دانشگاه سمنان
Semnan University

Nucleation aspects in growth of crystals

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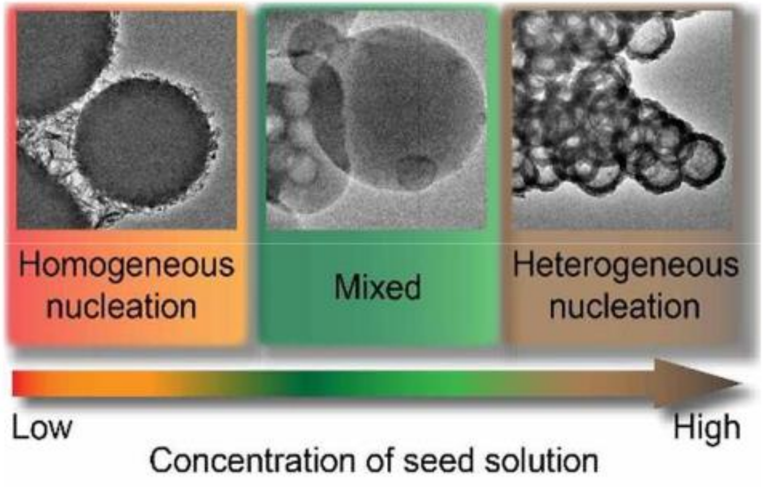
Definition

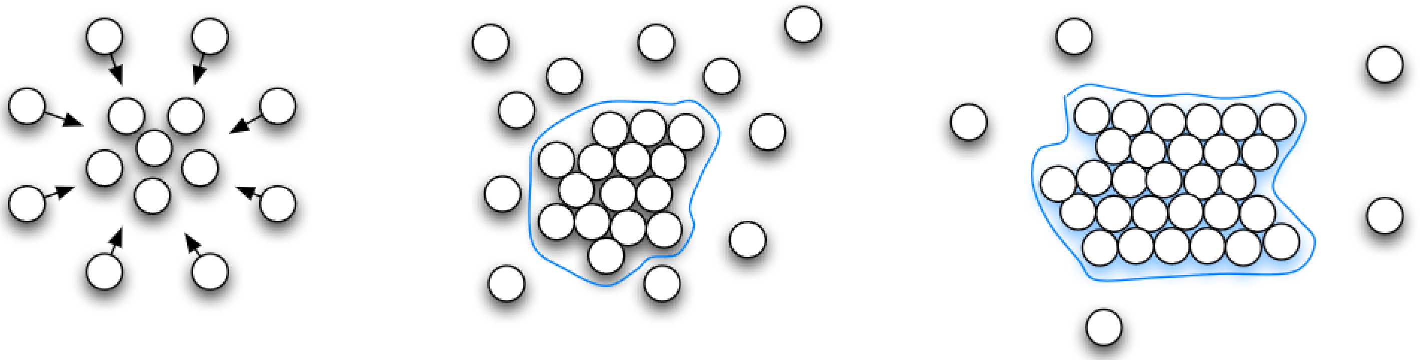
The formation of a new crystalline entity from a solution starts through the nucleation process. *Nucleation* is defined as the series of atomic or molecular processes by which the atoms or molecules of a reactant phase rearrange into a cluster of the product phase large enough as to have the ability to grow irreversibly to a macroscopically larger size.



Definition

During Solidification the atomic arrangement changes from a random or short-range order to a long range order or crystal structure.

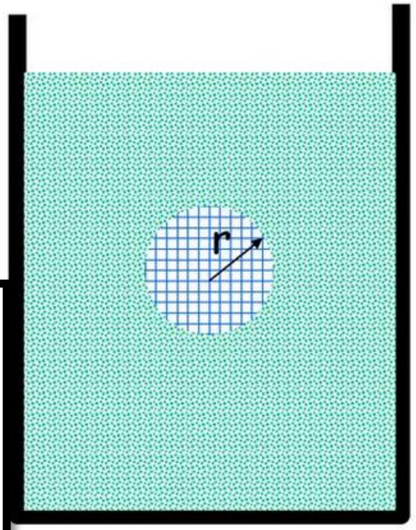
Nucleation occurs when a small nucleus begins to form in the liquid, the nuclei then grows as atoms from the liquid are attached to it.



The crucial point is to understand it as a balance between the free energy available from the driving force, and the energy consumed in forming new interface. Once the rate of change of free energy becomes negative, then an embryo can grow.

Types of nucleation

Homogeneous nucleation



Spherical ball of solid of radius R in the middle of the liquid at a temperature below T_m

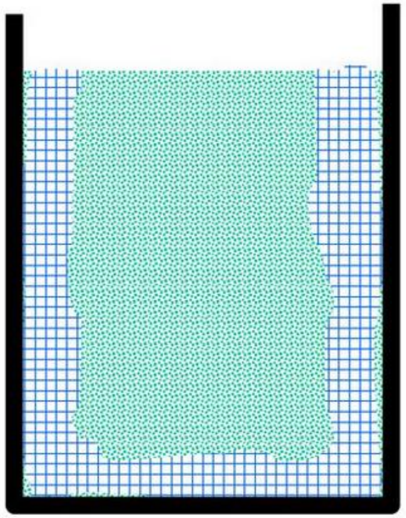
Homogeneous nucleation

G_L = free energy of liquid per unit volume

G_S = free energy of solid per unit volume

$$\Delta G = G_S - G_L$$

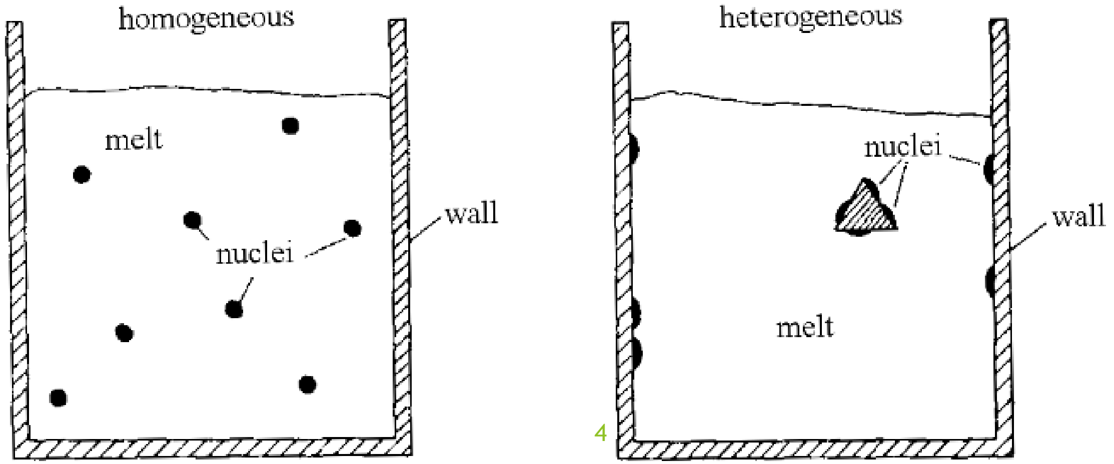
Heterogeneous nucleation



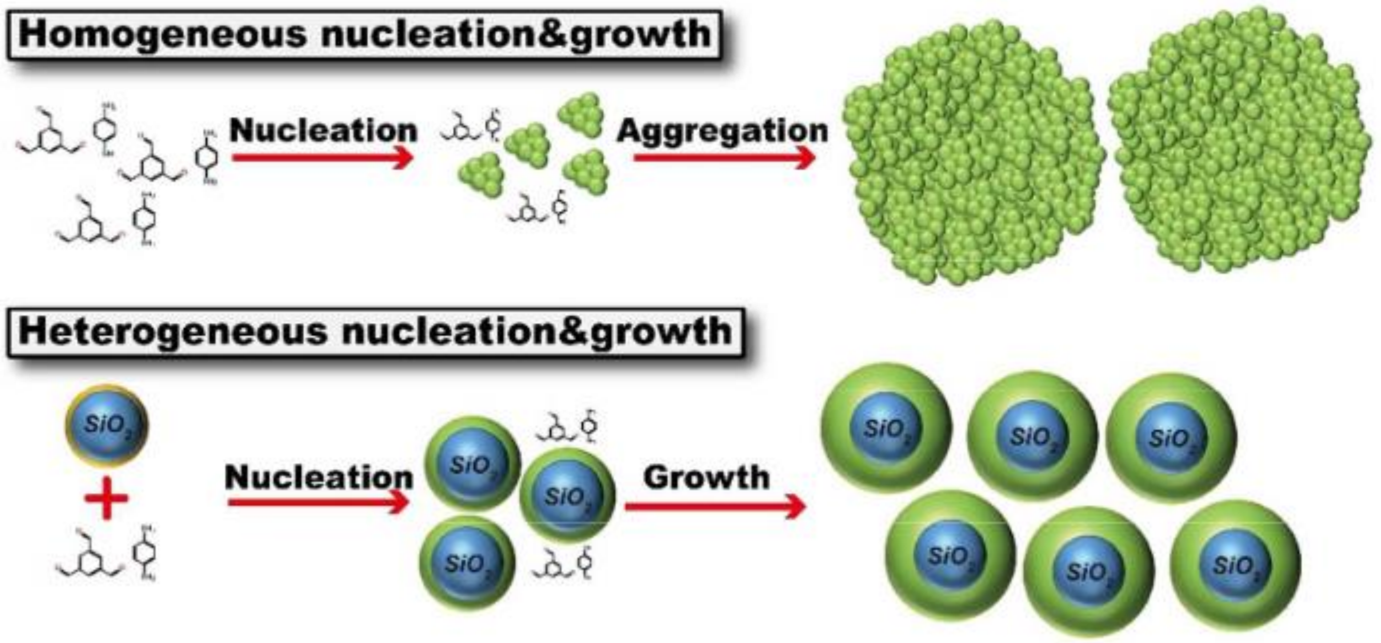
How does solidification begins?

Usually at the walls of the container

Heterogeneous nucleation.



Heterogeneous nucleation and growth of highly crystalline imine-linked covalent organic frameworks

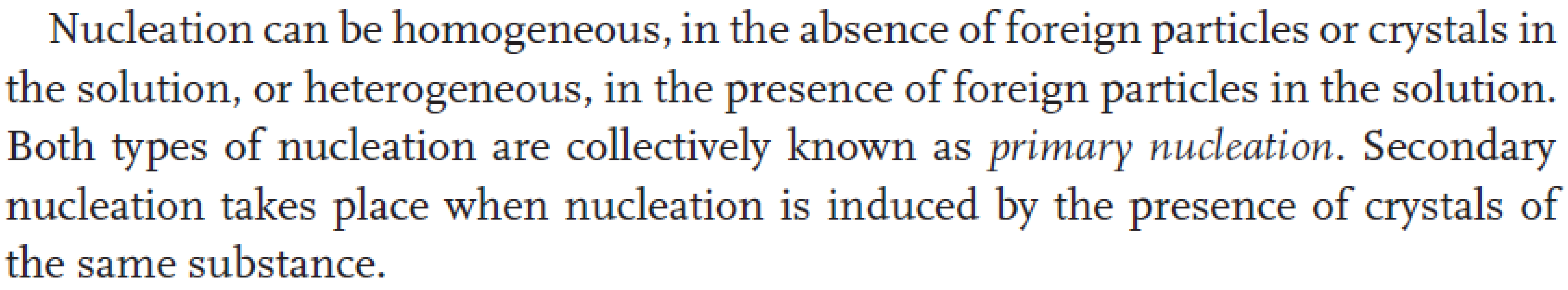


Scheme 2 Schematic process of the homogeneous and heterogeneous nucleation and growth.

- A heterogeneous nucleation and growth method is reported to synthesize imine-linked covalent organic frameworks (COFs). Excellent crystallinity and a high surface area are obtained.
- The introduction of heterogeneous nuclei suppresses the fast precipitation of amorphous structures at the early stage while promoting the crystallization of COFs during the growth process.

Yuan, Yuchen; Sun, Bing; Cao, An-Min; Wang, Dong; Wan, Li-jun (2018). *Heterogeneous nucleation and growth of highly crystalline imine-linked covalent organic frameworks. Chemical Communications, (), 10.1039.C8CC02381F–.*
doi:10.1039/C8CC02381F

Primary and secondary nucleation



Nucleation can be homogeneous, in the absence of foreign particles or crystals in the solution, or heterogeneous, in the presence of foreign particles in the solution. Both types of nucleation are collectively known as *primary nucleation*. Secondary nucleation takes place when nucleation is induced by the presence of crystals of the same substance.

- **Primary nucleation: the appearance of a new phase or first crystal that does not rely on a new phase**

- **Secondary nucleation: Crystal nuclei produced from a preexisting crystal**

Characteristics of nucleation

- 1-Nucleation time
- 2-It may occur slow or fast or does not occur
- 3-It is described by classical nucleation theory(CNT)
- 4-Effect of impurities

Examples of the nucleation

- Fluids (gases and liquids)
- Crystals
- Solids

Fluids (gases and liquids)

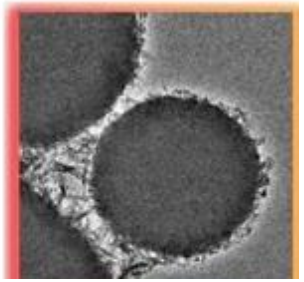
Nucleation of carbon dioxide bubbles around a finger

- Clouds form when wet air cools and many small water droplets nucleate from the supersaturated air.
- The excess vapor begins to nucleate and to form small water droplets which form a cloud.
- Nucleation of the droplets of liquid water is heterogeneous, occurring on particles referred to as cloud condensation nuclei.
- Cloud seeding is the process of adding artificial condensation nuclei to quicken the formation of clouds.
- Bubbles of carbon dioxide nucleate shortly after the pressure is released from a container of carbonated liquid.

Crystals

- The most common crystallization process on the Earth is the formation of ice.
- Liquid water does not freeze at 0 ˚C unless there is ice already present; cooling significantly below 0 ˚C is required to nucleate ice and so for the water to freeze.
- For example, small droplets of very pure water can remain liquid down to below -30 ˚C although ice is in a stable state below 0 ˚C.
- Many of the materials we make and use are crystalline but are made from liquids, e.g. crystalline iron made from a liquid iron cast into a mold, so the nucleation of crystalline materials is widely studied in industry
- For example, platinum deposited onto TiO2 nanoparticles catalyzes the liberation of hydrogen from water

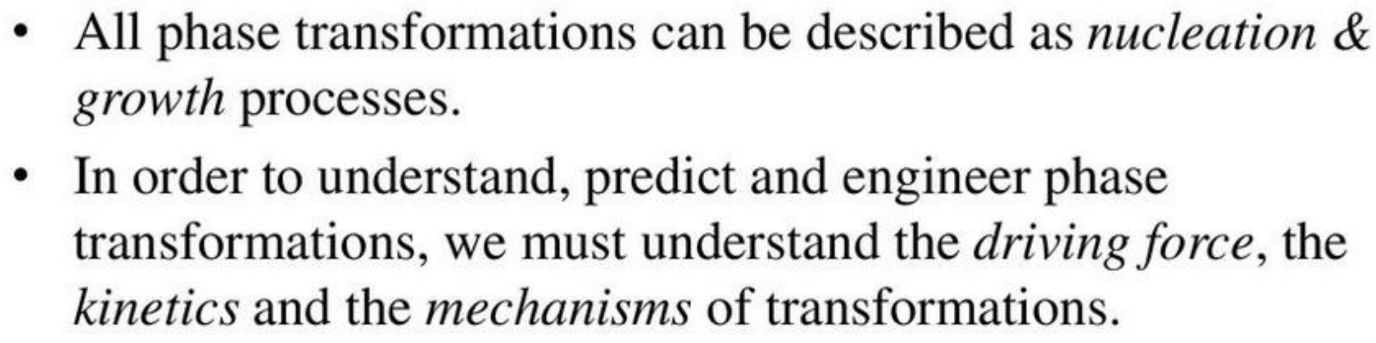
Solids



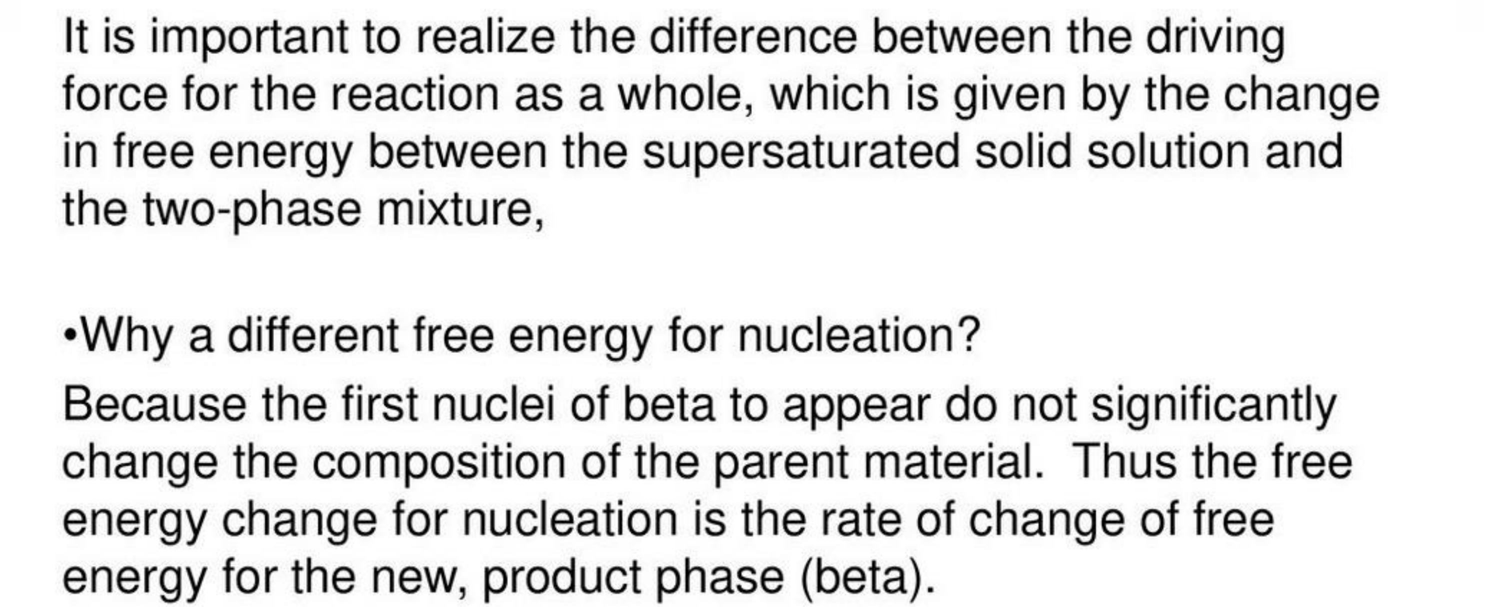
- In non-crystalline glasses, the nucleation and growth of impurity precipitate in crystals at, and between, grain boundaries are quite important in the industry.

- For example in metals solid-state nucleation and precipitate growth plays an important role in modifying mechanical properties like ductility, while in semiconductors it plays an important role e.g. in trapping impurities during integrated circuit manufacture.

Driving force for nucleation



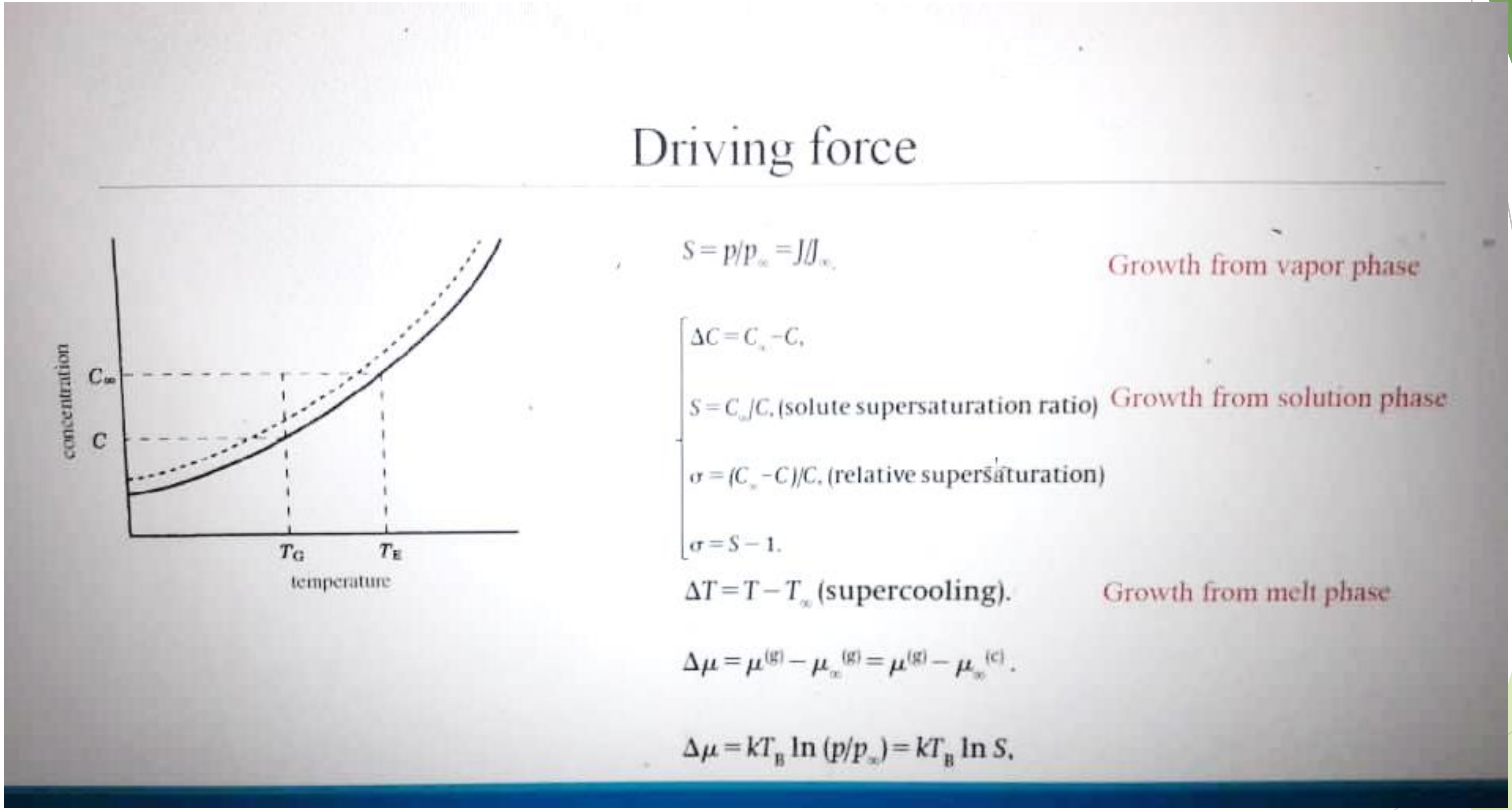
- All phase transformations can be described as *nucleation & growth* processes.
- In order to understand, predict and engineer phase transformations, we must understand the *driving force*, the *kinetics* and the *mechanisms* of transformations.



It is important to realize the difference between the driving force for the reaction as a whole, which is given by the change in free energy between the supersaturated solid solution and the two-phase mixture,

•Why a different free energy for nucleation?

Because the first nuclei of beta to appear do not significantly change the composition of the parent material. Thus the free energy change for nucleation is the rate of change of free energy for the new, product phase (beta).



Driving force

$S = p/p_\infty = J/J_\infty$ Growth from vapor phase

$\Delta C = C_\infty - C,$

$S = C_\infty/C,$ (solute supersaturation ratio) Growth from solution phase

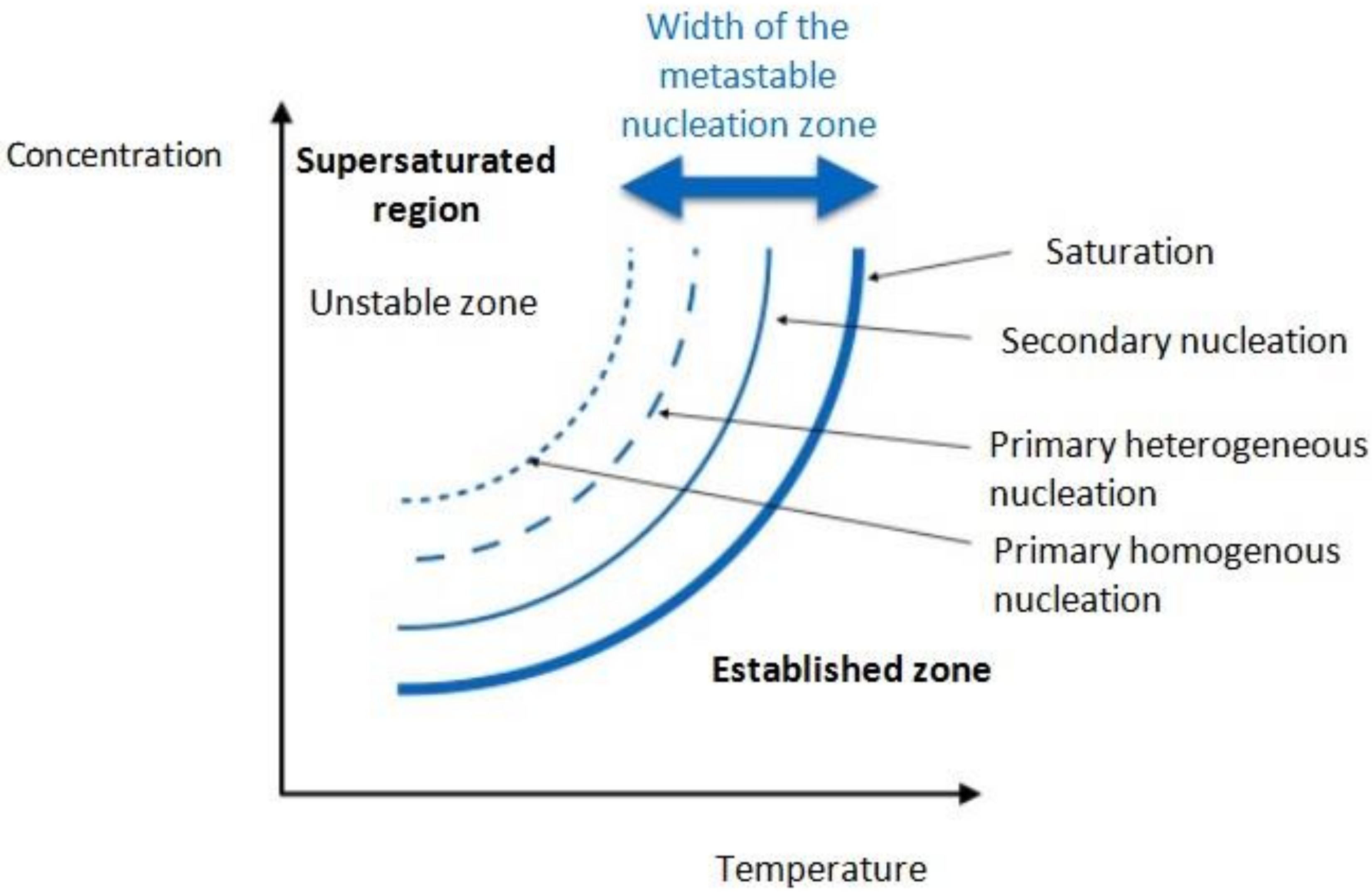
$\sigma = (C_\infty - C)/C,$ (relative supersaturation)

$\sigma = S - 1.$

$\Delta T = T - T_\infty$ (supercooling). Growth from melt phase

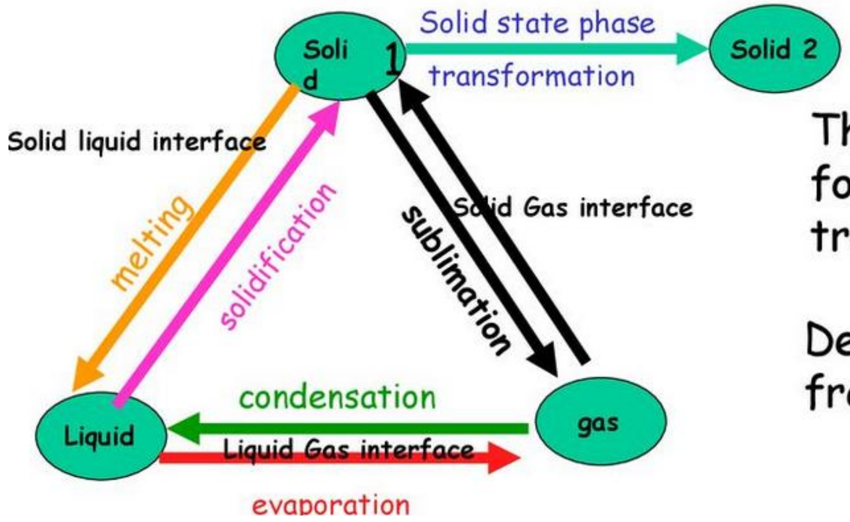
$$\Delta\mu = \mu^{(g)} - \mu_\infty^{(g)} = \mu^{(g)} - \mu_\infty^{(c)}.$$

$$\Delta\mu = kT_B \ln(p/p_\infty) = kT_B \ln S.$$


Width of the metastable nucleation zone
Concentration
Supersaturated region
Unstable zone
Saturation
Secondary nucleation
Primary heterogeneous nucleation
Primary homogenous nucleation
Established zone
Temperature

Driving force for nucleation

The driving force needed for the nucleation and growth of a crystal is referred to as *supersaturation* and is defined as the difference in chemical potential between a molecule in solution and that in the bulk of the crystal phase



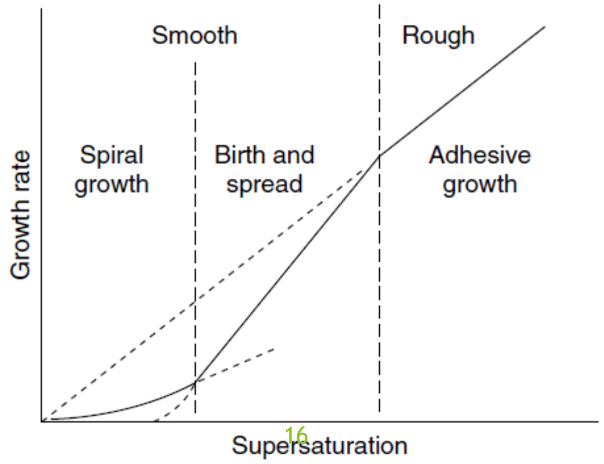
Thermodynamic driving force for a phase transformation

Decrease in Gibbs free energy

Supersaturation

- The growth mechanisms can be classified into three types depending on the interface structure:

- ❑ A surface will transform from smooth to rough at high driving force conditions (high supersaturation)
- ❑ At a low supersaturation, the interface is smooth and spiral growth is the mechanism of growth.
- ❑ After reaching a critical supersaturation for 2D nucleation, birth and spread dominate the growth.
- ❑ In these two domains, crystals are bound by crystallographically flat faces with Polyhedral morphologies.
- ❑ At high supersaturation, the surface transforms to a rough interface and adhesive-type growth dominates.



Mechanisms of growth as a function of supersaturation.

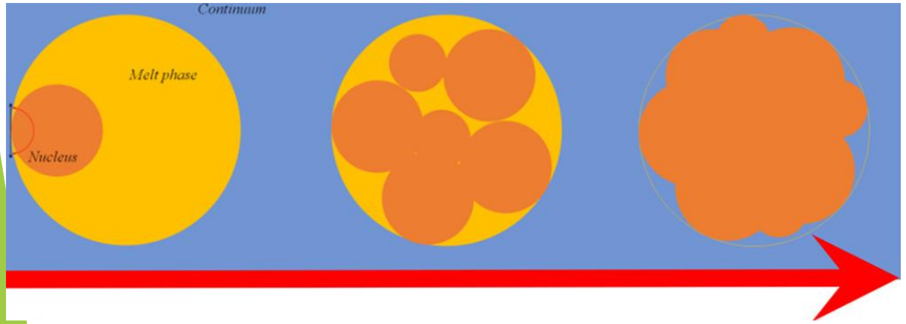
Energy consideration in nucleation

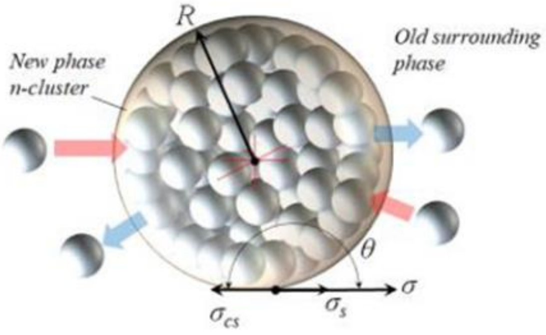
According to nucleation theory, the work necessary to form a cluster of n number of molecules is the difference between the free energy of the system in its final and initial states plus a term related to the formation of an interface between nucleus and solution. This can be expressed by (assuming a spherical nucleus):

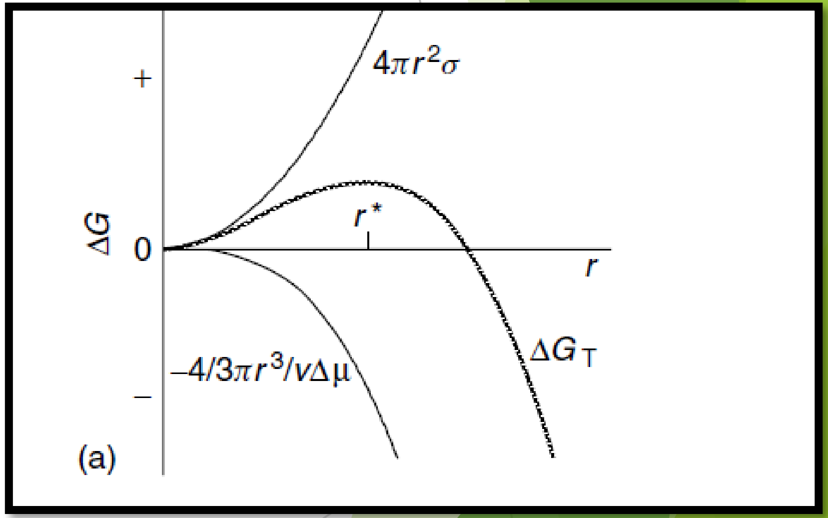
$$\Delta G_T = -n\Delta\mu + 4\pi \cdot r^2\sigma$$

where r is the radius of the nucleus and σ is the surface free energy. If each molecule in the crystal occupies a volume V, then each nucleus will contain $(4/3)\pi \cdot r^3/V$ molecules.

$$\Delta G_T = -\frac{4}{3}\pi \cdot \frac{r^3}{V}\Delta\mu + 4\pi \cdot r^2\sigma$$







(a) Total free energy versus cluster size.

Energy consideration in nucleation

ΔG_T as a function of r; it can be seen how the function reaches a maximum, which represents the energetic barrier that needs to be surpassed to achieve nucleation (ΔG^*). The *value of r at this maximum* (r^*) is defined as the critical radius or nucleus size

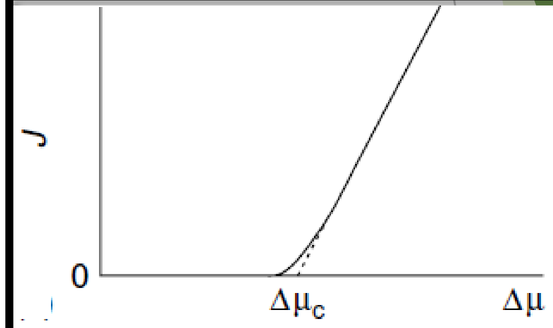
$$r^* = \frac{2\sigma \cdot V}{kT 1\text{n} S}$$

It has been proved that the value of r^* decreases (as well as that of ΔG^*) as the supersaturation increases [6], meaning that the probability of having nucleation in a given system will be higher, the higher the supersaturation.

The rate of nucleation (i.e., the number of nuclei formed per unit time per unit volume) can be expressed by an Arrhenius-type equation

$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right)$$

where A also depends on supersaturation. A typical plot of J as a function of supersaturation (S)



Nucleation rate as a function of supersaturation (showing the critical supersaturation).

This critical supersaturation ($\Delta\mu_c$)

defines the so-called metastable zone where crystal growth can proceed without concomitant nucleation taking place.

Induction Time

Induction time is defined as the amount of time elapsed between the achievement of a supersaturated solution and the observation of crystals. Its value will thus depend on the setting of $t = 0$ and the technique used to detect the formation of crystals.

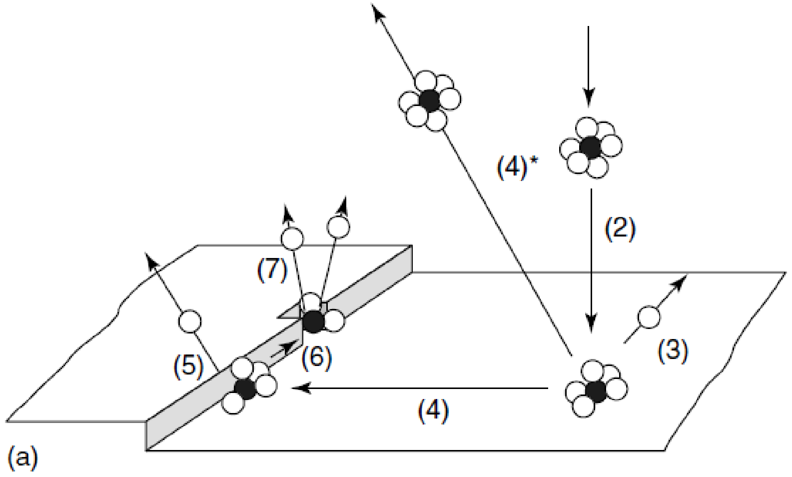
$$\boxed{t_{\mathrm{i}} = t_{\mathrm{r}} + t_{\mathrm{n}} + t_{\mathrm{g}}}$$

The induction time is separated into three periods: t_{r} is the relaxation time, required for the systems to achieve a quasi-steady-state distribution of molecular clusters; t_{n} is the time required for the formation of a nucleus; and t_{g} is the time required for the nucleus to grow to a detectable size.

Crystal Growth

Crystal growth is the series of processes by which an atom or a molecule is incorporated into the surface of a crystal, causing an increase in size. These different processes can be summarized into four steps

1) transport of atoms through solution;
2) attachment of atoms to the surface;
3) movement of atoms on the surface;
4) attachment of atoms to edges and kinks.



(a) Schematic representation of processes involved in the crystal growth: (1) Transport of solute to a position near the crystal surface; (2) diffusion through boundary layer; (3) adsorption onto crystal surface; (4) diffusion over the surface;

Artificial methods

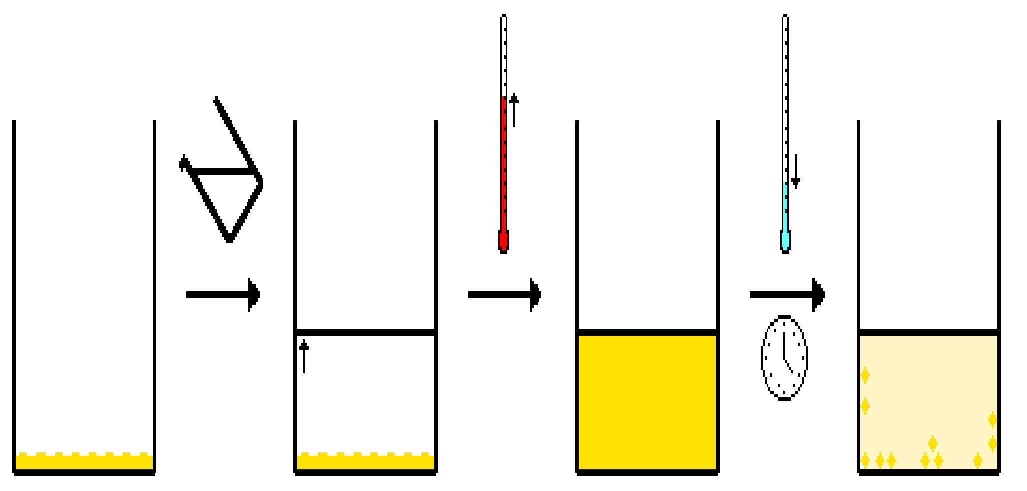
For crystallization (recrystallization) to occur from a solution it must be supersaturated.

This means that the solution has to contain more solute entities (molecules or ions) dissolved than it would contain under the equilibrium (saturated solution).

This can be achieved by various methods, with (1) solution cooling, (2) addition of a second solvent to reduce the solubility of the solute (technique known as antisolvent or drown-out), (3) chemical reaction and (4) change in pH being the most common methods used in industrial practice. Other methods, such as solvent evaporation, can also be used.

Recrystallization

- Typically, the mixture of "compound A" and "impurity B" are dissolved in the smallest amount of hot solvent to fully dissolve the mixture, thus making a saturated solution.
- The solution is then allowed to cool.
- As the solution cools the solubility of compounds in solution drops.
- This results in the desired compound dropping (recrystallizing) from solution.
- The slower the rate of cooling, the bigger the crystals formed.



Crystal Surface Structure

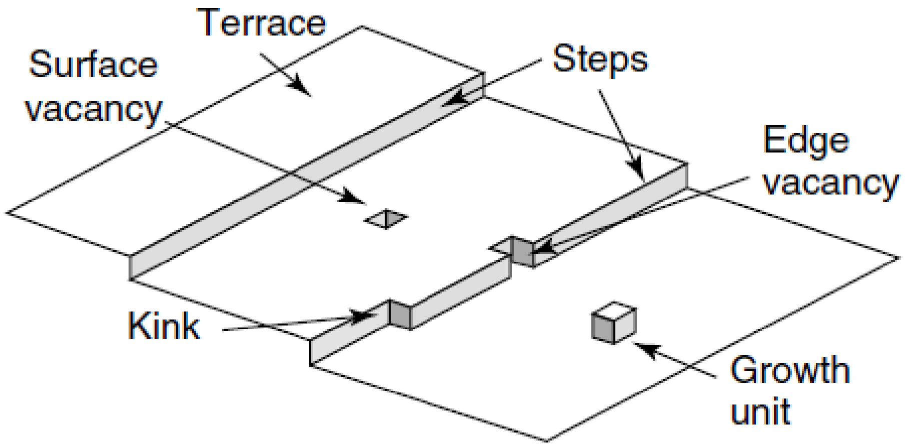
Crystal growth theories are based on considerations of the crystal surface structure

This model envisions the crystal surface as made of cubic units which form layers

These steps contain a number of monoatomic height, limited by steps (or edges).

The area between steps is referred to as a *terrace*, and

it may contain single adsorbed growth units, clusters, or vacancies.



Kossel model of a crystal surface.

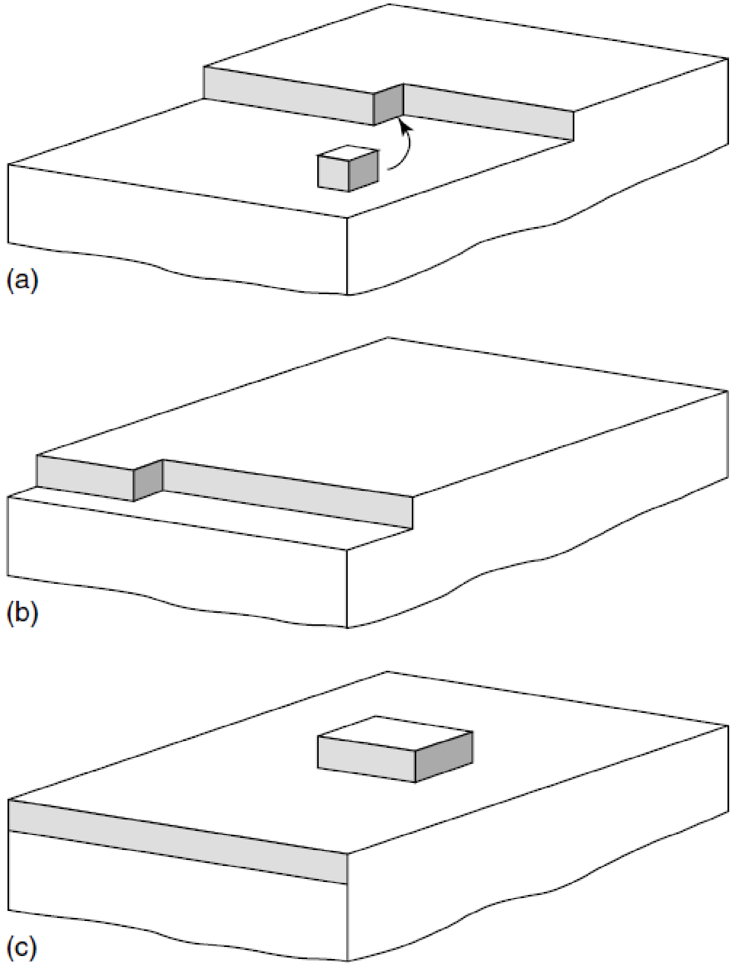
Multinucleation multilayer growth

The total free energy change due to the formation of a 2D nucleus of height *h* and radius *r* can be calculated by using Eq

$$\Delta G_{T-2D} = -\pi \cdot \frac{hr^2}{V}\Delta\mu + 2\pi \cdot rh\sigma$$

The maximum of this function defines the value of the critical radius which is given by

$$r_{2D}{}^{*} = \frac{\sigma \cdot V}{kT \ln S}$$

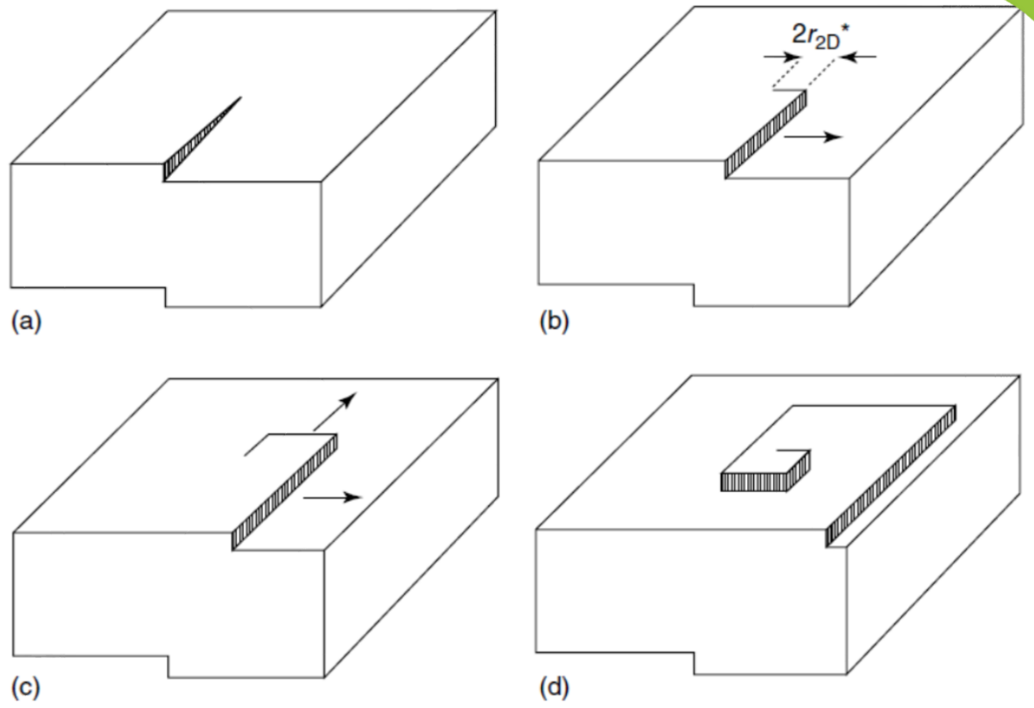


Schematic representation of layer growth. (a) Incorporation of growth units into step. (b) The step has almost advanced to the edge of the crystal. (c) Formation of 2D nucleus.

Spirals growth

The energetics of layer growth predicts that growth takes place at relatively high supersaturation!

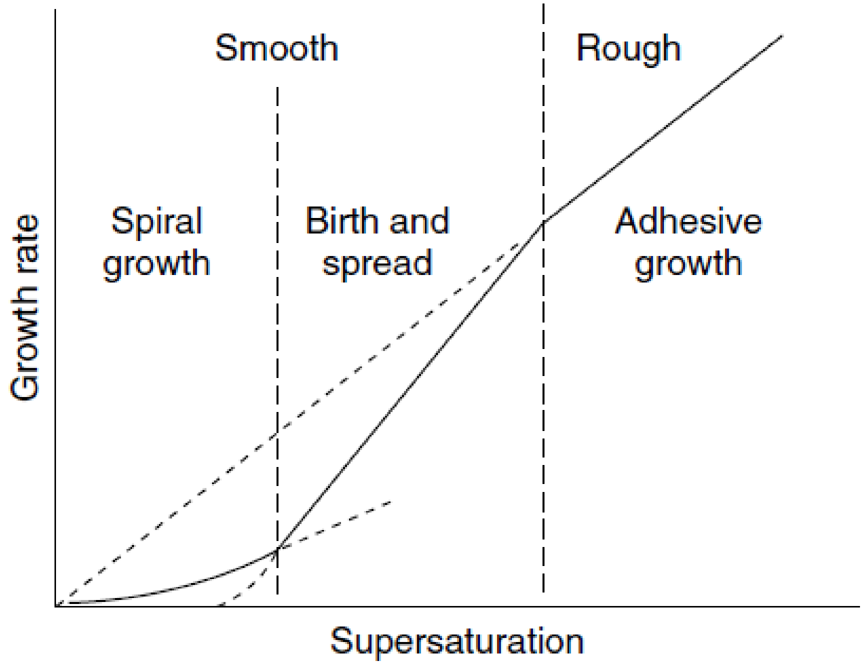
- ☐ **This dilemma was solved by Frank who postulated that crystal surfaces are intercepted by dislocations.**
- ☐ **These dislocations will create steps in the surface, obviating the necessity for 2D nucleation**



Development of a polygonal spiral.

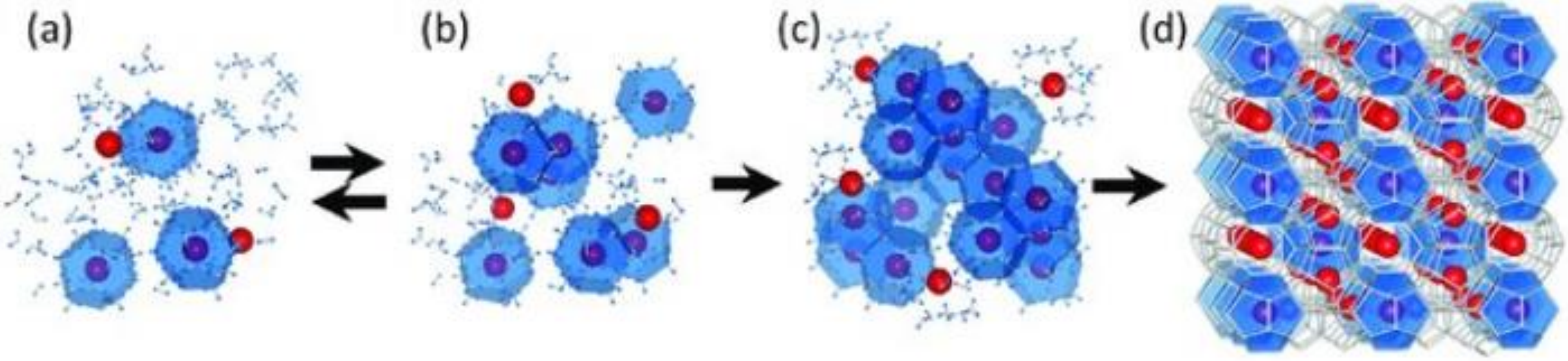
Growth Mechanisms: Rough and Smooth Surfaces

The growth mechanisms can be classified into three types depending on the interface structure.



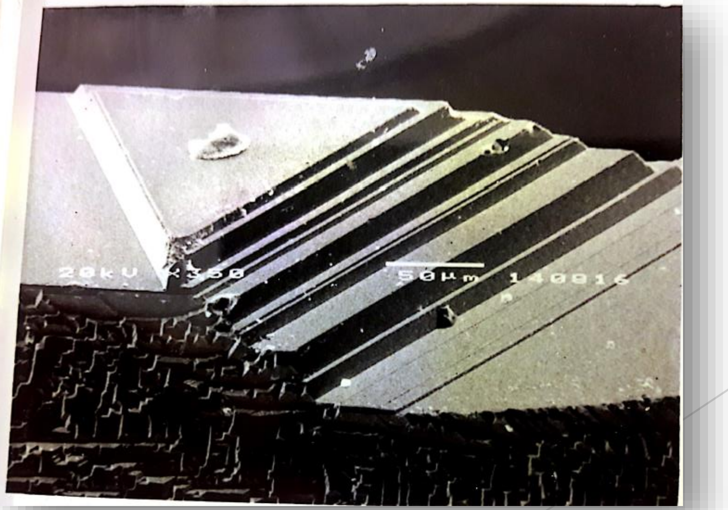
Mechanisms of growth as a function of supersaturation.

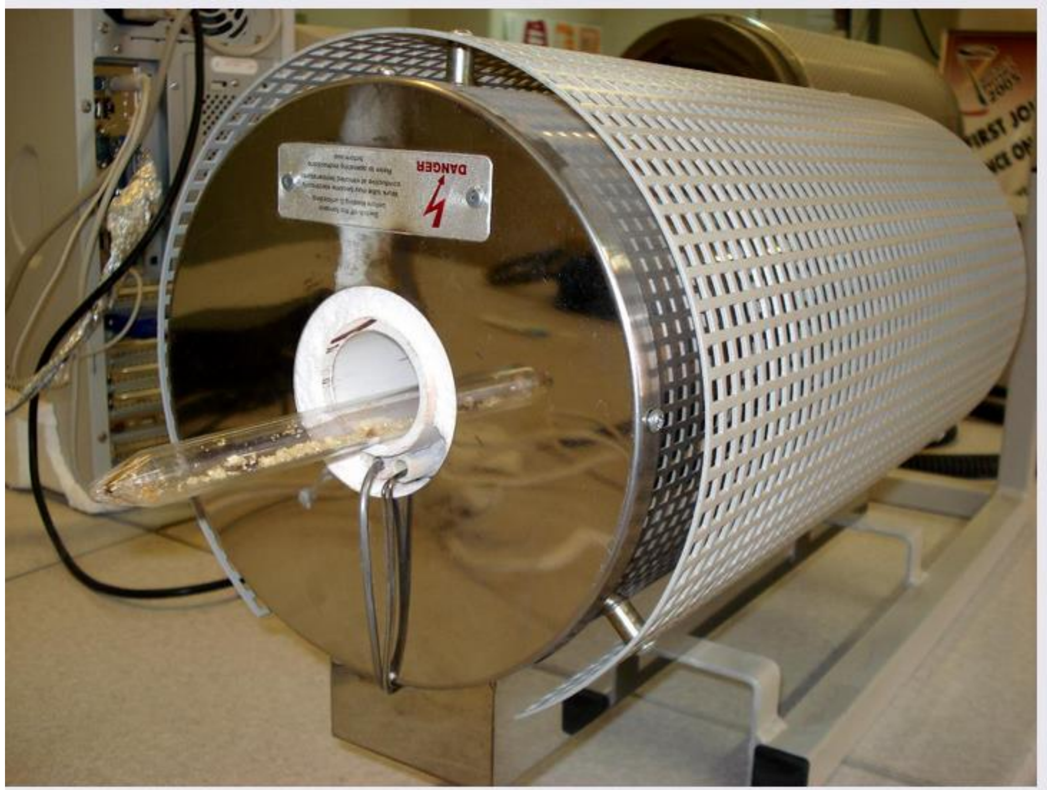
Labile-cluster model of hydrate nucleation: (a) labile-clusters, (b) agglomeration of clusters, (c) primary nucleolus, and (d) hydrate crystal.



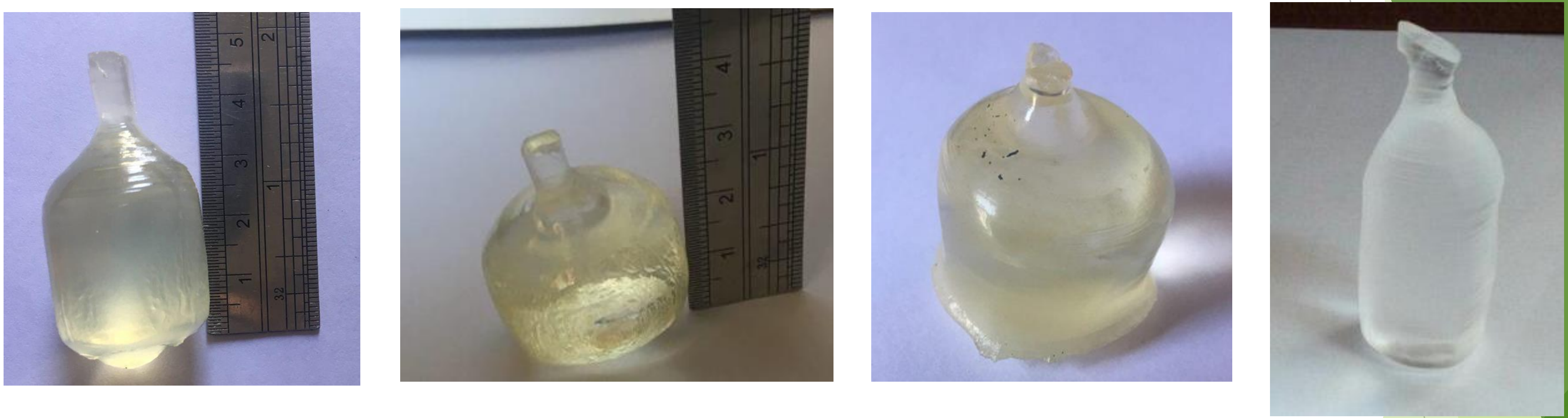

20kV X500
50µm 170828


140818


20kV X350
50µm 140916



Our works



Conclusion

Nucleation is a very sensitive and complicated process that should be controlled by different parameters to start and grow crystals under proper condition

- By considering the balance between the release of free energy by transformation and the cost of creating new interface, the critical free energy for nucleation and the critical size of the nucleus can be derived.
- The undercooling required for nucleation is increased by volume changes on transformation, but decreased by the availability of heterogeneous nucleation sites.

References

Synthesis Mechanism: Crystal Growth and Nucleation *Pablo Cubillas and Michael W. Anderson*

Yuan, Yuchen; Sun, Bing; Cao, An-Min; Wang, Dong; Wan, Li-jun (2018). Heterogeneous nucleation and growth of highly crystalline imine-linked covalent organic frameworks. Chemical Communications, (), 10.1039.C8CC02381F–. doi:10.1039/C8CC02381

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