
Phase Transitions & Interfaces

Chapter 6 of Atkins, 7th Ed. Chapter 4 and 18, 8th Ed.

Sections 6.7-6.10, 7th Ed.; 4.7, 18.7, 18.8 in 8th Ed.

Ehrenfest Classification of Phase Transitions

Physical Liquid Surface

Surface Tension

Curved Surfaces

Bubbles, cavities and droplets

Nucleation

Capillary Action

Ehrenfest Classification of Phase Transitions

Common phase transitions:

Fusion
Vapourization

Less common phase transitions:

Solid-Solid
Conducting-Superconducting
Fluid-Superfluid

Paul Ehrenfest came up with a classification scheme for phase transitions, based on the thermodynamic properties of substances

Many phase transitions are accompanied by changes in enthalpy and volume - these changes can alter the chemical potentials on both sides of the phase transition. For example, phase α changing to phase β :

$$\left(\frac{\partial \mu_{\beta}}{\partial p} \right)_T - \left(\frac{\partial \mu_{\alpha}}{\partial p} \right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{\text{trs}} V$$

$$\left(\frac{\partial \mu_{\beta}}{\partial T} \right)_p - \left(\frac{\partial \mu_{\alpha}}{\partial T} \right)_p = -S_{\beta,m} + S_{\alpha,m} = -\Delta_{\text{trs}} S = -\frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

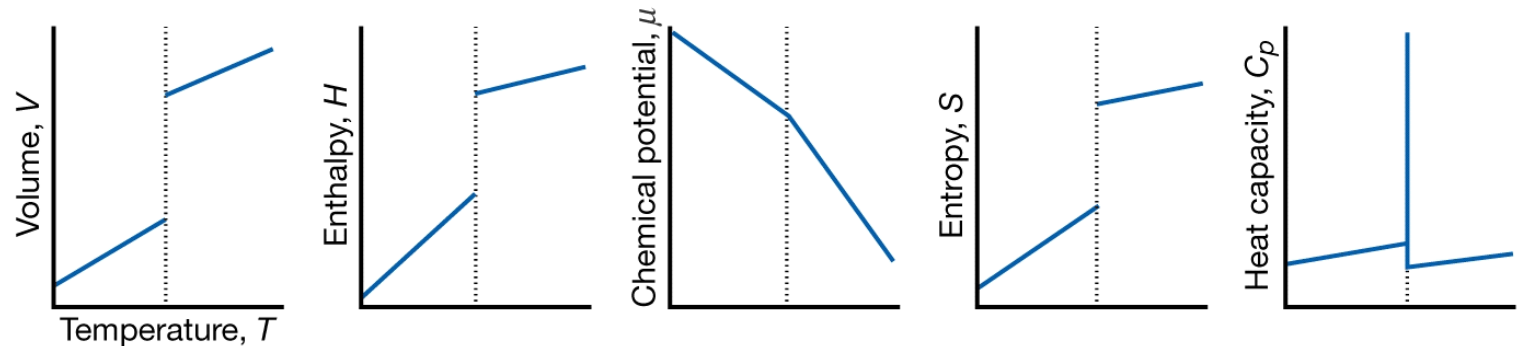
Ehrenfest Classification of Phase Transitions

$\Delta_{\text{trs}} V$ and $\Delta_{\text{trs}} H$ are nonzero for fusion and vapourization, so slopes of μ as functions of p or T on each side of the phase transition are different

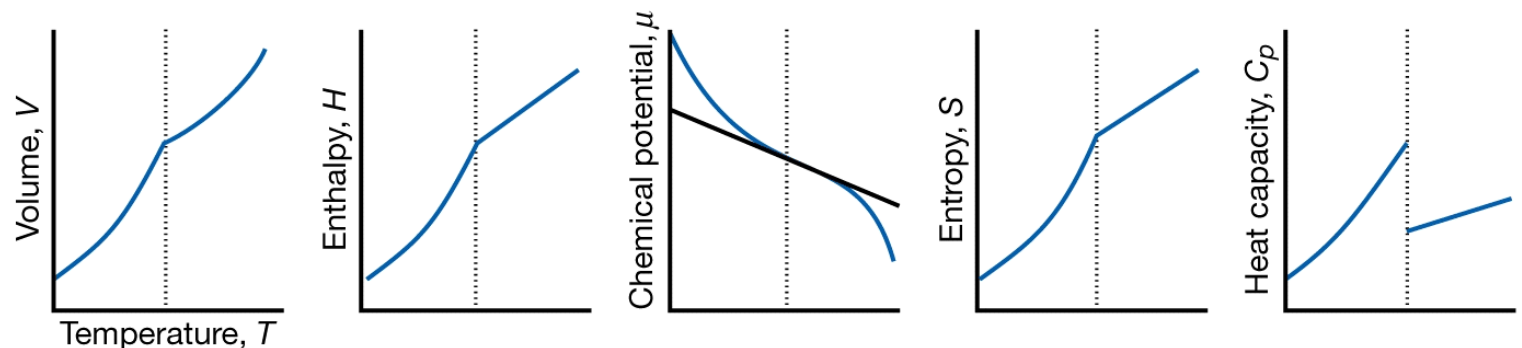
First order phase transition: first derivative of μ w.r.t. T is discontinuous

Second order phase transition: first derivative of μ w.r.t. T is continuous, but second derivative is discontinuous

(a) first order



(b) second order

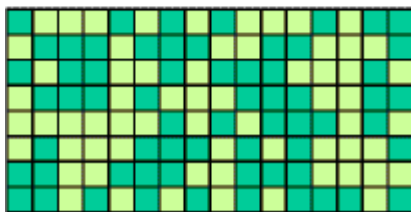
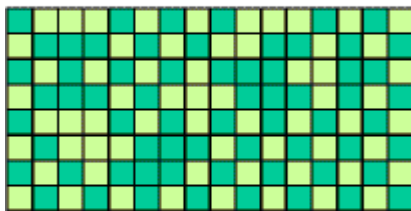
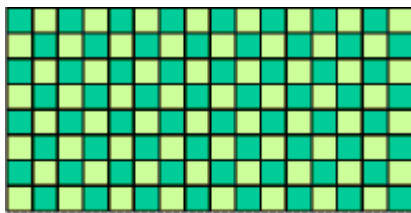


The C_p of a substance is the slope of the plot of enthalpy wrt temperature: at the transition, H changes by a finite amount, so at the transition, the heat capacity is **infinite**: i.e., **heat drives the transition instead of raising temperature**

λ -Transition

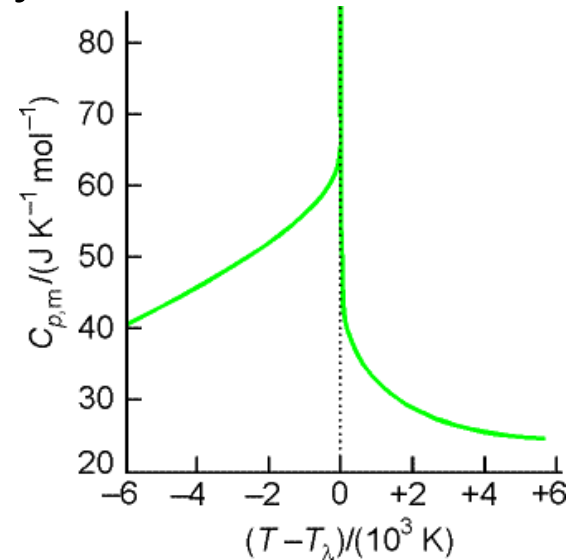
The λ -transition is a phase transition that is not first-order, but has infinite heat capacity at the transition - the heat capacity increases well before the transition, and occurs in:

- order-disorder transitions in alloys
- ferromagnetic materials
- fluid-superfluid transition in liquid helium



Order-disorder transition in β -brass (CuZn) is a λ -transition

- Low T phase: orderly arrangement of atoms
- Islands of disorder appear as T increased
- Islands grow and merge at the transition temperature (742 K), where heat capacity increases and drives the transition



Second-Order Phase Transition in a Solid

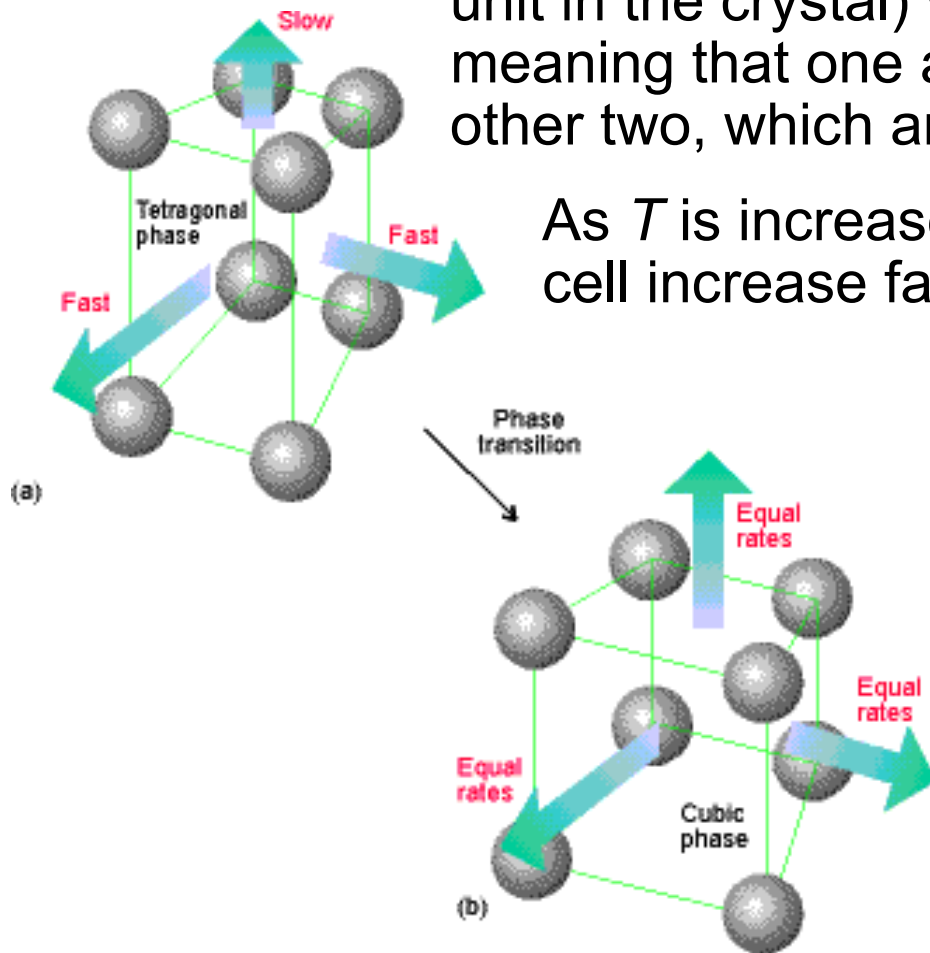
Change of symmetry of a crystal structure in a solid is an example of a **second-order phase transition**

At first, the crystal has a **unit cell** (smallest repeating unit in the crystal) which is **tetragonal** in symmetry, meaning that one axis of the unit cell is longer than the other two, which are equal

As T is increased, the shorter dimensions of the unit cell increase faster than the longer dimension

At some point, the sides of the unit cell become equal, and the crystal is said to have **cubic symmetry** at this point - after which, all sides of the unit cell increase at the same rate

This tetragonal-cubic solid-solid phase transition does not involve discontinuity in energy between atoms of the volume they occupy: so it is **not a first-order transition**



Liquid Surfaces: Surface Tension

A unique feature of behaviour of liquids is that they typically adopt a shape which **minimizes their surface area**

- Smallest surface-to-volume ratio: **spherical droplet**
- Maximum number of molecules in the bulk volume interacting with neighbouring molecules
- Other forces may compete against tendency to form an ideal shape (e.g., gravity flattens droplets into puddles, lakes and oceans)

Helmholz and Gibbs energies are used to describe the amount of work needed to change the surface area. Under different conditions, dA and dG are equal to the work done in changing the energy of a system

Work needed to change surface area, σ , of a sample by an infinitesimal amount $d\sigma$ is proportional to $d\sigma$

$$dw = \gamma d\sigma$$

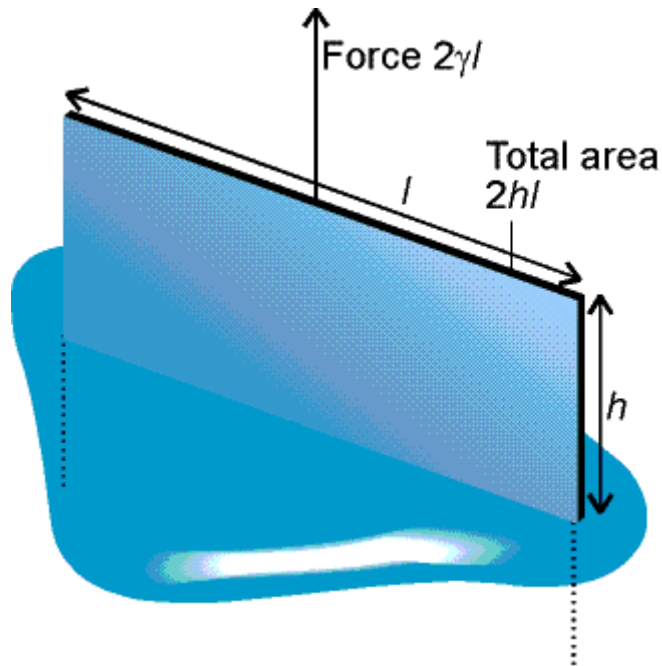
where γ is a proportionality constant known as **surface tension**, having dimensions J m^{-2} or N m^{-1} (since $1 \text{ J} = 1 \text{ N m}$). At constant V and T :

$$dA = \gamma d\sigma$$

Surface Tension

Helmholz energy decreases, $dA < 0$, if surface area decreases, $d\sigma < 0$, so surfaces have a natural tendency to **contract**

Example: Calculate work need to raise a wire of length L and to stretch the surface through liquid of height h as shown on the left



When wire of length L is raised by height h in increases the liquid surface area by twice the area of the rectangle (there is a surface on each side).

Total area increase: $2Lh$

Work done: $2\gamma Lh$

Because: $w = F \times d = 2\gamma L \times h$

γL is an **opposing force** on the wire of length L this is why γ is called **tension**, and units are chosen to be N m^{-1}

Surface Tension of Liquids: Bugs & Needles

Question:

Why can water beetles "walk" on the surface of water?

Answer:

At the interface between water and air there is an ordered arrangement of water molecules which are hydrogen bonded to one another and to the water molecules below. As a result, the water behaves as though it were coated with an invisible membrane which resists rupturing when stretched.



Surface tension is a "*measure of how difficult it is to stretch or break the surface of a liquid.*" The water beetles have a small mass which is equally distributed over a relatively large surface area. Therefore, they don't overcome the surface tension of the water and "float" on its surface.

Question:

Why don't all small objects float on water?

Answer:

It is not necessarily the size of the object that determines whether an object will float on the surface of the water. A small object will sink into water if enough of its mass is concentrated on a small area. For example, if a needle is placed point first on the surface of water, it sinks because there aren't enough hydrogen bonds to resist the concentrated force downward.

High Surface Tension of Water

Within the water, at least a few molecules away from the surface, every molecule is engaged in a tug of war with its neighbors on every side - strong **hydrogen bonding interactions**. For every "up" pull there is a "down" pull, and for every "left" pull there is a "right" pull, and so on, so that any given molecule feels no net force at all.

At the surface things are different. There is no up pull for every down pull, since of course there is no liquid above the surface; thus the surface molecules tend to be pulled back into the liquid. It takes work to pull a molecule up to the surface. If the surface is stretched - as when you blow up a bubble - it becomes larger in area, and more molecules are dragged from within the liquid to become part of this increased area. This "**stretchy skin**" effect is called **surface tension**. Surface tension plays an important role in the way liquids behave. If you fill a glass with water, you will be able to add water above the rim of the glass because of surface tension.

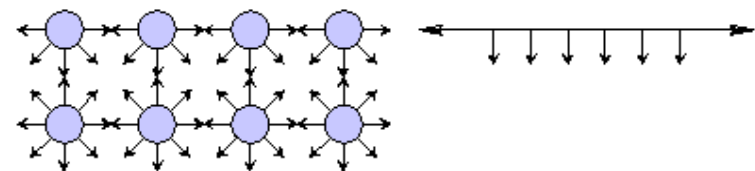
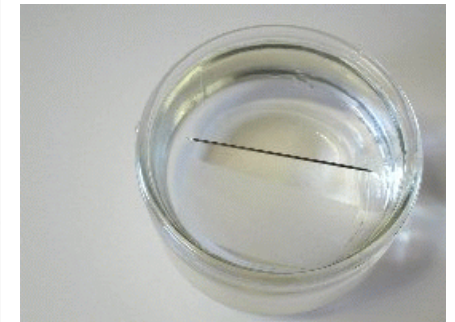
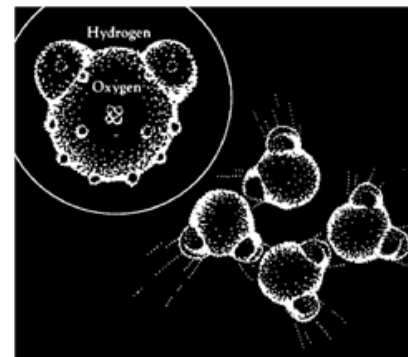
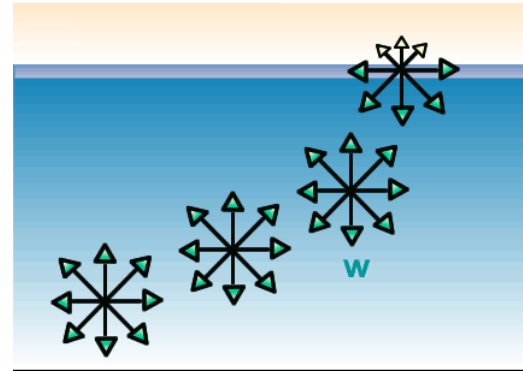
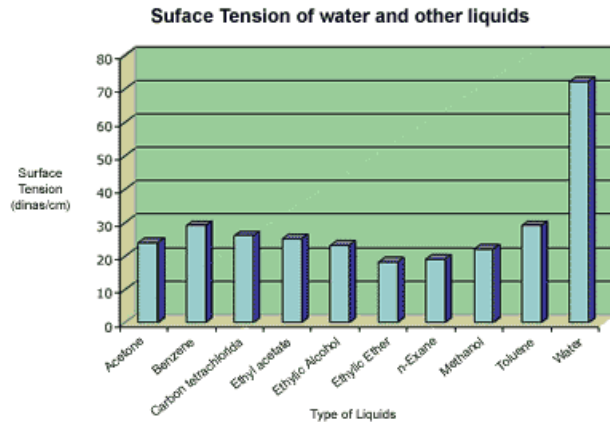


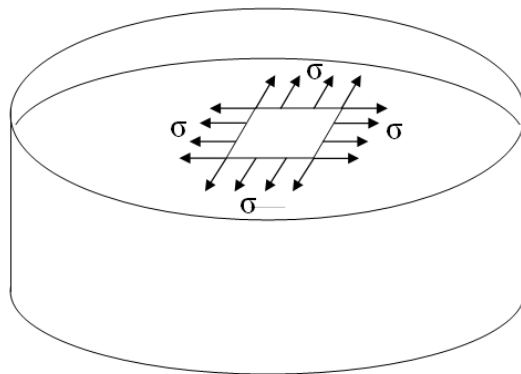
Figure 2 - Scheme of the attractive forces among the molecules of a liquid. The inner molecules are in equilibrium among them. Instead, the forces which act on the molecules of surface do not are balanced upward and from this originates an inward compression. Besides, the cohesion among the molecules determines a tension tangential to the surface. So, the surface of a fluid behaves like an elastic membrane. In this scheme the molecules are ordered, whereas in the reality the molecules of a liquid are not.

High Surface Tension of Water, 2

Water has a much high surface tension than most other liquids, due to the strong **cohesive** intermolecular interactions within the bulk material arising from hydrogen bonding. At the surface, there are additional **adhesive** forces.



The square area shown below on the surface of water is subject to forces of tension (N m^{-1}) in each direction, making the surface behave as a stretchy skin.



$$dw = \gamma d\sigma$$

Curved Surfaces

Surface area may be minimized by the formation of a curved surface, such as a **bubble**. There are two consequences of this curvature:

1. Vapour pressure of liquid depends on the curvature of its surface
2. Capillary rise and fall of liquids in narrow tubes

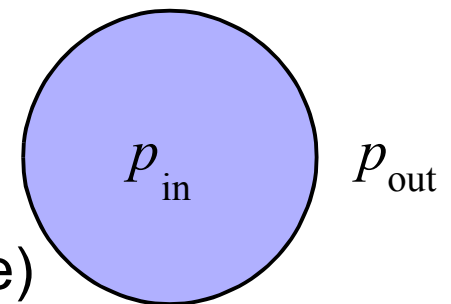
Bubble: A region in which vapour (possibly air as well) is trapped by a thin film - **two surfaces**, one on each side of the film

Cavity: A vapour-filled hole in a liquid (gas bubbles in liquids are strictly defined as cavities) - **one surface** touching a vapour

Droplet: Small volume of liquid at equilibrium surrounded by a vapour

Laplace equation: Pressure on the concave side of the interface, p_{in} is always greater than the pressure on the convex side, p_{out} , and these pressures are related by

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$



The difference in pressure decreases to zero as the radius of the curvature becomes infinite (i.e., flat surface)

Small cavities, small radii of curvature, produce huge pressure differences

Bubbles, Cavities and Droplets

Cavities in a liquid are at equilibrium when tendency for their surface area to decrease is balanced by a corresponding rise in internal pressure

If pressure in a cavity is p_{in} & radius = r , **outward force** is $p \times A = 4\pi r^2 p_{in}$

Inward forces arise from external pressure and surface tension, with magnitude $4\pi r^2 p_{out} + 8\pi\gamma r$

The latter is calculated as follows, the change in surface area when radius changes from r to $r + dr$ is

$$d\sigma = 4\pi (r + dr)^2 - 4\pi r^2 = 8\pi r dr$$

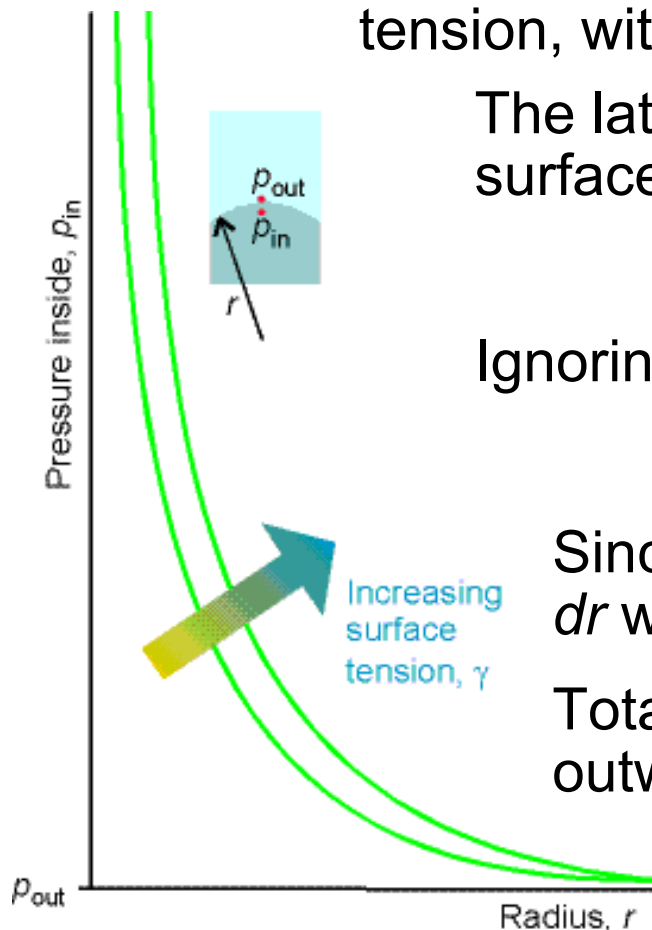
Ignoring the small $(dr)^2$, work done on the surface is

$$dw = 8\pi\gamma r dr$$

Since $w = F \times d$, force opposing stretching through dr when radius is r is $F = 8\pi\gamma r$

Total inward force is $4\pi r^2 p_{out} + 8\pi\gamma r$. At equilibrium outward and inward forces are balanced, so

$$4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi\gamma r$$



Bubbles, Cavities and Vapour Pressure

The vapour pressure of a liquid depends on the pressure applied to a liquid - since curving the surface gives rise to pressure difference of $2\gamma/r$, the vapour pressure above a curved surface should be different from a flat surface. We can use the Kelvin equation to calculate the vapour pressure of a liquid when dispersed as droplets of radius r

$$p = p^* e^{V_m \Delta P / RT}$$

If the applied pressure $\Delta P = 2\gamma/r$, then

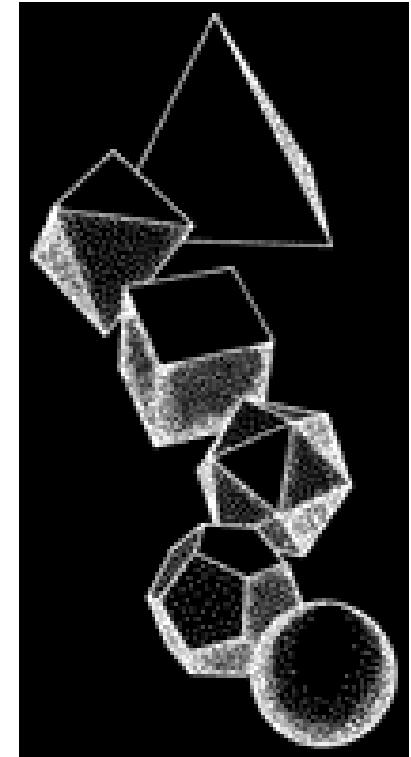
$$p = p^* e^{2\gamma V_m / rRT}$$

where p^* is the vapour pressure of the liquid

An analogous expression for the vapour pressure inside the cavity can also be obtained from the above equation: since the pressure outside the cavity is less than the pressure inside, we simply change the sign of the exponent.

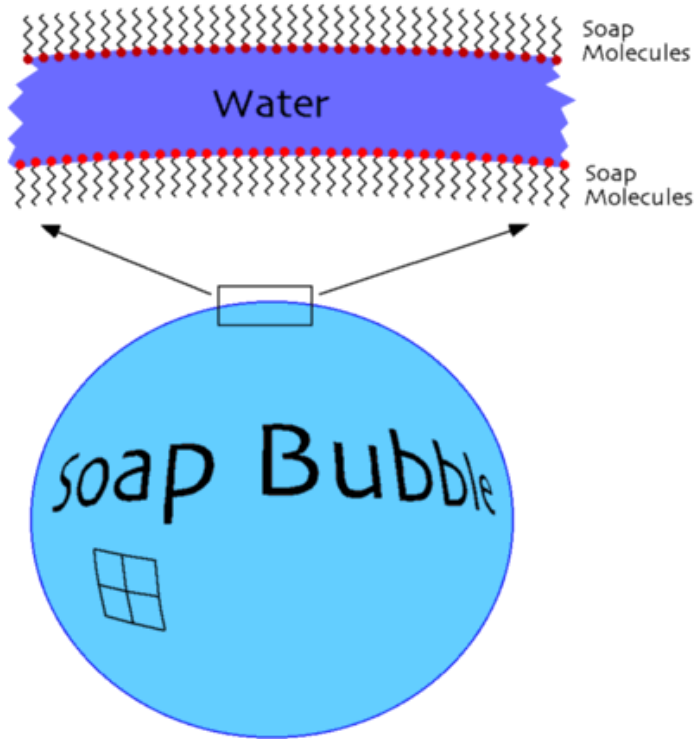
Shapes of Bubbles

A bubble, like a balloon, is a very thin skin surrounding a volume of air. The rubber skin of the balloon is elastic and stretches when inflated. The liquid skin of the bubble is stretchy, somewhat like a piece of thin rubber, and like a balloon it pushes the air out of the bubble, leaving a flat circle of soap in a bubble wand. Unlike a sheet of rubber that when unstretched loses all tension, a bubble always has its "stretch" no matter how small the surface becomes. If you blow a bubble and close the opening by flipping the wand over, the tension in the bubble skin tries to shrink the bubble into a shape with the smallest possible surface area for the volume of air it contains. That shape happens to be a sphere.



Shape	# of sides	Volume	Surface Area
Tetrahedron	4	1 cubic inch	7.21 square inches
Cube	6	1 cubic inch	6 square inches
Octahedron	8	1 cubic inch	5.72 square inches
Dodecahedron	12	1 cubic inch	5.32 square inches
Icosahedron	20	1 cubic inch	5.15 square inches
Sphere	infinite	1 cubic inch	4.84 square inches

What is a bubble?



- A **soap bubble** is simply a very thin sheet of water sandwiched between two layers of soap molecules (also called **surfactant molecules**).
- These molecules are called amphiphilic. This means that part of this molecule is attracted to water (hydrophilic) and another part is repelled from water (hydrophobic).
- When such a molecule is put in water, as many as possible will crowd to the surface, so that the heads can stay in the water, while the tails stick out into the air. This is why soap-like molecules are called surfactants, since they mostly affect the surface of water. It is these molecules that make soap bubbles stable.

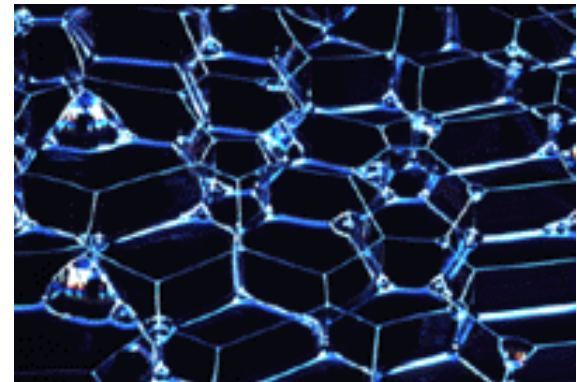
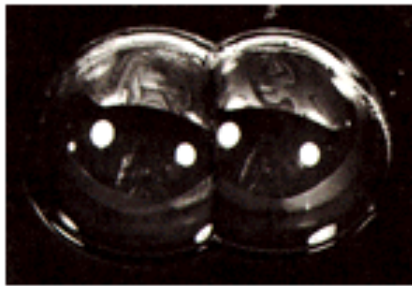
- Some bubbles result from **gas being trapped in solution** (such as CO_2 in soda and champagne, or N_2 in the blood of deep sea divers).
- Much study goes into understanding bubbles dissolved in gases, as well as the formation of large surfaces from surfactants used to construct bubbles (e.g., temperature, surface pressure, **nucleation** sites, etc.).



more information at: <http://home.earthlink.net/~marutgers/index.html>

When Bubble Meets Bubble

When one bubble meets with another, the resulting union is always one of total sharing and compromise. Since bubbles always try to minimize surface area two bubbles will merge to share a common wall. If the bubbles are the same size, this wall will be flat. If the bubbles are different sized, the smaller bubble, which always has a higher internal pressure, will bulge into the larger bubble.



Regardless of their relative sizes, the bubbles will meet the common wall at an angle of 120 degrees. This is easy to see in the bubble picture above. All three bubbles meet at the center at an angle of 120 degrees.

If you take two sheets of clear glass or plastic separated by about one-half inch, soak them in soapy solution and then blow bubbles between the sheets, you will get many bubble walls. If you look closely, you will notice that all of the vertices where three bubble walls meet form 120 degree angles. If your bubbles are of uniform size, you will notice that the cells form hexagons and start to look much like the cells of a beehive (very efficient distribution)

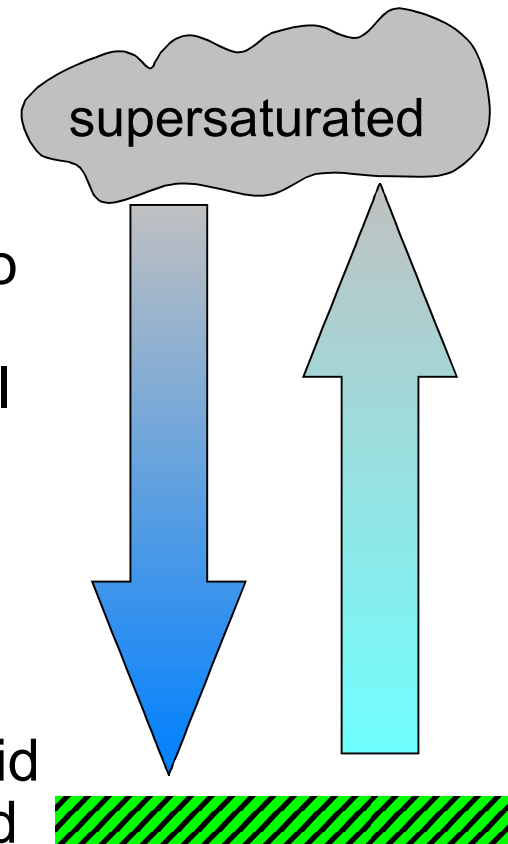
Nucleation

For water droplets of radius 1 μm and 1 nm, ratios p/p^* at 25°C are about 1.001 and 3, respectively (though in the latter case, the droplet is only 10 molecules in diameter, and the calculation is a bit suspect)

The effect is small, but can have some important consequences

Consider cloud formation:

- Warm moist air rises into atmosphere
- Temperature decreases, at some point vapour becomes thermodynamically unstable (i.e., wants to condense)
- Swarm of water molecules congregates into a small droplet, so small, that it has an enhanced vapour pressure - it is so small, instead of growing it evaporates (the vapour is stabilized, tendency to condense is overcome by heightened tendency to evaporate) that is, it is **supersaturated**:
 - thermodynamically unstable with respect to liquid
 - not unstable wrt small droplets before bulk liquid phase is formed



Nucleation, 2

Two mechanisms for cloud formation:

1. Sufficiently large number of molecules congregate into a large droplet so big that enhanced evaporation is negligible (**spontaneous nucleation**) - very low probability of this happening in a cloud
2. *Minute dust particles and other foreign matter nucleate* condensation (i.e., **centres are provided around which the condensation can occur**) - water molecules attach and condense

Liquids may be **superheated** above boiling temperatures and **supercooled** below freezing temperatures - thermodynamically stable phase is not achieved, on account of kinetic stabilization occurring in the absence of nucleation centres

Superheating: vapour pressure inside of a cavity is artificially low, so cavities that form tend to collapse (encountered in heating water in beaker without stirring - violent **bumping** occurs, from spontaneous nucleation leads to large bubbles big enough to survive) - small pieces of sharp edged glass or **porous activated carbon flakes** in the beaker prevent this, providing **nucleation centres** for the molecules in the heated liquid to attach themselves.

Nucleation, 3

Nucleation is necessary for phase transitions to occur at the normal phase transition temperatures - this is the formation of a small bubble (heating liquid-vapour) or crystal (cooling liquid-solid) that acts as the interface between the two phases. In the absence of nucleation sites, phase transition T 's change dramatically! Homogeneous or spontaneous nucleation is very improbable.

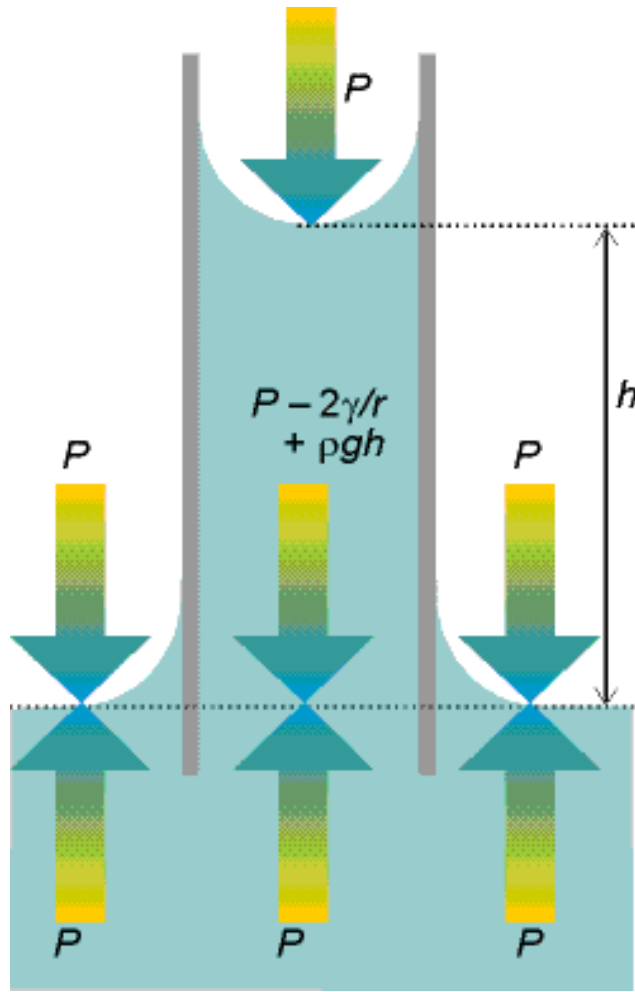
Example: H₂O freezes at -42 °C if it is cooled in a perfectly smooth container with no dust particles, crystals, etc. present to act as nucleation sites.

Example: For boiling liquids, nucleation most often happens on the heating surface, at so-called **nucleation sites**, which may be tiny crevices on a rough surface or rough particles introduced into the solution (e.g., CO₂ bubbles in pop bottles; bubbles on side of container during boiling). At these sites, tiny gas-liquid interfaces (surfaces) are thermodynamically stabilized. If a liquid is **de-gassed**, and heating surfaces are **clean and smooth**, superheating happens.

Suitably sized nuclei must grow or be present in order for phase transitions to occur. So, it is possible to **superheat** liquids above T_b and to **supercool** liquids below T_f , since there are energy barriers between the phases: a bubble or microcrystal (of the new phase) must form before the phase transition can proceed! So, a small bubble can't grow b/c of the surface tension σ : small bubbles pay a large cost in surface tension for a small gain in volume of the new phase. ***A nucleation surface helps to bypass this barrier!***

Capillary Action

The tendency of liquids to climb up capillary tubes (narrow bore tubes) is known as **capillary action**, and it results from **surface tension**



- Narrow tube is immersed in water, any liquid entering the tube adheres to the walls
- Energy is lowest when thin film covers as much of the glass as possible
- As the film creeps up the wall, the liquid surface becomes curved (**meniscus**)
- The pressure beneath the meniscus is less than the atmosphere by $2\gamma/r$, where r is the tube radius (assume hemispherical surface, and $p_{in} = p_{out} + 2\gamma/r$)
- Pressure immediately under the flat surface outside the tube is p , under the curved meniscus it is $p - 2\gamma/r$
- Excess external pressure forces the liquid up the tube until **hydrostatic equilibrium** has been achieved (equal pressures at equal depths)

Capillary Rise

Pressure exerted by a column of liquid of density of ρ and height h is

$$p = \rho gh$$

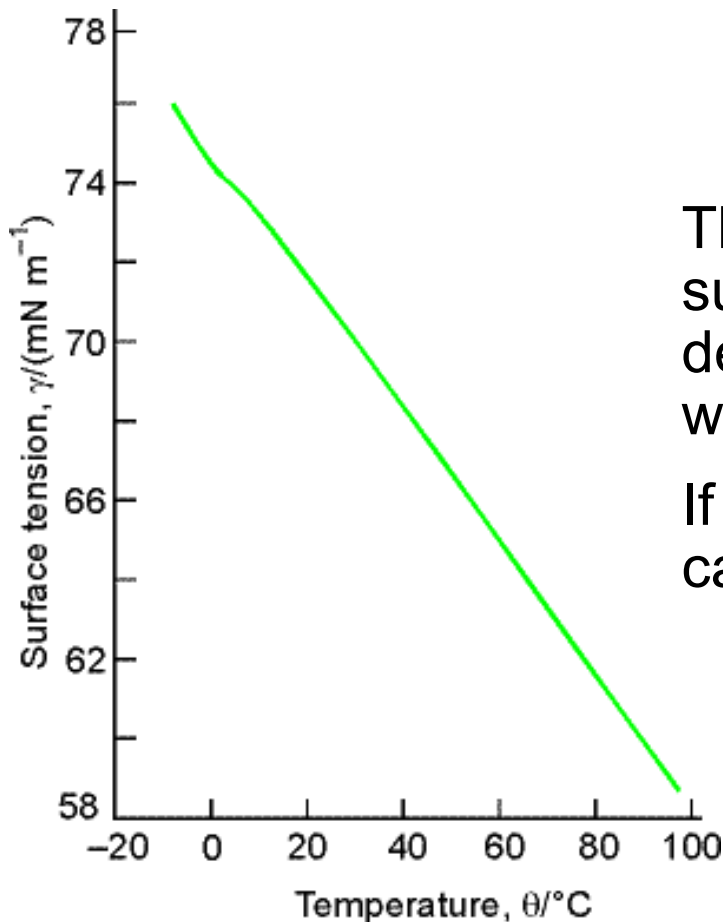
Hydrostatic pressure matches the pressure difference $2\gamma/r$ at equilibrium, so the height of the column is obtained by equating $2\gamma/r$ and ρgh

$$h = \frac{2\gamma}{\rho gr}$$

This is an easy way of now measuring the surface tension of liquids, which tend to decrease with increasing temperature (e.g., water is shown on the left)

If water at 25°C rises 7.36 cm in a 0.20 mm capillary tube, surface tension is:

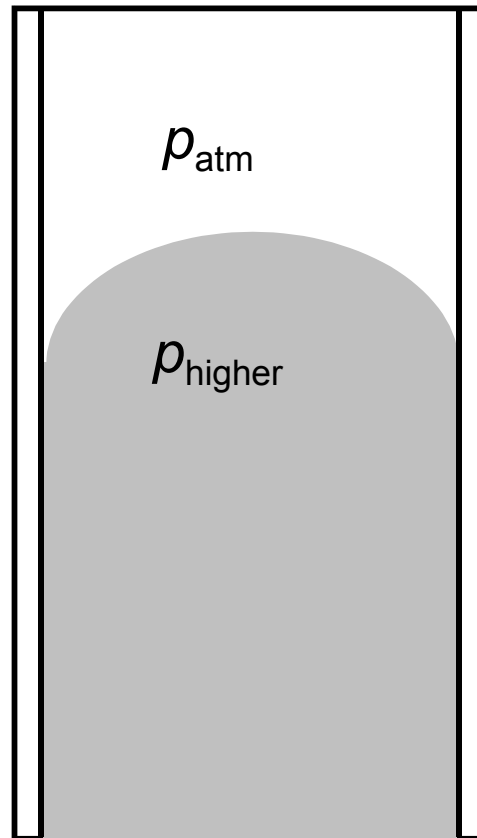
$$\begin{aligned}\gamma &= \frac{1}{2}\rho ghr = \frac{1}{2}(997.1 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \\ &\quad \times (7.36 \times 10^{-2} \text{ m}) \times (2.0 \times 10^{-4} \text{ m}) \\ &= 72 \text{ mN m}^{-1}\end{aligned}$$



Capillary Depression

If adhesive forces between the liquid and the wall are weaker than cohesive forces in the liquid (e.g., Hg in glass) liquid in the tube retracts from the walls, curving the surface with the high pressure concave side downwards (this is **capillary depression**). To equalize pressure at the same depth, surface falls to compensate for heightened pressure arising from its curvature

Mercury in a thermometer or barometer exhibits capillary depression



Contact Angle

There can be a non-zero contact angle between edge of meniscus and the wall of the capillary tube. If contact angle is θ_c , then

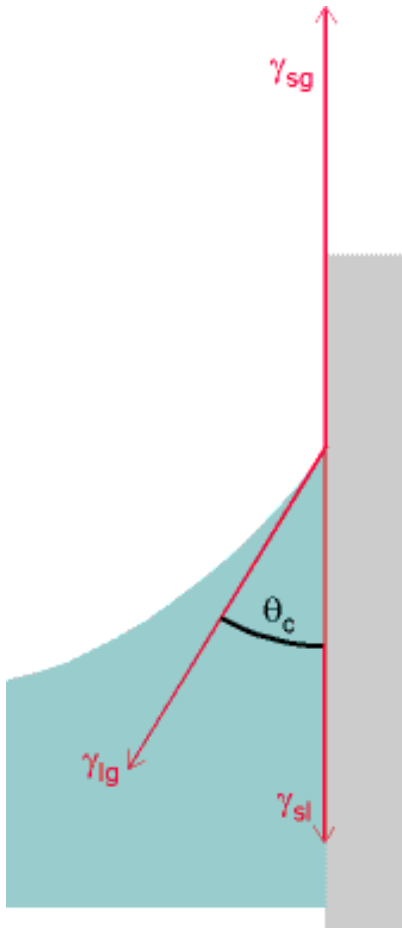
$$h = \frac{2\gamma}{\rho g r} \cos \theta_c$$

Contact angle comes from a balance of forces where the liquid and solid make contact (the **interface**). Vertical forces are in balance if surface tensions between all of the phase interfaces (energy need to create a unit area in each of the interfaces) obey

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta_c$$

solving for the contact angle:

$$\cos \theta_c = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$



Contact Angle

If work of adhesion of the liquid to the per area of unit contact is w_{ad} , then

$$w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$$

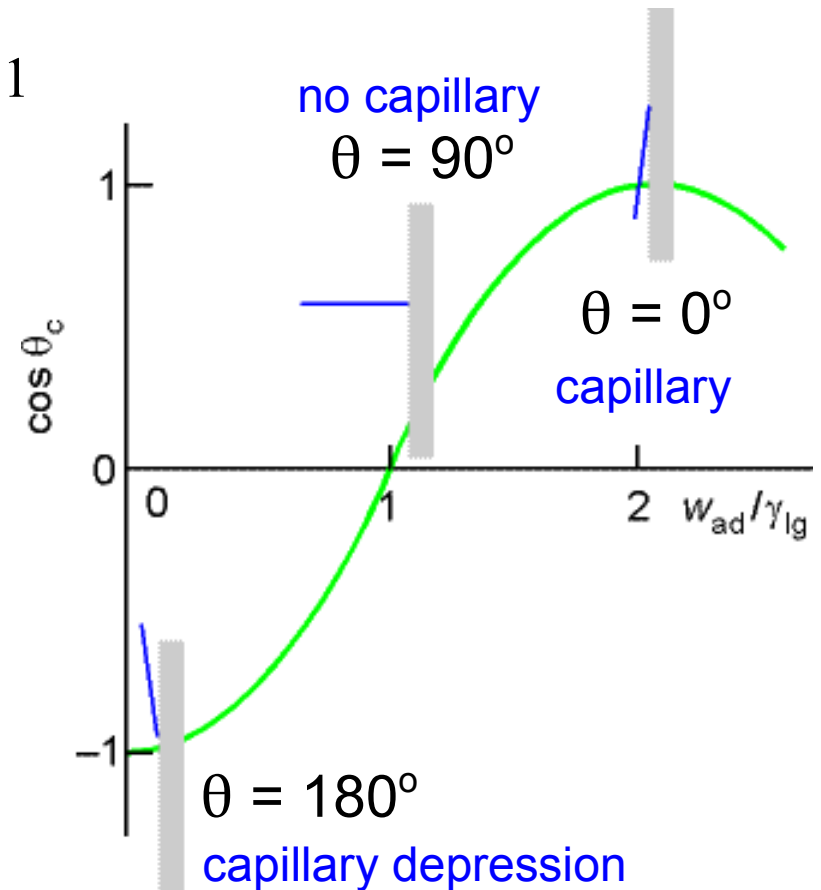
and the contact angle is rewritten as

$$\cos \theta_c = \frac{w_{ad}}{\gamma_{lg}} - 1$$

$\theta_c > 0^\circ$, $w_{ad} > \gamma_{lg}$, liquid completely spreads over (wets) the surface

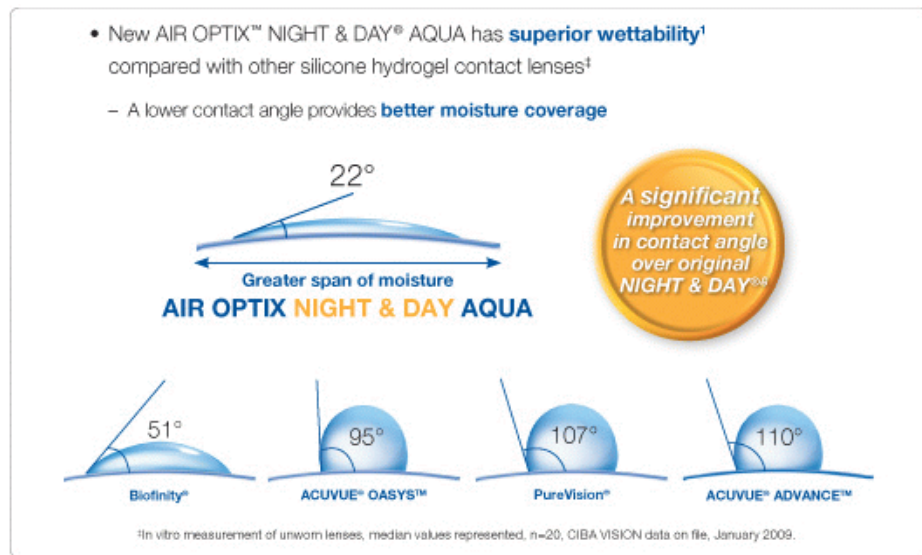
$\theta_c > 90^\circ$, $w_{ad} < \gamma_{lg}$, liquid does not spread over (does not wet) the surface

For mercury, $\theta_c = 140^\circ$, meaning $w_{ad}/\gamma_{lg} = 0.23$, indicating very low adhesion of the mercury to glass, because of the stronger cohesive forces in the mercury



Contact Angle & Wettability

Contact lenses: it is desirable to have low contact angles (water droplets) to assure **high wettability** and coverage of the lens with moisture (these surfaces are designed to be **hydrophilic**).



For top coatings on surfaces (cars, countertops, leaves, etc.), high contact angles assure **low wettability**, making the surfaces easy to clean (hydrophobic). The example above is for the lotus leaf.

LEFT: contact lenses: http://www.airoptix.com/.../AONDA_Wettability.shtml

RIGHT: :Lotus leaf and nanopatterning: www.npl.co.uk/.../wettability-and-nanopatterning