



**UNIVERSITY OF ROME "LA SAPIENZA"**  
**NANOTECHNOLOGIES ENGINEERING**

# **PRODUCTION AND CHARACTERIZATION OF MICROPARTICLES**

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## **MICROPARTICLES FUNDAMENTAL**

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# CRYSTALLIZATION

- The crystallization process is a separation process of a liquid bulk (solvent) from solids (solutes). At the end of the process, the bulk is less concentrated of the solutes which precipitates in form of crystals.
- Crystallization is one of the most common unit operations in Chemical Engineering to perform this kind of separation (10%). It is widely used for salt, sugar, fertilizer production as well as in pharmaceuticals.

# CRYSTALLIZATION FROM SOLUTION

- The solubility of one component is defined as the maximum mass of solute capable to dissolve in one unit of mass or volume of the solvent. It depends from the molecule, temperature and pressure.
- As soon as the solubility of a solute is exceeded, the solvent is in a state called of supersaturation; on the contrary, if the solvent is capable to dissolve more solute the state is called undersaturated.
- In case of supersaturation, the solvent is not capable to hold the total amount of solute in a dissolved state, and the solute will give rise to small solid crystals which separates from the bulk. These crystals may then grow up to millimeter scale.

# HOW TO GET TO A SUPERSATURATION CONDITION

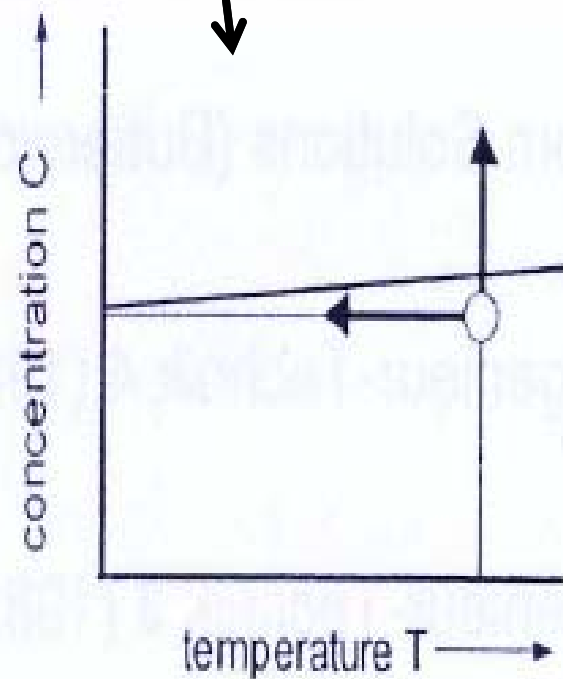
- By cooling or heating: since solubility is a function of temperature, temperature value changes may lead to different saturation conditions of the solvent. It depends if saturation of the specific solute is a positive or negative function of the saturation.
- By evaporation
- By chemical reaction with the solute
- By addition of another solvent or solute capable to change the saturation value of the target solute (salting-out)

The product of the crystallization process are on one side the mother liquor, that is the solvent residue, and on the other one the crystals.

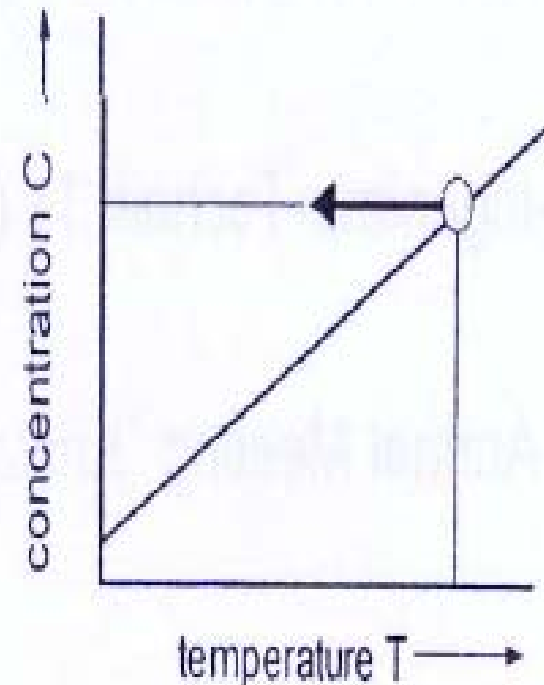
# HOW TO GET SUPERSATURATION

EVAPORATION if saturation changes slightly as a function of T

COOLING if saturation sensibly changes as a function of T



e. g.  
 $\text{NaCl}$   
 $\text{Na}_2\text{SO}_4$   
 $(\text{NH}_4)_2\text{SO}_4$   
 $\text{CaCl}_2$



e. g.  
 $\text{KCl}$   
 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$   
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
 $\text{AgNO}_3$   
melamine

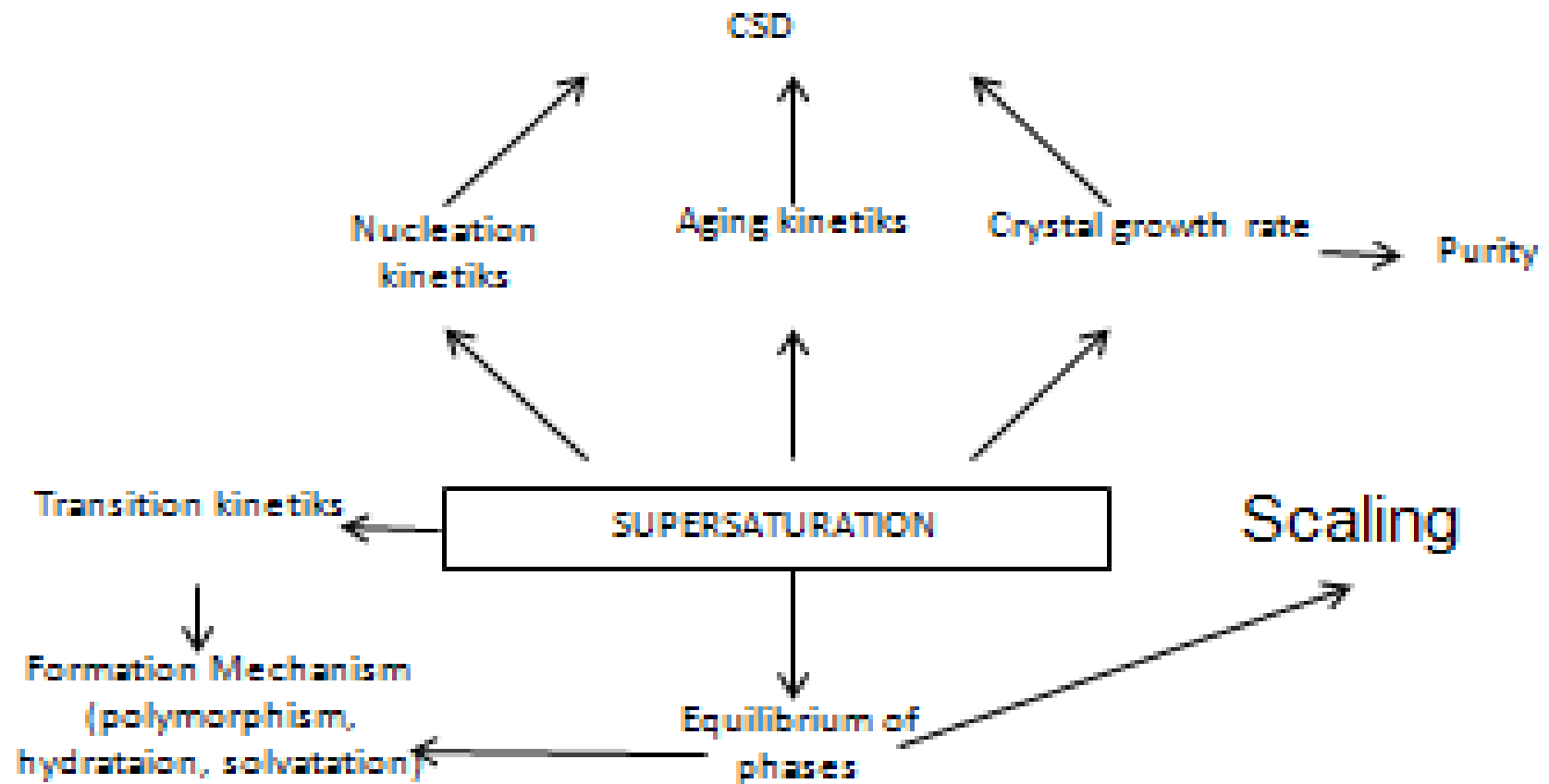
# PROCESS PERFORMANCES

The process performances are a function of:

1. the chemical composition of the obtained crystals (in case of solid production) or of the mother liquor (in case of purification processes)
2. The CSD (crystal size distribution) and their habit.

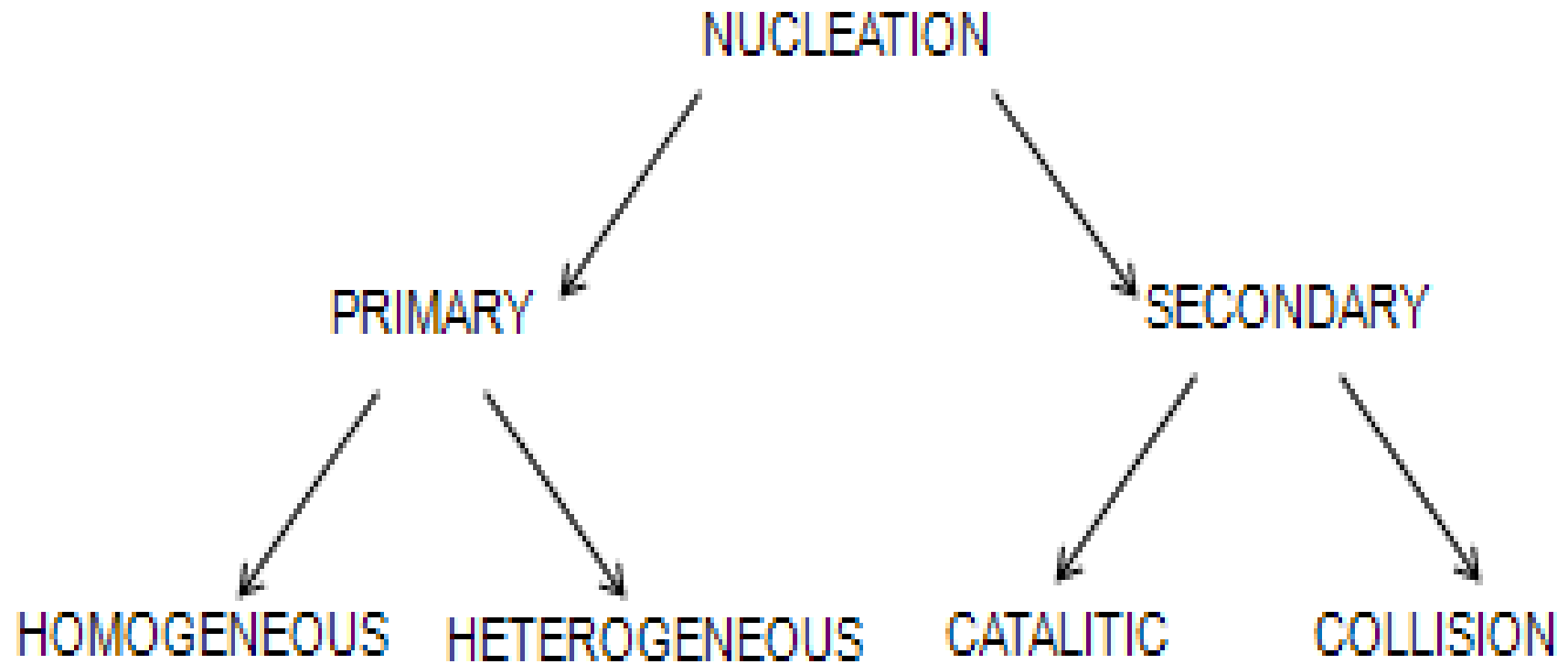
Given a certain purity, in many cases the main parameter is CSD, since the crystal size affects the (correct) use of the product.

# IMPORTANCE OF SUPERSATURATION





# CRYSTAL FORMATION



# NUCLEATION: OUTLINES

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- SUPERSATURATION UNITS
- METASTABLE ZONE
- PRIMARY NUCLEATION
  - HOMOGENEOUS
  - HETEROGENEOUS
- SECONDARY NUCLEATION
- NUCLEATION RATE EXPRESSIONS

## NUCLEATION: INTRODUCTION

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- The condition for **stable equilibrium** between two phases is the equality of their chemical potential.
- If the chemical potential of one of them turns out to be higher than that of the other, mass transport takes place until the chemical potentials become equal again throughout the system.
- The **driving force** of this transport is the difference between the chemical potentials in the two phases, designed as "generalised supersaturation",  $\Delta\mu$ .
- If one of the phases is supersaturated with respect to the state of equilibrium but the other phase is absent, the system is **metastable** and the formation of the missing phase is favourable.

## SUPERSATURATION UNITS

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The fundamental thermodynamic driving force for a crystallization process is the difference in chemical potential between the crystallizing substance  $i$  in the crystal,  $\mu_{i,c}$ , and in the solution or melt,  $\mu_{i,L}$ :

$$\Delta\mu_i = \mu_{i,c} - \mu_{i,L}$$

crystallization takes place when  $\Delta\mu_i < 0$  .

The definition of the chemical potential is as follows:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

where  $\mu_i^0$  is the chemical potential of a pure component and  $a_i$  is the solute activity.

## THE DIMENSIONLESS DRIVING FORCE

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The chemical potential of the solid is equal to that of the liquid solution at equilibrium, that is:

$$\mu_{i,c} = \mu_{i,L}^* = \mu_{i,L}^0 + RT \ln a_i^*$$

and

$$\Delta\mu_i = \mu_{i,L}^* - \mu_{i,L}$$

The dimensionless driving force for the crystallization process,  $\sigma_{\ln a_i}$ , can be written:

$$\sigma_{\ln a_i} = \frac{-\Delta\mu_i}{RT} = v_i \ln \frac{a_i}{a_i^*} = v_i \ln \left[ \frac{\gamma_i x_i}{\gamma_i^* x_i^*} \right]$$

where  $v$  is the number of the dissociated ions

## THE DIMENSIONLESS DRIVING FORCE

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Under the usual following approximation:

- $v_i$  is equal to unity
- The activity coefficient ratio,  $\gamma/\gamma^*$ , is unity.
- The expression  $(x-x^*)/x^*$  is  $\ll 1$ .

the dimensionless supersaturation becomes:

$$\sigma_{\ln a} \cong \sigma = \frac{x - x^*}{x^*}$$

The symbol  $\sigma$  is named **relative supersaturation**.

Other units are

The concentration driving force:

$$\Delta x = x - x^*$$

The supersaturation ratio:

$$S = \frac{x}{x^*}$$

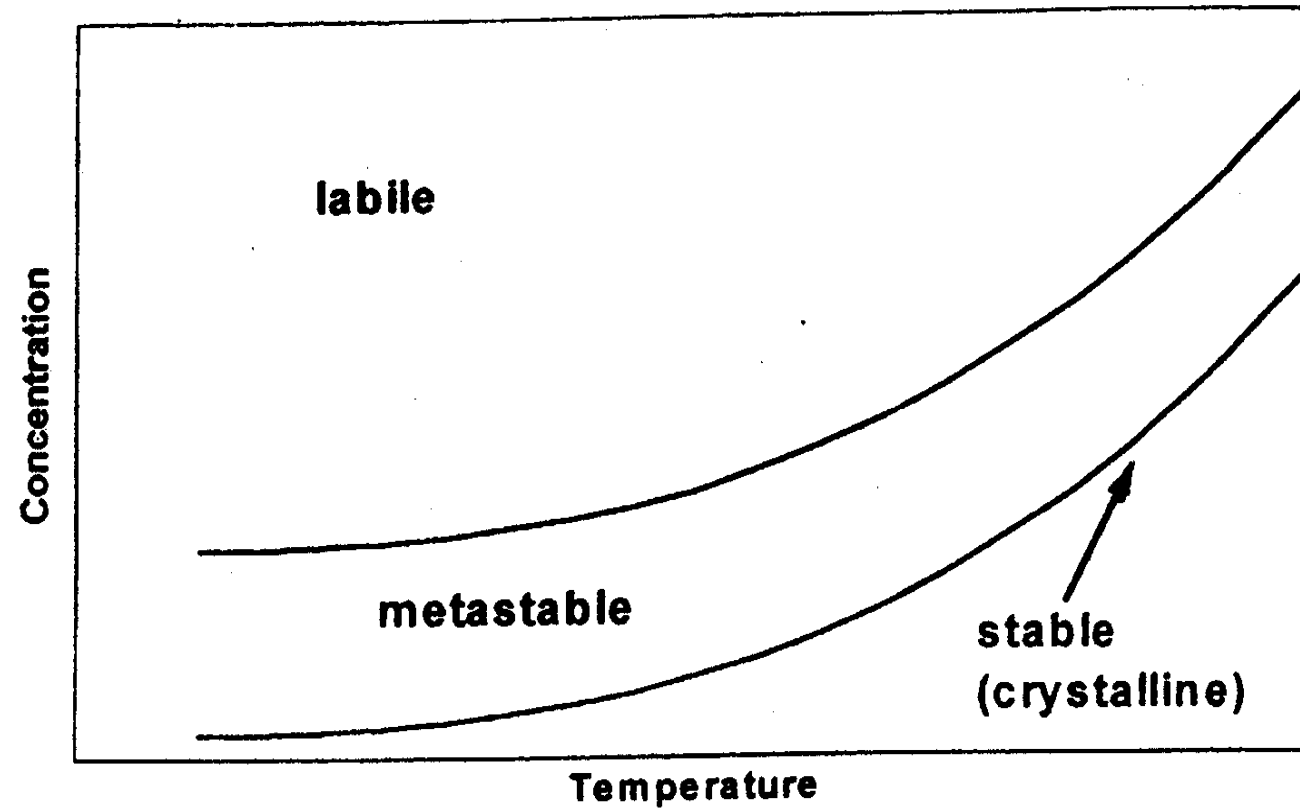
## METASTABLE ZONE

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- The metastable zone width is the maximum supersaturation achievable before nucleation occurs.
- It is usually expressed as the maximum undercooling.
- The nucleation is considered to take place where a significant change of the turbidimetry of the solution takes place.

## THE DIAGRAM CONCENTRATION - TEMPERATURE

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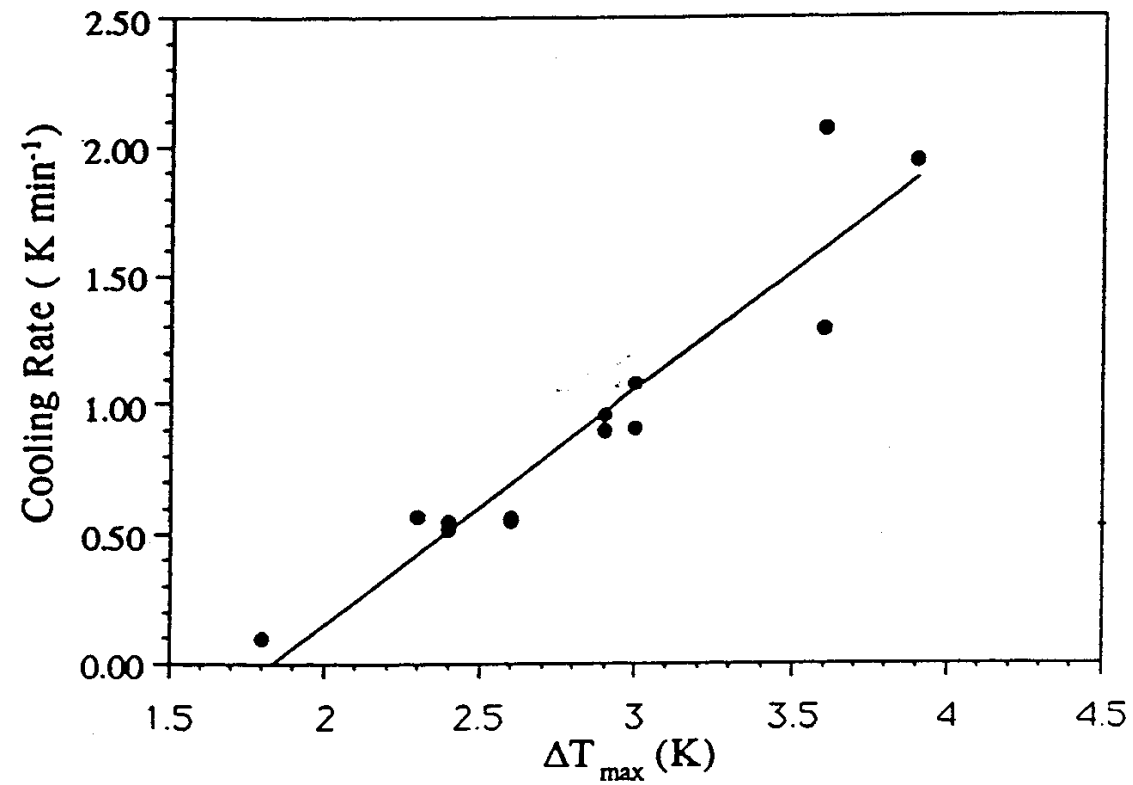




## EFFECT OF THE COOLING RATE ON THE METASTABLE ZONE WIDTH

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Metastable range with of pure caprolactam melt



# PRIMARY NUCLEATION

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In a supersaturated solution or melt, crystal nuclei may grow from a spontaneous centre (homogeneous nucleation) or from an artificial centre (heterogeneous nucleation). Both processes are referred to as primary nucleation processes.

The **free energy change** resulting from a crystal nucleating homogeneously from solution is given by:

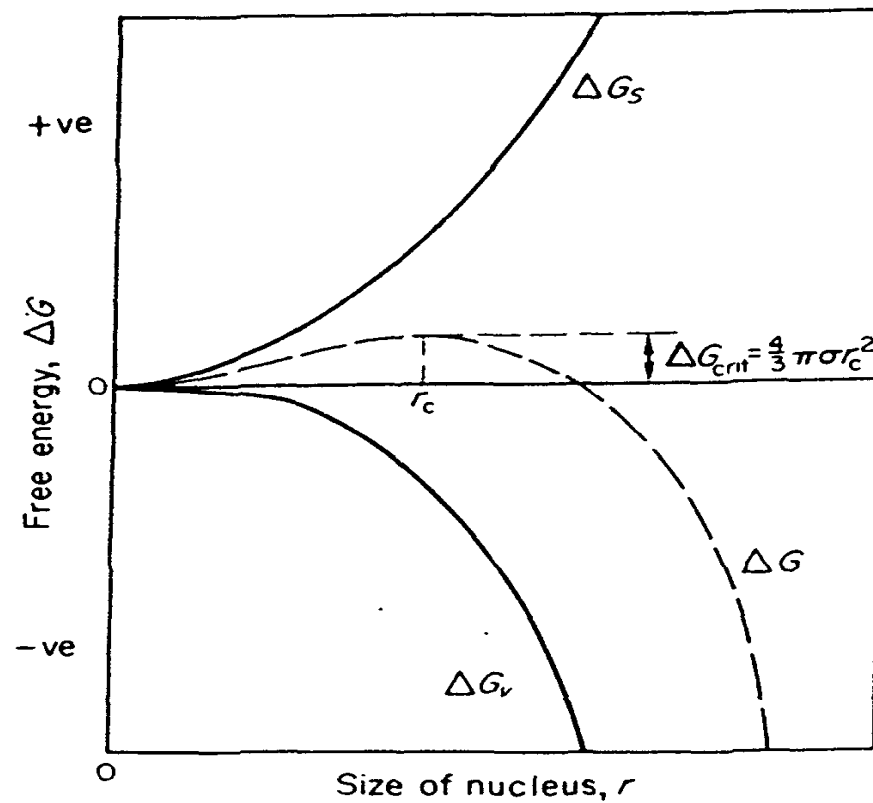
$$\Delta G = \Delta G_s + \Delta G_v$$

where  $\Delta G_s$  is the free energy change required to form the surface of the nucleus and  $\Delta G_v$  is the free energy change resulting when the solute changes from the liquid to the solid state

# FREE ENERGY DIAGRAM

$$\Delta G = 4\pi r^2 \gamma + (4/3)\pi r^3 \Delta G_v$$

$$\Delta G_{crit} = \frac{4}{3}\pi \gamma r_c^2$$



## HOMOGENEOUS NUCLEATION RATE

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The nucleation rate  $B^0$ , the number of nuclei produced per unit volume per unit time, can be expressed as

$$B^0 = A \exp(-\Delta G_{crit} / kT)$$

where

$$\Delta G_{crit} = \frac{4}{3} \pi \gamma_c r_c^2$$

The solubility of small crystals varies with solution concentration (Gibbs-Thompson equation), that is:

$$\ln(x / x^*) = \ln S = 2\gamma_v / kTr_c$$

The homogeneous nucleation rate can be derived:

$$B^0 = A \exp \left[ - \frac{16\pi\gamma^3 v^2}{3k^3 T^3 (\ln S)^2} \right]$$

# HETEROGENEOUS NUCLEATION

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For heterogeneous nucleation, foreign bodies in the solution or melt induce the nucleation at lower degrees of supersaturation and

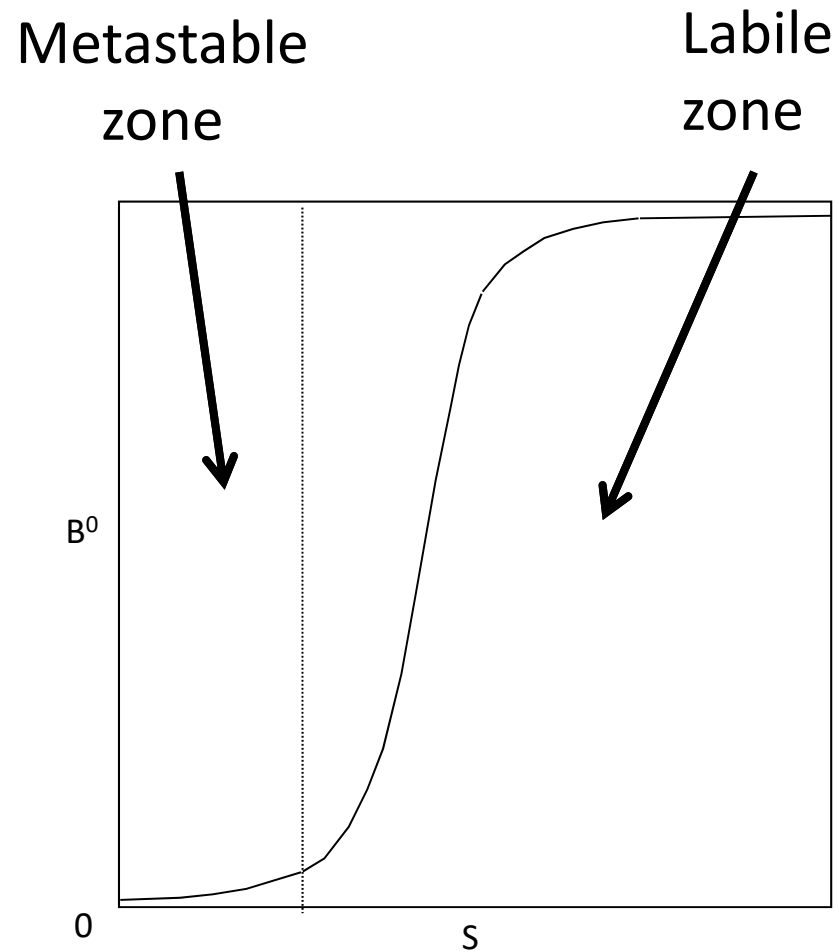
$$\Delta G_{crit}(\text{heterogeneous}) = \phi \Delta G_{crit}(\text{homogeneous})$$

where the factor  $\phi$ , less than 1, is related to the contact angle between the crystalline deposit and the foreign solid surface. Thus the **heterogeneous nucleation rate** is:

$$B^0 = A \exp \phi \left[ -\frac{16\pi\gamma^3\nu^2}{3k^3T^3(\ln S)^2} \right]$$

# The Form of $B^\circ$ Relationship

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# SECONDARY NUCLEATION

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Secondary nucleation is influenced by several factors.  
The hydrodynamics of the solution and the geometry of the crystallizer.

- ◆ The energy dispersed by the impeller or by the fluid re-circulation machine.
- ◆ The nature and the crystal habit of the crystals and the value of the magma density of the slurry.
- ◆ The supersaturation of the solution.

A suitable expression of the **secondary nucleation rate** is

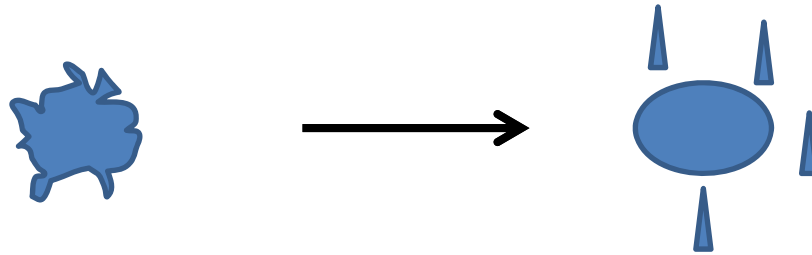
$$B^0 = k(T)\sigma^b \varepsilon^l M_T^j$$

# SECONDARY NUCLEATION

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- Secondary nucleation mechanisms are:

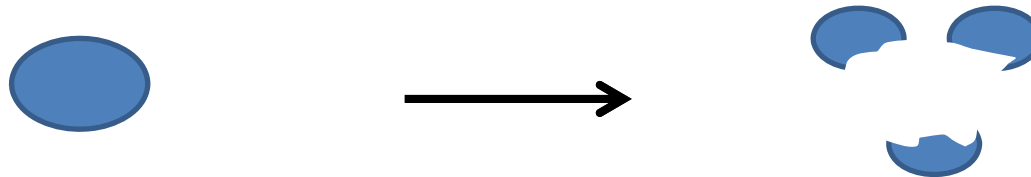
Abrasion



Attrition



Breakage





# SECONDARY NUCLEATION

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$$B^0 = k(T) \sigma^b \varepsilon^l M_T^j$$

$$B^0 = k(T) G^i N^h M_T^j$$

Power index	Range
b	1-3
h	1.5-4
i	0.5-3
l	0.5-1.3
j	1-2

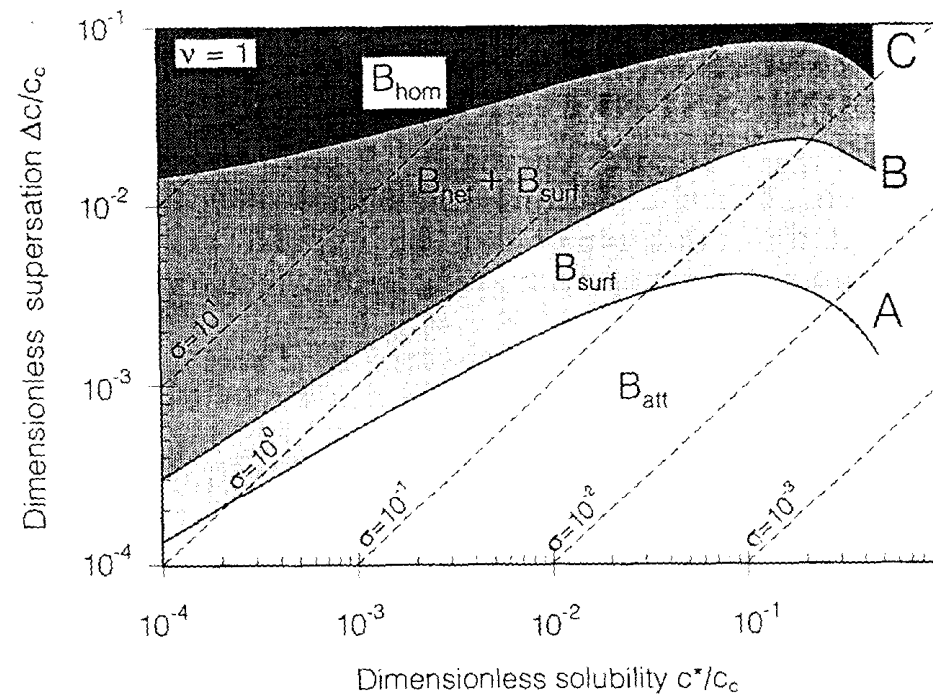
The secondary nucleation of caprolactam in a molten mixture CPL-water 1.5% by using a MSMPR crystallizer.

$$B^0 = 8.53 \cdot 10^{15} G^{1.85} N^{1.85} M_T^{1.29}$$

# PROCESSES CONTROLLING NUCLEATION

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Diagram proposed by Mersmann to evaluate the kind of nucleation;  $c_c$  is the crystal molar density



# INDUCTION TIME

The induction time is the time required to observe nucleation after saturation conditions were overcome.

Crystallization = more or tens minutes

Chemical precipitation = nanoseconds

