Phase Transformation

1.Diffusional

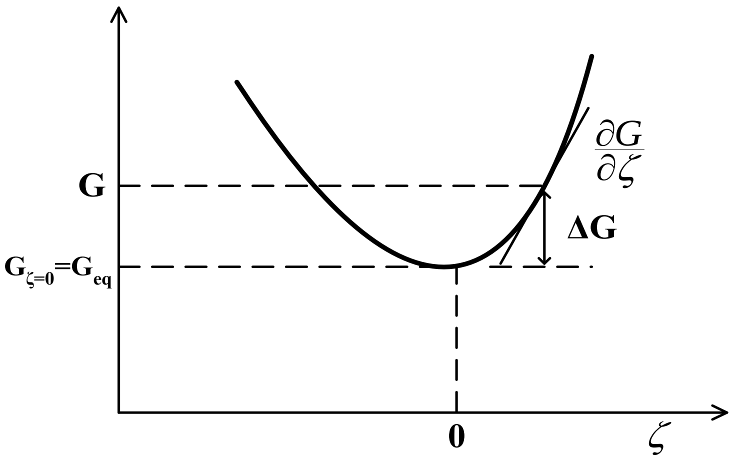
- Require movement of atoms by a diffusion process driven by a chemical potential gradient
    - a.**Nucleation and growth**
    - b.**Spinodal decomposition**

2.Displacive (Non-diffusional)

- Involve cooperative movement of atoms in a shearing action during phase transformation

e. g., **Martensitic transformation in steel**

- **Stability condition with respect to infinitesimal fluctuation**



$\Delta G > 0$ → the equilibrium is stable
$\Delta G = 0$ → the equilibrium is neutral
$\Delta G < 0$ → the equilibrium is unstable

$$\Delta G = G - G_{\xi=0}$$

$$= \left(\frac{\partial G}{\partial \zeta}\right)_{\xi=0}\delta\zeta + \frac{1}{2}\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{\xi=0}(\delta\zeta)^2 + \ldots + \frac{1}{n!}\left(\frac{\partial^n G}{\partial \zeta^n}\right)_{\xi=0}(\delta\zeta)^n$$

$$\Delta G = \delta G + \frac{1}{2}\delta^2 G + \ldots.\frac{1}{n!}\delta^n G$$

$$At \quad equilibrium \qquad \delta G = 0$$

$$\Delta G = \frac{1}{2}\delta^2 G + \ldots. = \frac{1}{2}\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_{\zeta=0}(\delta\zeta)^2 + \ldots.$$

Since $(\delta\zeta)^2$ is always positive

$$\Delta G > 0 \ when \ (\frac{\partial^2 G}{\partial \zeta^2})_{\zeta=0} > 0 \rightarrow stable$$

$$\Delta G < 0 \ when \ (\frac{\partial^2 G}{\partial \zeta^2})_{\zeta=0} < 0 \rightarrow unstable$$

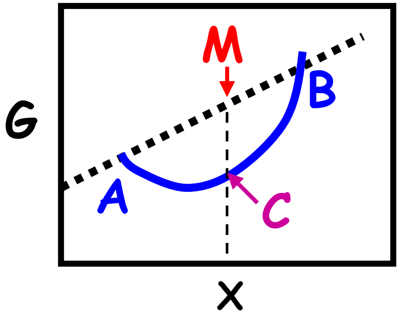
$$*When \ (\frac{\partial^2 G}{\partial \zeta^2})_{\zeta=0} = 0 \ \rightarrow \ \Delta G = \frac{1}{3!}(\frac{\partial^3 G}{\partial \zeta^3})_{\zeta=0}(\delta\zeta)^3 + ...$$

$if \ (\frac{\partial^3 G}{\partial \zeta^3})_{\zeta=0}$ has a value which is different from zero, it is possible to choose a value of ζ so as to make ΔG negative. Consequently, if $(\frac{\partial^3 G}{\partial \zeta^3})_{\zeta=0} \neq 0$ the equilibrium is unstable. If it is zero, the equilibrium is stable when $(\frac{\partial^4 G}{\partial \zeta^4})_{\zeta=0} > 0 \ \because (\delta\zeta)^4 > 0.$

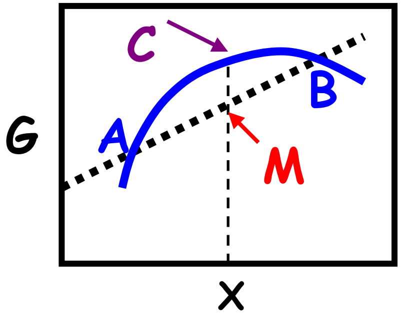
- Stability criteria for local compositional fluctuation

G_M < G_C →Decomposition

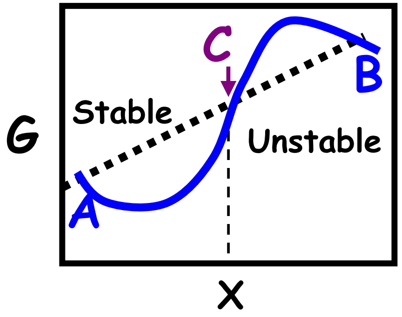
G_M > G_C →No Decomposition



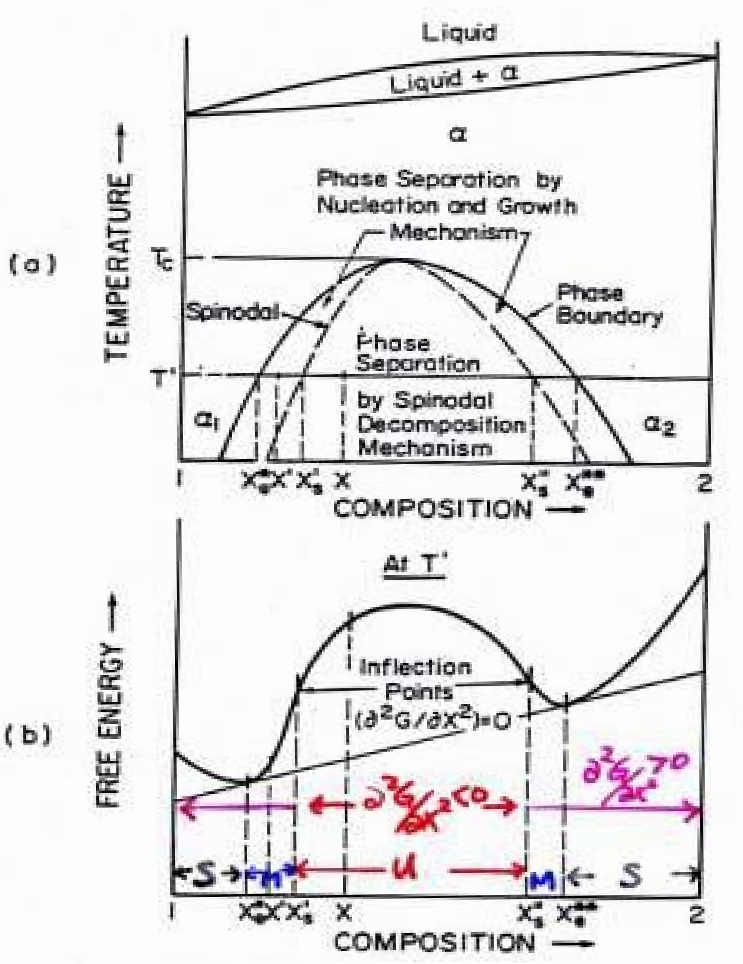
$$\frac{\partial^2 G}{\partial X^2} > 0, \ G_M > G_C, \ C \nrightarrow A+B$$



$$\frac{\partial^2 G}{\partial X^2} < 0, \ G_M < G_C, \ C \rightarrow A+B$$



$\frac{\partial^2 G}{\partial X^2} = 0$ Spinodal point separating stable and unstable regions

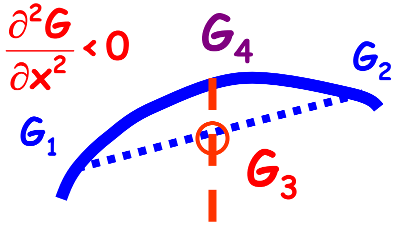


U: Unstable

M: Metastable

S: Stable

(a) Unstable region



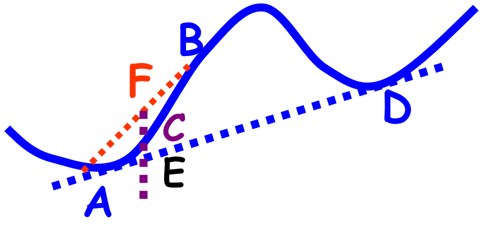
$$\frac{\partial^2 G}{\partial x^2} < 0$$

$G_3 < G_4$

- No energy barrier for decomposition
- Kinetics controlling process
- Spinodal decomposition

(b) Metastable region

$$\frac{\partial^2 G}{\partial x^2} > 0$$



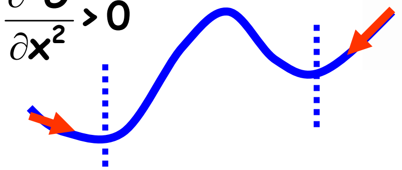
-Small fluctuation, C→A+B, and $G_C < G_F$, energetically unfavorable

-Large fluctuation, C→A+D and $G_C > G_E$, energetically favorable

-Nucleation and growth

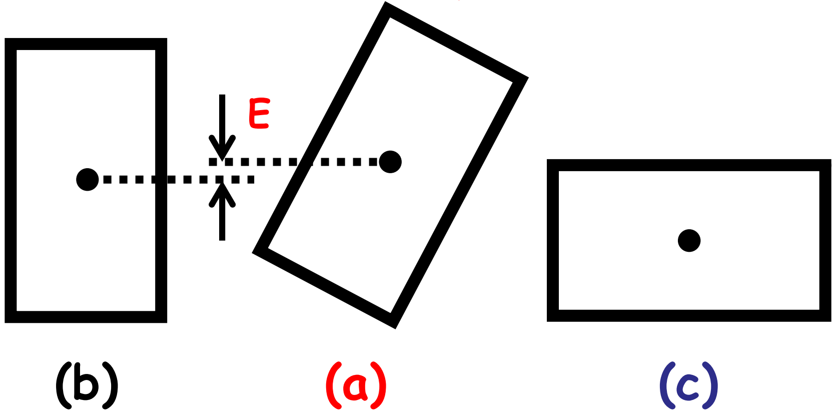
(c) Stable region

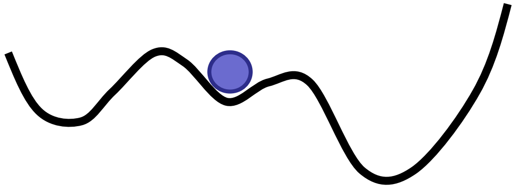
$$\frac{\partial^2 G}{\partial x^2} > 0$$



Mechanical Analogue

E: the minimum work required to render unstable





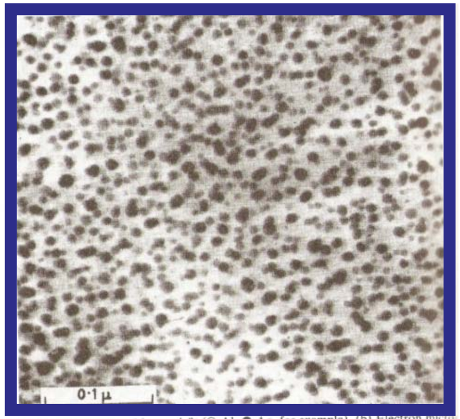
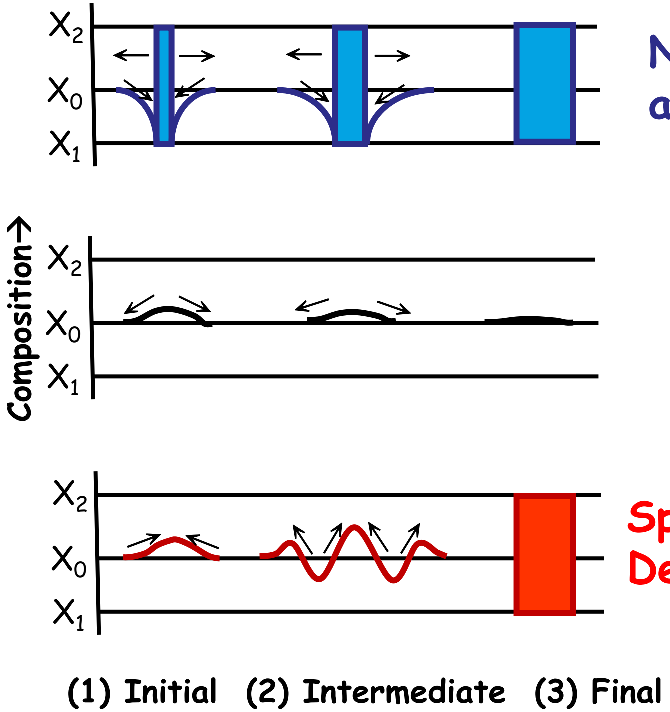


Fig. 3.39 (a) A zone with no misfit (○ Al, ● Ag, for example). (b) Electron micrograph of Ag-rich zones in an Al-4 atomic % Ag alloy (× 300 000). (After R.B. Nicholson, G. Thomas and J. Nutting, *Journal of the Institute of Metals*, **87** (1958– 1959) 431.)

(c) Metastable with a large fluctuation

(b) Metastable with a small fluctuation

(a) Unstable



Nucleation and Growth

Spinodal Decomposition

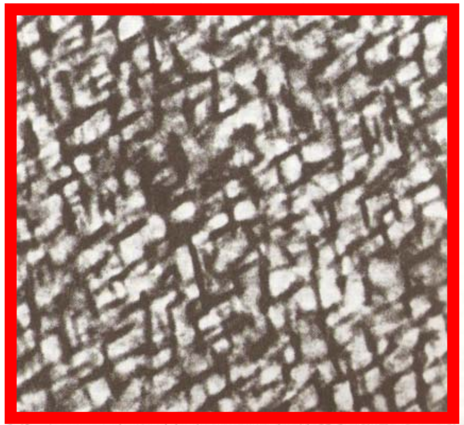
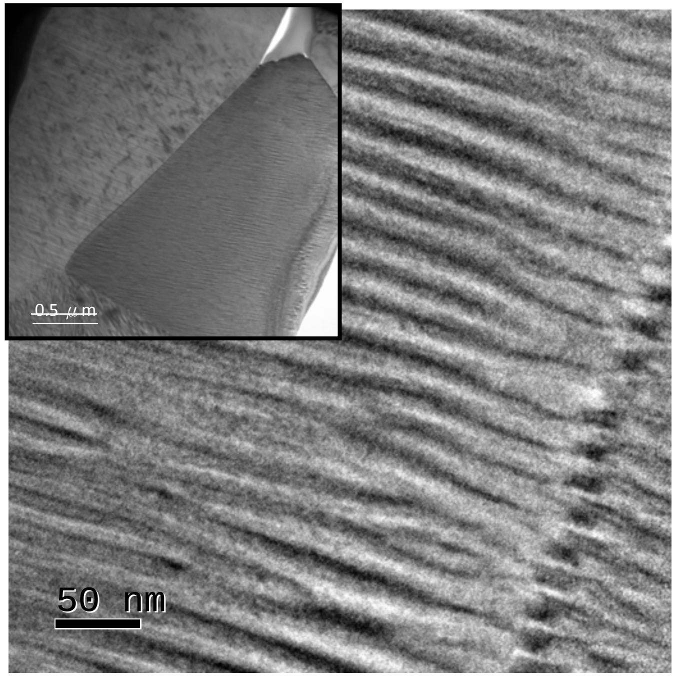


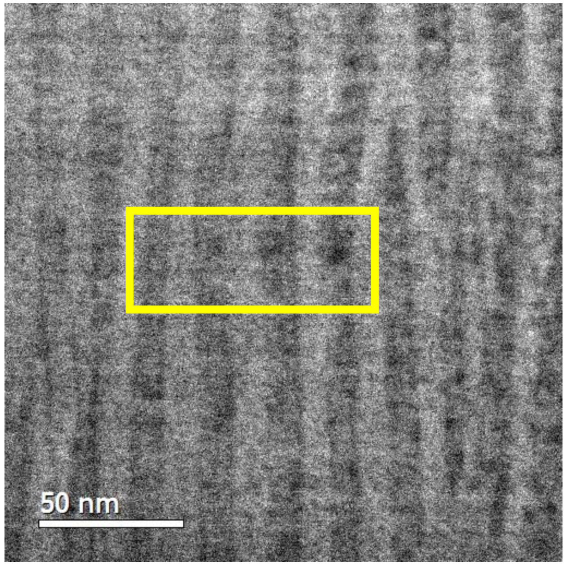
Fig. 5.42 A coarsened spinodal microstructure in Al–22.5 at% Zn–0.1 at% Mg solution treated 2 h at 400 °C and aged 20 h at 100 °C. Thin foil electron micrograph (× 314 000). (After K.B. Rundman, *Metals Handbook*, 8th edn., Vol. 8, American Society for Metals, 1973, p. 184.)

Spinodal decomposition of $V_{0.7}Ti_{0.3}O_2$ annealed at 450°C for 7 days in N_2

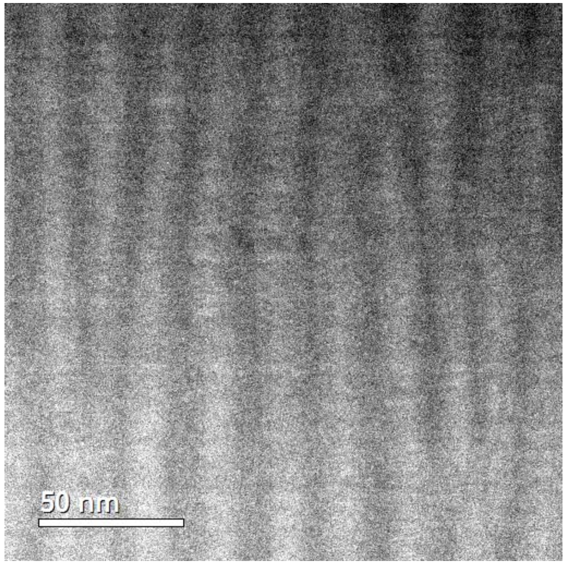


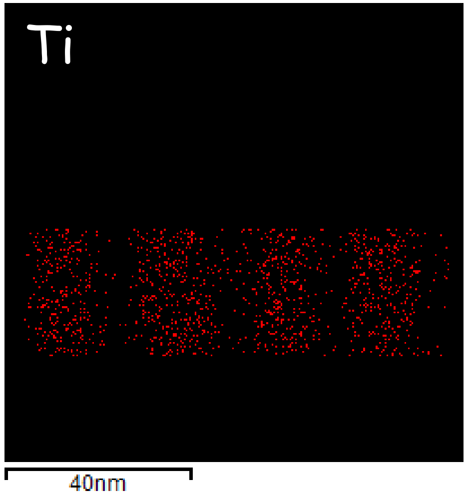
Wavelength of spinodal ≈ 22 nm

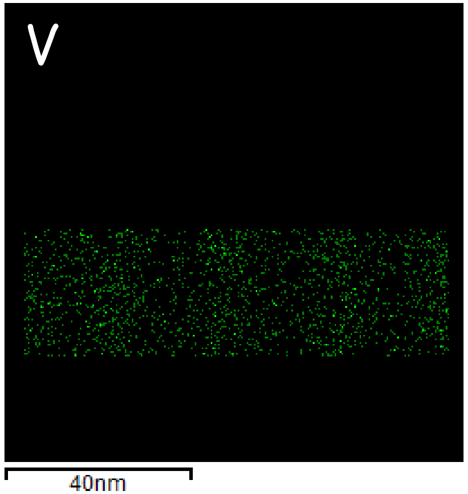
Bright field image



Dark field image







RY Tsai, 2017

Spinodal Decomposition

Composition fluctuation

$C_o \Rightarrow C_o + \delta C \text{ and } C_o - \delta C$

$$G_{C_o+\delta C} = G_{C_o} + (\pm\delta C)G'_{C_o} + 1/2(\pm\delta C)^2 G''_{C_o}$$

$$G'_{C_o} = \left(\frac{\partial G}{\partial C}\right)_{C_o}, \quad G''_{C_o} = \left(\frac{\partial G^2}{\partial^2 C}\right)_{C_o}$$

The change in Gibbs free energy accompanying the composition fluctuation

$$\Delta G = G_{C_o+\delta C} - G_{C_o}$$

$$= \frac{1}{2}[(\delta C)G'_{C_o} + \frac{1}{2}(\delta C)^2 G''_{C_o}]$$

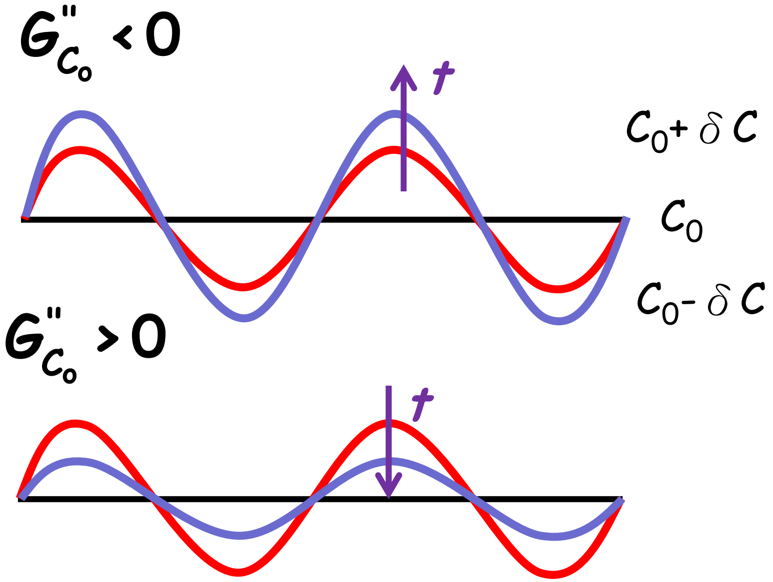
$$+ \frac{1}{2}[(-\delta C)G'_{C_o} + \frac{1}{2}(-\delta C)^2 G''_{C_o}]$$

$$= \frac{1}{2}(\delta C)^2 G''_{C_o}$$

$$G''_{C_o} < 0 \Rightarrow \Delta G < 0 \Rightarrow unstable$$

$$G''_{C_o} > 0 \Rightarrow \Delta G > 0 \Rightarrow stable$$

$$\Delta G = \frac{1}{2}(\delta C)^2 G''_{C_o}$$



$$C(x,t)=\frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

$$C(x,0)=\frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})$$

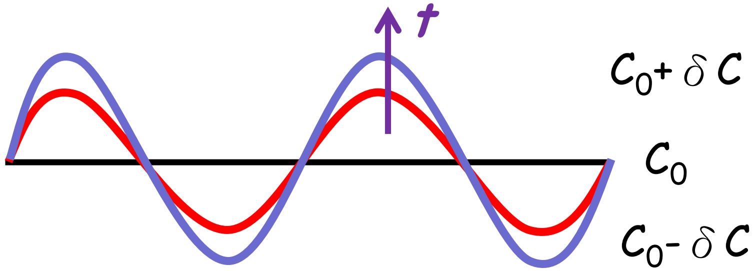
$$C(x,t)=C(x,0)\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

$$Amplification\quad Factor\quad (AF)=\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

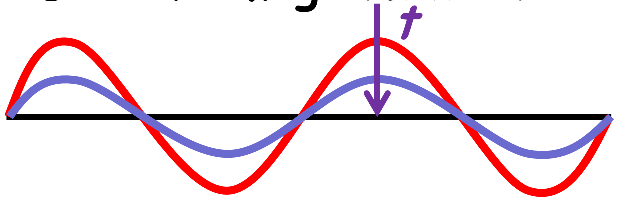
$$(1)D<0\Rightarrow\frac{d(AF)}{dt}>0\Rightarrow Spinodal\quad Decomposition$$

$$(2)D>0\Rightarrow\frac{d(AF)}{dt}<0\Rightarrow Homogenization$$

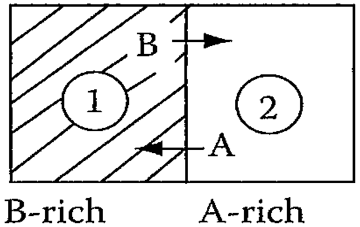
D<0: Decomposition



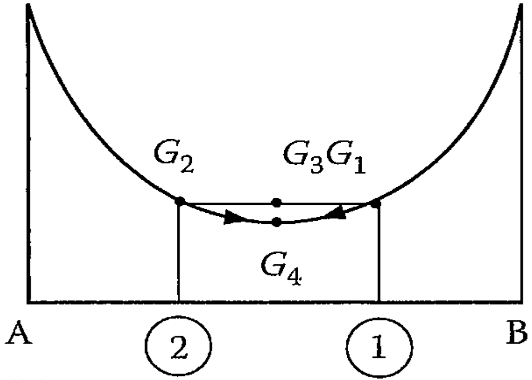
D>0: Homogenization



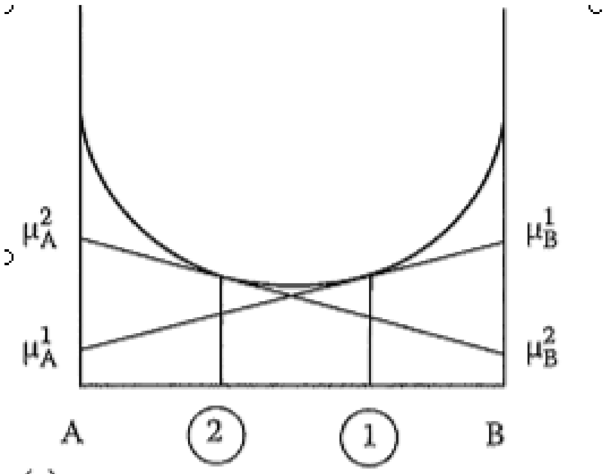
Down-Hill Diffusion



(a)

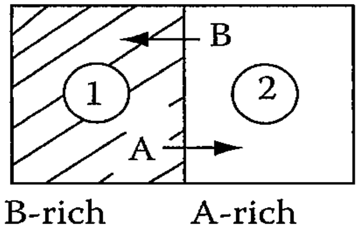


(b)

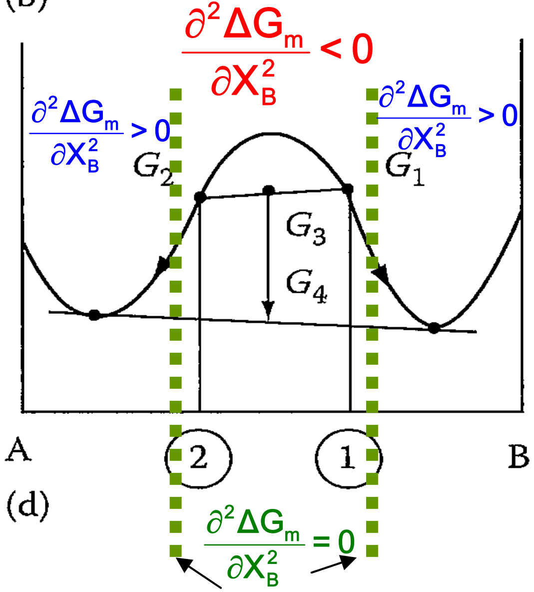


(e)

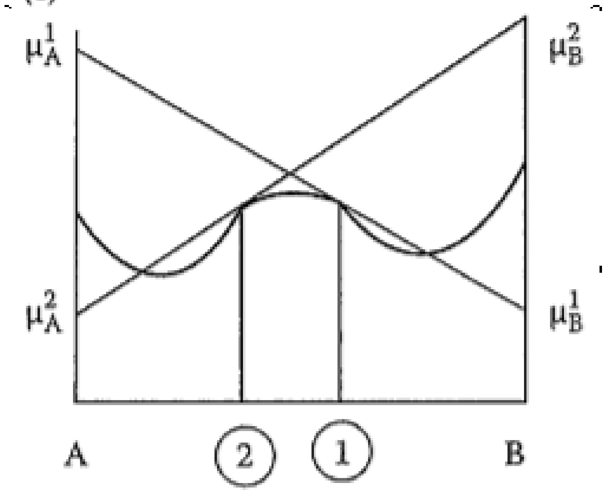
Up-hill Diffusion



(c)



(d)



(f)

$$\text{Driving force} \propto \frac{\partial \mu}{\partial x} \quad (\text{not } \frac{\partial C}{\partial x})$$

$$J = Cv = C \cdot (B \cdot F) = C \cdot B(-\frac{\partial \mu}{\partial x})$$

B : Mobility, F : Force

Regular Solution

$$\Delta H_m \neq 0 \quad \& \quad \Delta S_m^{exc} = 0$$

(Ideal Solution $\Delta H_m = 0 \quad \& \quad \Delta S_m^{exc} = 0$)

$\Delta H_m = \Omega X_A X_B$ where $\Omega = N_o Z \varepsilon$ and

$$\varepsilon = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB}, \quad \varepsilon_{XX} > 0$$

$$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Regular Solution

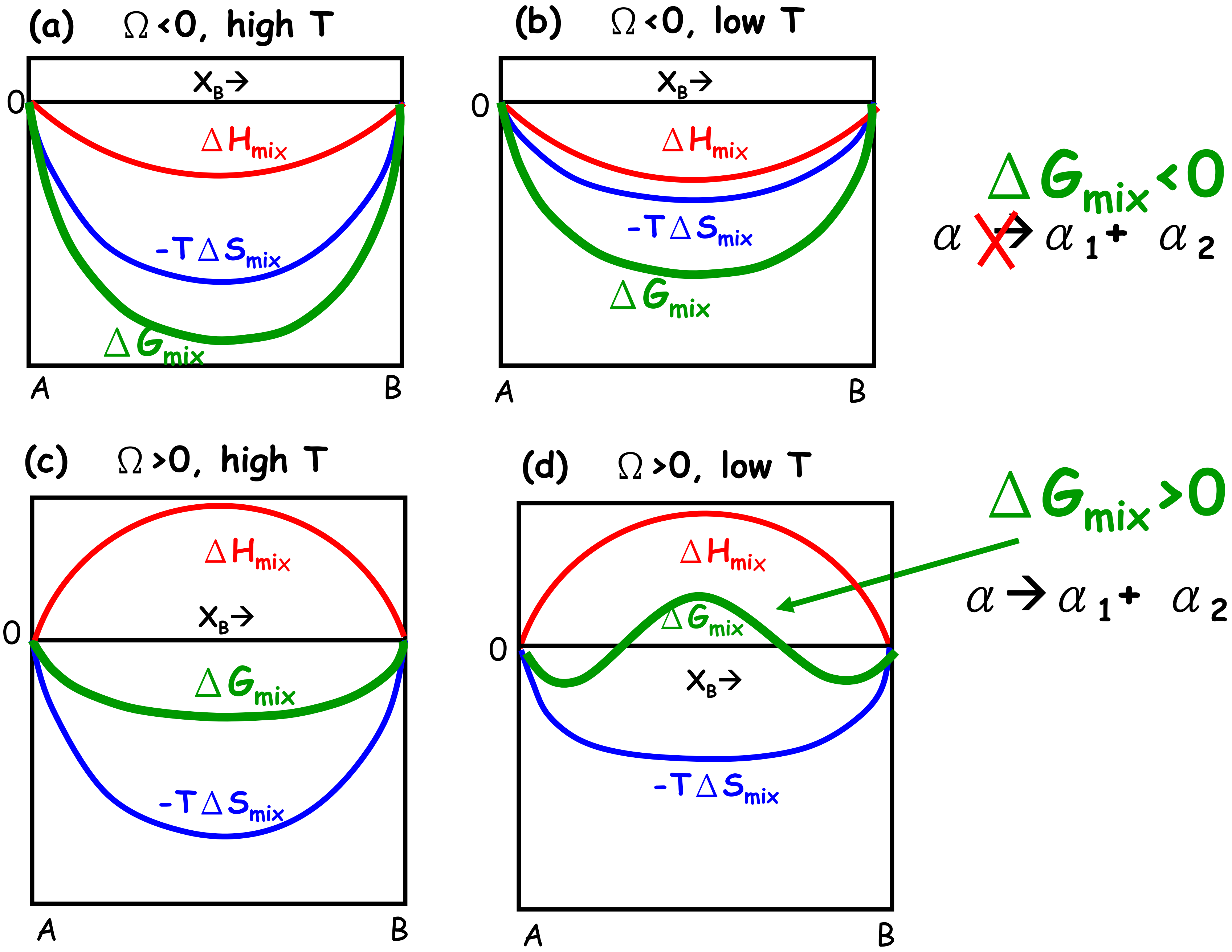
$\Delta H_m = P_{AB}(1/2(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB}) = P_{AB}\varepsilon$

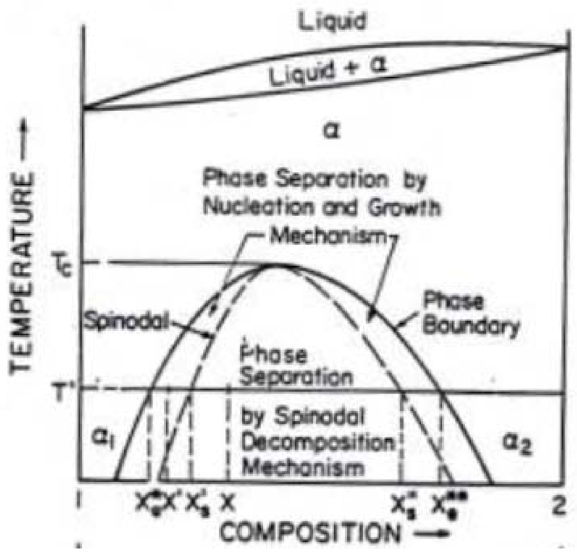
$P_{AB} = ((1/2)ZN_o)(2X_AX_B)$
$= ZN_oX_AX_B$: Probability to form A-B bonds

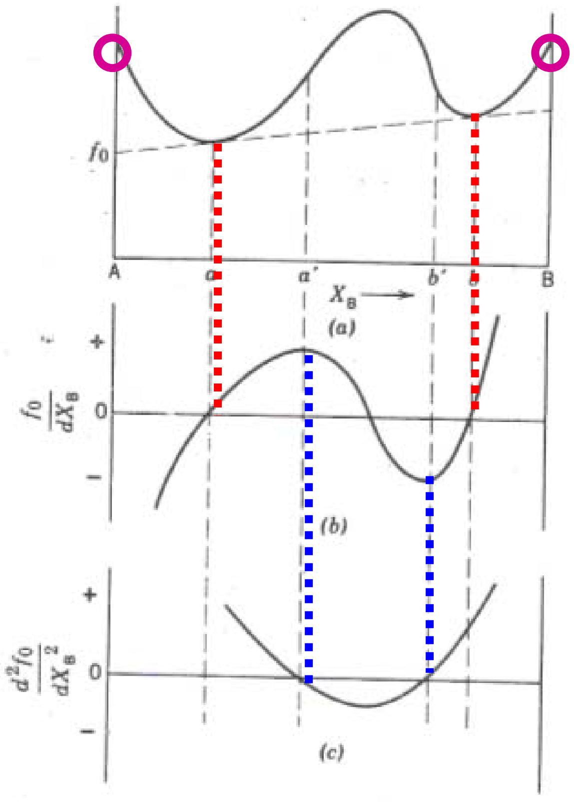
$\Delta H_m = ZN_oX_AX_B\varepsilon = ZN_o\varepsilon X_AX_B = \Omega X_AX_B$

$\Omega = ZN_o\varepsilon$
$\Omega < 0 \rightarrow$ attraction between unlike ions
$\rightarrow 1/2(\varepsilon_{AA} + \varepsilon_{BB}) < \varepsilon_{AB}$
$\Omega > 0 \rightarrow$ repulsion between unlike ions
$\rightarrow 1/2(\varepsilon_{AA} + \varepsilon_{BB}) > \varepsilon_{AB}$

For Ideal Solution
$1/2(\varepsilon_{AA} + \varepsilon_{BB}) = \varepsilon_{AB}$
$\varepsilon = 0 \rightarrow \Omega = 0 \rightarrow \Delta H_m = 0$


(a) Ω<0, high T
X_B →
0
ΔH_{mix}
$-T\Delta S_{mix}$
ΔG_{mix}
A
B
(b) Ω<0, low T
X_B →
0
ΔH_{mix}
$-T\Delta S_{mix}$
ΔG_{mix}
A
B
$\Delta G_{mix}<0$
$\alpha \not\rightarrow \alpha_1 + \alpha_2$
(c) Ω>0, high T
ΔH_{mix}
X_B →
0
ΔG_{mix}
$-T\Delta S_{mix}$
A
B
(d) Ω>0, low T
ΔH_{mix}
ΔG_{mix}
0
X_B →
$-T\Delta S_{mix}$
A
B
$\Delta G_{mix}>0$
$\alpha \rightarrow \alpha_1 + \alpha_2$





Regular Solution

$$\frac{\partial \Delta G_m}{\partial X_B} = RT(-\ln X_A + \ln X_B) + \Omega(1-2X_B)$$

$$\frac{\partial^2 \Delta G_m}{\partial X_B^2} = RT\left(\frac{1}{X_A} + \frac{1}{X_B}\right) - 2\Omega$$

$$\frac{\partial^3 \Delta G_m}{\partial X_B^3} = RT\left(\frac{1}{X_A^2} - \frac{1}{X_B^2}\right)$$

Spinodal line is determined where

$$\frac{\partial^2 \Delta G_m}{\partial X_B^2} = 0 \Rightarrow X_A X_B = \frac{RT}{2\Omega}, \quad (X_A + X_B = 1)$$

→ Spinodal parabola

Critical point is determined where

$$\left.\begin{array}{l} \dfrac{\partial \Delta G_m}{\partial X_B} = 0 \\[2ex] \dfrac{\partial^2 \Delta G_m}{\partial X_B^2} = 0 \end{array}\right\} \quad T_C = \frac{2X_B^C(1-X_B^C)\Omega}{R}$$

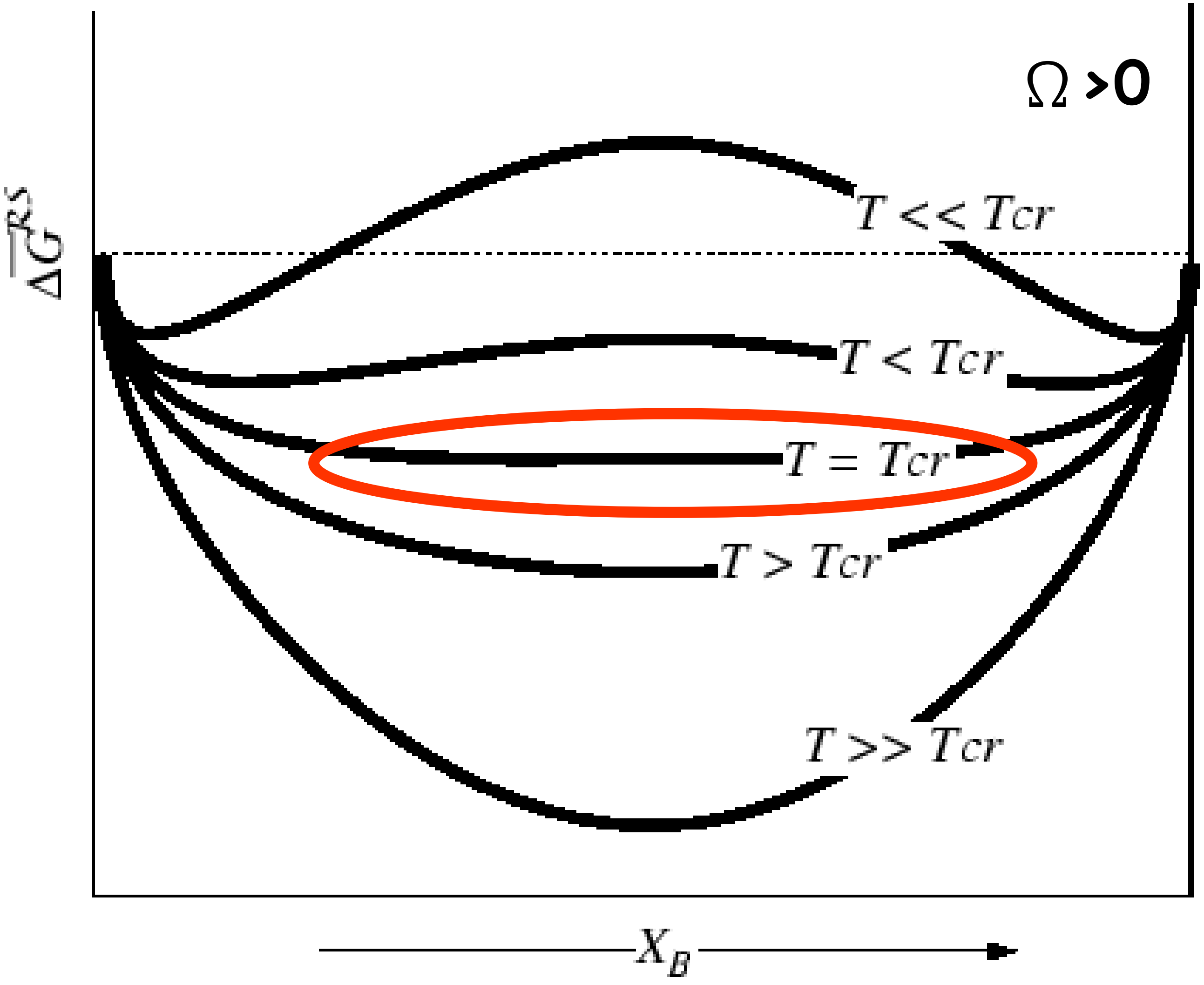
$T_C > 0$ → Ω must be positive

$$\frac{\partial^3 \Delta G_m}{\partial X_B^3} = 0 \rightarrow$$

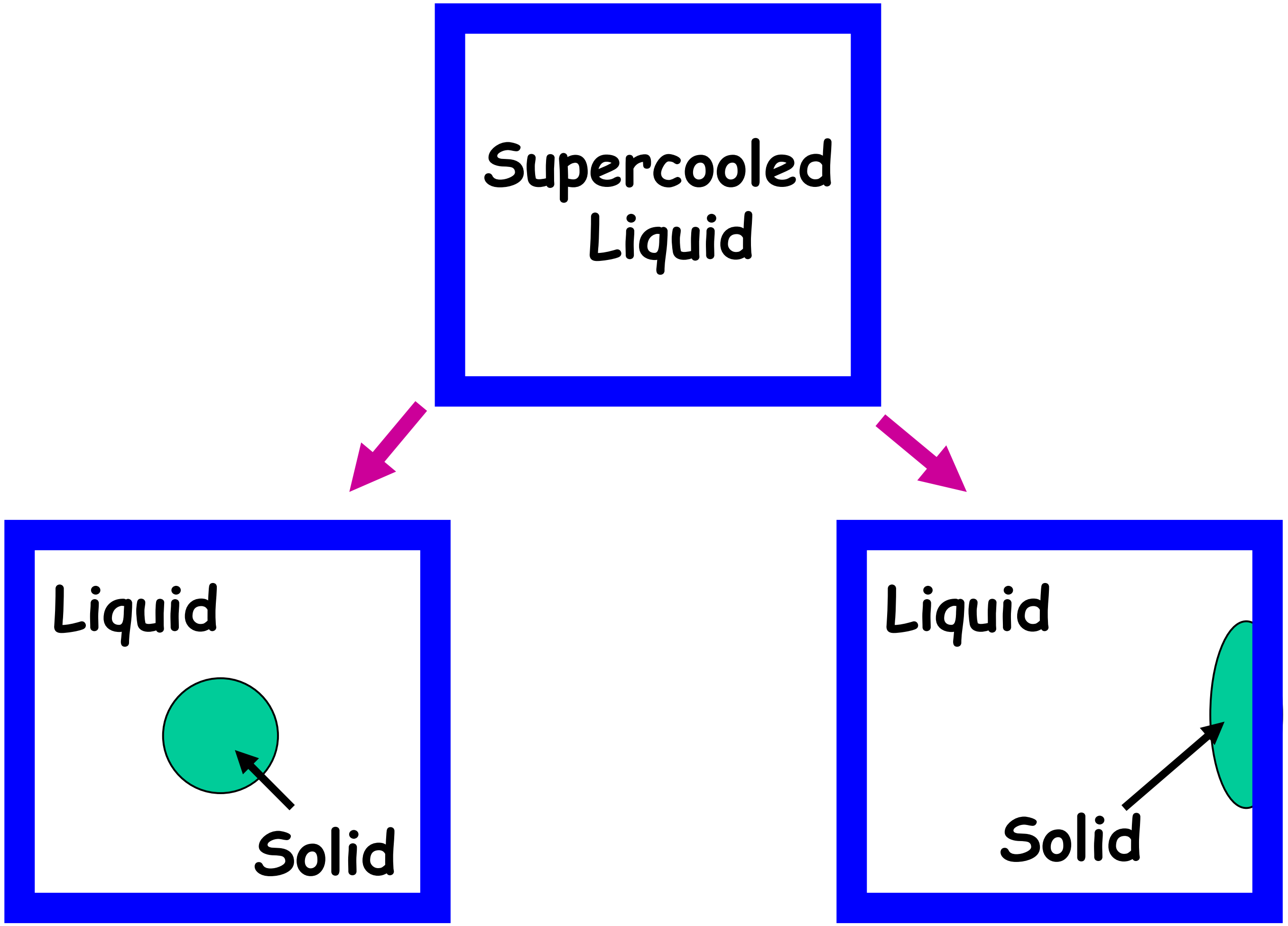
X_B^C is such that T_C is the maximum decomposition temperature associated with the miscibility gap

$$\rightarrow X_A = X_B = 0.5$$

$$\rightarrow T_C = \frac{\Omega}{2R}, \quad \Omega\uparrow T_C\uparrow$$


Ω >0
$\overline{\Delta G}^{RS}$
T << Tcr
T < Tcr
T = Tcr
T > Tcr
T >> Tcr
X_B

Nucleation



Supercooled Liquid

Liquid

Solid

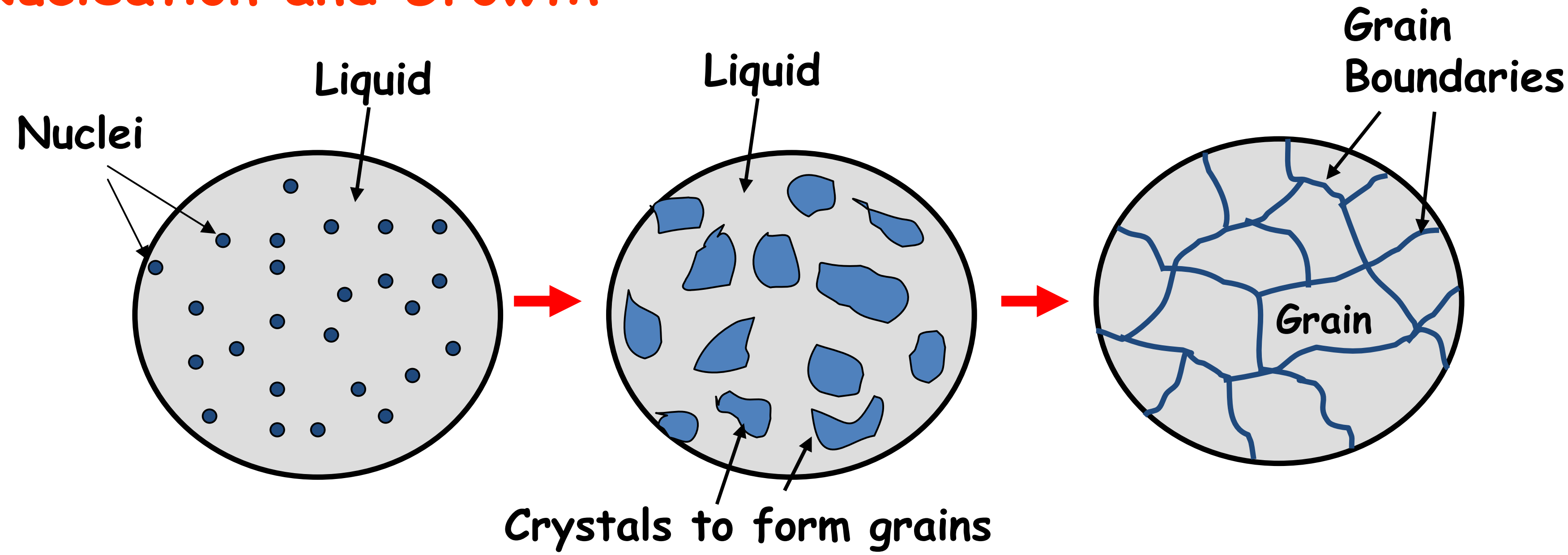
Liquid

Solid

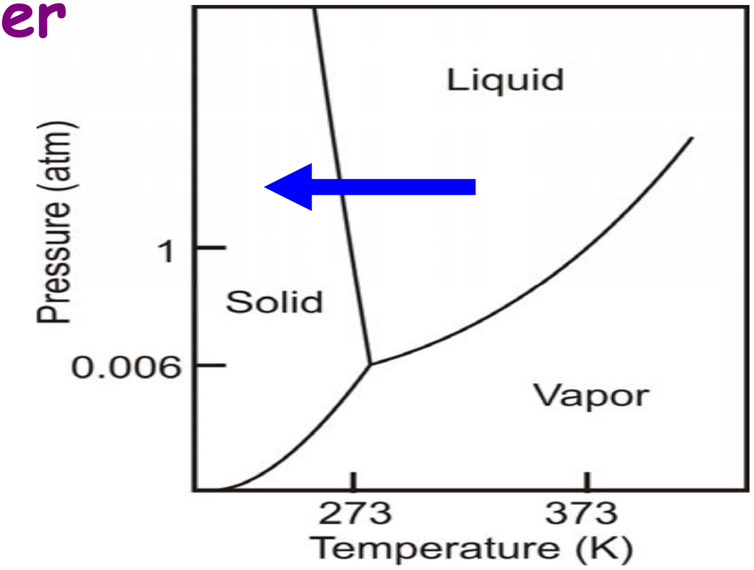
Homogeneous Nucleation

Heterogeneous Nucleation

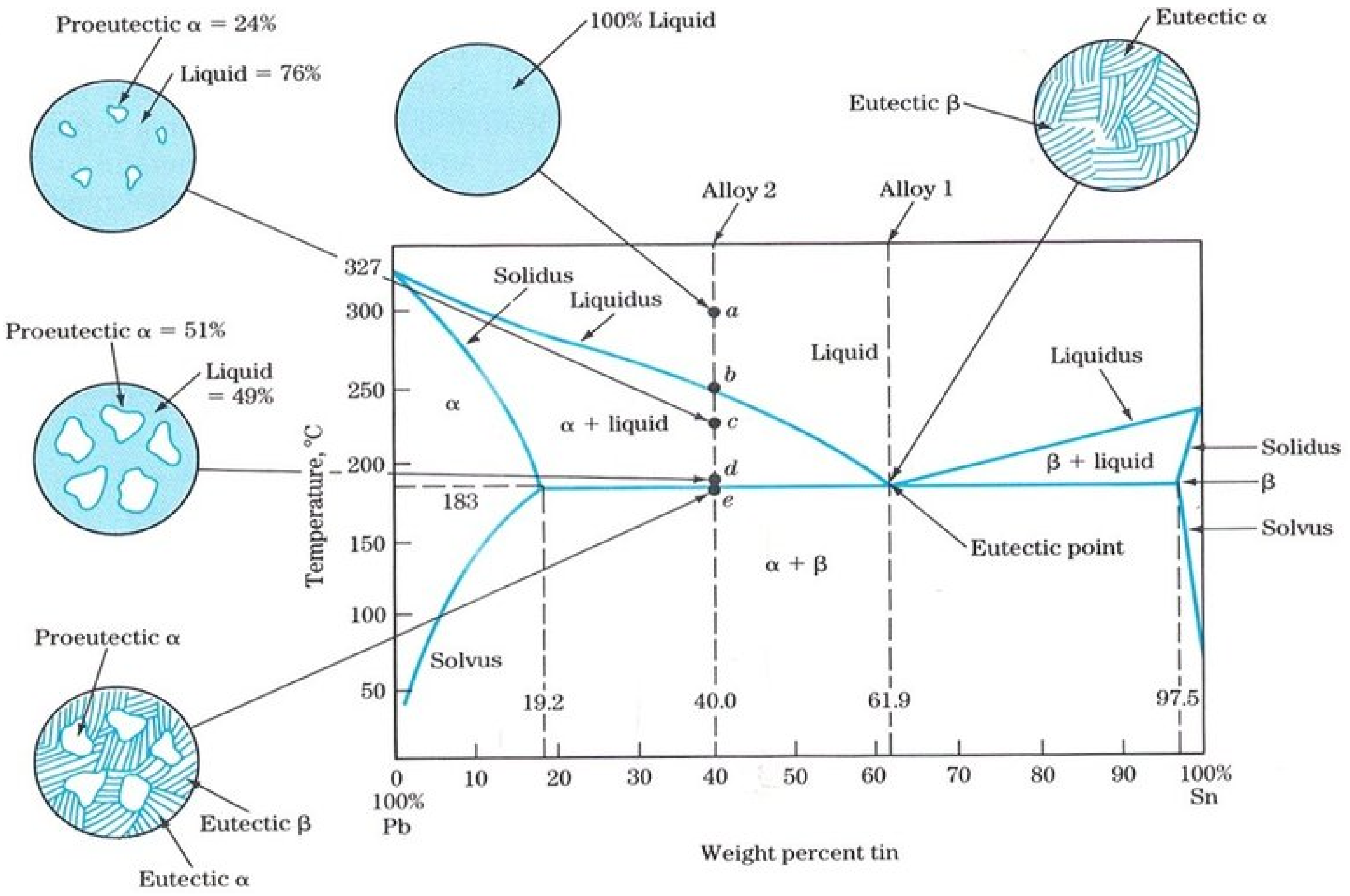
Nucleation and Growth



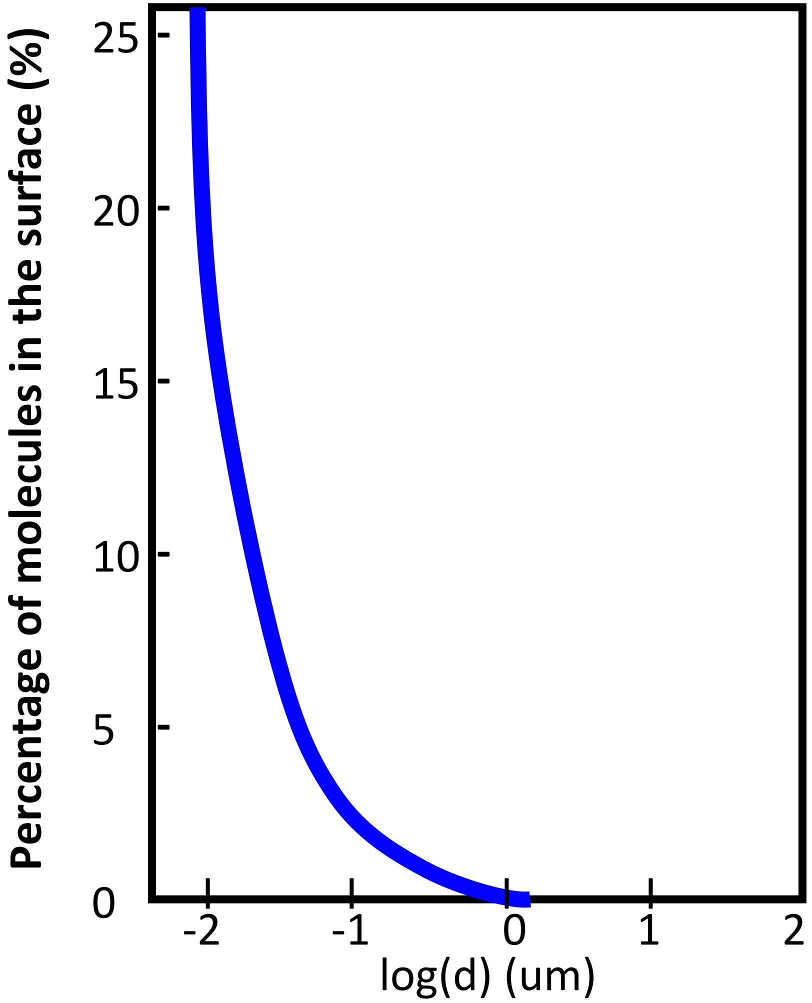
Freezing Water



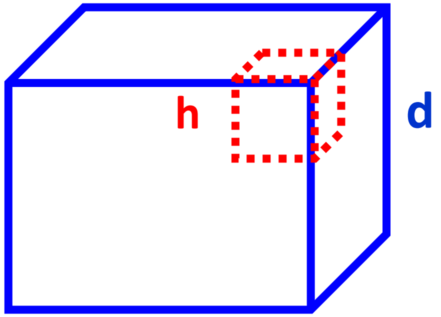
Phase Transformation in Pb-Sn Alloy System



Fraction of Molecules at Surface



AgBr with a molar volume of 30 cm³/mol
and a molecular dimension of h=0.37 nm



$$n_s = 6\left(\frac{d}{h}\right)^2$$

$$n_{total} = \left(\frac{d}{h}\right)^3$$

$$\frac{n_s}{n_{total}} = 6\left(\frac{h}{d}\right)$$

$\frac{n_s}{n_{total}}$ increases with decreasing d

Surface Tension & Energy

The surface stays under a tension or a stress (force per unit length, or work per unit area) which is called surface tension (γ_T)

$$\gamma_T = \frac{F}{L} = \frac{dW}{dA}$$

F:force; L:length

W:work; A:area

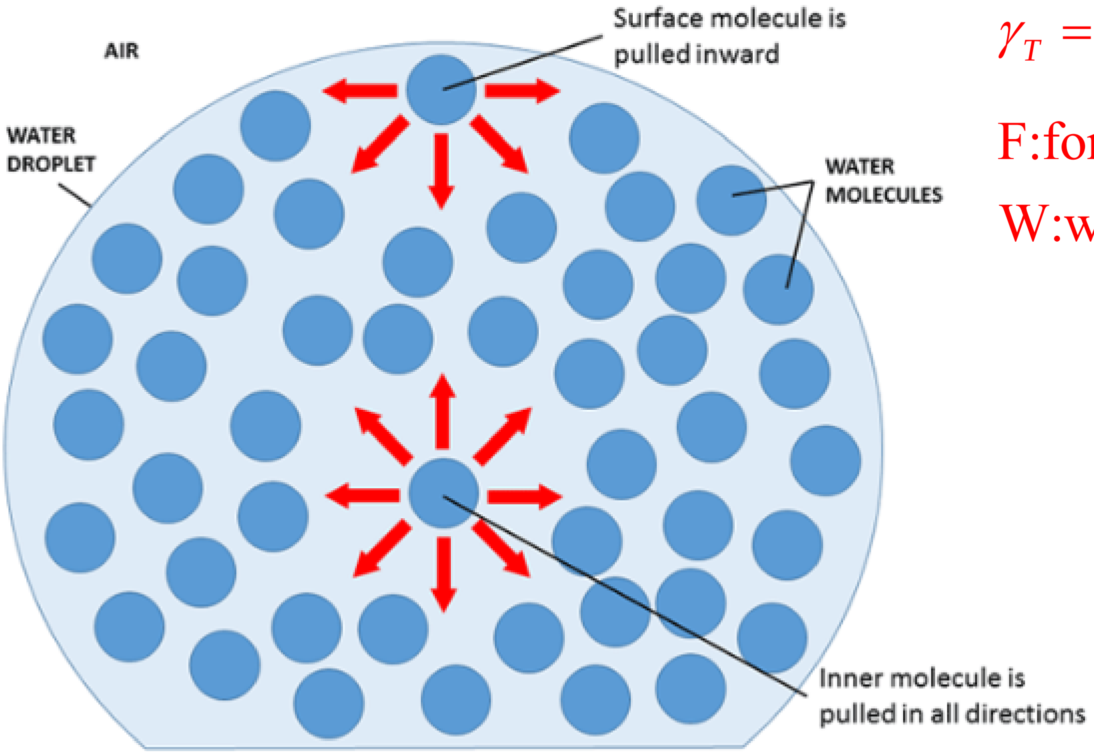


Diagram not to scale

Unbalanced forces for the molecules at the surface yield an excess free energy which is called Surface Energy

$$dG = -SdT + VdP + \gamma dA$$

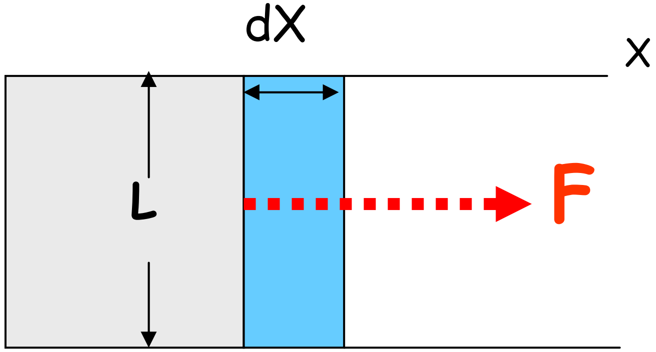
$$\Rightarrow \gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

The free energy of a system containing an interface of area A and excess free energy per unit area (surface energy: γ) is given by

$$G = G_o + \gamma A$$

where G_o is the bulk free energy.

$$dG = \gamma dA + A d\gamma$$



For a liquid film suspended by a wire frame, which is moved by a force of F

$$W(\text{work}) = Fdx$$

$$\text{Surface tension}(\gamma_T) = \text{Force/unit length} = F/L$$

$$\text{Then } W = \gamma_T Ldx = \gamma_T dA \text{ (work done on the system)} = dG$$

$$\gamma_T dA = \gamma dA + A d\gamma$$

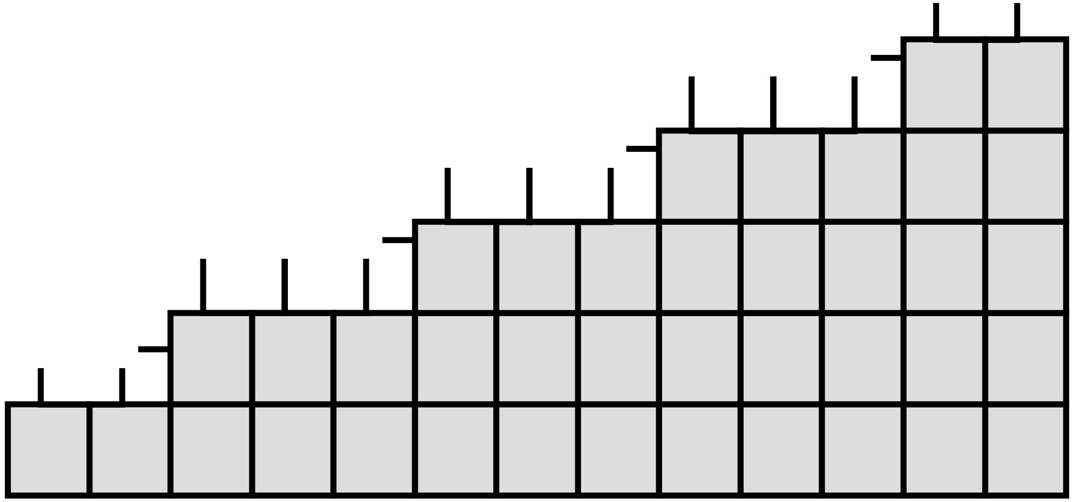
$$\gamma_T = \gamma + A\frac{d\gamma}{dA}$$

For liquid: Since the surface is unable to support shear stresses, the atoms within the liquid can rearrange during the stretching process and thereby maintaining a constant surface structure and energy; i.e., $d\gamma/dA = 0 \rightarrow \gamma_T = \gamma$

For solid: Since the atoms take much longer to move from the bulk to surface, the surface structure and energy will be changed when it is under stress. If this time is long in relative to the time of the experiment then $d\gamma/dA \neq 0 \rightarrow \gamma_T \neq \gamma$.

At temperatures near the melting point, however, $\gamma_T = \gamma$ because the mobility of atoms is fast enough to restore surface structure.

Broken-bond Model for surface energy

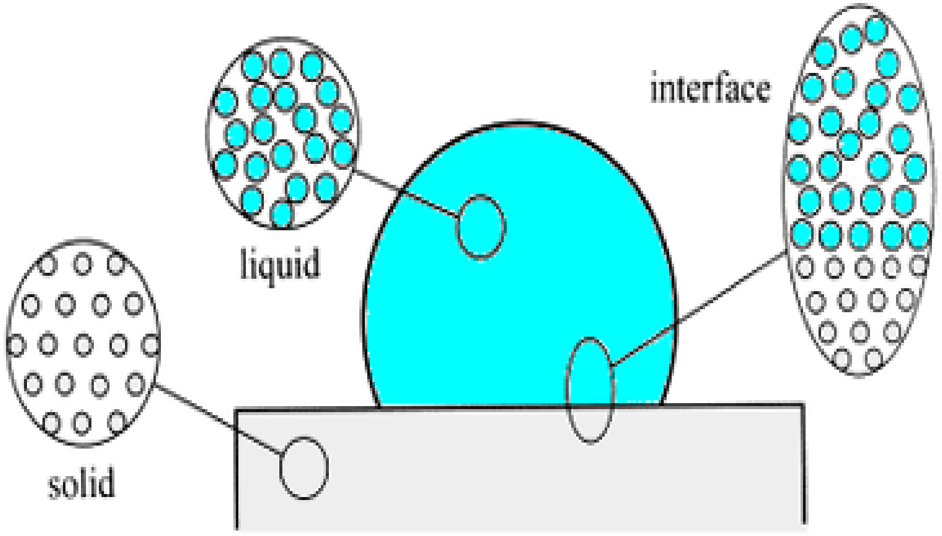


Average Surface Energies

Metals	T_m(°C)	γ_{SV} (mJm^{-2})
Sn	232	680
Al	660	1080
Ag	961	1120
Au	1063	1390
Cu	1084	1720
δ-Fe	1536	2080
Pt	1769	2280
W	3407	2650

H_2O: 72 mJm^{-2}

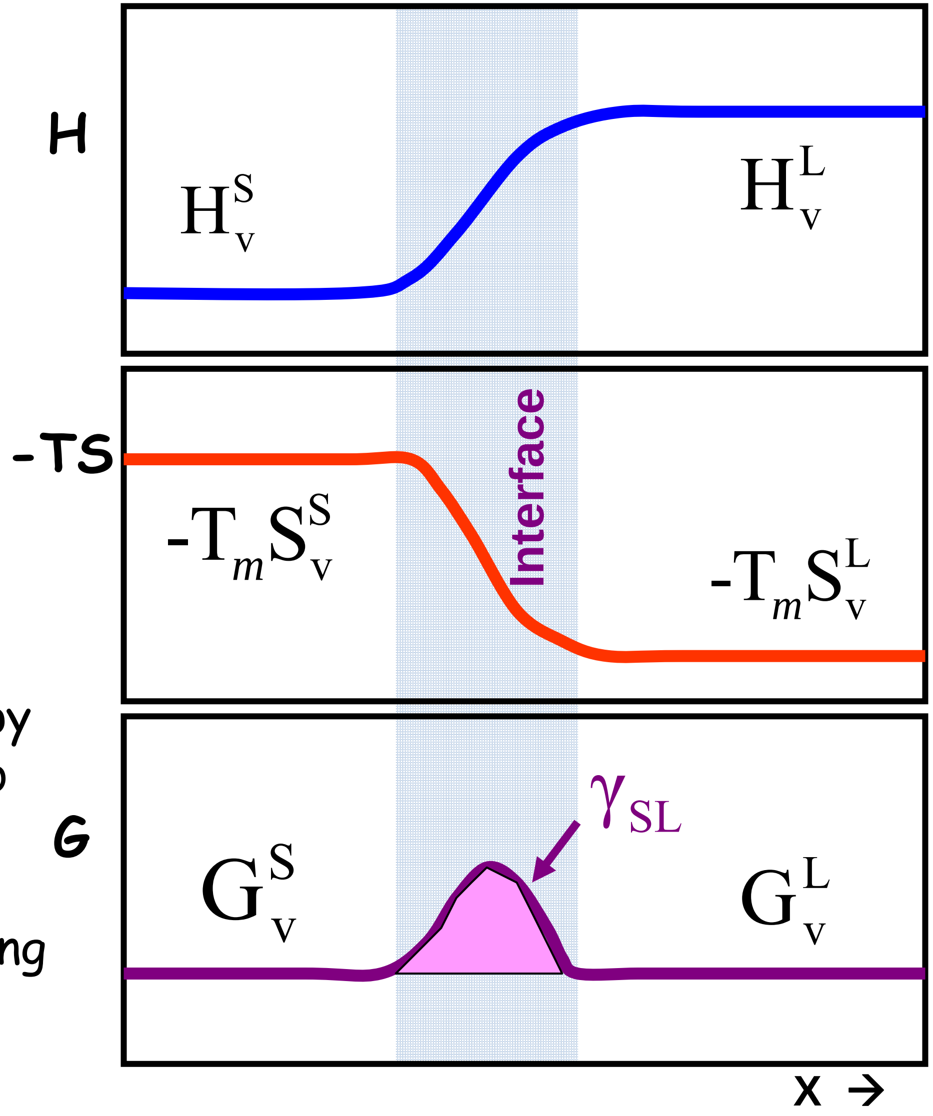
Interface of Solid/liquid



At the interface of solid/liquid, the inter-atomic bonds become gradually weakened, which increases the disorder. At equilibrium (e.g.,T_M), the high enthalpy of liquid is balanced by a high entropy so that both phases have the same free energy. In the interface, however, the balance is disturbed thereby resulting in an excess free energy of γ_{SL}.

$$G_v^L = H_v^L - TS_v^L$$

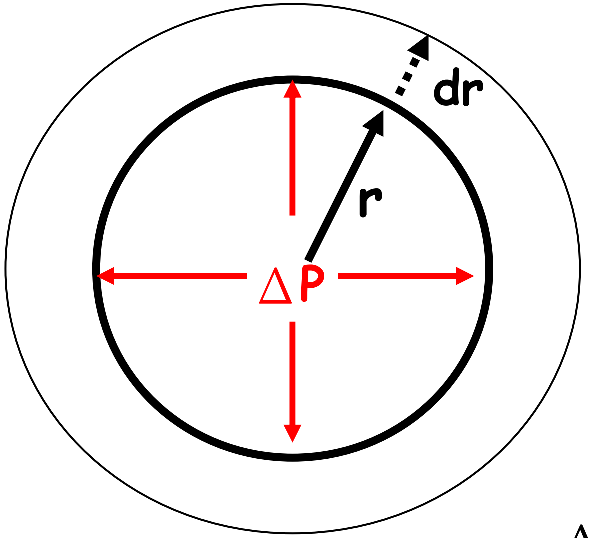
$$G_v^S = H_v^S - TS_v^S$$



Experimentally measured solid/liquid interfacial free energy

Metals	T_m(^oC)	γ_{SL} (mJm^{-2})
Sn	232	54
Pb	327	33
Al	660	93
Ag	961	126
Au	1063	132
Cu	1084	177
Mn	1220	206
Ni	1452	255
Co	1490	234
Fe	1536	204
Pd	1555	209
Pt	1769	240

Effect of Curvature



Work of expansion on the gas (ΔPdV)
=the reduction in surface energy (γdA)

$\gamma dA = \Delta P dV \rightarrow \Delta P = \gamma dA/dV$

$dV = 4\pi r^2 dr,\ dA = 8\pi r dr$

$\Delta P = \gamma(8\pi r dr)/4\pi r2dr$

$= 2\gamma/r$ (Young-LaPlace Eq.)

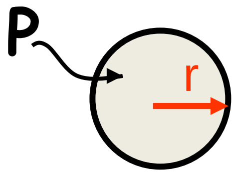
ΔP for water droplets of different radii

Radius (μm)	1000	100	1	0.01
ΔP (atm)	0.0014	0.0144	1.44	144

Stability of Droplet

Effects of Curvature

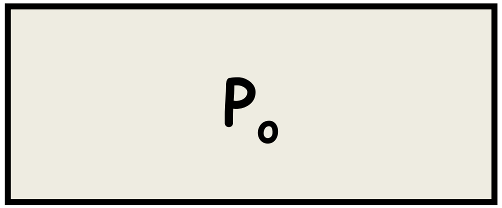
At constant T $dG = V_A^M dP$ V_A^M :molar volume of species A



$$\Delta G_A = G_A(P) - G_A^o(P_o) = G_A(r) - G_A^o(\infty)$$

$$= \int_{P_o}^{P} V_A^M dP = V_A^M (P - P_o)$$

$$= V_A^M \Delta P = V_A^M \left(\frac{2\gamma}{r}\right)$$

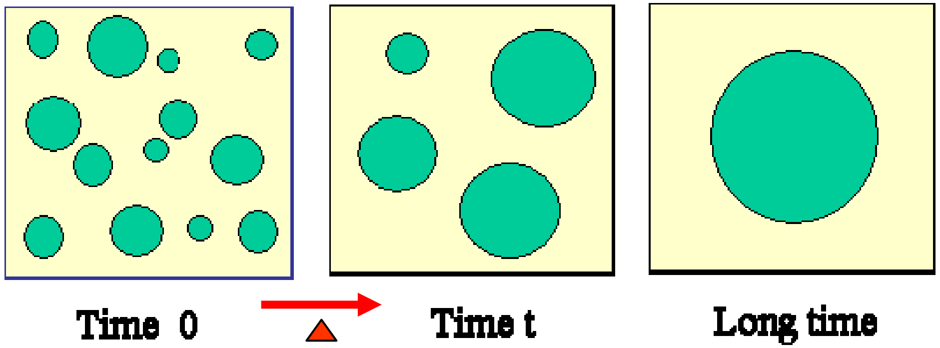


$$\mu_A(r) - \mu_A^o(\infty) = \frac{2\gamma V_A^M}{r}$$

$\mu_A^o(\infty)$: Chemical potential under a flat surface

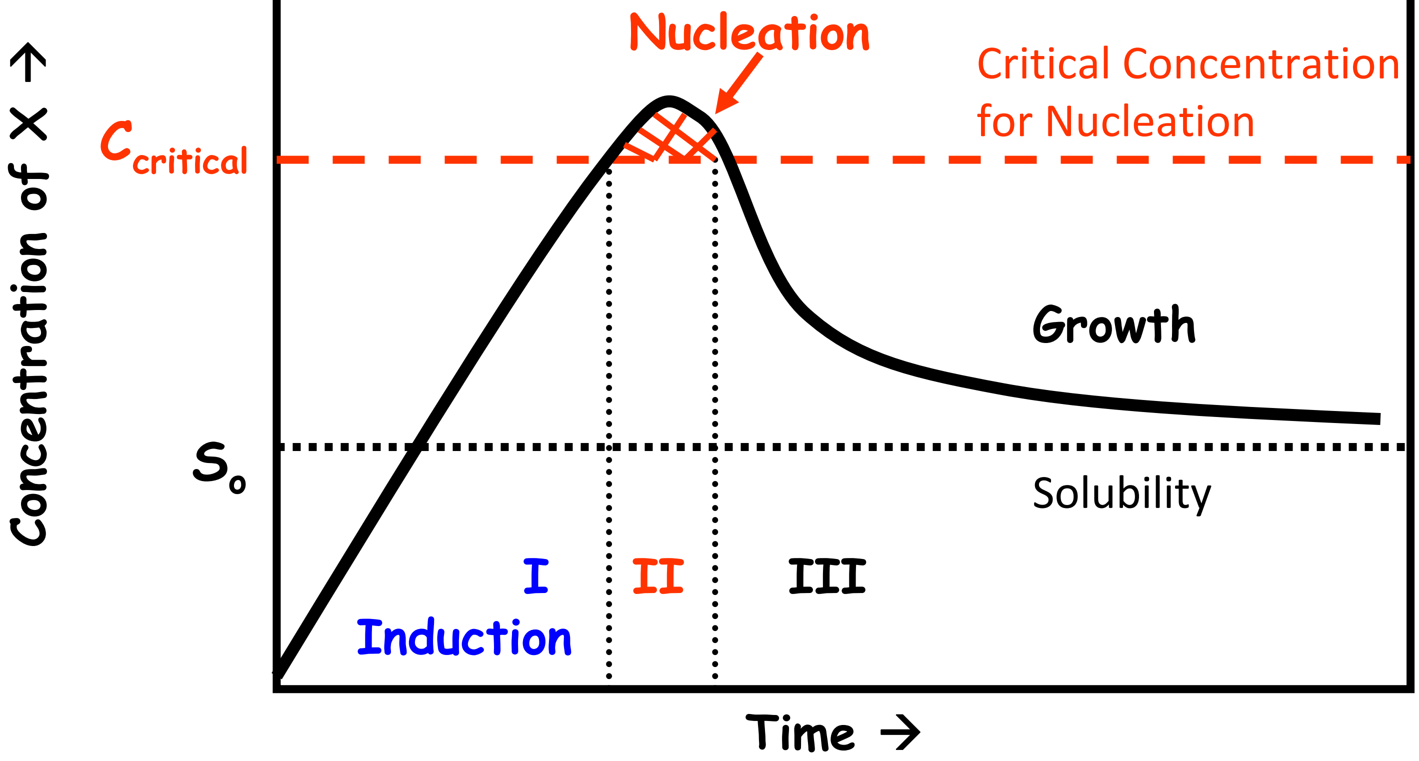
- Chemical potential increasing with decreasing particle size
- Smaller particles exhibiting higher solubility.

Ostwald Ripening (Coarsening): Larger particles grow at the expense of smaller particles



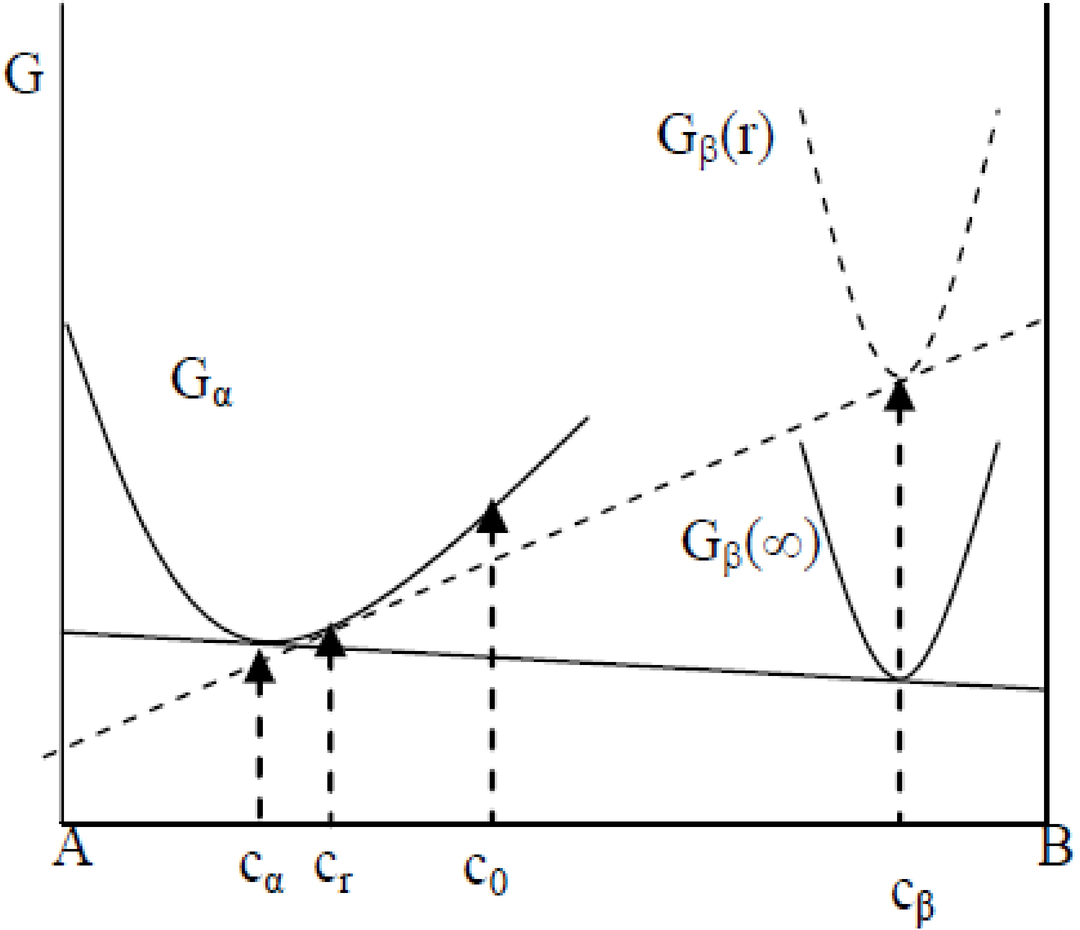
Precipitation from Homogeneous Solutions (PFHS)

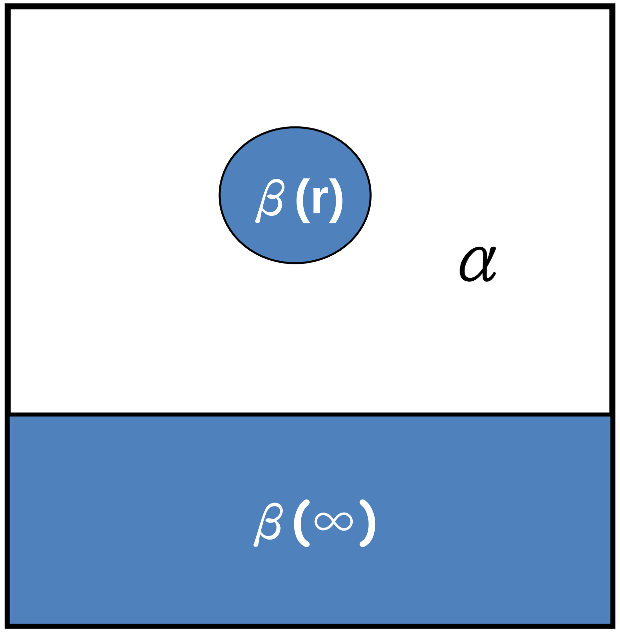
A + B ←→ X(s) + Y



- Approaches
    - Conductivity
    - Turbidity
    - Particle size measurement

Effect of Curvature





$$\mu_B^\alpha(C_r) = \mu_B^\beta(r) = \mu_B^\beta(C_\beta) + \frac{2\gamma_{\alpha\beta}V_B^M}{r}$$

$$= \mu_B^\beta(\infty) + \frac{2\gamma_{\alpha\beta}V_B^M}{r}$$

$$\mu_B^\alpha(C_\alpha) = \mu_B^\beta(C_\beta) \quad \text{or} \quad \mu_B^\alpha(\infty) = \mu_B^\beta(\infty)$$

Effects of Curvature on Solubility of Particles

$$C_r = C_\infty \exp\left(\frac{2\gamma_{\alpha\beta} V_B^M}{rRT}\right)$$

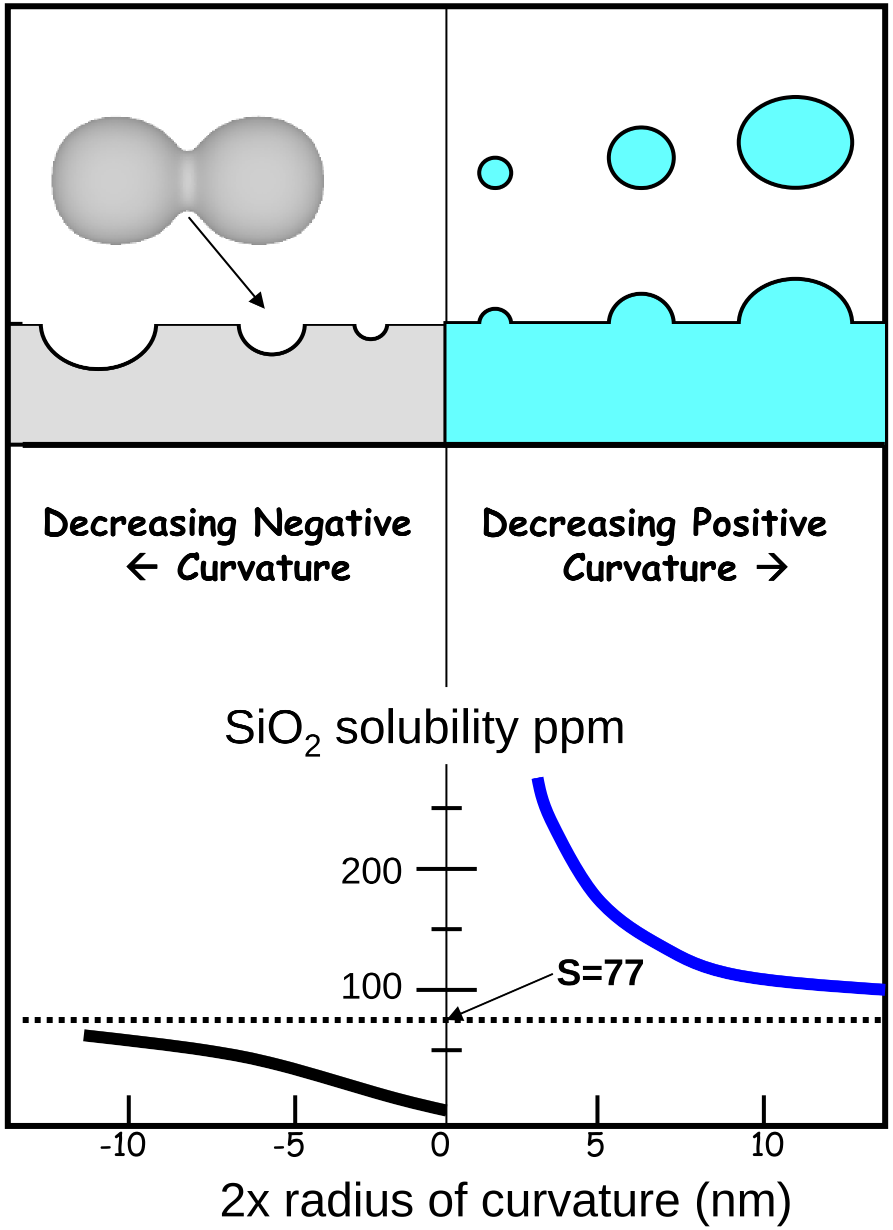
e.g., $\gamma_{\alpha\beta} = 0.5\ \mathrm{J/m^2}$; $V_B^M = 2.5\mathrm{x}10^{-5}\ \mathrm{m^3/mol}$; $T = 1000\mathrm{K}$

$$\text{if } r = 10^{-6}\,\mathrm{m}\ ; \frac{2\gamma_{\alpha\beta} V_B^M}{rRT} = 3\mathrm{x}10^{-3}$$

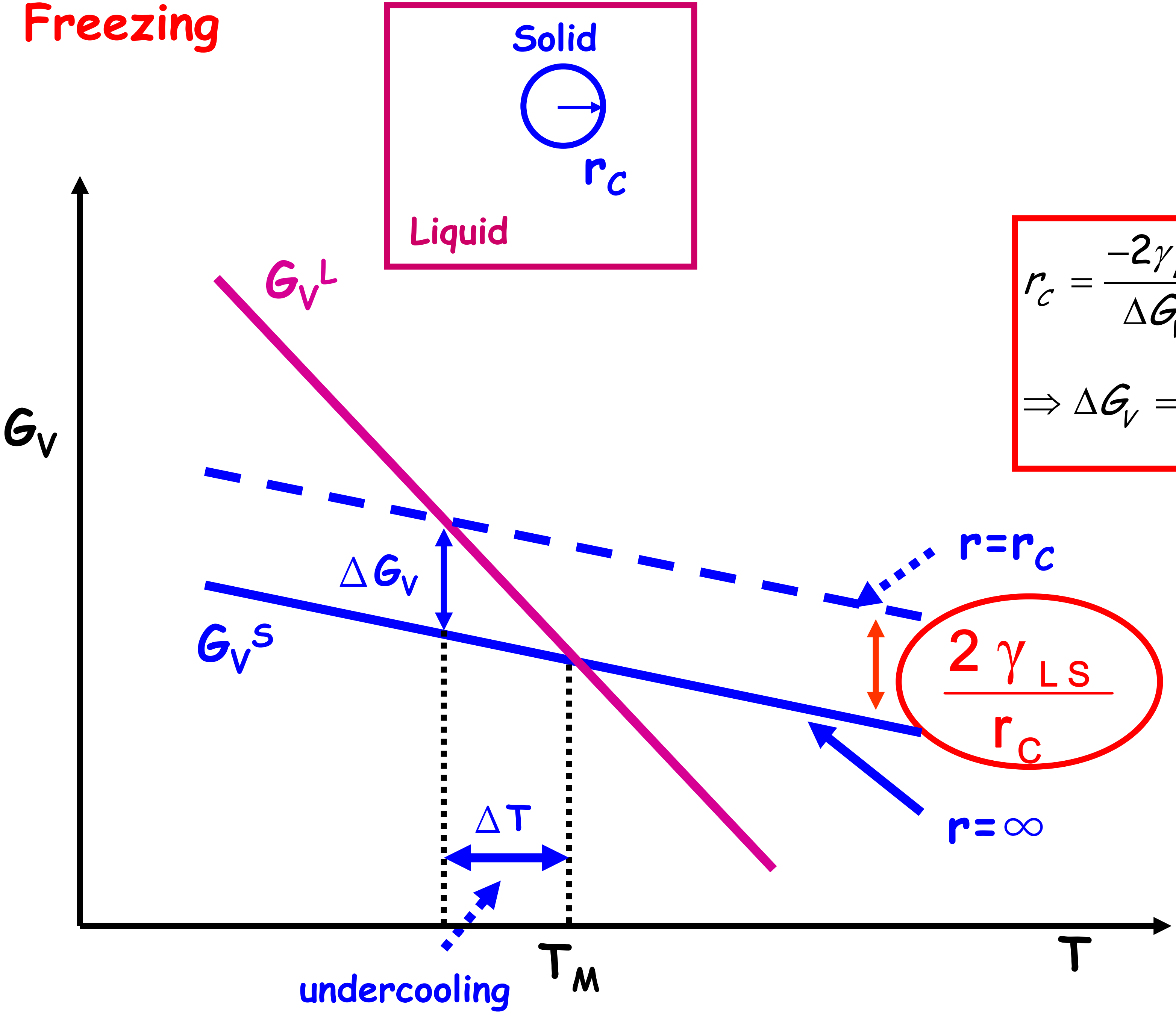
$$\Rightarrow \frac{C_r}{C_\infty} = \exp\left(\frac{2\gamma_{\alpha\beta} V_B^M}{rRT}\right) = 1.003$$

$$\text{if } r = 10^{-8}\,\mathrm{m}\ ; \frac{2\gamma_{\alpha\beta} V_B^M}{rRT} = 3\mathrm{x}10^{-1}$$

$$\Rightarrow \frac{C_r}{C_\infty} = \exp\left(\frac{2\gamma_{\alpha\beta} V_B^M}{rRT}\right) = 1.35$$



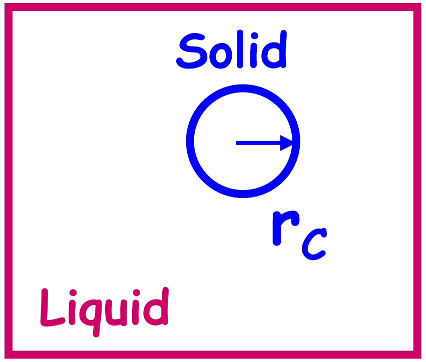
Freezing



$$r_c = \frac{-2\gamma_{LS}}{\Delta G_v}$$

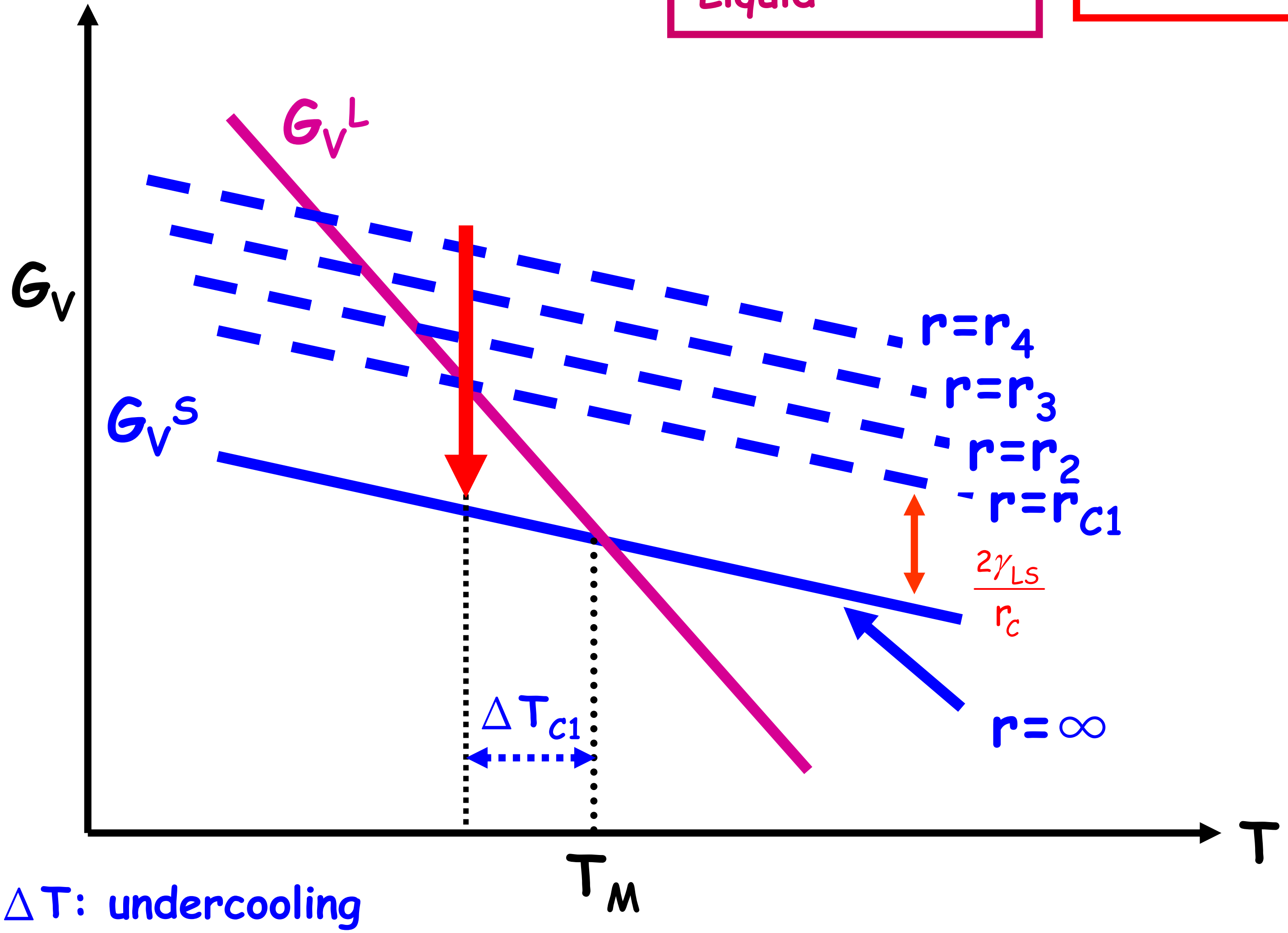
$$\Rightarrow \Delta G_v = \frac{-2\gamma_{LS}}{r_c}$$

Freezing



$$r_c = \frac{-2\gamma_{LS}}{\Delta G_V}$$

$$\Rightarrow \Delta G_V = \frac{-2\gamma_{LS}}{r_c}$$



ΔT: undercooling

Homogeneous Nucleation

e. g., Supersaturated Vapor→Liquid (V→L)

Assumption: A small liquid droplet has thermodynamic properties similar to bulk liquid

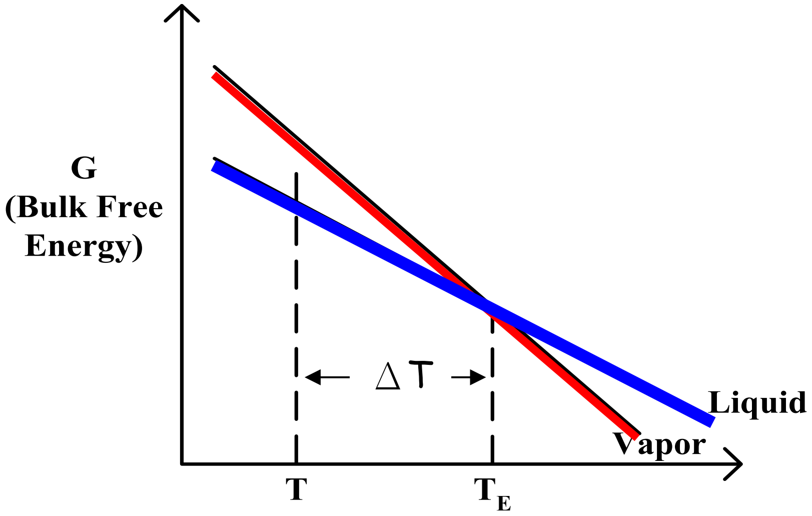
$$dG = -SdT + VdP + \gamma dA + \Sigma \mu_i dn_i$$

Isothermal transformation at constant pressure in one component system

$$dG = \gamma dA + \mu dn$$

Condensation

Vapor → Liquid



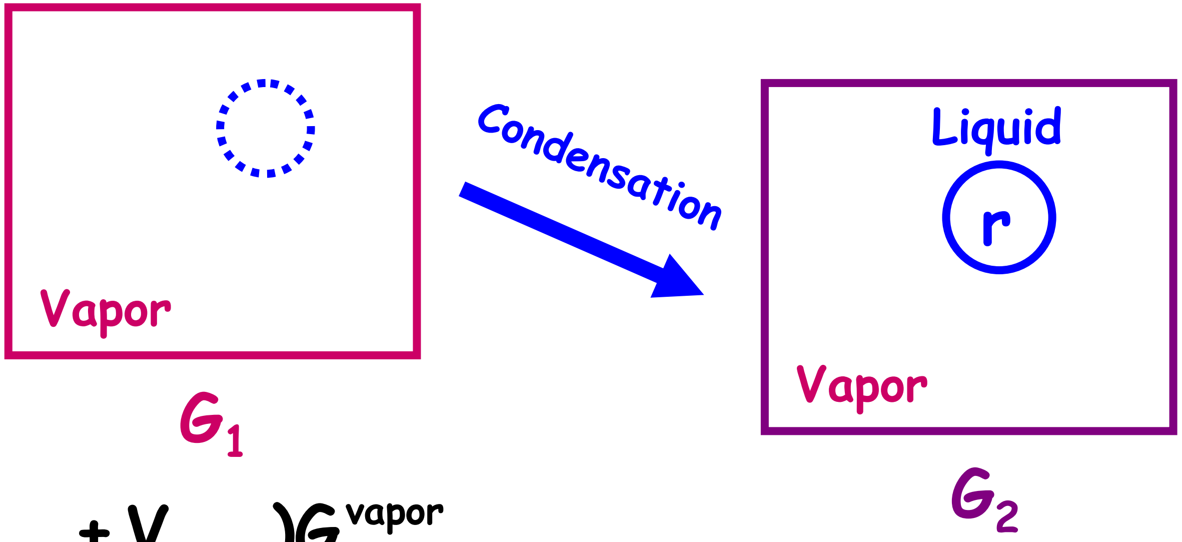
$$\Delta G_V = G_{liquid} - G_{vapor} = (-)\Delta G_{vap}$$

$T > T_E$ $G_{liq} > G_{vap}$ $\Delta G_v > 0$ *Liquid → Vapor*

$T < T_E$ $G_{liq} < G_{vap}$ $\Delta G_v < 0$ *Vapor → Liquid*

Vapor→Liquid

- **g^l and g^v : free energy per atom in the bulk phases**



$$G_1 = (V_{vapor} + V_{Liquid})G_V^{vapor}$$

$$G_2 = V_{vapor}G_V^{vapor} + V_{liquid}G_V^{liquid} + A_{LV}\gamma_{LV}$$

Total volume = $V_{vapor}+V_{Liquid}$

$$\boxed{\begin{aligned}\Delta G_r = G_2 - G_1 &= V_{liquid}(G_V^{liquid} - G_V^{vapor}) + A_{LV}\gamma_{LV} \\ &= \frac{4\pi r_{liquid}^3}{3}\Delta G_V + 4\pi r_{liquid}^2\gamma_{LV}\end{aligned}}$$

V:volume

Assuming that the liquid droplets are spherical and isotropic

$$\Delta G_r = \frac{4\pi r^3}{3V_l}(g^l - g^v) + 4\pi r^2 \gamma_{LV} \qquad (1)$$

$$= n(g^l - g^v) + \eta n^{2/3} \gamma_{LV}$$

g^l and g^v :
free energy per atom
in the liquid and vapor

where V_l: volume per atom in the liquid state, r: the radius of liquid droplet, n: number of atoms in the liquid droplet, and $\eta = (36\pi)^{1/3}(V_l)^{2/3}$

$$\frac{\partial \Delta G_r}{\partial r} = 0 = \frac{4\pi r^2}{V_l}(g^l - g^v) + 8\pi r \gamma_{LV}$$

$$r_C = (-)\frac{2\gamma_{LV} V_l}{g^l - g^v} \qquad (2)$$

Replacing eq. (2) into eq. (1)

$$\Delta G_C = \frac{16\pi \gamma_{LV}^3 V_l^2}{3(g^l - g^v)^2} \qquad (3)$$

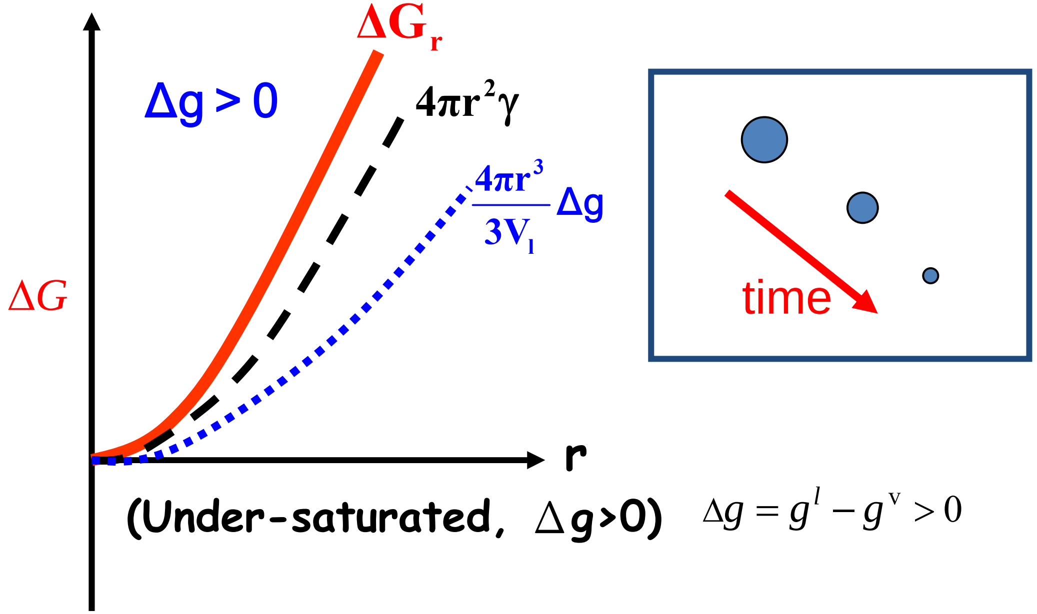
Replacing eq. (2) into eq. (3)

$$\Delta G_C = \frac{4\pi r^2 \gamma_{LV}}{3} = \frac{1}{3}(4\pi r^2 \gamma_{LV})$$

Critical free energy =1/3(total surface energy)

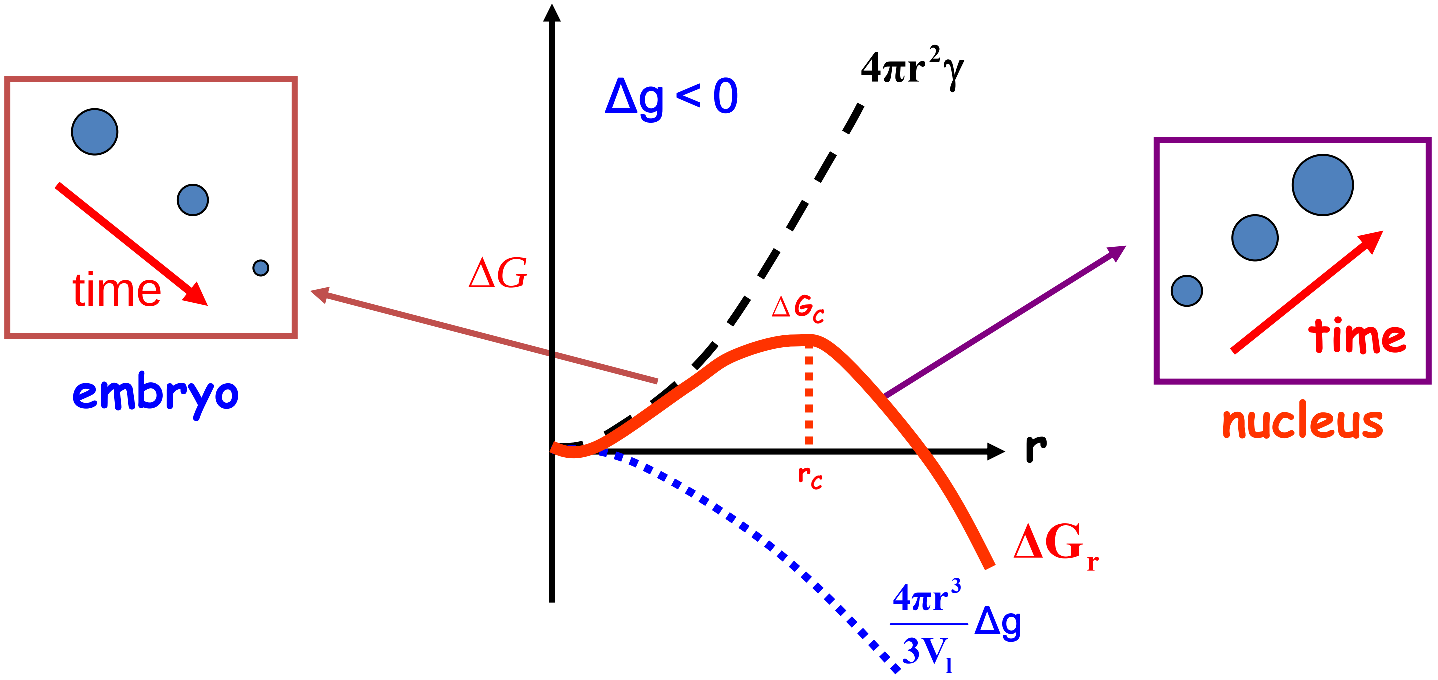
$$\Delta G = VdP = g^l - g^v$$

ideal gas: $V = \frac{RT}{P}$



(Under-saturated, Δg>0)

$\Delta g = g^l - g^v > 0$



(Supersaturated, Δg<0)

$\Delta g = g^l - g^v < 0$

$$\Delta G = n(g^l - g^v) + \eta n^{2/3} \gamma_{LV}$$

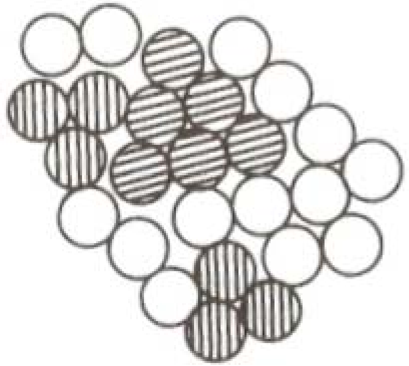
$$\left(\frac{\partial \Delta G}{\partial n}\right)_{n_c} = 0 \Rightarrow n_c = (-)\left(\frac{g^l - g^v}{\frac{2}{3}\gamma_{LV}\eta}\right)^{-3}$$

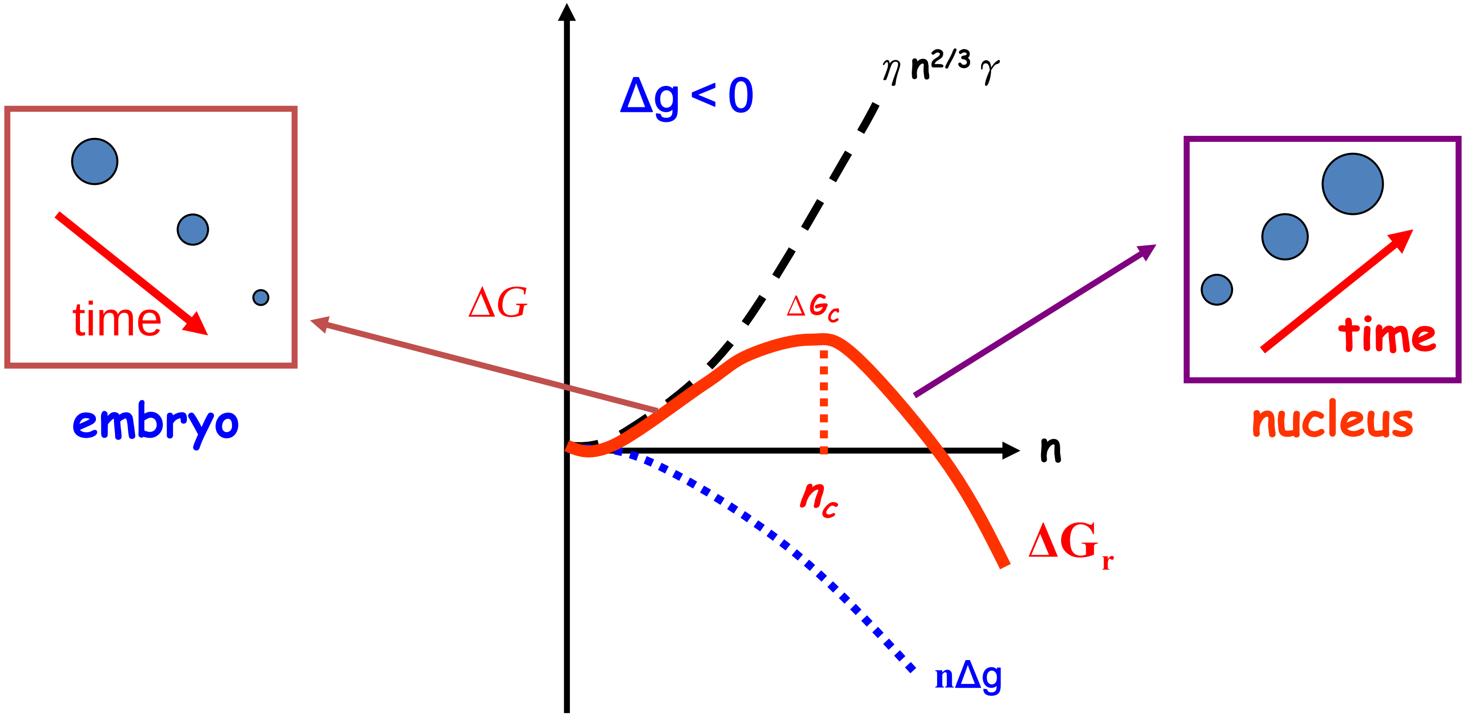
$$\eta = (36\pi)^{1/3}(V_l)^{2/3}$$

n_c: number of atoms in the critical nucleus

$$n_c = -\left(\frac{2\eta\,\gamma_{LV}}{3(g^l - g^v)}\right)^3 = -\frac{32\pi\,\gamma_{LV}^3 V_l^2}{3(g^l - g^v)^3}$$

$$\Delta G_c = \frac{4}{27}\frac{\gamma_{LV}^3 \eta^3}{(g^l - g^v)^2}$$



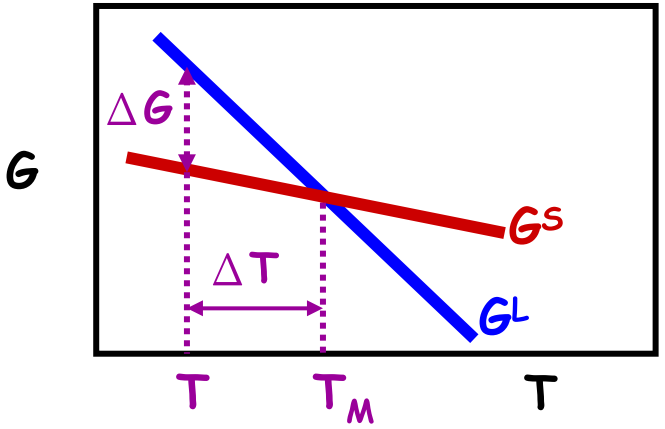


(Supersaturated, $\Delta g<0$)

$$\Delta g = g^l - g^v < 0$$

Freezing

L→ S



$$\Delta G = \Delta H - T\Delta S$$

$$\text{At}\quad T_m \rightarrow \Delta G = \Delta H_m - T_m \Delta S = 0$$

$$\Delta S = \frac{\Delta H_m}{T_m}$$

$$\text{At}\quad T \rightarrow \Delta G = \Delta H - T\Delta S = G^S - G^L$$

If ΔT is small and if ΔH and ΔS do not change significantly with temperature

$$\Delta G = \Delta H - T\frac{\Delta H_m}{T_m} \quad (if\ \Delta H \approx \Delta H_m)$$

$$\Delta G = \frac{\Delta H_m (T_m - T)}{T_m} = \frac{\Delta H_m \Delta T}{T_m} = \frac{T_m \Delta S \Delta T}{T_m} = \Delta S \Delta T$$

$$\Delta S < 0 \because L \rightarrow S$$

$$\Delta T > 0 \Rightarrow \Delta G < 0$$

Freezing or Solidification

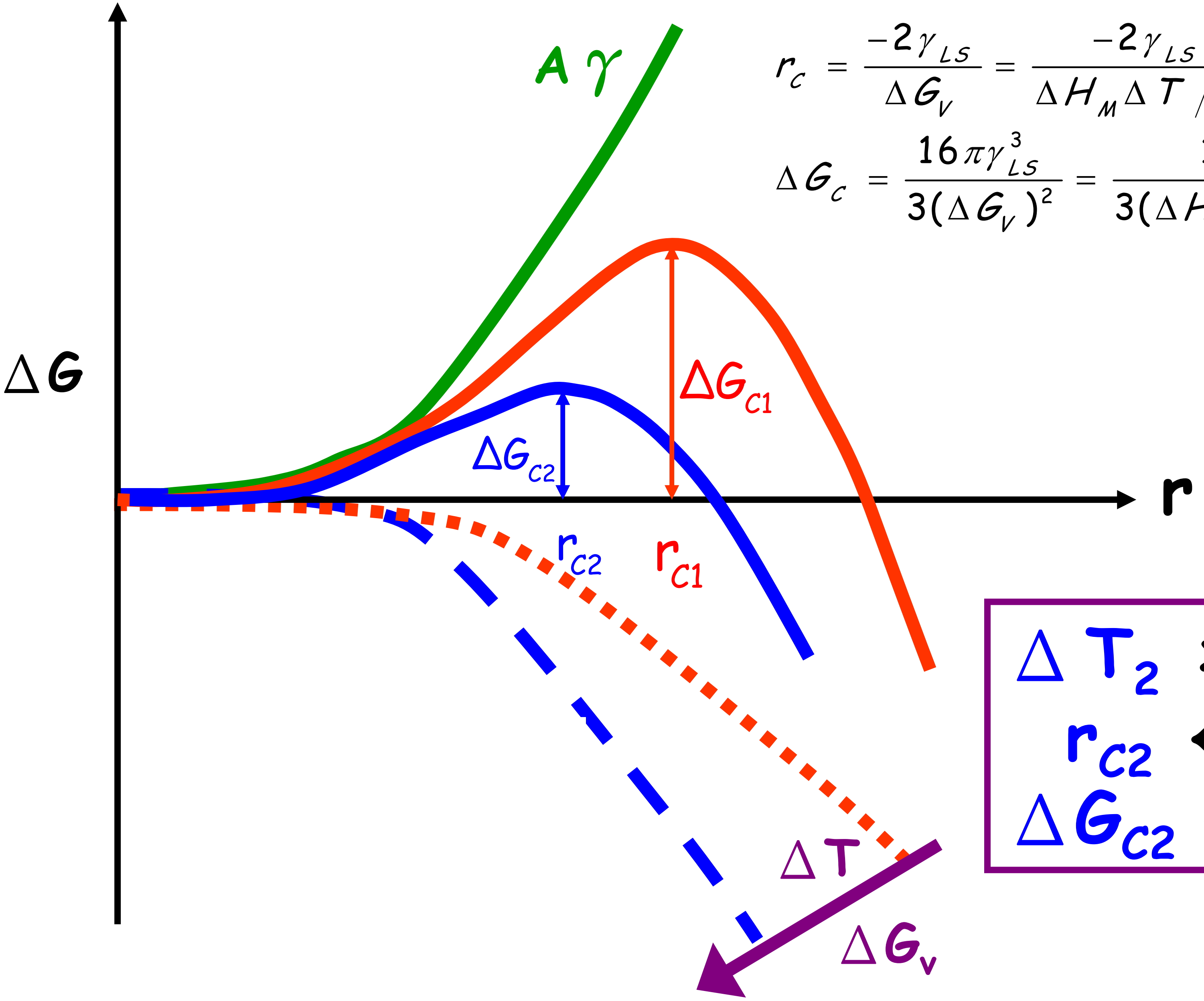
$$r_C = \frac{-2\gamma_{LS}}{\Delta G_V} = \frac{-2\gamma_{LS}}{\Delta H_M \Delta T / T_M}$$

$$\Delta G_C = \frac{16\pi\gamma_{LS}^3}{3(\Delta G_V)^2} = \frac{16\pi\gamma_{LS}^3}{3(\Delta H_M \Delta T / T_M)^2}$$

$$\Delta G_C = \frac{1}{3}\left(4\pi r_C^2 \gamma_{LS}\right)$$

As $T = T_M$, $\Delta T = 0$, then $r_C \longrightarrow \infty$ and $\Delta G_C \longrightarrow \infty$, barrier for nucleation is infinite at T_M, implying that *supercooling is needed for Homogeneous Nucleation.* For example, a liquid nickel can be supercooled by 250K below T_M (1453°C) without solidification, or pure water can be supercooled to as low as -42°C without being frozen into ice.

Effect of Undercooling



$$r_c = \frac{-2\gamma_{LS}}{\Delta G_V} = \frac{-2\gamma_{LS}}{\Delta H_M \Delta T / T_M}$$

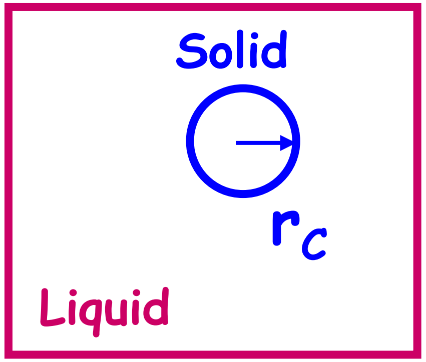
$$\Delta G_c = \frac{16\pi\gamma_{LS}^3}{3(\Delta G_V)^2} = \frac{16\pi\gamma_{LS}^3}{3(\Delta H_M \Delta T / T_M)^2}$$

$\Delta T_2 > \Delta T_1$

$r_{C2} < r_{C1}$

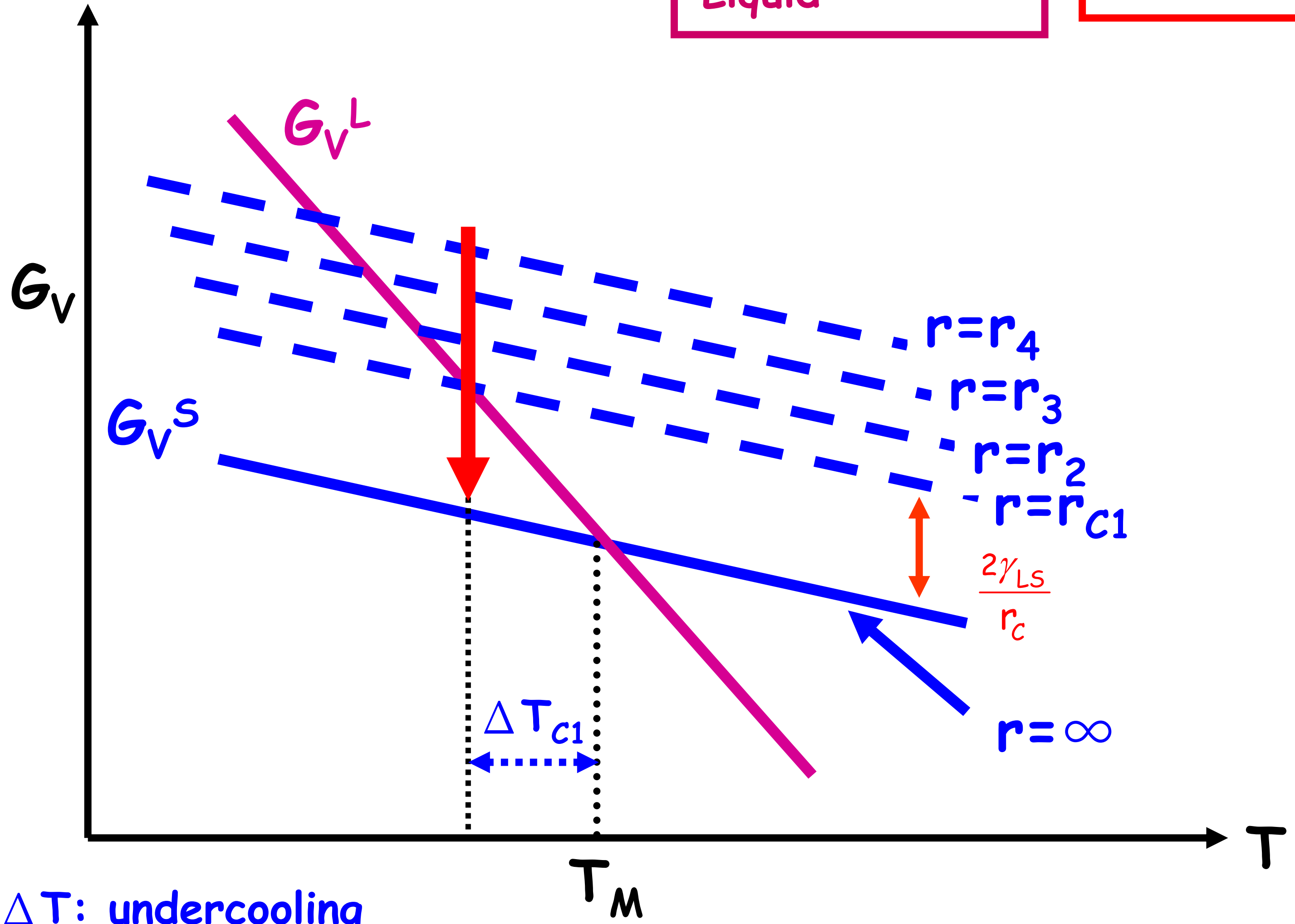
$\Delta G_{C2} < \Delta G_{C1}$

Freezing



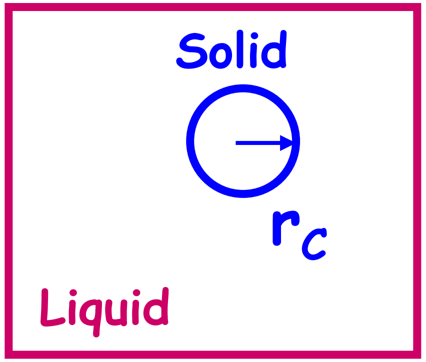
$$r_c = \frac{-2\gamma_{LS}}{\Delta G_V}$$

$$\Rightarrow \Delta G_V = \frac{-2\gamma_{LS}}{r_c}$$



ΔT: undercooling

Freezing

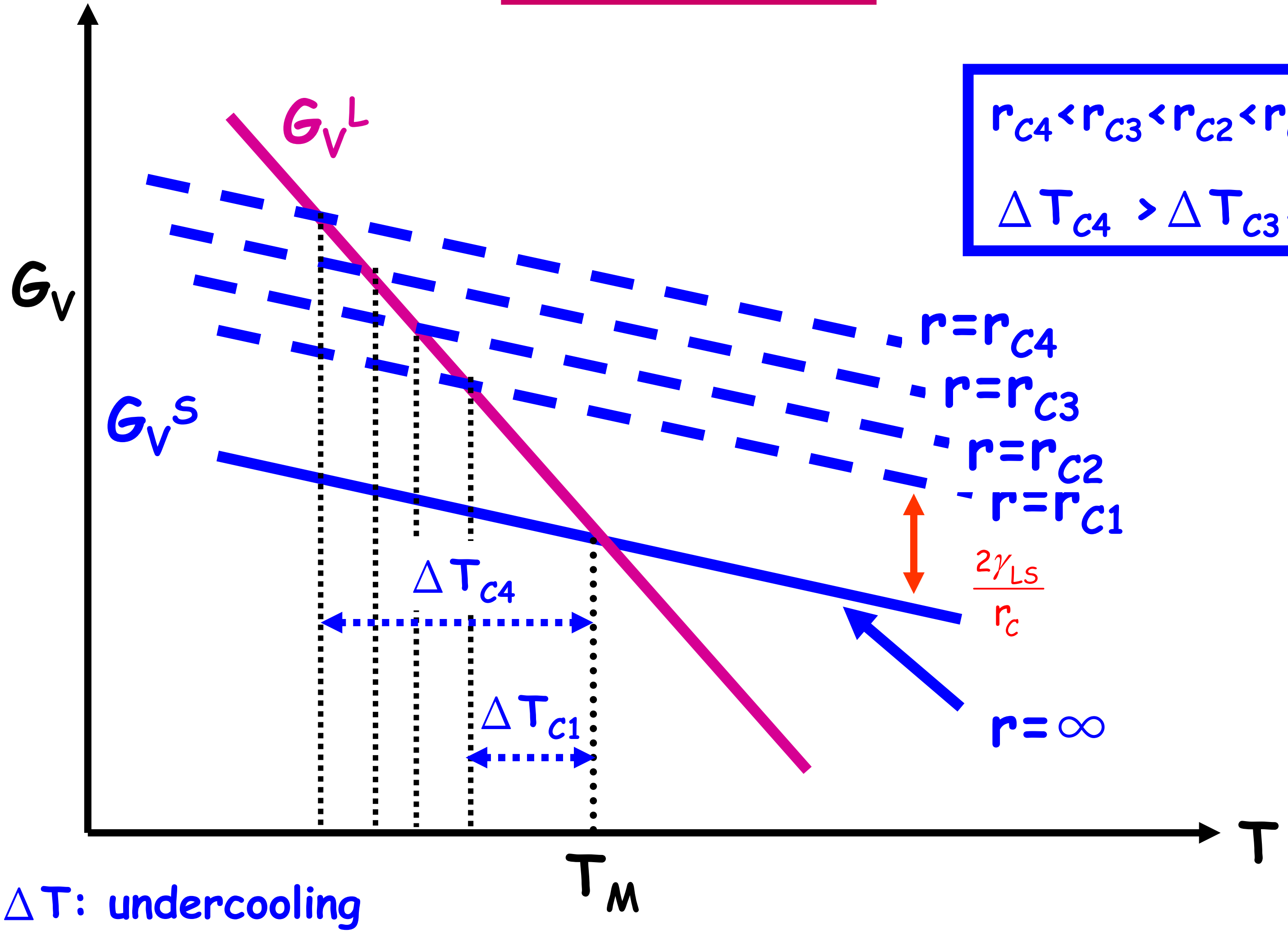


$$r_C = \frac{-2\gamma_{LS}}{\Delta G_V}$$

$$\Rightarrow \Delta G_V = \frac{-2\gamma_{LS}}{r_C}$$

$r_{C4} < r_{C3} < r_{C2} < r_{C1}$

$\Delta T_{C4} > \Delta T_{C3} > \Delta T_{C2} > \Delta T_{C1}$



ΔT: undercooling

Undercooling (ΔT) Required for Homogeneous Nucleation

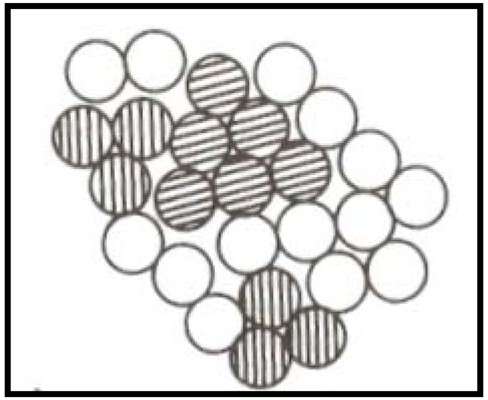
Size Distribution of Nuclei

$$\frac{n_r}{n_0} = \exp\left(-\frac{\Delta G_r}{RT}\right)$$

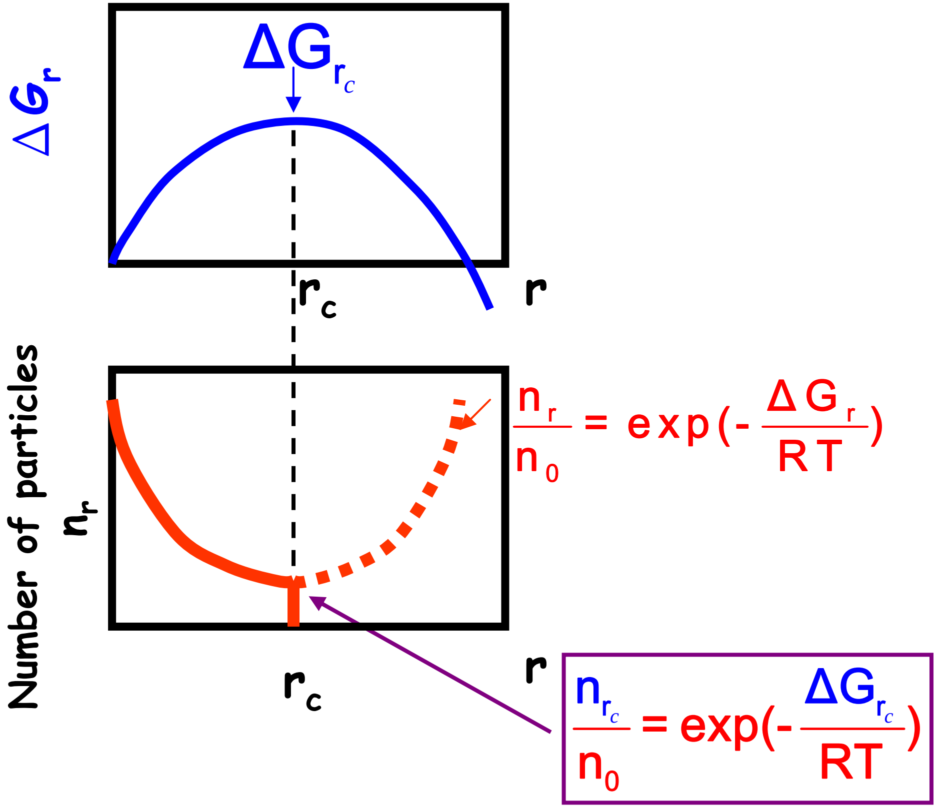
n_0: number of clusters having atomic radius

n_r: number of clusters having radius of r

ΔG_r: formation free energy of clusters with a radius of r



Clusters having a radius of r



$$\frac{n_r}{n_0} = \exp\left(-\frac{\Delta G_r}{RT}\right)$$

$$\boxed{\frac{n_{r_c}}{n_0} = \exp\left(-\frac{\Delta G_{r_c}}{RT}\right)}$$

Example: Ni T_m=1725K, $\Delta H_m/T_m$=-10 J mol^{-1}K^{-1}, γ_{LS}=0.25 J/m^2,
V (Molar volume) = 7 cm^3/mol

$$T = T_m \rightarrow \Delta G_V = 0$$

$$\Delta G_r = 4\pi r^2 \gamma_{LS}$$

$$r = 0.7nm \Rightarrow n_r = ?$$

$$\Delta G_r = 4\pi(7x10^{-10})^2(0.25)$$

$$= 1.54x10^{-18}\,J$$

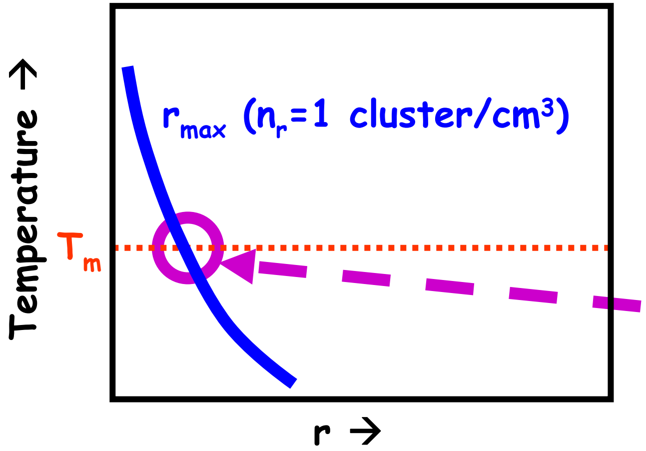
$$\boxed{n_o = \frac{6x10^{23}\ \text{atoms/mol}}{7\ \ \text{cm}^3\text{/mol}} = 8.6x10^{22}\ \text{atoms/cm}^3}$$

$$\frac{n_r}{n_0} = \exp(-\frac{\Delta G_r}{RT})$$

$$n_r = n_0\exp(-\frac{\Delta G_r}{RT})$$

$$= 8.6x10^{22}\exp(-\frac{1.54x10^{-18}}{1.38x10^{-23}\cdot 1725})$$

$$= 7.3x10^{-6}\ \text{clusters / cm}^3$$



Maximum cluster radius r_{max}
as a function of temperature

$T=T_m$

r (nm)	n_r (clusters/cm^3)
0.5	$4x10^9$
0.6	$2x10^2$
0.7	$7.3x10^{-6}$
0.8	$1.8x10^{-14}$
0.9	$4.4x10^{-35}$

Undercooling $\Delta T = 10K$

$$r_C = \frac{-2\gamma_{LS}}{\Delta G_V} = \frac{-2\gamma_{LS}}{\frac{\Delta H_M \Delta T}{T_M}\frac{1}{\overline{V}}} = \frac{-2\cdot 0.25}{-10\cdot 10\cdot \frac{1}{7x10^{-6}}}$$

$$= 35 \quad nm$$

$$\Delta G_C = \frac{16\pi\gamma_{LS}^3}{3(\Delta G_V)^2} = \frac{16\pi\gamma_{LS}^3}{3(\frac{\Delta H_M \Delta T}{T_M}\frac{1}{\overline{V}})^2}$$

$$= 1.3x10^{-15} J$$

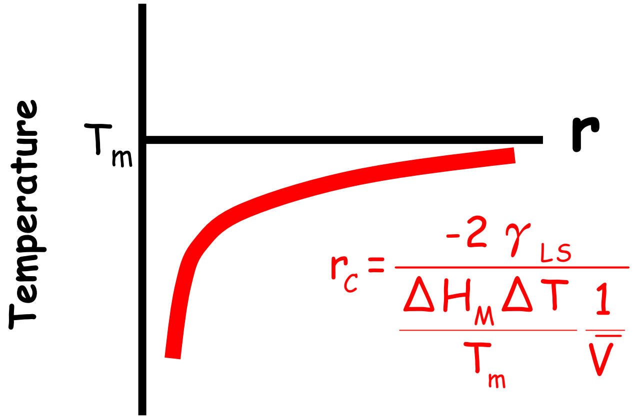
$$n_{r_C} = n_0 \exp(-\frac{\Delta G_C}{RT})$$

← Number of clusters having the critical radius of r_C

$$= 8.6x10^{22} \exp(\frac{-1.3x10^{-15}}{1.38x10^{-23}\cdot 1715})$$

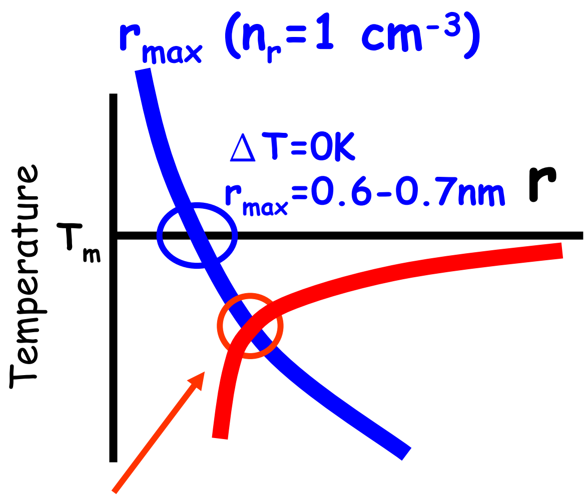
$$= 10^{-24000} cm^{-3}$$

Too low concentration→ Homogeneous nucleation does not take place



$$r_c = \frac{-2\gamma_{LS}}{\frac{\Delta H_M \Delta T}{T_m}\frac{1}{V}}$$

ΔT (K)	r_c (nm)	ΔG (J)	$n(r_c)$ (cm^{-3})
10	35.00	1.3×10^{-15}	10^{-24000}
100	3.50	1.3×10^{-17}	10^{-283}
300	1.17	1.4×10^{-18}	7×10^{-10}
325	1.07	1.2×10^{-18}	1.4×10^{-5}
340	1.03	1.1×10^{-18}	2.8×10^{-3}
			1
400	0.90	8.2×10^{-19}	3.7×10^{3}



ΔT=340-400K

r_c=0.9-1.03nm

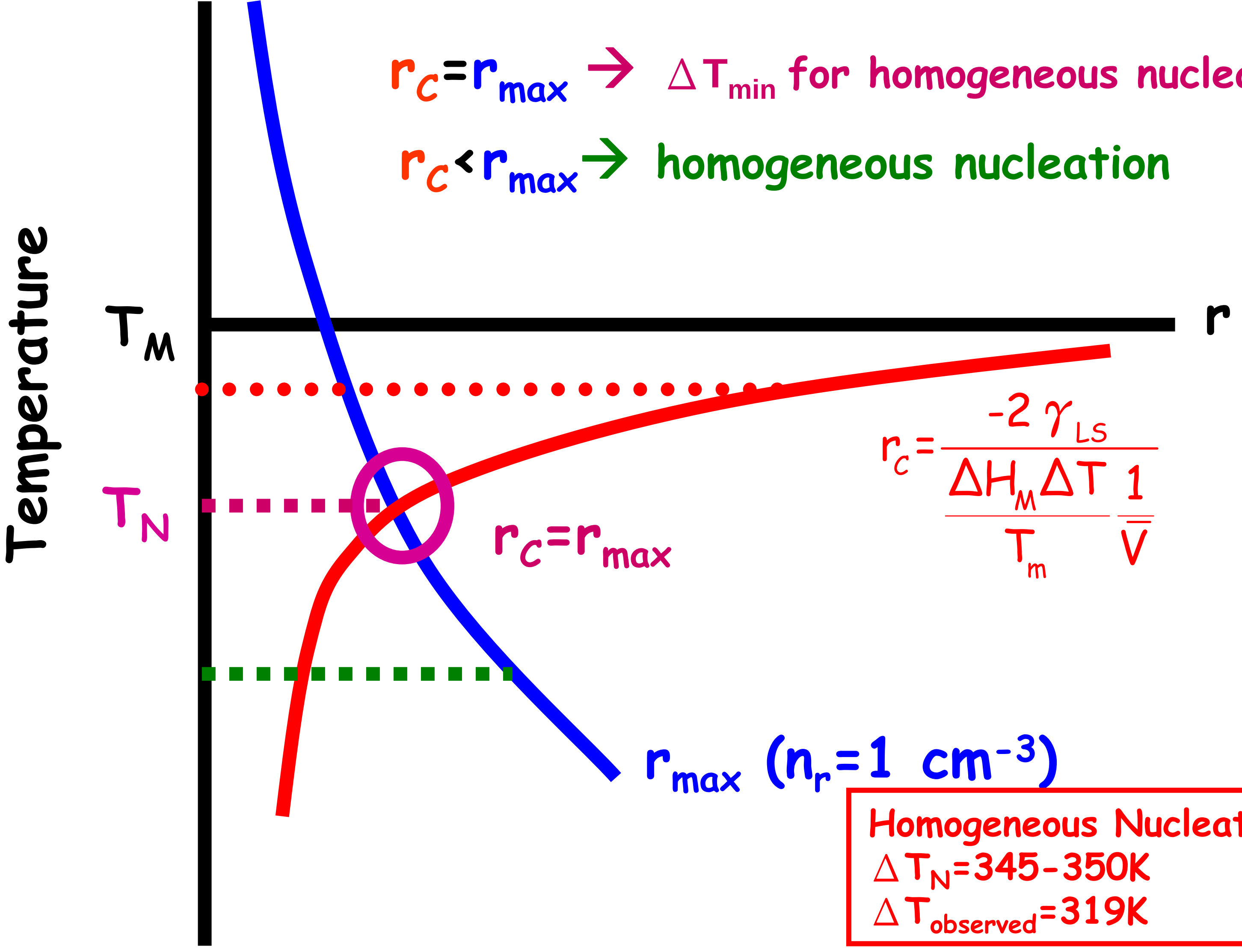
$$r_c = \frac{-2\gamma_{LS}}{\frac{\Delta H_M \Delta T}{T_m}\frac{1}{V}}$$

Undercooling required for homogeneous nucleation

$r_C > r_{max}$ → No homogeneous nucleation

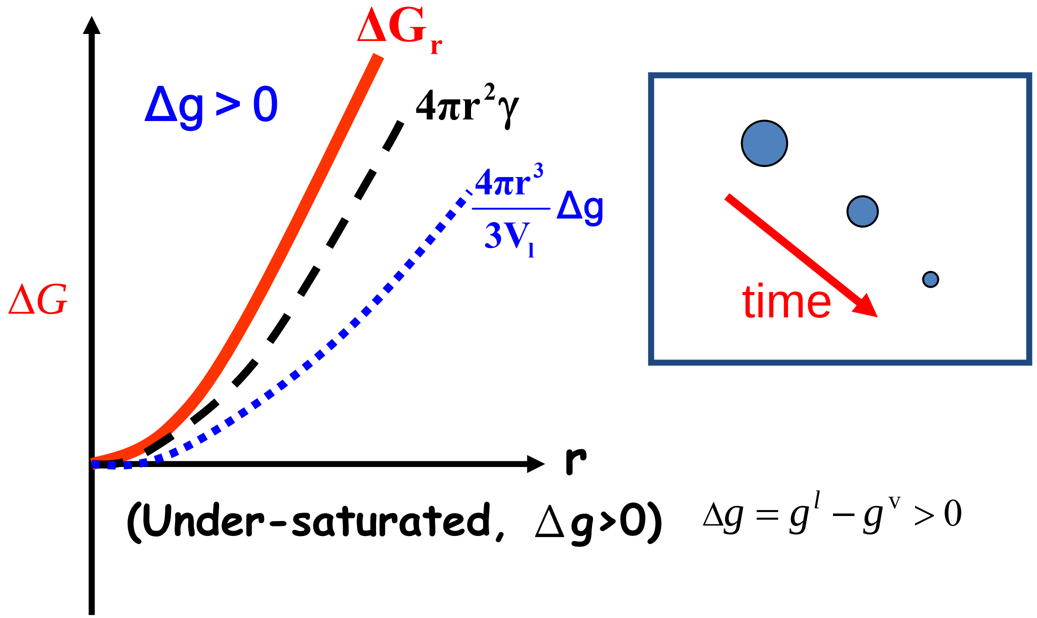
$r_C = r_{max}$ → ΔT_{min} for homogeneous nucleation

$r_C < r_{max}$ → homogeneous nucleation

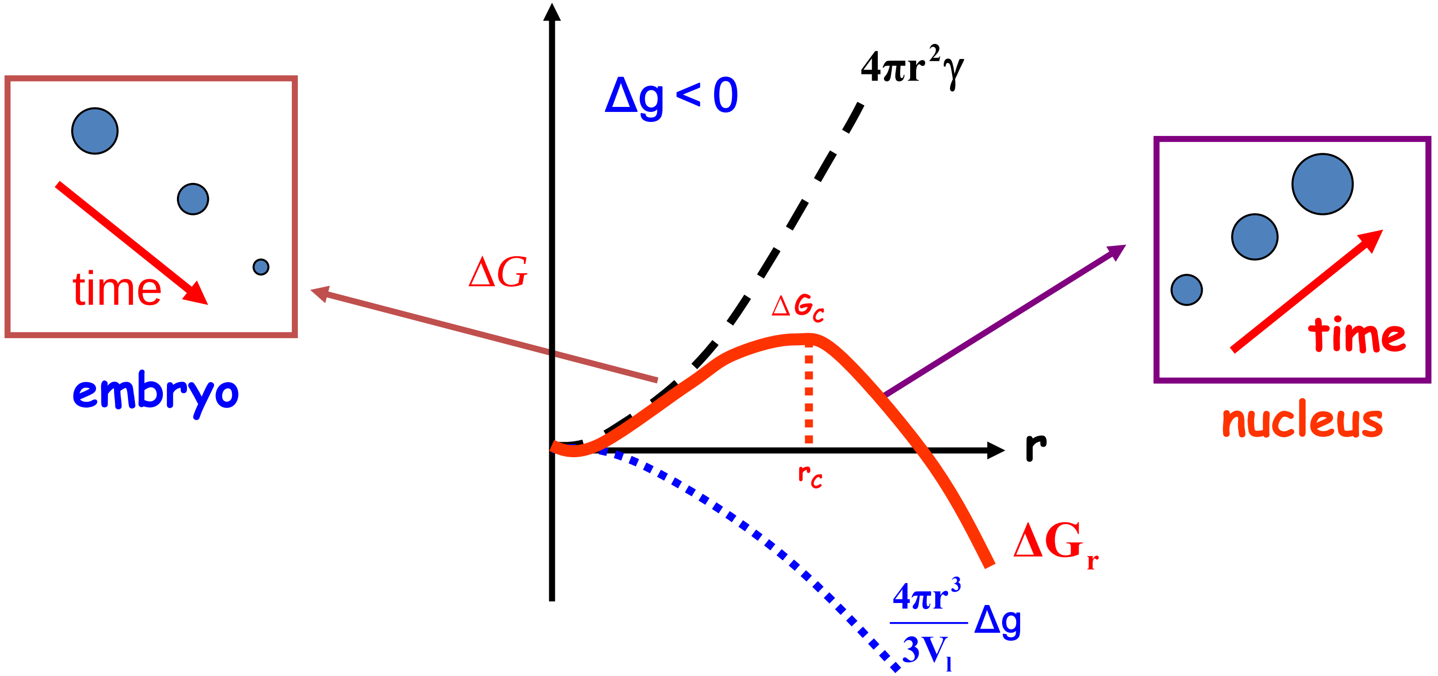


$$r_C = \frac{-2\gamma_{LS}}{\frac{\Delta H_M \Delta T}{T_m}\frac{1}{\overline{V}}}$$

Homogeneous Nucleation for Ni
$\Delta T_N = 345\text{-}350K$
$\Delta T_{observed} = 319K$



(Under-saturated, $\Delta g>0$) $\Delta g = g^l - g^v > 0$



(Supersaturated, $\Delta g<0$) $\Delta g = g^l - g^v < 0$

Homogeneous Nucleation Rate $I = q_0 O_c Z_c$

I = nucleation rate
q_o = jump frequency
O_c = area of critical nucleus
Z_c = number of critical nucleus

Volmer Theory

Assumptions

(1) Bimolecular process

$$\begin{aligned} &Q_1 + Q_1 \rightarrow Q_2 \\ &Q_2 + Q_1 \rightarrow Q_3 \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &Q_n + Q_1 \rightarrow Q_{n+1} \end{aligned}$$

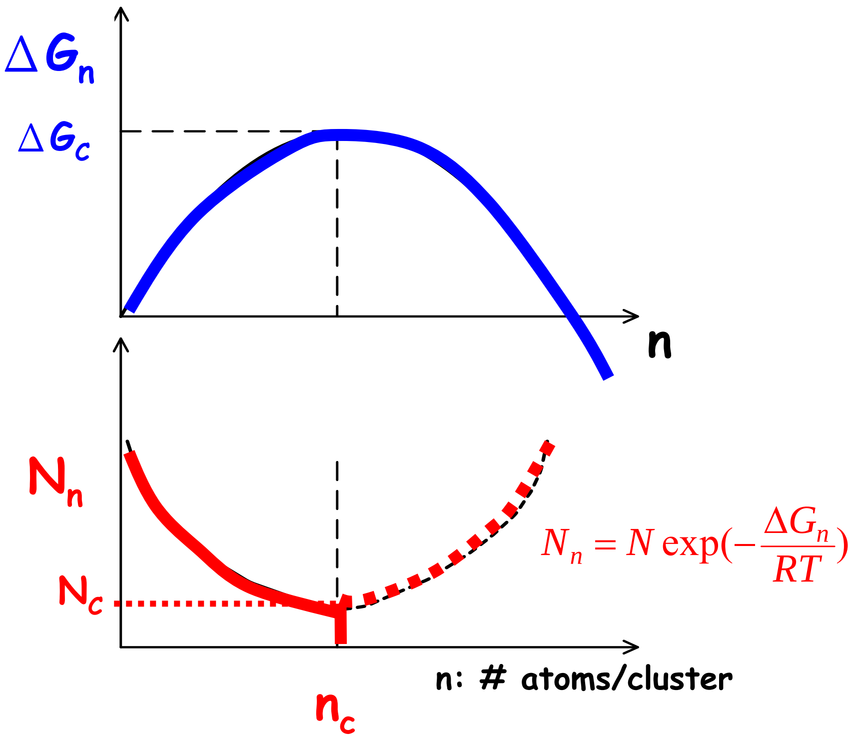
(2) Neglect the reverse reaction between embryos (irreversible process)

Note: If reversible process is considered, I=0

$$\because I = q_n O_n Z_n - q_{n+1} O_{n+1} Z_{n+1}$$

$$\text{Since } Z_n = Z_{n+1} \text{ (equilibrium distribution)}, I = 0.$$

(3) Equilibrium embryo size distribution



$$N_n = N\exp(-\frac{\Delta G_n}{RT})$$

:the statistical distribution function
for embryos containing n atoms

N: number of atoms in the vapor phase

ΔG_n:the standard free energy change resulting
from the conversion of vapor into embryos

$n < n_c \quad Z_n = N_n = N\exp(-\frac{\Delta G_n}{RT})$

$n > n_c \quad Z_n = 0$

$n = n_c \quad Z_c = N\exp(-\frac{\Delta G_c}{RT})$

Vapor→Liquid

$$I = q_0 O_c Z_c$$

$$= \frac{\alpha P}{\sqrt{2\pi MkT}} O_c N\exp(-\frac{\Delta G_c}{RT})$$

I: nucleation rate (sec^{-1})
q_o: probability per unit time
per unit area of capturing
one vapor atom
O_C: area of critical nucleus
Z_C: number of critical nucleus

(4) N_{C+1} is removed from the assembly

$$\Delta G_c = \frac{16\pi \gamma^3 (V_l)^2}{3(g^l - g^v)^2} = \frac{16\pi \gamma^3 (V_l)^2}{3(kT)^2[\ln(i)]^2}$$

$$i = \frac{P}{P_e} : \text{supersaturation}$$

$$j = i - 1 = \frac{P - P_e}{P_e} : \text{degree of supersaturation}$$

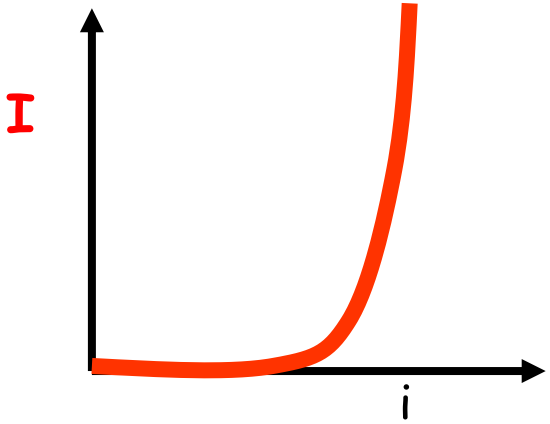
$$j = i - 1 \approx \ln(i)$$

$$\because \Delta G = VdP = g^l - g^v$$

$$ideal\ gas \Rightarrow V = \frac{kT}{P}$$

$$g^l - g^v = -kT \ln \frac{P}{P_e} = -\frac{2\gamma V_l}{r}$$

$$\therefore I = \frac{\alpha P}{\sqrt{2\pi MkT}} O_c N \exp\left(-\frac{16\pi \gamma^3 (v_l)^2}{3(kT)^3[\ln(i)]^2}\right)$$



Becker-Doring Theory

Assumptions

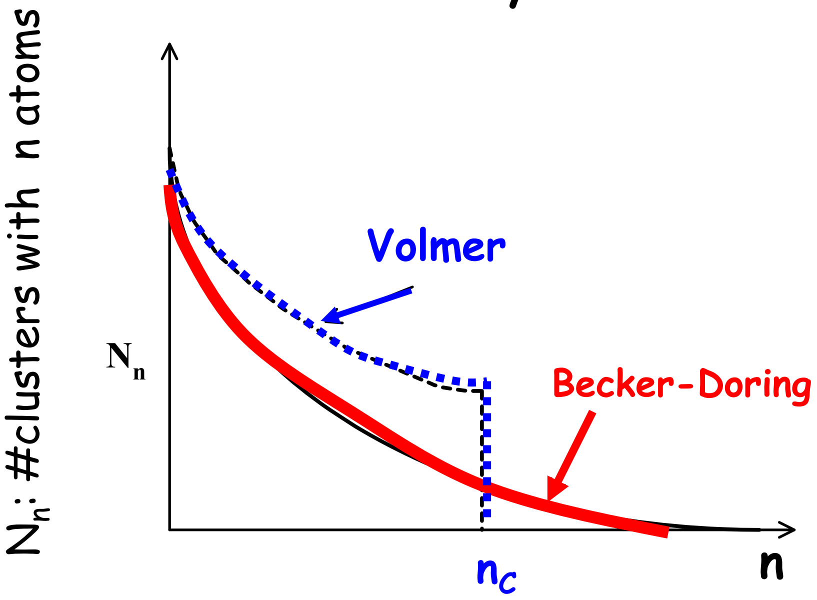
(1) Bimolecular process

(2) Reverse reaction considered

$$I = q_0 O_C Z_C - q_0 O_{C+1} Z_{C+1} \neq 0$$

(3) Embryo distribution
-steady state

(The number of embryos at a given size should remain effectively constant although embryos might grow or shrink in size (the probability for either direction is equal))



(n: # atoms/cluster)

$N_C \equiv N_{n_C}$

$$n \rightarrow 0 \quad Z_n \rightarrow N_n$$

$$n \rightarrow \infty \quad Z_n \rightarrow 0$$

$$I = q_0 O_C \cdot \left(\frac{\Delta G_C}{3\pi kT}\right)^{1/2} N_C^{-1} \cdot N \exp\left(-\frac{\Delta G_C}{kT}\right)$$

$$q_0 = \frac{\alpha P}{\sqrt{2\pi MkT}}$$

O_C= area of critical nucleus

Liquid→Solid: Nucleation of solid from liquid

- Kinetic theory of gaseous collision is no longer applicable
- q_0 replaced by diffusion in liquid

$$q_0 = \Gamma = \upsilon \exp\left(-\frac{\Delta g_n}{kT}\right)$$

$$= \frac{kT}{h}\exp\left(-\frac{\Delta g_n}{kT}\right)$$

$$I = \frac{NkT}{h}\left(\frac{O_C}{N_C}\right)\left(\frac{\Delta G_C}{3\pi kT}\right)^{1/2}\exp\left(-\frac{\Delta G_C + \Delta g_n}{kT}\right)$$

$$\left(\frac{O_C}{N_C}\right)\left(\frac{\Delta G_C}{3\pi kT}\right)^{1/2} \approx 10^1 \sim 10^2$$

$$\therefore I = \frac{NkT}{h}\exp\left(-\frac{\Delta G_C + \Delta g_n}{kT}\right)$$

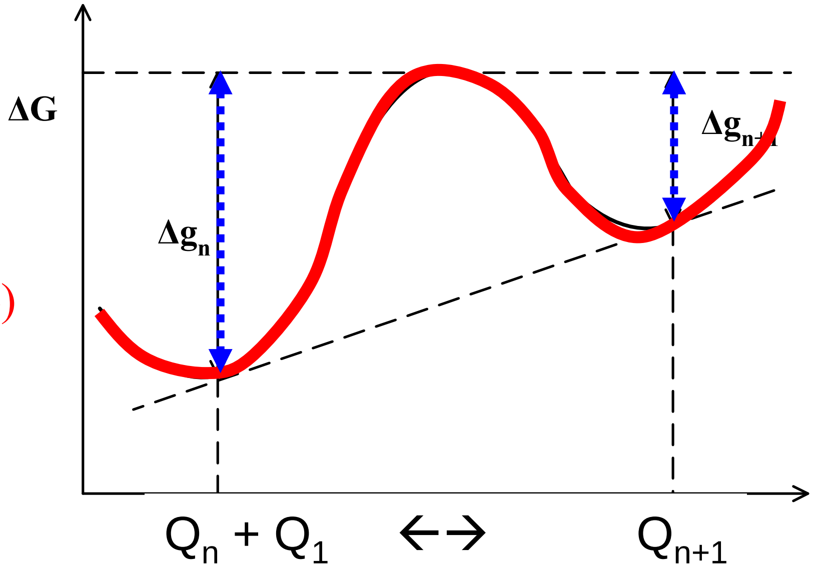
$${}^{v}I = \left(\frac{N}{V}\right)\left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta G_C + \Delta g_n}{kT}\right)$$

$$\frac{N}{V} \approx 10^{22} - 10^{23}\ cm^{-3}$$

$$\frac{kT}{h} = 10^{13}\ \sec^{-1}$$

$$\exp\left(-\frac{\Delta g_n}{kT}\right) \approx 10^{-2}\ for\quad L \rightarrow S$$

Δg_n~10 kJ/mol in liquid metals



$$\omega = \upsilon \exp\left(-\frac{\Delta G_m}{RT}\right)$$

$$\Gamma = Z\omega P_v$$

$$^{V}\mathrm{I} \approx 10^{33} \exp(-\frac{\Delta G_C}{kT})$$

$$\boxed{D = P_v w a_o^2}$$

$$Note: \ \frac{kT}{h} = \upsilon, \quad D = a_0^2 \upsilon$$

$$^{V}\mathrm{I} \approx N \cdot \frac{D}{a_0^2} \exp(-\frac{\Delta G_C}{kT})$$

$$D \approx 10^{-5}\ cm^2/\sec, \quad a_0^2 \approx 10^{-16} cm^2, \quad N \approx 10^{22} cm^{-3}$$

$$^{V}\mathrm{I} = 10^{33} \exp(-\frac{\Delta G_C}{kT})$$

For solidification

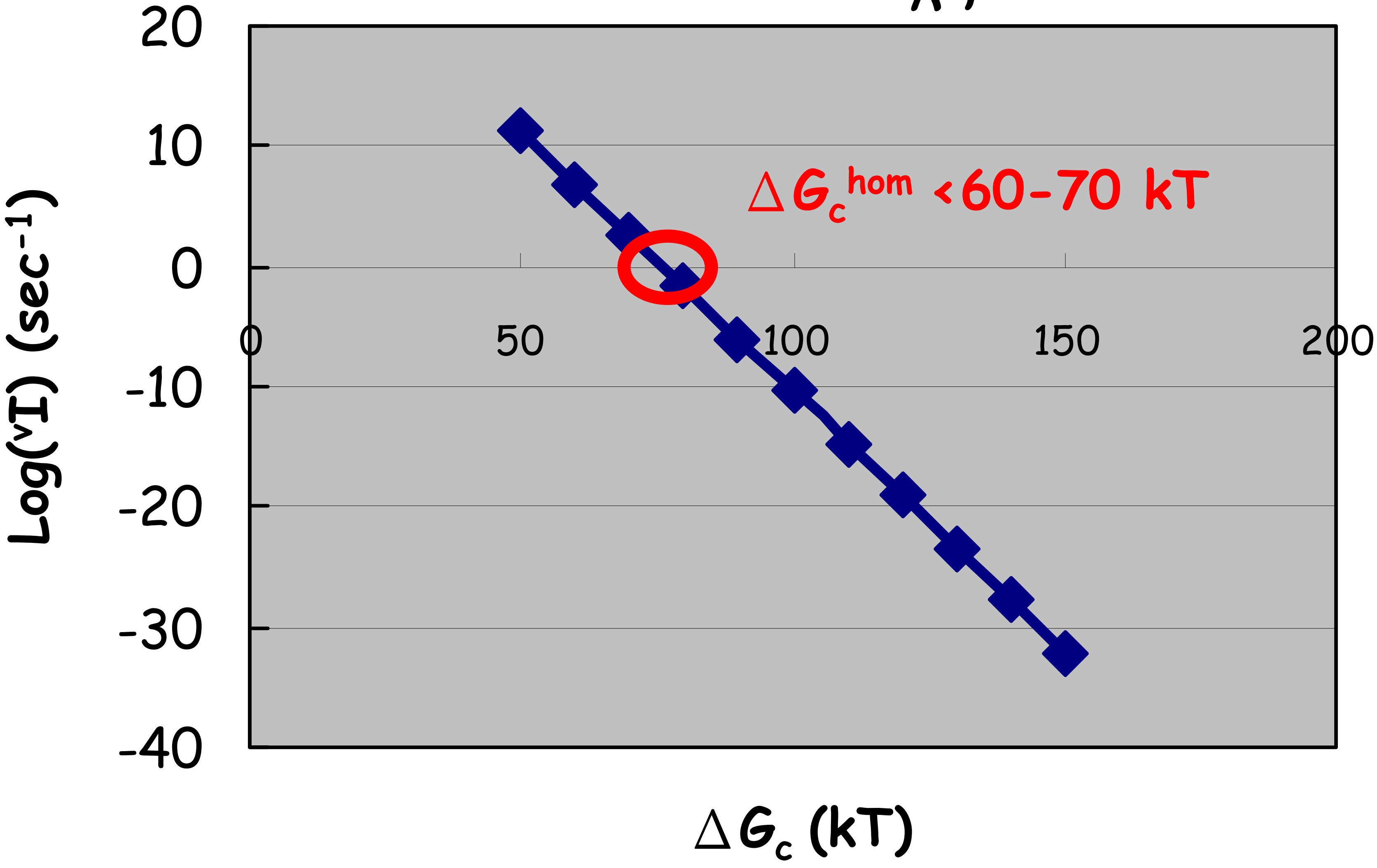
$$\Delta G_C = \frac{4\eta^3\gamma^3}{27(\Delta G_v)^2} = \frac{4\eta^3\gamma^3}{27(\frac{\Delta H_m \Delta T}{T_m})^2}$$

$$\because \Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

$$\therefore \ ^{V}\mathrm{I} \cong 10^{33} \exp[-\frac{4\eta^3\gamma^3 (T_m)^2}{27kT(\Delta H_m)^2(\Delta T)^2}]$$

Homogeneous Nucleation

$$^{V}I \approx 10^{33} \exp\left(-\frac{\Delta G_C}{kT}\right)$$



Liquid→Solid

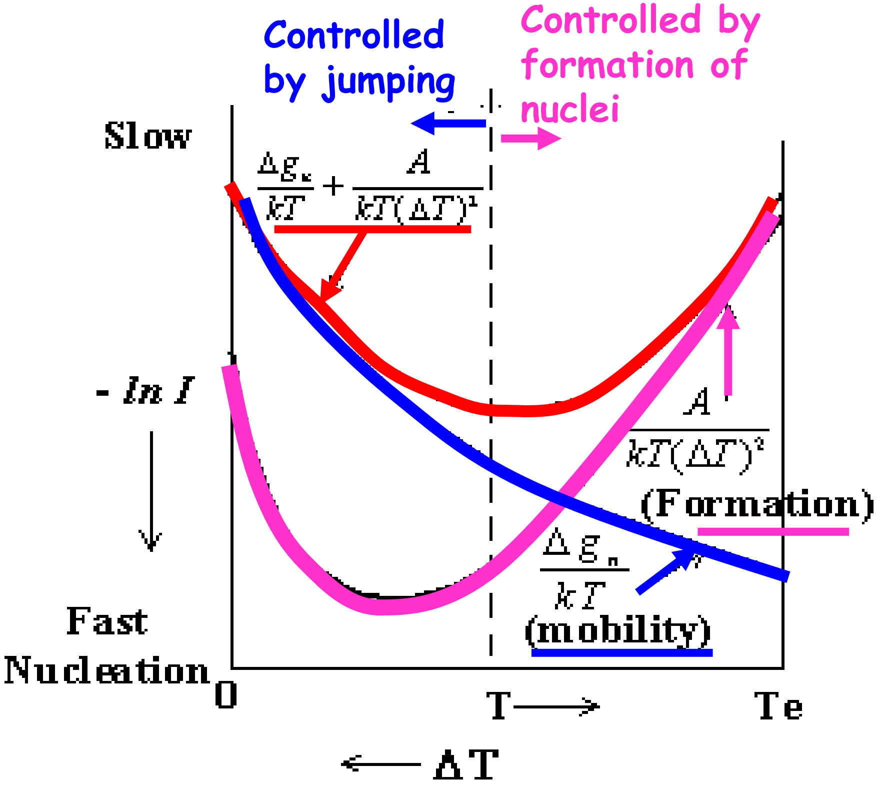
$$\Delta G_C = \frac{4\eta^3\gamma^3}{27(\frac{\Delta H_m \Delta T}{T_m})^2} = \frac{A}{(\Delta T)^2}$$

$$A = \frac{4\eta^3\gamma^3 T_m^2}{27(\Delta H_m)^2}$$

$$^{v}I = N \cdot \frac{kT}{h}\exp(-\frac{\Delta G_C + \Delta g_n}{kT})$$

$$\Delta G_c = \frac{4}{27}\frac{\eta^3\gamma^3}{(g^s - g^l)^2}$$

$$\Delta G_v = g^s - g^l = \frac{\Delta H_m \Delta T}{T_m}$$



Mobility term: $\frac{\Delta g_n}{kT}$

Formation term: $\frac{A}{kT(\Delta T)^2}$

$$-\ln(^{v}I) \ \alpha \ \frac{\Delta g_n}{kT} + \frac{A}{kT(\Delta T)^2}$$

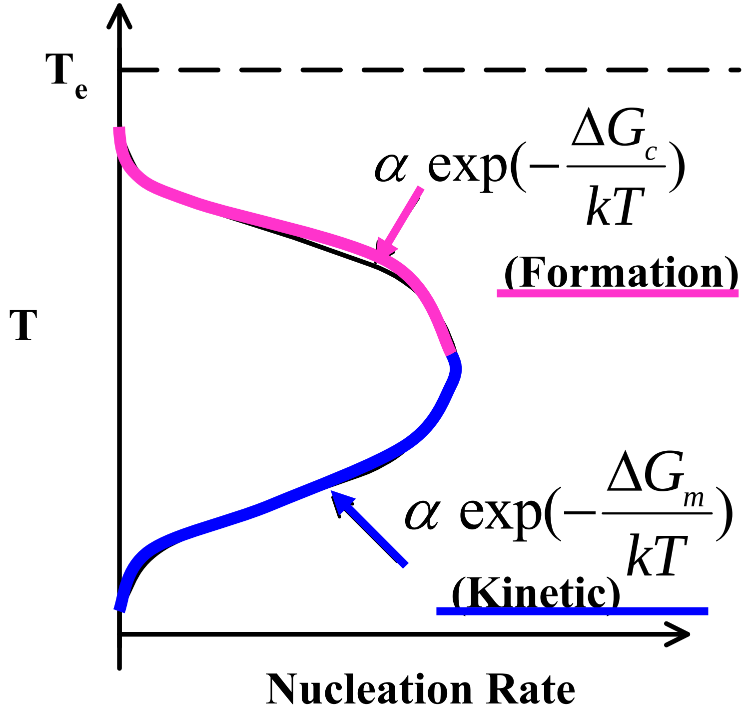
Solid→Solid

$$q_o = \frac{kT}{h}\exp(-\frac{\Delta G_m}{kT})$$

$$^{V}I = O_C \cdot \upsilon \exp(-\frac{\Delta G_m}{kT}) N \exp(-\frac{\Delta G_C}{kT})$$

$$\approx \frac{N \cdot D}{a_0^2}\exp(-\frac{\Delta G_C}{kT}) = 10^{29}\exp(-\frac{\Delta G_C}{kT})$$

$$D \approx 10^{-8}\ cm^2/\sec,\quad N \approx 10^{22},\quad a_0^2 \approx (3\times10^{-8})^2 \approx 10^{-15}$$



Phase Transformation in Solids

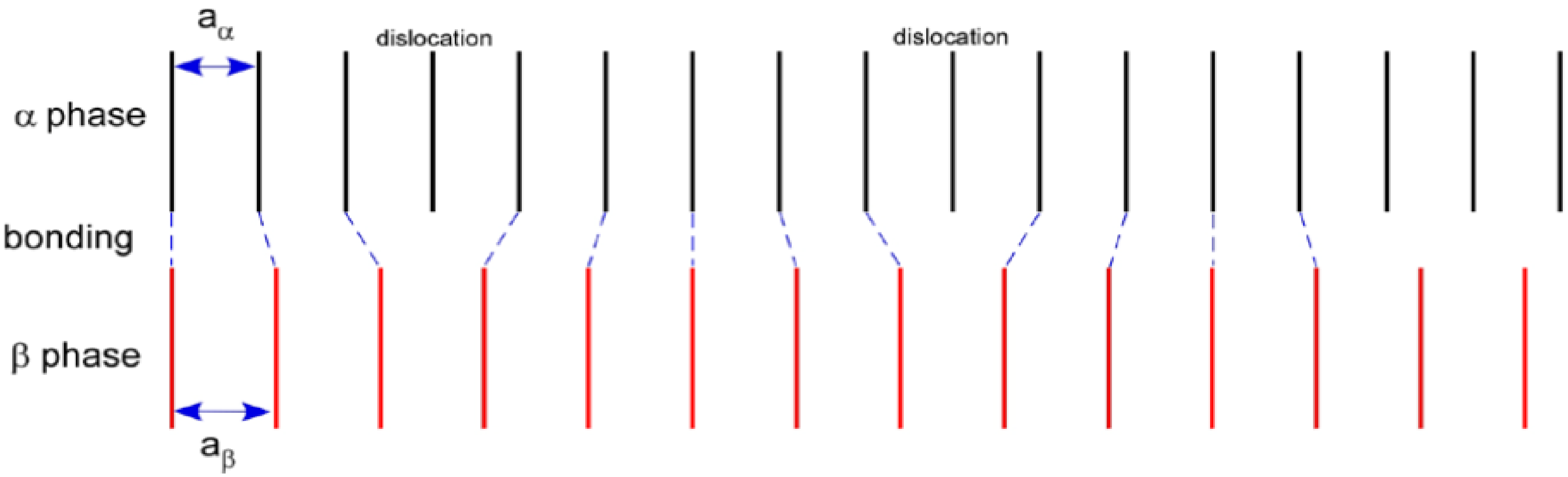
e.g., $\alpha \Leftrightarrow \beta$

The total interfacial energy ($\gamma_{\text{interface}}$) is the sum of surface energy contributed by chemical bonding at interface (γ_{Ch}) and the strain energy (γ_{St}).

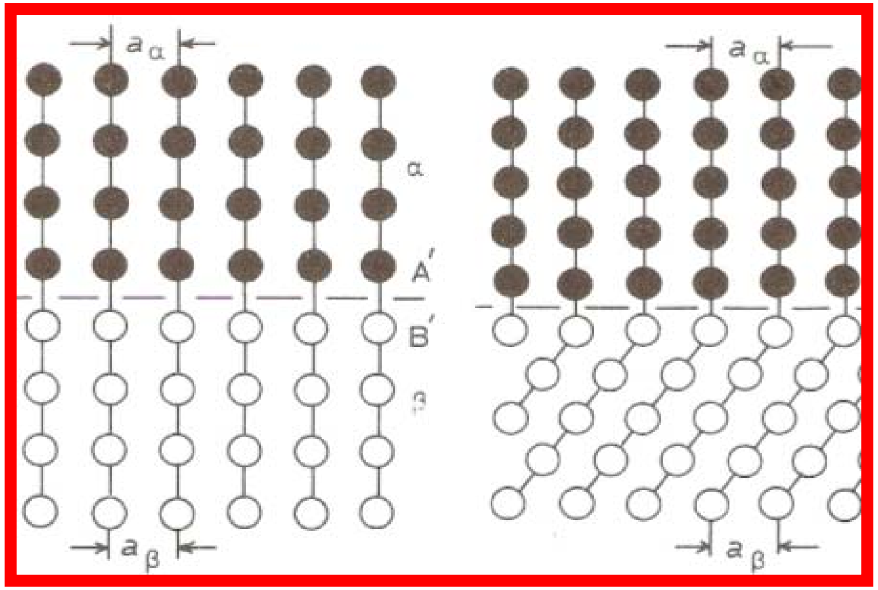
$$\gamma_{\text{interface}} = \gamma_{Ch} + \gamma_{St} = 4\pi r^2 \gamma_{\alpha\beta} + \frac{4\pi}{3} r^3 \cdot c\varepsilon^2$$

where c is the elastic constant and ε is the relative strain due to lattice mismatch.

$$\varepsilon \approx \frac{\left|a_\alpha - a_\beta\right|}{a_\alpha} \approx \frac{\left|a_\alpha - a_\beta\right|}{a_\beta}$$



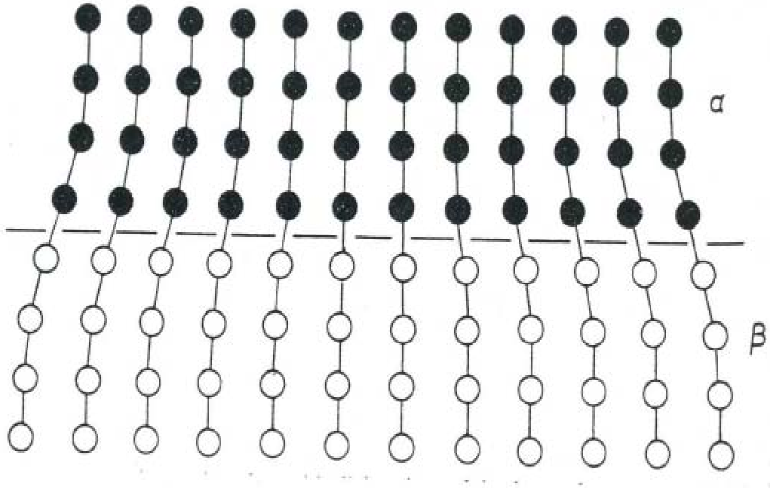
Coherent Interface



$$\gamma_{\text{interface}} = \gamma_{Ch} \;\; \alpha \; (\frac{dX}{dx})^2$$

$$\approx 0 - 200 \text{ mJ/m}^2$$

$$\frac{dX}{dx} : \text{concentration gradient}$$



$$\varepsilon \approx \frac{|a_\alpha - a_\beta|}{a_\alpha} \approx \frac{|a_\alpha - a_\beta|}{a_\beta} \leq 1\%$$

$$\gamma_{\text{interface}} = \gamma_{Ch} \;\; + \gamma_{St} \approx 0 - 200 \text{ mJ/m}^2$$

Gibbs free energy of an atom in a concentration gradient is not the same as the Gibbs free energy of that atom in a solution of uniform concentration

$$\gamma = \kappa\left(\frac{dX}{dx}\right)^2$$

Interfacial free energy is proportional to (composition gradient)^2

Regular Solution

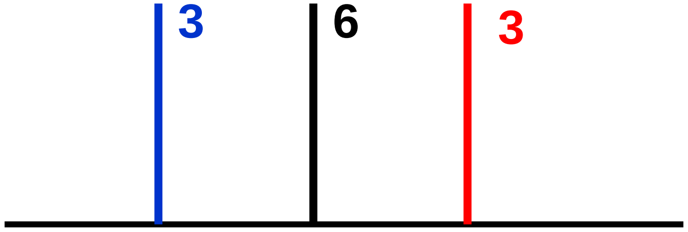
(1) In a uniform solution

$$\Delta H_m = \Omega X_A X_B = \Omega X_A (1 - X_A)$$

$$\Omega = Z[E_{AB} - \tfrac{1}{2}(E_{AA} + E_{BB})] = Z \cdot \Delta E$$

$$\Delta H_m = Z X_A (1 - X_A) \cdot \Delta E = 12C(1-C) \cdot \Delta E \qquad (Z=12)$$

(2) With a concentration gradient



$C_o-(dC/dx)\Delta x$
$=C_0-\Delta C$

C_o

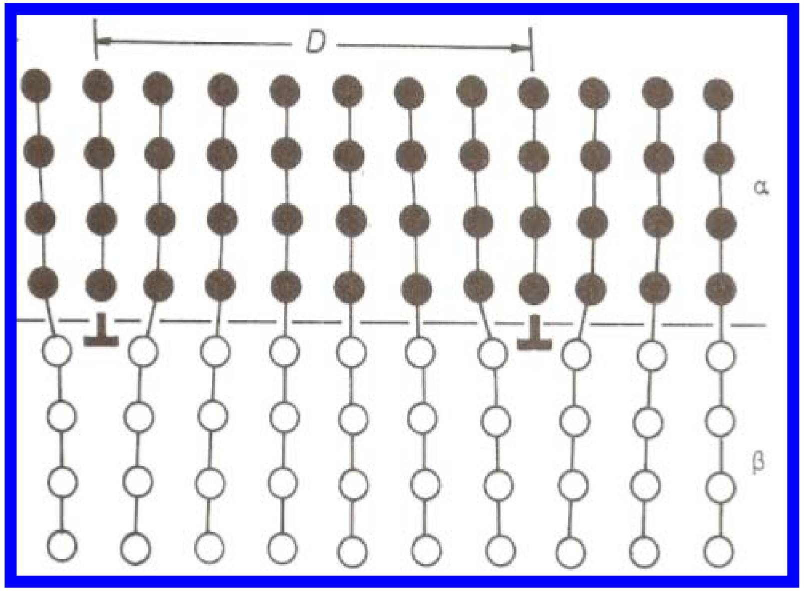
$C_o+(dC/dx)\Delta x$
$=C_0+\Delta C$

$$\begin{aligned}\Delta H_m &= 6C_o(1-C_o)\Delta E \\ &+ 3[(C_o+\Delta C)(1-(C_o+\Delta C))]\Delta E \\ &+ 3[(C_o-\Delta C)(1-(C_o-\Delta C))]\Delta E \\ &= 12C_o(1-C_o)\Delta E + 6(\Delta C)^2\Delta E \\ &= 12C_o(1-C_o)\Delta E + 6\left(\frac{dC}{dx}\right)^2(\Delta x)^2\Delta E\end{aligned}$$

Uniform concentration

Excess Gibbs free energy resulted from a non-uniform concentration

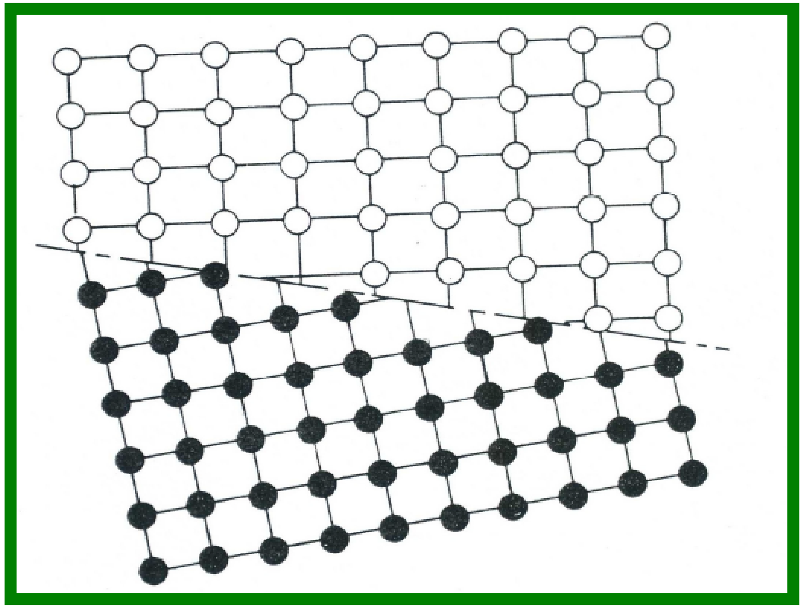
Semicoherent Interface



$$\varepsilon \approx \frac{|a_\alpha - a_\beta|}{a_\alpha} \approx \frac{|a_\alpha - a_\beta|}{a_\beta} \leq 25\%$$

$$\gamma_{\text{interface}} = \gamma_{Ch} + \gamma_{St} \approx 200 - 500 \text{ mJ/m}^2$$

Incoherent Interface



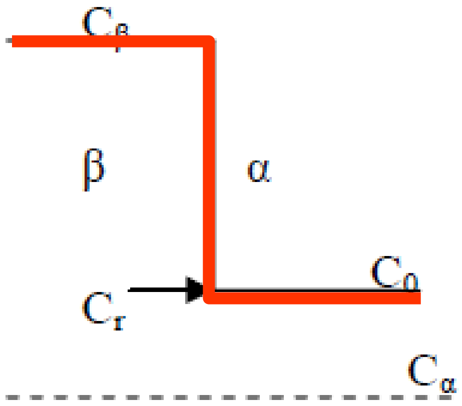
$$\varepsilon \approx \frac{|a_\alpha - a_\beta|}{a_\alpha} \approx \frac{|a_\alpha - a_\beta|}{a_\beta} > 25\%$$

$$\gamma_{\text{interface}} = \gamma_{Ch} + \gamma_{St} \approx 500 - 1000 \text{ mJ/m}^2$$

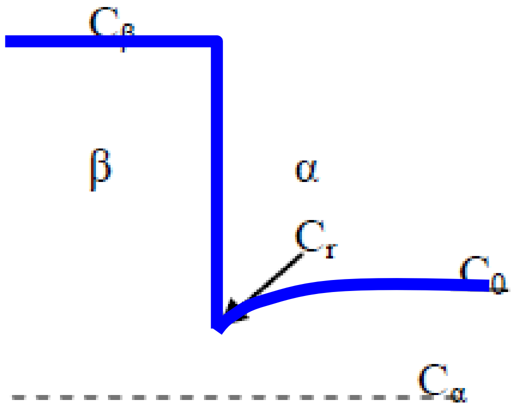
Effects of interface nature on Nucleation and Growth

For very small particles (though still larger than r_c), the term of strain energy is smaller than the surface energy (chemical contribution), and total interfacial energy is small (due to the limited surface area, and thus the limited number of interface chemical bonding), thereby it is energetically favorable to maintain coherent.

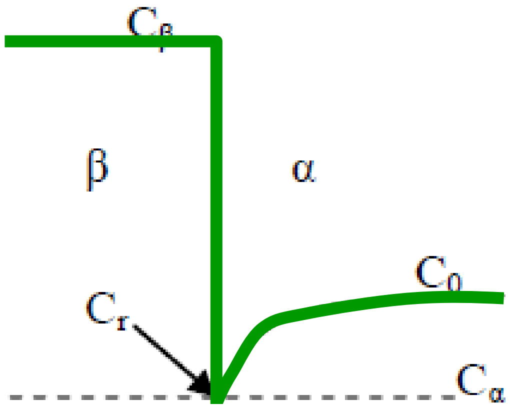
Diffusion normally occurs by a vacancy mechanism in substitutional solid solutions. In the case of the formation of a precipitate, a reconstruction of the lattice occurs, where involves the *creation and annihilation of vacancies,* if the interface is semicoherent or incoherent. However, if the interface is coherent, no such vacancies processes involved. The concentration profile across precipitate/matrix interface for the three different interfaces are shown below:



Coherent
(Reaction Controlling)



Semicoherent
(Mixed Controlling)



Incoherent
(Diffusion Controlling)

Boundary migration mobility (M)

M (coherent) < M (semicoherent) < M (incoherent)

Precipitates on Grain Boundary

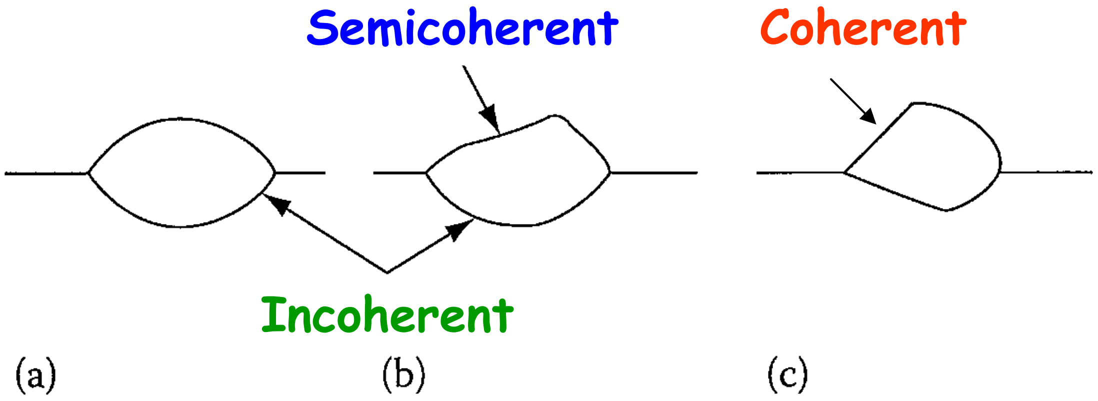


FIGURE 3.45
Possible morphologies for grain-boundary precipitates. Incoherent interfaces smoothly curved: coherent or semicoherent interfaces planar.

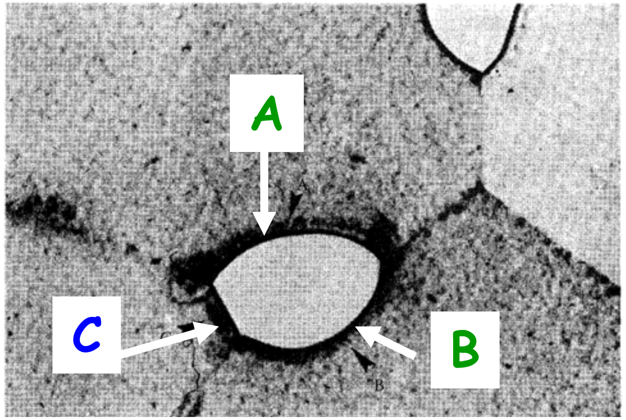
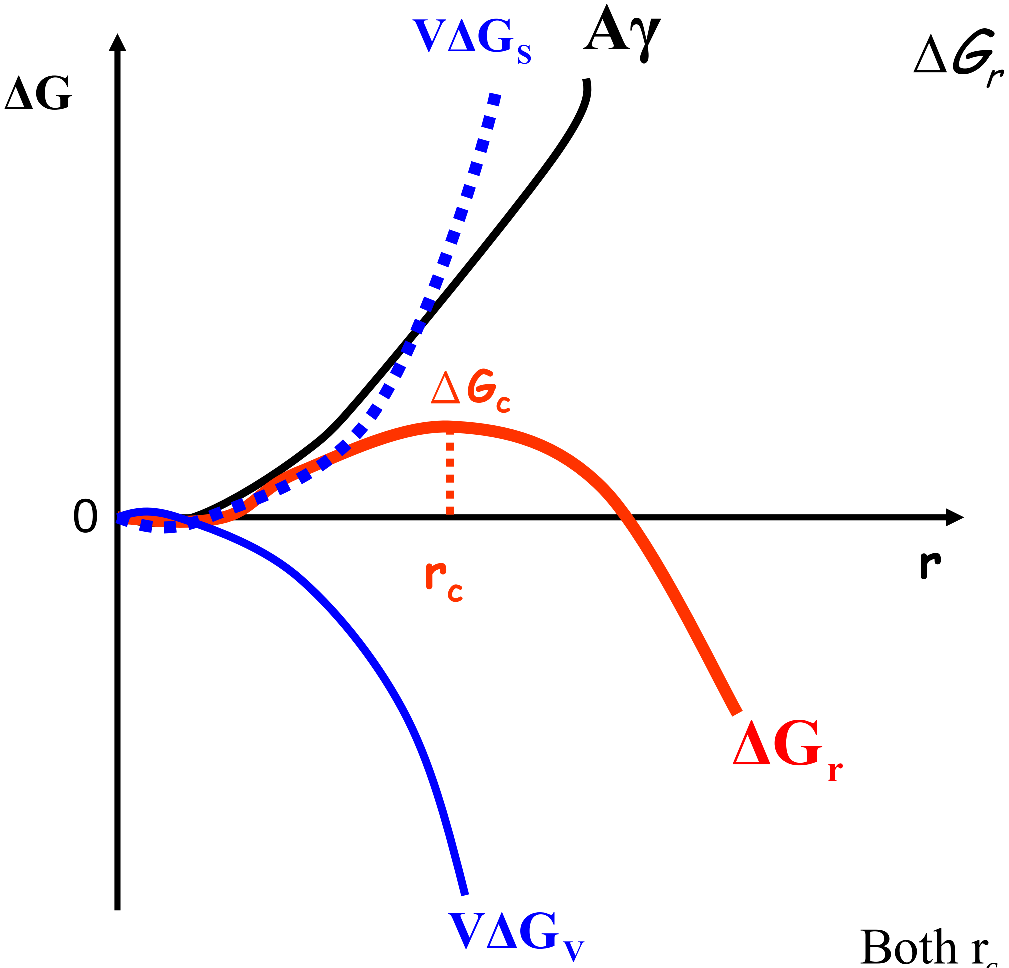


FIGURE 3.46
An α precipitate at a grain boundary triple point in an α–β Cu–In alloy. Interfaces A and B are incoherent, value C is semicoherent (×310). (After Chadwick, G.A., *Metallography of Phase Transformations*, Butterworths, London, 1972.)

Homogeneous Nucleation in Solids

Effects of Strain Energy (ΔG_S)



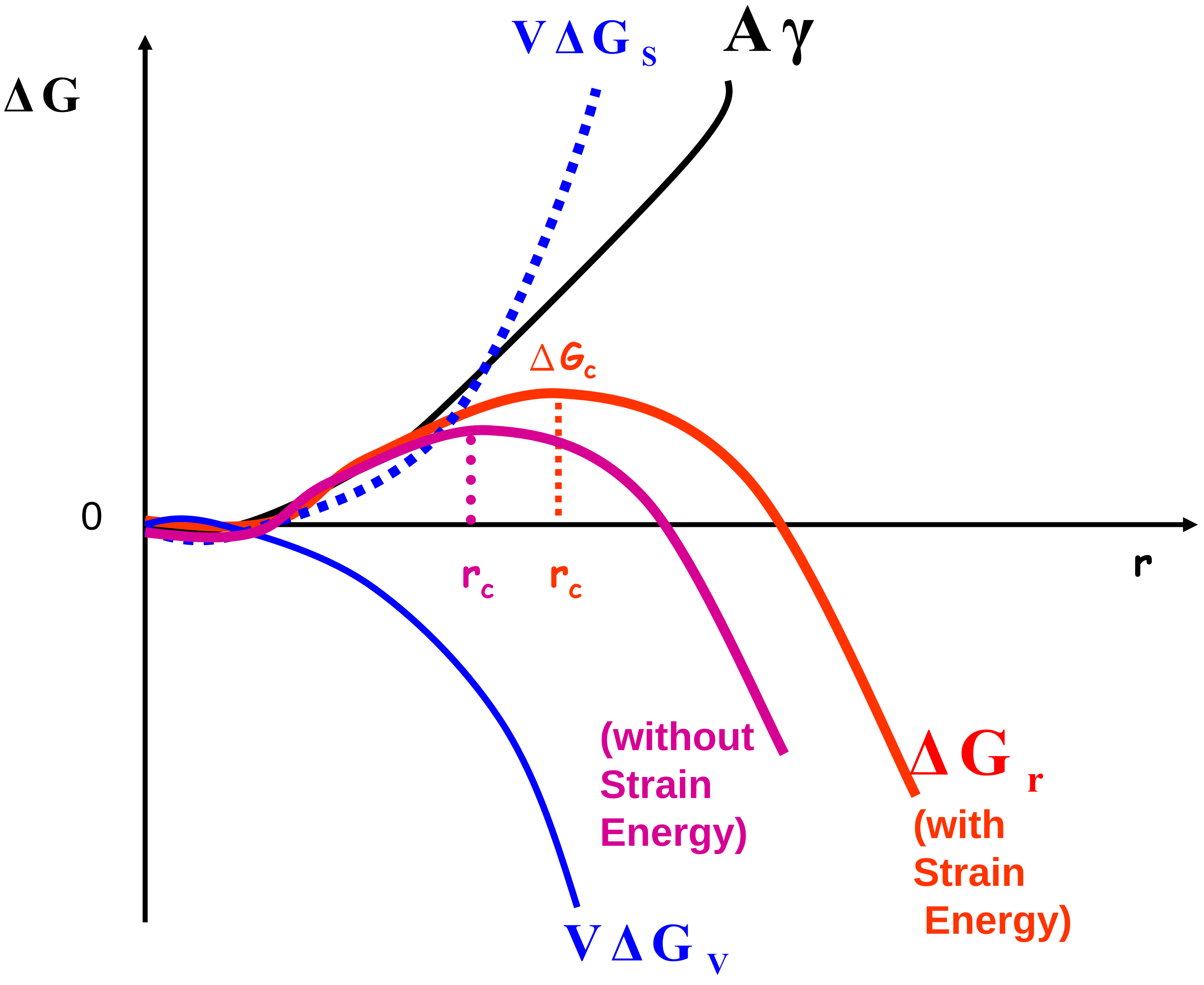
$$\Delta G_r = V\Delta G_V + A\gamma + V\Delta G_S$$
$$= \frac{4\pi r^3}{3}(\Delta G_V + \Delta G_S) + 4\pi r^2\gamma$$

$$r_c = \frac{-2\gamma}{\Delta G_V + \Delta G_S}$$

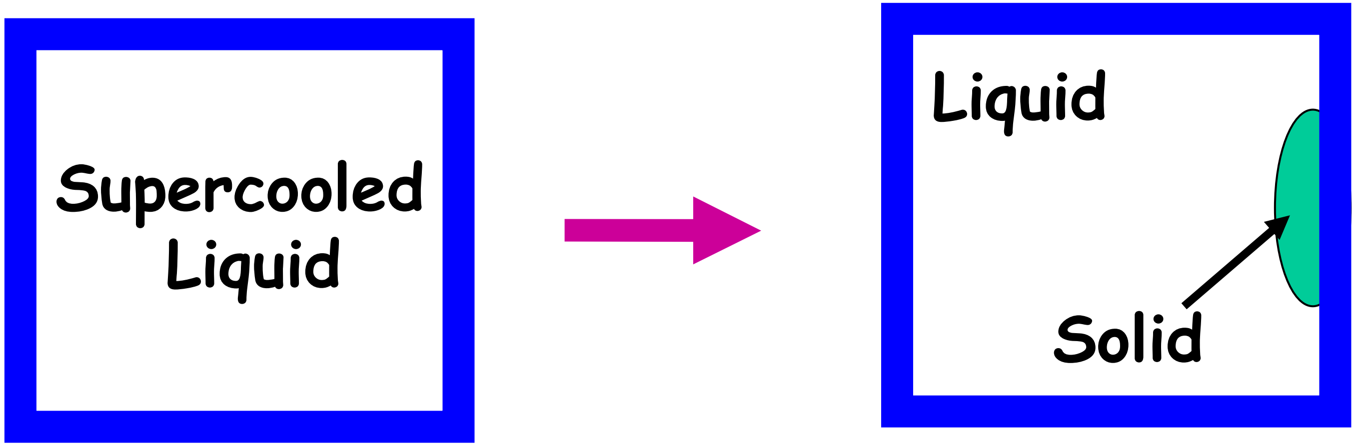
$$\Delta G_c = \frac{16\pi\gamma^3}{3(\Delta G_V + \Delta G_S)^2}$$

Both r_c and ΔG_c increase because $\Delta G_S > 0$.

Strain Energy Increasing Critical Nucleus Size and Free Energy



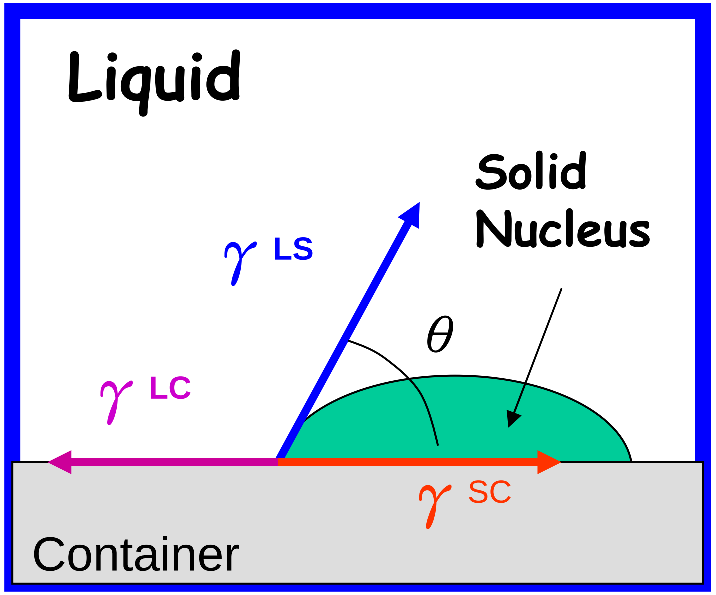
Heterogeneous Nucleation



Supercooled Liquid

Liquid

Solid



Liquid

Solid Nucleus

γ LS

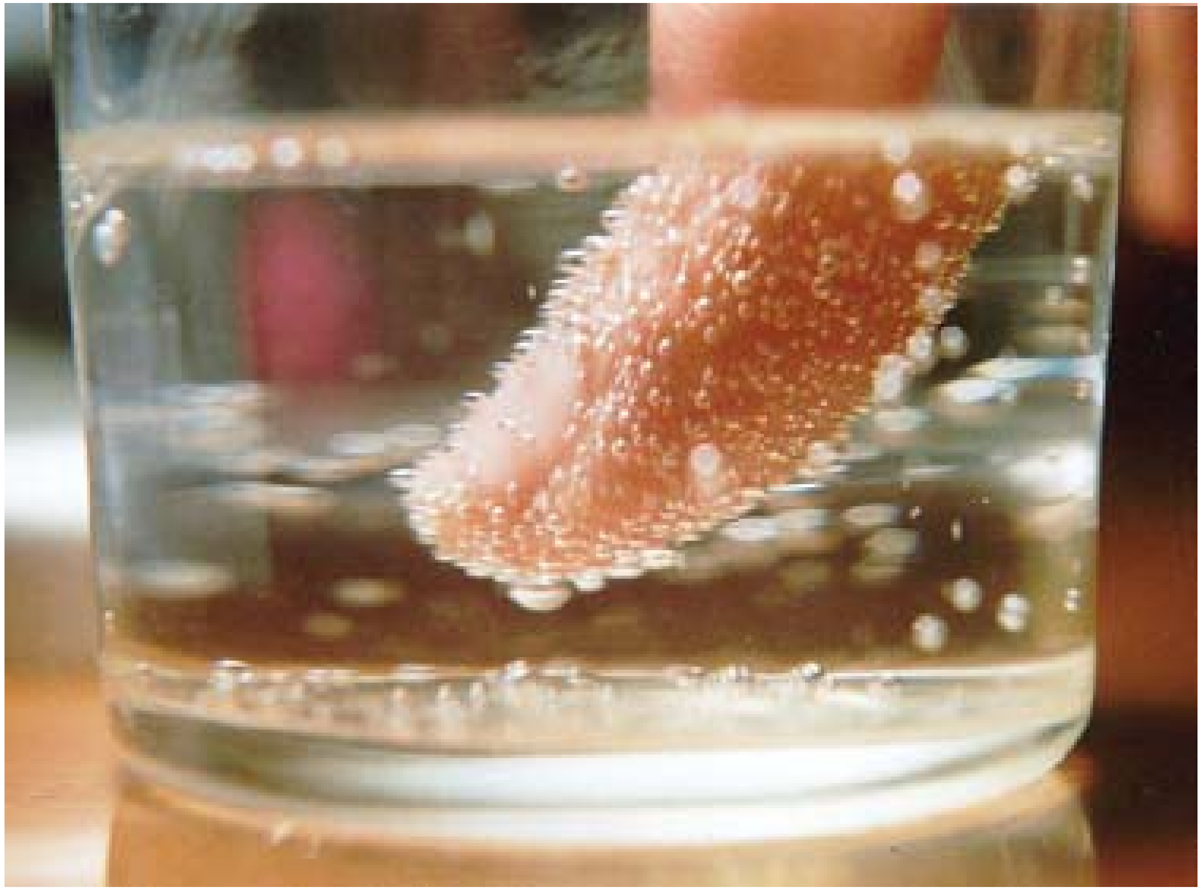
γ LC

θ

γ SC

Container

Heterogeneous Nucleation



Nucleation of CO_2 bubbles around a finger

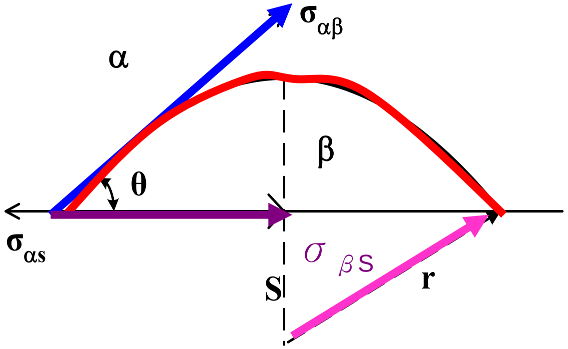
Heterogeneous Nucleation

-Impurities or strained regions of lattice enable nuclei to be formed with a much smaller free energy of activation than that of homogeneous nucleation

- α phase in contact with a solid phase of S, and β phase formed at the interface

-Assuming $\sigma_{\alpha\beta}$ is isotropic

-The volume of embryo = $\eta^{\beta} r^3$ and the surface area of contact with the α phase = $\eta^{\alpha\beta} r^2$, where η^{β} and $\eta^{\alpha\beta}$ are shape factors.



-The free energy of formation is

$$\Delta G^S = \frac{n^\beta r^3}{V^\beta}(g^\beta - g^\alpha) + r^2(n^{\alpha\beta}\gamma^{\alpha\beta} + n^{\alpha s}(\gamma^{\beta s} - \gamma^{\alpha s}))$$

$$\frac{\partial \Delta G^S}{\partial r} = 0 \Rightarrow r_c \text{ and } \Delta G_c^S$$

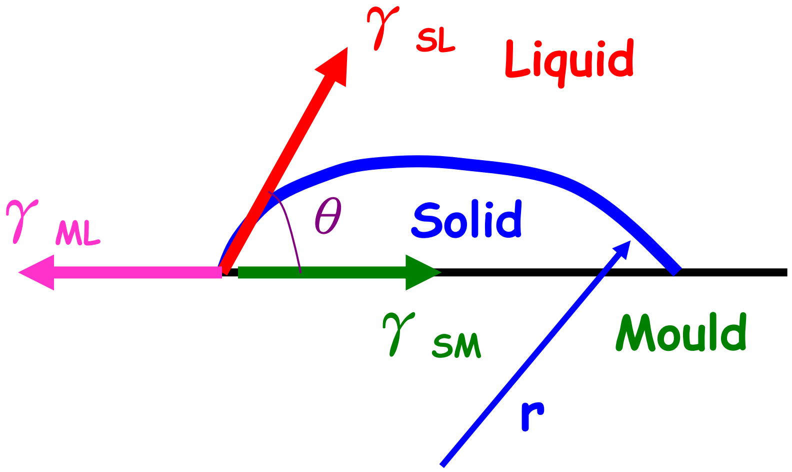
$$\Delta G_c^S = \frac{4}{27}\frac{[(n^{\alpha\beta}\gamma^{\alpha\beta} + n^{\alpha s}(\gamma^{\beta s} - \gamma^{\alpha s})]^3 (V^\beta)^2}{(n^\beta)^2 (g^\alpha - g^\beta)^2}$$

From the geometry of the figure

$$\eta^\beta = \pi(2 - 3\cos\theta + \cos^3\theta)/3$$

$$\eta^{\alpha\beta} = 2\pi(1 - \cos\theta)$$

$$\eta^{\alpha s} = \pi \sin^2\theta$$



$$\Delta G^{het} = V_s \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

$$A_{SL} = 2\pi r^2(1-\cos\theta)$$

$$A_{SM} = \pi r^2 \sin^2\theta$$

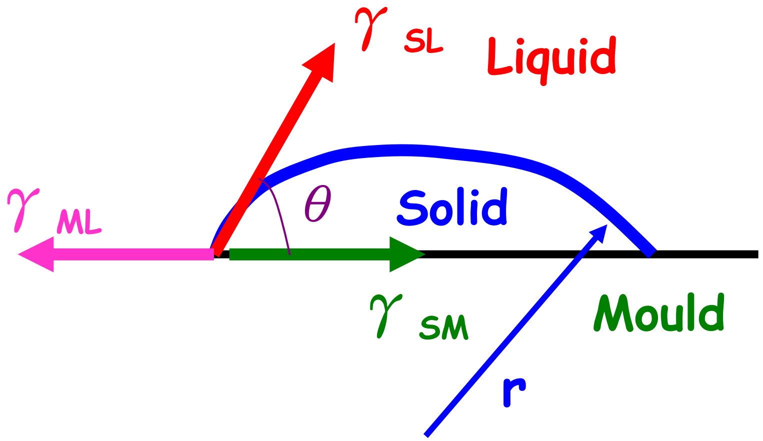
$$V_s = \pi r^3(2+\cos\theta)(1-\cos\theta)^2 \big/ 3$$

Heterogeneous Nucleation

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL}\cos\theta$$

$$\Rightarrow \cos\theta = \frac{\gamma_{ML} - \gamma_{SM}}{\gamma_{SL}}$$

θ : contact angle



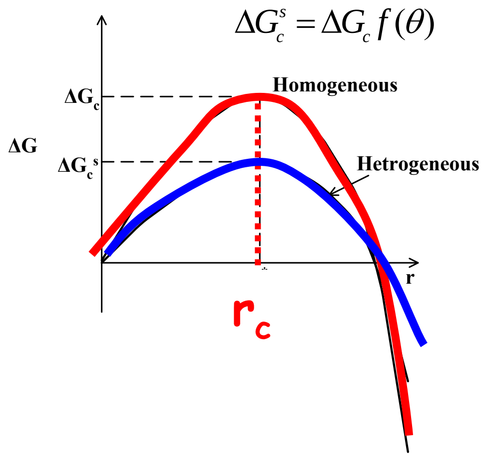
$$\Delta G^{het} = V_s\Delta G_V + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

$$\Delta G^{het} = \left(\frac{4\pi r^3}{3}\Delta G_V + 4\pi r^2\gamma_{SL}\right)f(\theta)$$

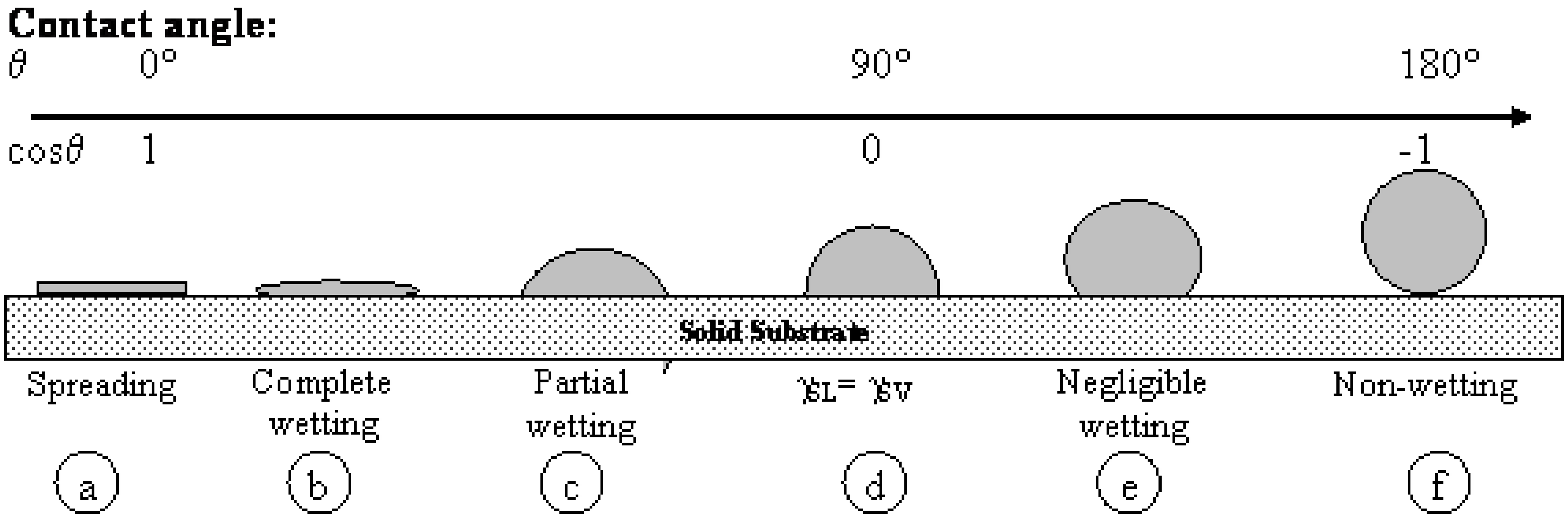
$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} = \frac{2-3\cos\theta+\cos^3\theta}{4} \le 1$$

$$\frac{\partial\Delta G^{het}}{\partial r} = 0 \Rightarrow \boxed{r_c^{het} = (-)\frac{2\gamma_{SL}}{\Delta G_V} = r_c^{hom}}$$

$$\Delta G_c^{het} = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}f(\theta) = \Delta G_c^{hom}f(\theta)$$

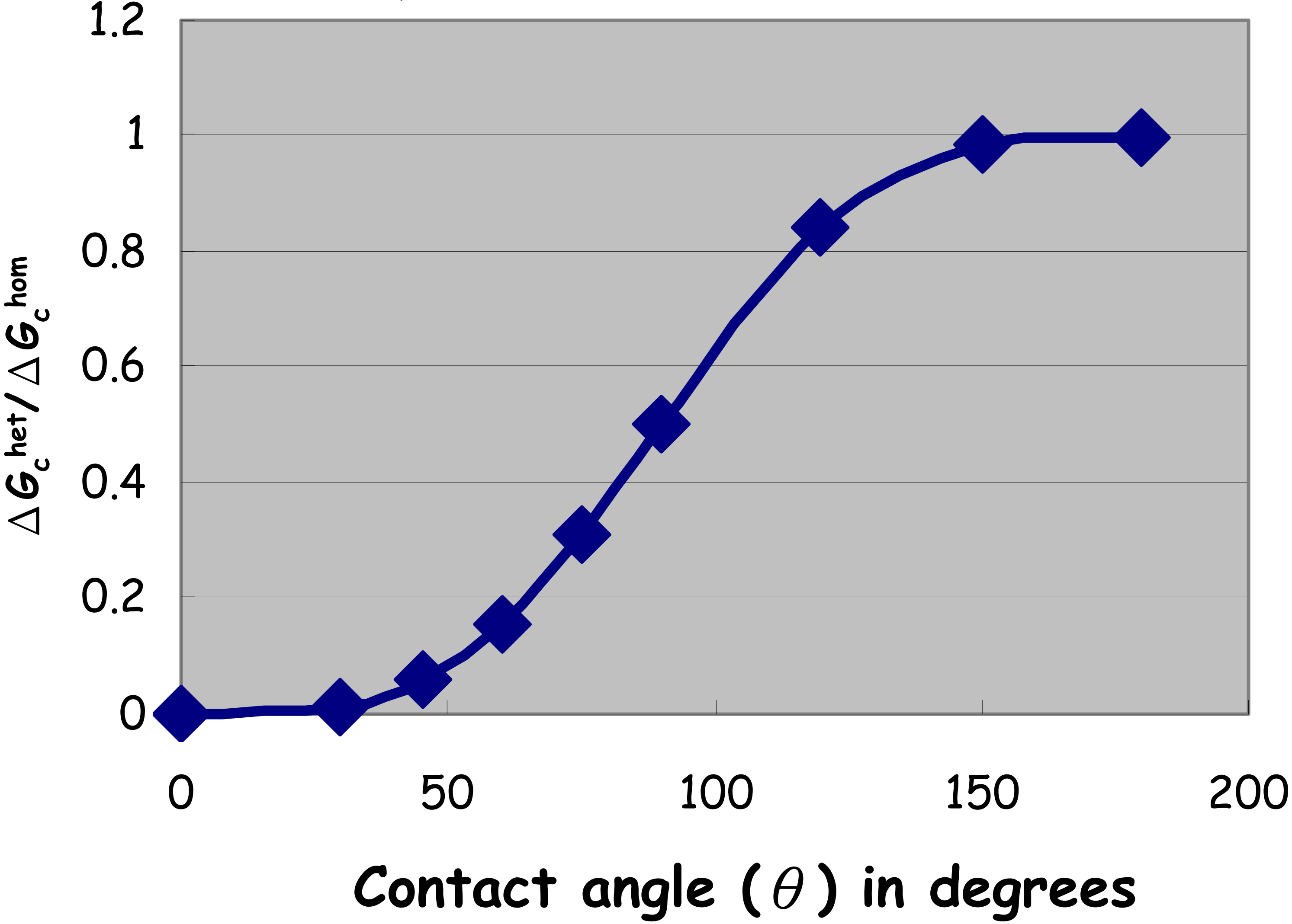


Contact Angle

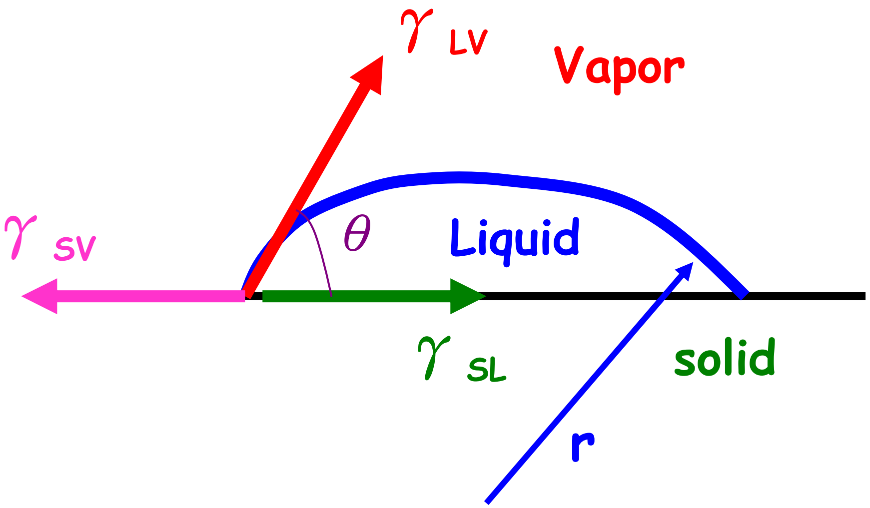


Liquid drop on solid surface. The condition $\theta < 90°$ *indicates that the solid is wet by the liquid, and* $\theta > 90°$ *indicates non-wetting, with the limits* $\theta = 0$ *and* $\theta = 180°$ *defining complete wetting and complete non-wetting, respectively*

$$\Delta G_c^{het} \Big/ \Delta G_c^{hom} = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$



Nucleation of Melting



$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos\theta \quad (\theta : \text{contact angle})$$

$$\Rightarrow \cos\theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}}$$

$$\gamma_{SV} >> \gamma_{LS} + \gamma_{LV} \Rightarrow \theta = 0$$

No superheating required for nucleation of liquid during melting

$$I = q_0 O_C N^S \exp(-\frac{\Delta G_c^S}{kT})$$

$$q_0 = \frac{\alpha P}{\sqrt{2\pi MkT}} \quad for \quad V \to L, \quad V \to S$$

$$I = (\frac{kT}{h}) N^S \exp(-\frac{\Delta G_c^S + \Delta g_n}{kT}) \quad for \quad L \to S, \quad S \to S$$

Note: The key difference between heterogeneous and homogeneous nucleation rates

1. N v.s. N^S
2. ΔG_c v.s. ΔG_c^S

$$\frac{\Delta G_c^S(hetero)}{\Delta G_c(homo)} = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

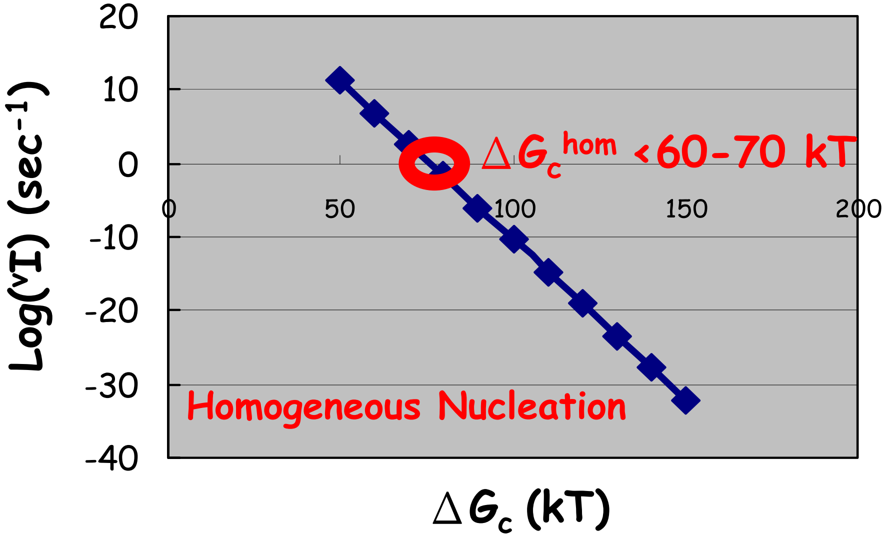
$$\theta > 0 \qquad \frac{\Delta G_c^S(hetero)}{\Delta G_c(homo)} > 0$$

$$\theta = \frac{1}{2}\pi \qquad \frac{\Delta G_c^S(hetero)}{\Delta G_c(homo)} = \frac{1}{2}$$

$$\theta = 0 \qquad \frac{\Delta G_c^S(hetero)}{\Delta G_c(homo)} = 0$$

$$\theta = \pi \qquad \frac{\Delta G_c^S(hetero)}{\Delta G_c(homo)} = 1$$

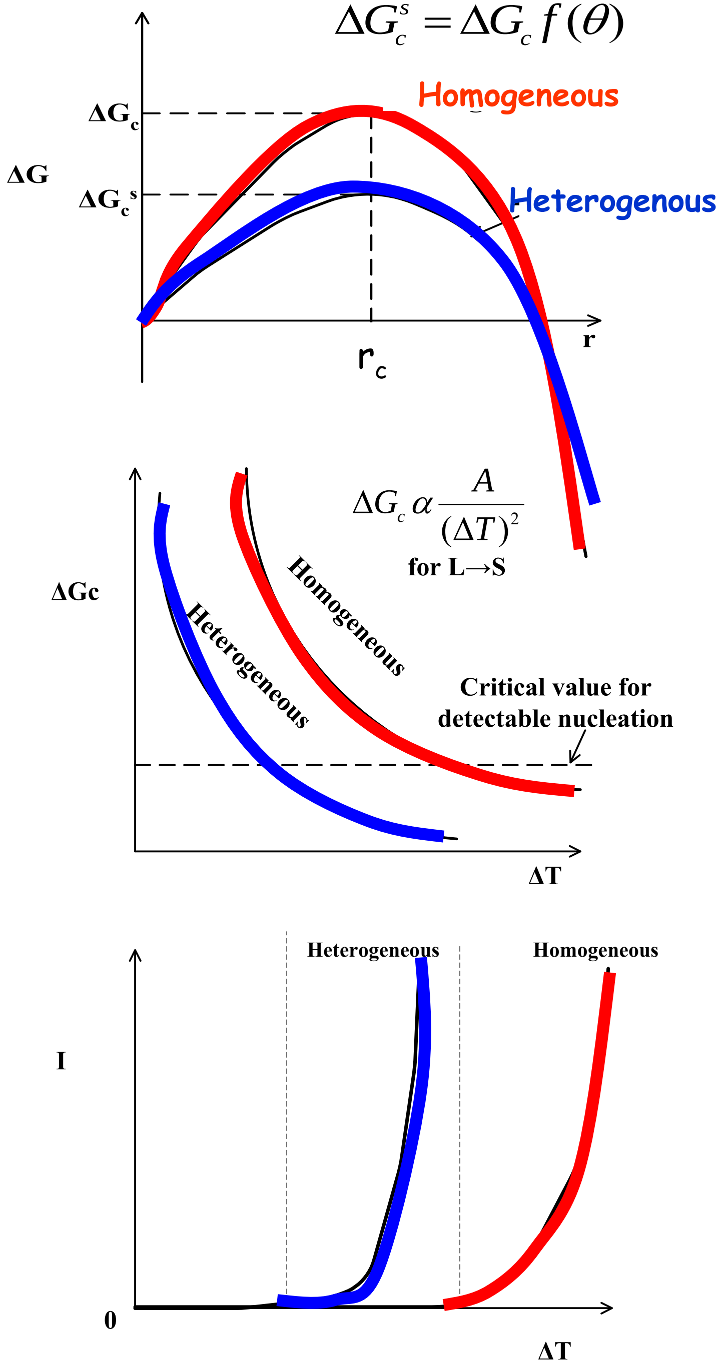
$${}^{V}I \approx 10^{33} \exp\left(-\frac{\Delta G_C}{kT}\right)$$



$$\Delta G_c^s = \Delta G_c f(\theta)$$

$$\Delta G_c \,\alpha\, \frac{A}{(\Delta T)^2}$$

for L→S

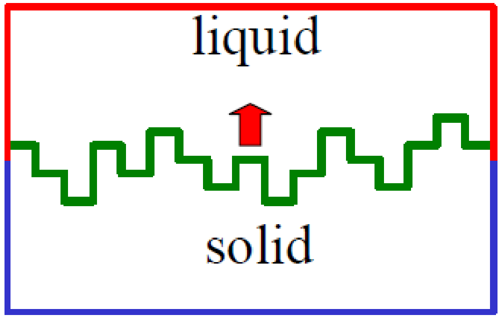


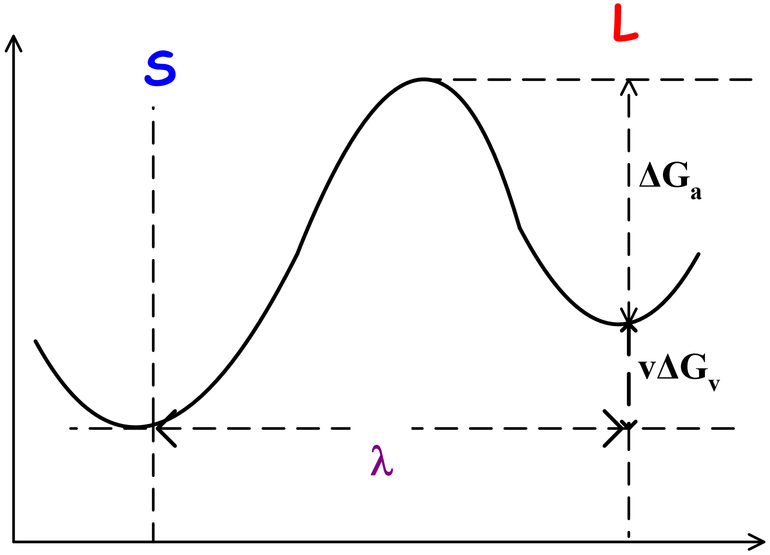
Growth (without composition change)

e.g., Crystal growth

I.Normal growth (continuous growth)

- Wilson-Frenkel model
- Every site is a growth site, or there is a constant number of growth sites
- Number of growth sites ≠ f (T)
- Rough interface on atomic scale (micro- roughness)





$$L \rightarrow S \quad (Lquid \rightarrow Solid)$$

$$\Gamma_{LS} = \nu_0 \exp(-\frac{\Delta G_a}{kT})$$

$$\Gamma_{SL} = \nu_0 \exp[-\frac{(\Delta G_a + V\Delta G_V)}{kT}]$$

$$\Gamma_{Net} = \Gamma_{LS} - \Gamma_{SL}$$

Γ_{Net} : Net frequency at the interface of Liquid/Solid

Velocity of interface approximated by wave equation

$$u = \lambda \Gamma_{net}$$

$$= \lambda \nu_0 \exp(-\frac{\Delta G_a}{kT})[1-\exp(-\frac{V\Delta G_V}{kT})]$$

$$= \lambda \Gamma_{LS}[1-\exp(-\frac{V\Delta G_V}{kT})]$$

(1) For small under-cooling (ΔT→0 and ΔG_V is small)

$$\Delta G_V << kT$$

$$\boxed{\begin{aligned}1-\exp(-\frac{V\Delta G_V}{kT}) &\approx 1-(1-\frac{V\Delta G_V}{kT}) \\ &= \frac{V\Delta G_V}{kT}\end{aligned}}$$

$$u = \lambda \nu_0 \exp(-\frac{\Delta G_a}{kT})(\frac{V\Delta G_V}{kT})$$

$$\Delta G_V = \frac{\Delta H \Delta T}{T_e}$$

$$u \approx \lambda \nu_0 \exp(-\frac{\Delta G_a}{kT})\frac{\Delta H \Delta T}{T_e}$$

$$u \ \alpha \ k(\Delta T)$$

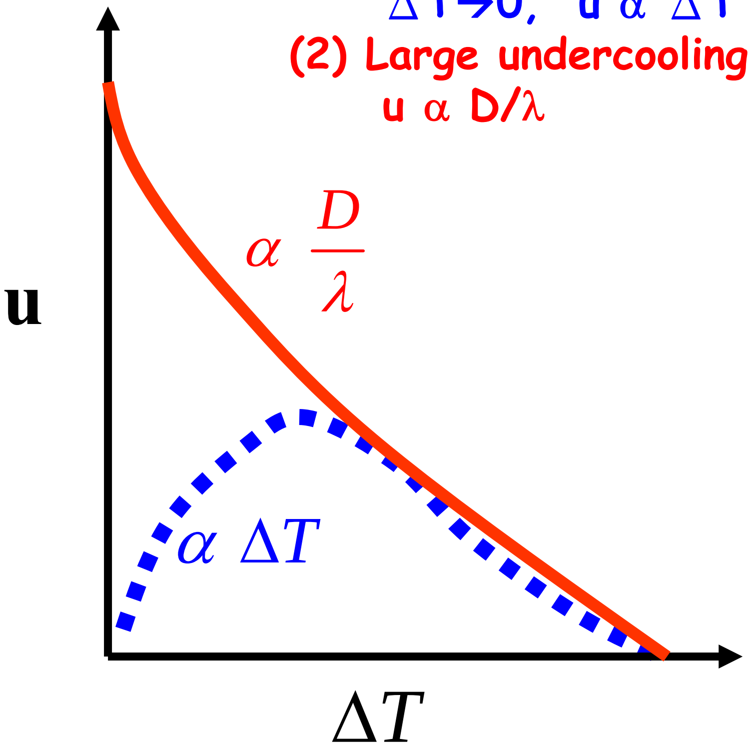
Growth rate is proportional to under-cooling when ΔT is small

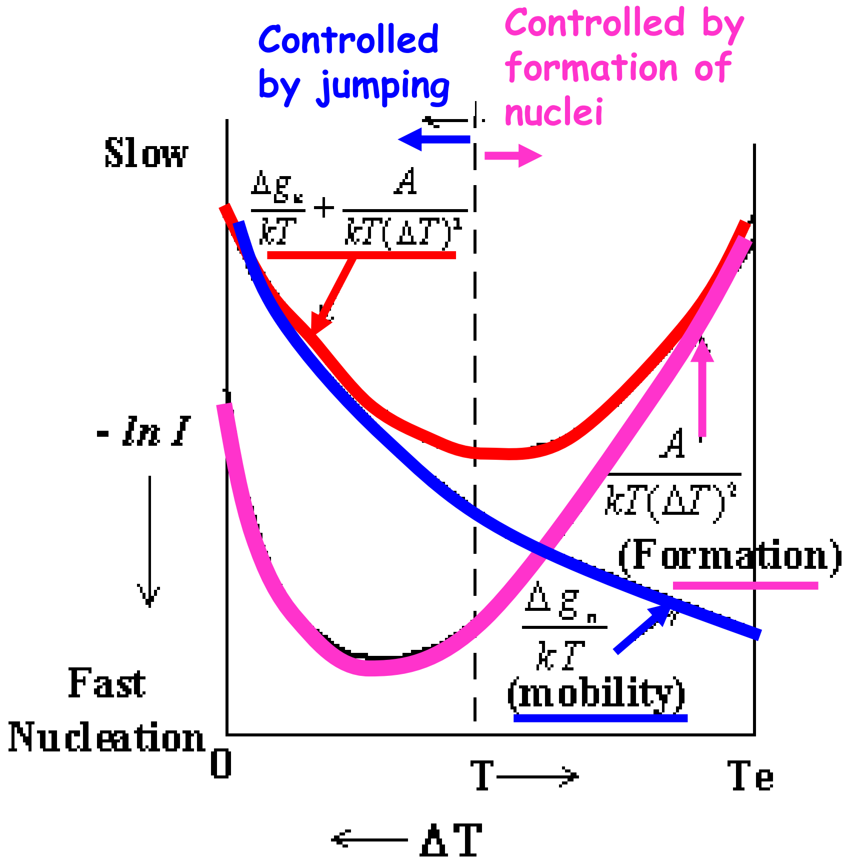
(2) For large under-cooling → $|V\Delta G_V| >> kT$

$$u = \lambda \nu_0 \exp(-\frac{\Delta G_a}{kT}) = \frac{D}{\lambda} \quad (D = \Gamma \lambda^2)$$

(1) Small undercooling
$\Delta T \rightarrow 0$, u α ΔT

(2) Large undercooling
u α D/λ





Grain Growth

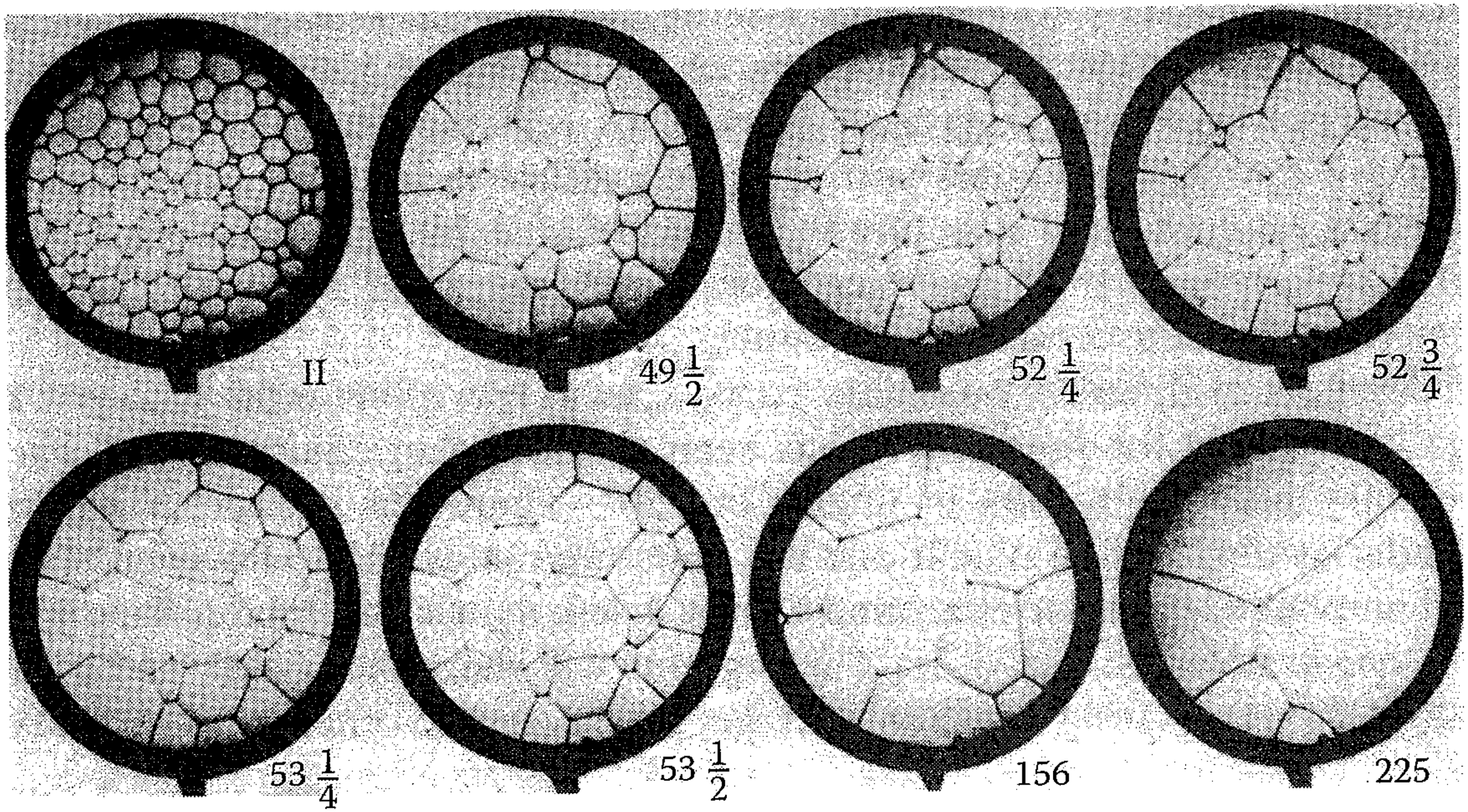
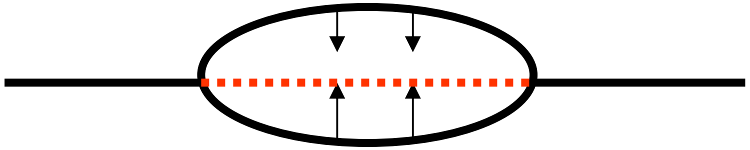
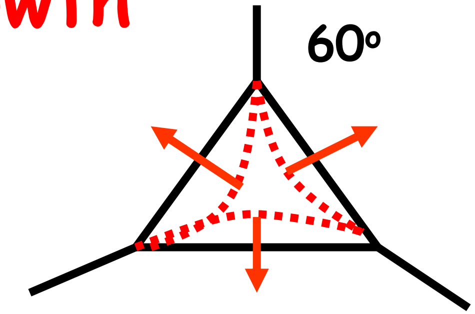
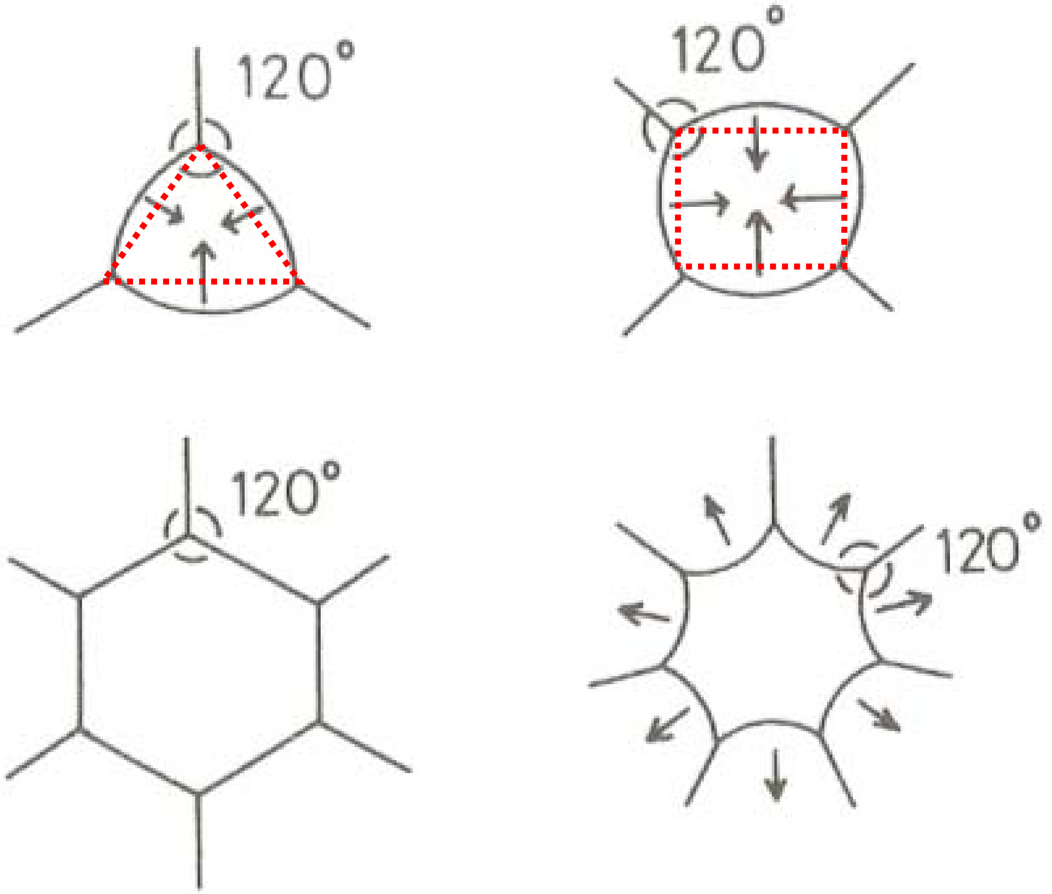


FIGURE 3.22
Two-dimensional cells of a soap solution illustrating the process of grain growth. Numbers are time in minutes. (After Smith, C.S., *Metal Interfaces*, American Society for Metals, Cleveland, 1952, 81.)

Grain Growth

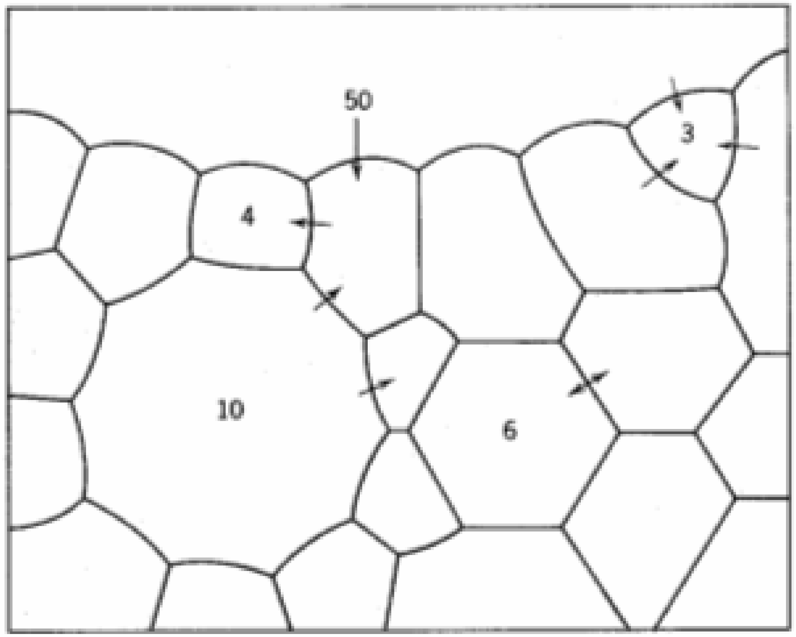


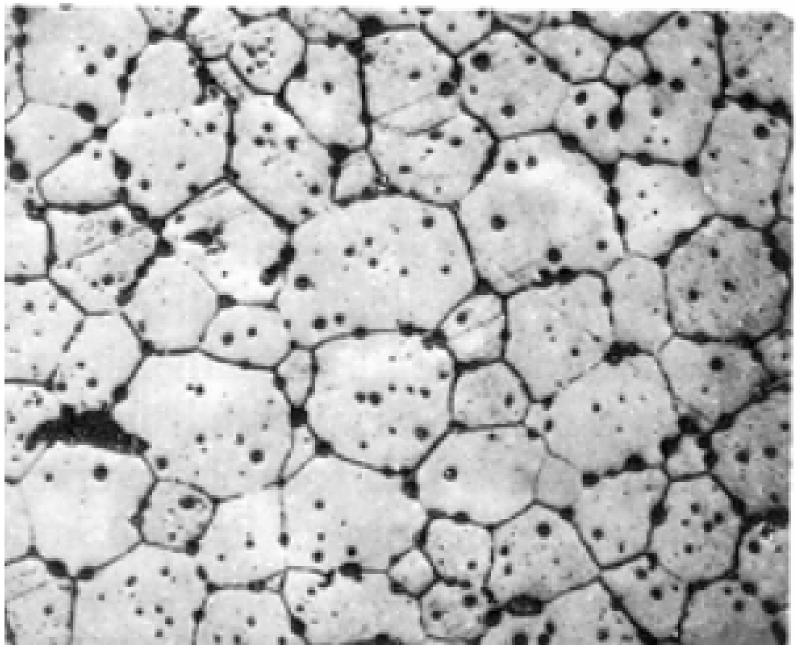




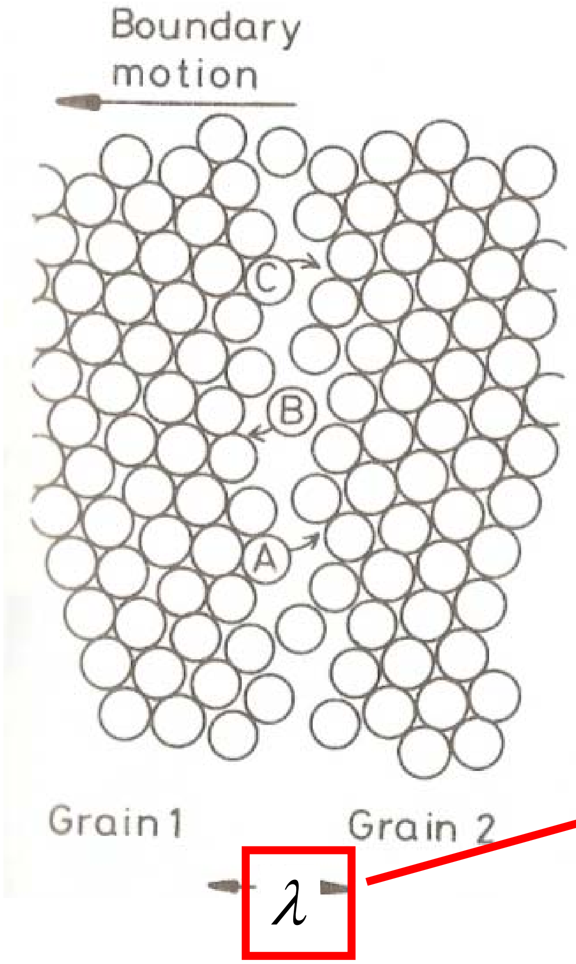
Grain Growth

The arrows indicate the directions in which grain boundaries migrate.

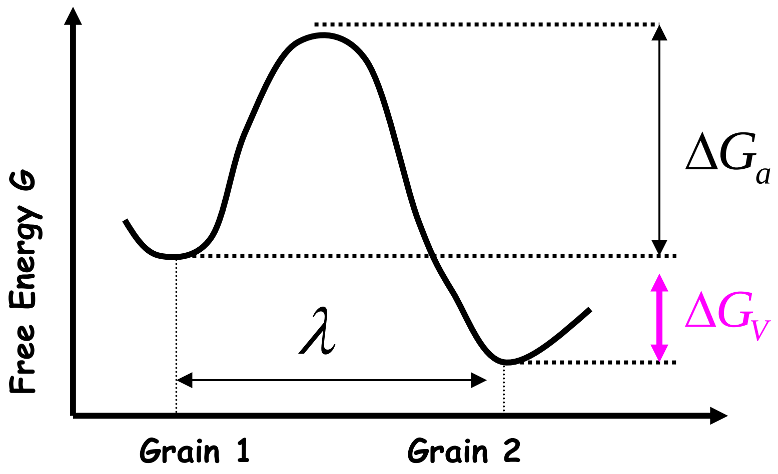




Grain Growth



λ is grain boundary width



$$\Delta G_V = \frac{2\gamma_{gb} V_M}{\bar{r}} = \Delta\mu$$

$\Delta G_V << kT$

$$u = \boxed{\lambda}\,\nu_o \exp\left(-\frac{\Delta G_a}{kT}\right)\left(\frac{V\Delta G_V}{kT}\right)$$

$$u = \frac{d\bar{r}}{dt} = K\frac{\gamma_{gb}}{\bar{r}}$$

$$\bar{r}^2 - \bar{r}_o^2 = Kt$$

$\bar{r}$: average grain size

II. Lateral Growth

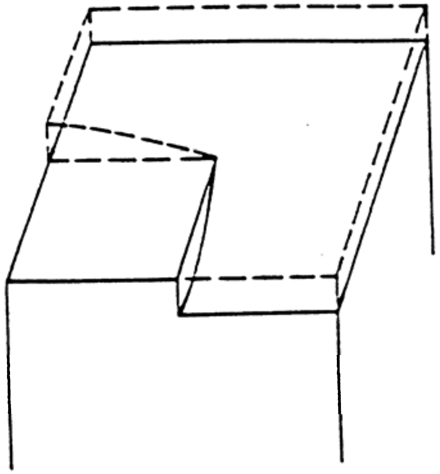
(1) Spiral Growth

- Interface is smooth on atomic scale, but imperfect
- Growth takes place only at the dislocation ledges; the fraction of preferred growth sites on the interface in growth from the melt is approximately by

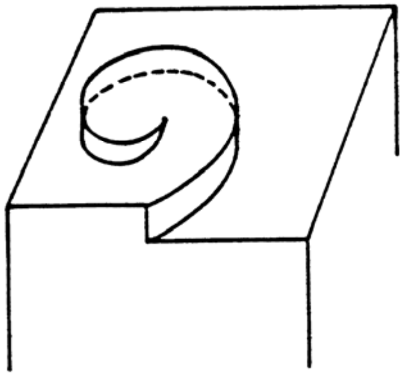
$$f \approx \frac{\Delta T}{2\pi T_E}$$

(Hilling & Turnbull, J. Chem. Phys. 24, 914 (1956))

(a)



(b)

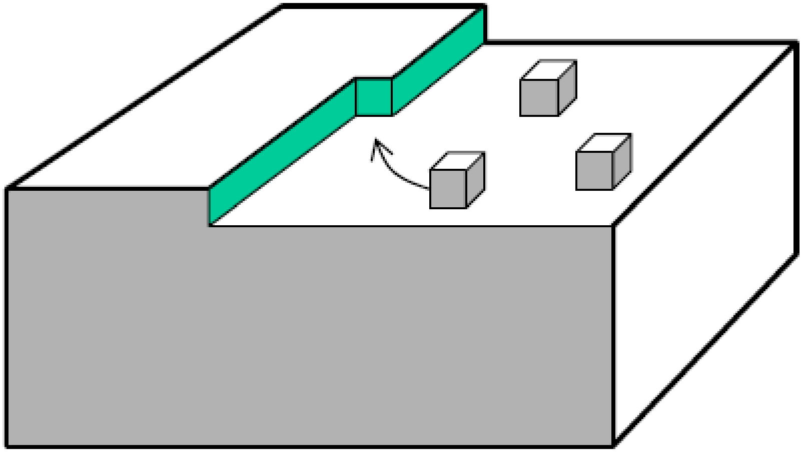


$$u = f \nu a_0 [1 - \exp(-\frac{V \Delta G_V}{kT})]$$

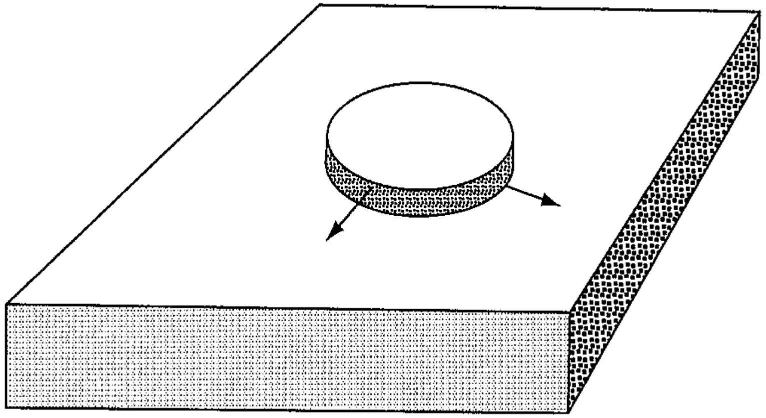
$*\text{Small } \Delta T, \; u \, \alpha \, (\Delta T)^2$

$*\text{Large } \Delta T, \; \text{model invalid}$

(2) Surface Nucleation



(a)

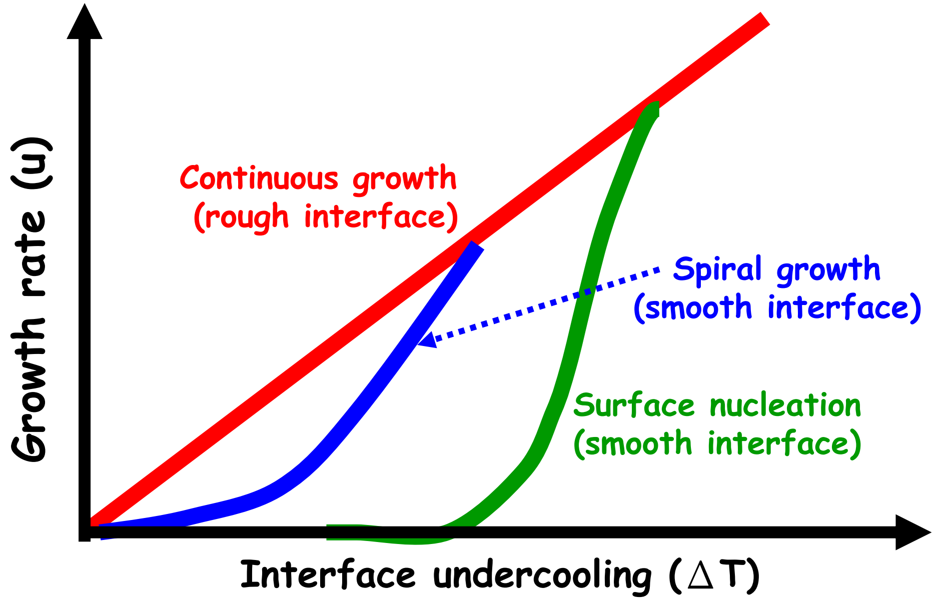


(b)

- Interface is smooth on atomic scale and perfect
- Growth takes place at step sites provided by two-dimension nuclei formed on the interface

$$u = A\nu \exp(-\frac{C}{T\Delta T})$$

where A and C are constants depending on specific models.



Small ΔT

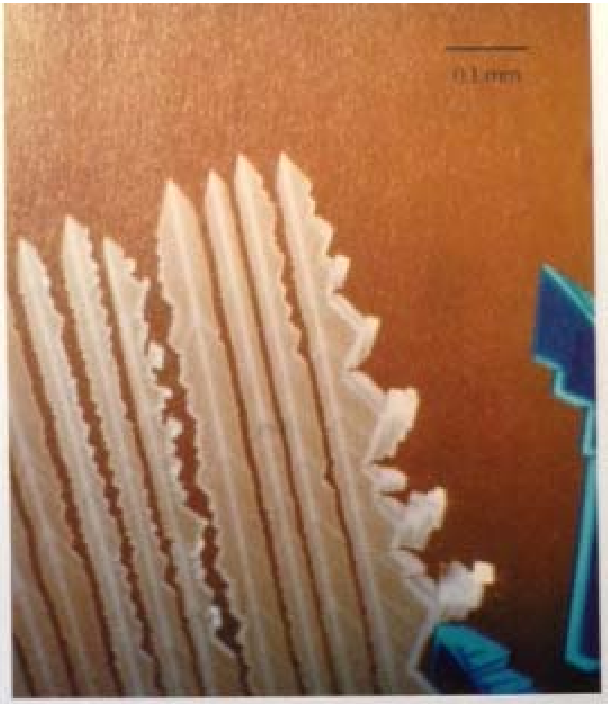
(1) Normal growth, $u \propto \Delta T$
(2) Spiral growth, $u \propto (\Delta T)^2$
(3) Surface-nucleation growth, $u \propto \exp(-1/\Delta T)$,
which requires $(\Delta T)_c$

Q: Can we predict whether a given material will have a rough or smooth interface?
If so, we have handled the kinetic models.

Note: Nucleation is required on smooth surfaces, but not for rough or imperfect surfaces

Faceted dendritic growth in tertiary butyl alcohol

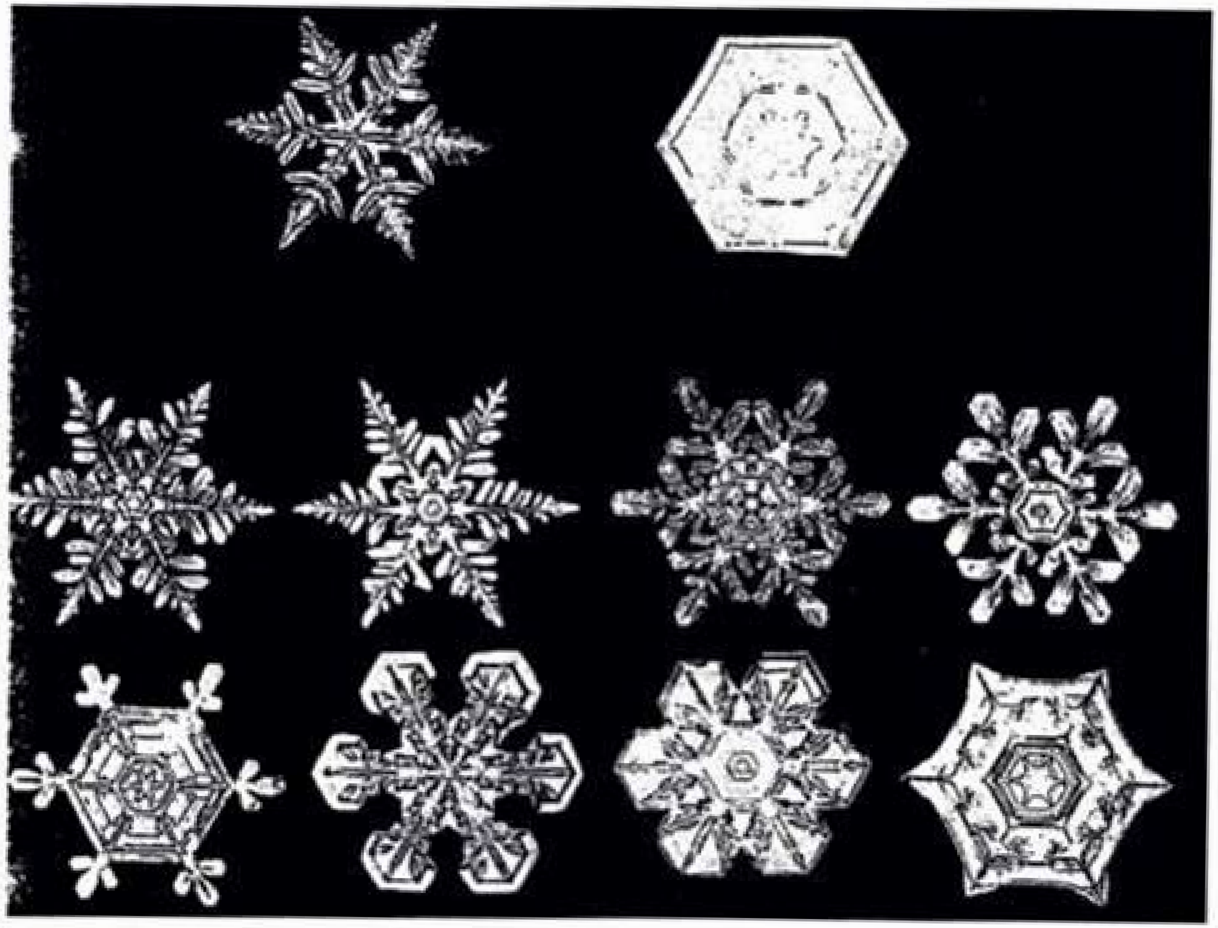
$\Delta S/R=3$



Faceted growth in benzil

$\Delta S/R=6$

re 21.18 Faceted



gure 21.8 Snow flakes. (From Bentley and Humphreys [7]).

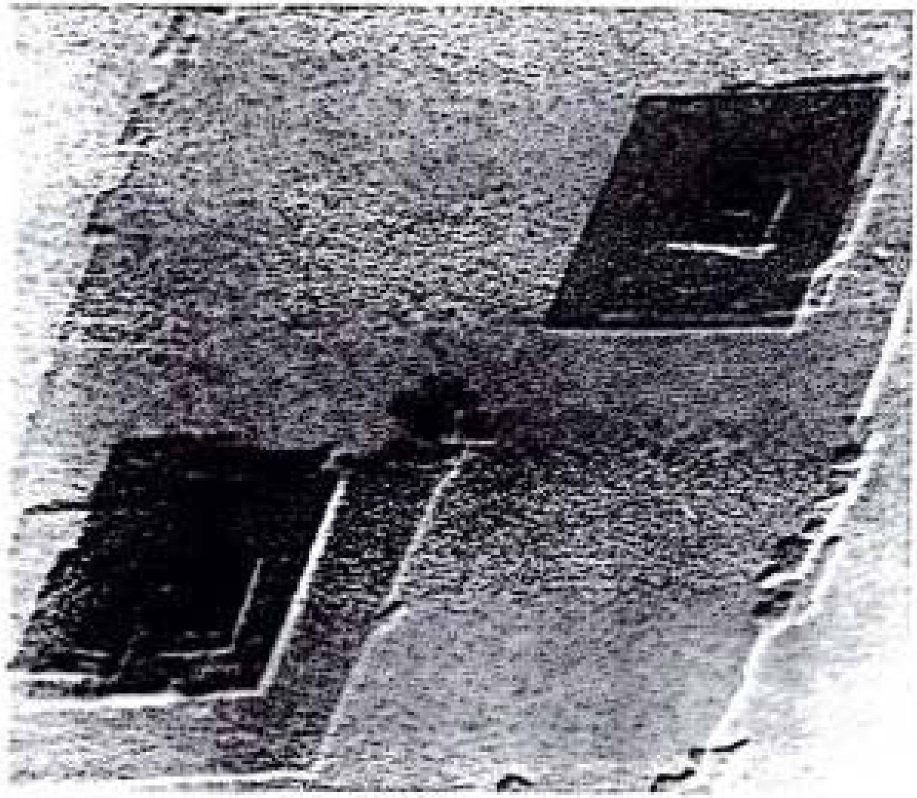


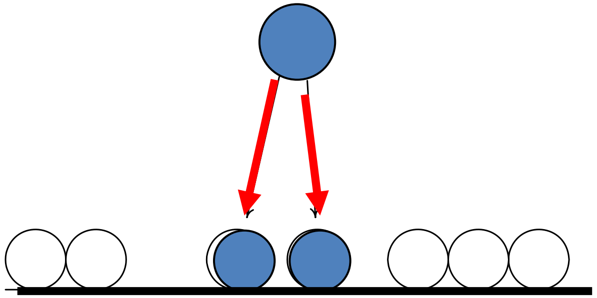
Figure 6.9 Polyethylene single crystal showing spiral growth [After Allen Sharples, "Introduction to Polymer Crystallization," London: Edward Arnold, Ltd., (1966)].

Jackson model of a crystal interface

Ref: K.H. Jackson, “Mechanism of Growth”, in Liquids, Metals, and Solidification, ASM, Cleveland, 1958, p174-186.

-**Thermodynamic Approach**: similar to regular solution

$$\Delta G_m = \Delta H_m - T\Delta S_m$$
$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$



$$\frac{\Delta G_s}{Nk_BT_E} = \alpha\theta(1-\theta) + \theta\ln\theta + (1-\theta)\ln(1-\theta)$$

where $\theta = \frac{N_A}{N}$

$$\frac{\Delta G_s}{Nk_BT_E} = \alpha\frac{N_A}{N^2}(N-N_A) - \ln\left(\frac{N}{N-N_A}\right) - \frac{N_A}{N}\ln\left(\frac{N-N_A}{N_A}\right) \quad (*)$$

$\frac{\Delta G_s}{Nk_BT_E}$: the normalized free energy change per atom added to surface

N: the total number of surface sites

N_A: the number of occupied surface sites

$$\alpha = \left(\frac{\Delta S_f}{k_B}\right) f_k = \left(\frac{\Delta H_f}{k_BT_E}\right) f_k$$

ΔH_f: Latent heat of transformation

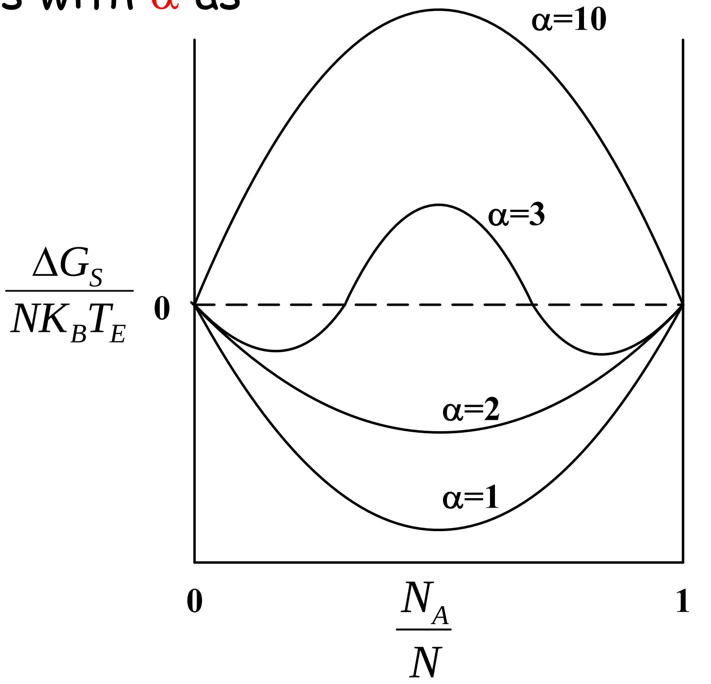
f_k: Crystallographic factor

-Fraction of all nearest neighbors lying in the plane parallel to the face under construction, e.g., (111) in FCC: 6 bonds out of 12 in plane, f_k=0.5.

In other words, α depends upon
(1) Crystallographic factor (f_k)
(2) Thermodynamic factor ($\Delta H_f / T_e$)
which can be used to predict "roughness of surface".

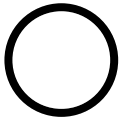
Equation (*) varies with α as

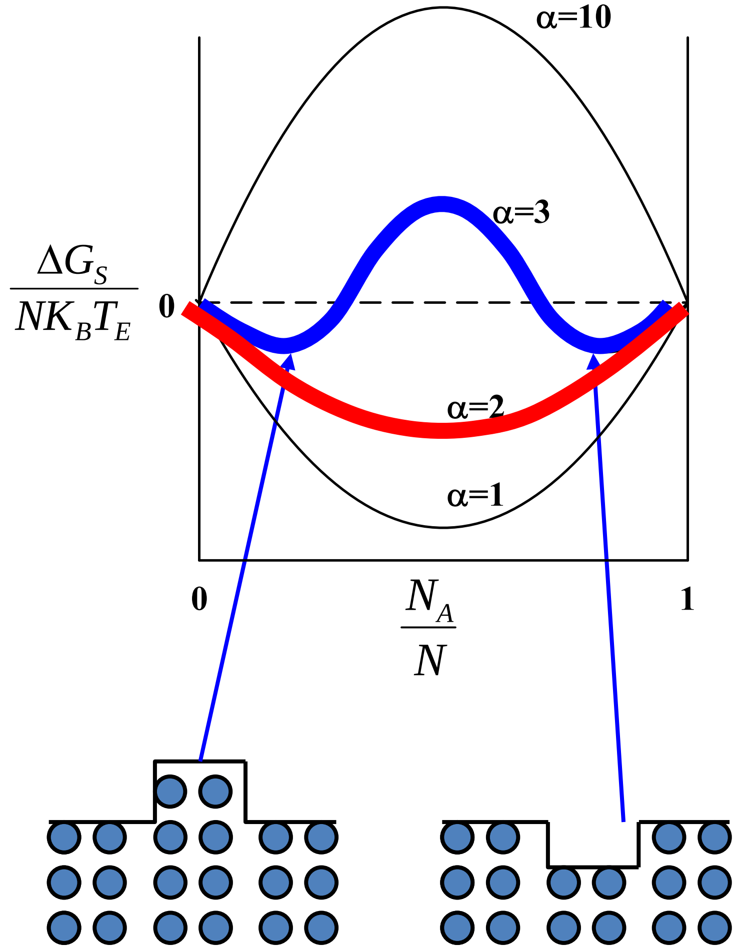
$$\frac{\Delta G_s}{N k_B T_E} = \alpha \frac{N_A}{N^2}(N - N_A) - \ln\left(\frac{N}{N - N_A}\right) - \frac{N_A}{N}\ln\left(\frac{N - N_A}{N_A}\right)$$



0<α<2

- -The lowest free energy occurs when half the available surface sites are filled, i.e., $N_A/N=0.5$. This is a "rough" surface.
- - Little anisotropy in growth rate
- - Normal growth→ non-faceting
- -Micro-roughness → macro-smoothness
- -Diffusion-controlling process mostly





$$\frac{\Delta G_s}{Nk_BT_E} = \alpha\theta(1-\theta) + \theta\ln\theta + (1-\theta)\ln(1-\theta)$$

$$\frac{d(\frac{\Delta G_s}{Nk_BT_E})}{d\theta} = 0 = \alpha(1-2\theta) + \ln\theta - \ln(1-\theta)$$

$$\text{or} \quad \frac{\theta}{1-\theta} = \exp[-\alpha(1-2\theta)]$$

For large α, the minimum is located at

$\theta \approx \exp(-\alpha) \Rightarrow micro-smoothness$

For small α, the minimum is located at

$\theta = \frac{1}{2} \Rightarrow micro-roughness$

$$\frac{d^2(\frac{\Delta G_s}{Nk_BT_E})}{d\theta^2} = -2\alpha + \frac{1}{\theta} + \frac{1}{1-\theta}$$

$$= -2\alpha + 4, \quad \text{for } \theta=\frac{1}{2}$$

So the critical value of α is $\alpha_c = 2$

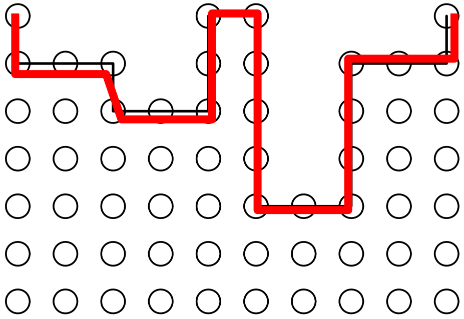
The free energy has two minima for α>2,

and only one, at $\theta=\frac{1}{2}$ for α<2.

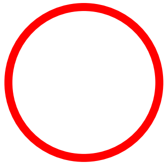
$\alpha > 2$

- The lowest free energy occurs when there are new extra atoms on the plane and a few atoms missing from the plane below. This is a "smooth" surface.
- Surface nucleation required
- Growth rate → anisotropy → faceting
- Macro-roughness → micro-smoothness
- Interface-controlling process mostly

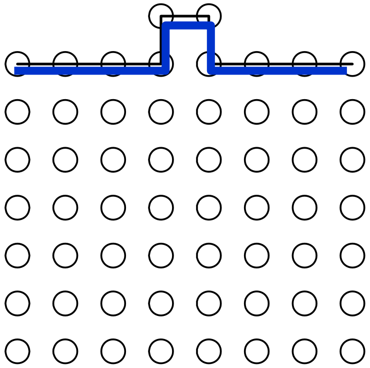
Low α



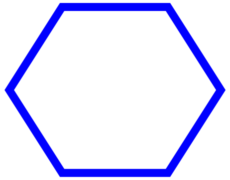
Micro-roughness
Macro-smoothness
Non-faceting



High α



Micro-smoothness
Macro-roughness
Faceting



$\frac{\Delta H_f}{RT_E} < 2$

- Most metals in solid-liquid transformation
- Inorganic glass formers such as SiO_2 (α=0.6) and GeO_2 (α =1.3)

$\frac{\Delta H_f}{RT_E} > 2$

- Most organics on solidification
- Multi-component inorganic glass/metallic oxide systems

$Na_2O \cdot 2SiO_2\ (\alpha = 4)$

$PbO \cdot 2B_2O_3\ (\alpha = 30)$

Tri-α-naphthylbenzene $(\alpha = 10.7)$

$\frac{\Delta H_f}{RT_E} \approx 2$

- Semimetals

$Ga\ (\alpha = 2.2), Bi(\alpha = 2.4)$

- Elementary semiconductors

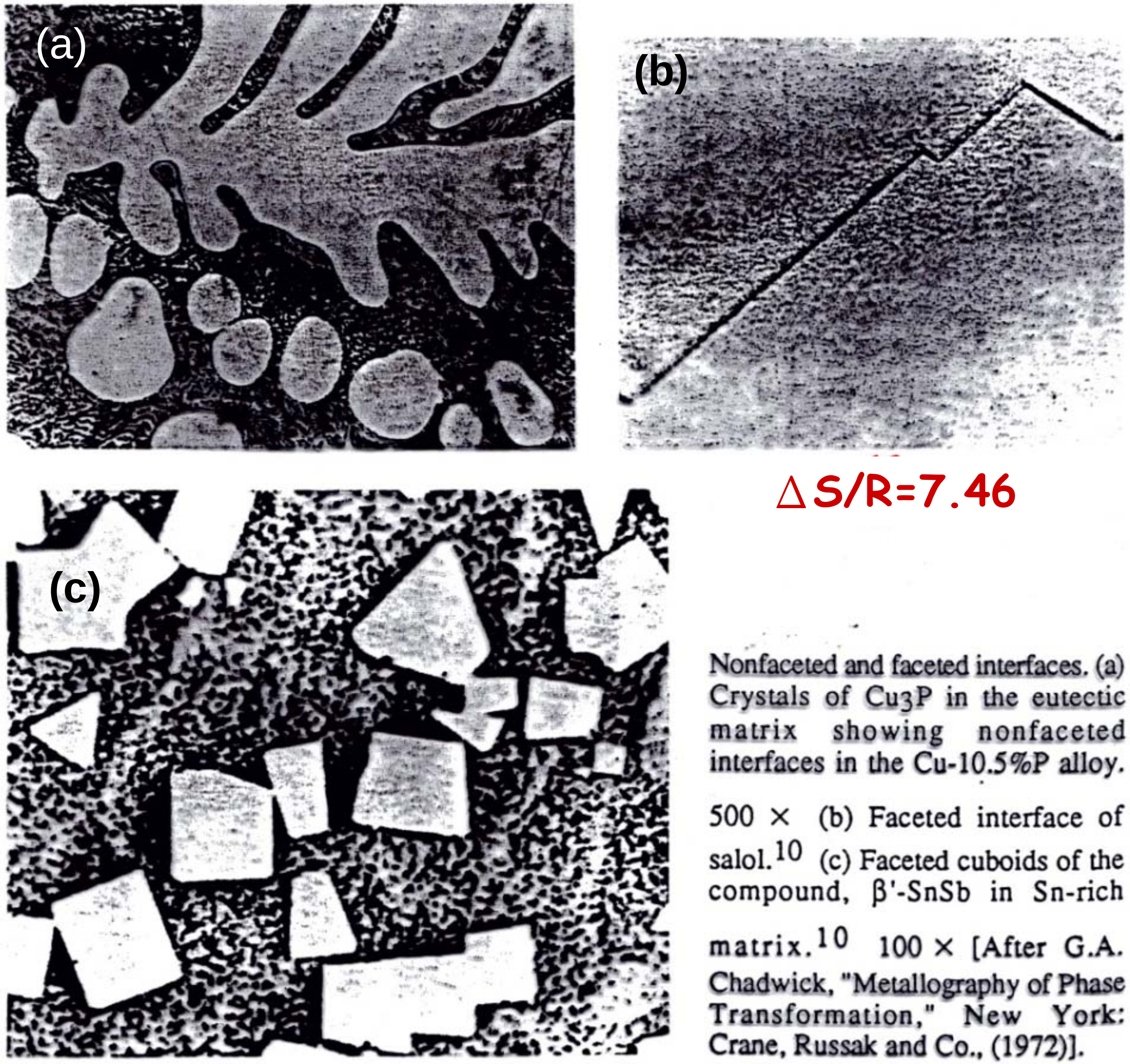
$Si\ (\alpha = 3.24), Ge(\alpha = 3.0), H_2O(\alpha = 2.63)$

e.g., (111) faces of Si and Ge

$$f_k = \frac{3}{4}, \quad \alpha > 2$$

-For small ∆T, both grow with large flat surface
→faceting

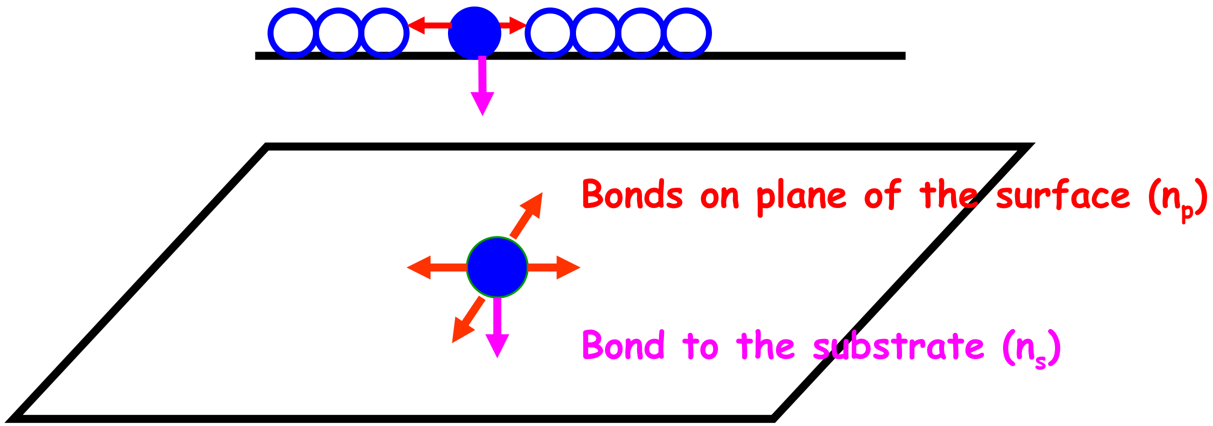
-At large ∆T (30K for Ge and 90K for Si) flat surface disappears→ roughness in the form of dendrites.



$\Delta S/R=7.46$

Nonfaceted and faceted interfaces. (a) Crystals of Cu_3P in the eutectic matrix showing nonfaceted interfaces in the Cu-10.5%P alloy. 500 × (b) Faceted interface of salol.[10] (c) Faceted cuboids of the compound, β'-SnSb in Sn-rich matrix.[10] 100 × [After G.A. Chadwick, "Metallography of Phase Transformation," New York: Crane, Russak and Co., (1972)].

f_k

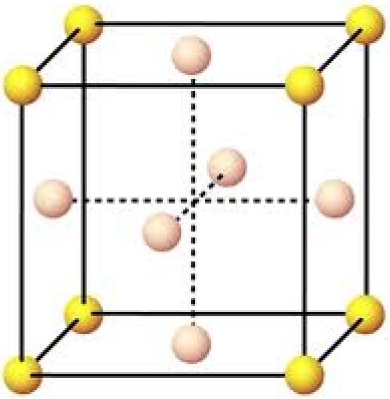


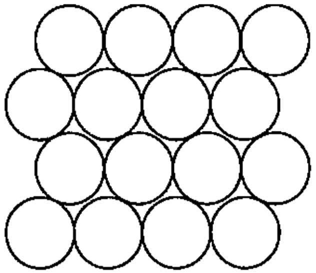
$$Z = n_P + 2n_S$$

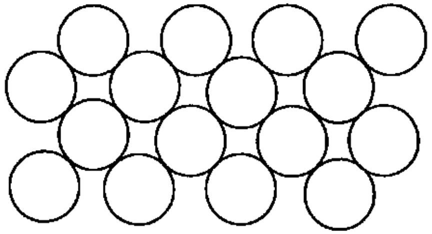
Z : the total number of nearest neighbors

$$f_k = \frac{n_P}{Z}$$

for FCC (111) 1/2; (100) 1/3, (110) 1/6




111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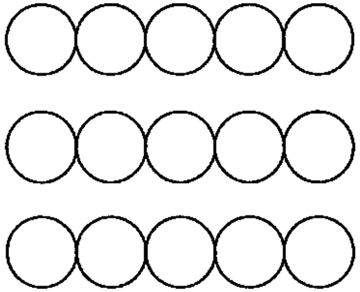
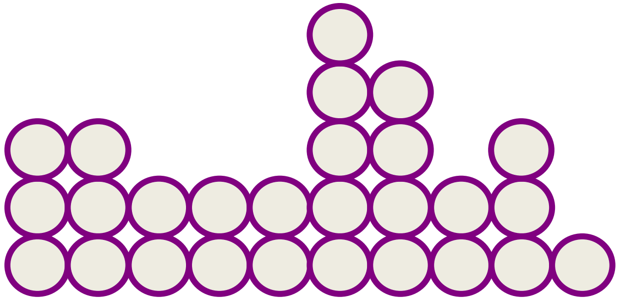
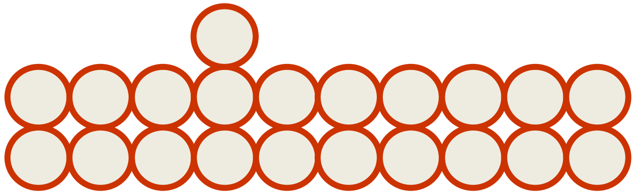

220

Low entropy change



High entropy change



$$\Delta S_f = \frac{\Delta H_f}{T_E} : \text{entropy change on crystallization}$$

Metals from the melt	1
Si, Ge, Sb, Ga from the melt	3
Many organic compounds	6
Metals from the vapor	10
Complex molecules	20
Polymers	>100

Homogeneous Nucleation in Solids with Composition Change

$T_e \rightarrow T_2$

$\alpha \rightarrow \alpha + \beta$

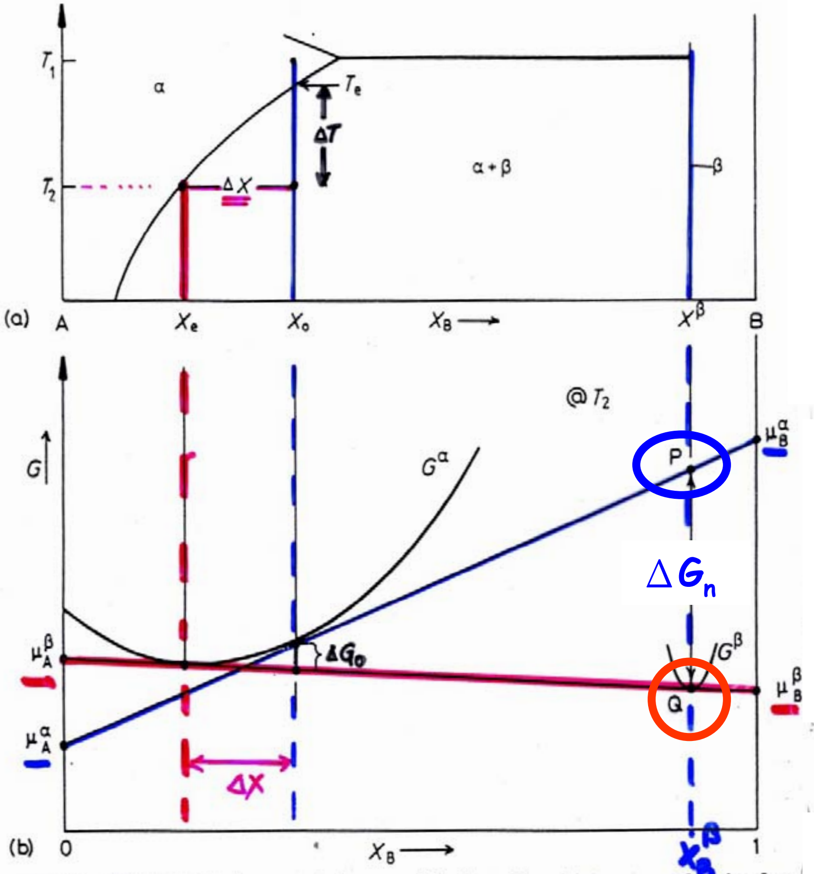


Fig. 5.3 Free energy changes during precipitation. The driving force for the first precipitates to nucleate is $\Delta G_n = \Delta G_v V_m$. ΔG_0 is the total decrease in free energy when precipitation is complete and equilibrium has been reached.

Composition change

$X_0 \rightarrow X_e + X^\beta \ (\Delta X = X_0 - X_e)$

Total free energy change: ΔG_0

To nucleate β in α phase, however, the composition does not change significantly

$X_0 \approx X_0^\alpha$

Free energy change: ΔG_n (nucleation)

At point P: per mole of β removed from α phase

$$\Delta G_P = X_A^\beta \mu_A^\alpha + X_B^\beta \mu_B^\alpha$$

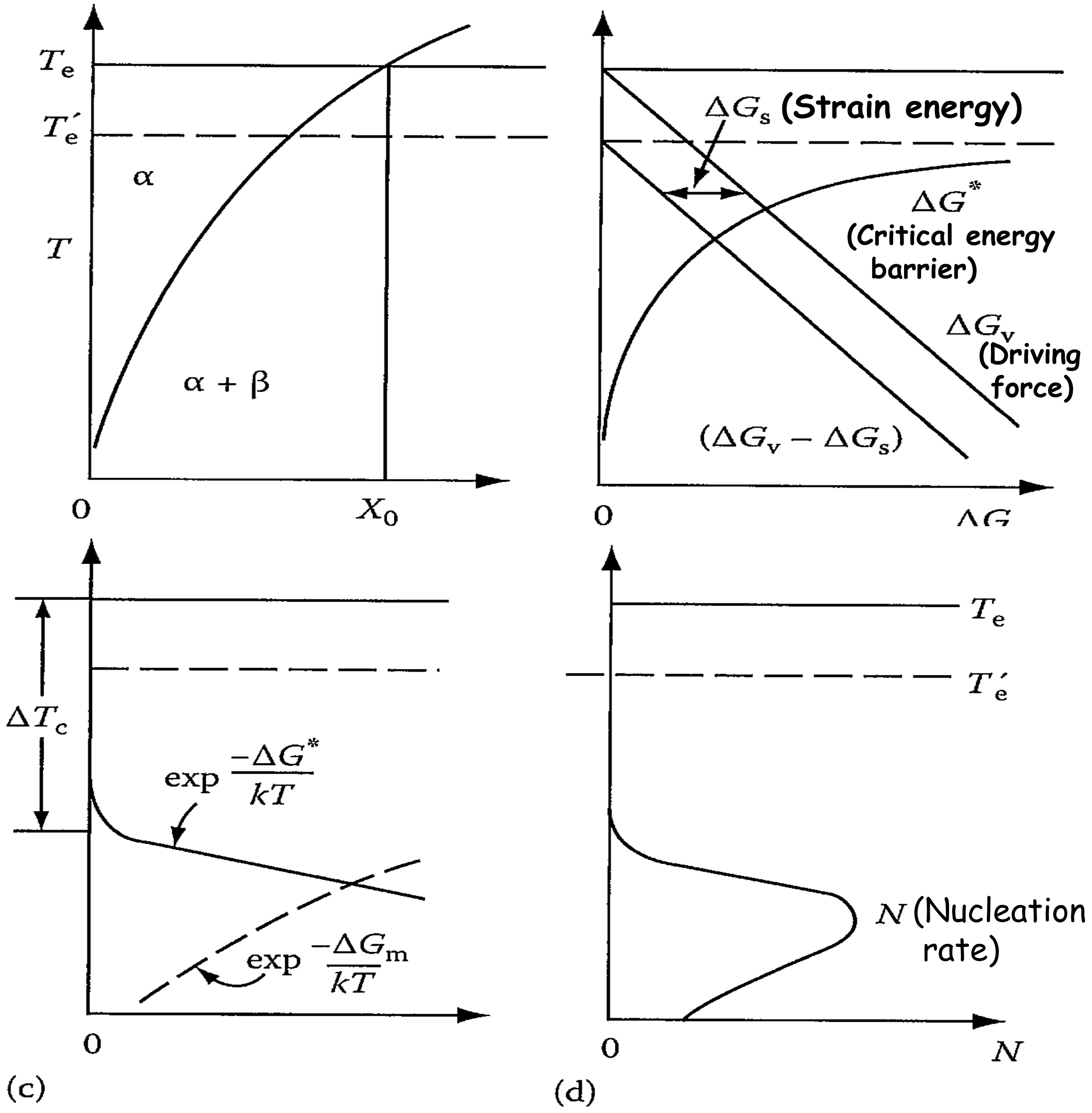
At Point Q: per mole of β formed

$$\Delta G_Q = X_A^\beta \mu_A^\beta + X_B^\beta \mu_B^\beta$$

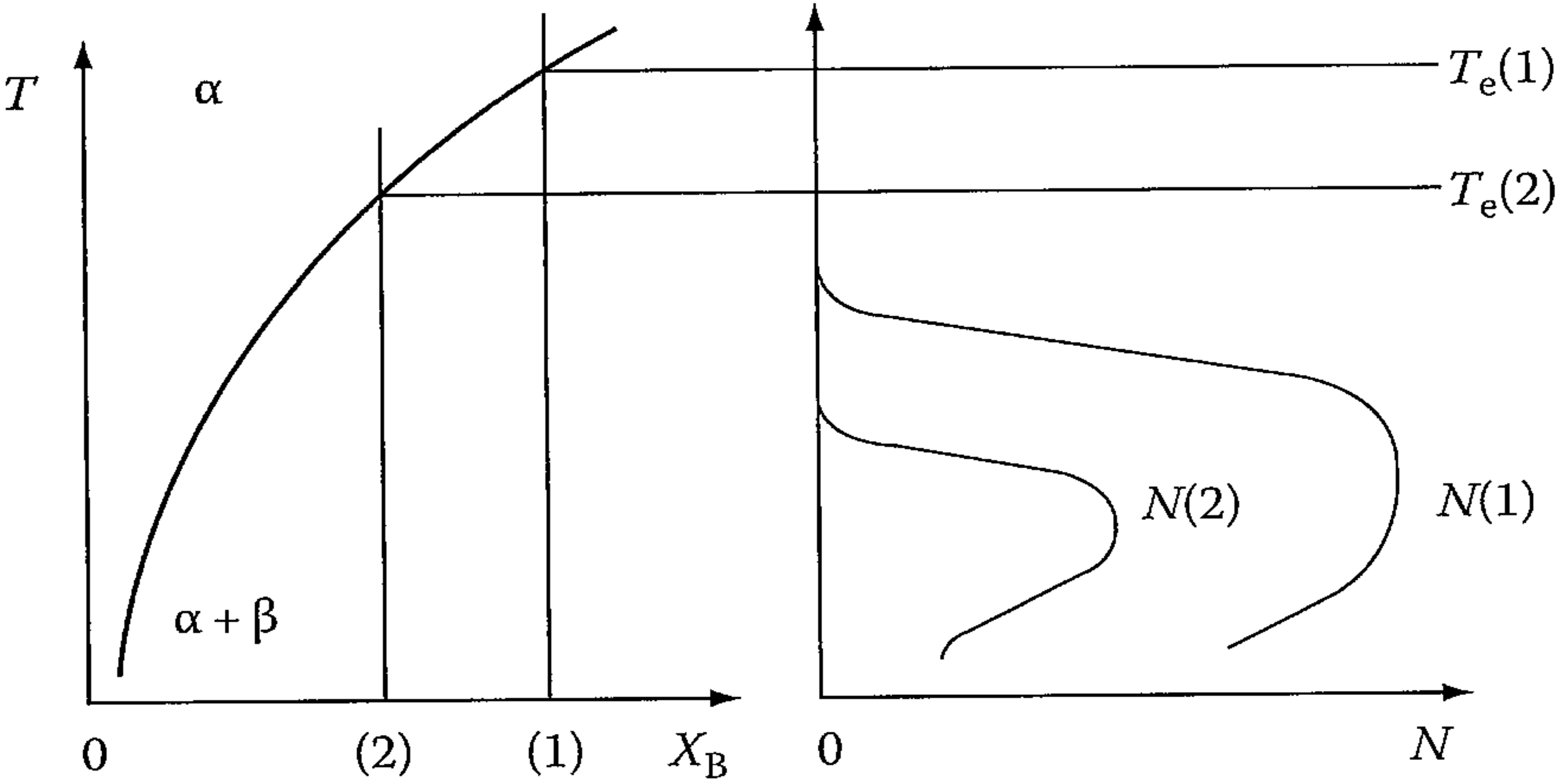
$$\Delta G_n = \Delta G_P - \Delta G_Q = X_A^\beta (\mu_A^\alpha - \mu_A^\beta) + X_B^\beta (\mu_B^\alpha - \mu_B^\beta)$$

:Driving force for nucleation

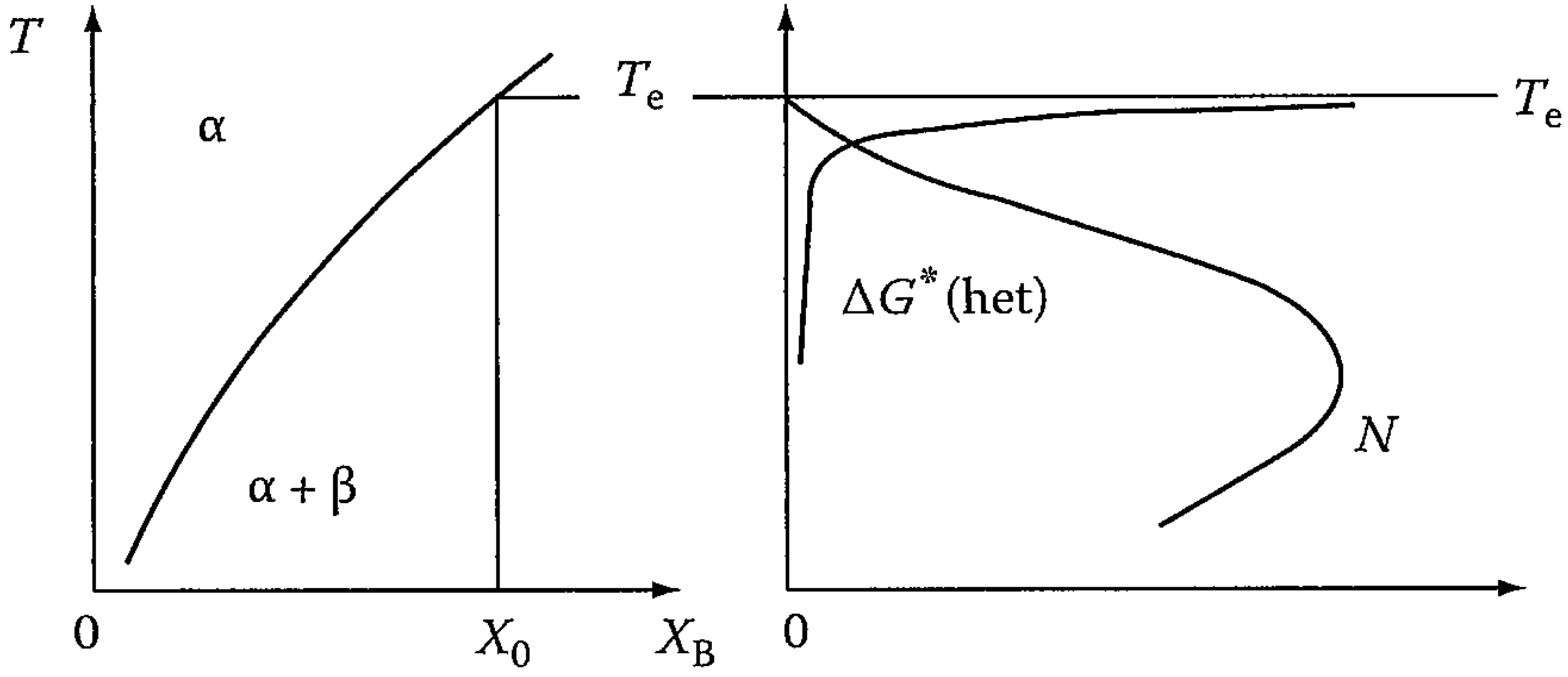
Effects of Interfacial Strain Energy on Homogeneous Nucleation in Solids



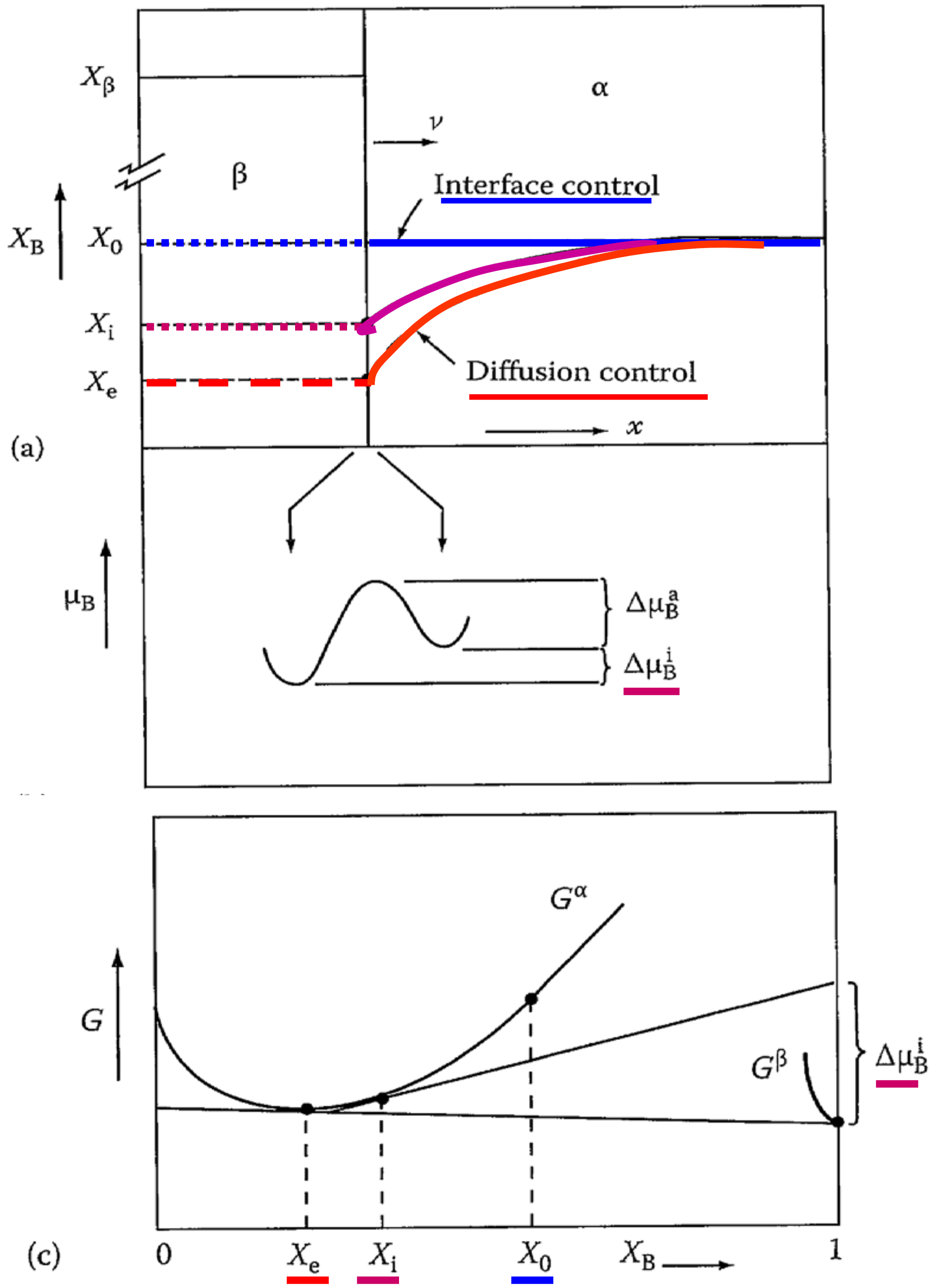
Effects of Alloy Composition on Nucleation Rate



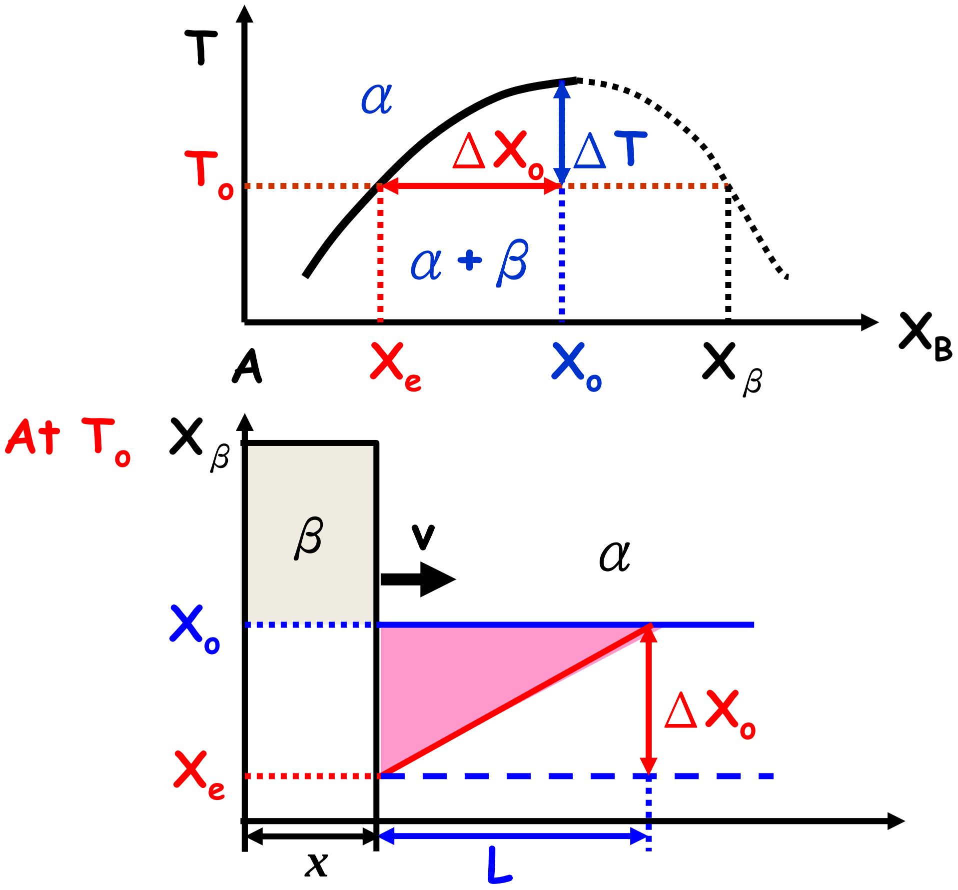
Effects of Undercooling on Heterogeneous Nucleation Rate



Growth Kinetics with Composition Change



Diffusion Controlling Growth with Composition Change

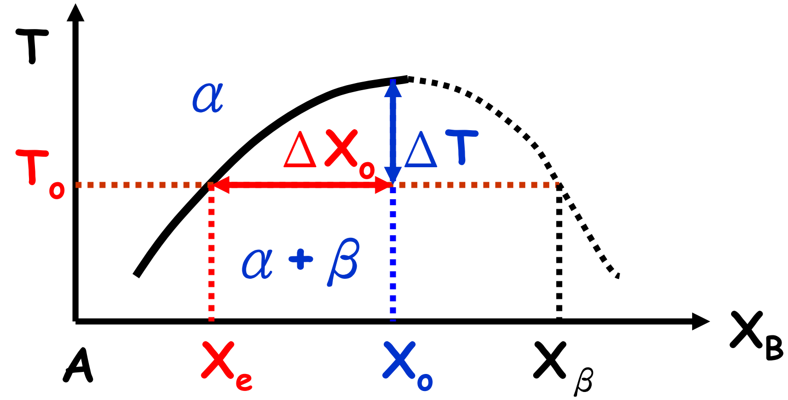


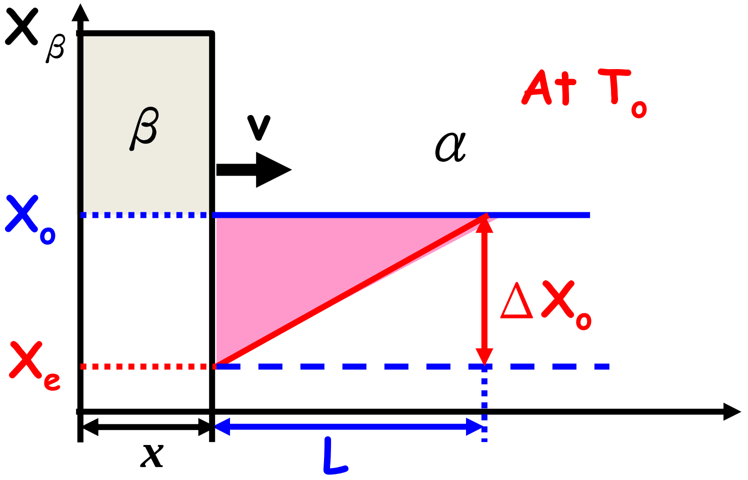
$$J = C \cdot v$$

$$v = \frac{dx}{dt} = \frac{J}{C} = \frac{D\, dC/dx}{(X_\beta - X_e)}$$

(-) : toward right

Diffusion Controlling Growth with Composition Change





$$J = C \cdot v$$

$$v = \frac{dx}{dt} = \frac{D\, {}^{dX}\!/_{dx}}{(X_\beta - X_e)}$$

(-): toward right

The same area (Accumulation = Depletion)

$$(X_\beta - X_o)\cdot x = (X_o - X_e)\cdot {}^{L}\!/_{2} = \Delta X_o \cdot {}^{L}\!/_{2}$$

$$v = \frac{dx}{dt} = \frac{D\, {}^{dX}\!/_{dx}}{(X_\beta - X_e)} = \frac{D\, {}^{\Delta X_o}\!/_{L}}{(X_\beta - X_e)}$$

$$\because {}^{dX}\!/_{dx} \approx {}^{\Delta X_o}\!/_{L}$$

$$\because L = \frac{2(X_\beta - X_o)\cdot x}{\Delta X_o}$$

$$v = \frac{dx}{dt} = \frac{D(\Delta X_o)^2}{2(X_\beta - X_e)(X_\beta - X_o)\cdot x}$$

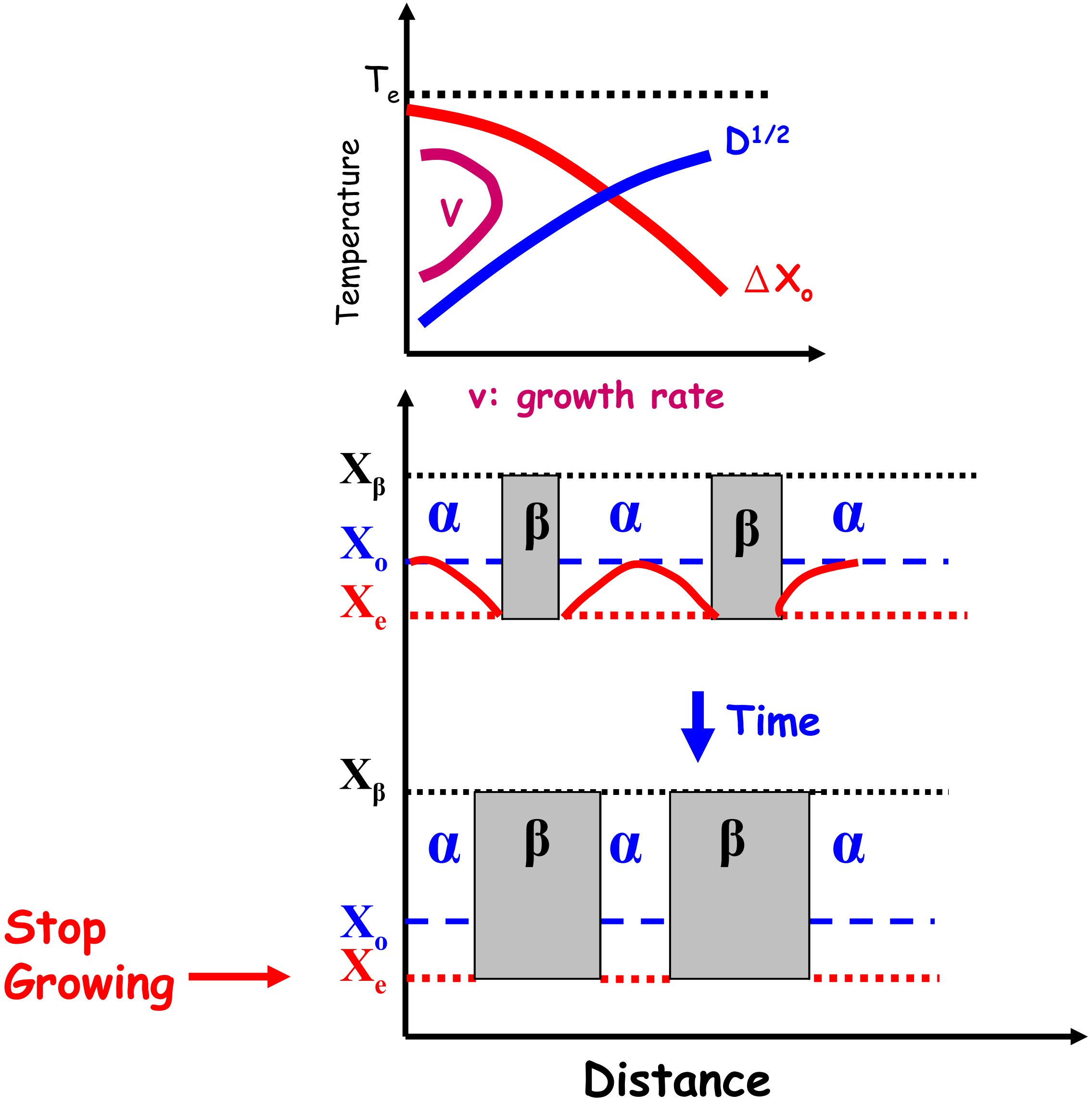
$$x = \frac{\Delta X_o}{[(X_\beta - X_e)(X_\beta - X_o)]^{1/2}}\sqrt{Dt}$$

X : molar fraction

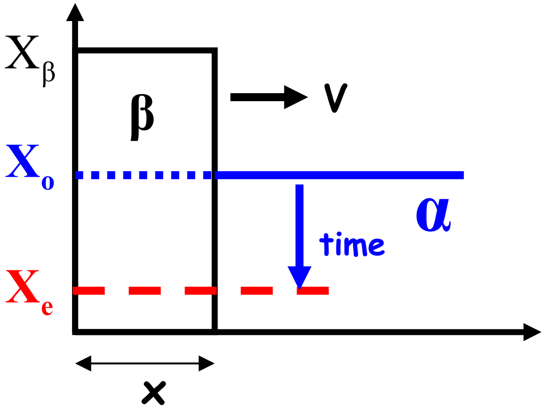
x : thickness of precipitate

$$v = \frac{dx}{dt} = \frac{\Delta X_o}{2[(X_\beta - X_e)(X_\beta - X_o)]^{1/2}} \sqrt{\frac{D}{t}}$$

→ Parabolic Growth Rate



Reaction Controlling Growth Kinetics with Composition Change



$$v = \frac{dx}{dt} = \frac{J}{C} = \frac{K_S(X_o - X_e)}{(X_\beta - X_o)}$$

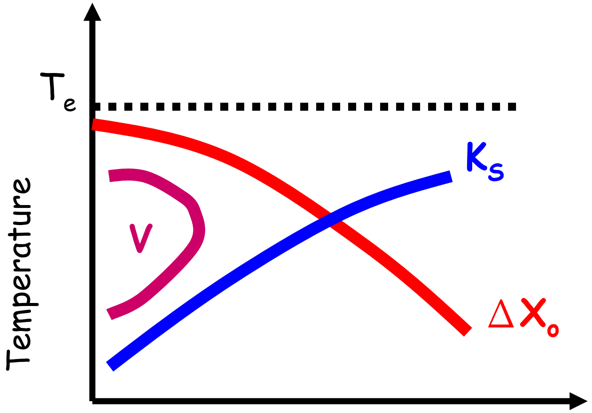
K_S: Reaction rate constant at the interface of α/β, assuming first order chemical reaction

$$x = \frac{K_S(X_o - X_e)}{(X_\beta - X_o)} \cdot t = \frac{K_S \Delta X_o}{(X_\beta - X_o)} \cdot t$$

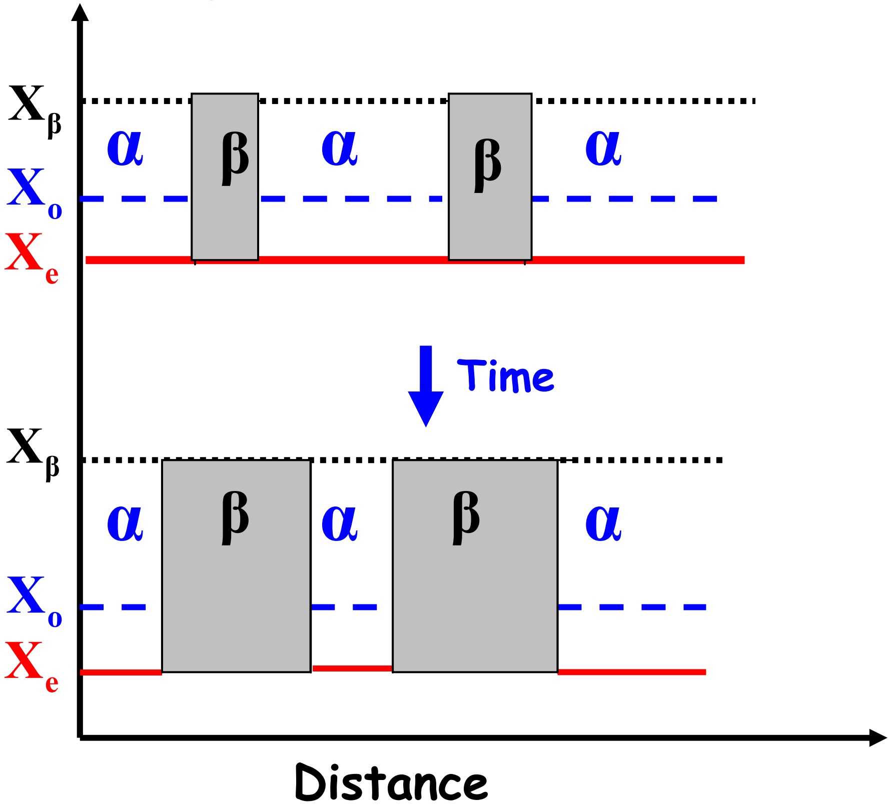
$$v = \frac{dx}{dt} = \frac{K_S \Delta X_o}{(X_\beta - X_o)} = \frac{K_S \Delta X_o}{(X_\beta - X_e - \Delta X_o)}$$

v is constant only at the early stage of growth or when $\Delta X_o \Rightarrow 0$;

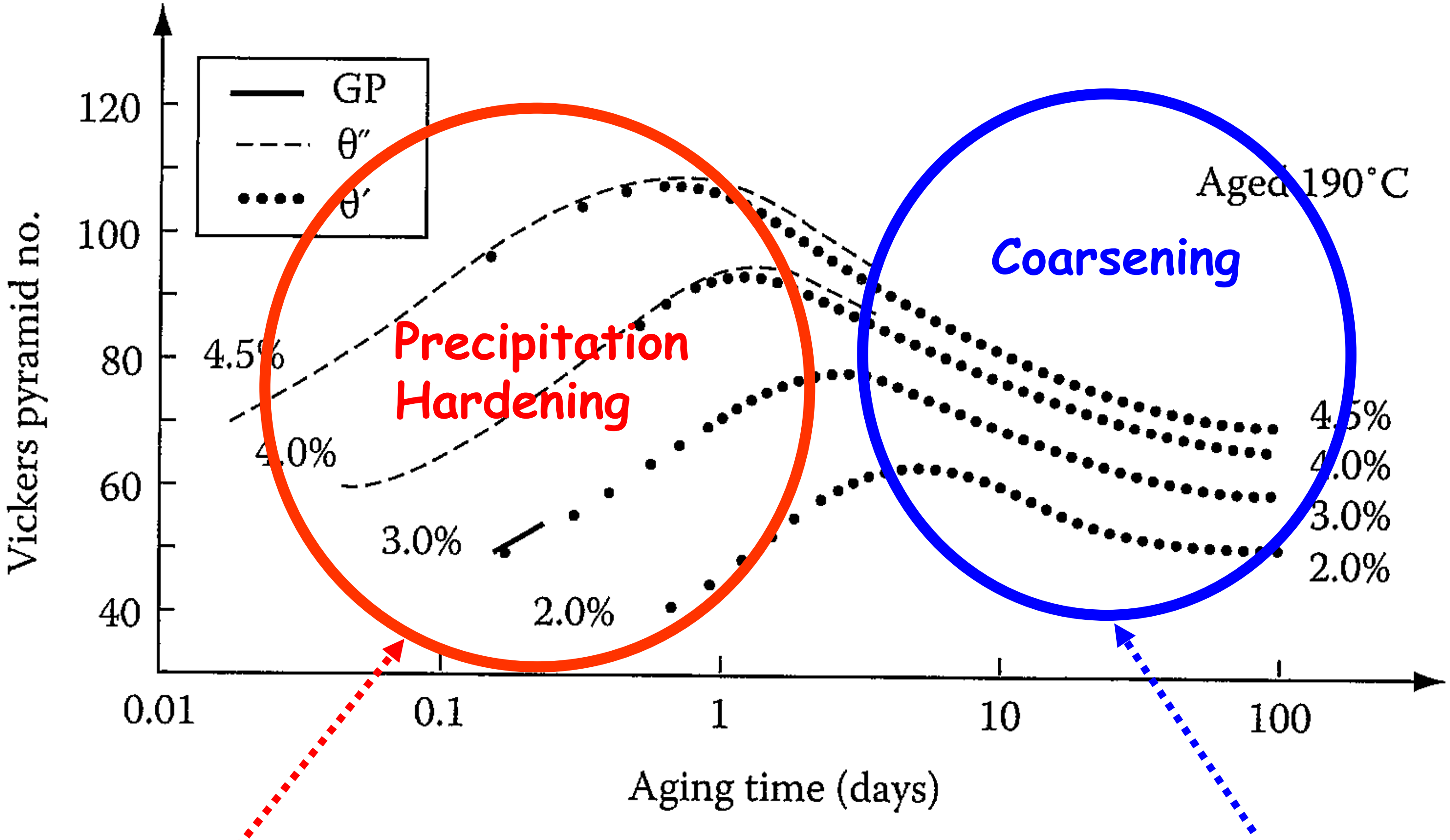
otherwise v decreases with increasing time because X_o keeps reducing.

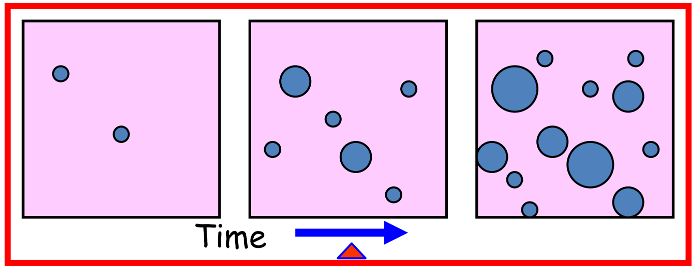


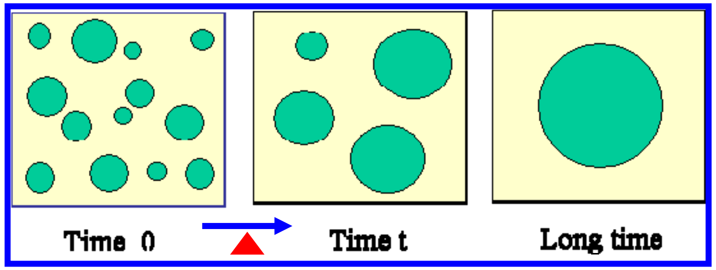
v: growth rate



Age Hardening of Al-Cu Alloys







Isothermal Kinetics of Transformation by Nucleation and Growth

1. J. W. Christian, p15-22, (1975).
2. Johnson and Mehl, Trans. AIME, 135, 416 (1939)
3. Avrami, J. Chem. Phys., 7, 1103 (1939); Avrami, J. Chem. Phys., 8, 212 (1940); Avrami, J. Chem. Phys., 9, 177 (1941)
4. Burke and Turnbull, Prog. In Metal Phys., 3, 220 (1952)

Goal: Develop kinetic equations for volume fraction transformed (X vs. t)

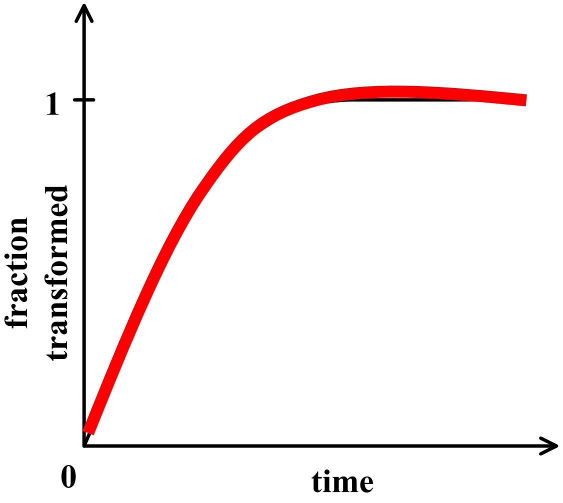
In a homogeneous reaction, the volume transforming in a short time interval is proportional to the volume remaining untransformed at the beginning of this interval, and this leads to a first order rate reaction process.

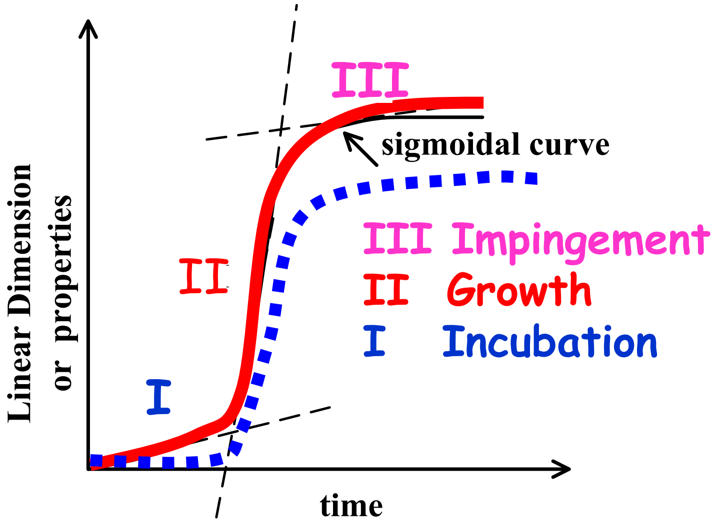
For a reaction $\alpha \rightarrow \beta$

$$\frac{dV^{\beta}}{dt} = k(V - V^{\beta})$$

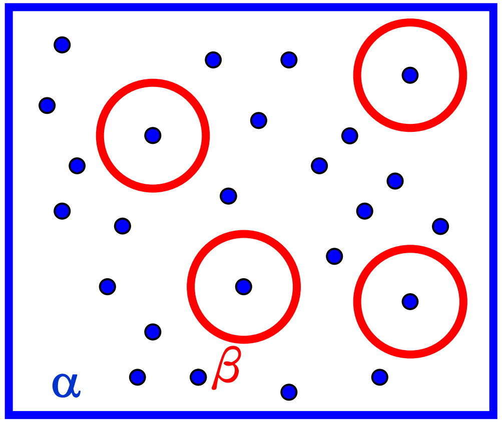
$$\frac{V^{\beta}}{V} = 1 - \exp(-kt) = X \quad \text{(Volume fraction transformed)}$$

where V is the total volume, V^{β} is the transformed volume and k is the rate constant.





Formal Theory of Transformation Kinetics



- Randomness of active nucleation sites
- ^{V}I (Nucleation Rate) = number of nuclei formed per unit volume of α per unit time
- Number of particles formed between τ and τ +d τ =$^{V}IV^{\alpha}d\tau$ where τ is an incubation time.
- Volume of each β particle formed is

$$t<\tau,\ V_{\tau}^{\beta}=0$$

$$t>\tau,\ V_{\tau}^{\beta}=\frac{4\pi}{3}[u(t-\tau)]^{3}$$

assuming that u is constant in time, which is true for the system without composition change.

At early stage of transformation, $V^{\beta} \ll V^{\alpha}$ and impingement can be ignored, and volume of β phase increases as

$$dV^{\beta}=V_{\tau}^{\beta}\,{}^{V}I\,V^{\alpha}d\tau$$

V_{τ}^{β} : **Volume of each β particle**

$^{V}IV^{\alpha}d\tau$: number of particles formed

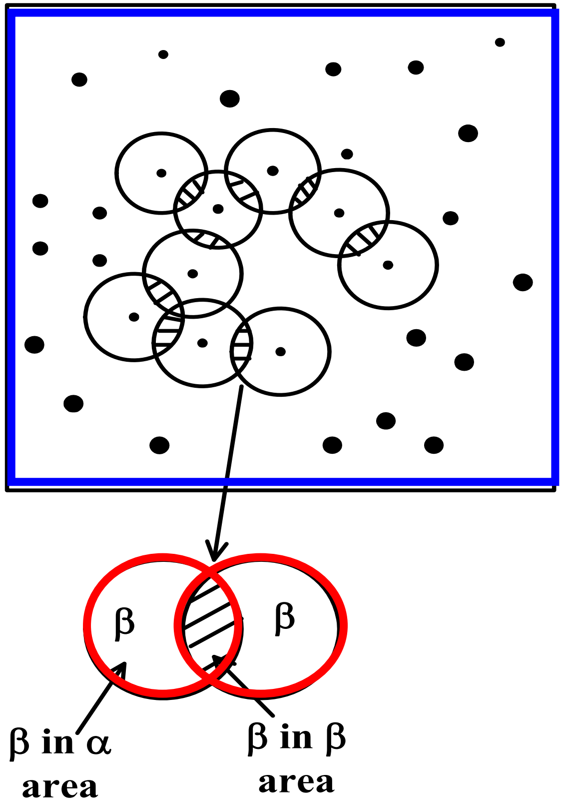
$$V^{\beta}=\frac{4\pi}{3}V\int_{0=\tau}^{t=\tau}{}^{V}Iu^{3}(t-\tau)^{3}dt$$

$$V=V^{\alpha}+V^{\beta}$$

Assuming that ^{V}I and u are constants

$$X=\frac{V^{\beta}}{V}=\frac{\pi}{3}{}^{V}Iu^{3}t^{4}$$

∵ $V^{\beta} \ll V^{\alpha}$, $V \approx V^{\alpha}$
at early stage of transformation



Mutual interference or impingement need to be considered at later stage of transformation. In this case, there are ${}^{V}IV^{\alpha}d\tau$ newly transformed regions nucleated in the α area, and ${}^{V}IV^{\beta}d\tau$ newly transformed regions nucleated in the β area, and Arvami called ${}^{V}IV^{\beta}d\tau$ as phantom nuclei and defined an "extended volume" of transformed material V_e^{β}

$$dV_e^{\beta} = ({}^{V}IV^{\beta}d\tau + {}^{V}IV^{\alpha}d\tau)V_{\tau}^{\beta}$$

$$= (V^{\alpha} + V^{\beta})({}^{V}Id\tau)V_{\tau}^{\beta}$$

$$= (V)({}^{V}Id\tau)(\frac{4\pi}{3}[u(t-\tau)]^3)$$

$$V_e^{\beta} = \frac{4\pi}{3}V\int_0^t {}^{V}Iu^3(t-\tau)^3\,dt$$

V_e^{β} differs from the actual volume of transformed materials:

(1) it counts phantom regions, nucleated in already transformed area

(2) treating all regions as though they continue growing irrespective of other regions

$$dV^{\beta} = (1 - \frac{V^{\beta}}{V})dV_e^{\beta}$$

fraction of increment due to transformation occurring in α phase

$$V_e^{\beta} = -V\ln(1-\frac{V^{\beta}}{V})$$

Substituting into $$V_e^{\beta} = \frac{4\pi}{3}V\int_0^t {}^{V}\mathrm{I}u^3(t-\tau)^3\,d\tau$$

$$\ln(1-X) = -\frac{4\pi}{3}u^3\int_0^t {}^{V}\mathrm{I}(t-\tau)^3\,d\tau$$

$$X = 1-\exp(-\frac{\pi u^3\,{}^{V}\mathrm{I}t^4}{3})$$

(assuming ^{v}I and *u* are constants)

Early stage of transformation (t→0)

$$X = \frac{\pi}{3}\,{}^{V}\mathrm{I}u^3t^4$$

Note: In general, ^{v}I is not constant, but may either increase or decrease with time.

Avrami assumed that nucleation rate was not fixed

$${}^{V}\mathrm{I} = f(t)$$

$${}^{V}N = {}^{V}N_0\exp(-\upsilon t)$$

$^{v}N_o$: number of nucleation sites per unit volume initially

$${}^{V}\mathrm{I(t)} = -\frac{d\,{}^{V}N}{dt} = {}^{V}N_0\upsilon\exp(-\upsilon t) = {}^{V}N\upsilon$$

$$\ln(1-X) = \frac{4\pi}{3}u^3\int_0^t {}^{V}\mathrm{I}(t-\tau)^3\,d\tau$$

$$= \frac{4\pi}{3}u^3\int_0^t {}^{V}N_0\upsilon\exp(-\upsilon t)(t-\tau)^3\,d\tau$$

Integrating by parts gives

$$X = 1-\exp[(\frac{-8\pi\, {}^{v}N_0 u^3}{\upsilon^3})\{\underbrace{\exp(-\upsilon t)-1+\upsilon t-\frac{\upsilon^2 t^2}{2}+\frac{\upsilon^3 t^3}{6}}_{(**)}\}]$$

Two limiting cases

(1) ν t is small, implying that ^{v}I is constant

$$e^{-\upsilon t} = 1-\upsilon t+\frac{\upsilon^2 t^2}{2}-\frac{\upsilon^3 t^3}{6}+\frac{\upsilon^4 t^4}{24}-\frac{\upsilon^5 t^5}{120}+\ldots\ldots$$

$$\because \text{small } \upsilon t,\quad {}^{V}\mathrm{I}(t) = {}^{v}N_0\upsilon\exp(-\upsilon t) \cong {}^{v}N_0\upsilon$$

Eq (**) becomes $\upsilon^4 t^4/24$

3-Dimension, spherical ^{v}I and u are constant, n=4 in $X=1-\exp(-kt^n)$

$$X = 1-\exp[(\frac{-8\pi\, {}^{v}N_0 u^3}{\upsilon^3}\cdot\frac{\upsilon^4 t^4}{24})$$

$$= 1-\exp[\frac{-\pi\, {}^{v}N_0 \upsilon u^3 t^4}{3}]$$

$$= 1-\exp[\frac{-\pi\, {}^{V}\mathrm{I} u^3 t^4}{3}]$$

→ the same as that of constant ^{v}I and u.

(2) ν t is large, indicating that ^{v}I goes to zero quickly. All nucleation centers will be exhausted at early stage of the transformation

Eq (**) becomes $\upsilon^3 t^3/6$

$$Note:\ \exp(-\upsilon t)-1+\upsilon t-\frac{\upsilon^2 t^2}{2}+\frac{\upsilon^3 t^3}{6} \approx \frac{\upsilon^3 t^3}{6} \qquad (\exp(-\upsilon t)=0 \text{ when } \upsilon \text{ is large})$$

$$X = 1 - \exp[(\frac{-8\pi\,{}^{v}N_0 u^3}{\upsilon^3} \cdot \frac{\upsilon^3 t^3}{6})$$

$$= 1 - \exp[\frac{-4\pi\,{}^{v}N_0 u^3 t^3}{3}]$$

3-Dimension, spherical
${}^{v}I=0$, and u is constant,
n=3 in $X=1-\exp(-kt^{n})$

→ Nucleation is rapid, and X is controlled by growth.

Avrami proposed that a 3-D nucleation and growth process, the equation of transformation kinetics is

$$X = 1 - \exp(-kt^n) \qquad (*)$$

$$or \quad X = 1 - \exp(-(kt)^n)$$

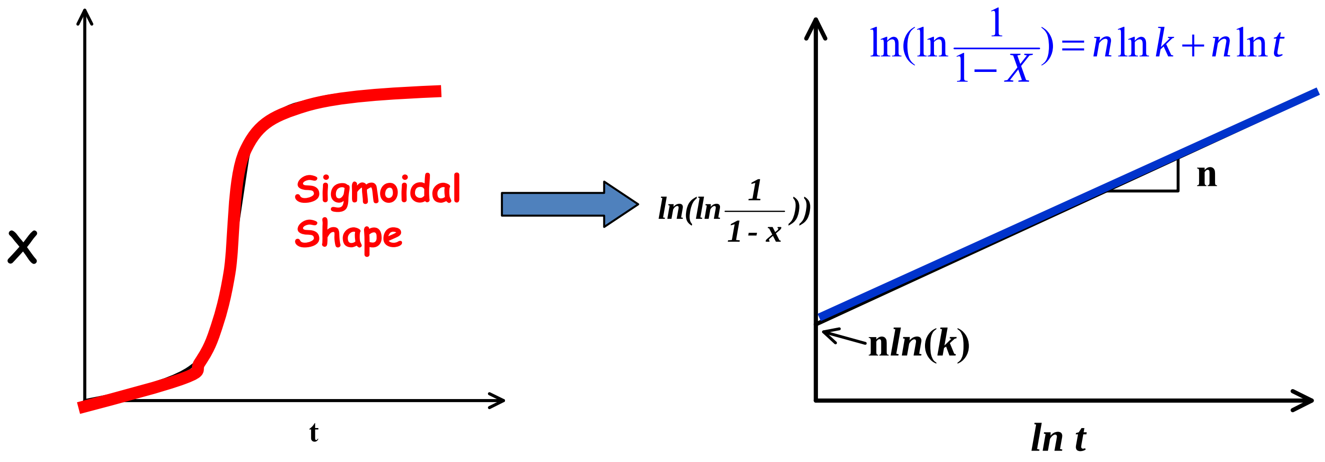
where 3≤n≤4. This should cover all cases in which ${}^{v}I$ is some decreasing function of time, up to the limit when ${}^{v}I$ is constant.

Note that the above equation (*) is similar to chemical reaction kinetics of many heterogeneous systems

$$\frac{dX}{dt} = nk^n t^{n-1}(1-X)$$

$$X = 1 - \exp(-(kt)^n)$$

$$\ln(\ln\frac{1}{1-X}) = n\ln k + n\ln t$$



$$\ln(\ln\frac{1}{1-X}) = n\ln k + n\ln t$$

3-D: Volume of transformed region = $\frac{4\pi}{3}[u(t-\tau)]^3$

2-D: Volume of transformed region = $\pi\delta\cdot[u(t-\tau)]^2$

1-D: Volume of transformed region = $\pi\delta^2 u(t-\tau)$

Diffusion-controlling Growth
(Parabolic growth,
$x=kt^{1/2}$, and $u=kt^{-1/2}/2$)

	n (Constant ^{v}I)	n (Zero ^{v}I)
3-D	2.5	1.5
2-D	2.0	1.0
1-D	1.5	0.5

Reaction-controlling Growth
(Linear growth, $x=kt$, and $u=k$)

	n (Constant ^{v}I)	n (Zero ^{v}I)
3-D	4	3
2-D	3	2
1-D	2	1

Parabolic Growth

$x = k\sqrt{t}$, $u = \frac{dx}{dt} = \frac{k}{2\sqrt{t}}$

volume of transformed region=

$3-D: \frac{4\pi}{3}u^3t^3$

$2-D: \pi\delta u^2t^2$

$1-D: \pi\delta^2 ut$

^{v}I is constant, u α $t^{-1/2}$

3-D

$$\ln(1-x) = -\frac{4\pi}{3}\int_0^t {}^{v}Iu^3t^3dt$$

$$x = 1-\exp(-\frac{\pi}{15}{}^{v}I\cdot k^3t^{\frac{5}{2}})$$

2-D

$$\ln(1-x) = -\pi\delta\int_0^t {}^{v}Iu^2t^2dt$$

$$x = 1-\exp(-\pi\delta\,{}^{v}I\cdot\frac{k^2}{8}t^2)$$

1-D

$$\ln(1-x) = -\pi\delta^2\int_0^t {}^{v}I\cdot u\cdot tdt$$

$$x = 1-\exp(-\pi\delta^2\,{}^{v}I\cdot\frac{k}{3}t^{\frac{3}{2}})$$

^{v}I=0, u α $t^{-1/2}$, number of nuclei=N_0

3-D

$$\ln(1-x) = -\frac{4\pi}{3}N_0u^3t^3$$

$$x = 1-\exp(-\frac{\pi}{6}N_0k^3t^{\frac{3}{2}})$$

2-D

$$\ln(1-x) = -\pi\delta N_0u^2t^2$$

$$x = 1-\exp(-\pi\delta N_0\frac{k^2}{4}t)$$

1-D

$$\ln(1-x) = -\pi\delta^2N_0u\cdot t$$

$$x = 1-\exp(-\pi\delta^2N_0\frac{k}{2}\cdot t^{\frac{1}{2}})$$

Linear Growth

$$x=kt, \quad u=\frac{dx}{dt}=k$$

volume of transformed region=

$$3-D: \frac{4\pi}{3}u^3t^3$$

$$2-D: \pi\delta u^2t^2$$

$$1-D: \pi\delta^2 ut$$

${}^{v}I$, and u are constant

3-D

$$\ln(1-x) = -\frac{4\pi}{3}\int_0^t {}^{v}Iu^3t^3dt$$

$$x = 1-\exp(-\frac{\pi}{3}\,{}^{v}Iu^3t^4)$$

2-D

$$\ln(1-x) = -\pi\delta\int_0^t {}^{v}Iu^2t^2dt$$

$$x = 1-\exp(-\pi\delta\,{}^{v}Iu^2\frac{t^3}{3})$$

1-D

$$\ln(1-x) = -\pi\delta^2\int_0^t {}^{v}I\cdot u\cdot tdt$$

$$x = 1-\exp(-\pi\delta^2\,{}^{v}I\cdot u\frac{t^2}{2})$$

${}^{v}I=0$, u=constant, number of nuclei=N_0

3-D

$$\ln(1-x) = -\frac{4\pi}{3}N_0u^3t^3$$

$$x = 1-\exp(-\frac{4\pi}{3}N_0u^3t^3)$$

2-D

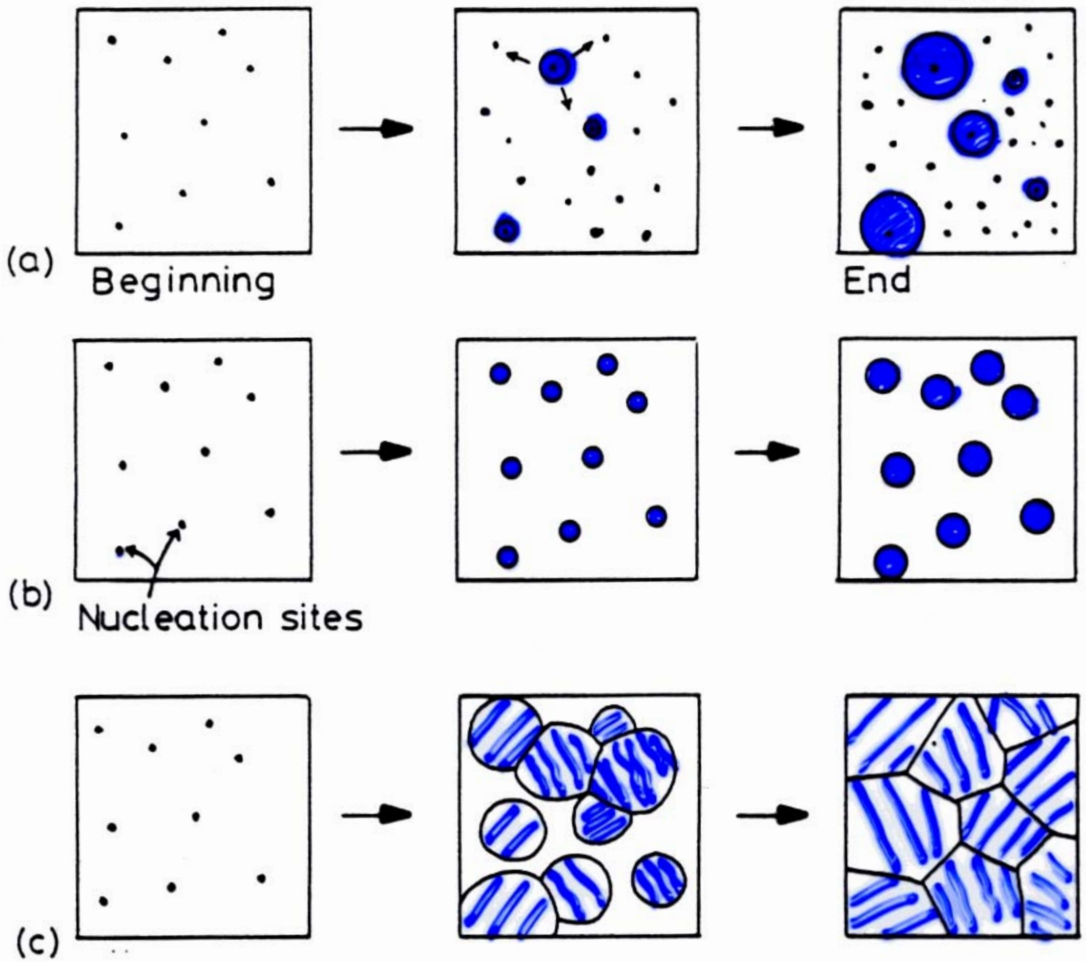
$$\ln(1-x) = -\pi\delta N_0u^2t^2$$

$$x = 1-\exp(-\pi\delta N_0u^2t^2)$$

1-D

$$\ln(1-x) = -\pi\delta^2N_0u\cdot t$$

$$x = 1-\exp(-\pi\delta^2N_0u\cdot t)$$



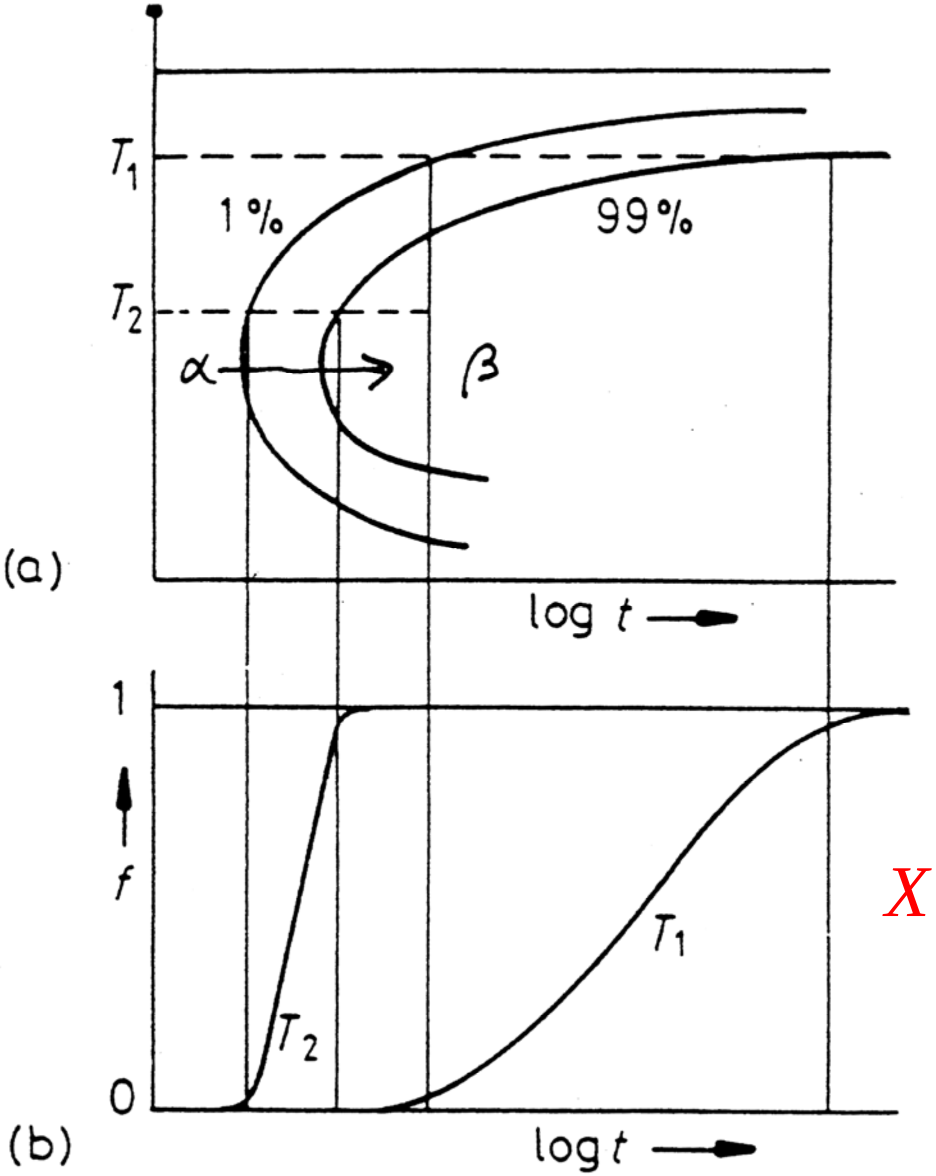
Constant ^{v}I,
Broad size
distribution

Zero ^{v}I,
Narrow size
distribution

Impingement

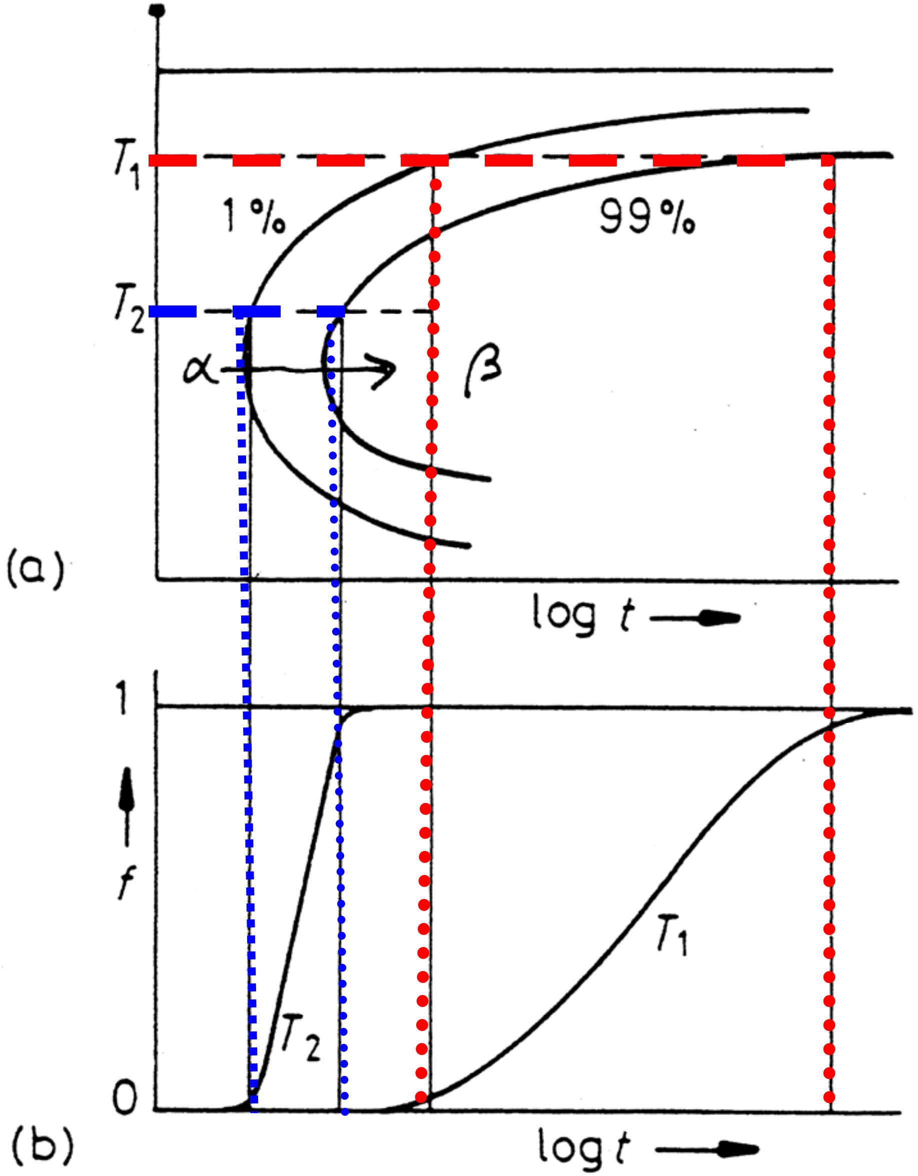
Fig. 5.24 (a) Nucleation at a constant rate during the whole transformation. (b) Site saturation—all nucleation occurs at the beginning of transformation. (c) A cellular transformation.

Time-Temperature-Transformation (TTT) Curves

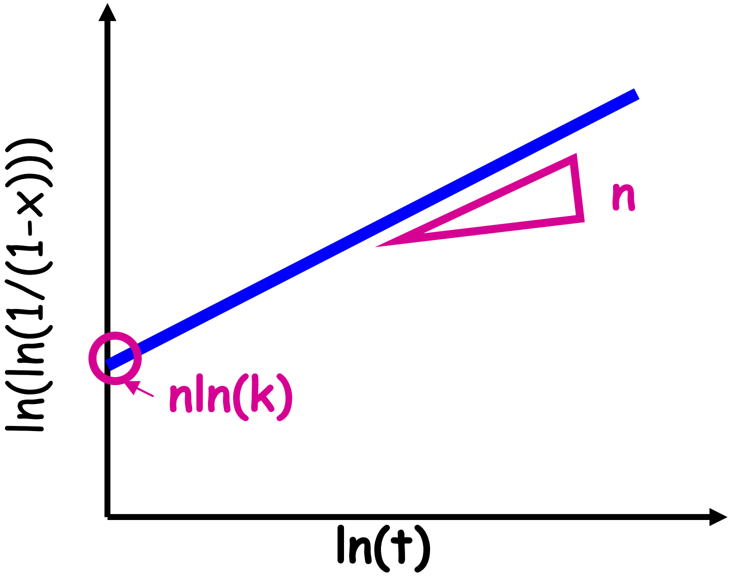


$$X = 1 - \exp(-kt^n)$$

Time-Temperature-Transformation (TTT) Curves



$$X = 1 - \exp(-kt^n)$$



Constant ${}^{V}I$ and u

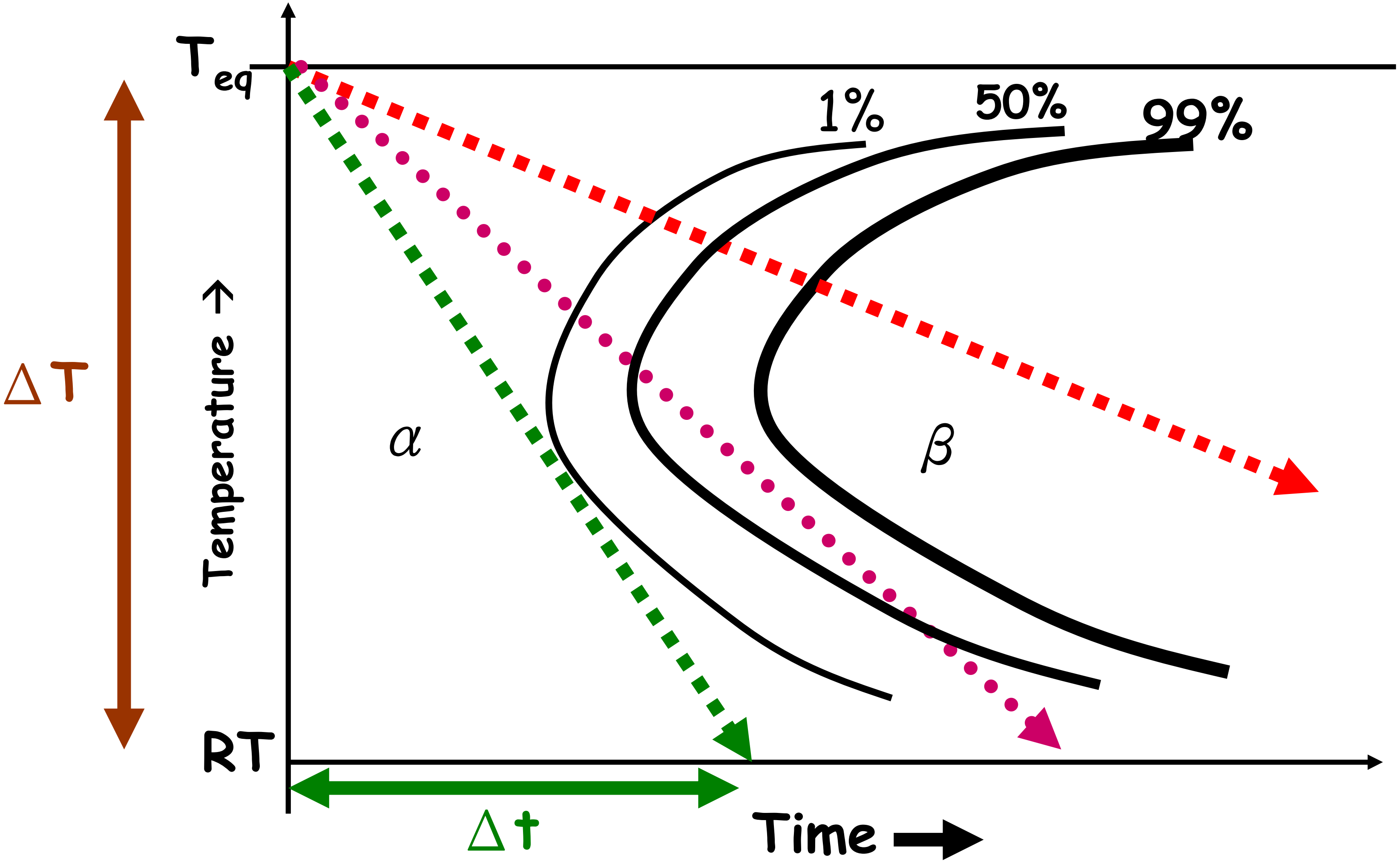
$$X = 1 - \exp[\frac{-\pi\, {}^{V}I u^3 t^4}{3}]$$

Zero ${}^{V}I$ but constant u

$$X = 1 - \exp[\frac{-4\pi\, {}^{V}N_0 u^3 t^3}{3}]$$

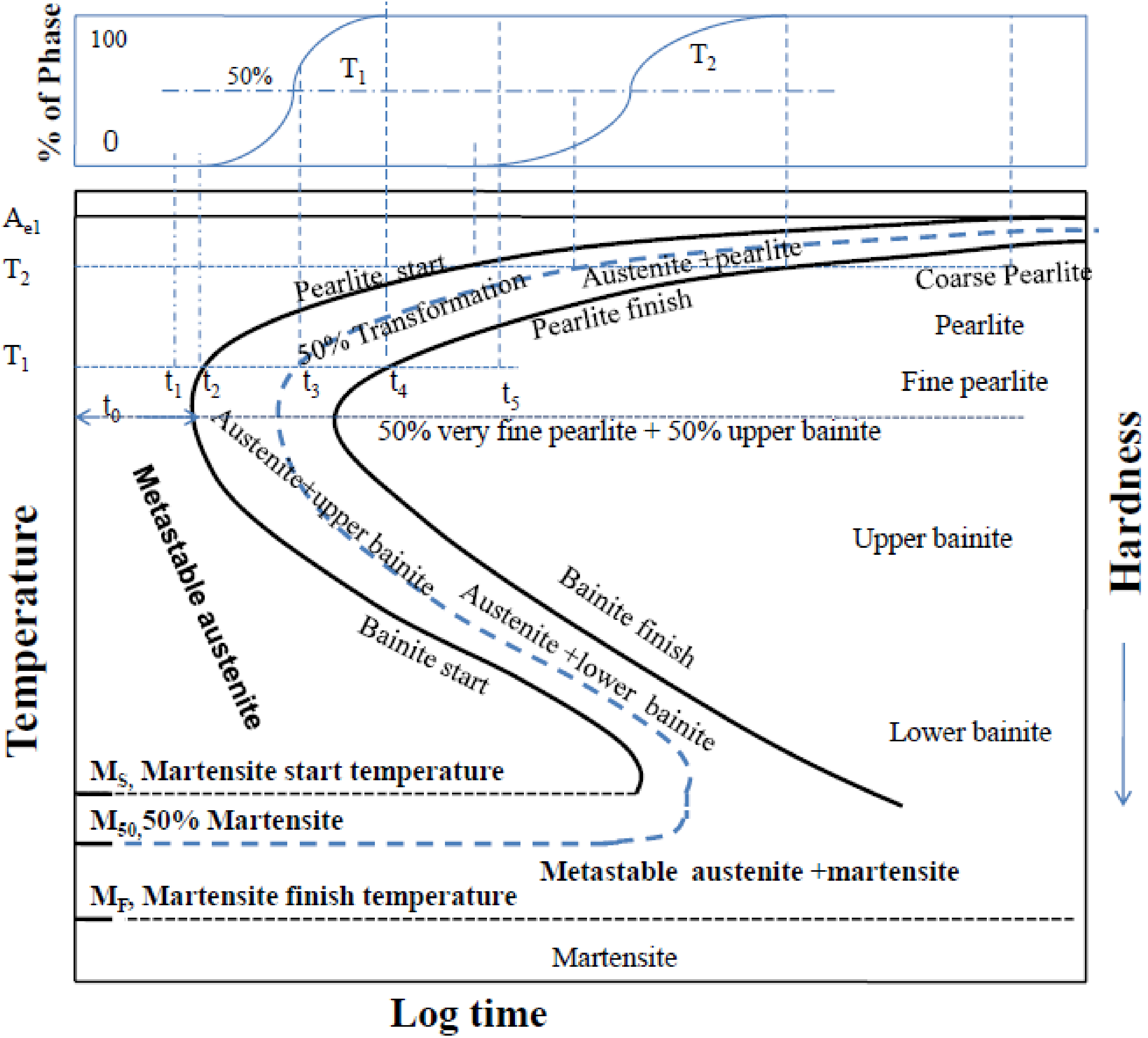
Time-Temperature-Transformation (TTT) Curves

Continuous Cooling Transformation (CCT) Curves



Cooling Rate required = $\Delta T / \Delta t$ to avoid $\alpha \rightarrow \beta$

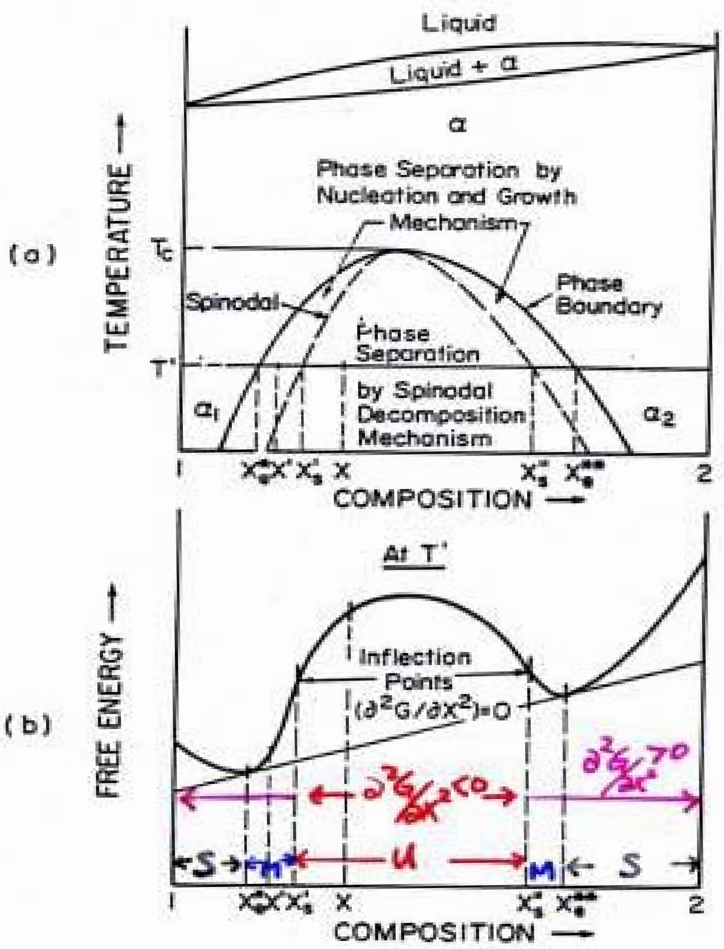
Fig.4: Time temperature transformation (schematic) diagram for plain carbon eutectoid steel



At T_1, incubation period for pearlite=t_2, Pearlite finish time =t_4

Minimum incubation period t_0 at the nose of the TTT diagram,

M_S=Martensite start temperature
M_{50}=temperature for 50% martensite formation
M_F= martensite finish temperature

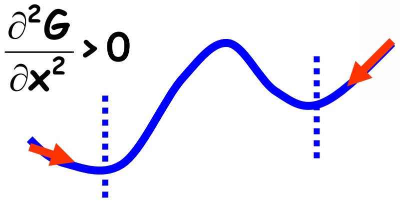


U: Unstable

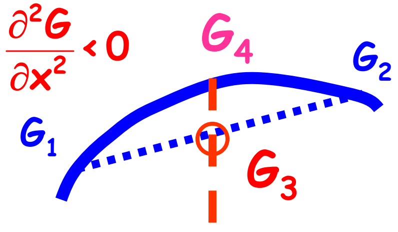
M: Metastable

S: Stable

(c) Stable region



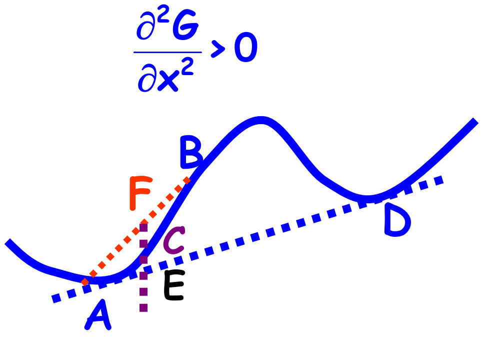
(a) Unstable region



$G_3 < G_4$

- No energy barrier for decomposition
- Kinetics controlling process
- Spinodal decomposition

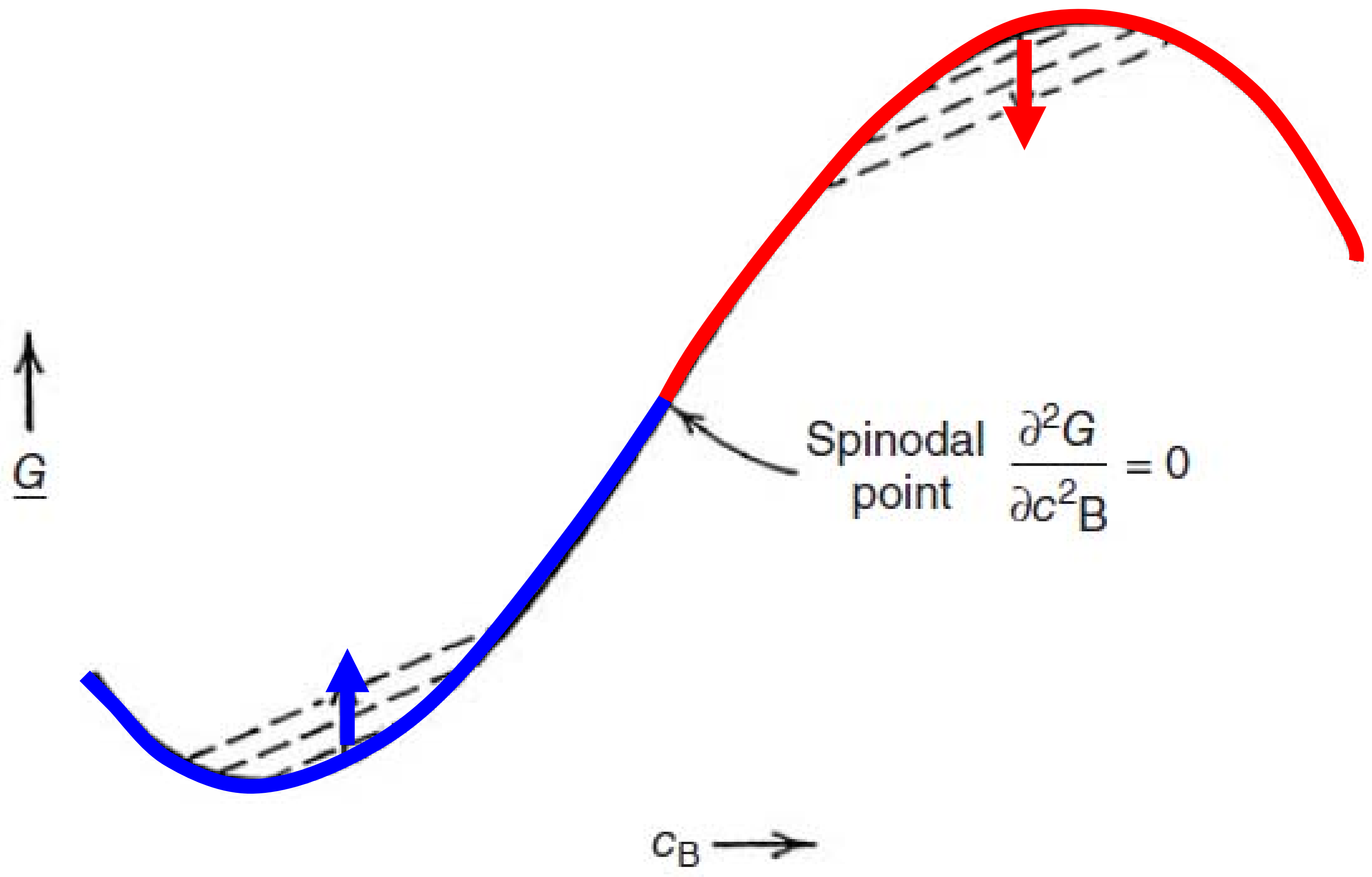
(b) Metastable region



-Small fluctuation, C→A+B, and $G_C<G_F$, energetically unfavorable

-Large fluctuation, C→A+D and $G_C>G_E$, energetically favorable

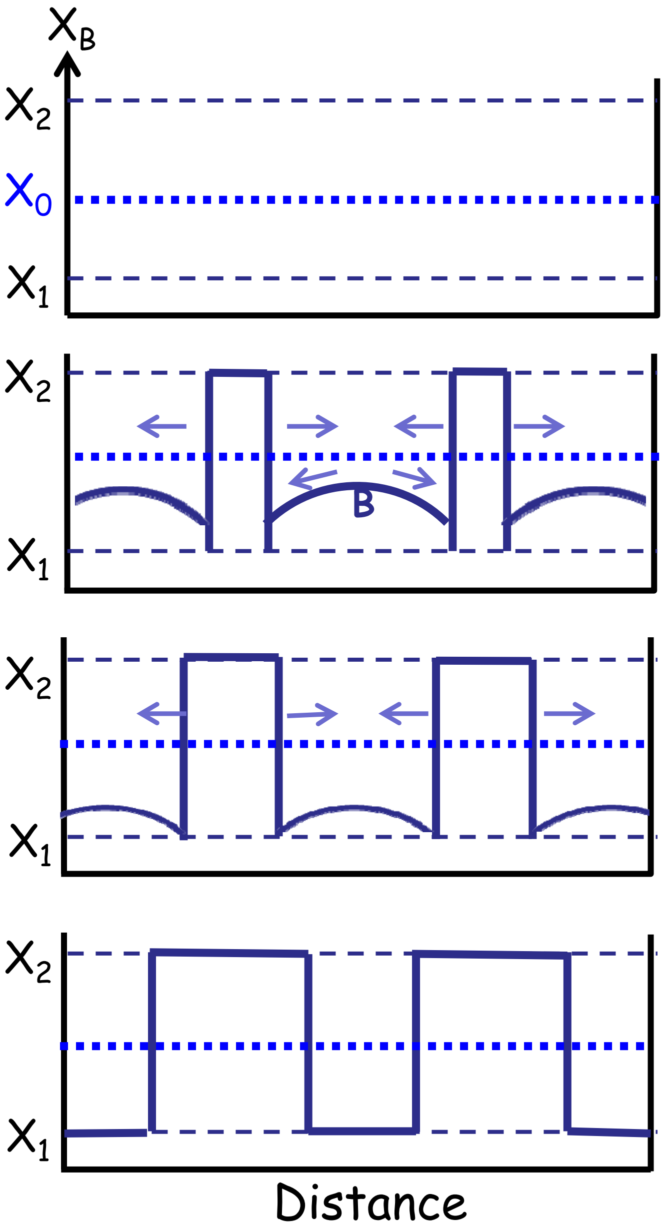
-Nucleation and growth



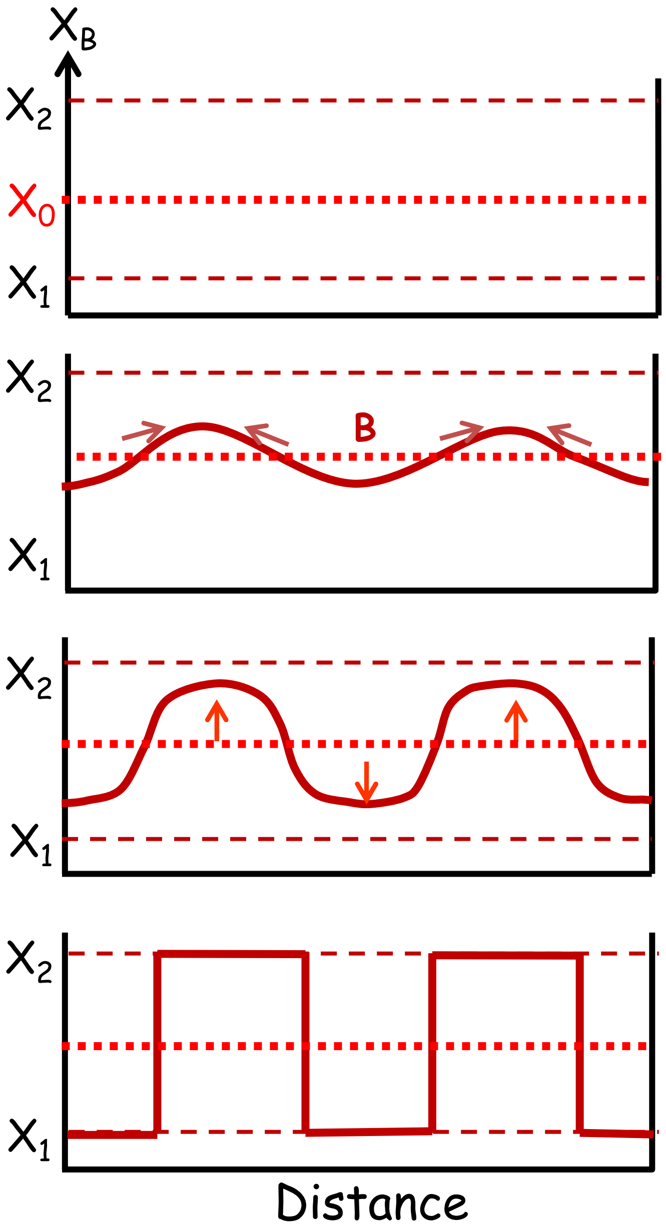
Small compositional fluctuation in the unstable area: $\frac{\partial^2 G}{\partial X^2} < 0,\quad G_M < G_C,\quad C \rightarrow A + B$

in the stable/meta-stable areas: $\frac{\partial^2 G}{\partial X^2} > 0,\quad G_M > G_C,\quad C \nrightarrow A + B$

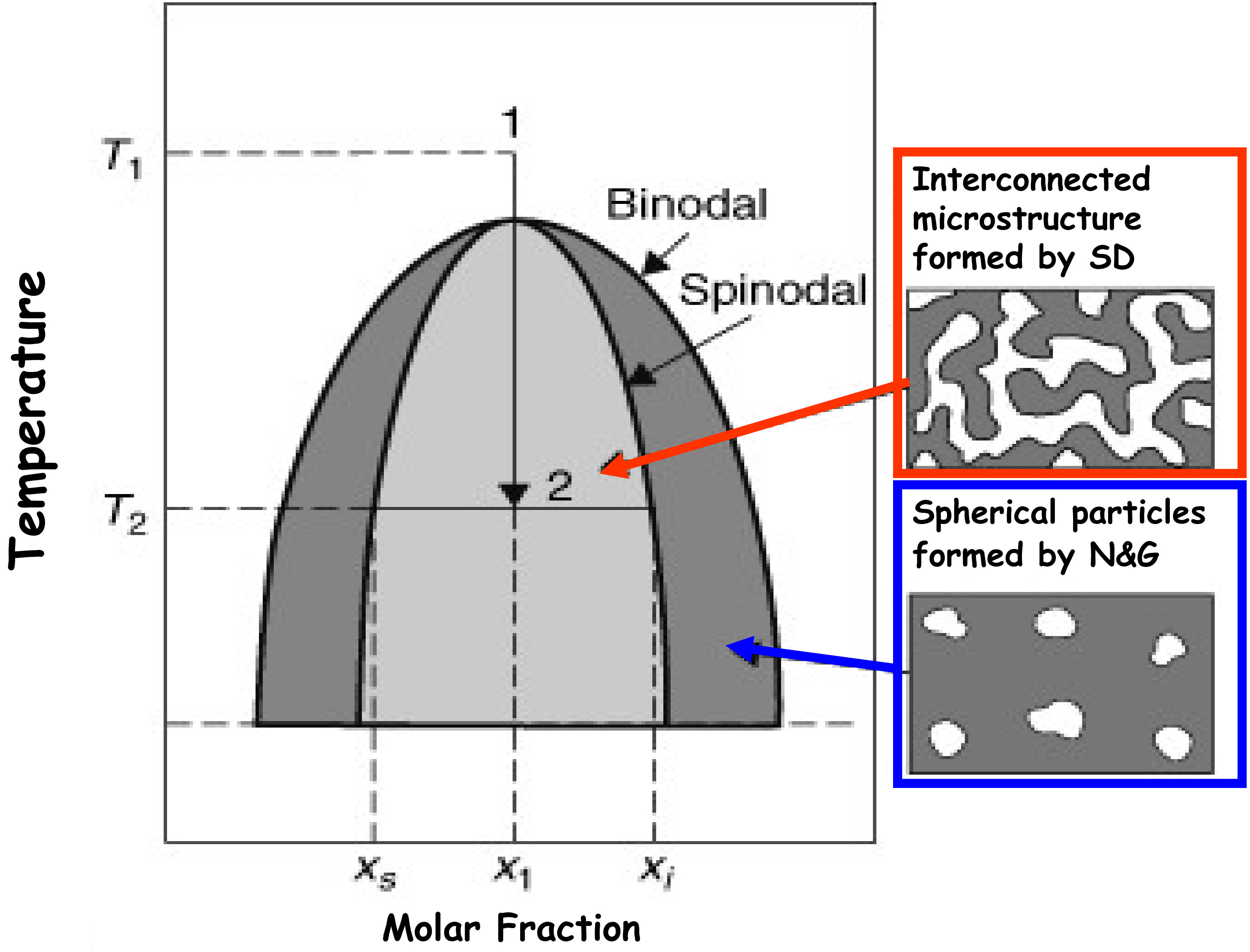
Nucleation and Growth



Spinodal Decomposition



Phase Separation

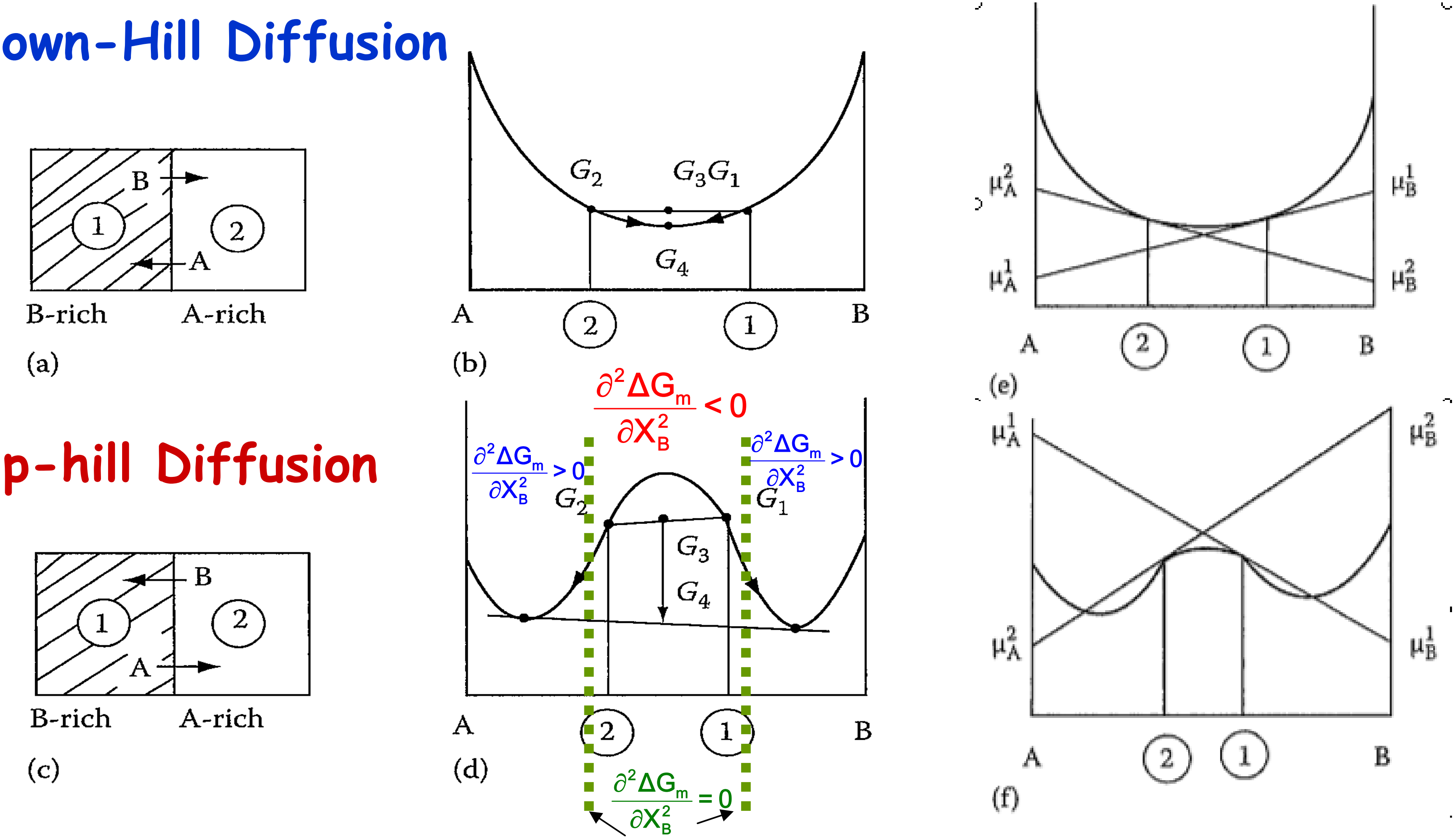


Interconnected microstructure formed by SD

Spherical particles formed by N&G

Down-Hill Diffusion

Up-hill Diffusion

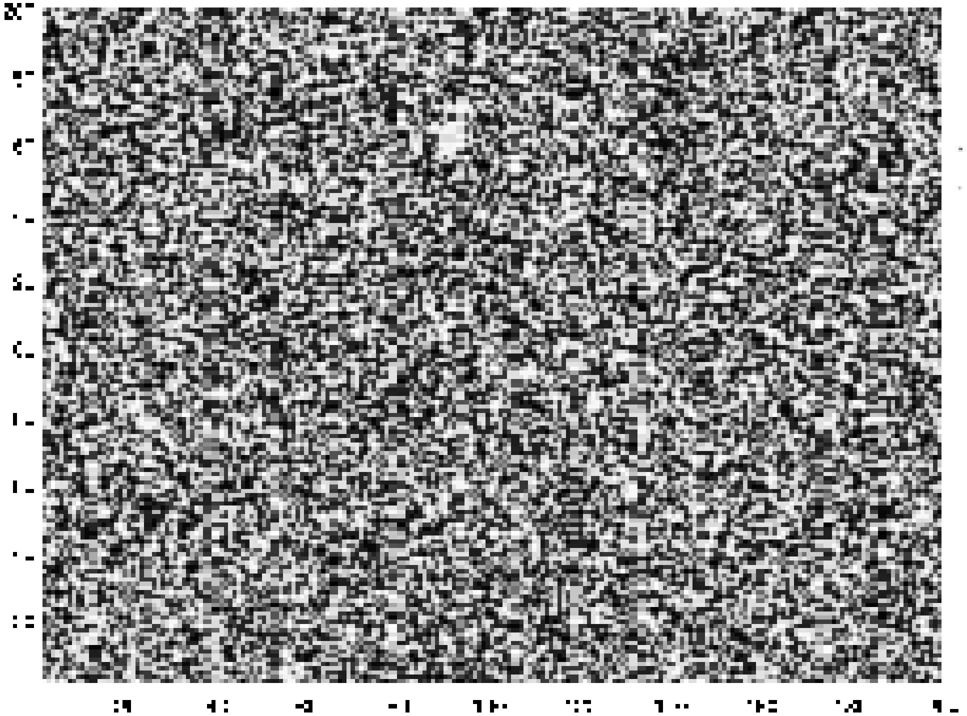


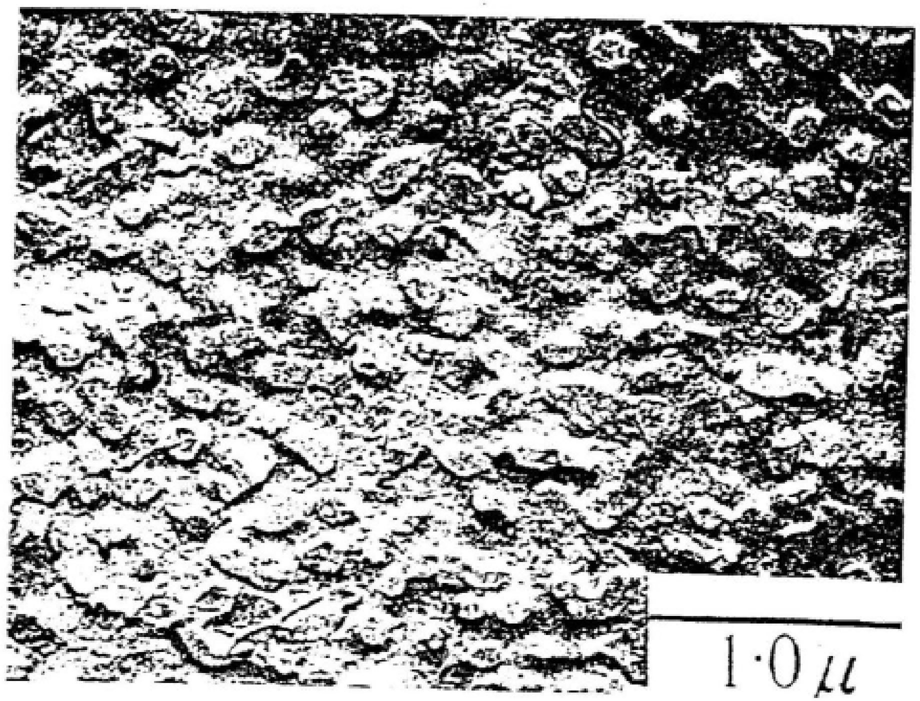
$$Driving\ \ force\ \ \alpha\ \ \frac{\partial \mu}{\partial x}\ \ (not\ \frac{\partial C}{\partial x})$$

$$J = Cv = C\cdot(B\cdot F) = C\cdot B(-\frac{\partial \mu}{\partial x})$$

B : Mobility, F : Force

Spinodal Decomposition





Spinodal Decomposition

Characteristics of spinodal decomposition

(1) No energy barrier
(2) Continuous variation of composition between transformed and untransformed, diffuse interface between transformed and initial phases
(3) $\Delta H_{mix} > 0$ → positive deviation ($\gamma > 1$)
(4) Uphill diffusion → Negative diffusivity
(5) Periodic and highly connected of transformed phases
(6) Systems: Al-Cu, B_2O_3-SiO_2 glass, CoO-MgO, $MgAl_2O_4$-Al_2O_3, etc.

Characteristics of nucleation and growth

(1) With energy barrier
(2) Sharp interface
(3) Random distribution of particle sizes and position in transformed matrix
(4) Invariance of transformed phase composition with time
(5) Tendency toward spherical particles

Kinetics of Spinodal Decomposition

(1)J. W. Cahn, Acta. Meta. 9 (1961), p. 795
(2)J. W. Cahn, Trans. Met. Soc. AIME,242 (1968), p. 166
(3)J. E. Hillard in "Phase Transformation", ASM (1970), p. 497
(4)A. K. Jena and M.C. Chaturved, "Phase Transformations", Chap. 9 (1992)

The flux of each constituent in a binary system with a moving lattice, viewed from the edge of sample (stationary coordinate)

$$\mathrm{J_B = j_B + v_x C_B; \quad J_A = j_A + v_x C_A} \qquad \mathrm{v_x}: \text{velocity of lattice flow}$$

$$\mathrm{J_{net} = J_A + J_B = j_A + j_B + v_x (C_A + C_B) = 0}$$

$$\mathrm{v_x} = \frac{\mathrm{-(j_A + j_B)}}{\mathrm{(C_A + C_B)}} = \frac{1}{\mathrm{(C_A + C_B)}}\left(D_A^I \frac{\partial \mathrm{C_A}}{\partial x} + D_B^I \frac{\partial \mathrm{C_B}}{\partial x}\right) = \frac{1}{\mathrm{(C_A + C_B)}}(D_A^I - D_B^I)\frac{\partial \mathrm{C_A}}{\partial x}$$

$$\therefore \mathrm{J_B = j_B} + \frac{C_B}{\mathrm{C_A + C_B}}\left(D_A^I \frac{\partial \mathrm{C_A}}{\partial x} + D_B^I \frac{\partial \mathrm{C_B}}{\partial x}\right) = \mathrm{j_B} - X_B(\mathrm{j_A + j_B}) = -\tilde{D}\frac{\partial C_B}{\partial x}$$

where $$j_B = C_B \mathrm{v}_B = X_B C \cdot B_B F_B = X_B C \cdot B_B\left(-\frac{\partial(\mu_B/N)}{\partial x}\right)$$

$$j_A = -(1 - X_B) C \cdot B_A\left(\frac{\partial(\mu_A/N)}{\partial x}\right)$$

v_B: atomic velocity
X_B: molar fraction
$C=C_A+C_B$: #atoms/unit volume
B_A, B_B: mobility
μ: chemical potential per mole
$N= 6\times10^{23}$
x: distance

J_i: Flux under stationary coordinate
j_i: Flux under moving coordinate

$$J_B = -\tilde{D}\frac{\partial C_B}{\partial x} = -(X_A D_B^I + X_B D_A^I)\frac{\partial C_B}{\partial x}$$

$$j_B = -D_B^I \frac{\partial C_B}{\partial x}$$

$$J_B = j_B - X_B(j_A + j_B)$$

$$= \frac{-X_B(1-X_B)C}{N}\{[(1-X_B)B_B + X_B B_A](\frac{\partial \mu_B}{\partial x} - \frac{\partial \mu_A}{\partial x}) + (B_B - B_A)[X_B \frac{\partial \mu_B}{\partial x} + (1-X_B)\frac{\partial \mu_A}{\partial x}]\}$$

$X_B \frac{\partial \mu_B}{\partial x} + (1-X_B)\frac{\partial \mu_A}{\partial x} = 0 \rightarrow$ Gibbs-Duhem equation

Hence $J_B = -\frac{BC}{N}[\frac{\partial(\mu_B - \mu_A)}{\partial x}]$

where $B = X_B(1-X_B)[(1-X_B)B_B + X_B B_A]$

:the resultant mobility of the binary system

$$\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x} = (\frac{BC}{N})[\frac{\partial^2(\mu_B - \mu_A)}{\partial x^2}]$$

$$\mu_B - \mu_A = \overline{G}_B - \overline{G}_A = \frac{dG}{dX_B}$$

G : Gibbs free energy per mole

It is convenient to use free energy per unit volume (*f*)

$$f = g_{\text{at P=1 atm}} = \frac{GC}{N}$$

f: Helmholtz free energy per unit volume
g: Gibbs free energy per unit volume
C: Number of atoms per unit volume

$$\mu_B - \mu_A = \frac{\partial({}^{fN}\!/\!_{C})}{\partial X_B} = \frac{N}{C}\frac{\partial f}{\partial X_B}$$

$$\therefore J_B = -\frac{BC}{N}\left[\frac{\partial(\frac{N}{C}\frac{\partial f}{\partial X_B})}{\partial x}\right] = -B\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial X_B}\right) = -B\frac{\partial}{\partial X_B}\left(\frac{\partial f}{\partial X_B}\right)\left(\frac{\partial X_B}{\partial x}\right)$$

$$\because J_B = -\tilde{D}\frac{\partial C_B}{\partial x} = -\tilde{D}C\frac{\partial X_B}{\partial x}$$

$$\therefore \tilde{D} = \frac{B}{C}\frac{\partial^2 f}{\partial X_B^2} = \frac{B}{N}\frac{\partial^2 G}{\partial X_B^2} \qquad (\because f = {}^{GC}\!/\!_{N})$$

within spinodal $\frac{\partial^2 G}{\partial X_B^2} < 0 \Rightarrow \tilde{D} < 0$

Fick's 2nd law $$\frac{\partial C_B}{\partial t} = \tilde{D}\frac{\partial^2 C_B}{\partial x^2} = \frac{B}{C}\left(\frac{\partial^2 f}{\partial X_B^2}\right)\frac{\partial^2 C_B}{\partial x^2} = \frac{Bf''}{C}\frac{\partial^2 C_B}{\partial x^2}$$

$$\text{General Solution}: C_B - \overline{C}_B = A(\beta,0)\exp\left(-\beta^2\left(\frac{Bf''}{C}\right)t\right)\exp(i\beta x)$$
$$= A(\beta,t)\exp(i\beta x)$$

where $\beta = \frac{2\pi}{\lambda}$:wavenumber

$$C(x,t)=\frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

$$C(x,0)=\frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})$$

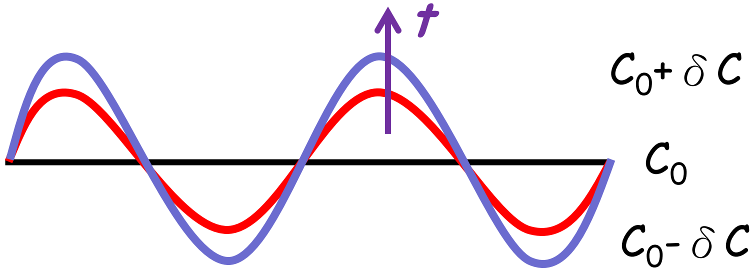
$$C(x,t)=C(x,0)\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

$$Amplification\quad Factor\quad (AF)=\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

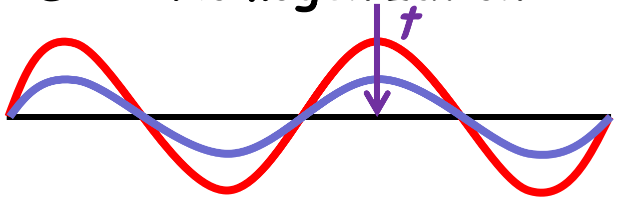
$$(1)D<0\Rightarrow\frac{d(AF)}{dt}>0\Rightarrow Spinodal\quad Decomposition$$

$$(2)D>0\Rightarrow\frac{d(AF)}{dt}<0\Rightarrow Homogenization$$

D<0: Decomposition



D>0: Homogenization



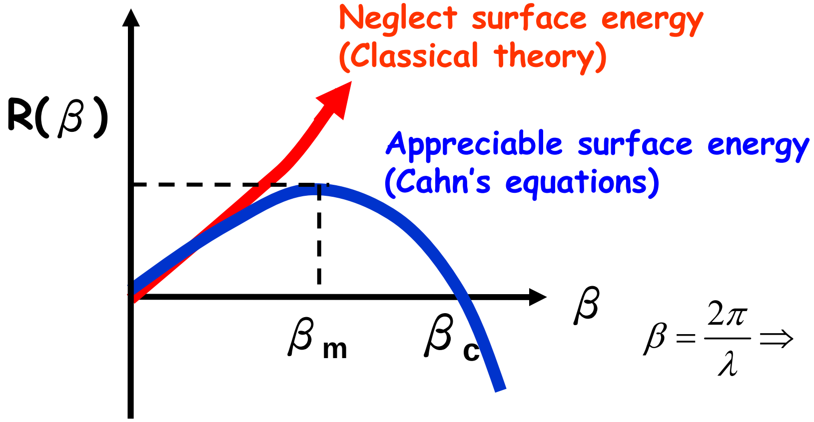
- λ is the wavelength of the composition modulation
- $\overline{c}$ is the average concentration
- A(β ,0) is the amplitude of the composition modulation of wave number β at time zero

$$A(\beta,t) = A(\beta,0)\exp(-\beta^2(\frac{Bf''}{C})t)$$
$$= A(\beta,0)\exp(R(\beta)t)$$

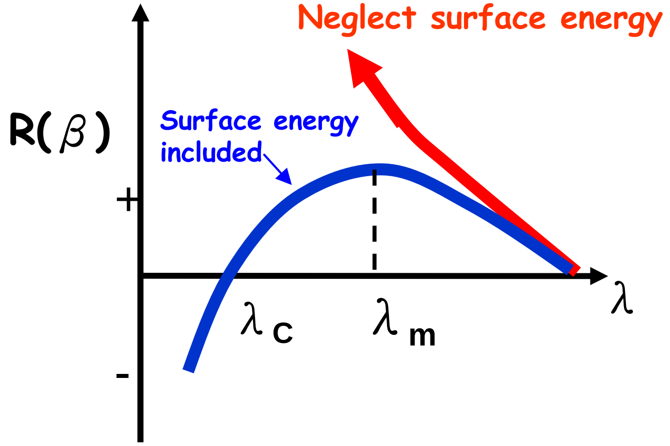
- A(β ,t) is the amplitude of the Fourier component of wave number β at time t
- R(β) is an amplification factor

$$R(\beta) = -\beta^2(\frac{B}{C})f''$$

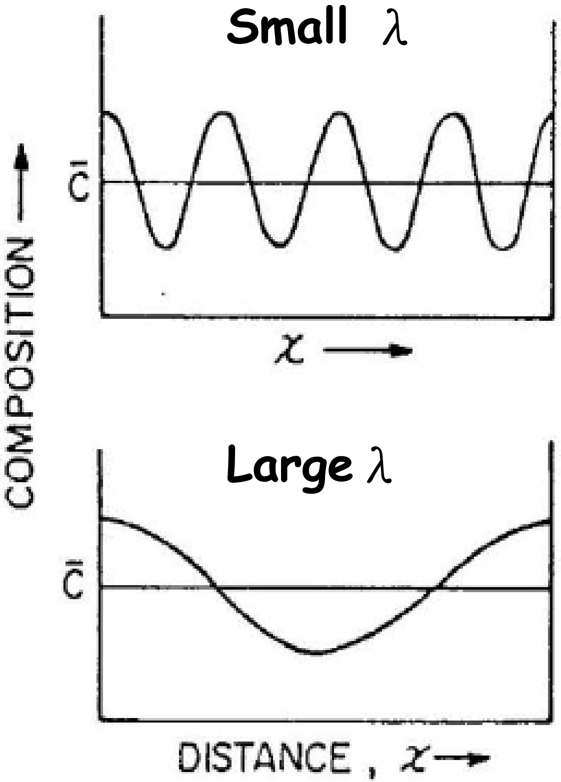
f"<0 within spinodal→ R(β) >0 and the sinusoidal composition modulations are amplified



$$\beta = \frac{2\pi}{\lambda} \Rightarrow$$



The amplitude of the composition fluctuation is less at larger wavelength because of the longer diffusion distance, and more at smaller wavelength because of the shorter diffusion distance.



* $\lambda \rightarrow 0,\ \beta \rightarrow \infty,\ R(\beta) \rightarrow \infty$

→ a continuous microstructure should be observed.

* However, $\lambda_{measured} \approx 10\ nm$ is always observed.

* Strain energy or interfacial free energy has to be included.

Modified diffusion equations - Effect of composition gradient

- Excess interfacial free energy existing in the diffuse interface between two phases
- The interfacial free energy is positive, which decreases the driving force for spinodal decomposition
- The interfacial free energy increases with decreasing wavelength

Helmholtz free energy of a homogeneous system

$$F = \int f(X_B)dV$$

The change in free energy due to the change in concentration of δX_B

$$\delta F = \int [\frac{\partial f}{\partial X_B}\delta X_B]dV \qquad \text{Note:} \frac{\partial f}{\partial X_B} = \frac{C}{N}\Delta\mu$$

$f(X_B)$: Helmholtz free energy/unit volume of homogeneous material with a composition X_B. Since the interfacial free energy (γ) is proportional to the square of the composition difference between the coexisting phases across the interface (dX_B / dx)

$$\gamma = k(\frac{dX_B}{dx})^2 \qquad k\text{: gradient energy coefficient}$$

Helmholtz free energy of an inhomogeneous system is

$$F = \int [f(X_B) + \kappa(\frac{dX_B}{dx})^2]dV$$

The change in free energy due to the change in concentration of δX_B

$$\delta F = \int [\frac{\partial f}{\partial X_B}\delta X_B + (\frac{\partial \kappa}{\partial X_B})(\frac{\partial X_B}{dx})^2 \delta X_B + 2\kappa(\frac{\partial X_B}{\partial x})\delta(\frac{\partial X_B}{\partial x})]dV$$

$$= \int [\frac{\partial f}{\partial X_B} - (\frac{\partial \kappa}{\partial X_B})(\frac{\partial X_B}{dx})^2 - 2\kappa(\frac{\partial^2 X_B}{\partial x^2})]\delta X_B dV = \int [\frac{\partial f}{\partial X_B} - 2\kappa(\frac{\partial^2 X_B}{\partial x^2})]\delta X_B dV$$

Gibbs free energy of an atom in a concentration gradient is not the same as the Gibbs free energy of that atom in a solution of uniform concentration

$$\gamma = \kappa \left(\frac{dX_B}{dx}\right)^2$$

Interfacial free energy is proportional to (composition gradient)^2

Regular Solution

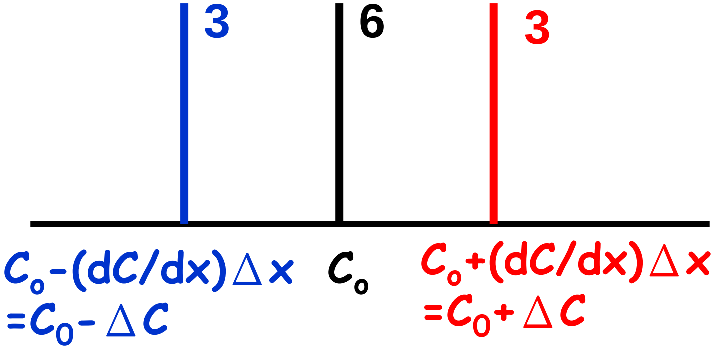
(1) In a uniform solution

$$\Delta H_m = \Omega X_A X_B = \Omega X_A (1 - X_A)$$

$$\Omega = Z[E_{AB} - \tfrac{1}{2}(E_{AA} + E_{BB})] = Z \cdot \Delta E$$

$$\Delta H_m = Z X_A (1 - X_A) \cdot \Delta E = 12C(1 - C) \cdot \Delta E \qquad \text{(Z=12)}$$

(2) With a concentration gradient



$$\Delta H_m = 6C_o(1 - C_o)\Delta E$$

$$+ 3[(C_o + \Delta C)(1 - (C_o + \Delta C))]\Delta E$$

$$+ 3[(C_o - \Delta C)(1 - (C_o - \Delta C))]\Delta E$$

$$= 12C_o(1 - C_o)\Delta E + 6(\Delta C)^2 \Delta E$$

$$= 12C_o(1 - C_o)\Delta E + 6\left(\frac{dC}{dx}\right)^2 (\Delta x)^2 \Delta E$$

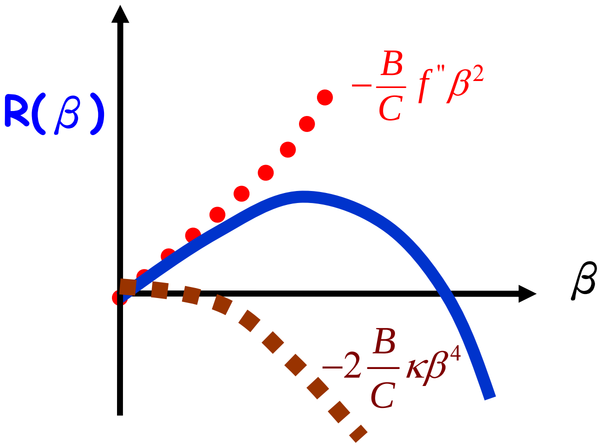
Uniform concentration

Excess Gibbs free energy resulted from a non-uniform concentration

$$J_B = -B\frac{d}{dx}\left(\frac{\partial f}{\partial X_B} - 2k\frac{\partial^2 X_B}{\partial x^2}\right)$$

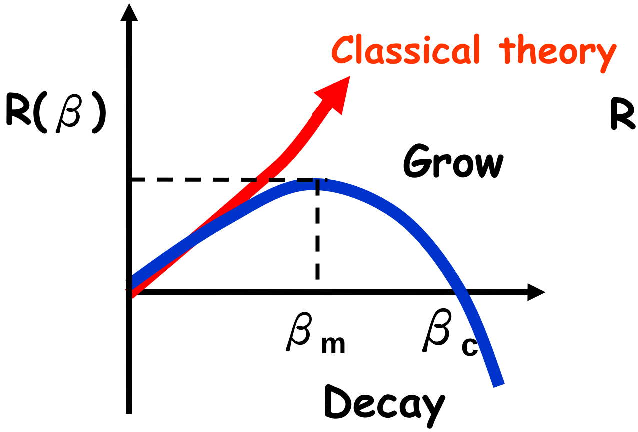
$$\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x} = +\frac{B}{C}\left(f''\frac{\partial^2 C_B}{\partial x^2} - 2\kappa\frac{\partial^4 C_B}{\partial x^4}\right)$$

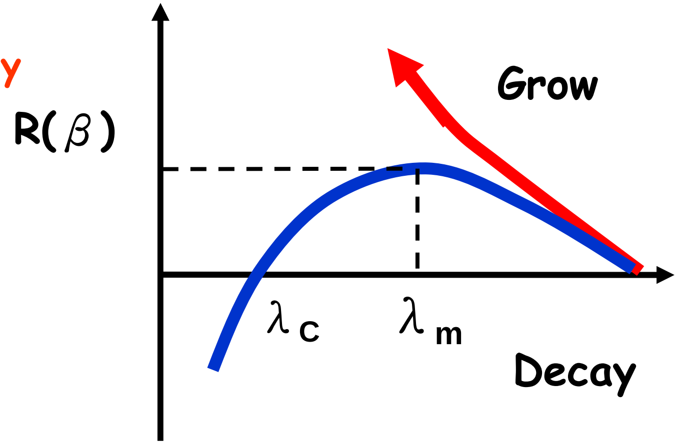
Hence $R(\beta) = -\frac{B}{C}f''\beta^2 - 2\frac{B}{C}\kappa\beta^4$



(1) At a large wavelength, β is small→ β^2 dominates and the amplification factor, R(β) is positive because f″ is negative. R(β) tends to approach zero with an increase in wavelength.

(2) At a small wavelength, β is large→ β^4 becomes predominant, and R(β) tends to be negative.





Note: * When λ is large, decreasing λ means decreasing the diffusion distance → R(β) increases

* When λ is small ($\lambda < \lambda_m$), the gradient energy term is large enough to offset the driving force (f″), then R(β) decreases with decreasing λ.

$\lambda < \lambda_C$

→Spinodal fluctuation decays
→Spinodal decomposition will not happen

However, the solid solution can still decompose to its equilibrium state by Nucleation and Growth, but not by the spinodal decomposition.

Effect of coherent strain energy

- Lattice parameter in general varies with composition. Work has to be performed in straining the lattice if the lattice is to remain coherent in the presence of a composition modulation. To maintain the coherence, it will reduce the driving force for phase transformation.
- Coherent strain energy generally is a function of crystallographic direction, which is to determine the morphology of transformed phase.
- The growth rate will be the maximum in the elastically softest direction.

$$W = Y\delta^2 \quad \text{(Elastic Strain Energy)}$$

$$Y = \frac{E}{1-\upsilon} \quad \text{(Isotropic)}$$

Y: Stiffness

E:Young's modulus

υ: Poisson's ratio

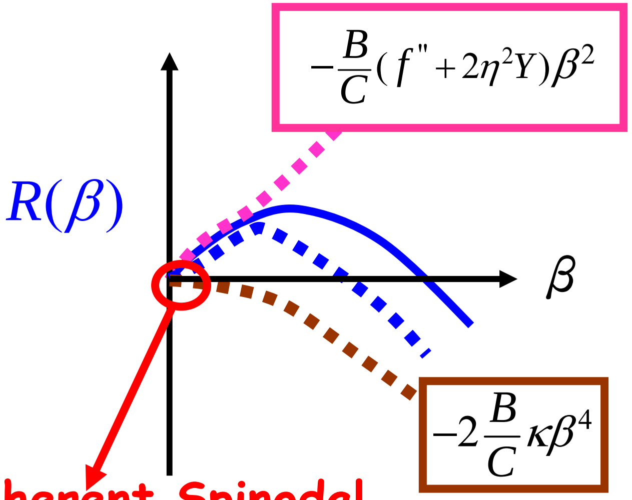
$$\delta = \eta(X_B - \overline{X_B}) : \text{disregistry}$$

X_B: Composition

$\bar{X}_B$: Average composition

$$f_{strain} = Y\delta^2 = Y\eta^2(X_B - \overline{X_B})^2$$

:Coherent strain energy per unit volume



Coherent Spinodal

$$\boxed{f''+2\eta^2Y=0 \text{ and } \beta=0}$$

$$\boxed{R(\beta)=-\frac{B}{C}(f''+2\eta^2Y+2\kappa\beta^2)\beta^2}$$

$$\boxed{R(\beta)=-\frac{B}{C}(f''+2\kappa\beta^2)\beta^2}$$

$$F=\int[f(X_B)+\eta^2Y(X_B-\overline{X_B})^2+k(\frac{dX_B}{dx})^2]dV$$

$$J_B=-B\frac{d}{dx}(\frac{\partial f}{\partial X_B}+2\eta^2Y(X_B-\overline{X_B})-2k\frac{\partial^2X_B}{\partial x^2})$$

$$\frac{\partial C_B}{\partial t}=-\frac{\partial J_B}{\partial x}=\frac{B}{C}[(f''+2\eta^2Y)\frac{\partial^2C_B}{\partial x^2}-2k\frac{\partial^4C_B}{\partial x^4})$$

$$R(\beta)=-\frac{B}{C}(f''+2\eta^2Y+2k\beta^2)\beta^2$$

-Therefore, for an alloy to decompose by spinodal mechanism the $f''+2\eta^2Y$ must be negative as the surface energy term $2k\beta^2$ is always positive Consequently, the boundary corresponding to $\boxed{f''+2\eta^2Y=0}$ is defined as the **coherent spinodal** at which β→0, λ→∞ (Ignore the effect of surface energy).

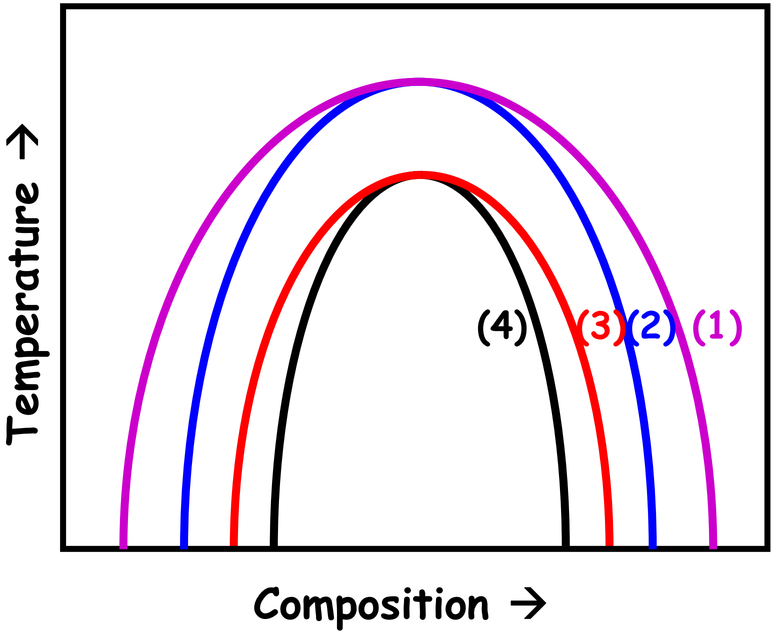
- $2\eta^2Y$ will be absent at high temperature which is to be relieved by plastic deformation. $2k\beta^2$ is significant only when λ is small (λ≈10 nm).

-To grow, R(β) has to be positive. Since β is inherently positive, R(β) is positive only if $f''+2\eta^2Y+2k\beta^2\le 0$. For a system with spinodal decomposition, κ is expected to be positive. Thus $f''+2\eta^2Y\le 0$. Since Y varies with the direction of crystal, the temp will be maximum for those directions that minimize $2\eta^2Y$.

$$* \ R(\beta) = 0 \Rightarrow f'' + 2\eta^2 Y + 2\kappa\beta^2 = 0$$

$$\beta_C^2 = -\frac{(f'' + 2\eta^2 Y)}{2k}$$

$$f'' + 2\eta^2 Y = 0 \rightarrow \beta_C = 0 \Rightarrow \text{Coherent Spinodal}$$



(1) Incoherent miscibility curve (Strain-free) →f'=0

(2) Chemical spinodal curve (Strain-free) →f"=0

(3) Coherent miscibility curve
f = free energy change + strain energy
→f'=0

(4) Coherent spinodal curve →$f'' + 2\eta^2 Y = 0$

T_S^* is the temperature for coherent spinodal

$$f'' + 2\eta^2 Y = 0 \rightarrow \beta_C^2 = 0 \rightarrow f''(T_s^*) + 2\eta^2 Y = 0$$

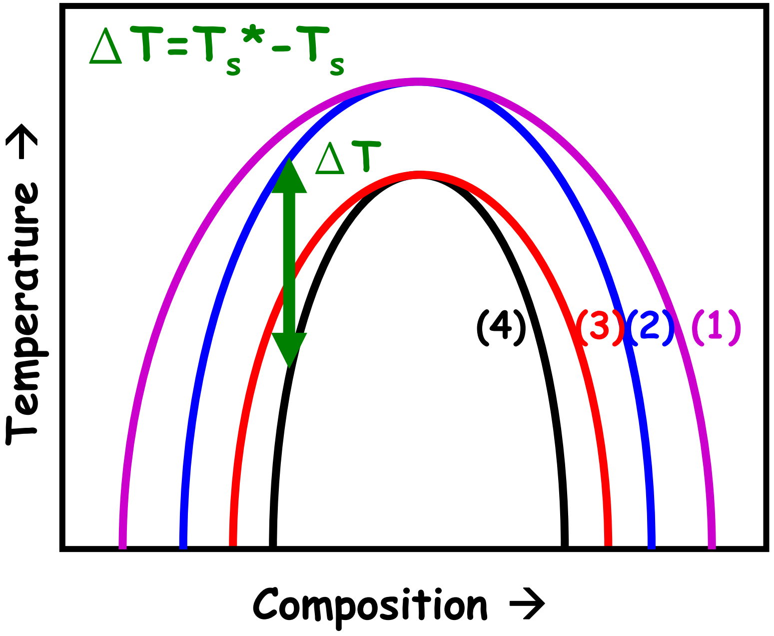
T_S is the temperature for chemical spinodal

$$f''(T_s) = 0$$

$$f''(T_s^*) = f''(T_s) + \frac{\partial f''}{\partial T}(T_s^* - T_s)$$

$f''(T_S) = 0$ at chemical spinodal

$$\therefore T_s^* - T_s = \frac{f''(T_s^*)}{\partial f'' / \partial T}$$



$$\frac{\partial f''}{\partial T} = -S'' \Rightarrow T_s^* - T_s = \frac{f''(T_s^*)}{-S''}$$

$$f''(T_s^*) = -2\eta^2 Y$$ **Coherent spinodal**

$$\therefore T_s^* - T_s = \frac{2\eta^2 Y}{S''}$$

$$\because S'' = \frac{-C_0 k}{X_B(1 - X_B)} < 0$$

$$\therefore T_s^* - T_s < 0 \Rightarrow T_s^* < T_s$$

Small Coherency Strain

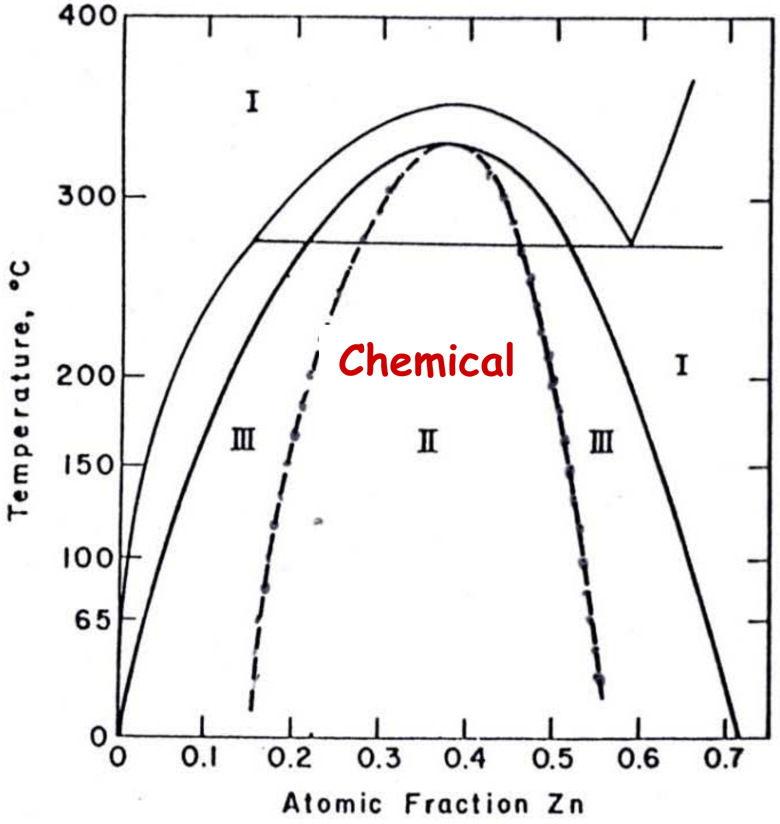


Fig. 7—The coherent phase diagram (heavy line) and spinodal (dashed line) in the Al-Zn system in which coherency strains are small.[24]

Large Coherency Strain

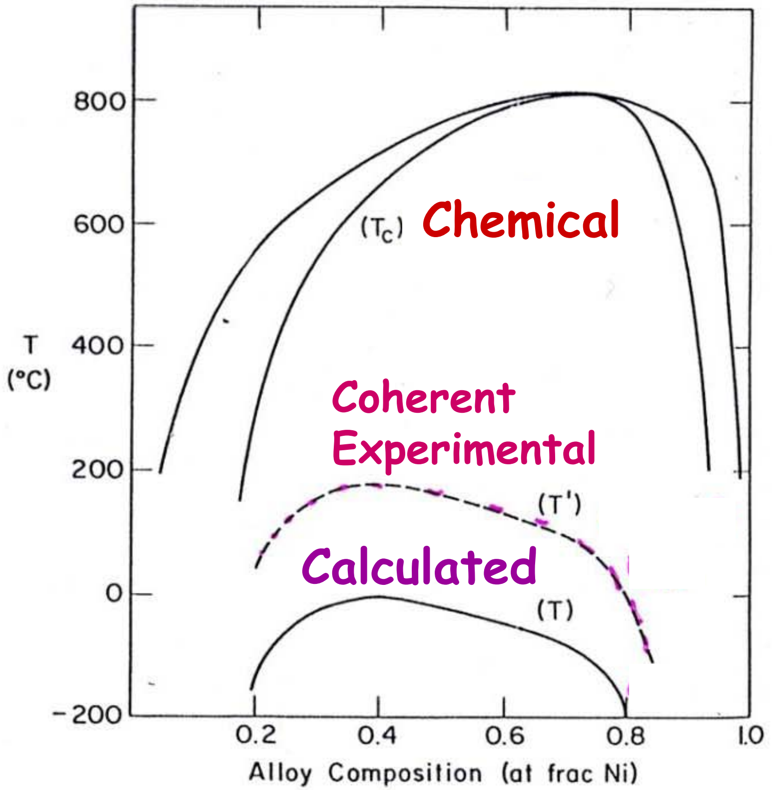
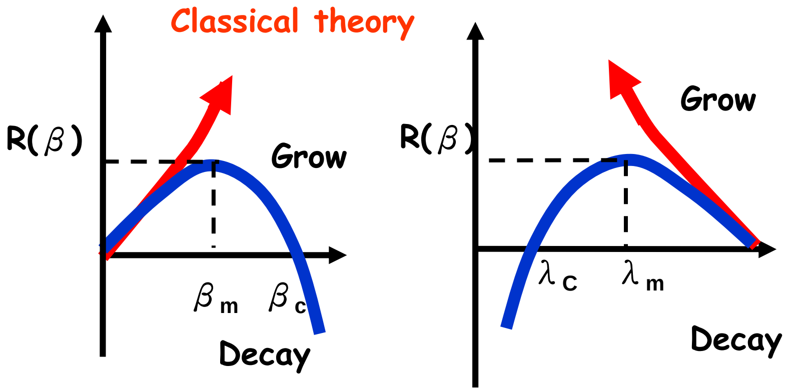


Fig. 8—The coherent spinodal (dashed line) in Au-Ni where the coherency strain is large and in which elastic moduli vary strongly with composition.[25] T_c is the chemical spinodal; T' and T are, respectively, an experimental and theoretical estimate of the coherent spinodal.



$$R(\beta) = -(f'' + 2\eta^2 Y + 2\kappa\beta^2)\beta^2 \cdot \frac{B}{C}$$

$$\beta_C^2 = -\frac{(f'' + 2\eta^2 Y)}{2\kappa}$$

$$R(\beta) = 2\kappa(\beta_C^2 - \beta^2)\beta^2 \cdot \frac{B}{C}$$

$$\frac{\partial R(\beta)}{\partial \beta} = 0 \Rightarrow \beta_m = \frac{\beta_C}{\sqrt{2}}$$

$$R(\beta_m) = \left(\frac{2\kappa B}{C}\right)\beta_m^4 = \left(\frac{\kappa B}{2C}\right)\beta_C^4$$

$$\beta_m^2 = -\left(\frac{f'' + 2\eta^2 Y}{4\kappa}\right) = -\left(\frac{S''(T_s^* - T)}{4\kappa}\right)$$

$$\therefore R(\beta_m) = \left(\frac{2\kappa}{C}\right)\left(B_0 \exp\left(-\frac{Q}{RT}\right)\right)\left(\frac{S''(T - T_s^*)}{4\kappa}\right)^2$$

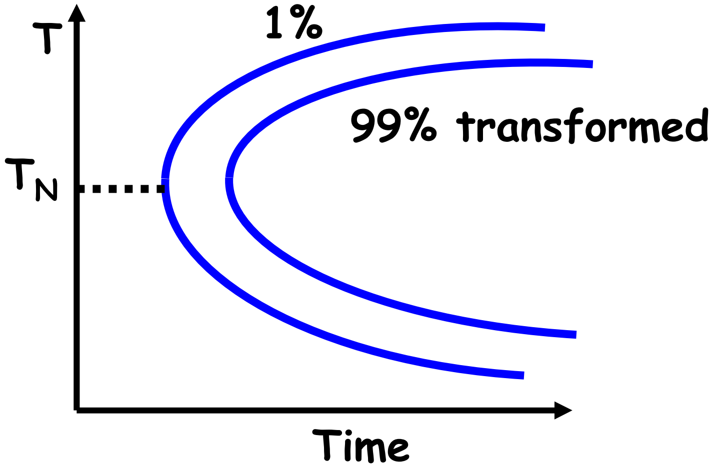
$$\ln(R(\beta_m)) = \ln\left(\frac{2\kappa B_0}{C}\right) - \frac{Q}{RT} + \ln\left(\frac{S''(T - T_s^*)}{4\kappa}\right)^2$$

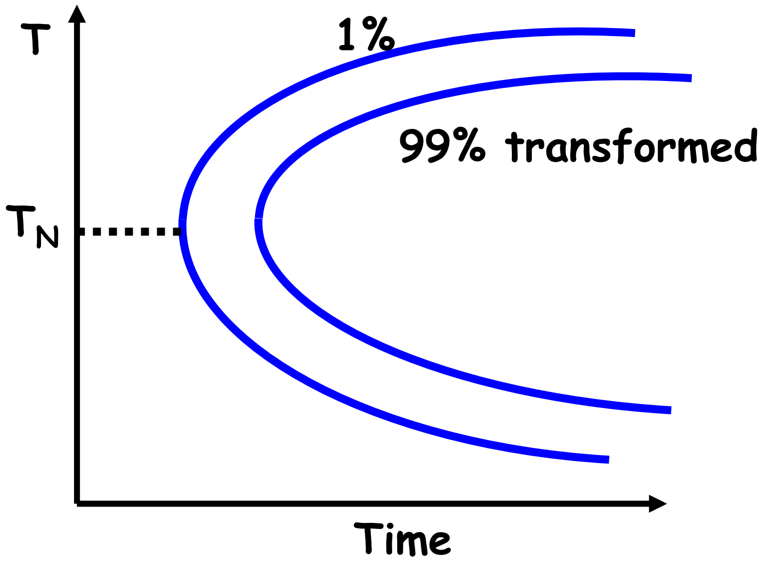
$$\frac{\partial \ln(R(\beta_m))}{\partial T} = \frac{Q}{RT^2} + \frac{2}{T - T_s^*} = 0 \Rightarrow T_N$$

$$\frac{Q}{RT_N^2} + \frac{2}{T_N - T_s^*} = 0 \Rightarrow \frac{T_s^* - T_N}{T_N} = \frac{2RT_N}{Q}$$

$$C - \overline{C} = A(\beta,0)\exp\left(-\beta^2\left(\frac{Bf''}{C}\right)t\right)\exp(i\beta x)$$
$$= A(\beta,t)\exp(i\beta x)$$

$$A(\beta,t) = A(\beta,0)\exp\left(-\beta^2\left(\frac{Bf''}{C}\right)t\right)$$
$$= A(\beta,0)\exp(R(\beta)t)$$





- $T>T_N$ → Driving force increases with decreasing temp., $\beta_m \propto \Delta T$.
- $T<T_N$ → Mobility decreases with decreasing temp

$$\left(\frac{2\pi}{\lambda_m}\right)^2 = \beta_m^2 = \frac{(T-T_s^*)S''}{4\kappa} = \frac{(T-T_s)S'' - 2\eta^2 Y}{4\kappa}$$

(1) $\beta_m \uparrow$ *when* $T\downarrow \rightarrow \lambda_m \downarrow,\ T\downarrow\ (\Delta T\uparrow)$

(2) $2\eta^2 Y\uparrow \quad \beta_m\downarrow \quad \lambda_m\uparrow$

(3) $\kappa\uparrow \quad \beta_m\downarrow \quad \lambda_m\uparrow$

Q: Is it possible to suppress spinodal decomposition by quenching?

Recall

$$R(\beta_m) = -\frac{B}{2C}(f'' + 2\eta^2 Y)\beta_m^2 \equiv \frac{1}{t}$$

$$\beta_m = \frac{2\pi}{\lambda_m} \quad \text{and} \quad \tilde{D} = \frac{B}{C} f''$$

equivalent to $\frac{1}{t} \;\alpha\; \tilde{D}(\frac{1}{\lambda_m})^2$

$$x^2 \approx \tilde{D}t \quad (\lambda = \lambda_m)$$

$$x = \lambda_m = 10 \text{ nm} \quad \text{(measured)}$$

$$(10^{-6})^2 = 10^{-9} \text{ cm}^2/\text{sec} \cdot \text{t}$$

$$\because \tilde{D} = 10^{-9} \text{ cm}^2/\text{sec} \quad \text{for solid,}$$

$$\tilde{D} = 10^{-6} \text{ cm}^2/\text{sec} \quad \text{for liquid}$$

$$t \approx 10^{-3} \text{ sec for solid,}$$

$$t \approx 10^{-6} \text{ sec for liquid}$$

→ Transformation time is so short, therefore, it is hard to suppress spinodal decomposition by quenching