# 03_Contact Angle (Heterogeneous Nucleation)

# Overview

•Surface Energy and Surface Tension

•Equilibrium shape of a droplet on a surface

•Heterogeneous nucleation (the significance of the volume of the critical nucleus and the contact angle)

•Incubation time - why does a nucleus grow when the energy slope is unfavorable (upwards).

# Surface Energy and Surface Tension

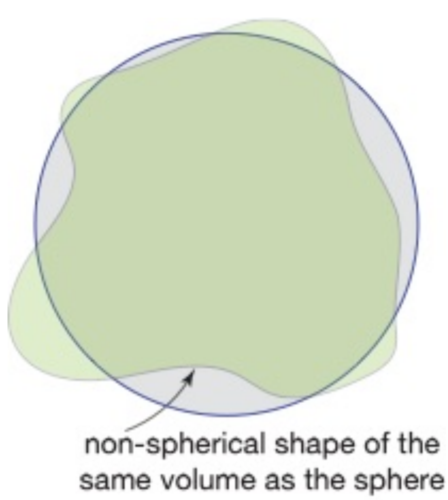
## Experimental Manifestation

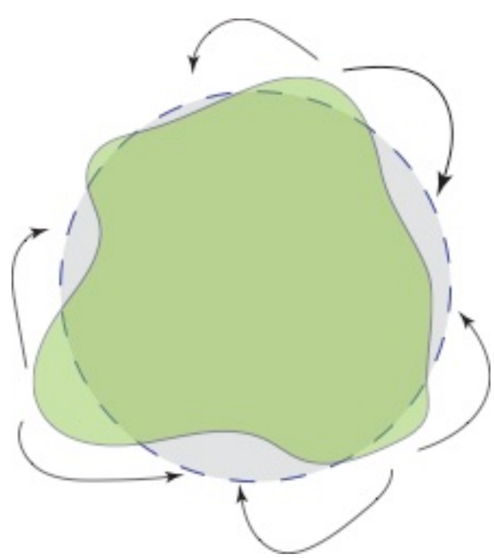
### Surface Energy

Three dimensional objects seek to minimize their surface area to achieve low surface energy. It is intuitively obvious that the lowest energy shape of three-dimensional form is a "sphere", which has the lowest surface area.

Units are J m$^{-2}$

The non-spherical shape has a larger volume than the perfect sphere, and therefore wants to assume a spherical shape.



In the picture on the right the spherical shape is obtained by transported mass from protrusions into the valleys, that is from regions with positive curvature to regions with negative curvature.

The driving force for the transport is therefore related to

$$+\frac{2\gamma_S}{r^{+convex}}-\frac{2\gamma_S}{r^{-concave}} \qquad (1)$$

since the surface with a positive curvature has a higher energy than the surface with a negative curvature.

Compare to $r^*=\dfrac{2\gamma_S}{\Delta G^*}$

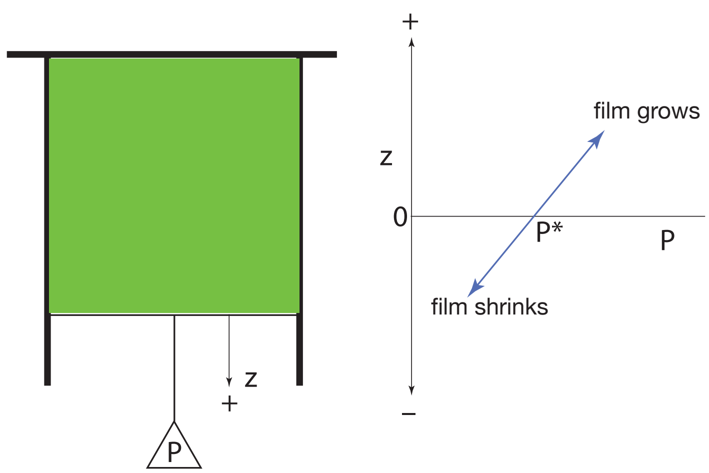
we can write the equation as follows: $\Delta G^*=\dfrac{2\gamma_S}{r^*}$ (2)

where $\Delta G^*$ was the driving force in the nucleation problem. Therefore Eq. (1) becomes the driving force for smoothing the surface into the shape of a sphere.

The mass transport occurs at high temperature. It is called diffusion. The process is called spheroidization.

## Surface Tension

It has units of N m$^{-1}$, that is force per unit length.




At P* there is mechanical equilibrium between surface tension and the applied load

The experiment consists of a thin film (made from soapy water) which is bounded within a rectangular wire frame, where the bottom leg can slide up and down (ideally frictionless movement). Now to hold the film unfolded we must apply a weight to the sliding wire.

Say the length of the wire is L. Then the applied force per unit length is given by

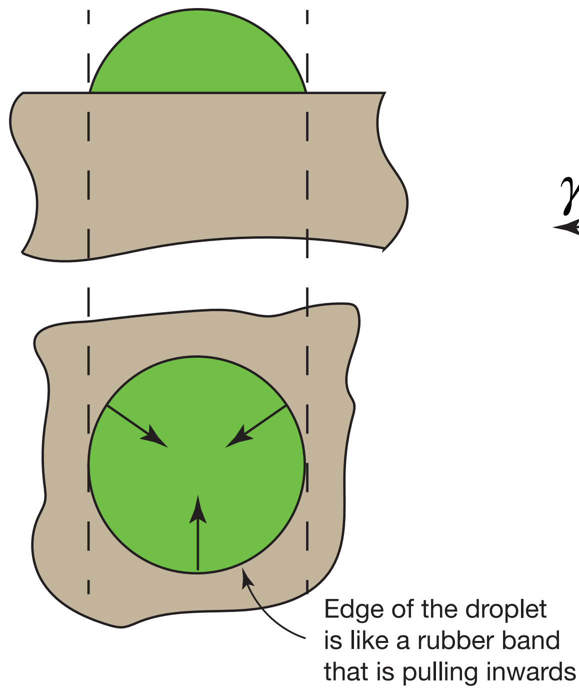
$\dfrac{P}{L}$ which has units of N m$^{-1}$.

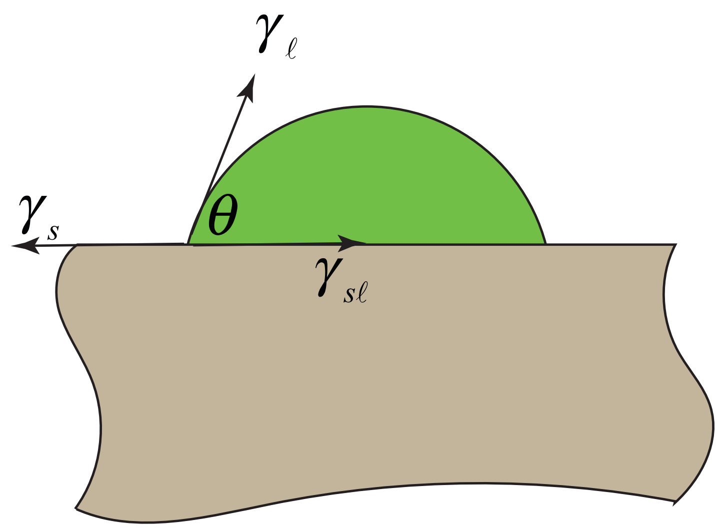
Therefore at equilibrium

$$2\gamma_\ell=\frac{P^*}{L}$$

This is now we measure the surface tension of liquids.

# Equilibrium shape of a droplet on a surface




We ask what will be the equilibrium shape of the droplet on a solid surface (water droplet on a crystal of potassium iodide)

Strictly speaking the equilibrium shape will be determined by minimizing the change in all components of the interfacial energy of which there are three

•surface energy of the liquid $\gamma_\ell$

•Surface energy of the free surface of the solid, $\gamma_S$

•Interfacial energy of the solid-liquid interface, $\gamma_{S\ell}$

For rigorous analysis we need to consider how the total surface energy is affected by shape (for example if the free surface area of the solid increases then the solid - liquid interface area must decrease).

The Simple Solution is Given by the Contact Angle

$$\gamma_S = \gamma_{S\ell} + \gamma_\ell \cos\theta \qquad (3)$$

The contact angle is a handbook value related to a specific solid and a specific liquid.

A smaller contact angle implies better wetting.

# Application to Heterogeneous Nucleation

We have learned that the probability of nucleation depends on the volume of the critical nucleus. The radius of the nucleus does not change but its volume reduces from homogeneous to heterogeneous nucleation, AND the volume depends on the contact angle.

From geometry:

The volume of the critical nucleus is given by

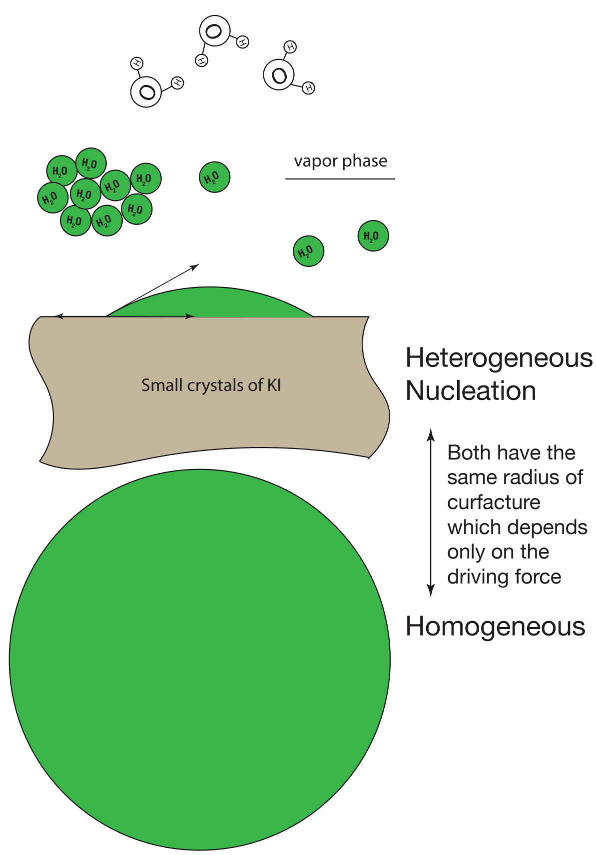
$$V^* = r^{*3} F_V(\theta) \qquad (4)$$

where,

$$F_V(\theta) = \frac{2\pi}{6}\left(2 - 3\cos\theta + \cos^3\theta\right)$$

Note that $F_V \rightarrow 0, \text{ if } \theta \rightarrow 0$. It becomes equal to a hemisphere if $\theta \rightarrow \frac{\pi}{2}$ .

# Homogeneous vs Heterogeneous Nucleation




The principal difference between homogeneous and heterogeneous nucleation is related to the volume of the nucleus of a critical size. The volume of the nucleus informs about the number of atoms that must aggregate to form a cluster of critical size. The probability of nucleation falls steeply as these number of atoms increase.

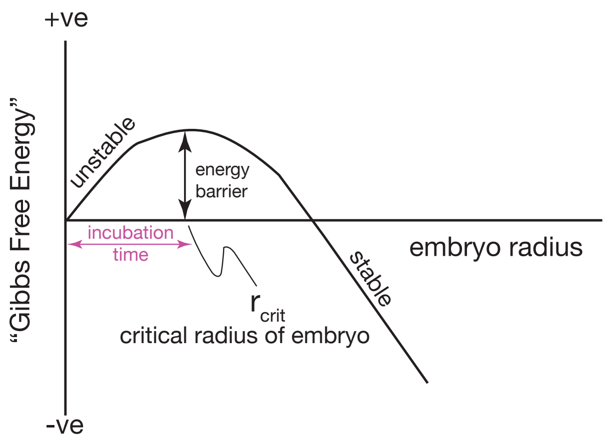
The volume of the nucleus depends (i) on the radius of curvature of the surface of the nucleus - which is the same for homogeneous and heterogeneous nucleation:

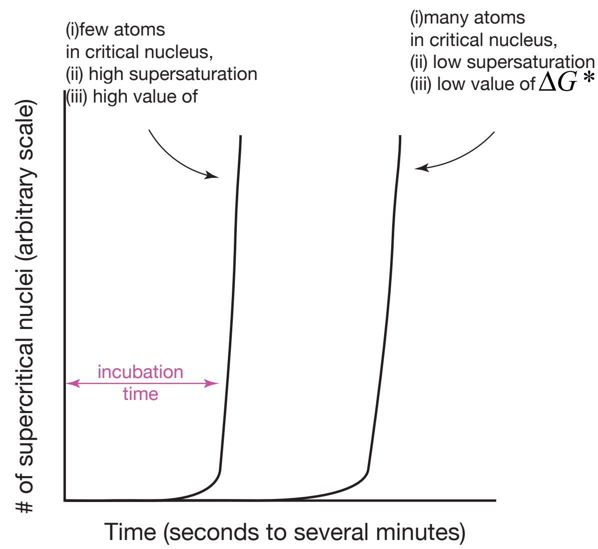
$$r^* = \frac{2\gamma_s}{\Delta G^*}$$

and (ii) on the nucleation site. The site can have a very large effect on the volume of the nucleus.

As shown on the right the full sphere and a segment of the sphere on the surface have the same radius of curvature but very different volume. The volume on the surface depends on the contact angle which was discussed just above. It is for this reason that heterogeneous nucleation is so effective; this is the reason why cloud seeding with potassium works. KI has a very low wetting angle for water droplets.

# Incubation Time




The question can be asked why does the embryo grow at all when the free-energy is rising, which is contrary to usual thinking where things happen only if the free-energy decreases. Answer lies in understanding how the embryo grows.

Imagine a cloud of many $H_2O$ molecules that are in a state where they want to condense. To do so they must nucleate that is, form a cluster of atoms (actually molecules) that is supercritical (which we have related just above to a certain number of atoms in the cluster).

The "abnormal" growth of the embryo before it becomes "supercritical", that is $r < r^*$, is related to the atomistic mechanism of the attachment of atoms arriving at the surface from vapor and then either sticking to the surface or being released back to the vapor phase.

Thus, the interaction between the vapor and a surface can involve three events:

i. The arrival rate of atoms on the surface (this is related to the vapor pressure). We write the rate of arrival in terms of the time interval, $\Delta t_{in}$, between each impingement event; the subscript "in" stands for incoming atoms.

ii. The emission rate of the atoms back into the vapor phase. We write the rate of emission in terms of the time interval, $\Delta t_{out}$, between each emission event back to the vapor; the subscript "out" stands for the atoms leaving the surface back to the vapor phase.

Clearly, the embryo will grow if $\Delta t_{out} > \Delta t_{in}$, that is the residence time is greater than the arrival time, that is, the arrival rate is faster than the etching rate. When the embryo is supercritical then the atoms stick because they reduce the free energy of the embryo; therefore, $\Delta t_{out} \gg \Delta t_{in}$.

The key question is how the embryo can grow, albeit very slowly, even when going uphill in free energy, when the embryo is subcritical? To understand we must consider the atomic process by which atoms (or molecules) arrive on a surface and then, may be, re-emitted into the vapor. The rate of re-emission depends on the local bonding environment that the host offers to the arriving atom. At some sites the local environment will have strong bonding, and in other places it will be weaker (than the average). Thus the distribution for $\Delta t_{out}$ will have a bell-shaped curve; atoms with longer $\Delta t_{out}$ will have a chance of sticking.

The time between arrivals will depend on the vapor pressure. The vapor pressure is related to $\Delta G^*$, which is related to the supercooling:

$$\Delta G^* = \Delta H \frac{\Delta T}{T_{\text{dew-point}}}, \quad (5)$$

the critical radius is given by

$$r^* = \frac{2\gamma_s}{\Delta G^*} \quad (6)$$

and, the number of atoms in an embryo of critical size is given by

$$n^* = \frac{r^{*3} F_V(\theta)}{\Omega} \quad (7)$$

It can be analyzed from above equations, as shown in the figure at the start of this section, that larger supercooling leads to smaller number of atoms in the embryo of critical size. It also leads to a higher vapor pressure, relative to the equilibrium vapor pressure. Both of these factors hasten the formation of a critical embryo:

i. The higher vapor pressure increases the impingement rate that is reduces $\Delta t_{in}$,

ii. Smaller critical radius reduces the volume of the critical nucleus, that is the cluster needs to have fewer atoms to render it critical,

iii. Heterogeneous nucleation also reduces the volume as explained above in terms of the contact angle, which significantly reduces the number of atoms in a critical nucleus.

The smaller the number of atoms in an embryo of critical size the shorter is the incubation time. Indeed this relationship is highly non-linear.