Surface Energy Density and Surface Tension

It is an experimental observation that liquids tend to draw up into spherical drops.

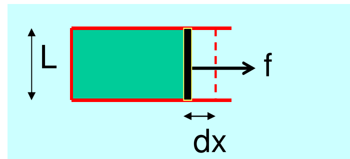
A sphere is the geometric form which has the smallest surface area for a given volume.

Thus it is clear that the surface of the liquid must have a higher energy than the bulk.

This energy is known as the free surface energy density γ, with units of Jm^{-2} and typical values of $30\text{-}70 \cdot 10^{-3} Jm^{-2}$.

Sometimes the unit is given equivalently as Nm^{-1}, particularly when quoted as a surface tension.

We can use a virtual work argument to show this for a force ***f*** acting on an area ***dA*** and moving through a distance ***dx***:



$$f\,dx = \gamma\,dA = \gamma\,L\,dx$$

Thus $\gamma = f / L$

The **surface energy density** is: $(f\,dx) / (L\,dx) = f/L = \gamma$, i.e. equal to the surface tension.

Surface Energy Density & Surface Tension: For a "pure" liquid/vapour surface or liquid/liquid interface , they are the same thing.

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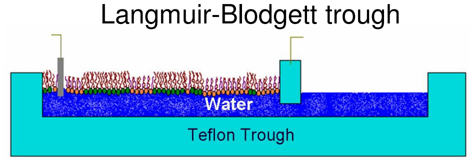
Surface Energy Density and Surface Tension

Langmuir-Blodgett trough



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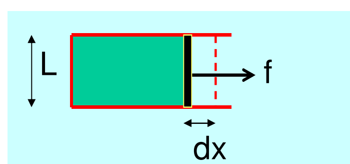

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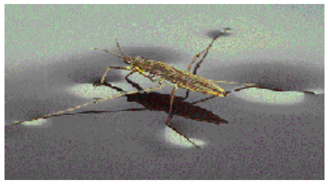
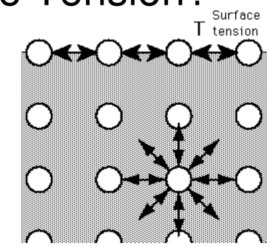
Why is there a Surface Tension?





At the simplest level, we can ascribe the existence of surface tension to the reduction in favourable bonds for molecules at the liquid surface.

Formally it is the additional free energy per unit area required to remove molecules from the bulk to create the surface.

Denoted by

$$\gamma = \left(\frac{\partial U}{\partial A}\right)_{S,V,n_i} = \left(\frac{\partial F}{\partial A}\right)_{T,V,n_i} = \left(\frac{\partial G}{\partial A}\right)_{T,P,n_i}$$

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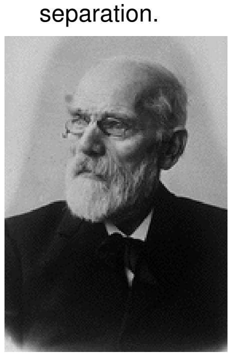
Van der Waals

Van der Waal's attraction between molecules $\propto 1/r^6$, where r is separation.



Johannes van der Waals 837-1923
Nobel Prize in Physics 1910

It arises from interactions between dipoles in the two surfaces.

Energy U due to dipole moment **p** in local field $\mathbf{E_L}$ is $-\mathbf{p}.\mathbf{E_L}$

where $$\mathbf{E_L} = \frac{2\mathbf{p}}{4\pi\varepsilon_o r^3}$$

and **p** is the induced dipole due to the field $\mathbf{E_L}$ so that $\mathbf{p} \propto \mathbf{E_L}$ so that

$$U \propto -\mathbf{p}.\mathbf{E_L} \propto -\mathbf{E_L}^2$$

$$\therefore U \propto -\frac{1}{r^6}$$

$$\boxed{U = -\iint_{V_1 V_2} \frac{A}{|\mathbf{x}_1 - \mathbf{x}_2|^6} n(\mathbf{x}_1) n(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2}$$

Always attraction! The "Hamaker constant" is a function of molecular (local) dielectric polarisability of the two interacting objects. There are various levels of accuracy for its value.

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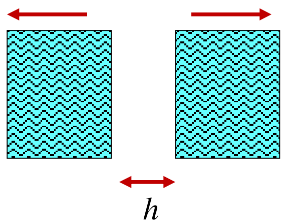
Continuum Approach

Imagine cutting a volume of liquid and pulling it apart



$f(h)$ is the force between the two halves of the liquid

$$\gamma = \frac{1}{2}\int_a^\infty f(h)dh \cdot \frac{1}{(\text{area})}$$

where a is a cut-off at very short distances

Assuming a Van der Waals interaction, then the force can be worked out by summing pairwise interactions between the two surfaces (**see QS for proof of this**):

$$f(h) = \frac{A}{6\pi h^3}\cdot(\text{area})$$

where A is the Hamaker constant, typically $\sim 10^{-20}$J. Then

$$\gamma = \frac{A}{24\pi a^2}$$

The cut-off a could be taken, e.g. as half the average intermolecular distance, but this leads to values systematically too small: this picture has only dealt with a static case, and more sophisticated analysis is required to get better agreement

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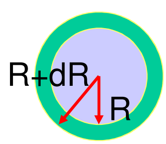
Bubbles and Droplets

Imagine expanding a droplet from radius R to $R+dR$, with a corresponding increase in surface area ΔA



Work done is $\Delta p \cdot 4\pi R^2 dR$, where Δp is the difference in internal and external pressure, i.e. is the pressure driving the expansion.

This must balance the work done in expanding the interface $\gamma \Delta A = \gamma 8\pi R dR$

Therefore $$\Delta p = \frac{2\gamma}{R}$$

And the pressure has to be higher <u>inside</u> the drop.

For a bubble (as in a soap bubble) which is an air-filled film, there are two separate surfaces, and

$$\Delta p = \frac{4\gamma}{R}$$

For a more general (non-spherical) drop, with two principal radii of curvature R_1 and R_2

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

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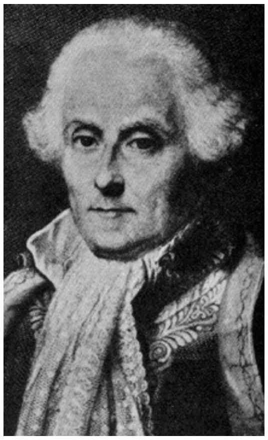
Pierre-Simon Laplace
1749-1827



The Laplace disjoining pressure

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

is one of his less familiar contributions.

Laplace was particularly interested in 'Celestial Mechanics'

Laplace had to survive the French Revolution and Napoleon…

He briefly (for 6 weeks) served as Interior Minister, but was deemed by Napoleon a 'mediocre administrator' despite his scientific fame.

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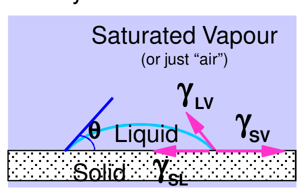
Wetting and Contact Angle

When a liquid is deposited on a surface, it may not form a continuous film but instead break up into droplets.

The shape of the droplets is defined by the relative surface energies.

This is generic, e.g. equally true for a solid drop forming from its melt on a surface.

S denotes Solid, *V* - vapour and *L* - liquid , respectively



Balancing forces (recall surface energy ≡ surface tension per unit length) at the contact line, where the solid, liquid and vapour phases meet

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

(γ_{SV} denotes surface energy between substrate and vapour, etc)

This is known as the Young equation.

Condition for complete wetting is that there is no real solution for θ.

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Thomas Young (1773-1829)

Thomas Young
(1773-1829)

- His epitaph states
  "...a man alike eminent in almost every department of human learning."
- Through his medical practice he got interested in the human eye.
- This led him to study optics, and led to his famous Young's slits experiments.
- Discovered the cause of astigmatism.
- Postulated how the receptors in the eye perceive colour.
- And he also managed to find time to give a formal meaning to energy: he assigned the term ***energy*** to the quantity mv^2 and defined *work done* as *(force* x *distance),* proportional to *energy.*
- Plus he derived the equation for surface tension, and also defined Young's modulus

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Wetting and Spreading

The spreading parameter S is sometimes defined by

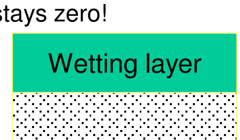
$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$$

It is a measure of the difference in surface energy between the substrate dry and wet.

If S>0, the liquid spreads completely to cover the surface and lower its surface energy:

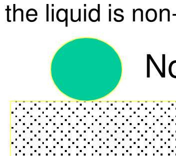
$$\cos\theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}}$$

When the fraction is ≥ 1, then θ is zero and stays zero!



If S<0, partial wetting is said to occur, with a finite contact angle θ.

When the fraction is ≤ -1, then contact angle θ is 180°, and stays it! The liquid forms a complete sphere and the liquid is non-wetting.



Acqueous liquids will spread on highly polarisable substrates such as metal and glass.

They may or may not on plastics – if the liquid is less polarisable than the substrate, it will.

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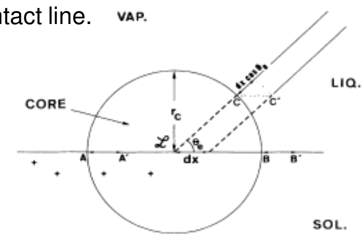
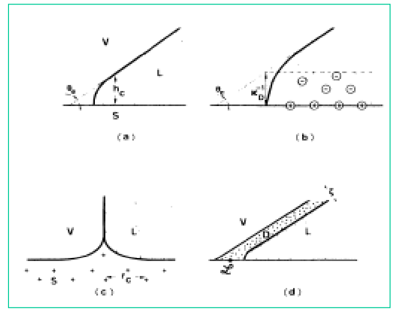
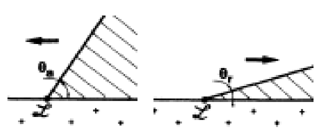
Wetting and Contact Angle

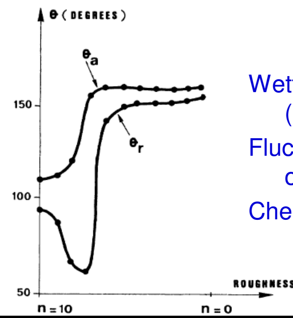
More details / delicate issues lie in the “core structure” of the contact line.





Contact angle hysteresis:
advancing or receding edge





Wetting phase transitions (1st or 2nd order)

Fluctuations and elasticity of the contact line

Chemical propulsion

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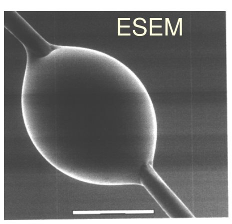
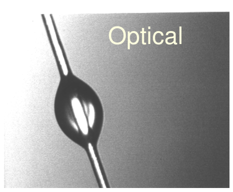
Imaging Drops

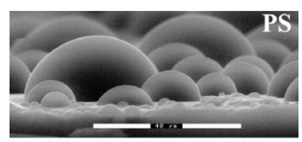


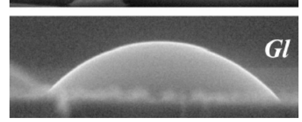


Water droplets on a cellulose fibre.

Accuracy of measuring small droplets using optical microscopes can be limited due to refraction at interface.

Using Environmental SEM offers a potentially more accurate route.





A smaller contact angle is seen for water droplets on the polar glass substrate (lower) compared with the polystyrene (upper) surface.

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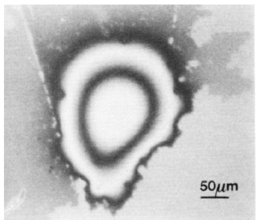
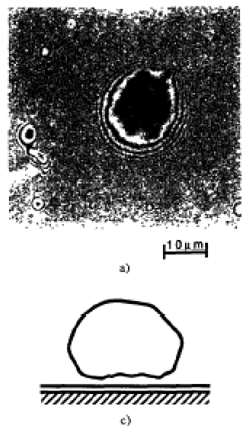
Using Interference to probe ‘Droplet’ Shape



Interference fringes can be used to monitor drop shape/thickness, and the way in which the droplet spreads.

The dynamics of spreading can thus be followed in real time.



Similar approaches have been developed to study cell adhesion.

Here a phospholipid vesicle is examined.

Thermal fluctuations and surface defects (roughness) mean the shape is far from spherical.

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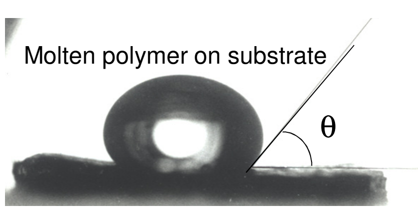
Measuring Surface Tension

Measuring the contact angle is obviously a good way of determining the surface energy of a liquid on a particular substrate, if the other surface energy terms are known.

A goniometer can be used to measure the angle accurately, or photographs taken on which measurements are made.

However, there are experimental difficulties to take into account.



Roughness: If the surface is rough, then the local contact angle and the macroscopic (measured) contact angle will differ. This is a very hard problem to deal with, both theoretically and experimentally.

If the droplet grows, the advancing and receding angles will differ due to hysteresis effects. These are also not well understood. In general the advancing angle is used, although sometimes both are quoted.

Surface cleanliness is a major issue. Finger grease, for instance, can completely change the measurements.

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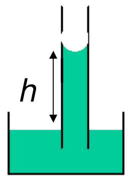
Measuring Surface Tension

Capillary Rise Experiments



$$\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\rho g h$$

As the liquid rises up the tube, wetting the side of the, we must have a balance of forces at equilibrium, arising from the pressure difference across the meniscus and the drop in pressure over capillary rise

Constraint on capillary diameter.

The capillary length: $l_c = \sqrt{\gamma / \rho g}$

For a circular capillary of uniform radius R, $R_1=R_2$ and this can be arranged to give

$$\gamma = \frac{\rho g h R}{2}$$

where ρ is the density of the fluid

h is the meniscus rise.

This method works well for low viscosity, simple liquids.

It assumes 'complete wetting'. Otherwise we need to calculate the actual curvature of the liquid surface, which is no longer = R

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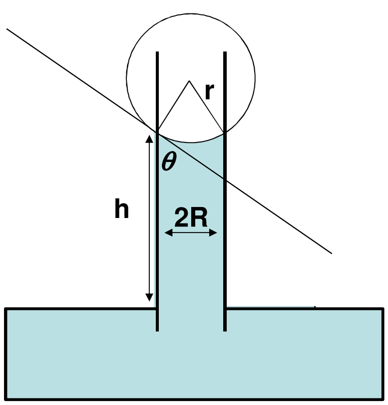
Measuring Surface Tension

If the contact angle is finite, then we must modify our earlier analysis.



If the meniscus has the same radius for each of its radii of curvature, then

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

This equation implies that we can determine the surface tension γ, or θ, if one or the other are measured independently.

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Interface between two liquids

(an extension of the 'Flory-Huggins phase separation')

Free energy of mixing (cf. Thermal & Statistical)

Entropy terms:

$$S = -N_{\text{tot}}\, k_B \sum_i p_i \ln p_i$$

where *i* are the states of the system, and p_i is their probability.

If there are two species, **P** and **S** (historically: for 'polymer' and 'solvent'), then the probability of finding one or the other is proportional to their concentration, and:

$$S = -N_{\text{tot}}\, k_B \left(\phi_p \ln \phi_p + \phi_s \ln \phi_s\right)$$

This is called the *entropy of mixing* (in its simplest form).

.

Energy terms:

Assume pair interactions.

Three characteristic energies measured by their 2nd virial coef: ε_{PP}, ε_{SS}, ε_{PS}

Need to estimate the number of pair 'contacts' between each species, knowing only the concentration of P-species: ϕ_P

$$N_{pp} = \tfrac{1}{2} N_{\text{tot}}\, \phi_p^{\,2}$$

$$N_{ss} = \tfrac{1}{2} N_{\text{tot}}\, \phi_s^{\,2} = \tfrac{1}{2} N_{\text{tot}}\, (1-\phi_p)^2$$

$$N_{pp} = N_{\text{tot}}\, \phi_p \phi_s = N_{\text{tot}}\, \phi_p (1-\phi_p)$$

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'Flory-Huggins free energy of mixing'

Energy terms continued:

Energy per particle is

$$u_{\text{int}} = \tfrac{1}{2}\left[\varepsilon_{pp}\phi_p^{\,2} + \varepsilon_{ss}(1-\phi_p)^2 + 2\varepsilon_{ps}\,\phi_p(1-\phi_p)\right]$$

Noting that the energy of the completely un-mixed state is:

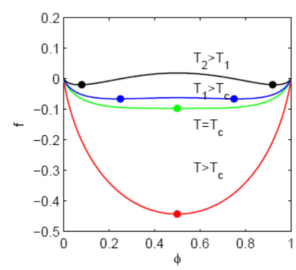
$$u_0 = \tfrac{1}{2}\left[\varepsilon_{pp}\phi + \varepsilon_{ss}(1-\phi_p)\right]$$

Taking the difference gives the "energy of mixing":

$$u_{\text{mix}} = k_B T\, \chi\ \phi_p (1-\phi_p) + const.$$

Where the parameter χ is:

$$\boxed{\chi\, k_B T = \tfrac{1}{2}\left[2\varepsilon_{ps} - \left(\varepsilon_{pp} + \varepsilon_{ss}\right)\right]}$$



Combining the entropy and energy density terms gives the *free energy per particle:*

$$\frac{F}{k_B T} = \phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi\ \phi(1-\phi)$$

Look at the low concentration expansion of the osmotic pressure, and at the phase behaviour of the regular solution model.

Examine $dF/d\phi$, $d^2F/d^2\phi$, find the critical point T_c as a function of χ, etc.

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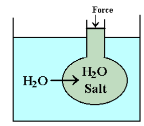
Free energy and osmotic pressure

The Flory-Huggins theory has the free energy function (in full):

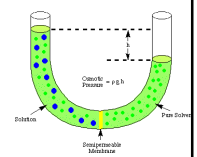
$$\boxed{F_{\text{mix}} = U_{\text{mix}} - TS_{\text{mix}} = N_{\text{tot}}\, k_B T \left(\chi \cdot \phi(1-\phi) + \phi \ln\phi + [1-\phi]\ln[1-\phi]\right)}$$

With the non-dimensional "Flory χ–parameter"



Osmotic pressure in the mixture:

$$\Pi = -\frac{\partial F_{\text{mix}}}{\partial V} = -\frac{\partial F_{\text{mix}}}{v_0\, \partial N} = -\frac{k_B T}{v_0}\left[\ln(1-\phi) + \chi\phi^2\right] \quad \text{since } \phi = N_{\text{p}}/N_{\text{tot}}$$



At small concentration of the species $\{p\}$ the osmotic pressure expands:

$$\Pi \approx \frac{k_B T}{v_0}\left[\phi + \tfrac{1}{2}(1-2\chi)\phi^2 + \ldots\right] = \boxed{\frac{N_{\text{p}} k_B T}{V}} + \frac{N_{\text{p}}^2}{V^2} k_B T \cdot \tfrac{1}{2} v_0 (1-2\chi) + \ldots$$

Most chemists/biologists work with this part only $\quad \Pi_i = M_i RT$

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A closer look at interface between fluids

In the Flory-Huggins model the concentration ϕ is not position-dependent. Hence the free energy density also is not position dependent. This implies "infinitely sharp" interfaces, which is not physical.

Extend the previous model from:

$$F_{\text{mix}} = N_{\text{tot}}\, k_B T \left(\chi \cdot \phi(1-\phi) + \phi \ln\phi + [1-\phi]\ln[1-\phi]\right)$$

to:

$$F = \frac{k_B T}{v_0} \int d\mathbf{x} \left[\chi \cdot \phi(1-\phi) + \phi\ln\phi + [1-\phi]\ln[1-\phi] + g\left(\nabla\phi\right)^2\right]$$

2 changes:

This free energy contains spatial information in $\phi(\boldsymbol{x})$

Also there is a new term that penalises strong gradients

F is now a functional (the integral of a function $\phi(\boldsymbol{x})$, the concentration profile). What does it mean in this case to minimise ***F*** ?

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A closer look at interface between fluids

$$F = \frac{k_B T}{v_0} \int d\mathbf{x} \left[\chi \cdot \phi(1-\phi) + \phi \ln \phi + [1-\phi] \ln[1-\phi] + g (\nabla \phi)^2 \right]$$

This is too difficult to miminise analytically, because of all the logarithms, but we can readily compare it with the Ginzburg-Landau expansion (see Thermal Stat. Phys. course) for concentrations near ϕ =½, which is the critical value for the underlying Flory-Huggins theory:

$$\phi(x) = \frac{1}{2} + \psi(x) \quad \text{where } \psi \text{ is small.}$$

This gives:

$$F \approx \frac{k_B T}{v_0} \int d\mathbf{x} \left[(2-\chi) \cdot \psi^2 + \frac{4}{3} \psi^4 + g (\nabla \psi)^2 \right] + const.$$

This is a standard 'Landau expansion' with the **gradient term** added:

$$F \approx \int d\mathbf{x} \left[A \cdot \psi^2 + C \cdot \psi^4 + g \cdot (\nabla \psi)^2 \right]$$

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A closer look at interface between fluids

$$F \approx \frac{k_B T}{v_0} \int d\mathbf{x} \left[(2-\chi) \cdot \psi^2 + \frac{4}{3} \psi^4 + g (\nabla \psi)^2 \right] + const.$$

How to minimise a functional? Recall the Lagrangian method:

$$\delta F = \frac{k_B T}{v_0} \int d\mathbf{x} \left[\frac{\partial f}{\partial \psi} \delta\psi + \frac{\partial f}{\partial (\nabla \psi)} \delta(\nabla \psi) \right]$$

$$= \frac{k_B T}{v_0} \int d\mathbf{x} \left[\frac{\partial f}{\partial \psi} - \nabla \left(\frac{\partial f}{\partial (\nabla \psi)} \right) \right] \delta\psi = 0$$

Boundary conditions: away from interface the gradient is negligible, setting :

$$\psi_0 = \pm \sqrt{\frac{A}{2C}}$$

Gives the **Euler–Lagrange equation:**

$$\frac{\partial f}{\partial \psi} - \nabla \left(\frac{\partial f}{\partial (\nabla \psi)} \right) = A \cdot \psi + 2C \cdot \psi^3 - g \cdot \nabla^2 \psi = 0$$

Choosing the coordinate ***z*** perpendicular to the interface, and taking the parameter **A** to be negative (below the critical point χ_c) we have the solution:

$$\boxed{\psi(z) = \sqrt{\frac{A}{2C}} \tanh \left(z/w \right)}$$

$w = \sqrt{2g/A}$ is the "width" of the interface.
Remember that A→ 0 at the critical temperature, like ($T-T_c$)....

Interface between two fluids

We have calculated the equilibrium profile for a system with an interface.

The difference between the free energy of the system with the interface, and a system of two bulk phases with no interface is given by evaluating the free energy functional in the two cases.

$$\frac{\Delta F}{\text{Area}} = \gamma \approx \frac{k_B T}{v_0} \cdot 2g \int_{-\infty}^{+\infty} dz \left(\frac{d\psi}{dz} \right)^2$$

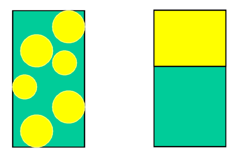
Therefore with the hyperbolic tangent profile:

$$\gamma = \frac{k_B T}{v_0} \cdot \frac{A}{2C} \cdot \frac{4}{3w} = \frac{2k_B T}{3v_0} \cdot \frac{\sqrt{2g}}{C} A^{3/2}$$

γ goes to zero at phase transition.

Important points on surface tension:

- There is an interfacial tension between two liquids in contact.
- The more different the liquids (e.g. in polarity) the larger tension this will be.
- The surface tension is related to the intermolecular interactions, and also to the temperature.



Immiscible phases will tend to separate into a state which minimises the interface area.

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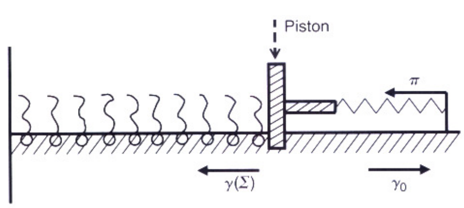
Surfactants: amphiphilic molecules

Usually these have a polar head and a hydrophobic tail, and are similar to the lipids which turn up in cell membranes.

Preferentially they will adsorb to an air-water (or water-oil) interface.

Let Σ^{-1} be the monolayer surface density (Σ is the area per polar head, in later slides it's called a).

The molecules can be compressed at the surface of a "Langmuir trough".



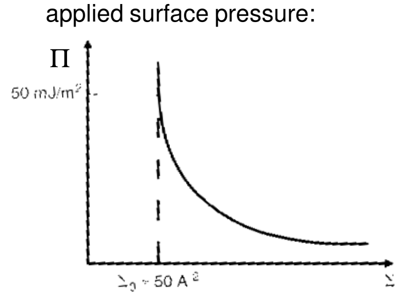
Surface pressure Π to compress a monolayer related to free energy per molecule:

$$\Pi(\Sigma) = -\left(\frac{\partial f}{\partial \Sigma} \right)_T$$

Piston is in equilibrium when

$$\gamma(\Sigma) = \gamma_o - \Pi$$

This yields the form of the equilibrium curve relating surface area Σ to applied surface pressure:



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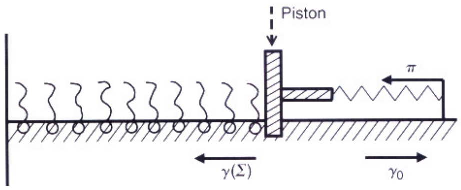
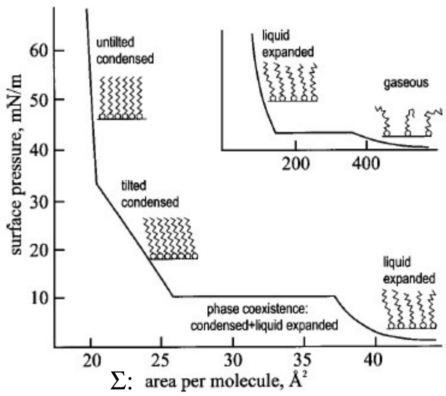
Surfactants: amphiphilic molecules





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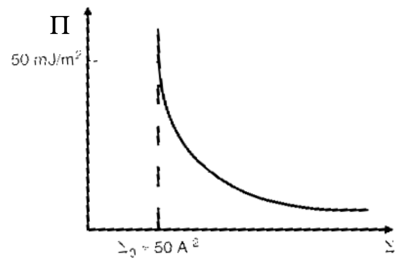

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Reduction in Surface Tension due to Surfactant

Σ is the area per molecule: $\Sigma = A/n$

Chemical potential of neutral surfactant at the air-water surface where concentration is not dilute (where $f(\Sigma)$ is free energy per molecule in the bulk):

$$\mu_{surf} = f(\Sigma) + \Sigma.\Pi(\Sigma)$$

And (at constant T)

$$d\mu_{surf} = \Sigma.d\Pi$$

Therefore

$$\mu_{surf} = \mu^o_{surf} + \int_0^{\Pi} \Sigma.d\Pi$$

where μ^o_{surf} is the free energy of a single surfactant molecule at the surface.

In equilibrium, the chemical potentials for the bulk and surface are equal at the interface .

Thus if c is <u>bulk</u> surfactant concentration, a **relation between Σ, c and γ** emerges (μ^o_w is the standard chemical potential of bulk pure water and is > μ^o_{surf} since the surfactant is not completely immersed) .

In equilibrium (for a dilute solution of a non-ionic surfactant)

$$\mu^o_W + k_B T \ln c = \mu_{surf}$$

$$\therefore k_B T \ln c = \Delta\mu + \int_0^{\Pi} \Sigma.d\Pi$$

or

$$k_B T \frac{dc}{c} = +\Sigma.d\Pi = -\Sigma.d\gamma(\Sigma)$$

$$\text{or} \quad \frac{1}{\Sigma} = -\frac{1}{k_B T}\left(\frac{\partial \gamma}{\partial \ln c}\right)_T$$

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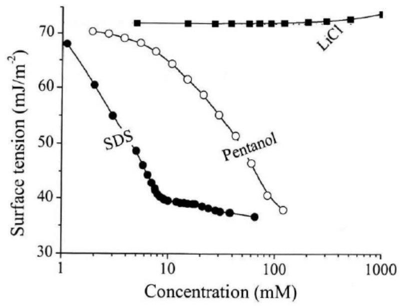
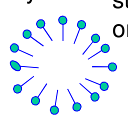
Dependence of Surface Tension on surfactant Concentration



Typically there is a substantial reduction in surface tension, down to some plateau

The surface tension decreases to the point where there is an energetically more favourable arrangement of molecules.

This is when micelles start to form.



As we shall see, this occurs when $\mu_{surf} > \mu_{micelle.}$ and we reach the cmc (defined fully in section on self-assembly).

Thereafter more micelles form in preference to more surface adsorption.

The concentration at which this occurs is known as the critical micelle concentration (cmc).

The micelles themselves may migrate to the interface.

In principle for oil-water interfaces it is possible for the interfacial tension to fall to zero (free surfaces will have zero tension only at the critical point).

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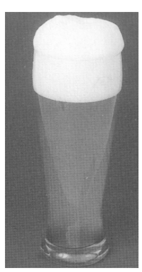
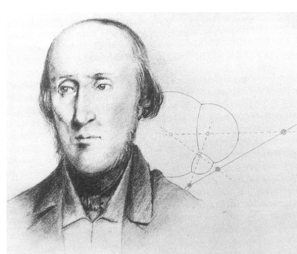
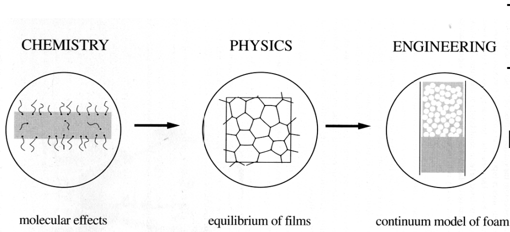
Foams





Joseph Plateau 1801-83. Did most of his work on soap when he was blind.



Surfactants play a key role in stabilising foams, such as beer froth or whipped cream. This allows the foam to survive for longer.

The films between the bubbles are known as Plateau Borders.

STATICS:

They sit at the surface of the liquid film between the gas bubbles and lower the surface energy there.

DYNAMICS:

They also slow the drainage and rupture of the liquid film.

This allows the foam to survive for longer.

In many everyday products, getting the drainage right is hugely important for its function .

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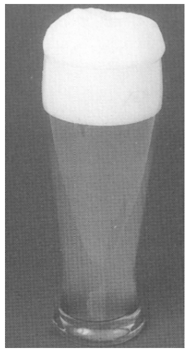
Good foams, Bad foams

Foam: air/water
Emulsion: oil/water
"wet" and "dry" foams depending on the volume fraction of air.



Destabilising foams and emulsions can be as important as stabilising them... and is often more difficult.

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Hydrophobic and Hydrophilic Surfaces

Hydrophobic surfaces are obviously ones that repel water whereas hydrophilic ones are covered with a wetting water layer.

Different applications have different requirements.

Hydrophobic surfaces

Leaves, duck feathers etc are designed so that water rapidly forms droplets and rolls off them ('water off a duck's back').

Aircraft are sprayed with a hydrophobic liquid so that a continuous film of water does not form which can transform into solid ice during flight, substantially increasing weight.

Teflon frying pans and saucepans are used to prevent most things – not just water – sticking. Made from polytetrafluorine ethylene (PTFE).

Hydrophilic surfaces

Contact lenses must be made out of materials that favour wetting, and prevent the lens adhering to the cornea.

In many industrial processes such as paper coating, wetting must be achieved very fast to cope with the speed of the process (m's per second).

Likewise with adhesives, you need a continuous film to form to give good adhesive strength.

Super-Hydrophobic surfaces

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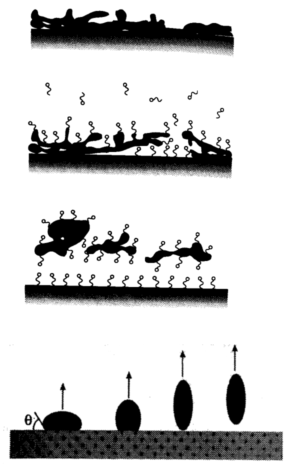
How does Soap Work?



Soap – sodium and potassium salts of fatty acids traditionally – have long been used.

However because they react with Ca^{2+} and Mg^{2+} ions to form scum, modern detergents use different chemistry, but follow the same physical principles.

The molecule must wet the substrate (fabric etc) so that it comes into contact with the surface and the dirt.

If the contaminant is an oily fluid, the molecule must increase the surface contact angle.

It removes the oil by a 'rollup' mechanism.

The dirt is then solubilised, and can then be removed mechanically.

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Interactions between Surfaces

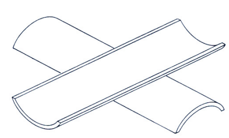
Van der Waals' $U \propto 1/r^6$ form of the potential is correct for pairwise interactions between two dipoles.

Between macroscopic surfaces one must sum over all appropriate such pairs, and hence this depends on the geometry of the objects.

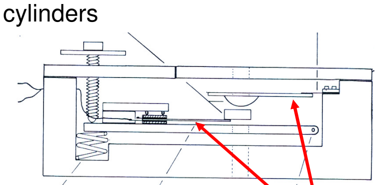
Also, a correction needs to be made at larger distances, since the force between the two dipoles are said to be 'retarded'; basically this means they are out of phase.

At large distances, the result for dipoles turns out to be $U \propto 1/r^7$

Experiments carried out at the Cavendish by Tabor and Winterton

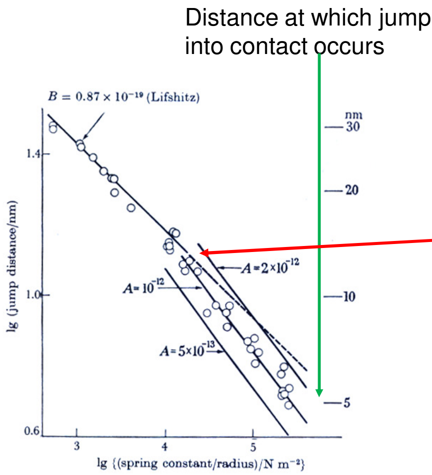


Configuration: crossed mica cylinders



Measure separation via interferometry.
Use springs of different stiffness.
Determine when attraction is sufficient to cause surfaces to jump together into contact.

Results from Surfaces Force Apparatus



Tabor and Winterton, Proc Roy Soc 1969

A is Hamaker's constant; theoretical fits plotted.

Change in slope indicates transition from $1/r^6$ to $1/r^7$ behaviour.

Confirms theoretical ideas.

Subsequent modifications to the "surface force" apparatus permitted actual force measurements to be made – and also study the friction laws ($F=\mu R$ and such)

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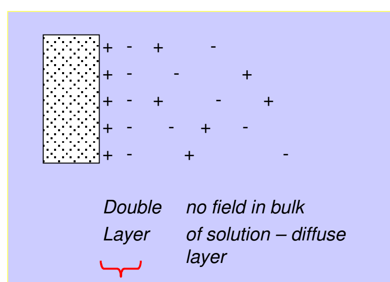
Charged surface in contact with electrolyte

This is a "primer" – a generic problem that occurs in great many situations when objects are immersed in water.

(Water is not unique in being able to carry dissociated charges – but it is of special interest to us)

When a liquid (water) comes in contact with a surface of a solid, it often causes some dissociation and "takes away" some ions – which leaves the remaining **surface charged**.

The bulk of a liquid carries a lot of oppositely-charged ions: the ones taken from the surface make a negligible contribution



Counter-ions line up to form a *double layer* next to the surface (co-ions are repelled).

However, thermal fluctuations cause the double layer to be somewhat diffuse (not dissimilar to the sedimentation problem).

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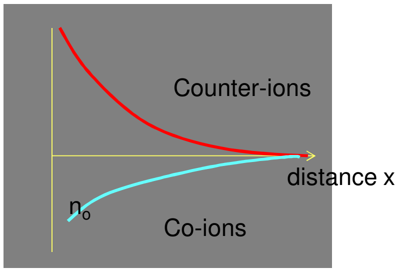
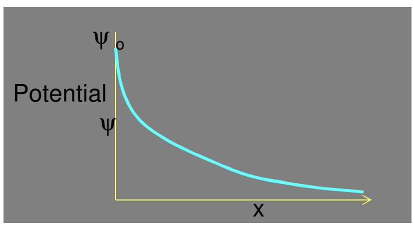
Potential and charge distributions near the surface



Ion distribution must have this form, and hence potential must also fall away from the surface.



Let us construct a model to evaluate these parameters <u>assuming</u>:

- Surfaces are perfectly flat with a uniform charge density σ.
- In the liquid, charges are point-like and obey the Boltzmann distribution.
- The influence of the solvent is limited to its dielectric permittivity ε, which is assumed constant.
- The electrolyte is assumed to be symmetrical (1:1) with a charge q= ± ze.

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Debye-Hückel Theory

Flat surface: Poisson - Boltzmann

The potential at the surface is ψ_o, and at a distance x from surface it is ψ(x).

Assume the surface is positively charged.

Bulk ion concentration n_o. Then

$$n_+(x) = n_o \exp\left(\frac{-ze\psi(x)}{k_B T}\right)$$

$$n_-(x) = n_o \exp\left(\frac{+ze\psi(x)}{k_B T}\right)$$

Hence the local charge density ρ is

$$\rho = ze(n_+ - n_-)$$

$$\rho = zen_o\left(\exp\left(-\frac{ze\psi}{k_B T}\right) - \exp\left(+\frac{ze\psi}{k_B T}\right)\right)$$

$$= -2zen_o \sinh\left(\frac{ze\psi}{k_B T}\right)$$

The charge obeys the laws of electrostatics (Poisson eq.), we are only interested in the distance away from the surface:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon\varepsilon_o} = \frac{2zen_o}{\varepsilon\varepsilon_o}\sinh\left(\frac{ze\psi}{k_B T}\right)$$

with boundary conditions:

$\psi = \psi_o$ at x = 0 and

ψ = 0 and dψ/dx = 0 at x = ∞

People say that this has a solution, but I'm not able to verify this:

$$\psi = \frac{2k_B T}{ze}\ln\left(\frac{1+\gamma\exp(-\kappa x)}{1-\gamma\exp(-\kappa x)}\right)$$

$$\gamma = \frac{\exp\left(ze\psi_o/2k_B T\right)-1}{\exp\left(ze\psi_o/2k_B T\right)+1}$$

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Debye-Hückel Theory

The Debye-Hückel approximation:

$$\frac{ze\psi_o}{k_B T} << 1$$

(thermal energy of an ion is much greater than the electrostatic energy). For a single-e charge at room T this is valid for $\psi_o \le 30$mV.

Then:

$$\frac{d^2\psi}{dx^2} \approx \left[\frac{2z^2e^2n_o}{\varepsilon\varepsilon_o k_B T}\right]\psi$$

We certainly know how to solve <u>this</u>:

$$\psi = \psi_o \exp(-\kappa x)$$

where the parameter: $$\kappa = \left[\frac{2e^2n_o z^2}{\varepsilon\varepsilon_o k_B T}\right]^{1/2}$$

This shows the potential has an exponential fall off with distance and $1/\kappa$ is the distance over which the potential falls by a factor of e.

The characteristic decay distance $1/\kappa$ is called the Debye screening length

$\kappa_{DH} \propto \sqrt{n_o}$ and $\propto z$, meaning that if we put <u>more dissociated ions</u> (or increase their charge) – the surface electrostatic potential $\psi(x)$ will fall away much faster.

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Debye-Hückel Theory

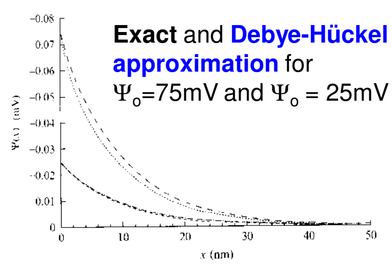
For a monovalent ion, typical values of the Debye screening length:

Conc. of monovalent ion	$1/\kappa$
0.1M	1nm
0.001M	10nm

ψ_o can be related to surface charge density σ within DH approximation. From charge neutrality:

$$\sigma_o = -\int_0^\infty \rho\, dx \sim \varepsilon\varepsilon_o \kappa \psi_o$$

The surface potential therefore depends on both the surface charge density and the ionic composition of the medium.



Exact and **Debye-Hückel approximation** for Ψ_o=75mV and Ψ_o = 25mV

There are a series of further refinements possible, but this is good enough to help us understand colloidal stability.

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