Understanding surfaces in ‘depth’

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Contents

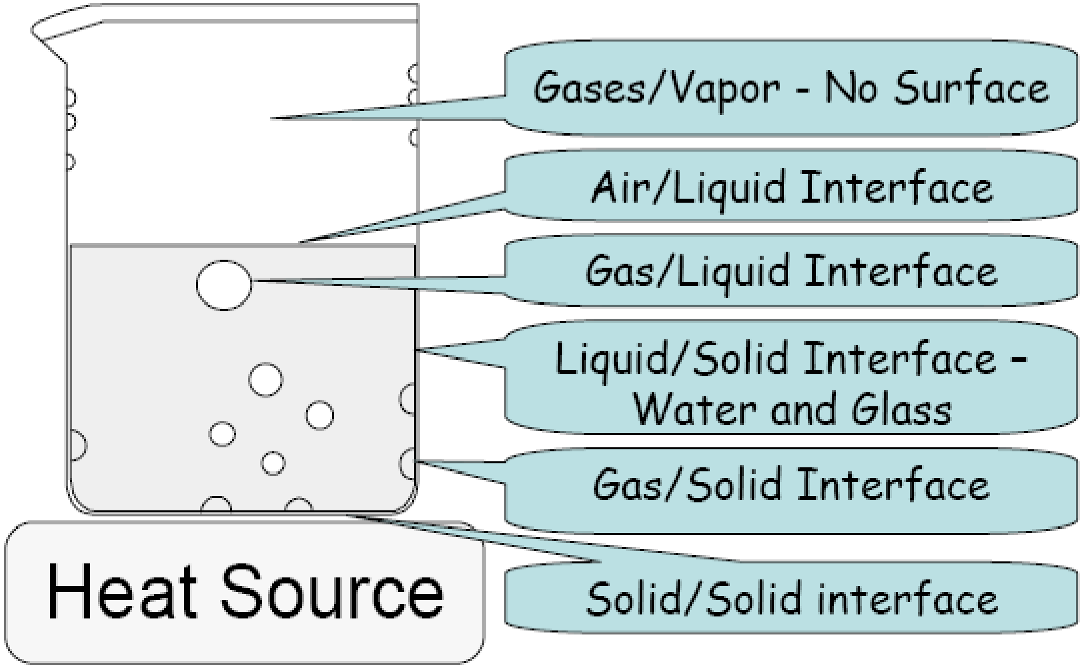
Interfaces

- Substance can exist in any of 3 phases: gas, liquid or solid.
- When two phases meet, **the boundary** between them is called **an interface**

Terminology

- Only the boundary between non-gaseous phases and vacuum can be named as a surface.
- The boundary between liquid or solid phase and their vapors can be approximated as surface.
- In other cases, the boundary is an interface.
- How many surfaces / interfaces are there between the kettle of water and the heater ??

- Where are the surfaces?
- What kind of surfaces are they?



Gases/Vapor - No Surface

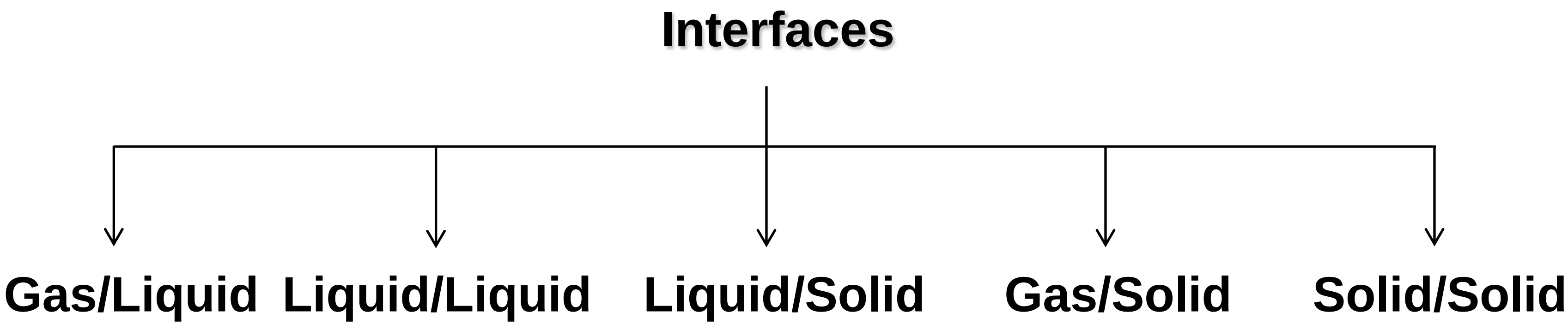
Air/Liquid Interface

Gas/Liquid Interface

Liquid/Solid Interface – Water and Glass

Gas/Solid Interface

Solid/Solid interface



Interfaces

Gas/Liquid **Liquid/Liquid** **Liquid/Solid** **Gas/Solid** **Solid/Solid**

Gas/Liquid

- **Bubbles/Foam**
- **Surfactants**
- **Adsorption**
- **Liquid Crystals**
- **Insoluble monolayers**

Liquid/Liquid

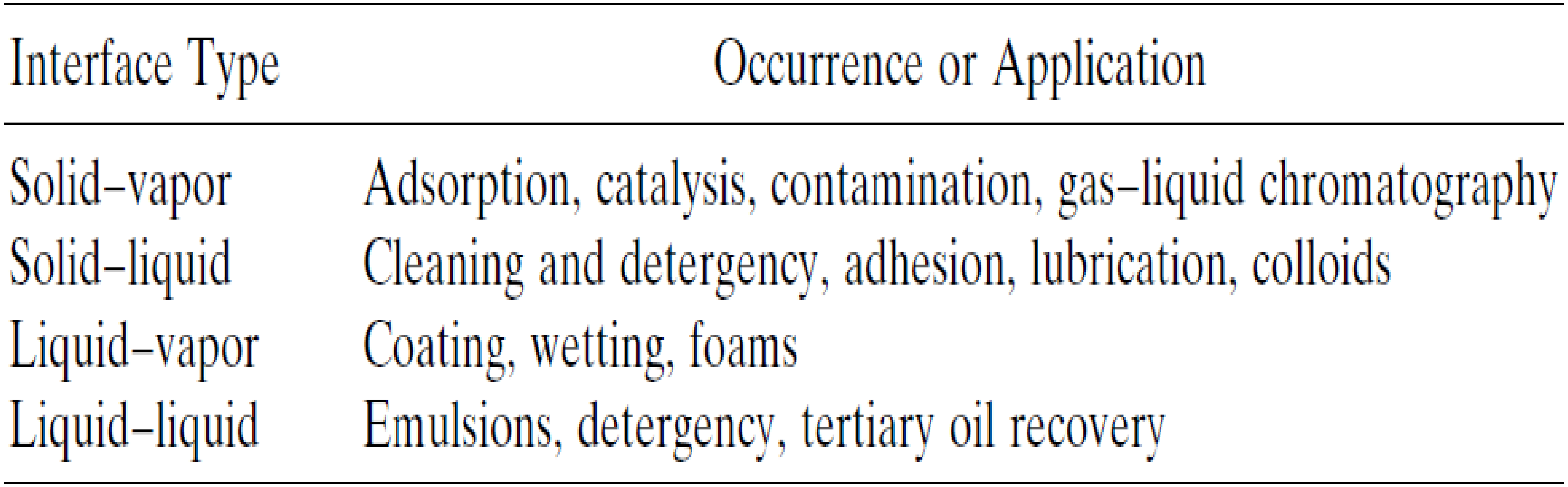
- **Emulsions**
- **Detergency**
- **Reverse Micelles**
- **Aerosols**

Direct Application of Surface and Colloidal Phenomena

Lubrication
Adhesion
Foams
Wetting and waterproofing
Control of rheological properties
Emulsions
Emulsion and dispersion polymerization
Drilling muds
Electrophoretic deposition

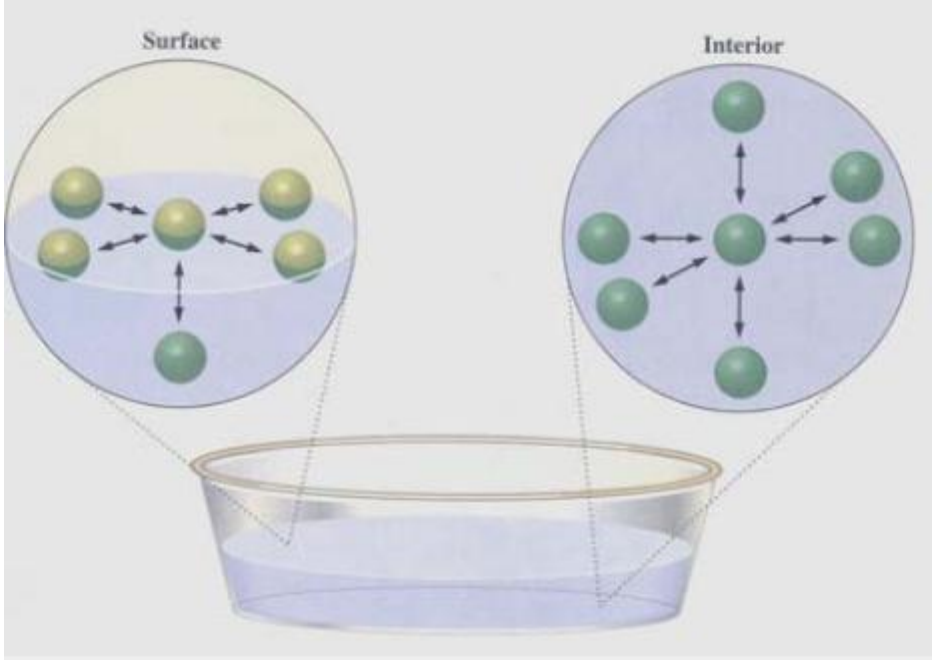
Physiological Applications

Respiration
Joint lubrication
Capillary phenomena in liquid transport
Arteriosclerosis
Blood transport
Emulsification of nutrients
Enzymes
Cell membranes



Interface Type	Occurrence or Application
Solid–vapor	Adsorption, catalysis, contamination, gas–liquid chromatography
Solid–liquid	Cleaning and detergency, adhesion, lubrication, colloids
Liquid–vapor	Coating, wetting, foams
Liquid–liquid	Emulsions, detergency, tertiary oil recovery

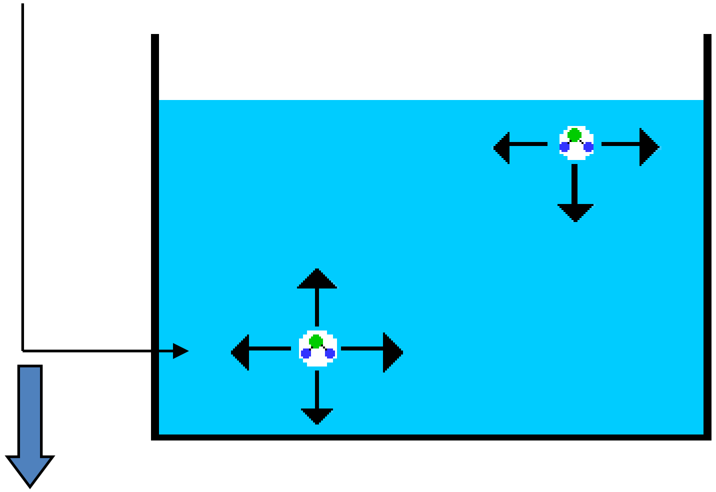
What is the difference?



So What?

A water molecule deep within the liquid is pulled equally from all sides

A water molecule at the surface lacks neighbouring water molecules (toward the interface)



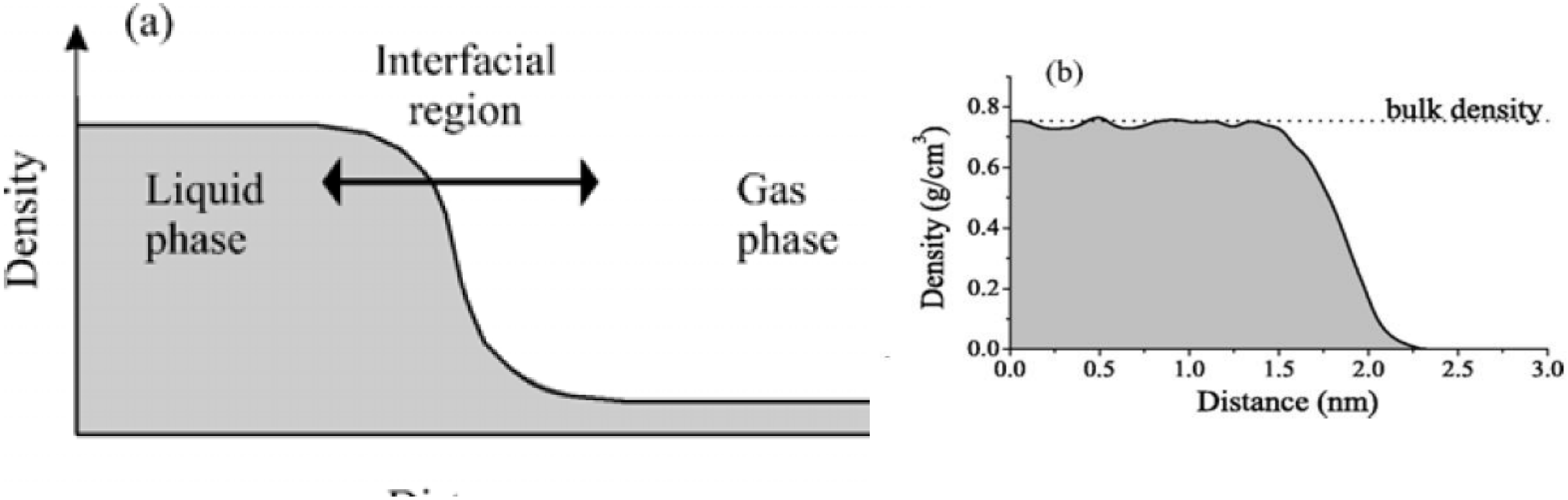
net force is not zero!

net force = zero

- This unequal attraction causes the water at the air-water interface to act as a cohesive surface.
- and the liquid to shrink to the smallest possible surface area.

Microscopic picture of the liquid surface

- A surface is not an infinitesimal sharp boundary in the direction of its normal, but it has a certain thickness.
- For example, if we consider the density ρ normal to the surface we can observe that, within a few molecules, the density decreases from that of the bulk liquid to that of its vapour



Density of a liquid versus the coordinate normal to its surface: (a) is a schematic plot

(b) results from molecular dynamics simulations of *n*-tridecane ($C_{13}H_{28}$) at 27° C

Tridecane is practically not volatile.
For this reason the density in the vapour phase is negligible.

- When two phases are in contact, there is a transition region of molecular dimensions in which the composition of the system changes from that of one phase to that of the other.

- In the case of a non volatile molecularly smooth solid surface in contact with an inert gas, the transition r egion will be essentially one molecule in thickness.

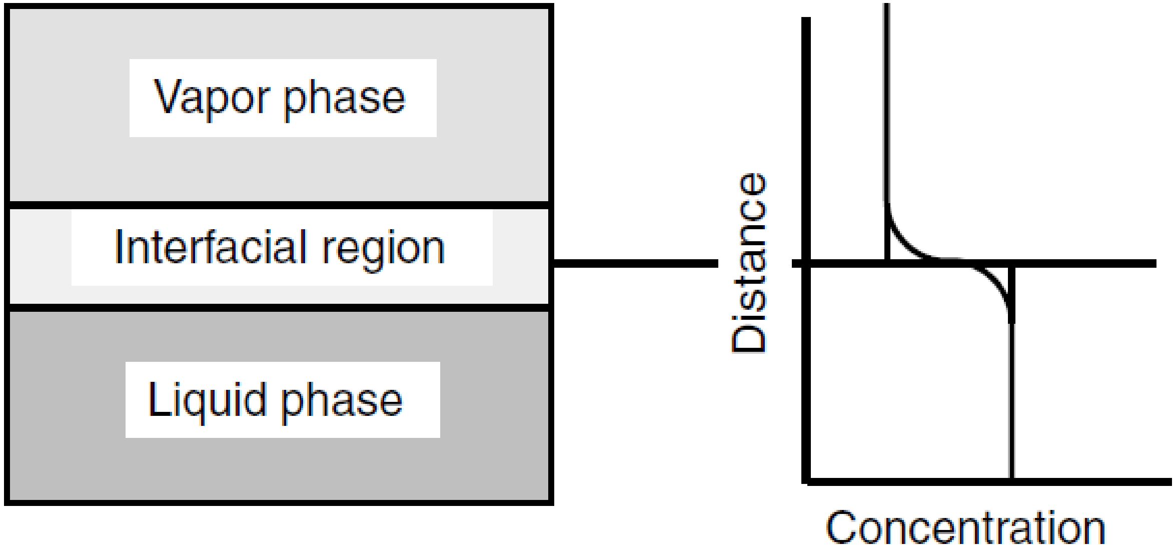
- Thus, there will be a sharp boundary at which the composition will change abruptly from molecules of the solid to molecules of the gas.

- For a pure liquid in contact with its vapour, the transition will be much less abrupt, going from a molecular density corresponding to the bulk material,through a zone where the unit concentration gradually decreases until the density reaches that of the pure vapour.

- In such a case, the transition region may be found to be several unit diameters thick.

- At a mixed liquid–vapuor interface, each component will have its own concentration profile depending on such factors as volatility and miscibility.

- For example, the vapor region directly adjacent to the liquid phase may have a higher concentration of liquid phase units which then decreases (relative to other vapor-phase components) with distance from the interface.



- The density is only one criterion to define the thickness of an interface. Another possible parameter is the orientation of the molecules.

- For example, water molecules at the surface prefer to be oriented with their negative sides “out” towards the vapor phase.

- This orientation fades with increasing distance from the surface.

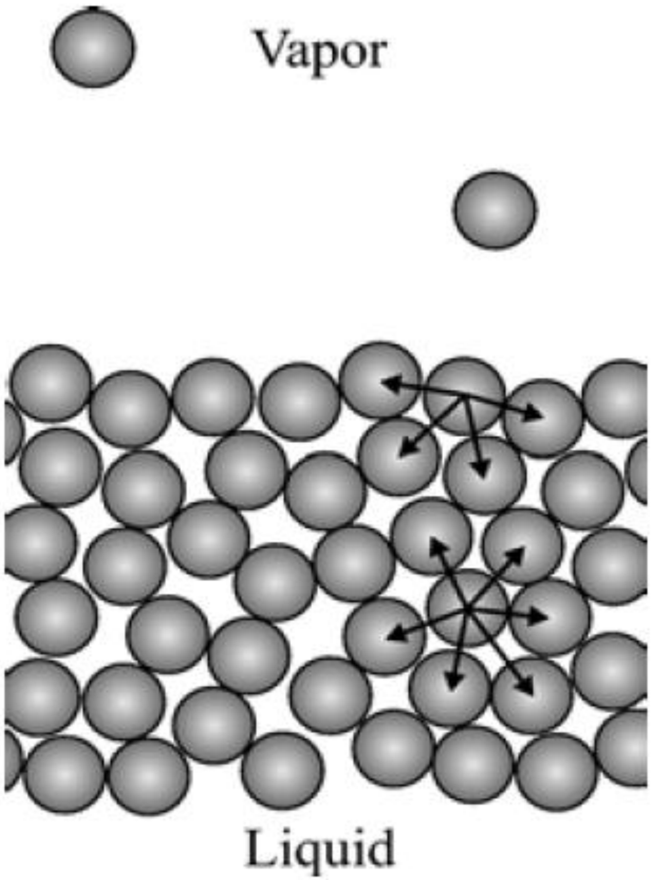
- At a distance of 1–2 nm the molecules are again randomly oriented.

Which thickness do we have to use?

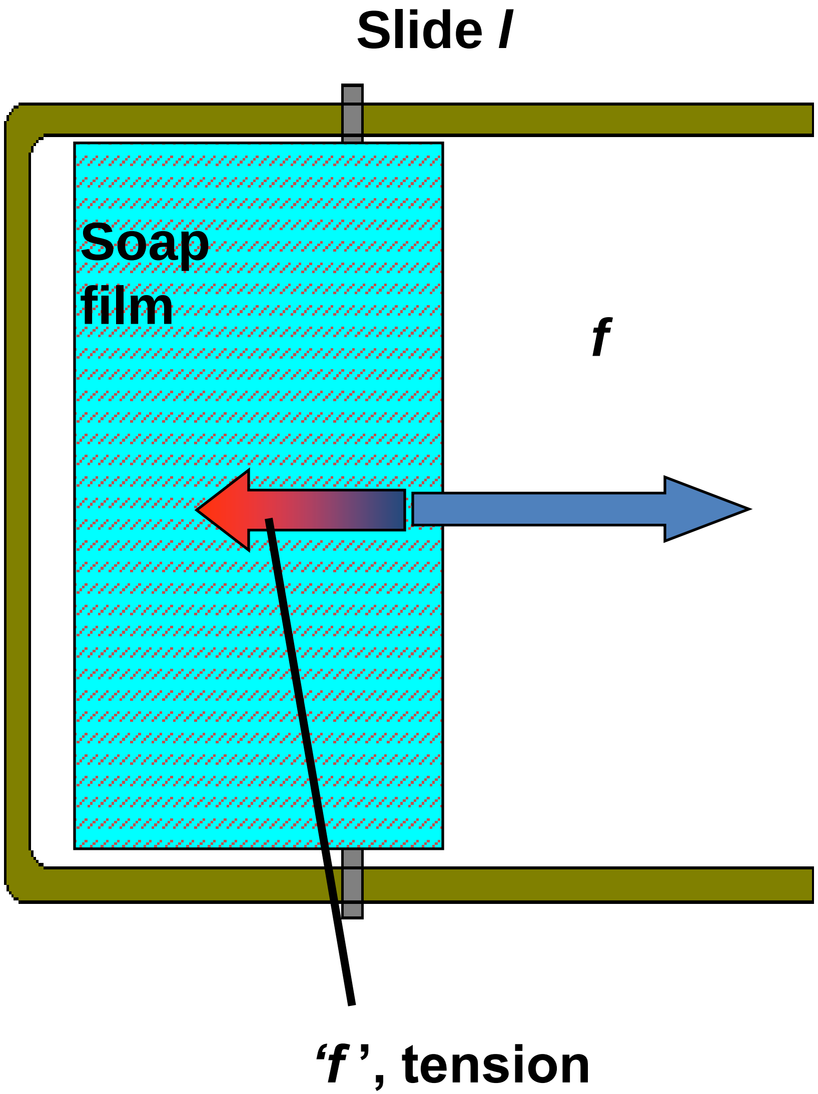
- This depends on the relevant parameter.
- If we are for instance, interested in the density of a water surface, a realistic thickness is in the order of 1 nm.
- Let us assume that a salt is dissolved in the water. Then t he concentration of ions might vary over a much larger distance (characterized by the Debye length.
- With respect to the ion concentration, the thickness is thus much larger. In case of doubt, it is safer to choose a large value for the thickness.

- The surface of a liquid is a very turbulent place.
- Molecules evaporate from the liquid into the vapor phase and vice versa.
- In addition, they diffuse into the bulk phase and molecules from the bulk diffuse to the surface.
- Typically 10^7 water molecules /s hit a surface area of 10 Å^2.
- In equilibrium the same number of molecules escape from the liquid phase.
- 10 Å^2 is approximately the area covered by one water molecule. Thus, the average time a water molecule remains on the surface is of the order of 0.1 μs

Surface Tension and surface energy



An experimental ‘film’



The soap film contracts spontaneously. To prevent contraction, a force *f* must be applied. If *f* decreases slightly, contraction occurs, and if *f* is increased, the film extends.

This suggests that there exists a force ‘*f*’ that makes the film shrink.

Surface tension manifested in terms of surface force.

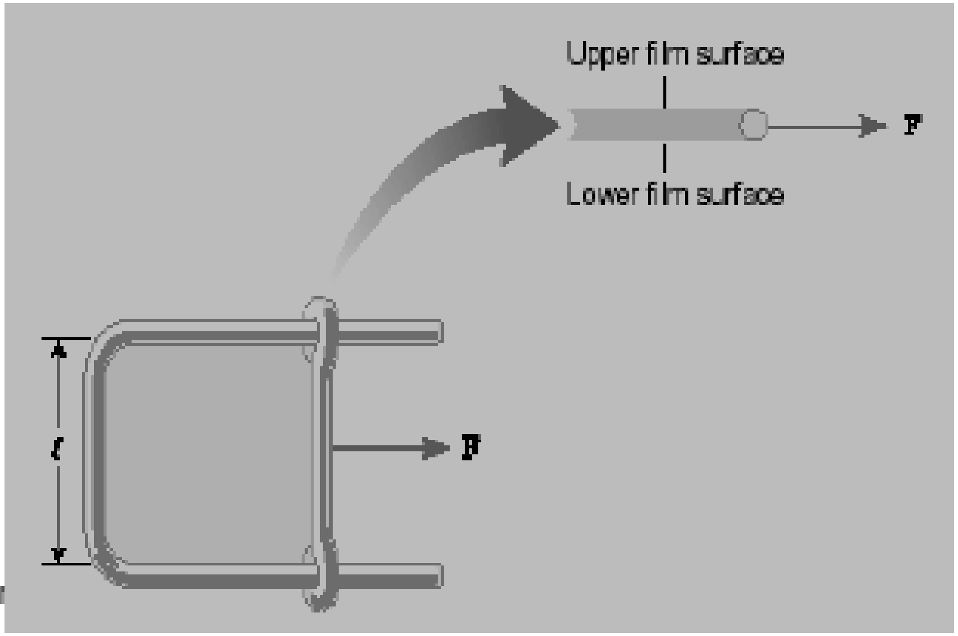
- The surface tension (γ) of the solution film **is a function of the force f** that must be applied to break the film over the length of the movable bar.

- *As a general definition*: Surface tension is the magnitude of the force, exerted parallel to the surface of a liquid, divided by the length L of the line over which it acts.

$$\gamma = f/ L$$

- For the specific case illustrated in this example. There is an upper surface & a lower surface , thus the force acts along a total length of 2 L.

$$\gamma = f/ 2L$$

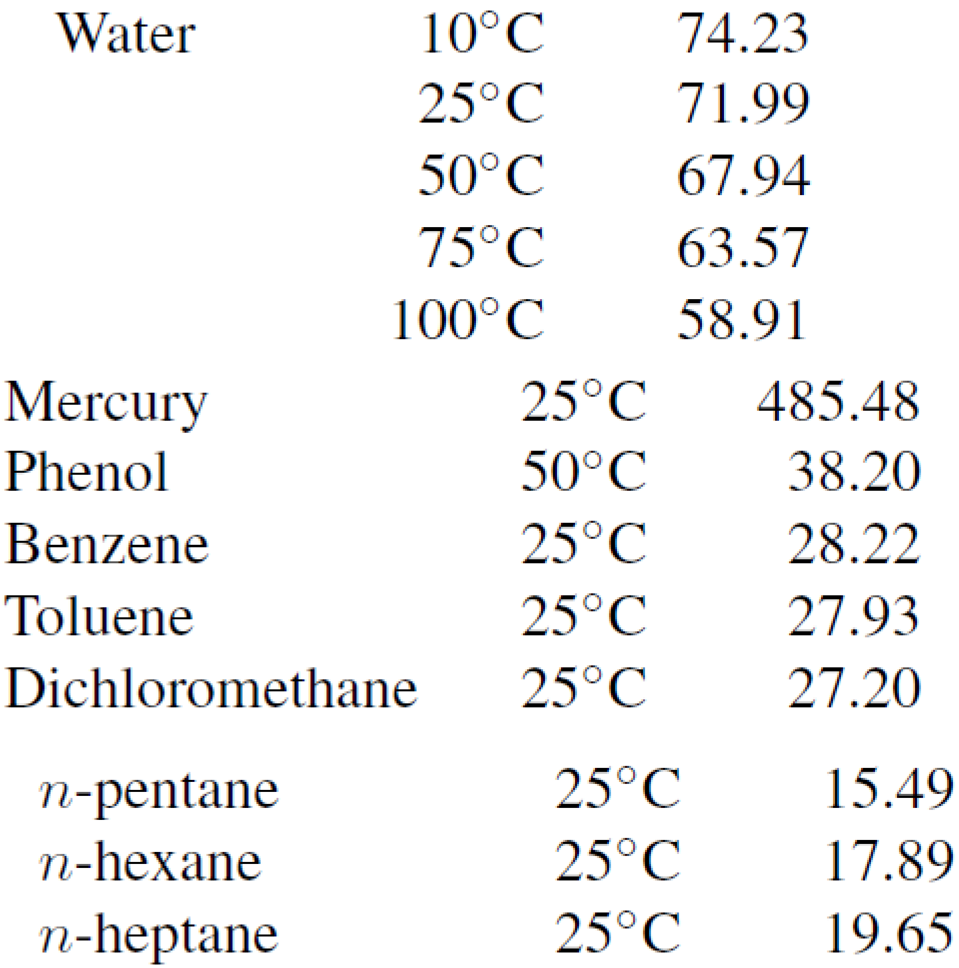


The term “surface tension” is tied to the concept that the surface stays under a tension. In a way, this is similar to a rubber balloon, where also a force is required to increase the surface area of its rubber membrane against a tension.

There is, however, a difference:

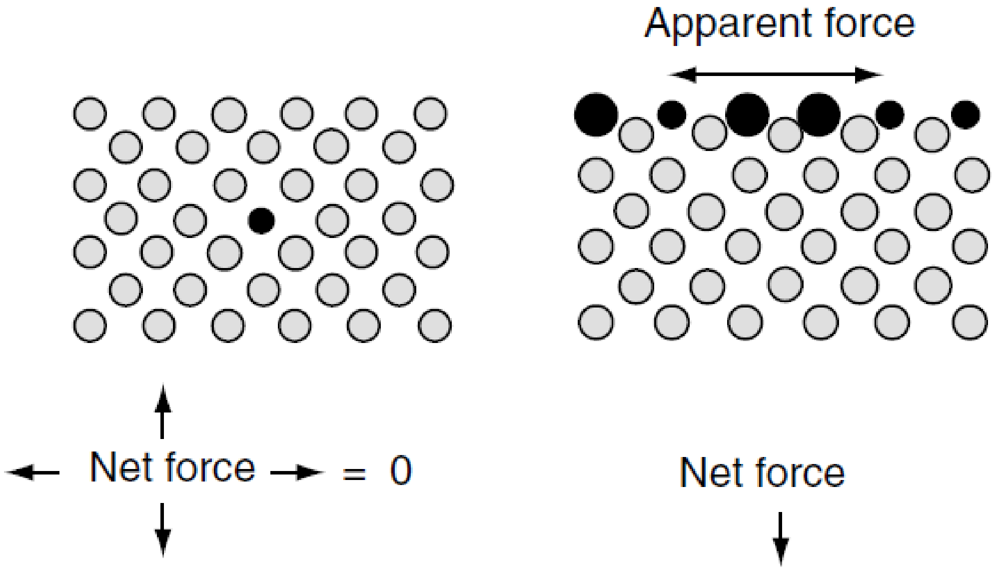
While the expansion of a liquid surface is a plastic process the stretching of a rubber membrane is usually elastic.

Surface tensions γ of some liquids at different temperatures T.



Water	10°C	74.23
	25°C	71.99
	50°C	67.94
	75°C	63.57
	100°C	58.91
Mercury	25°C	485.48
Phenol	50°C	38.20
Benzene	25°C	28.22
Toluene	25°C	27.93
Dichloromethane	25°C	27.20
n-pentane	25°C	15.49
n-hexane	25°C	17.89
n-heptane	25°C	19.65

Surface Energy



At the surface, molecules are only partially surrounded by other molecules and the number of adjacent molecules is small in the bulk (Fig)

This is energetically unfavorable. **Why?**

In order to bring a molecule from the bulk to the surface, work has to be done. With this view *γ* can be interpreted as the energy required to bring molecules from inside the liquid to the surface and to create new surface area. Therefore often the term “surface energy” is used for *γ*.

Estimate the surface tension of cyclohexane from the energy of vaporization $\Delta_{vap}U = 30.5$ kJ/mol at 25°C.
The density of cyclohexane is $\rho = 773$ kg/m and its molecular weight is $M = 84.16$ g/mol.

Assume that in the bulk and at the surface each molecule of the HC is surrounded by six and five nearest neighbors in a cubic arrangement.

Solution

Each molecule is surrounded by 6 nearest neighbors. Thus each bond contributes roughly $\Delta_{vap}U/6$ = 5.08 kJ/mol.

At the surface one neighbor and hence one bond is missing. Therefore we estimate a surface tension equivalent to 5.08 kJ/mol

To estimate the surface tension we need to know the surface area occupied by one molecule.
If the molecules form a cubic structure, the volume of one unit cell is a^3, where a is the distance between nearest neighbors.
This distance can be calculated from the density:

$$\begin{aligned} a^3 &= \frac{M}{\rho N_A} = \frac{0.08416\ \mathrm{kg/mol}}{773\ \mathrm{kg/m^3} \cdot 6.02 \times 10^{23}\ \mathrm{mol^{-1}}} = 1.81 \times 10^{-28}\ \mathrm{m^3} \Rightarrow \\ a &= 0.565\ \mathrm{nm} \end{aligned}$$

The surface area per molecule is a^2. For the surface energy we estimate

$$\gamma = \frac{\Delta_{vap}U}{6N_A a^2} = \frac{5080\ \mathrm{Jmol^{-1}}}{6.02 \times 10^{23}\ \mathrm{mol^{-1}} \cdot (0.565 \times 10^{-9}\ \mathrm{m})^2} = 0.0264\ \frac{\mathrm{J}}{\mathrm{m^2}}$$

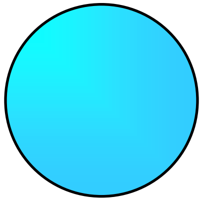
Experimental value = 0.0247 J/m^2

- The units for surface tension and specific excess surface free energy are dimensionally equivalent and, for a pure liquid in equilibrium with its vapor, numerically equal

- For two pure, mutually immiscible liquids having a common flat interface we can define the terms ‘‘interfacial tension’’ and ‘‘excess interfacial free energy,’’ based on the same concepts used for the liquid–vapor systems

Curved surfaces and additional pressure

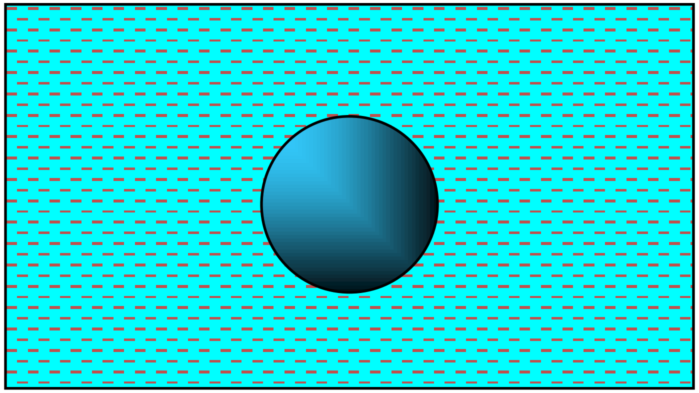
Curved liquid surface



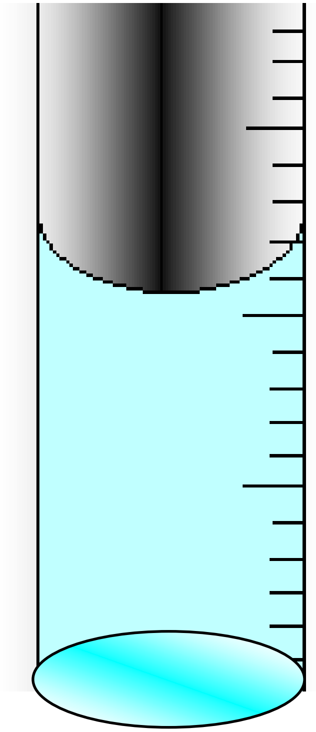
Drop

Convex
surface

Concave surface



Bubble



Pipette

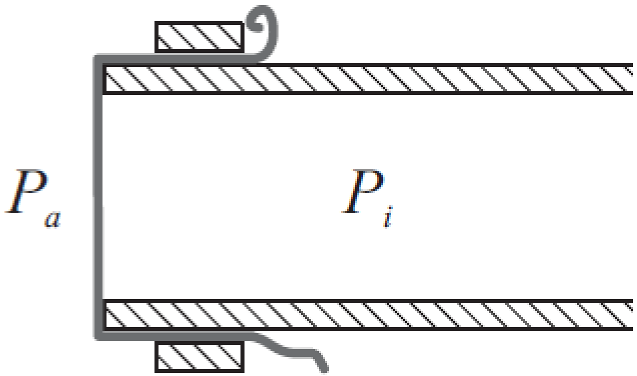
Curved liquid surfaces

- If in equilibrium a liquid surface is curved, there is a pressure difference across it.In order to curve the surface, the pressure on one side must be larger than on the other side.

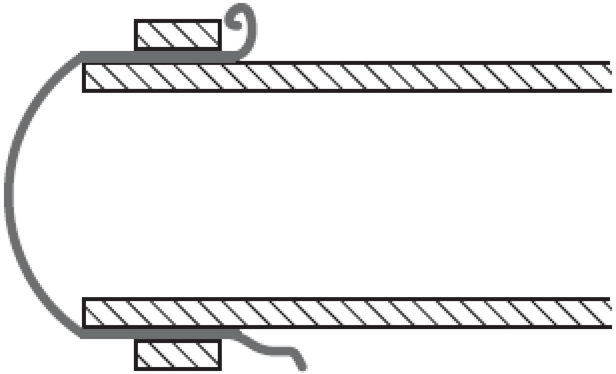
- For instance, take a tube and close one end with a rubber membrane, the membrane will be planar (provided the membrane is under some tension).It will remain planar as long as the tube is open at the other end and the pressure inside the tube is equal to the outside pressure.

- If we now blow carefully into the tube, the membrane bulges out and becomes curved due to the increased pressure inside the tube.

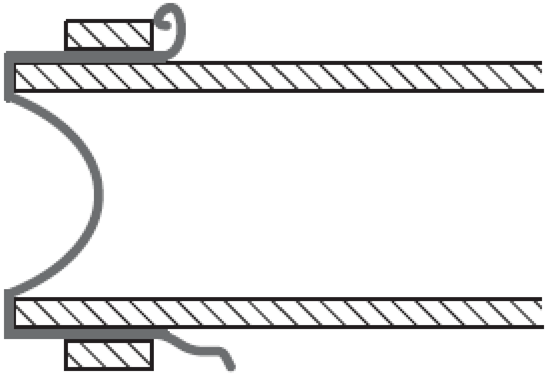
- If we suck on the tube, the membrane bulges inside the tube because now the outside pressure is higher than the pressure inside the tube.



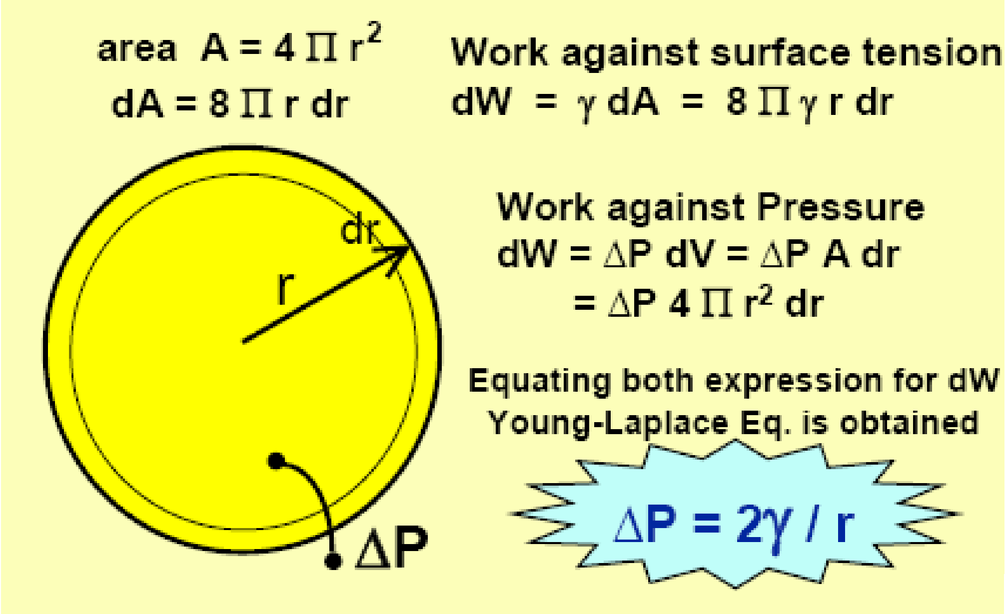
$P_a = P_i$



$P_a < P_i$



$P_a > P_i$



area $A = 4 \Pi r^2$

$dA = 8 \Pi r \, dr$

Work against surface tension

$dW = \gamma \, dA = 8 \Pi \gamma r \, dr$

Work against Pressure

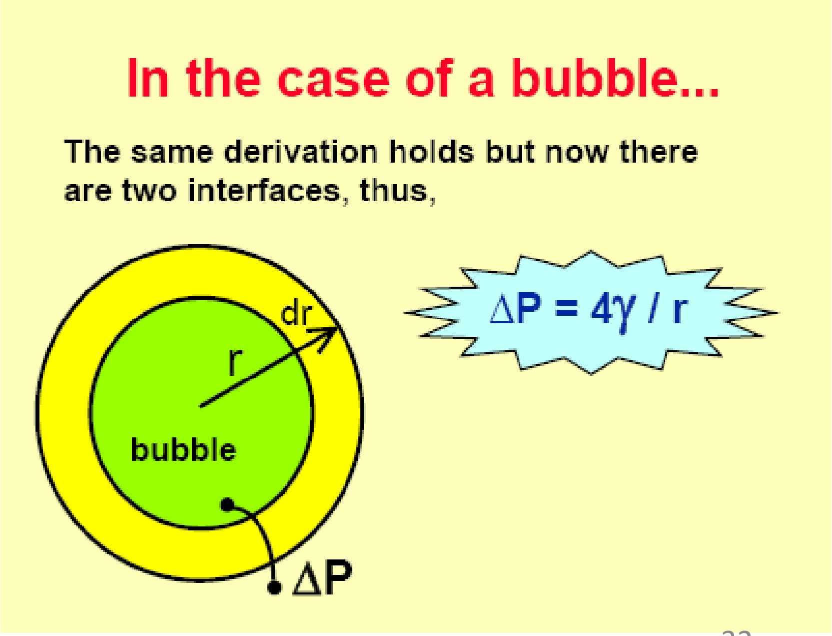
$dW = \Delta P \, dV = \Delta P \, A \, dr$

$= \Delta P \, 4 \Pi r^2 \, dr$

Equating both expression for dW

Young-Laplace Eq. is obtained

$$\Delta P = 2\gamma / r$$



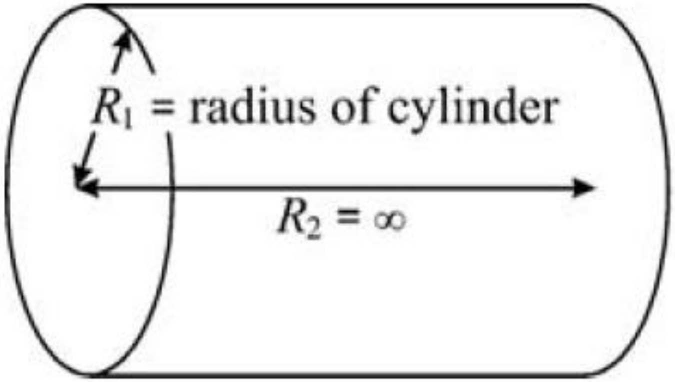
In the case of a bubble...

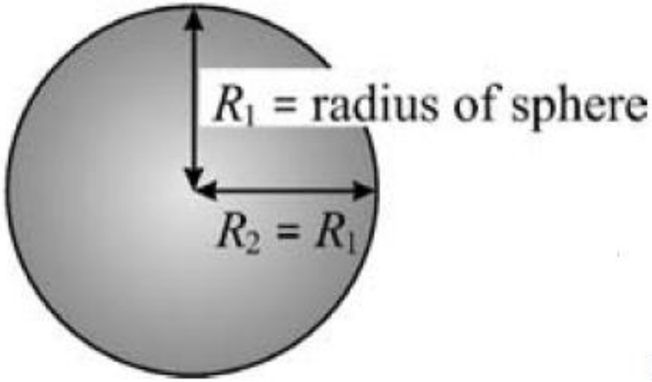
The same derivation holds but now there are two interfaces, thus,

$$\Delta P = 4\gamma / r$$

The Young–Laplace equation relates the pressure difference between the two phases ΔP and the curvature of the surface

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



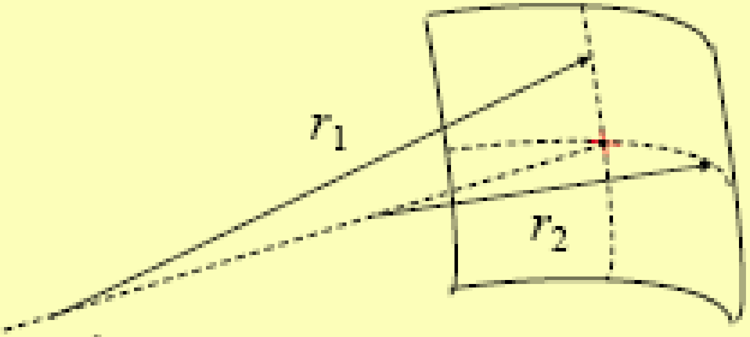


For a cylinder of radius r a convenient choice is $R_1 = r$ and $R_2 = \infty$ so that the curvature is $1/r + 1/\infty = 1/r$.
For a sphere with radius R , $R_1 = R_2$ and the curvature is $1/R + 1/R = 2/R$

Generalized Young-Laplace Eqn.

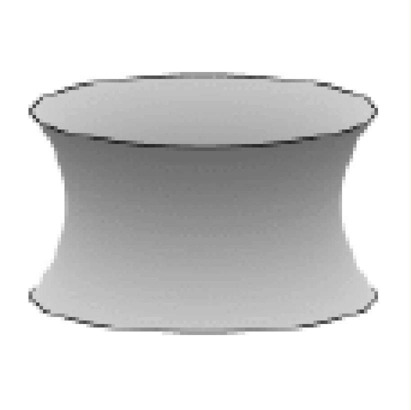
$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$or \;\; \Delta P = \gamma 2H$$



$$H = mean\ curvature = \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Shape	r_1	r_2	ΔP
Sphere	r	r	$2\gamma/r$
Plane	∞	∞	0
Cylinder	r	∞	γ/r
Saddle point	r	$-r$	0



How large is the pressure in a spherical bubble with a diameter of 2 mm and a bubble of 20 nm diameter in pure water, compared with the pressure outside?

Solution :

For a bubble the curvature is identical to that of a sphere: $R_1 = R_2 = R$. Therefore,

$$\Delta P = \frac{2\gamma}{R} \qquad \text{With } R = 1\ \text{mm}$$

$$\Delta P = 0.072\ \frac{\text{J}}{\text{m}^2} \times \frac{2}{10^{-3}\text{m}} = 144\ \text{Pa}$$

With $R = 10$ nm

$$\Delta P = 0.072\ \text{J/m}^2 \times 2/10^{-8}\,\text{m} = 1.44 \times 10^7\ \text{Pa}$$

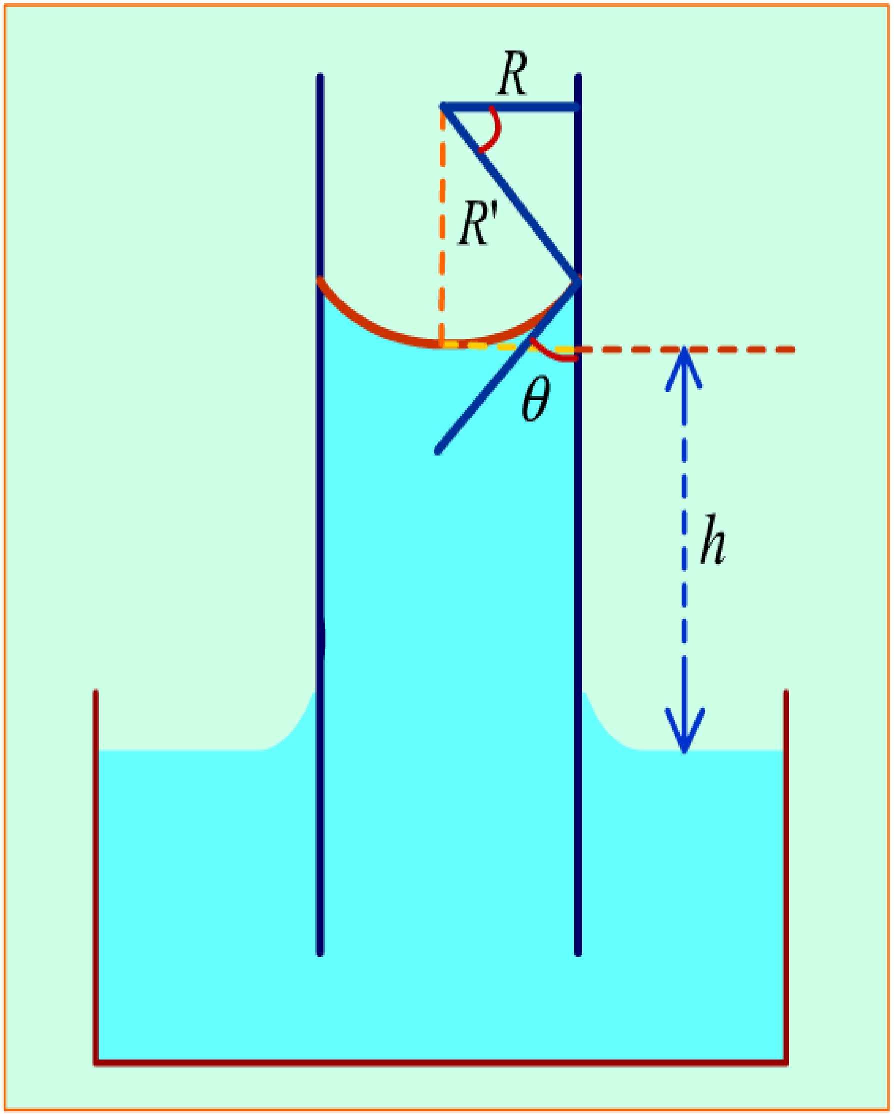
$$= 144\ \text{bar.}$$

Capillary rise

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

$$R = R' \cos\theta$$

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



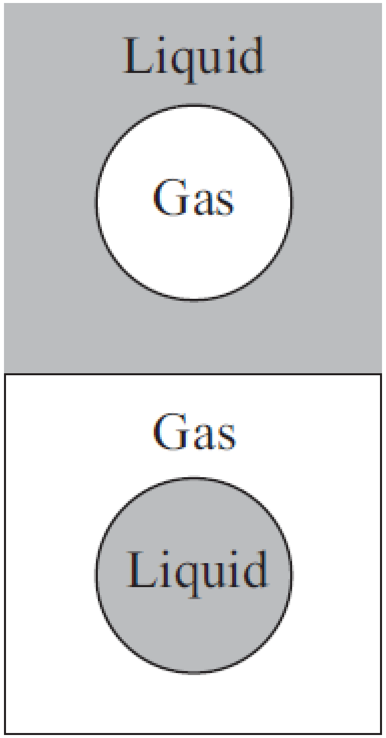
Some implications of capillary rise

Water travels through trunk from roots to leaves by capillarity.

Pen deliveries ink from the tube to the tip by capillarity.

Lamp burns the alcohol which is supplied by the capillary action of the wick.

When applying the equation of Young and Laplace to simple geometries it is usually obvious at which side the pressure is higher. For example, both inside a bubble and inside a drop, the pressure is higher than outside.



For a drop in a gaseous environment, the two principal curvatures are positive and given by $C_1 = C_2 = 1/R$.
The pressure difference is positive, which implies that the pressure inside the liquid is higher than outside.

For a bubble in a liquid environment the two principal curvatures are negative: $C_1 = C_2 = -1/R$. The pressure difference is negative and the pressure inside the liquid is lower than inside the bubble

The Kelvin equation

- The subject of the Kelvin equation is when the liquid surface is curved, the vapor pressure changes.
- The vapor pressure of a drop is higher than that of a flat, planar surface.
- In a bubble the vapor pressure is reduced.
- The Kelvin equation tells us how the vapor pressure depends on the curvature of the liquid.

$$RT \cdot \ln \frac{P_0^{\mathrm{K}}}{P_0} = \gamma V_m \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

Drop in its vapor

- The vapor pressure of a drop is higher than that of a liquid with a planar surface.
- One consequence is that an aerosol of drops (fog) should be unstableLet us assume that we have a box filled with many drops in a gaseous environment.
- Some drops are larger than others.
- The small drops have a higher vapor pressure than the large drops.Hence, more liquid evaporates from their surface. This tends to condense into large drops.
- Within a population of drops of different sizes, the bigger drops will grow at the expense of the smaller ones — a process called Ostwald ripening6. These drops will sink down and, at the end, bulk liquid fills the bottom of the box.

- For a given vapor pressure, there is a critical drop size. Every drop bigger than this size will grow.Drops at a smaller size will evaporate.

- If a vapor is cooled to reach over-saturation, it cannot condense (because every drop would instantly evaporate again), unless nucleation sites are present. In that way it is possible to explain the existence of over-saturated vapors and also the undeniable existence of fog.

Bubble in a liquid

A negative sign has to be used for a bubble because of the negative curvature of the liquid surface.

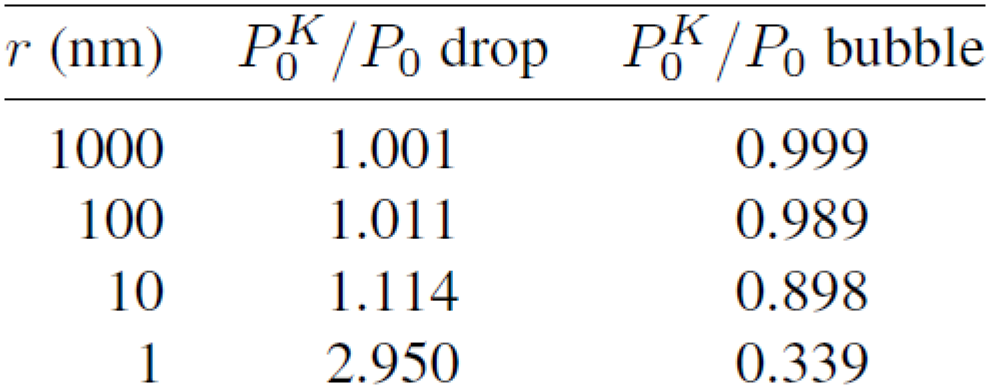
As a result we get,

$$RT \cdot \ln \frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r}$$

The vapor pressure inside a bubble is therefore reduced.

This explains why it is possible to overheat liquids:

When the temperature is increased above the boiling point (at a given external pressure) occasionally, tiny bubbles are formed. Inside the bubble the vapor pressure is reduced, the vapor condenses, and the bubble collapses.Only if a bubble larger than a certain critical size is formed, is it more likely to increases in size rather than to collapse.



r (nm)	P_0^K/P_0 drop	P_0^K/P_0 bubble
1000	1.001	0.999
100	1.011	0.989
10	1.114	0.898
1	2.950	0.339

Relative equilibrium vapour pressure of a curved water surface at 25 °C for spherical drops and bubbles of radius *r*.

Nucleation theory

The formation of a new phase in the absence of an external surface is called homogeneous nucleation.
Homogeneous nucleation first small clusters of molecules are formed. These clusters grow due to the condensation of other molecules. In addition, they aggregate to form larger clusters.
Finally macroscopic drops form.
Usually this happens only if the vapor pressure is significantly above the saturation vapor pressure.
In most practical situations we encounter heterogeneous nucleation, where a vapor condenses onto a surface such as a dust particle.

In order to describe nucleation, we calculate the change in the Gibbs free energy for the condensation of *n* moles vapour at a vapour pressure *P* :

we first consider $G_L - G_V$.

Here, G_L = Gibbs free energy of the liquid drop

G_V = Gibbs free energy of the corresponding number of molecules in the vapour phase.

G_V is given by,

$G_V = nG_0 + nRT$ (ln P assuming that the vapour behaves as an ideal gas)

To calculate G_L we use the fact that it is equal to the Gibbs free energy of a (hypothetical) vapour, which is in equilibrium with the liquid drop. This hypothetical vapour has a pressure Po^K and its Gibbs free energy is

$$G_L = G_V^{hypothetical} = nG^0 + nRT \cdot \ln P_0^K$$

Since the drops have a curved surface of radius *r* the vapor pressure $P^{K\,0}$ is higher than that of the flat liquid surface. Thus, the difference in the Gibbs energies is

$$G_L - G_V = nRT \cdot \ln P_0^K - nRT \cdot \ln P = -nRT \cdot \ln \frac{P}{P_0^K}$$

This, however, is not the whole energy difference.
In addition, the drop has a surface tension which has to be considered.

The total change in the Gibbs free energy is

$$\Delta G = -nRT \cdot \ln \frac{P}{P_0^K} + 4\pi\gamma r^2$$

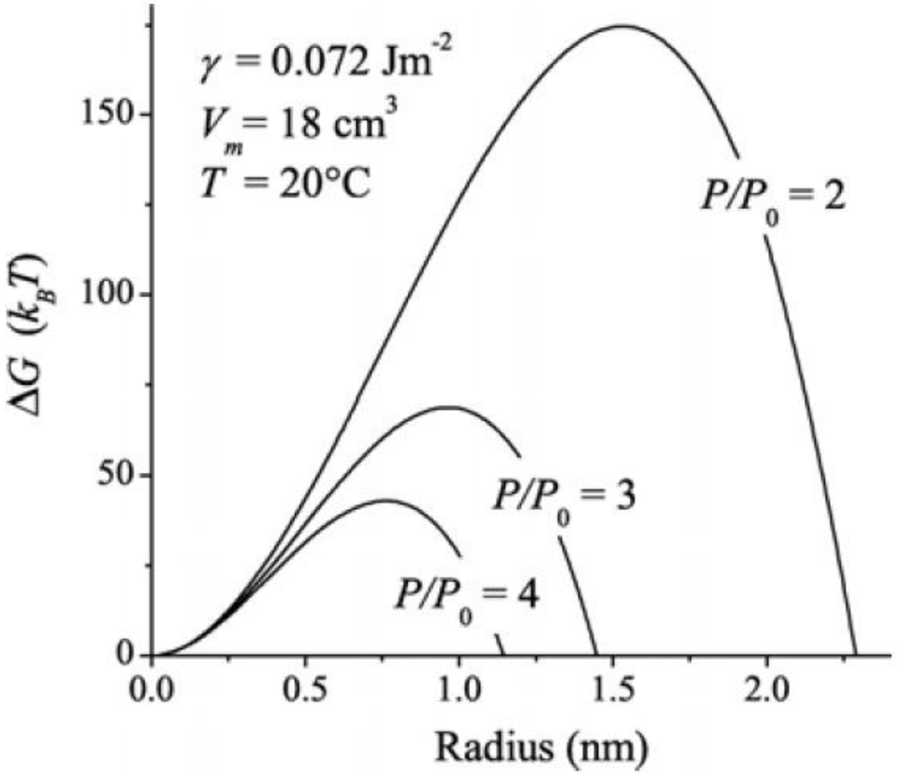
In a drop of radius r there are $n = 4\pi r^3/3V_m$ moles of molecules, where V_m is the molar volume of the liquid phase. Inserting leads to

$$\Delta G = -\frac{4\pi RTr^3}{3V_m} \cdot \ln \frac{P}{P_0^K} + 4\pi\gamma r^2$$

This is the change in Gibbs free energy upon condensation of a drop from a vapor phase with partial pressure P.

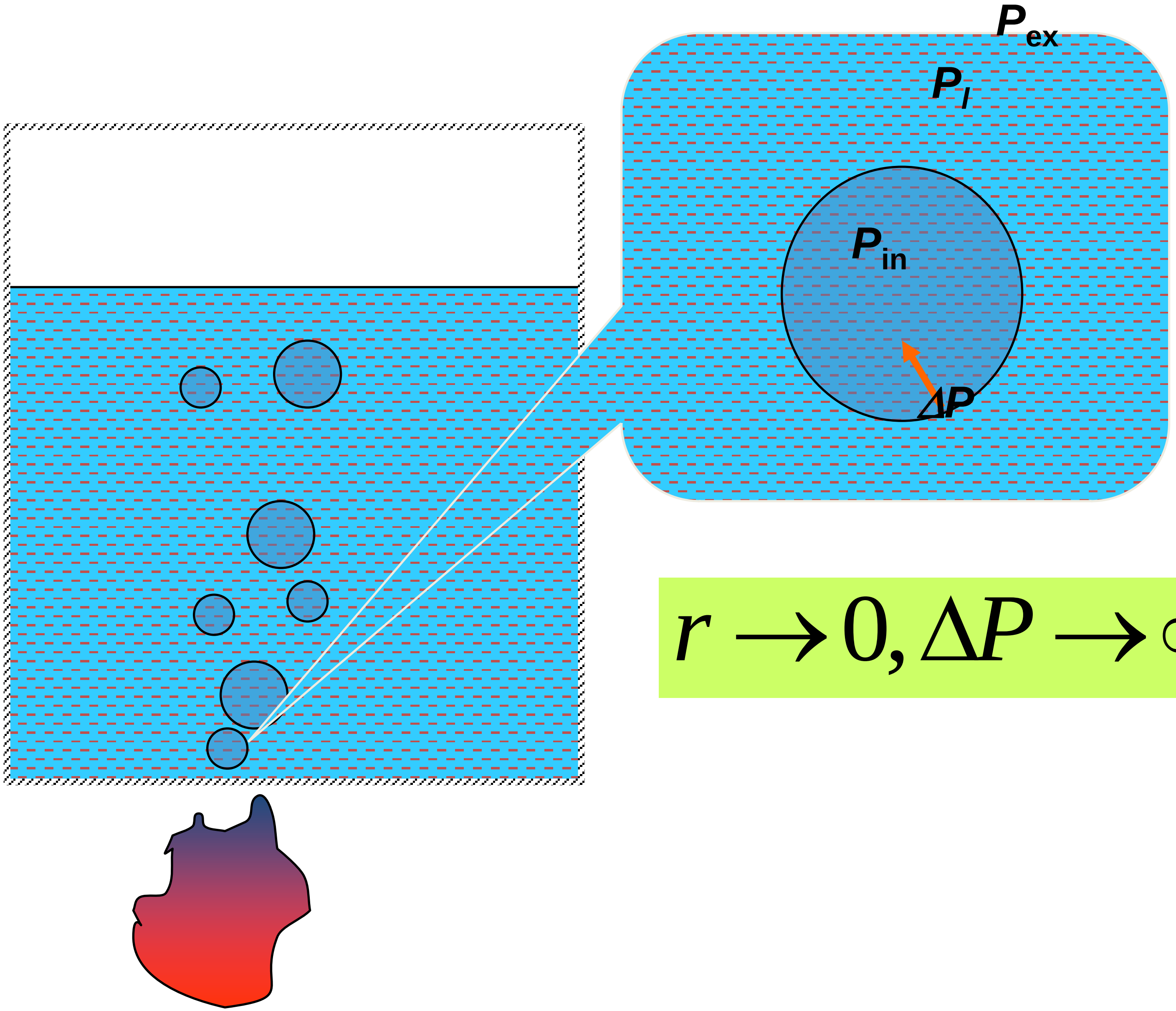
Any drop, which is formed by randomly clustering molecules will evaporate again.
No condensation can occur.
For $P > PK$ 0 , ΔG increases with increasing radius, has a maximum at the so-called critical radius $r*$ and then decreases again.
At the maximum we have $d\Delta G/dr = 0$, which leads to a critical radius of

$$r^* = \frac{2V_m\gamma}{RT \cdot \ln\left(P/P_0^K\right)}$$



For water at $T = 0^\circ$C and a supersaturation $P/P^0 = 4$,
the critical radius is $R* = 8$ Å.
This corresponds approximately to 70 molecules.
There $\Delta G_{max} = 1.9 \times 10^{-19}$ J.

Superheated liquid



$$r \rightarrow 0, \Delta P \rightarrow \infty$$

Superheating

.

$$\frac{1}{T} - \frac{1}{T_0} = -\frac{R}{\Delta H_v} \ln\left(1 - \frac{2\sigma}{rP_0}\right)$$

Thomson Equation

The smaller the bubble, the higher the boiling temperature.

For water with air bubble with diameter of 10^{-6} meter as seed, it boils at 123 °C.

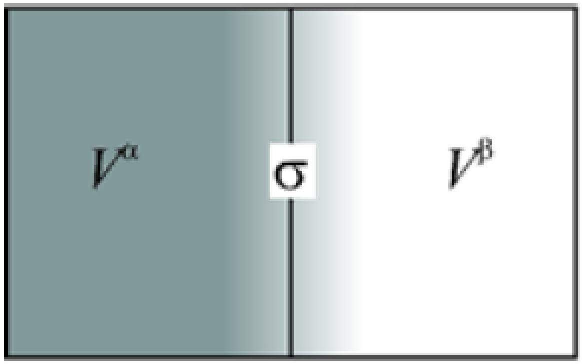
Once the bubble of relative large diameter formed, the evaporation would proceed in a vigorous manner.

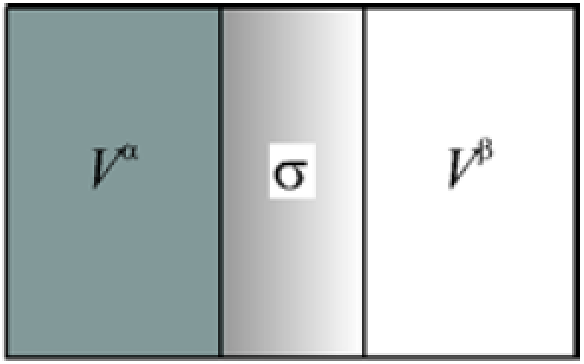
Surface Excess

The presence of an interface influences generally all thermodynamic parameters of a system.

To consider the thermodynamics of a system with an interface, we divide that system into three parts:

The two bulk phases with volumes $V\alpha$ and $V\beta$, and the interface σ.





In the Gibbs model the interface is ideally thin ($V^\sigma = 0$) and the total volume is

$$V = V^\alpha + V^\beta$$

All other extensive quantities can be written as a sum of three components:
one of bulk phase α, one of bulk phase β, and one of the interfacial region σ.
Examples are the internal energy U, the number of molecules of the ith substance N_i, and the entropy S:

$$U = U^{\alpha} + U^{\beta} + U^{\sigma}$$

$$N_i = N_i^{\alpha} + N_i^{\beta} + N_i^{\sigma}$$

$$S = S^{\alpha} + S^{\beta} + S^{\sigma}$$

The contributions of the two phases and of the interface are derived as follows.
Let u_{α} and u_{β} be the internal energies per unit volume of the two phases.
The internal energies $u\alpha$ and $u\beta$ are determined from the homogeneous bulk regions of the two phases.
Close to the interface they might be different.
Still, we take the contribution of the volume phases to the total energy
of the system as $u\alpha V\alpha + u\beta V\beta$. The internal energy of the interface is

$$U^\sigma = U - u^\alpha V^\alpha - u^\beta V^\beta$$

At an interface, the molecular constitution changes.
The concentration (number of molecules per unit volume) of the i^{th} material is, in the two phases, respectively *cαi*
and *cβi* .
The additional quantity that is present in the system due to the interface is

$$N_i^\sigma = N_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta$$

With the above equation it is possible to define something like a surface concentration, the so called **interfacial excess**

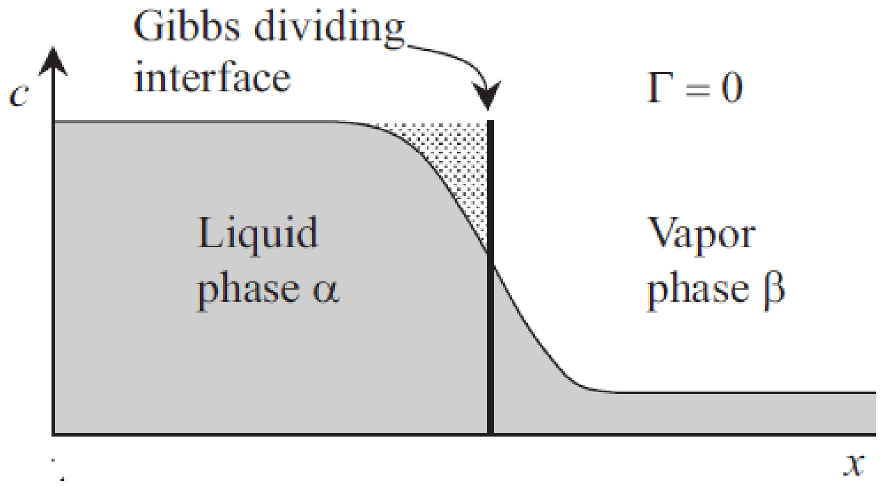
$$\Gamma_i = \frac{N_i^\sigma}{A}$$

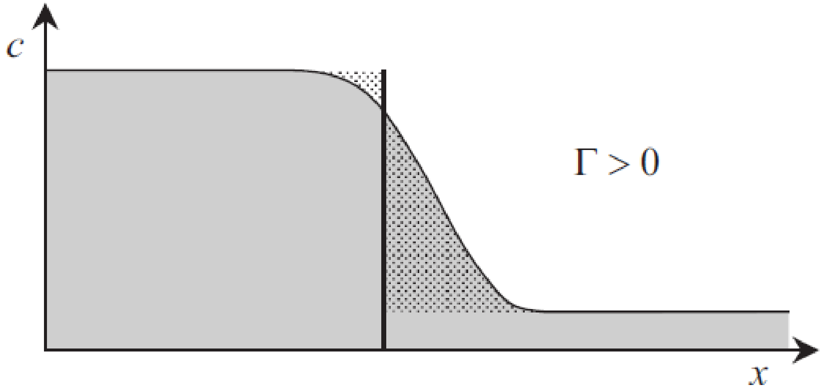
In the Gibbs model of an ideal interface there is one problem: where precisely do we position the ideal interface?

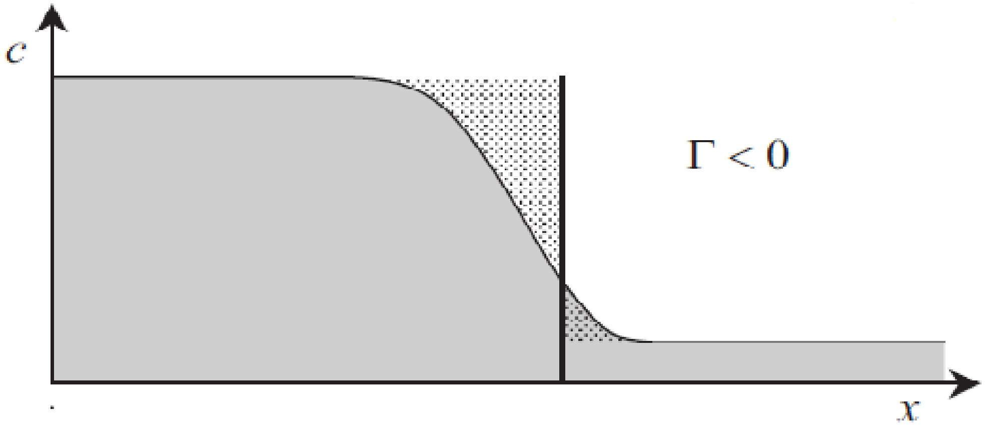
Let us therefore look at a liquid–vapor interface of a pure liquid

more closely.

The density decreases continuously from the high density of the bulk liquid to the low density of the bulk vapor


Gibbs dividing interface
c
Γ = 0
Liquid phase α
Vapor phase β
x


c
Γ > 0
x


c
Γ < 0
x

It is natural to place the ideal interface in the middle of the interfacial region so that $\Gamma = 0$.
In this case the two dotted regions, left and right from the ideal interface, are equal in size.
If the ideal interface is placed more into the vapor phase the total number of molecules extrapolated from the bulk densities is higher than the real number of molecules

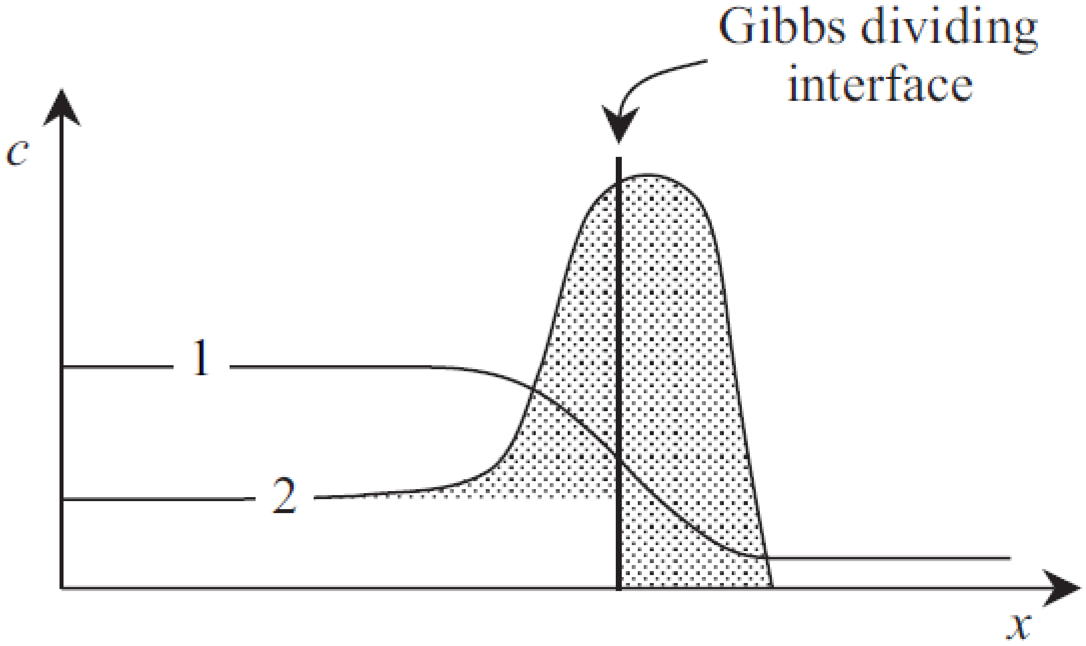
$N < c\alpha$
$V \alpha + c\beta V \beta$.
Therefore the surface excess is negative.

Vice versa:
if the ideal interface is placed more into the liquid phase, the total number of molecules extrapolated from the bulk densities is lower
than the real number of molecules
$N > c\alpha V \alpha + c\beta V \beta$, and the surface excess is positive

Let us consider a two- or multi-component liquids such as a solvent with dissolved substances.
Substituting $V\alpha = V - V\beta$ we can write

$$N_1^\sigma = N_1 - c_1^\alpha V + \left(c_1^\alpha - c_1^\beta\right) V^\beta$$

The first component which is taken to be the solvent.
For all other components we get similar equations


Gibbs dividing
interface
c
1
2
x

Gibbs energy and definition of the surface tension

$$dG = -SdT + V^\alpha dP^\alpha + V^\beta dP^\beta + \sum \mu_i dN_i + \gamma dA$$

$$dG = -SdT + VdP + \sum \mu_i dN_i + \gamma dA$$

What have we assumed here?

$$\left.\frac{\partial G}{\partial A}\right|_{T,P,N_i} \equiv \gamma$$

The surface tension of pure liquids

For pure liquids the description becomes much simpler.
We start by asking, how is the surface tension related to the surface excess quantities, in particular to the internal energy?

For pure liquids we choose the Gibbs dividing plane such that Γ = 0.
Then the surface tension is equal to the free surface energy per unit area

$$f^{\sigma} = \frac{F^{\sigma}}{A} = \gamma$$

Gibbs adsorption isotherm

It is well known that the surface tension of water decreases when a detergent is added.

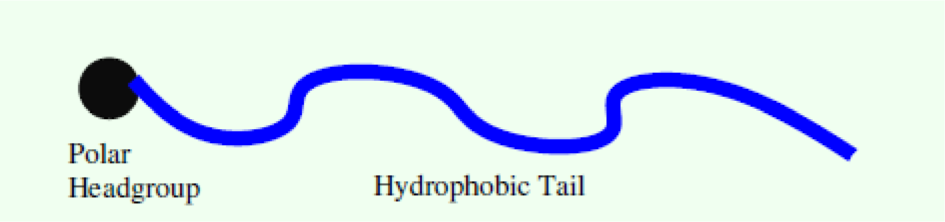
Detergents are strongly enriched at the surface, which lowers the surface tension.

This change of surface tension upon adsorption of substances to the interface, is described by the Gibbs adsorption isotherm

$$\Gamma_2^{(1)} = -\frac{a}{RT} \cdot \left.\frac{\partial \gamma}{\partial a}\right|_T$$

when a solute is enriched at the interface ($\Gamma(1)^{2} > 0$), the surface tension decreases when the solution concentration is increased. Such solutes are said to be surface active and they are called **surfactants** or surface active agents.

Often the term amphiphilic molecule or simply amphiphile is used.
An amphiphilic molecule consist of two well-defined regions:
One which is oil-soluble (lyophilic or hydrophobic) and one which is water-soluble (hydrophilic
When a solute avoids the interface ($\Gamma(1)^{2} < 0$), the surface tension increases by adding the substance



You add 0.5 mM SDS (sodium dodecylsulfate, NaSO4(CH2)11CH3) to pure water at 25°C. This leads to a decrease in the surface tension from 71.99mJ/m^2 to 69.09 mJ/m^2. What is the surface excess of SDS?

At such low activities and as an approximation we replace the activity *a* by the concentration *c* and get

$$\frac{\partial\gamma}{\partial a} \approx \frac{\Delta\gamma}{\Delta c} = \frac{(0.06909 - 0.07199)\mathrm{Nm}^{-1}}{(0.0005 - 0)\mathrm{molm}^{-3}} = -5.80\ \frac{\mathrm{Nm}^2}{\mathrm{mol}}$$

$$\Gamma = -\frac{a}{RT} \cdot \frac{\partial \gamma}{\partial a} = -\frac{0.0005\ \mathrm{molm}^{-3}}{8.31 \cdot 298\ \mathrm{Jmol}^{-1}} \cdot (-5.80)\frac{\mathrm{Nm}^2}{\mathrm{mol}} = 1.17 \times 10^{-6}\frac{\mathrm{mol}}{\mathrm{m}^2}$$

Can you calculate area / molecule?

Every molecule occupies an average surface area of 1.42 nm^2.

Surfaces coming in contact

How two phases will behave when brought in contact with each other?

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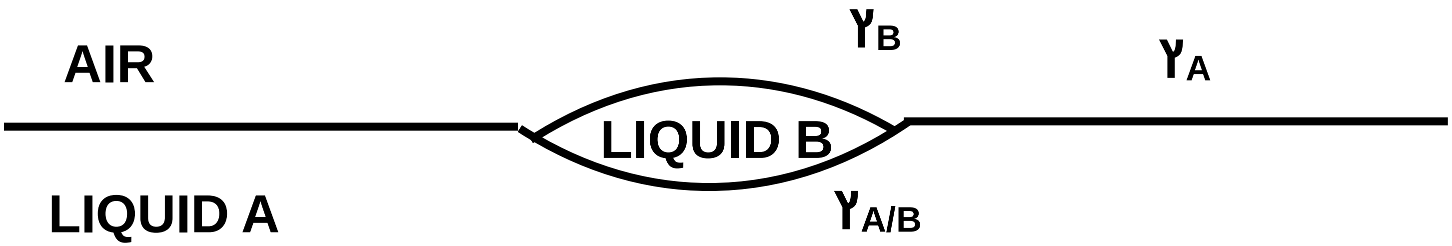
A liquid on solid/ liquid surfaces, can remain retracted (withdraw/revoke) in the form of a drop or lens

or

It may exhibit a tendency to spread (film) and cover the surface of the liquid or solid.



γ_B

AIR

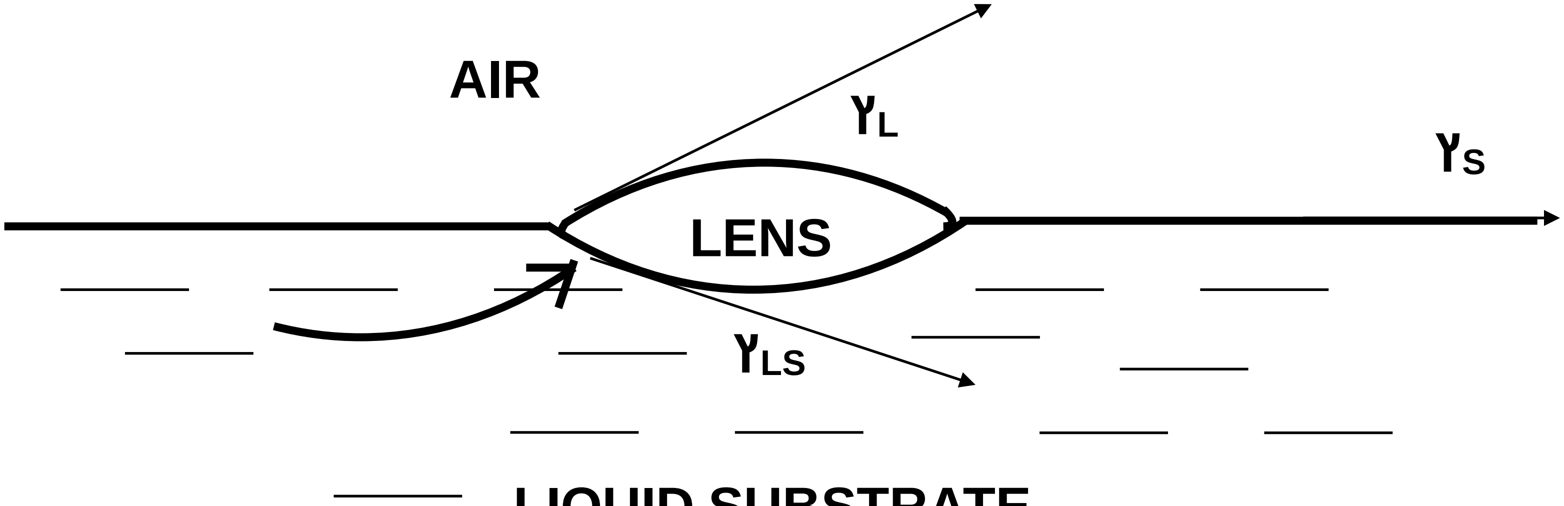
γ_A

LIQUID B

LIQUID A

$\gamma_{A/B}$

SPREADING OF ONE LIQUID ON ANOTHER



AIR

γ_L

γ_S

LENS

γ_{LS}

LIQUID SUBSTRATE

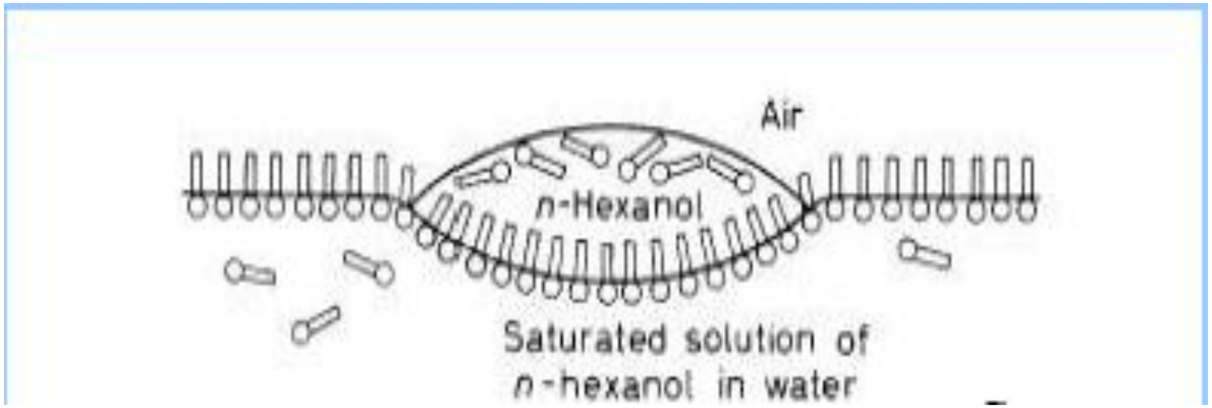
- It is apparent that the individual phases will exhibit a tendency to minimize the area of contact with other phases.

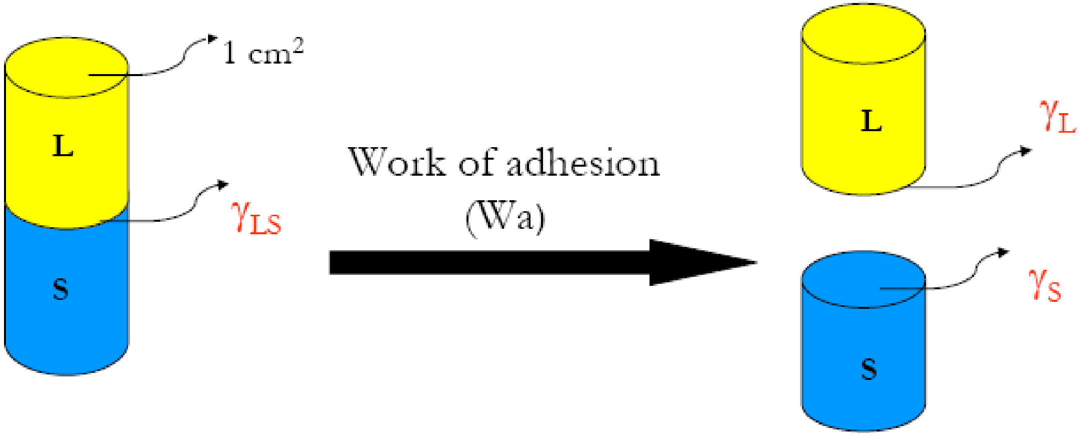
- The tendency for interaction at the new interface leads to spontaneous spreading of one substance over the other.

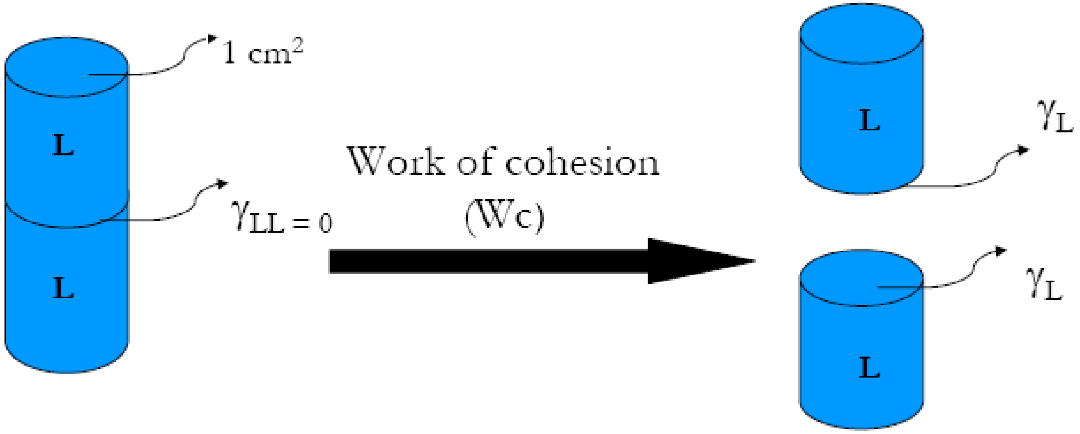
- Phase affinity is increased as the forces of attraction b/w different phases (adhesion forces) become greater than the forces of attraction b/w molecules of the same phases (cohesion forces.

- Spreading Coefficient is the difference between the work of adhesion and the work of cohesion.

$$S_{12} = -\left(\frac{dG}{dA}\right)_{T,P}$$







$\gamma_{LL} = 0$, because no interface exists between like molecules

The work required for separation Wc:

$$Wc = 2\,\gamma_L$$

$$S = Wa - Wc = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma$$

$$S = \gamma_S - (\gamma_L + \gamma_{LS})$$

Spreading occurs (S is positive) when the surface tension of the sub-layer liquid is greater than the sum of the surface tension of the spreading liquid and the interfacial tension between the sub-layer and the spreading liquid.

If $(\gamma_L + \gamma_{LS})$ is larger than Y_S , (S is negative) the substance forms globules or a *floating lens* and fails to spread over the surface.

Factors affecting spreading coefficient

Molecular Structure

- Higher polarity of the molecule more positive is [S]
- For organic acids, as oleic acid, longer the carbon chain decrease in polar character thus decrease [S]
- Some oils can spread over water because they contain polar groups such as -COOH and -OH

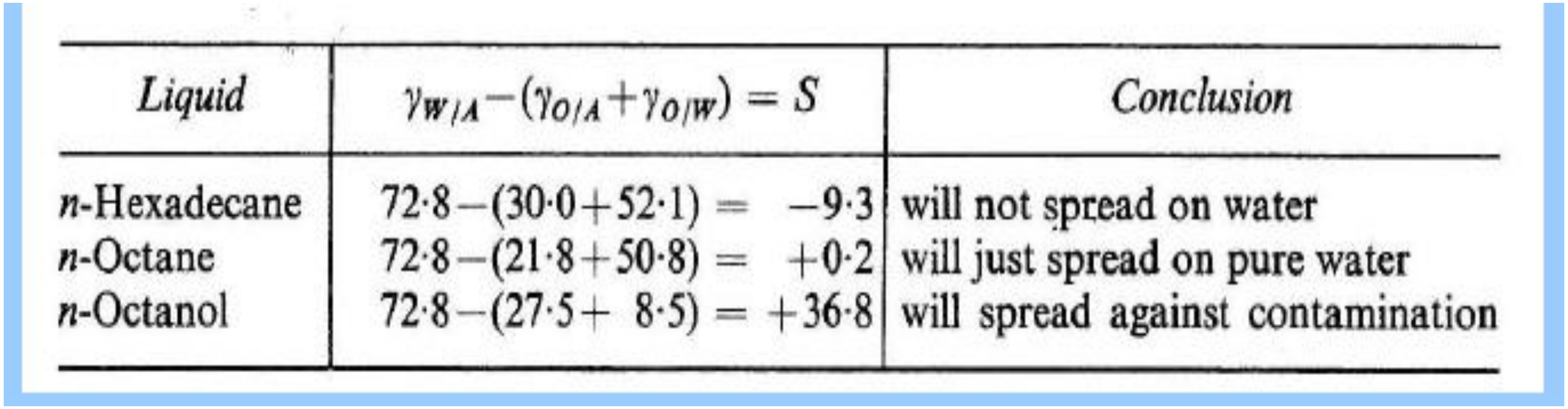
Cohesive forces

- Benzene spreads on water not because it is polar but because the cohesive forces between its molecules are much weaker than the adhesion with water.

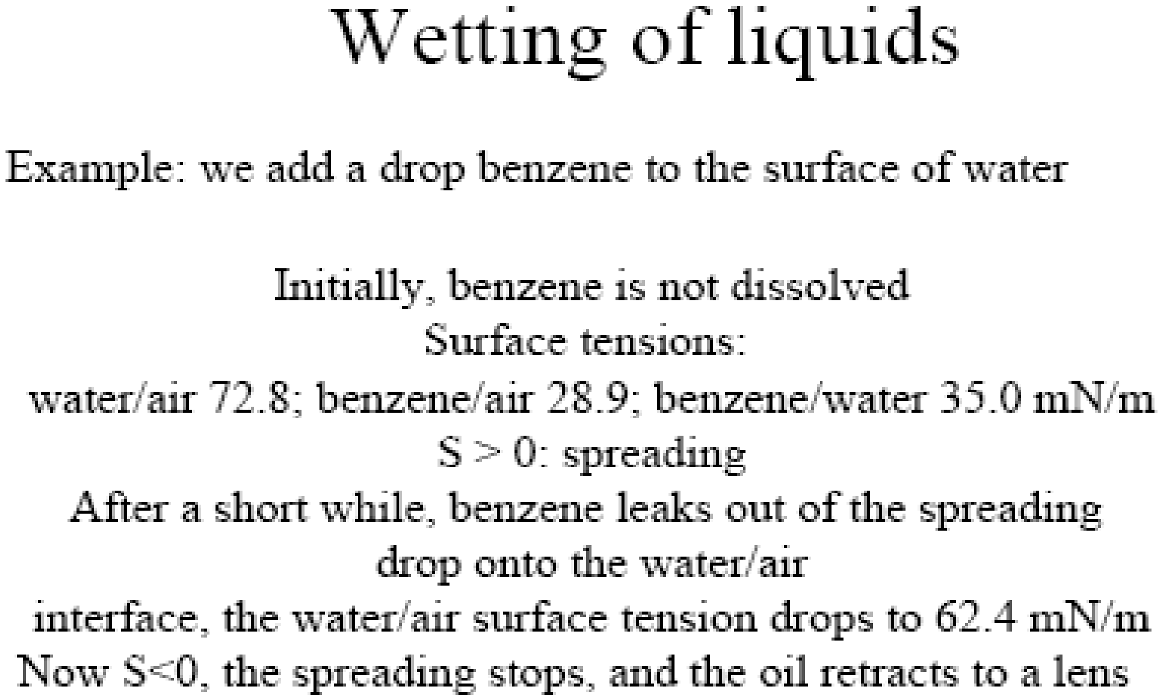
- When two immiscible liquids are placed in contact, the bulk liquids will eventually become mutually saturated.

- This will change the values of the various surface (ST) and interfacial tensions (IT).

- There is an initial spreading coefficient which is an immediate value, and a final spreading coefficient after mutual saturation has taken place.



Liquid	$\gamma_{W/A}-(\gamma_{O/A}+\gamma_{O/W}) = S$	*Conclusion*
n-Hexadecane	$72{\cdot}8-(30{\cdot}0+52{\cdot}1) = -9{\cdot}3$	will not spread on water
n-Octane	$72{\cdot}8-(21{\cdot}8+50{\cdot}8) = +0{\cdot}2$	will just spread on pure water
n-Octanol	$72{\cdot}8-(27{\cdot}5+8{\cdot}5) = +36{\cdot}8$	will spread against contamination



Wetting of liquids

Example: we add a drop benzene to the surface of water

Initially, benzene is not dissolved
Surface tensions:
water/air 72.8; benzene/air 28.9; benzene/water 35.0 mN/m
S > 0: spreading
After a short while, benzene leaks out of the spreading
drop onto the water/air
interface, the water/air surface tension drops to 62.4 mN/m
Now S<0, the spreading stops, and the oil retracts to a lens

Contact angle

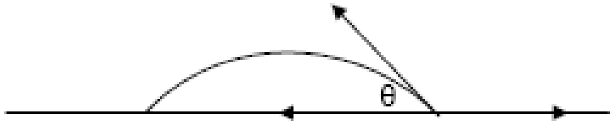
- The contact angle (CA) is the angle b/w a liquid droplet and the surface over which it spreads.

Or

- The angle made by the liquid with the solid surface at the point of contact.

Force Balance at a Triple Interface

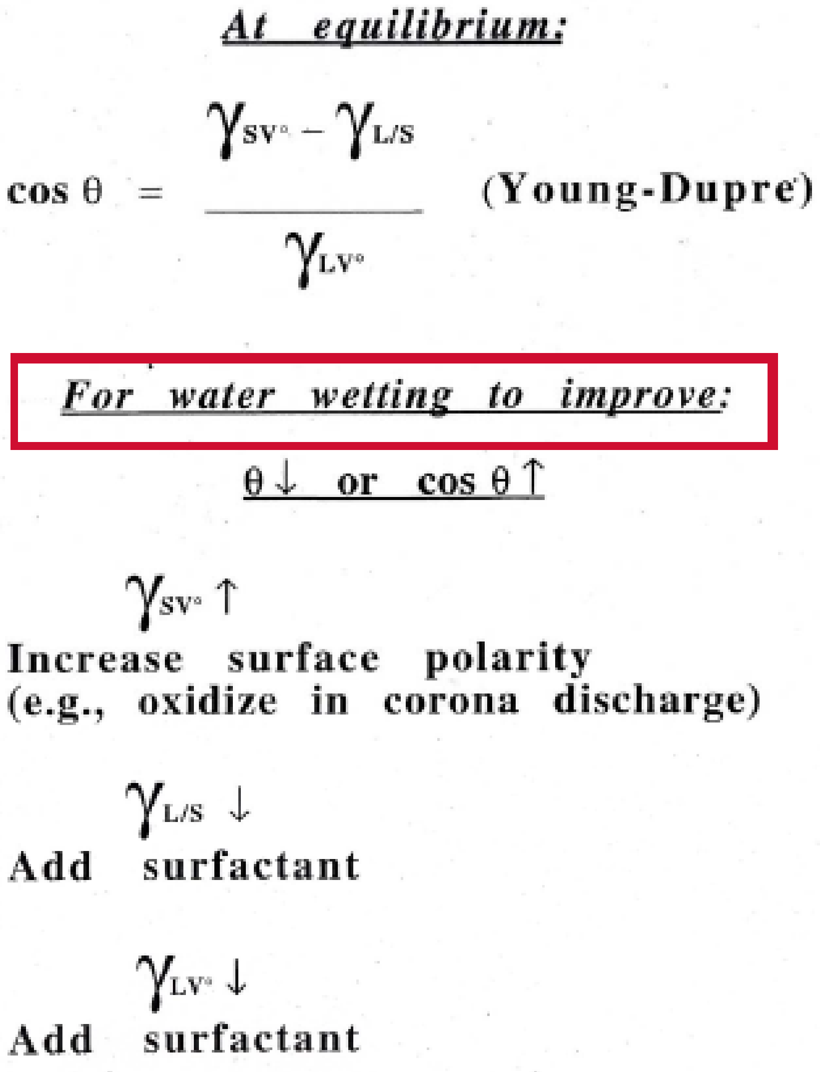
- In most cases a liquid placed on a solid will not wet it but remains as a drop having a definite angle of contact between the liquid and solid phases. The force balance at a triple interface represents Young's equation.



$$\boxed{\gamma_{SL} - \gamma_{SV} + \gamma_{LV}\cos\theta = 0}$$

Substrate	θ
Teflon	110
PMMA	59.3
Platinum	40
Glass	small
Gold	0

Practical application of the Young-Dupre equation



At equilibrium:

$$\cos\theta = \frac{\gamma_{SV^\circ} - \gamma_{L/S}}{\gamma_{LV^\circ}} \qquad \text{(Young-Dupre)}$$

For water wetting to improve:

$\theta\downarrow$ or $\cos\theta\uparrow$

$\gamma_{SV^\circ}\uparrow$

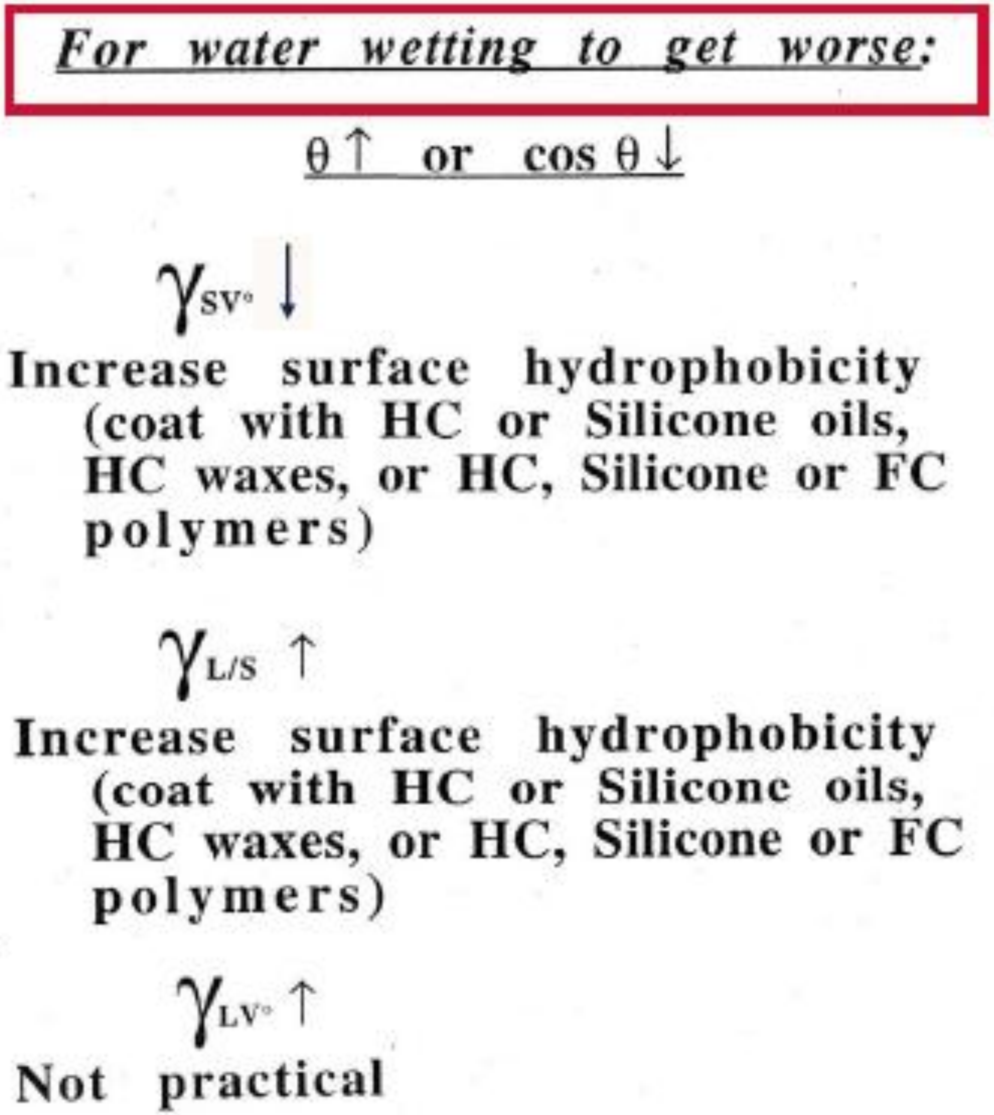
Increase surface polarity
(e.g., oxidize in corona discharge)

$\gamma_{L/S}\downarrow$

Add surfactant

$\gamma_{LV^\circ}\downarrow$

Add surfactant



For water wetting to get worse:

$\theta \uparrow$ or $\cos\theta \downarrow$

$\gamma_{SV^\circ} \downarrow$

Increase surface hydrophobicity (coat with HC or Silicone oils, HC waxes, or HC, Silicone or FC polymers)

$\gamma_{L/S} \uparrow$

Increase surface hydrophobicity (coat with HC or Silicone oils, HC waxes, or HC, Silicone or FC polymers)

$\gamma_{LV^\circ} \uparrow$

Not practical

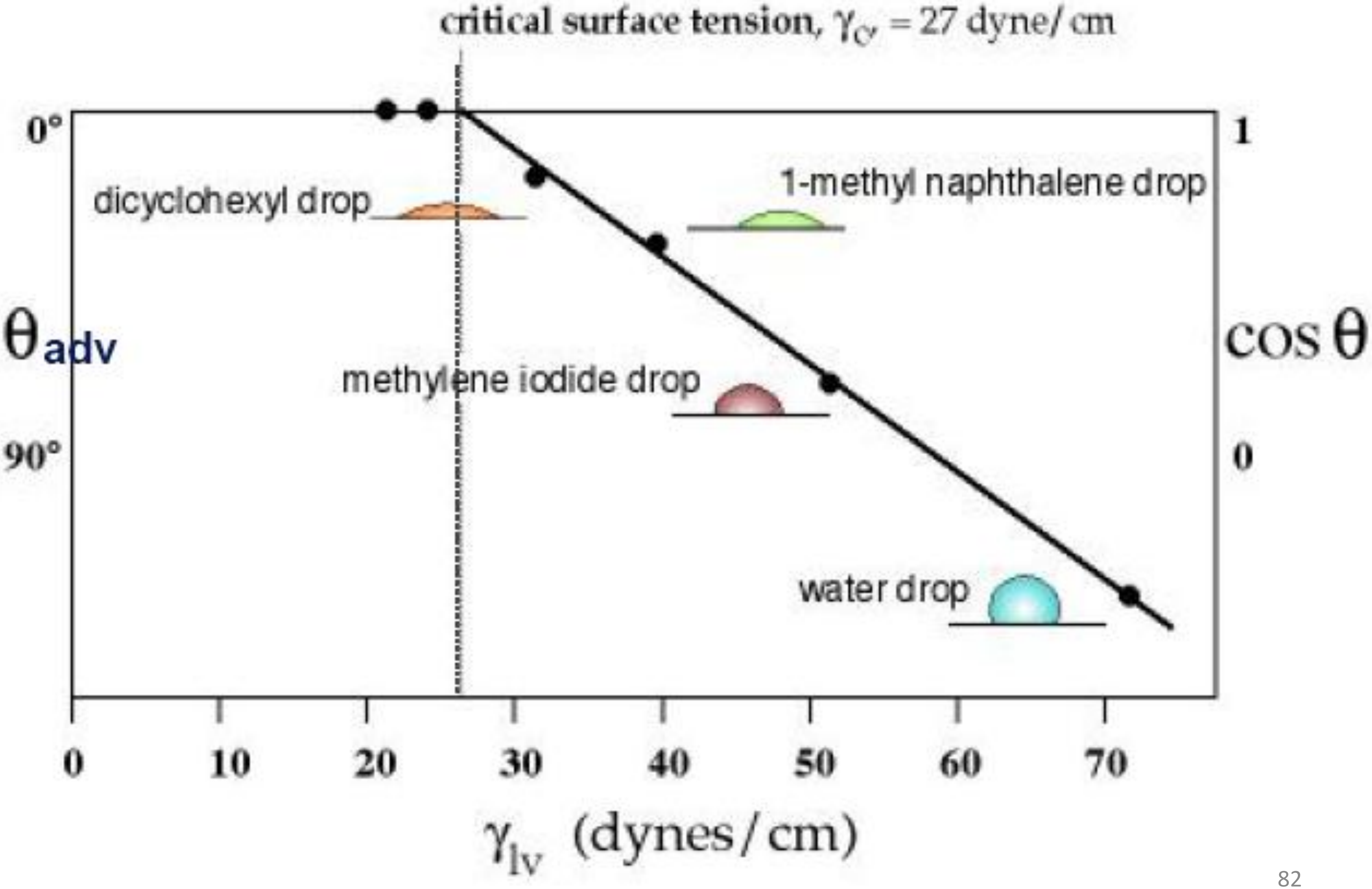
Critical Surface Tension, γ_c

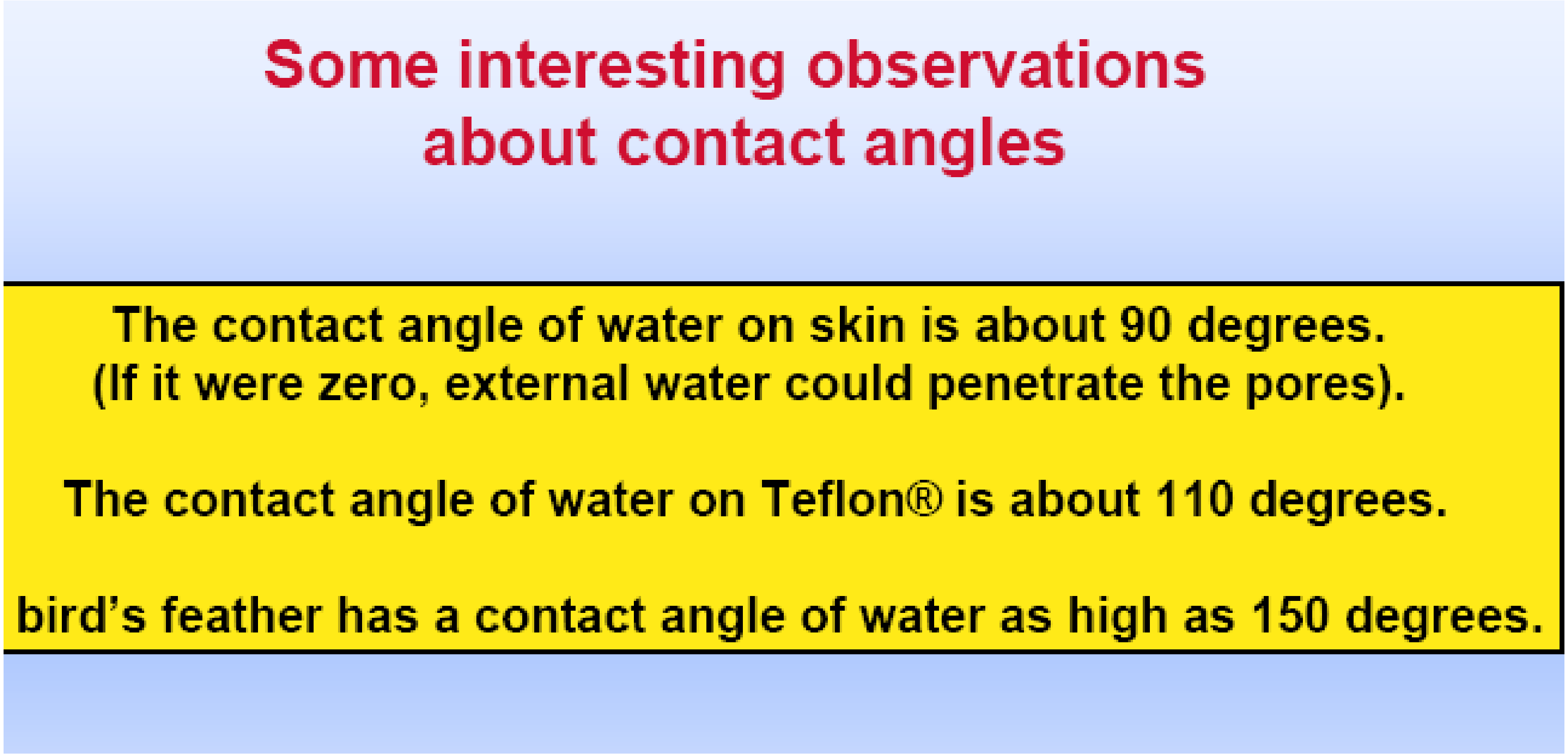
Measure θ_{adv} on one surface for a series of liquids varying in surface tension.

Plot $\cos\theta_{adv}$ vs. γ_{lv}

Extrapolate to $\cos\theta_{adv} = 1.0$ $(\theta_{adv} = 0°)$

Define $\gamma_c = \gamma_{lv}$ at $\cos\theta_{adv} = 1.0$ $(\theta_{adv} = 0°)$


critical surface tension, $\gamma_{C'} = 27$ dyne/ cm
0°
90°
θadv
1
0
cos θ
dicyclohexyl drop
1-methyl naphthalene drop
methylene iodide drop
water drop
0
10
20
30
40
50
60
70
γ_{lv} (dynes / cm)

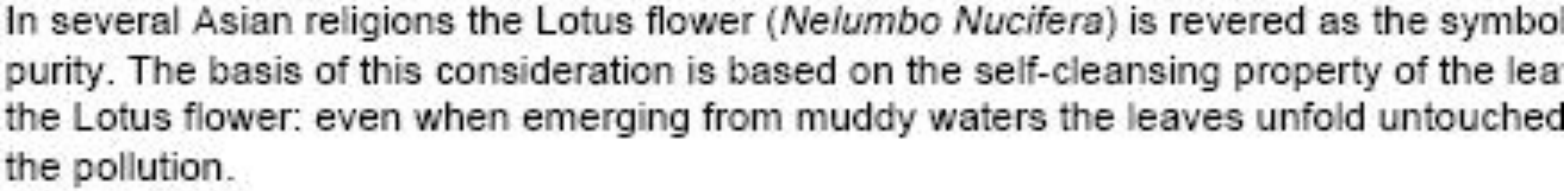


Some interesting observations about contact angles

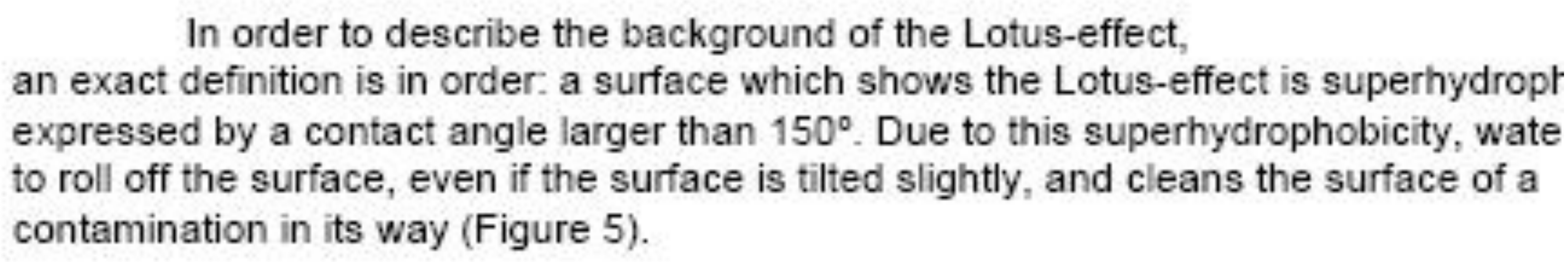
The contact angle of water on skin is about 90 degrees.
(If it were zero, external water could penetrate the pores).

The contact angle of water on Teflon® is about 110 degrees.

bird’s feather has a contact angle of water as high as 150 degrees.



In several Asian religions the Lotus flower (*Nelumbo Nucifera*) is revered as the symbol purity. The basis of this consideration is based on the self-cleansing property of the lea the Lotus flower: even when emerging from muddy waters the leaves unfold untouched the pollution.



In order to describe the background of the Lotus-effect, an exact definition is in order: a surface which shows the Lotus-effect is superhydroph expressed by a contact angle larger than 150°. Due to this superhydrophobicity, wate to roll off the surface, even if the surface is tilted slightly, and cleans the surface of a contamination in its way (Figure 5).