

Zero-Dimensional Nanostructures: Nanoparticles

Principles of homogeneous
nucleation

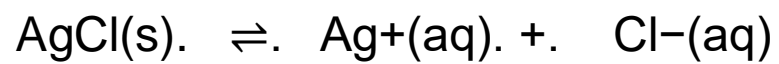
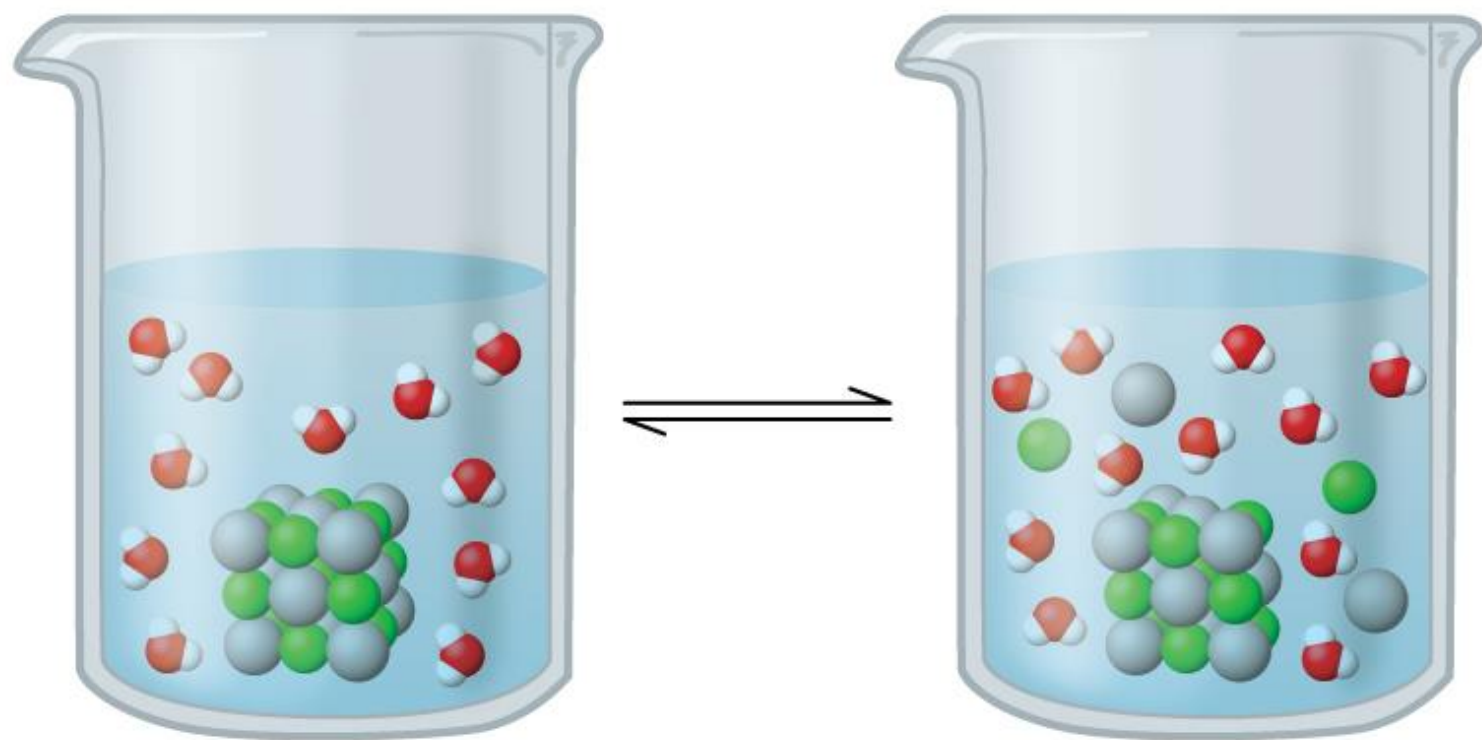
Video

Reaction between AgNO_3 and NaCl (Silver nitrate + Sodium Chloride)

<https://www.youtube.com/watch?v=0AyLFP26r4o>

Reflection:

- 1) How much Cl^- is needed to precipitate the Ag^+ ?
- 2) Assume that you take away all the Na^+ and the NO_3^- ions, and you are just left with the AgCl . What happens afterward?

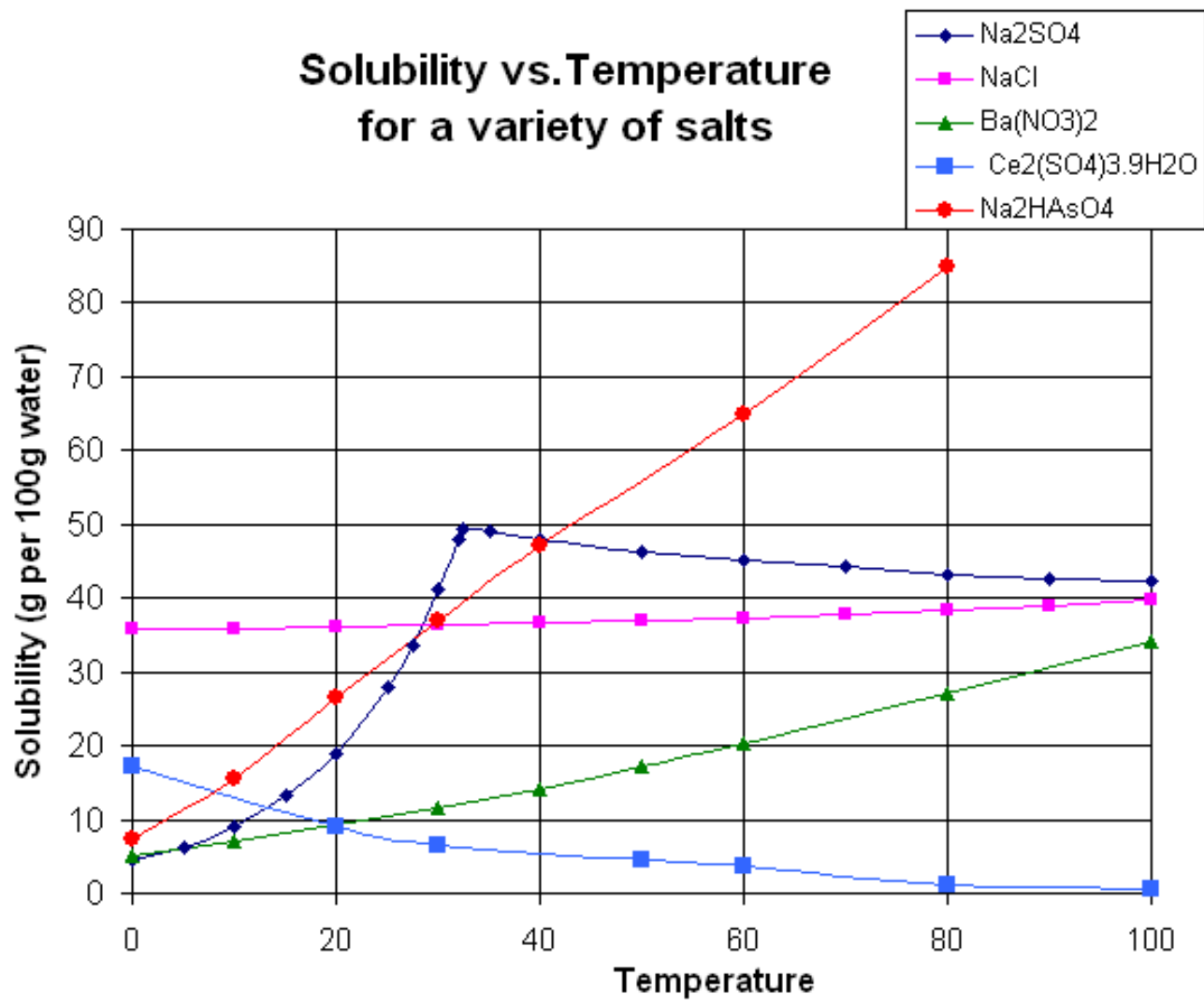


$$K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$$

Constantes del Producto de Solubilidad

Apéndice C

Compuesto	Nombre	Kps
AgBr	Bromuro de plata	5×10^{-13}
AgCl	cloruro de plata	$1,8 \times 10^{-10}$
AgI	yoduro de plata	$8,3 \times 10^{-17}$
AgBrO ₃	bromato de plata	4×10^{-5}
AgIO ₃	yodato de plata	$3,0 \times 10^{-8}$
Ag ₂ S	sulfuro de plata	$2,1 \times 10^{-49}$
Ag ₃ PO ₄	fosfato de plata	$1,3 \times 10^{-20}$
Ag ₂ CO ₃	carbonato de plata	$6,2 \times 10^{-12}$
Ag ₂ Cr ₂ O ₇	dicromato de plata	$2,7 \times 10^{-11}$
Ag ₂ SO ₄	sulfato de plata	$1,6 \times 10^{-5}$
Ag ₃ AsO ₄	arseniato de plata	$1,0 \times 10^{-22}$
AgCN	cianuro de plata	$1,2 \times 10^{-16}$
Ag ₂ CrO ₄	cromato de plata	$1,9 \times 10^{-12}$
Al(OH) ₃	hidróxido de aluminio	5×10^{-33}
AuCl	cloruro de oro(I)	$2,0 \times 10^{-13}$
AuCl ₃	cloruro de oro(III)	$3,2 \times 10^{-25}$
BaCO ₃	carbonato de bario	$8,1 \times 10^{-9}$
BaC ₂ O ₄	oxalato de bario	$1,7 \times 10^{-7}$
BaCrO ₄	cromato de bario	$1,2 \times 10^{-10}$
BaF ₂	fluoruro de bario	$2,4 \times 10^{-5}$
Ba(IO ₃) ₂	yodato de bario	$6,0 \times 10^{-10}$
Ba(OH) ₂	hidróxido de bario	5×10^{-3}
BaSO ₄	sulfato de bario	$1,1 \times 10^{-10}$
Be(OH) ₂	hidróxido de berilio	$2,0 \times 10^{-18}$
Bi ₂ S ₃	sulfuro de bismuto(III)	$3,0 \times 10^{-96}$
CaCO ₃	carbonato de calcio	$4,8 \times 10^{-9}$
CaC ₂ O ₄	oxalato de calcio	$2,6 \times 10^{-9}$
CaCrO ₄	cromato de calcio	$7,1 \times 10^{-4}$

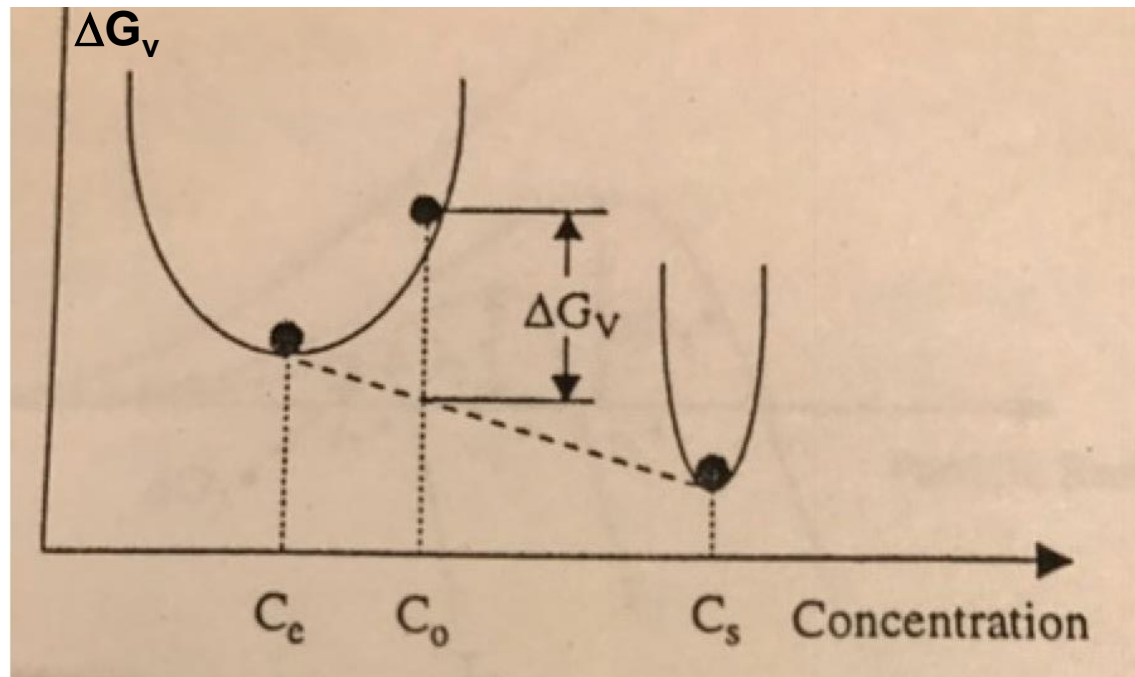


Thermodynamic Approach

$$\Delta G_v = -\frac{kT}{W} \ln\left(\frac{C}{C_0}\right) = -\frac{kT}{W} \ln(1 + S)$$

W Atomic volume

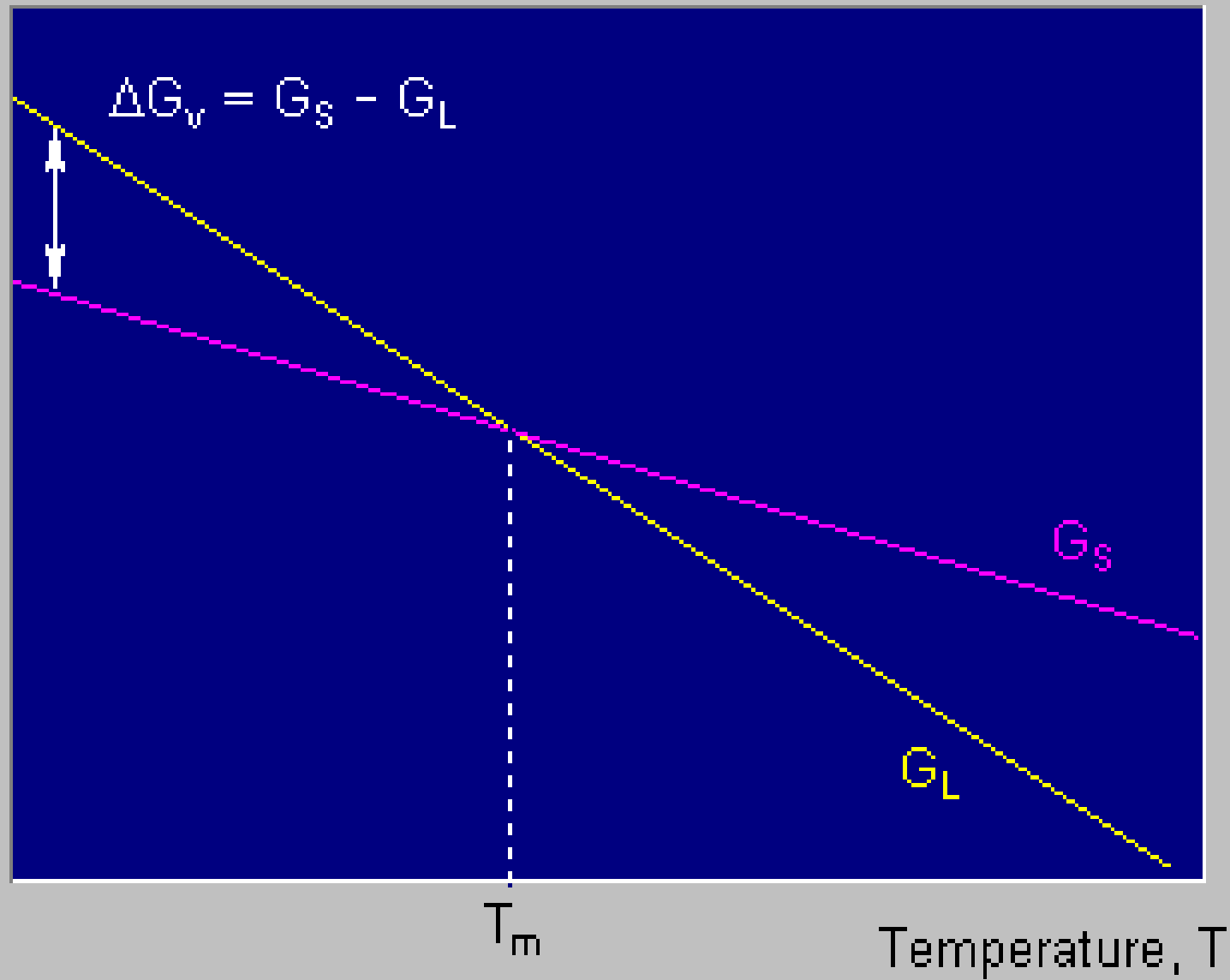
$$S = (C - C_0)/C_0$$



Solidification

- Solidification of metals and alloys usually represents a **transformation** from a **non-crystalline liquid** to a **crystalline solid**.
- If a liquid metal is cooled below its equilibrium **melting point, T_m** , the system can lower its free energy ($G = H - T S$) by forming a **solid phase**.

Free Energy, G_v (Jm^{-3})



The change in free energy for solidification, $\Delta G_v = G_S - G_L$, or

$$\Delta G_v = \Delta H_v - T \Delta S_v \quad (1)$$

where ΔH_v and ΔS_v are the changes in enthalpy and entropy.

At the equilibrium melting temperature, T_m , the driving force for transformation, $\Delta G_v = ?$

$$\begin{aligned} \Delta H_v - T_m \Delta S_v &= 0 \\ \Delta S_v &= \Delta H_v / T_m \end{aligned}$$

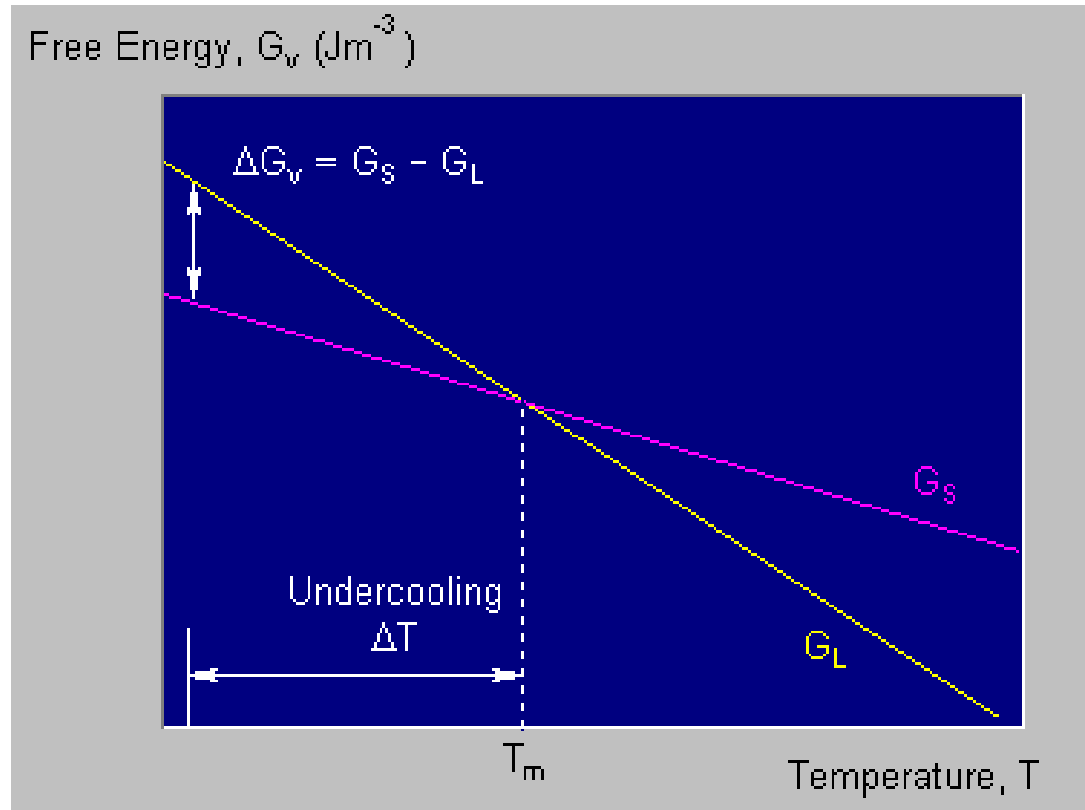
Substituting this expression for ΔS_v into Equation (1):

$$\begin{aligned} \Delta G_v &= \Delta H_v - (T \Delta H_v / T_m) \\ &= \Delta H_v (1 - T / T_m) \\ &= \Delta H_v (T_m - T) / T_m \end{aligned}$$

But $T_m - T = \Delta T$, the undercooling, and so we have:

$$\Delta G_v = \Delta H_v \Delta T / T_m$$

$$\Delta G_V = \frac{\Delta H_V \Delta T}{T_m}$$



This energy change is the **driving force** for solidification.

Although solidification cannot occur without a **thermodynamic** driving force, the rate (**kinetics**) cannot be predicted from this alone.

Yes, this is the thermodynamic explanation, but...

How is the phenomenon at the molecular/atomic level?

Principles of phase transformation

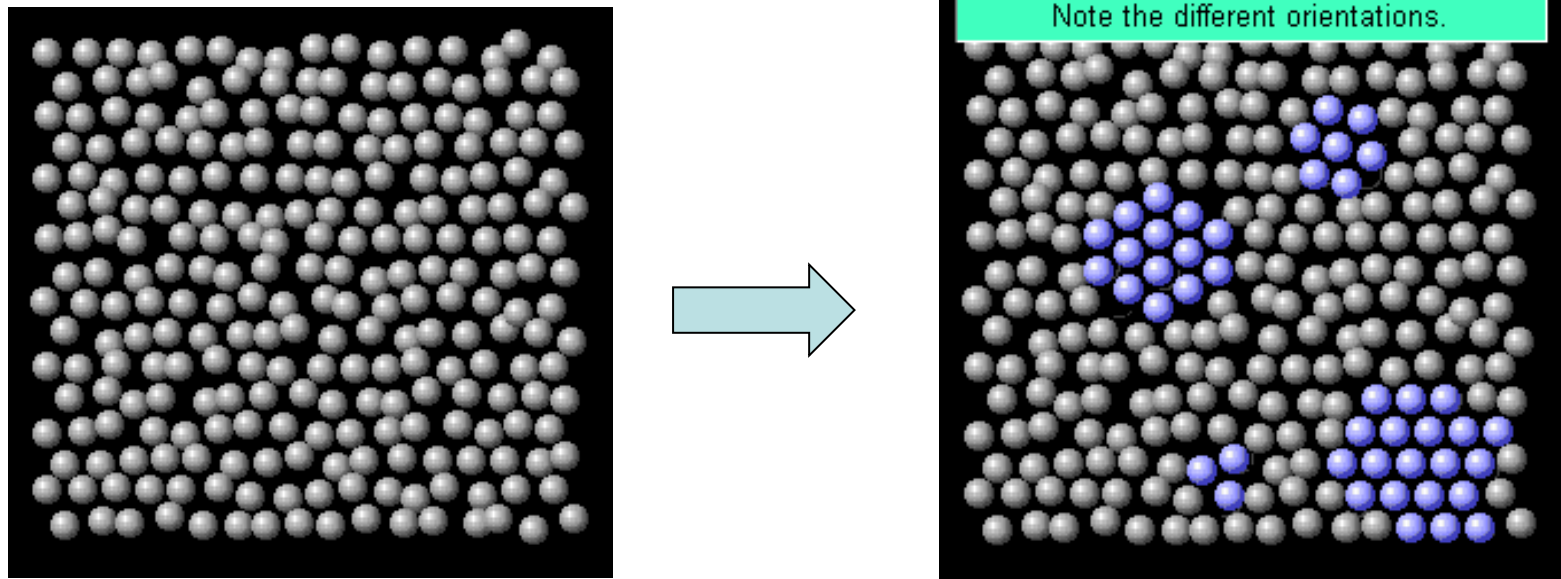
- **Nucleation:**

- The physical process by which a new phase is produced in a material. In the case of solidification, this refers to the **formation of a tiny, stable solid particles in the liquid.**

- **Growth:**

- The physical process by which a new phase increases in size. In the case of solidification, this refers to the **formation of a stable solid as the liquid freezes.**

Nucleation is the **initial stage** of formation of one phase from another phase (L o S)

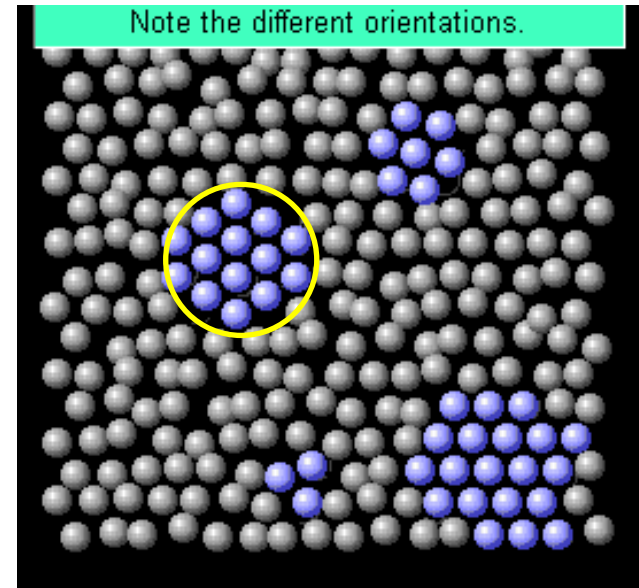
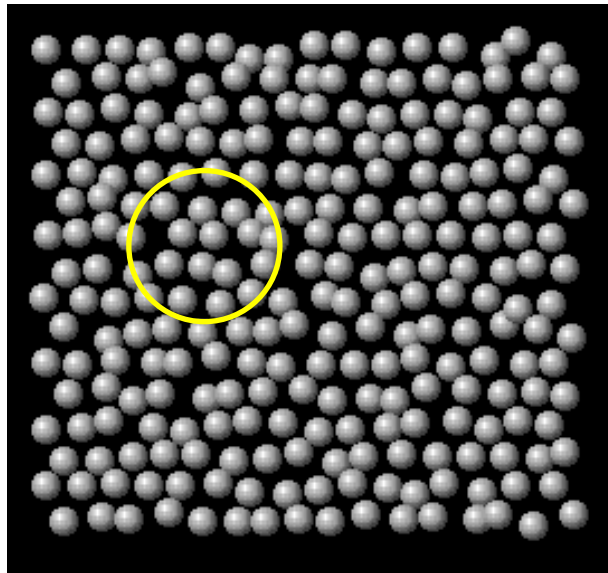


When a liquid metal is cooled towards the melting temperature, some atoms are already beginning to **randomly arrange** themselves into small **crystal**-like clusters.

The formation of such clusters arises from the **random motion** of the atoms within the liquid.

The average cluster **size increases** as the temperature falls **below T_m** .

When the cluster form we have:

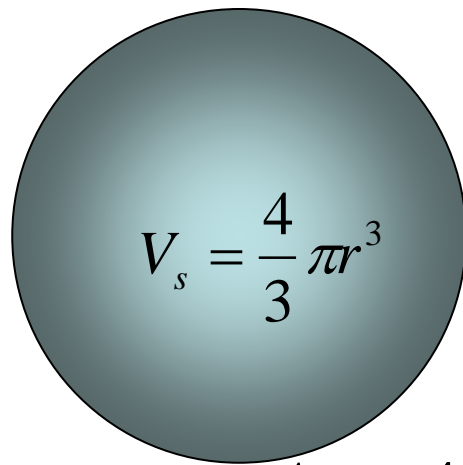


Total Free Energy Change \Rightarrow Volume Free Energy Change + Surface Free Energy Change

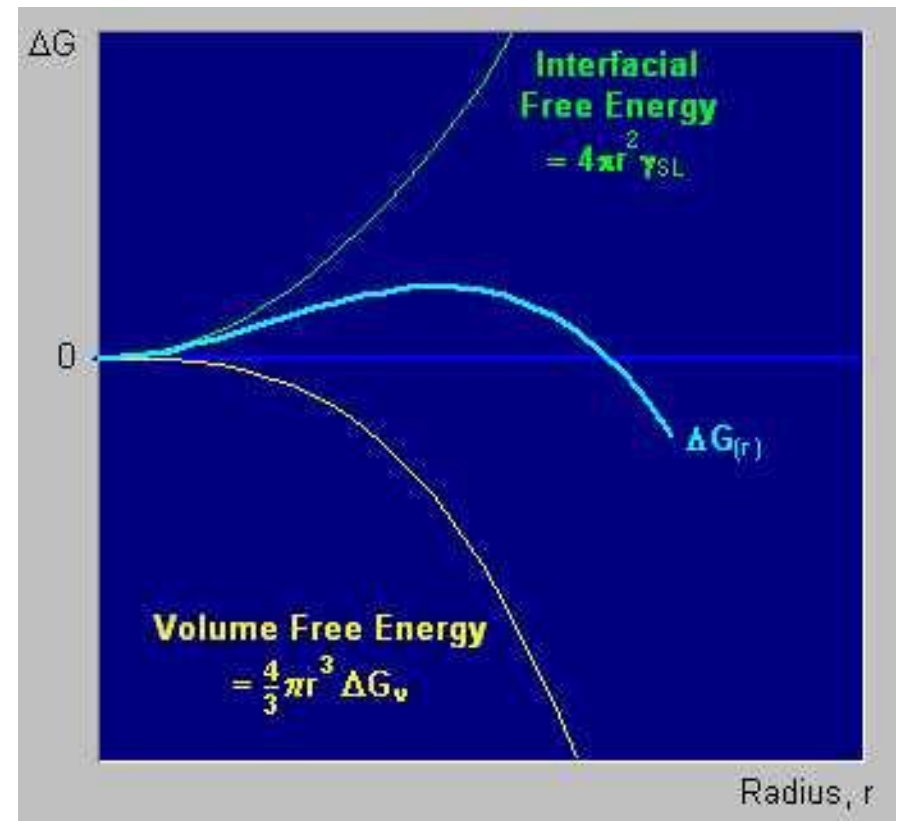
$$\Delta G = V_s \Delta G_V + A_{sl} \sigma_{sl}$$

Assuming the interfacial free energy is isotropic, the cluster will grow spherically.

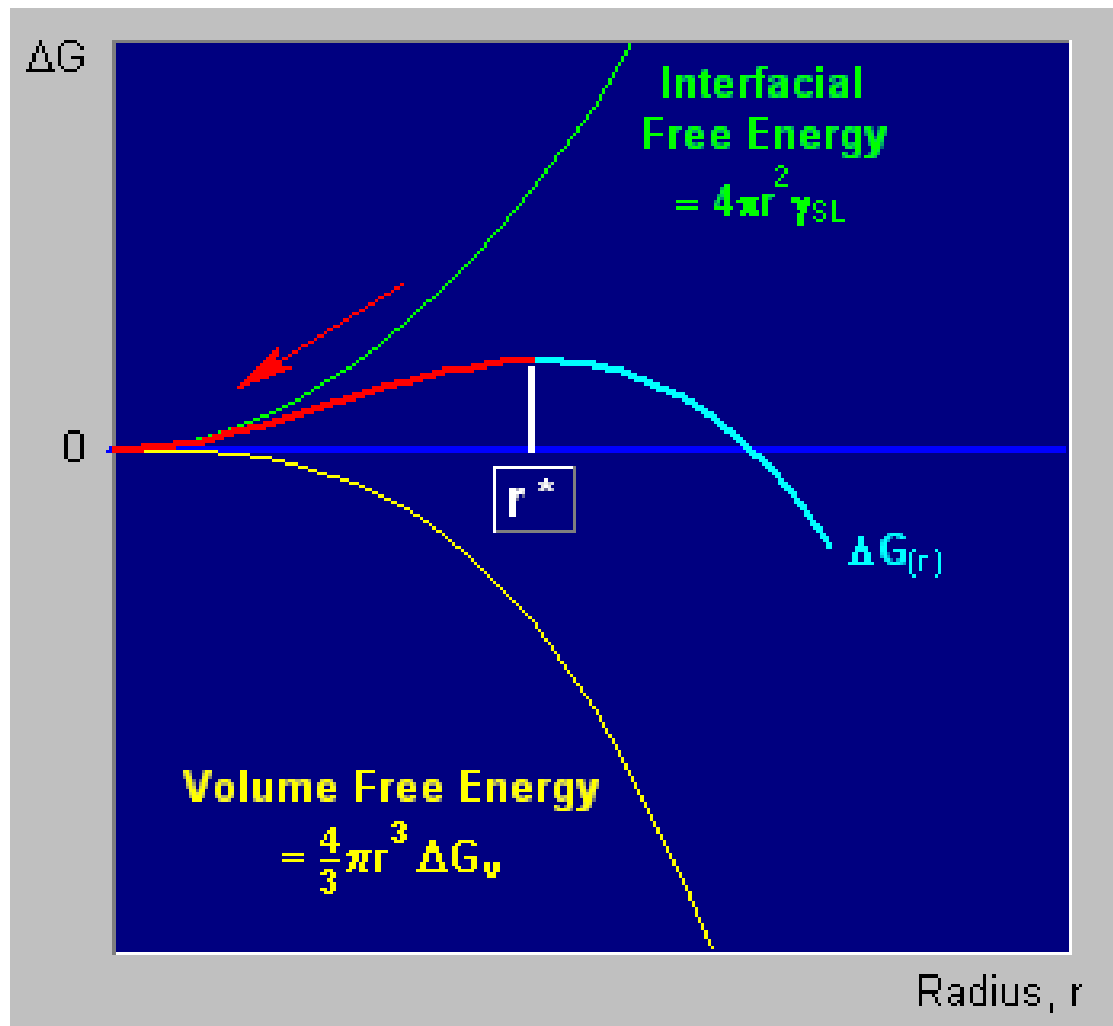
$$\Delta G = V_s \Delta G_V + A_{sl} \sigma_{sl}$$



$$A_{sl} = 4\pi r^2$$



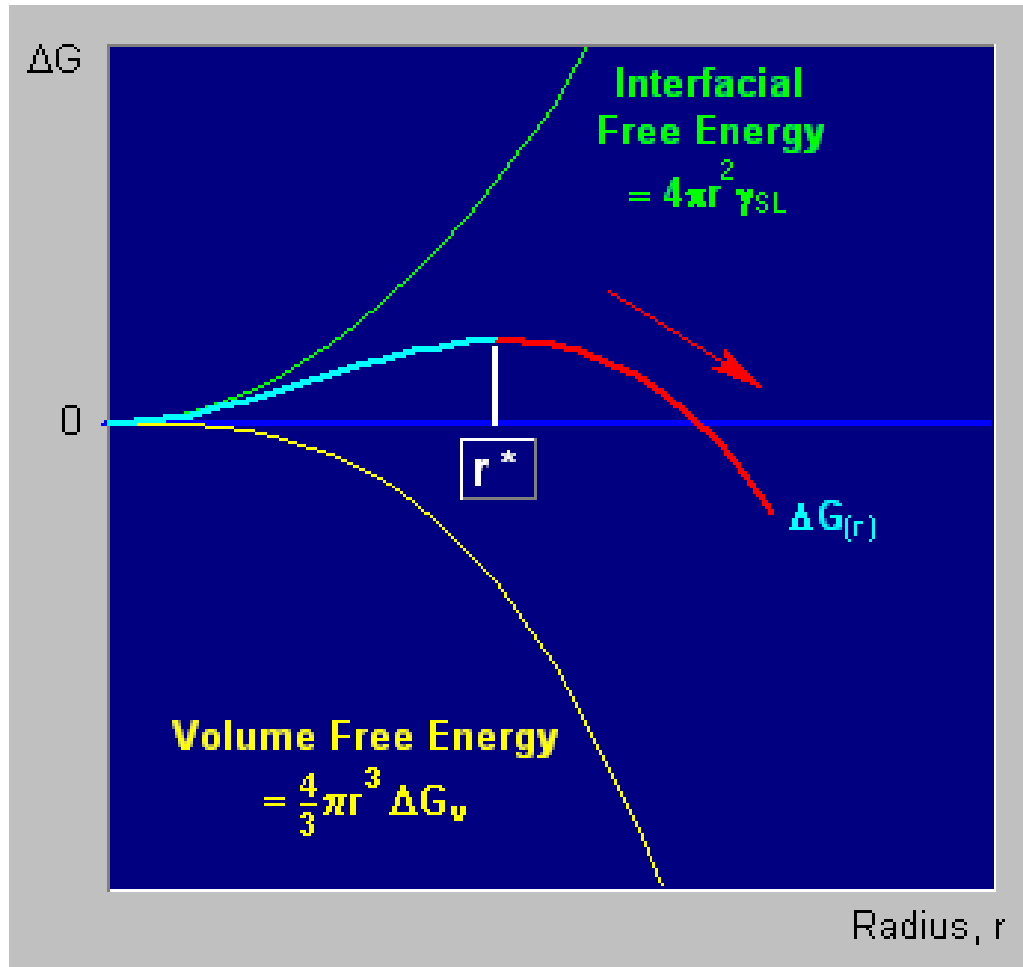
$$R_{\text{embryo}} < r^*$$



Free energy increase.

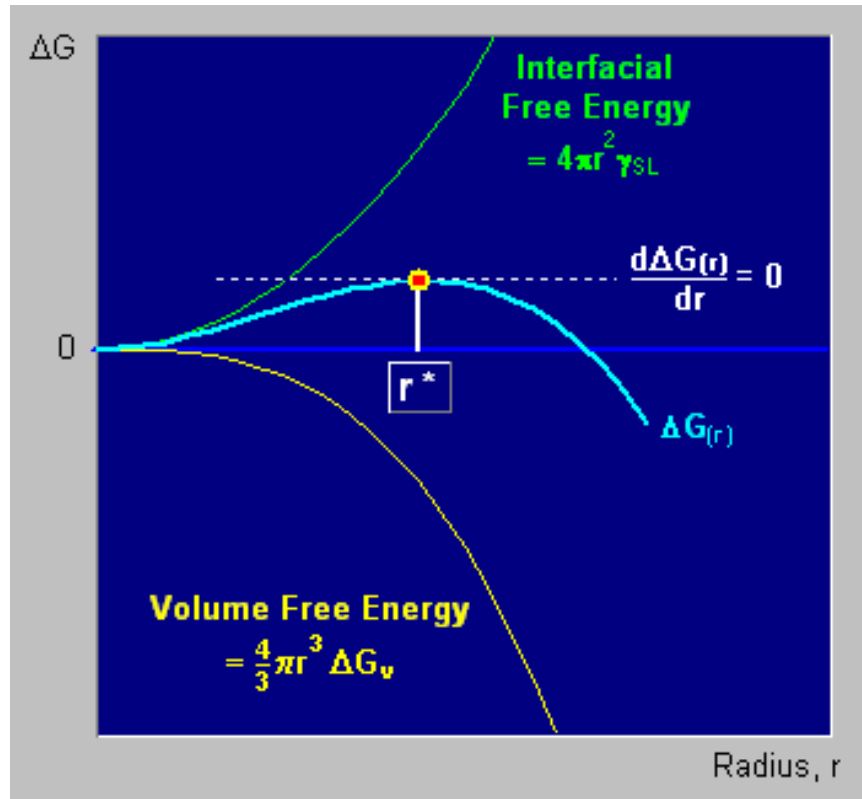
The solid remelts,

$$R_{\text{embryo}} > r^*$$



The solid will
grow,
free energy
decrease.

r^* to Homogeneous Nucleation



$$\Delta G = V_s \Delta G_V + A_{sl} \sigma_{sl}$$

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \sigma_{sl}$$

$$4 \pi r^{*2} \Delta G_V + 8 \pi r^* \sigma_{sl} = 0$$

$$r^* = \frac{-2 \sigma_{sl}}{\Delta G_V}$$

$$\Delta G_V = \frac{\Delta H_V \Delta T}{T_m}$$

$$r^* = \frac{2 \sigma_{sl} T_m}{\Delta H_V \Delta T}$$

TABLE 8-1 ■ Values for freezing temperature, latent heat of fusion, surface energy, and maximum undercooling for selected materials

	Freezing Temperature (T_m)	Heat of Fusion (ΔH_f)	Solid-Liquid Interfacial Energy (σ_{sl})	Typical Undercooling for Homogeneous Nucleation (ΔT)
Metal	(°C)	(J/cm ³)	(J/cm ²)	(°C)
Ga	30	488	56×10^{-7}	76
Bi	271	543	54×10^{-7}	90
Pb	327	237	33×10^{-7}	80
Ag	962	965	126×10^{-7}	250
Cu	1085	1628	177×10^{-7}	236
Ni	1453	2756	255×10^{-7}	480
Fe	1538	1737	204×10^{-7}	420
NaCl	801			169
CsCl	645			152
H ₂ O	0			40

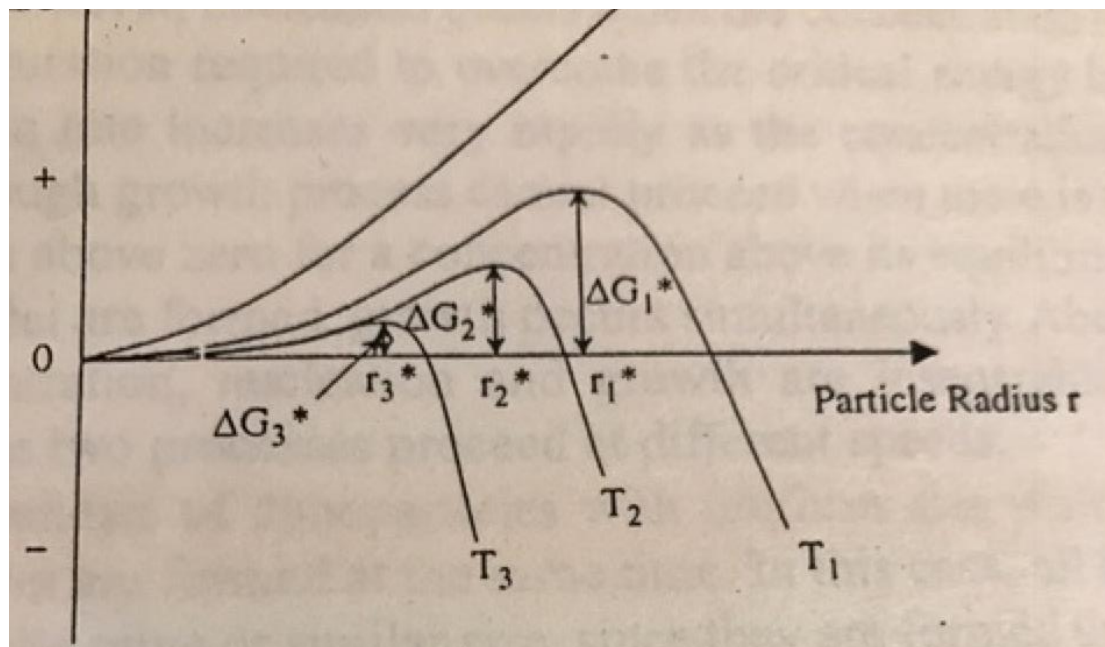
Is it possible to reduce the r^*

$$r^* = -2 \frac{\gamma}{\Delta G_v}$$

The free energy is a function of T and supersaturation (C-Co)/Co

However...

the supersaturation decreases as T increases
the surface tension _____ as T increases



Important considerations

- Identical size
- Identical shape or morphology
- Identical chemical composition and crystal structure
- Individually disperse or monodispersed

Debate

Debate...

Based on the information provided so far...

Depict a process to get small particles with the narrowest size distribution possible

Synthesis Methods

- Thermodynamic approach
 - i. supersaturation
 - ii. nucleation
 - iii. growth
- Kinetic approach

Desirable features

- Uniform size distribution
- Identical shape or morphology
- Identical chemical composition and crystal structure
- Individually dispersed

Critical size (r^*)

How to reduce the value of r^* ?

$$r^* = -2 \frac{\gamma}{\Delta G_V} \qquad \Delta G^* = \frac{16\pi\gamma}{(3\Delta G_V)^2}$$

Energy barrier to overcome, so nucleation can start

so $\Delta G_V \uparrow\uparrow$

but remember that... $\Delta G_V = \frac{kT}{\Omega} \ln\left(\frac{C}{C_0}\right) = \frac{kT}{\Omega} \ln(1 + \sigma)$

$$C \uparrow$$

$$T \uparrow \longrightarrow$$

It affects surface energy (specially near roughening temperature)

Other variables affecting r^*

Besides of C and T:

- Solvent type (polarity)
- Additives (i.e.: viscosity)
- Impurities

Rate of nucleation (R_N)

$$R_N = f(n, P, \Gamma)$$

n is the number of growth species/volume

P is the probability of fluctuations of the critical free energy ΔG^*

Γ is the frequency of species jumping from one growing site to another one

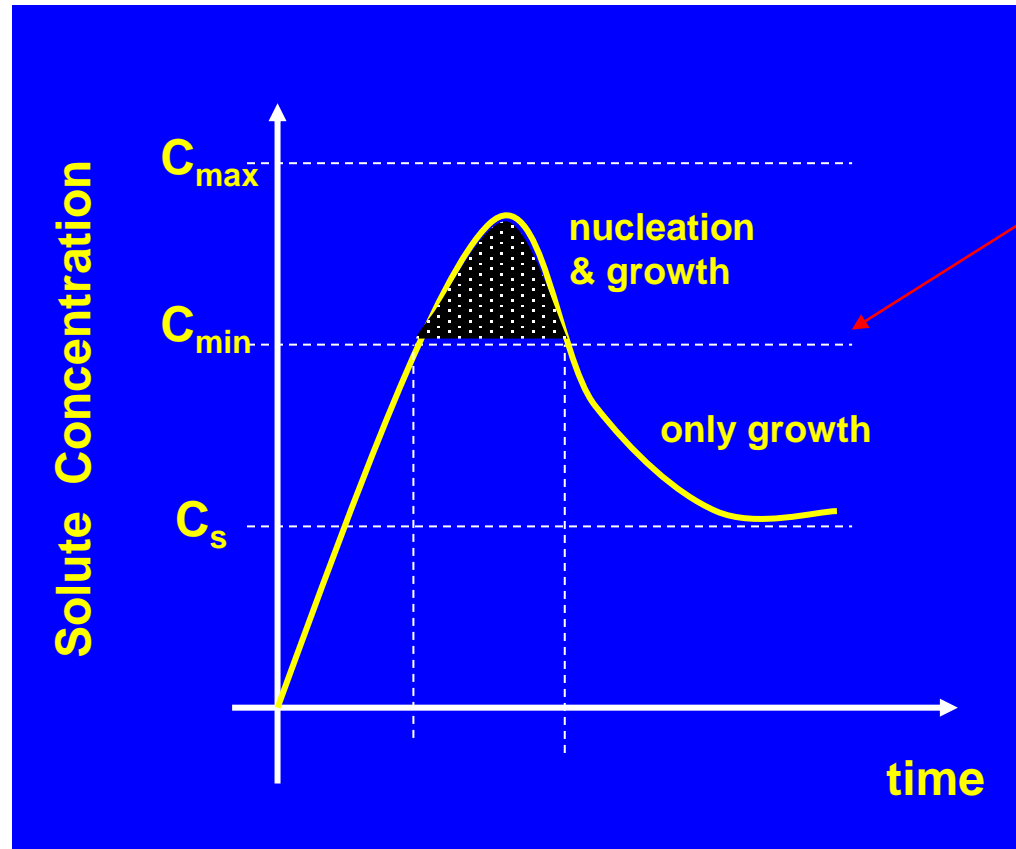
$$P = \exp\left(\frac{-\Delta G^*}{kT}\right)$$

$$\Gamma = \frac{kT}{3\pi\lambda^3\eta}$$

$$R_N = nP\Gamma = \left[\frac{C_0 kT}{3\pi\lambda^3\eta}\right] \exp\left[\frac{-\Delta G^*}{kT}\right]$$

$$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2}$$

$$\Delta G_v = \frac{kT}{\Omega} \ln\left(\frac{C}{C_0}\right) = \frac{kT}{\Omega} \ln(1 + \sigma)$$



below C_{\min}
nucleation
ceases,
so...

Growth of the nuclei

Steps:

- generation of the species
 - diffusion from the bulk to the surface
 - adsorption onto the growth surface
 - surface growth onto the solid surface
-
- diffusion limited**
- growth limited**

Diffusion controlled growth

Promotes the formation of uniformly sized particles

$$\frac{dr}{dt} = D(C - C_s) \frac{V_m}{r}$$

D is the diffusion coefficient

$$r dr = D(C - C_s) V_m dt$$

at time $t=0$, $r = r_o$

$$r^2 = 2D(C - C_s) V_m t + r_o^2$$

$$r^2 = k_D t + r_o^2$$

where: $k_D = 2D(C - C_s) V_m$
is the diffusion constant

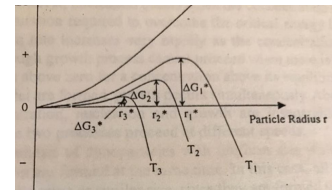
For this type of growth the radius difference among particles is given by:

$$r \delta r = r_o \delta r_o$$

$$\delta r = \frac{r_o \delta r_o}{r}$$

Therefore such difference decreases with time as well as with higher values of r_o and higher k_D

$$\delta r = \frac{r_o \delta r_o}{\sqrt{k_D t + r_o^2}}$$



Surface controlled growth

Does not promote the formation of uniformly sized particles

- Monolayered

If the radius of the nuclei increases, then the radius difference among particles increases:

$$\frac{dr}{dt} \propto \text{surface area}$$

$$\frac{dr}{dt} = k_m r^2$$

$$\frac{dr}{r^2} = k_m dt$$

$$\frac{1}{r} = \frac{1}{r_0} - k_m t$$

$$\delta r / r^2 = \delta r_0 / r_0^2$$

$$\delta r = \frac{r^2 \delta r_0}{r_0^2}$$

substitution of r:

$$\delta r = \frac{\delta r_0}{(1 - k_m r_0 t)^2}$$

therefore:

as t increases...

Surface controlled growth

Does not promote the formation of uniformly sized particles

Polinuclear growth

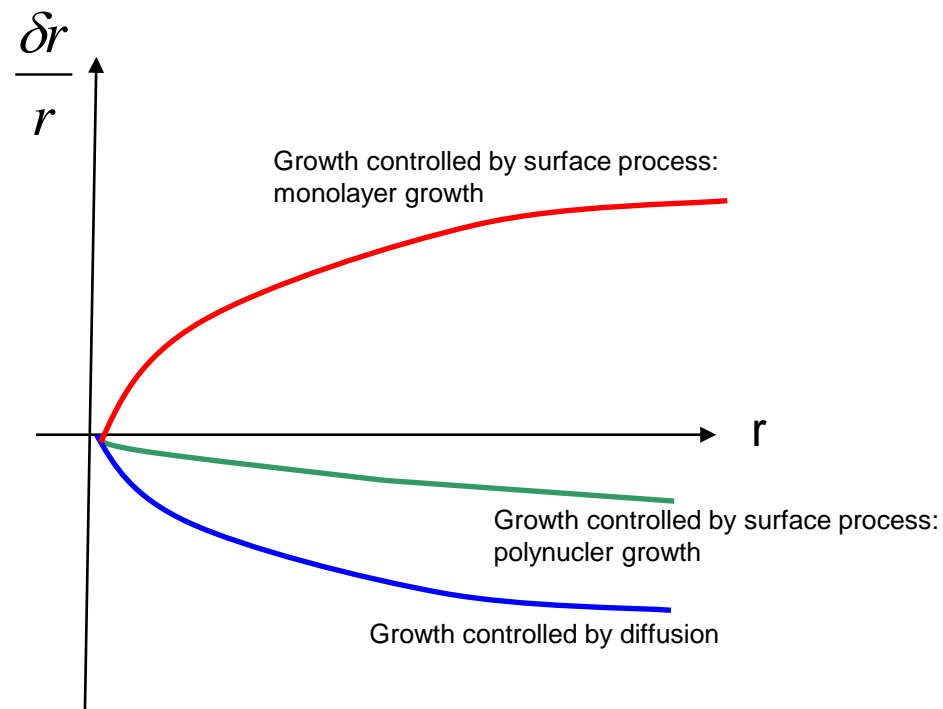
surface process is very fast,
growth rate is constant

$$\frac{dr}{dt} = k_p$$

$$r = k_p t + r_0$$

Therefore, the radius difference
remains constant:

$$\delta r = \delta r_0$$



Advantages of solution processes

It is easy to:

- prevent agglomeration
- extract
- do surface modifications and applications
- control the process
- have mass production