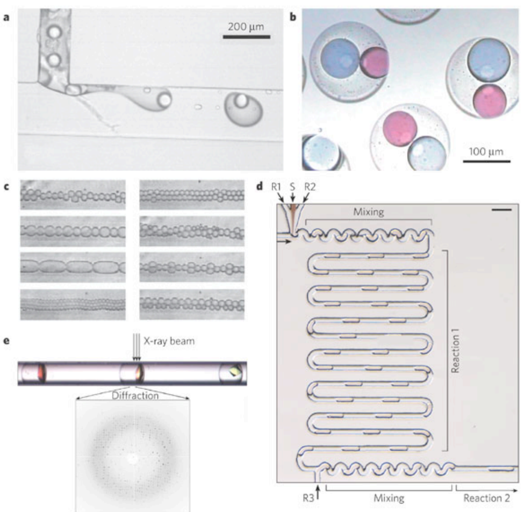
- Marangoni Flow – flow resulting from local differences in surface tension.
- Causes of Variation in Surface Tension:
  - Local temperature differences
  - Local differences in composition due to differential evaporation
  - Electric charges at surfaces
  - Local compression or dilatation of absorbed films.

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	$grad(\sigma) = \tau_\alpha + \tau_\beta$

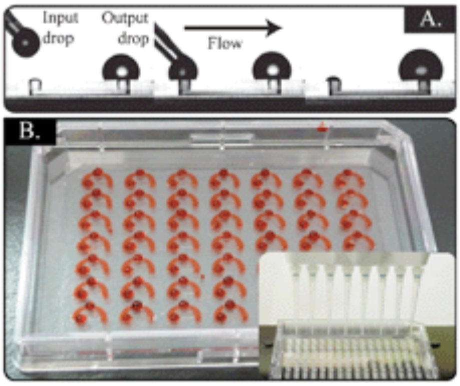
Control Micro/Nanofluidic Interfaces

- Microfluidic technology allows droplets to be generated that can be used as containers in which different kind of reactions can be carried out in a controlled way.

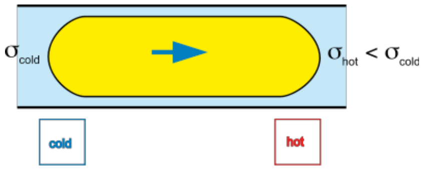


Surface Tension-Driven Flow

It is possible to move droplet or bubbles squeezed in microchannels, even if there liquid is totally wetting the solid. The method is to modify the liquid-gas surface tension (instead of the solid-liquid surface tension).

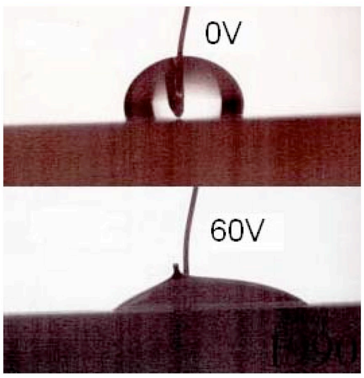


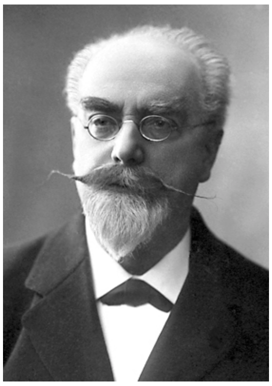
Heating a liquid decreases its surface tension (it is the reverse with the solid-liquid surface tension).



Electrowetting

- The electrowetting behavior of mercury and other liquids on variably charged surfaces was probably first explained by Gabriel Lippmann in 1875 and was certainly observed much earlier.

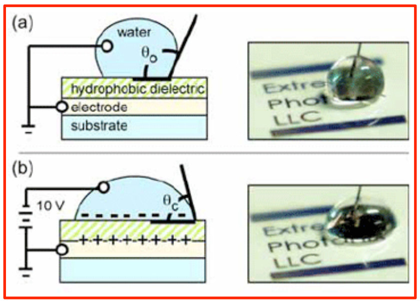




Electrowetting on Dielectric (EWOD)

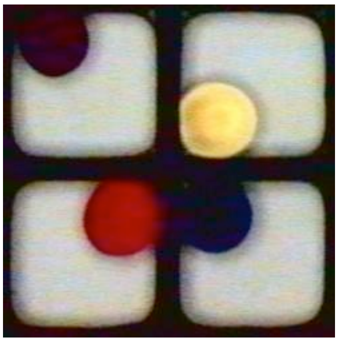
- The simplest derivation of electrowetting behavior is given by considering its thermodynamic model. While it is possible to obtain a detailed numerical model of electrowetting by considering the precise shape of the electrical fringing field and how it affects the local droplet curvature, such solutions are mathematically and computationally complex.

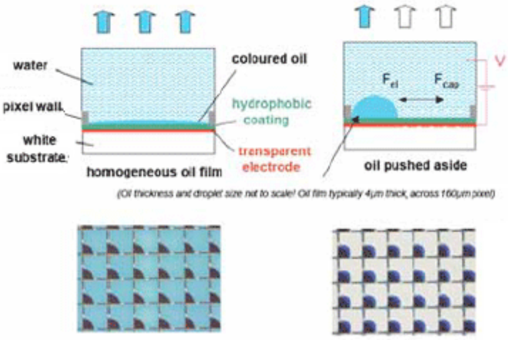
$$\theta = \cos^{-1}\left(\frac{\gamma_{ws}^{0} - \gamma_{s} - \frac{CV^2}{2}}{\gamma_{w}}\right)$$



Electrowetting Display

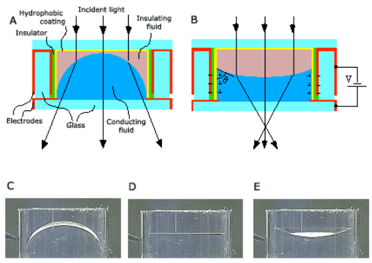
- Using the principle of Electrowetting, *Liquavista* is developing a range of products based on a variety of architectures.

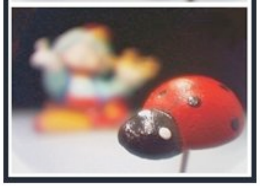




Electrowetting Lens

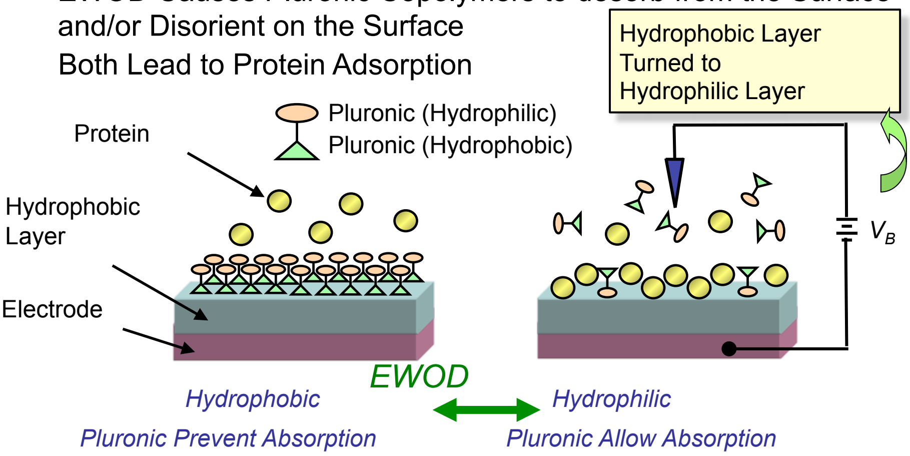
- Philips' fluid lenses bring things into focus; unique variable-focus with no mechanical moving parts.





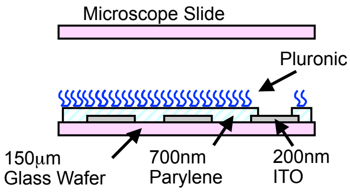
Electrowetting Protein/Cell Patterning

- Approach: *Electrowetting on Dielectric (EWOD)*
- EWOD Causes Pluronic Copolymers to desorb from the Surface and/or Disorient on the Surface
  Both Lead to Protein Adsorption

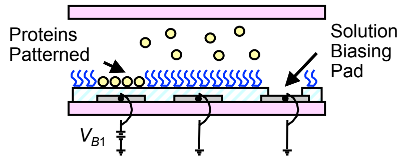


Electrowetting Protein/Cell Patterning

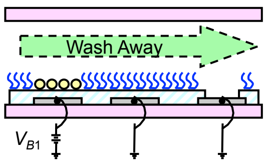
Step 1:
- *Flow proteins into the chamber*
- *No bias at this time*



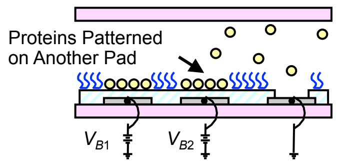
Step 2:
- *Turn on the selected patterns*
- *Proteins ONLY bind onto those patterns*



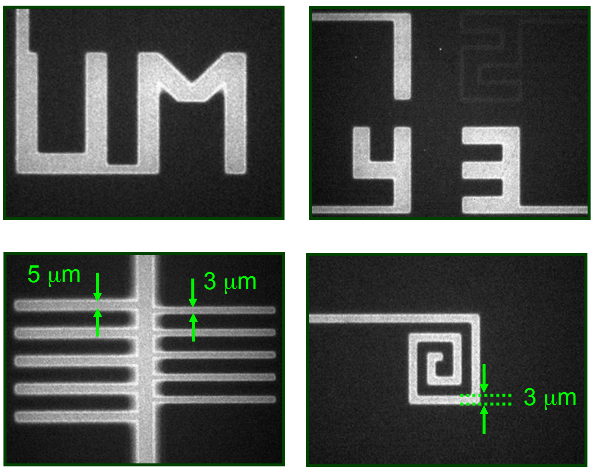
Step 3:
- *Wash out unbounded proteins*



Step 4:
- *Flow proteins into the chamber*
- *Switch on other patterns*



Electrowetting Protein/Cell Patterning



Testing Conditions

- *Pluronic Coating*
  40mg/ml incubated in chamber for 3min
- *Protein Solution*
  300μl of 0.3mg/ml TMR-BSA solution (pH 6.86 in 2.7mg/ml K-Pipe buffer) incubated in chamber for 3min
- *Washing*
  1000μl buffer washing away unbounded proteins

Electrowetting Protein/Cell Patterning