ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

Μάθημα 5ο

Ακαδημαϊκό έτος 2017-2018

Driving force for melt crystallization

$$\Delta\mu = \mu_L(T) - \mu_S(T)$$

For cooling crystallization from melts or solutions

$$\Delta\mu = \frac{\Delta H_{eq}}{T^*} \cdot \Delta T$$

$$\Delta T = T - T^*$$

$$\Delta c = c - c^*$$

Melt crystallization under pressure:

$$\Delta\mu = \Delta V_{molar} \Delta P = \frac{\Delta\rho}{\rho_{melt}\rho_{solid}} \cdot \Delta P$$

Supersaturation Ratio

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

Relative supersaturation

$$\sigma = \frac{c - c^*}{c^*} = \frac{\Delta c}{c^*} = S - 1$$

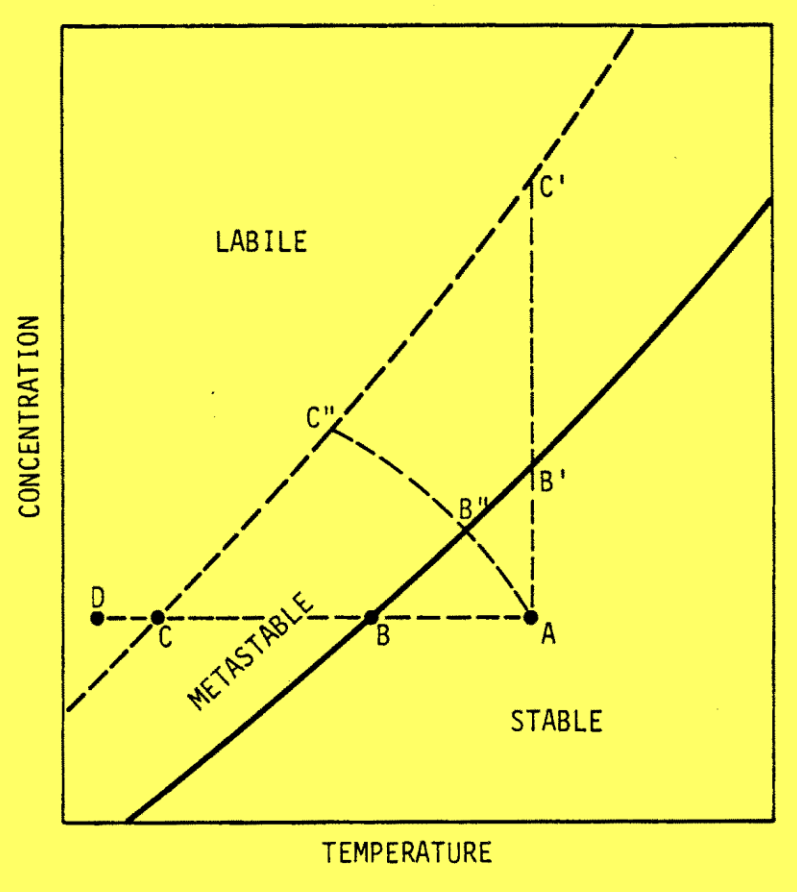
Driving force for the separation of one component of a mixture in one (continuous) phase and the development of discontinuity :

- **Departure from equilibrium-Metastable state Measure**
- **Υπερκορεσμός (Supersaturation)-(Solubility= equilibrium)**

The creation of a new phase in a continuous medium

- Physical(e.g. condensation, crystallization, solid state phase transformations) and chemical processes (e.g. heterogeneous reactions) in vapours, melts or solutions of different systems , take place via the formation of 3D nuclei of the new phase.
- Necessary condition is that the continuous medium is supersaturated with respect to the new phase.
- The formation of new nuclei is accompanied with chnages of the system's Gibbs free energy

Methods for the preparation of suersaturated solutions



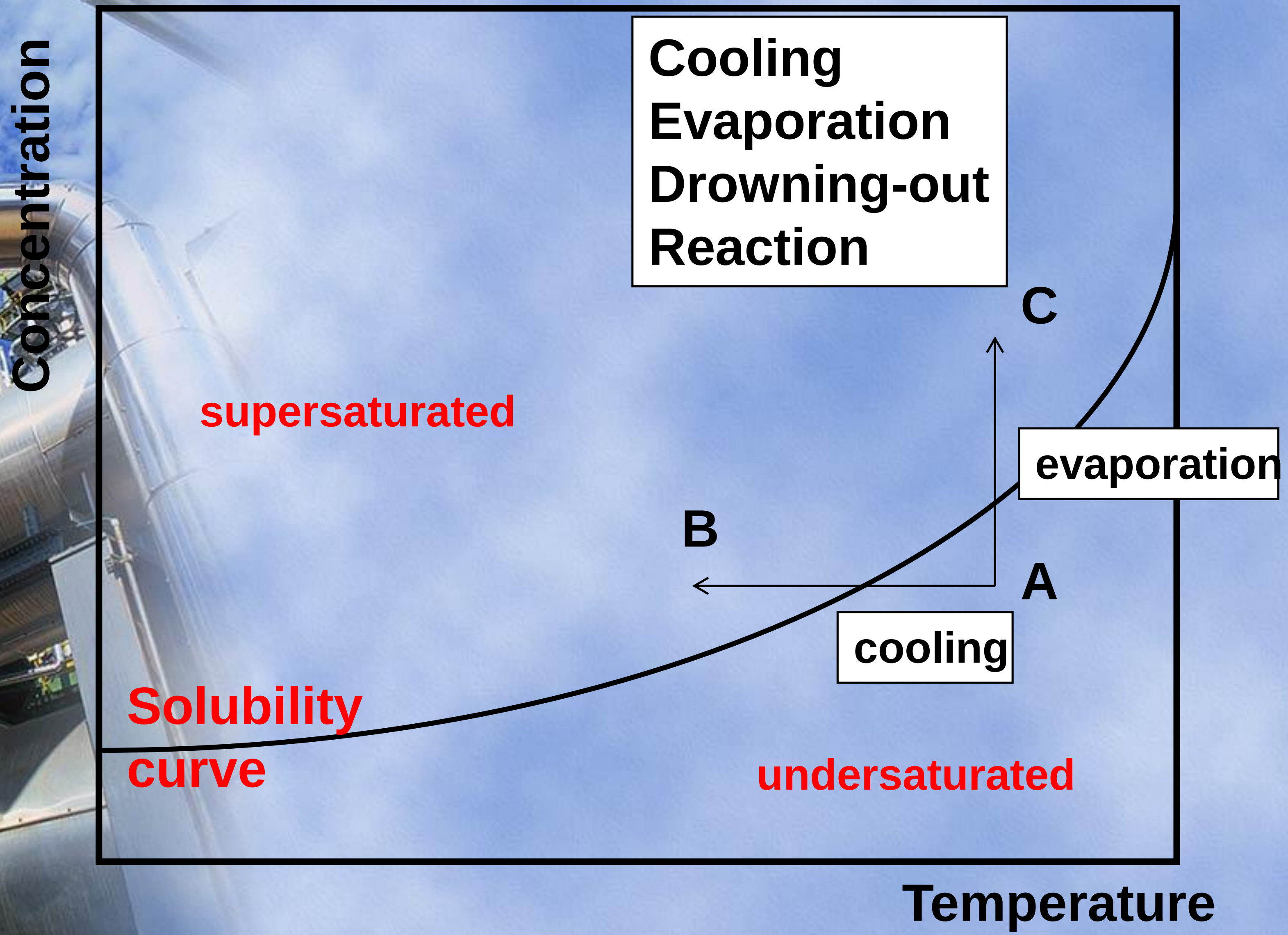
(1) Heating (solids with inverse solubility)

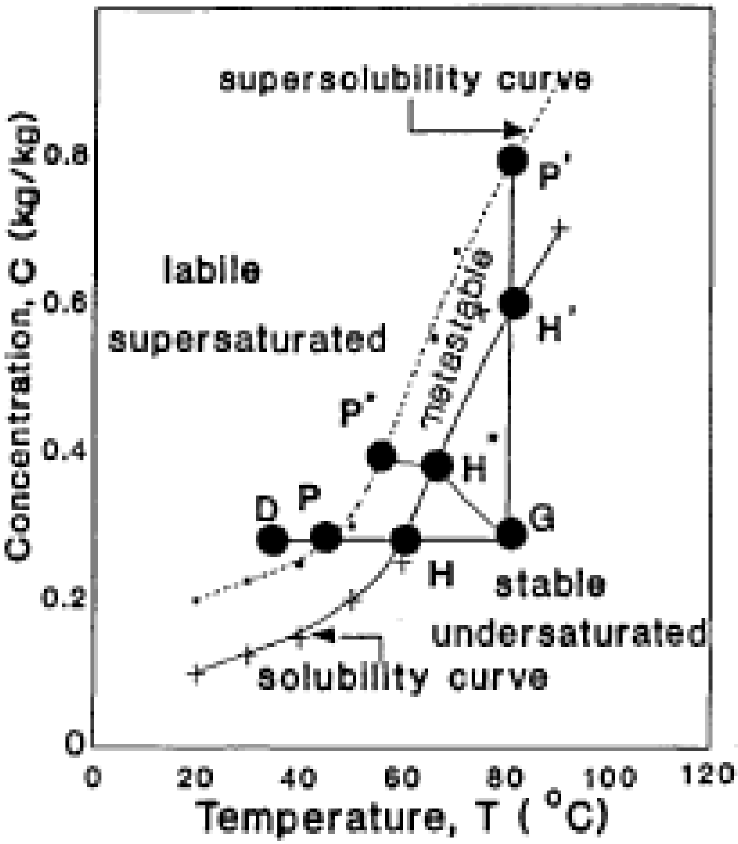
(2) Solvent evaporation

(3) drowning out — addition of an antisolvent fully miscible with the solvent but immiscible with the solute, which we aim at separating

(4) Chemical reaction the product of which is the formation of an insoluble compound (proton addition or removal, hydrolysis, large molecules combination).

Generation of supersaturation



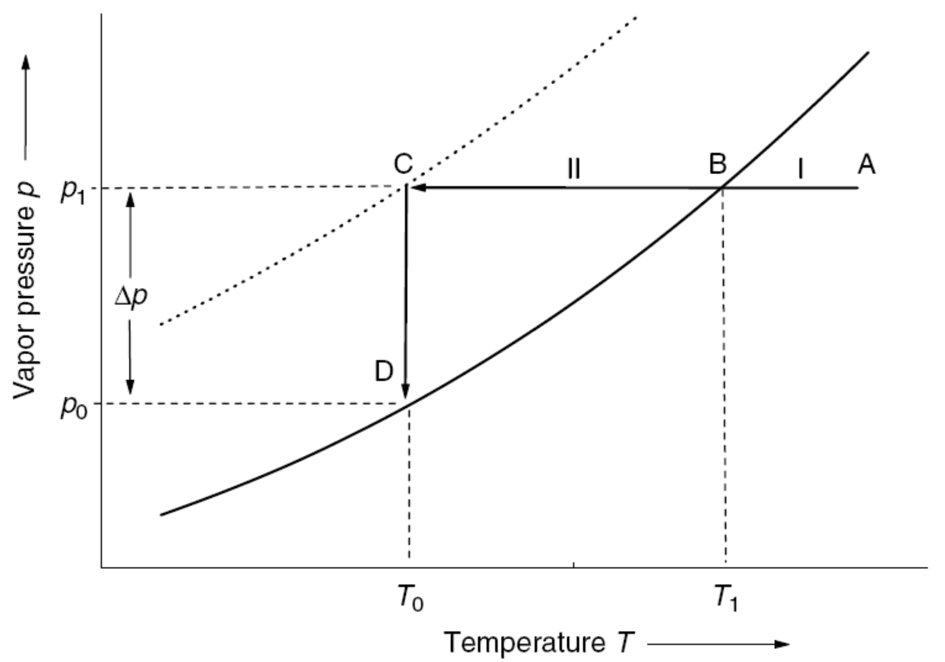


$$aA + bB \rightarrow cC + dD$$

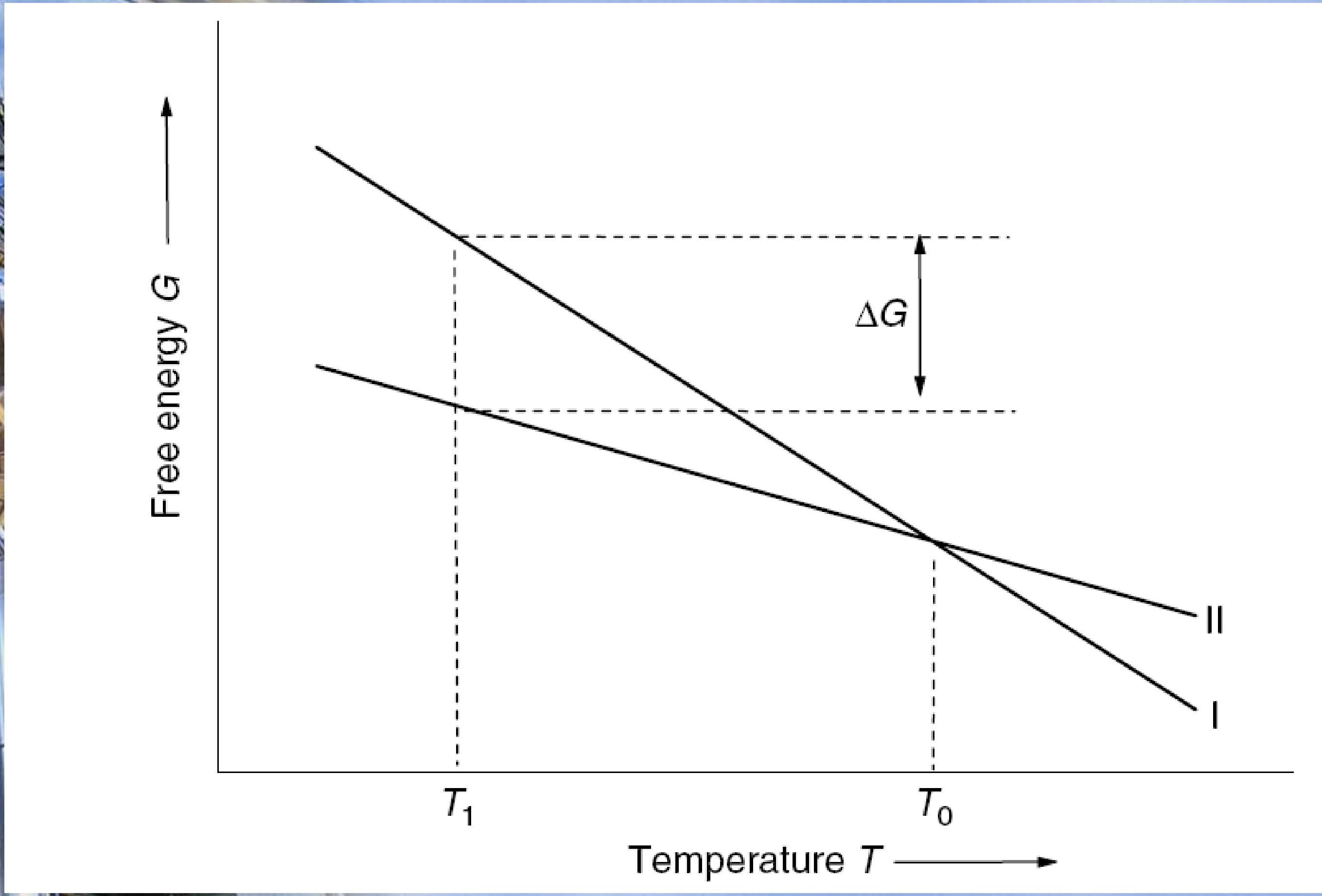
$$\Delta G = (cG_C + dG_D) - (aG_A + bG_B) < 0$$

$$\Delta G = G_{II} - G_I = \Delta H - T\Delta S$$

$$\Delta H = H_{II} - H_I \qquad \Delta S = S_{II} - S_I$$



The dependence of Gibbs energy on temperature



Equilibrium
for ΔG=0 (T_0)

$$\Delta S = \Delta H / T_0$$

Out of equilibrium

$$\Delta G = \Delta H - T\Delta H / T_0 = \Delta H \Delta T / T_0$$

$$\Delta T = T - T_0.$$

i components with a number of moles n_i

$$\Delta G = \sum_i \Delta \mu_i n_i$$

$$\Delta \mu = k_B T \ln(p/p_0)$$

For solutions

$$\Delta \mu = k_B T \ln(a/a_0) = k_B T[\ln(f/f_0) + \ln(c/c_0)]$$

$$\Delta\mu = \Delta H \Delta T / T_0 n$$

$$\Delta\mu = k_B T \ln(1 + \sigma)$$

For small values of relative supersaturation

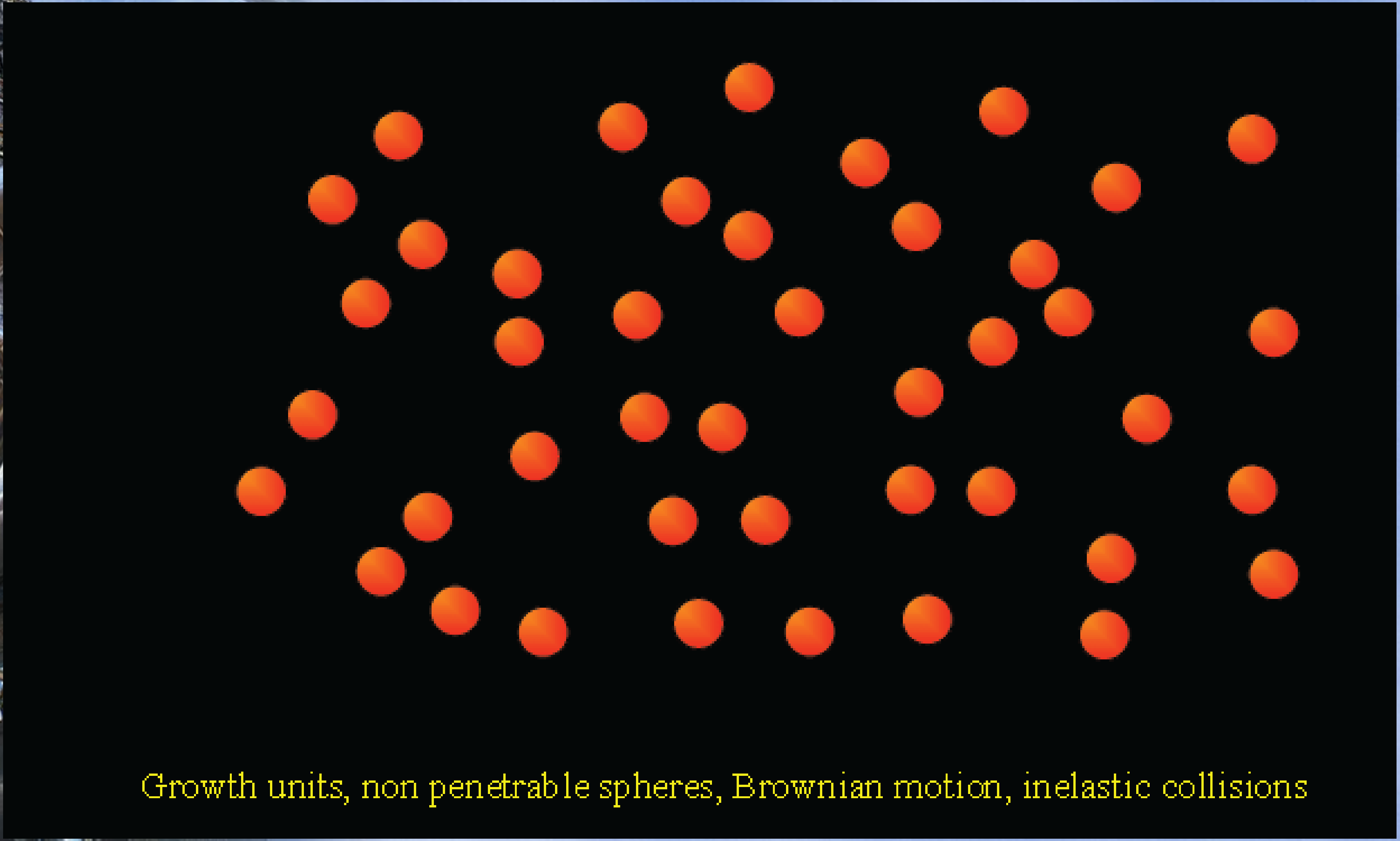
$$\ln(1 + \sigma) \approx \sigma,$$

$$\Delta\mu = k_B T \sigma$$

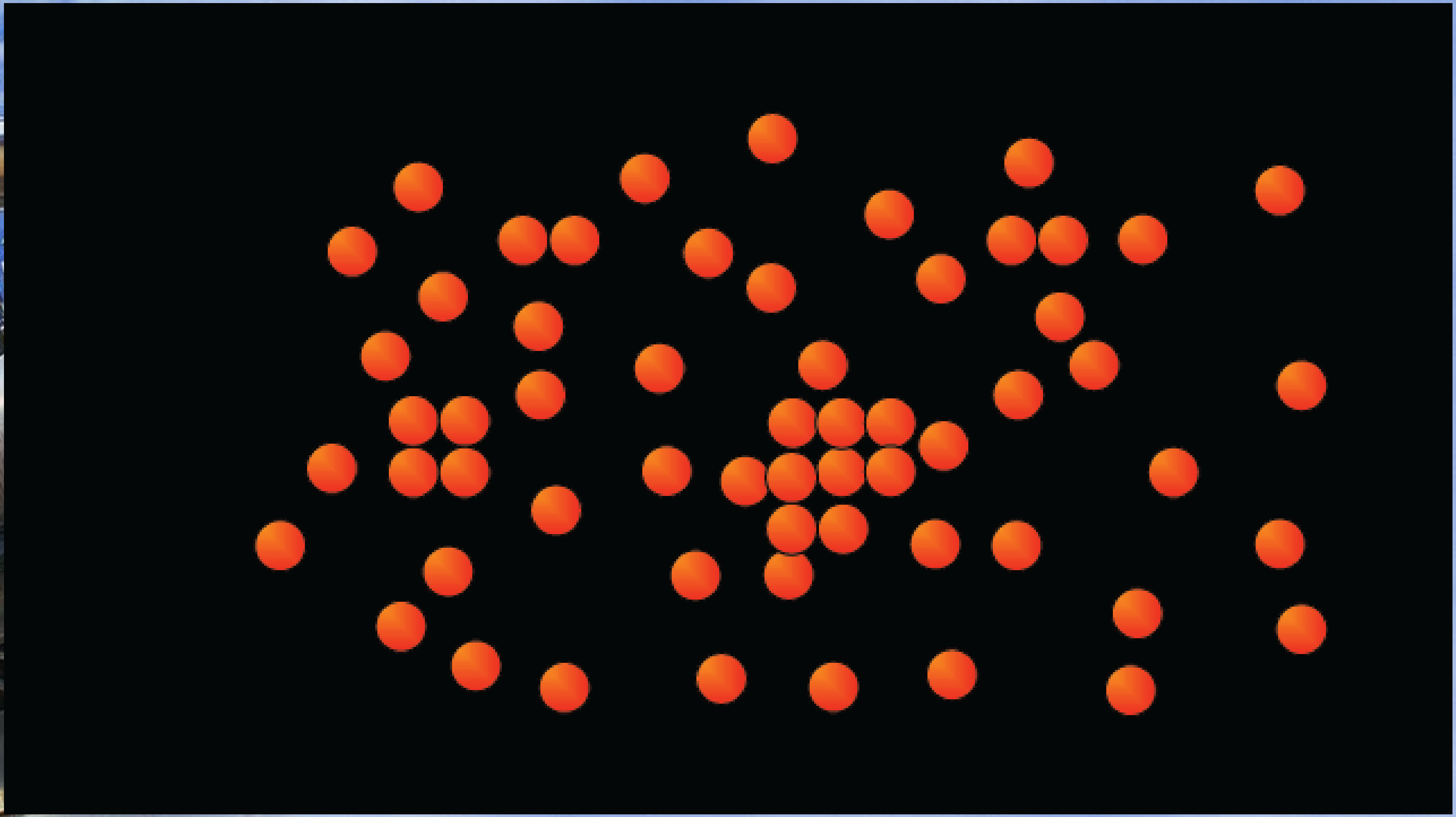
For electrolyte solutions

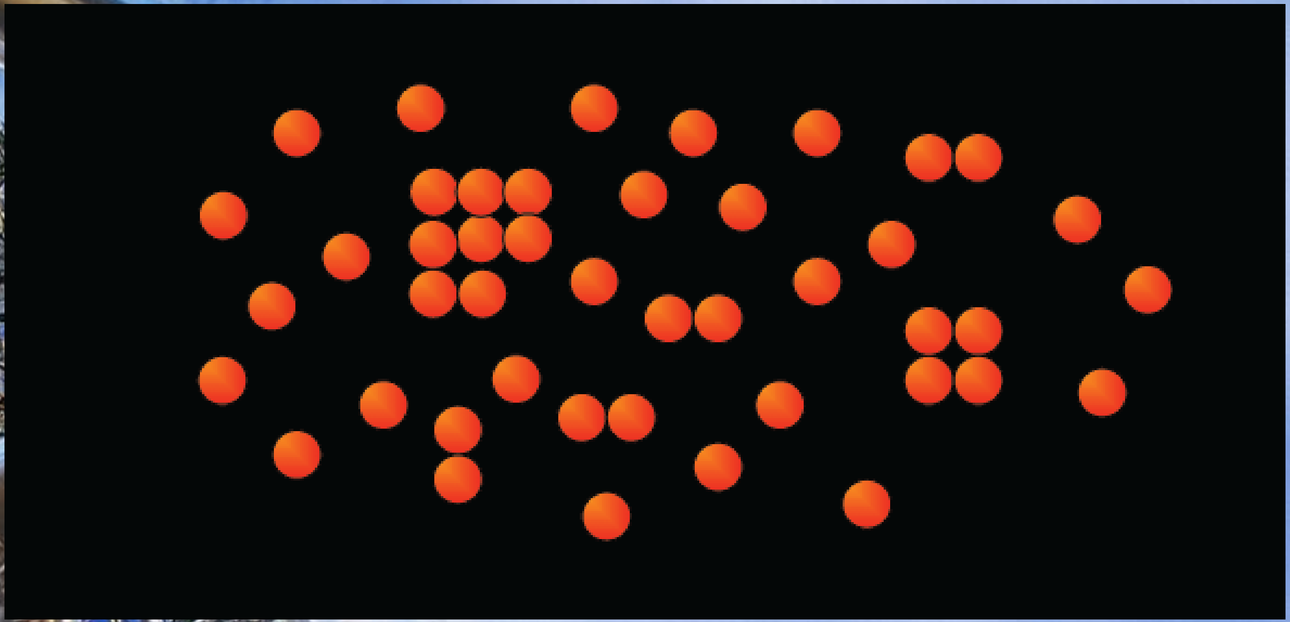
$$\Delta\mu / k_B T = \ln S = \ln(a / a_0) = \ln[(a_{\text{cation}} a_{\text{anion}}) / K_s]$$

In supersaturated solutions there are structural units, or embryos or nuclei of the crystals

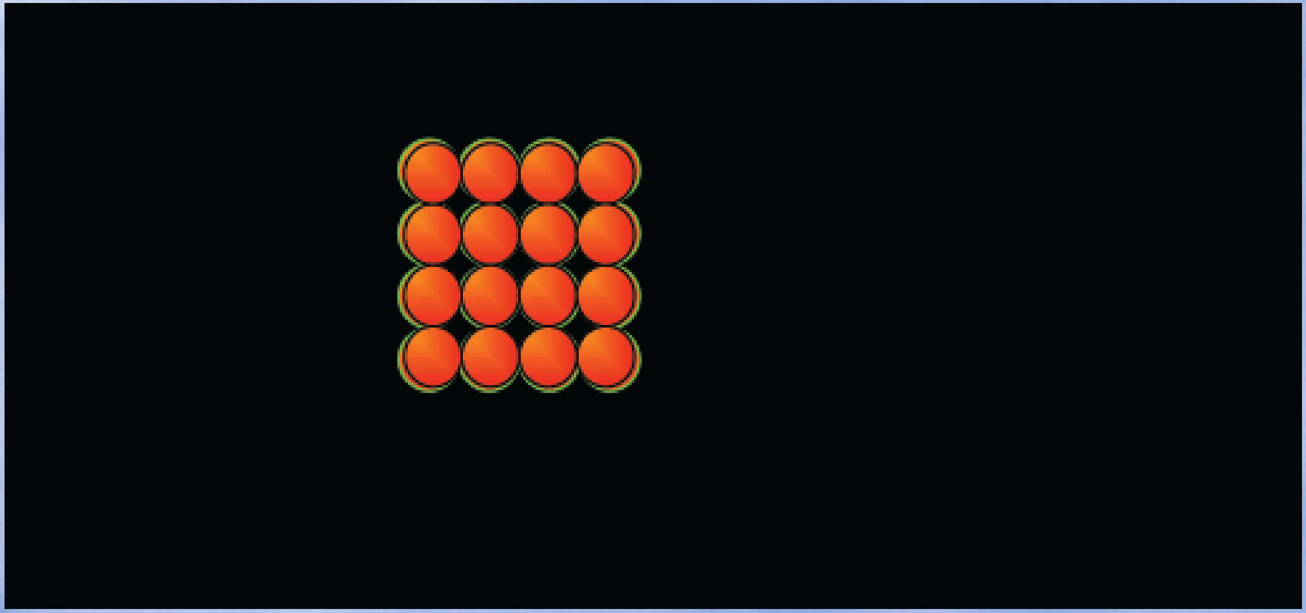


Depending on conditions- Distance from equilibrium



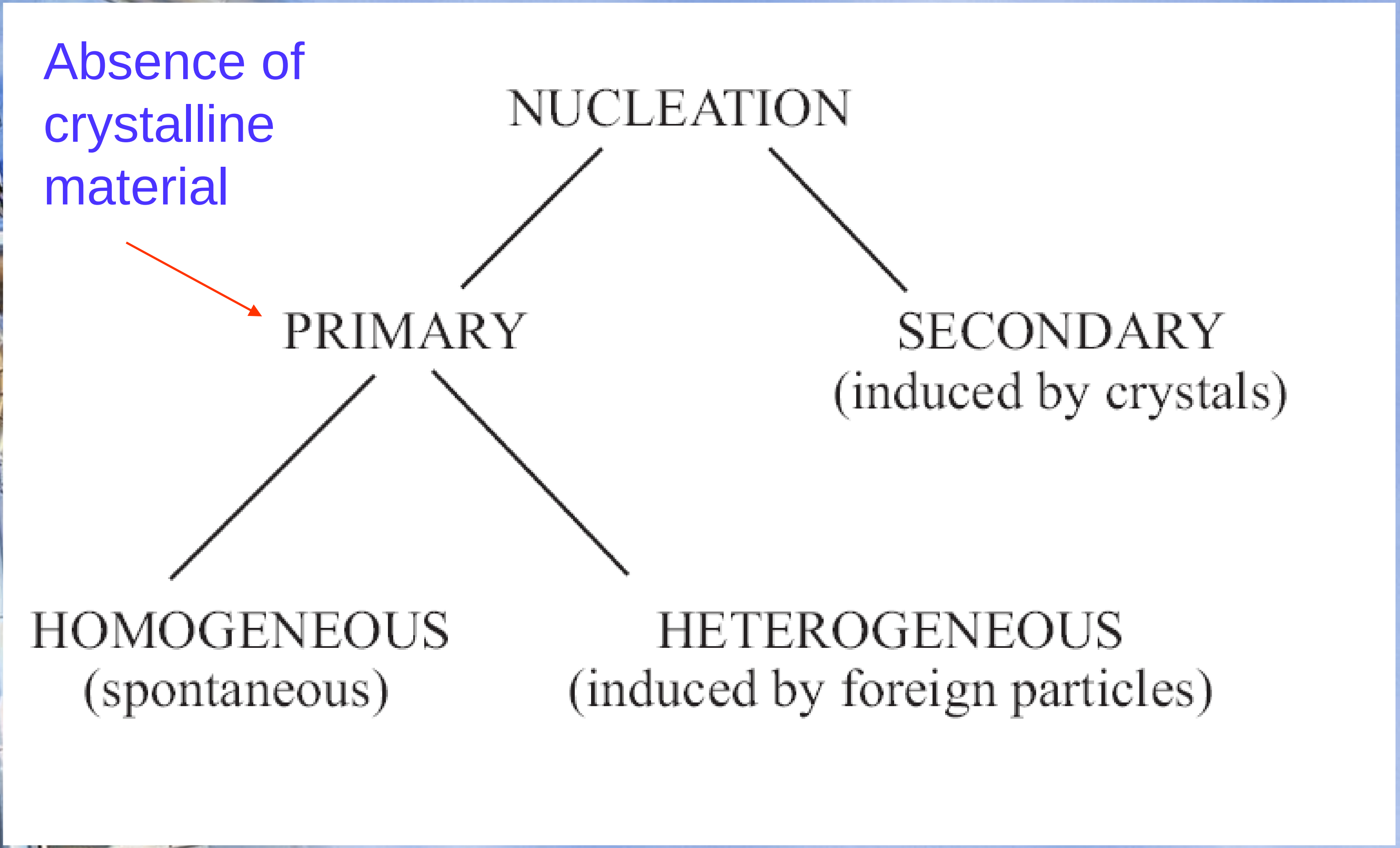


Phase separation-nucleation



Nucleation(πυρηνογένεση) = generation of nuclei of new crystals in a continuum

- **Primary homogeneous** nucleation: It can be realized in particle-free systems. Occurs via an autocatalytic mechanism through the formation of clusters.
- Necessary condition for the formation of macroscopic crystals from the nuclei, is that nuclei grow to a size exceeding a critical size, called size of critical nucleus or simply critical size


Absence of crystalline material
NUCLEATION
PRIMARY
SECONDARY
(induced by crystals)
HOMOGENEOUS
(spontaneous)
HETEROGENEOUS
(induced by foreign particles)

Mechanism

$$A \quad + A \rightleftharpoons A_2$$

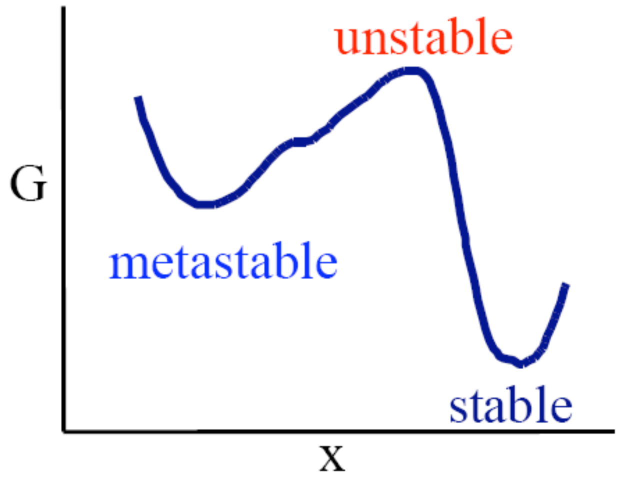
$$A_2 \quad + A \rightleftharpoons A_3$$

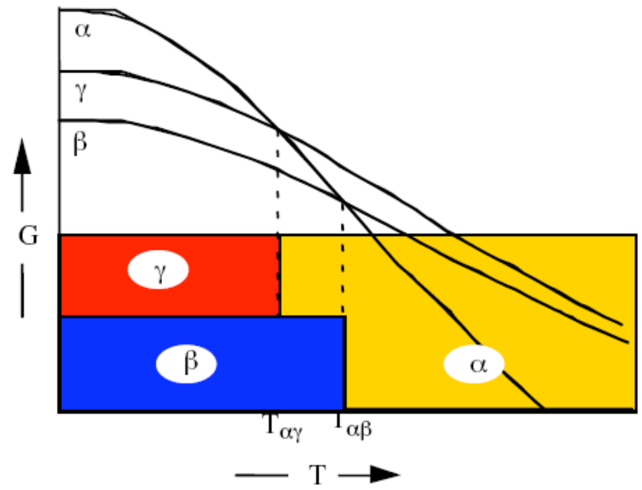
$$A_{n-1} + A \rightleftharpoons A_n \quad \text{(critical cluster)}$$

Nucleation and further crystal growth

- The nuclei forming in a supersaturated solution may either develop further to a critical or supercritical size or it may re-dissolve. In all cases the process shall be in the direction of reduction of the overall free energy of the particle
- The critical size, is therefore the size corresponding to the smallest possible stable nucleus
- Particles (clusters) with size below the critical shall be re-dissolved or re-evaporated in the supersaturated solutions or vapors
- Particles with size larger than the critical shall continue to grow (crystal growth)

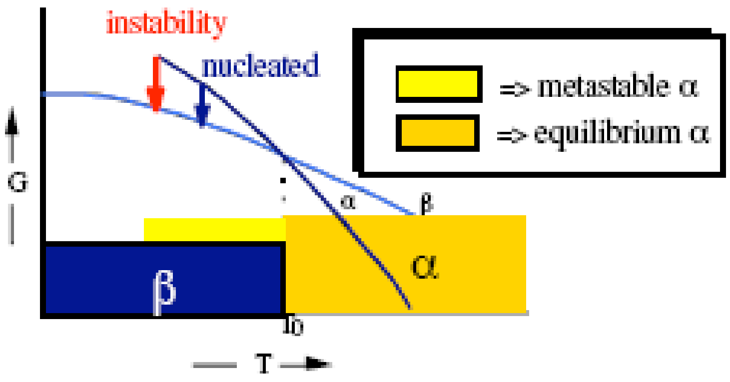
Global Equilibrium:
Kinetics of Phase Transformations

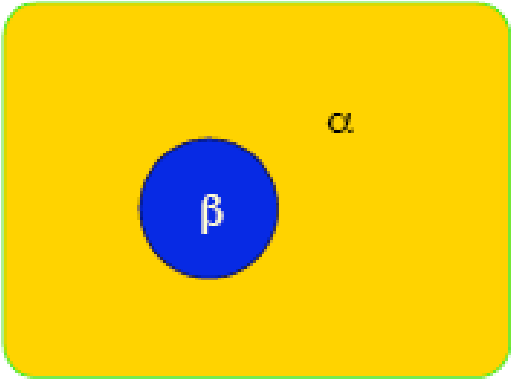




- “Phases” usually represent distinct free energy minima
  - Requires a finite change to accomplish “phase transformation”
  - Phase may be preserved in a “metastable” state
- Phase transformations (“1st order”)
  - Thermodynamics: driving force is free energy difference
  - Kinetics: rate of transformation depends on mechanism (path)

Basic Mechanisms of Phase Transformations





- Two basic mechanisms of phase transformation
- Nucleation and growth
  - A discrete particle of β phase forms in the interior of α
  - Grows to consume α phase
- Instability
  - Parent phase becomes internally unstable; must transform

Nucleation of a solid phase-component

- Development of a new phase in a continuum
- Appearance of a separating surface
- New phase detectable directly or indirectly from changes in the physicochemical properties of the fluid phase (pH, pIon, sp.conductivity, optical density etc)

What about free energy?

- In a fluid, the (macroscopic) free energy is everywhere the same (constant)
- At the microscopic level there are fluctuations, as there are fluctuations in molecular motion
- There are regions in which the supersaturation is larger and the energy is also larger and sufficient for nucleation to take place.