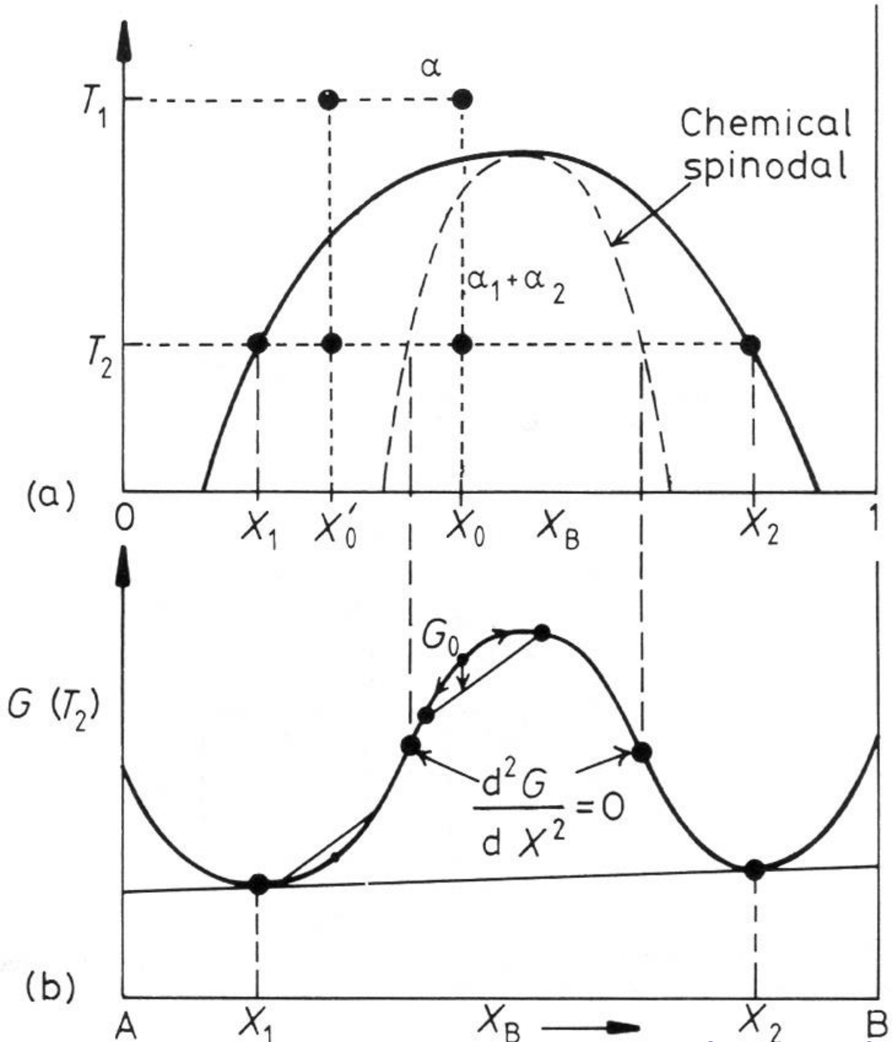
5.5.5 Spinodal Decomposition

No barrier for nucleation

Phase diagram with a miscibility gap

$$\Omega > 0$$



- ✓ $\frac{d^2G}{dX^2} < 0$: chemical spinodal
- ✓ Small fluctuation in composition will produce A and B rich region
- ✓ Up-hill diffusion until the equilibrium composition X_1 and X_2

- ✓ $\frac{d^2G}{dX^2} > 0$: meta-stable

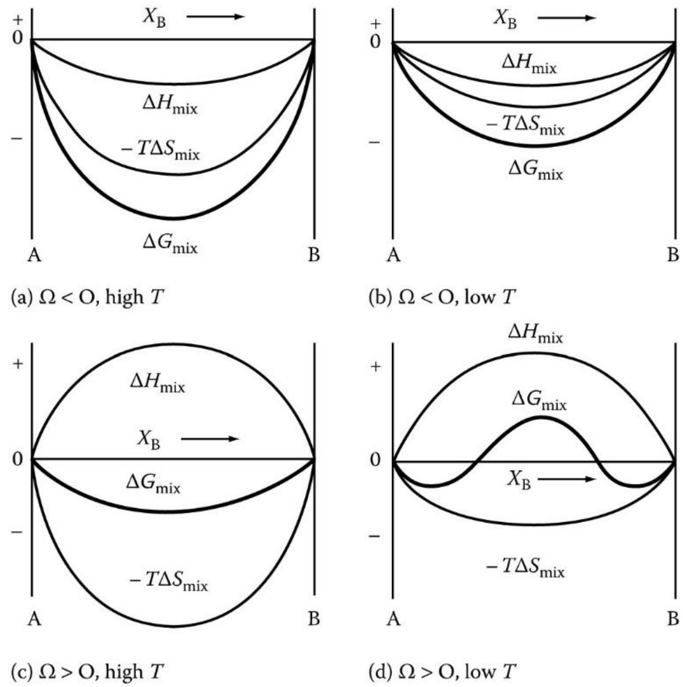
  nucleation and Growth

From Ch1

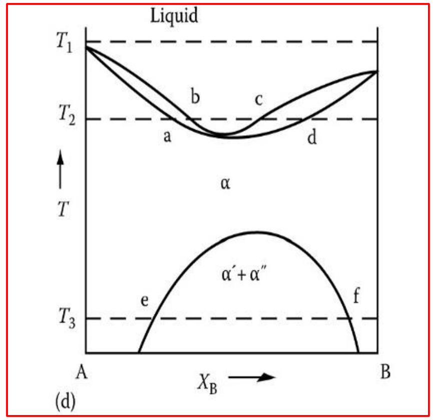
❖ **The Effect of ΔH_{mix} and T on ΔG_{mix}**

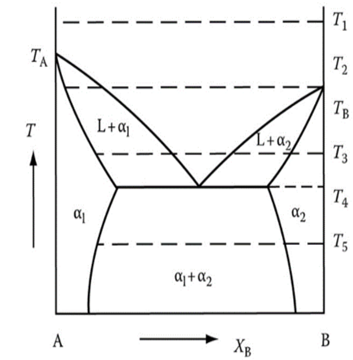
$\Omega < 0$

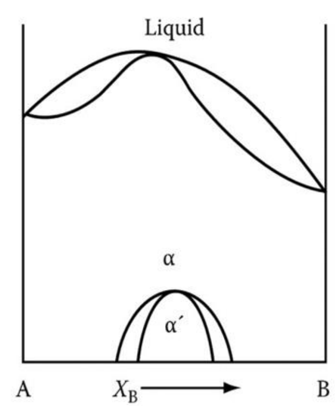
$\Omega > 0$

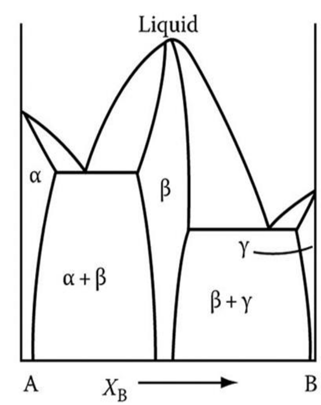


(a) Ω < O, high T
(b) Ω < O, low T
(c) Ω > O, high T
(d) Ω > O, low T



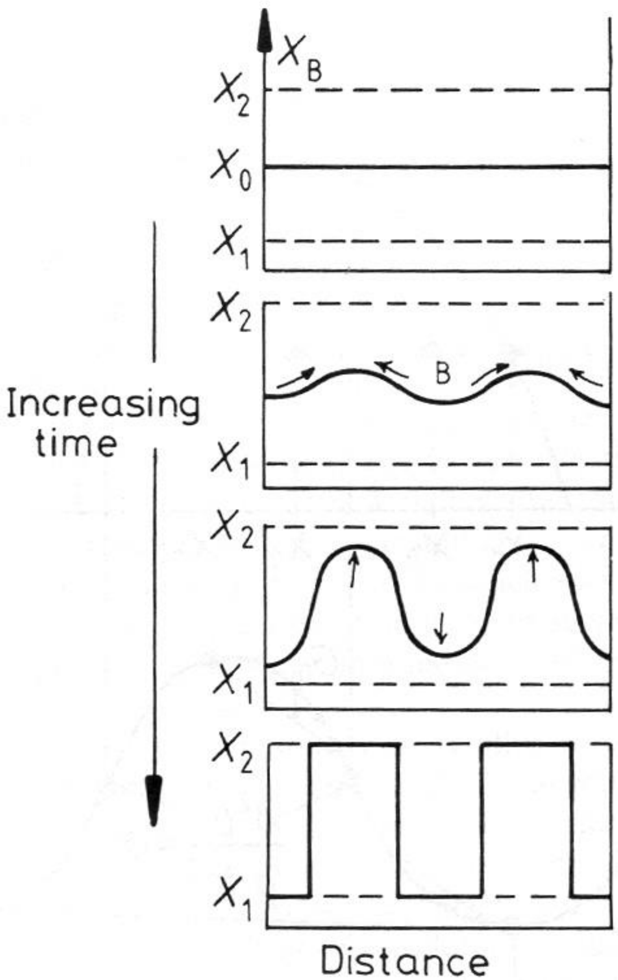




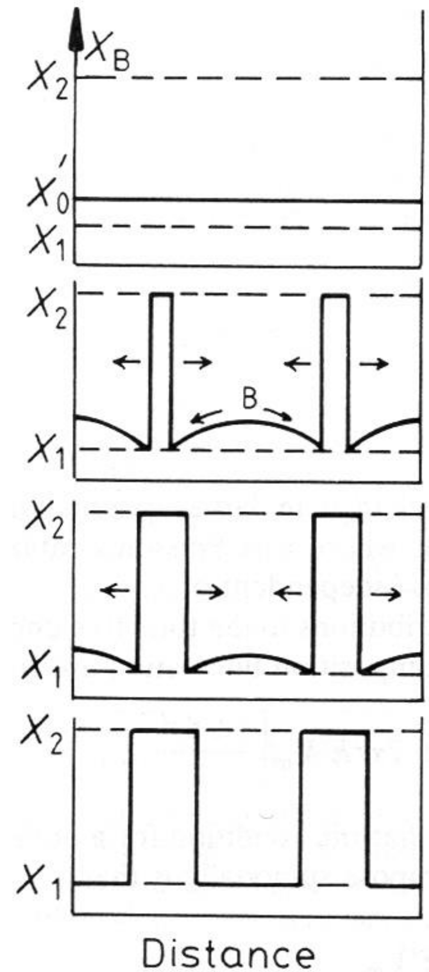


5.5.5 Spinodal Decomposition

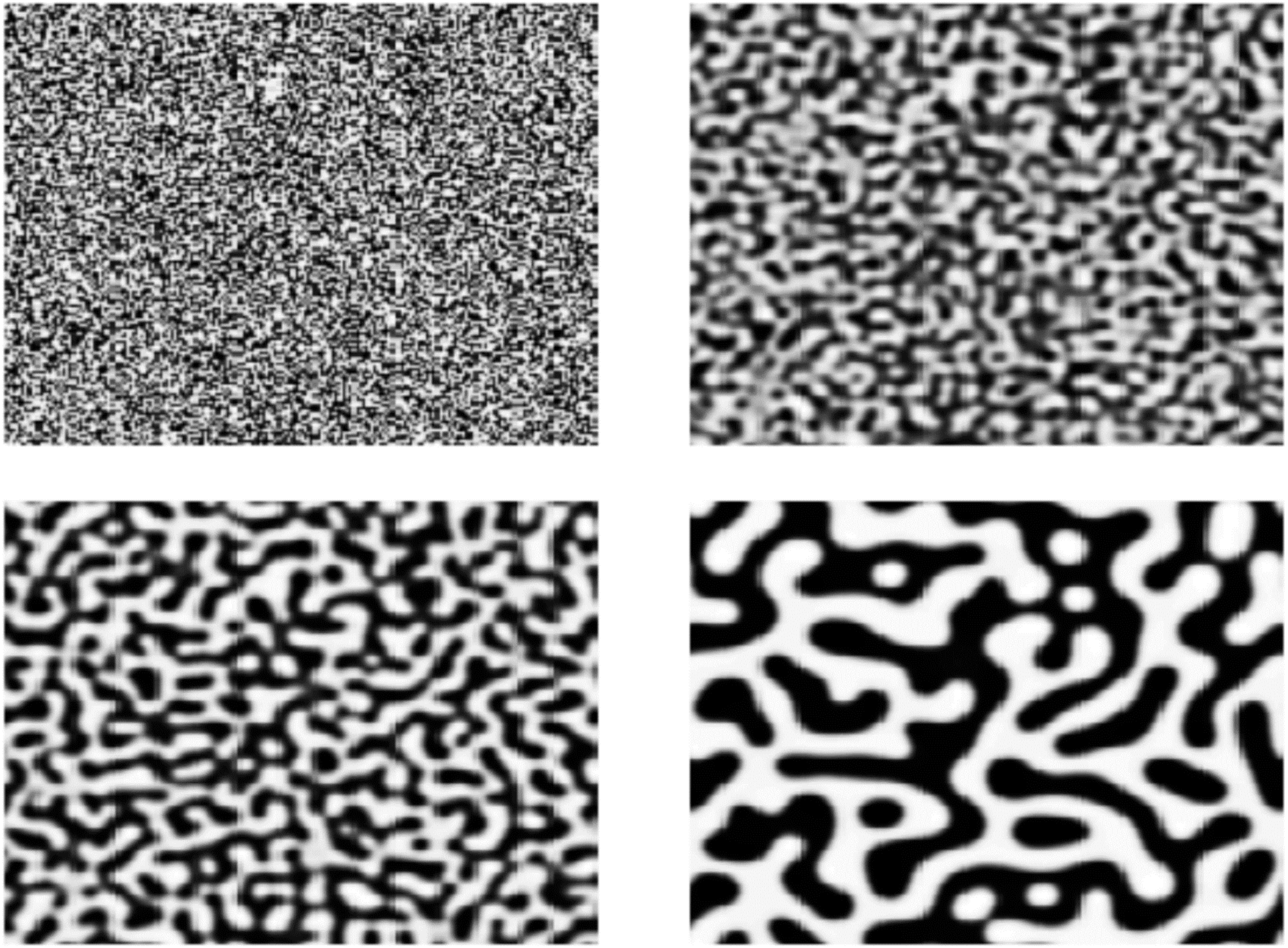
❖ Composition profiles in an alloy quenched into the spinodal region



❖ Composition profiles in an alloy outside the spinodal points



Spinodal decomposion



5.5.5 Spinodal Decomposition

❖ **The Rate of Spinodal Transformation**

✓ Rate controlled by interdiffusion coefficient $\tilde{D}$

✓ Within the spinodal $\tilde{D} < 0$

✓ Composition fluctuation $\propto \exp(-\frac{t}{\tau})$ $\tau = -\lambda^2 / 4\pi^2 D$

- τ : characteristic time constant
- λ : wavelength of the composition modulation (1-D assumed)

- Transfer rate ↑ as λ ↓

- However, there is a minimum value of λ below which spinodal decomposition cannot occur

- To calculate λ, it is need to take care of

1) interfacial energy , and 2) coherency strain energy

5.5.5 Spinodal Decomposition

✓ Homogeneous alloy X_o => decomposed $X_o + \Delta X$ and $X_o - \Delta X$

Total chemical free energy change

$$\Delta G_C = \frac{1}{2}\frac{d^2G}{dX^2}(\Delta X)^2$$

Interfacial energy (gradient energy)

$$\Delta G_\gamma = K\left(\frac{\Delta X}{\lambda}\right)^2$$

- Initially small, but getting bigger
- Origin: Increase of unlike nearest neighbours
- K : propotional constant dependent on the difference in the bond energies

Coherency strain energy

$$\Delta G_S \propto E\delta^2$$

$$\delta = \left(\frac{da}{dX}\right)\left(\frac{\Delta X}{a}\right)$$

$$\Delta G_S = \eta^2(\Delta X)^2 E' V_m$$

$$where \quad \eta = \frac{1}{a}\left(\frac{da}{dX}\right)$$

$$E' = \frac{E}{1-\nu}$$

(indepenent of λ)

5.5.5 Spinodal Decomposition

Total free energy change

$$\Delta G = \left\{ \frac{d^2 G}{dX^2} + \frac{2K}{\lambda^2} + 2\eta^2 E' V_m \right\} \frac{(\Delta X)^2}{2}$$

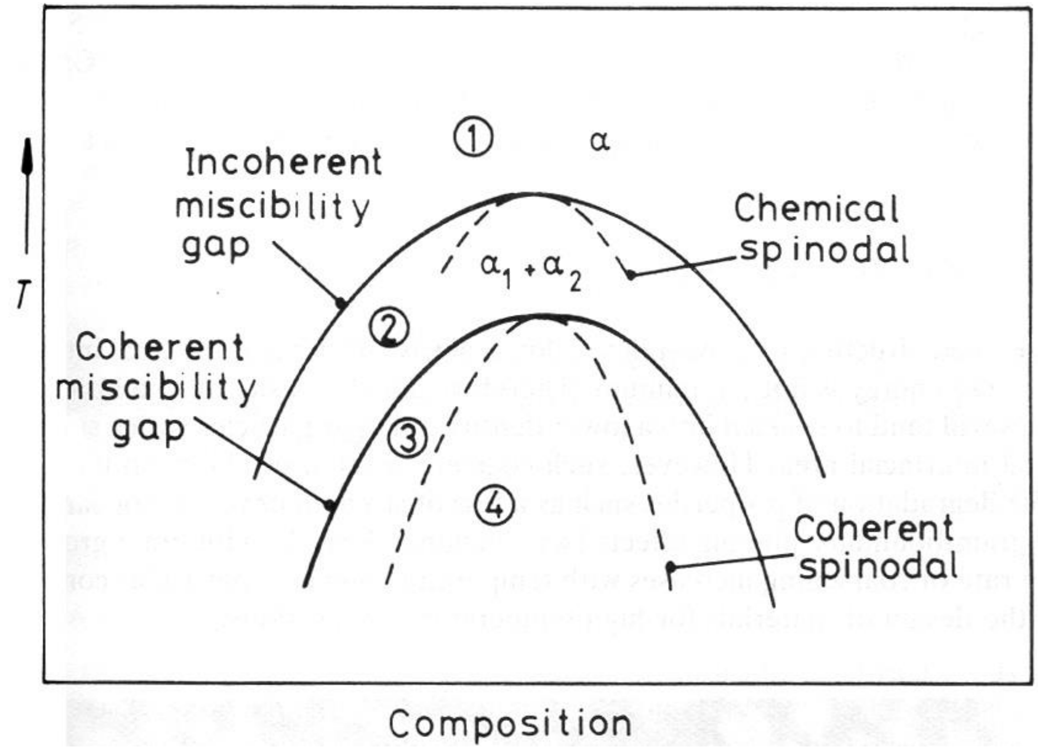
Condition for Spinodal decomposition

$$-\frac{d^2 G}{dX^2} > \frac{2K}{\lambda^2} + 2\eta^2 E' V_m$$

The limit for the decomposition
(λ = infinite)

$$\frac{d^2 G}{dX^2} = -2\eta^2 E' V_m$$

Coherent Spinodal

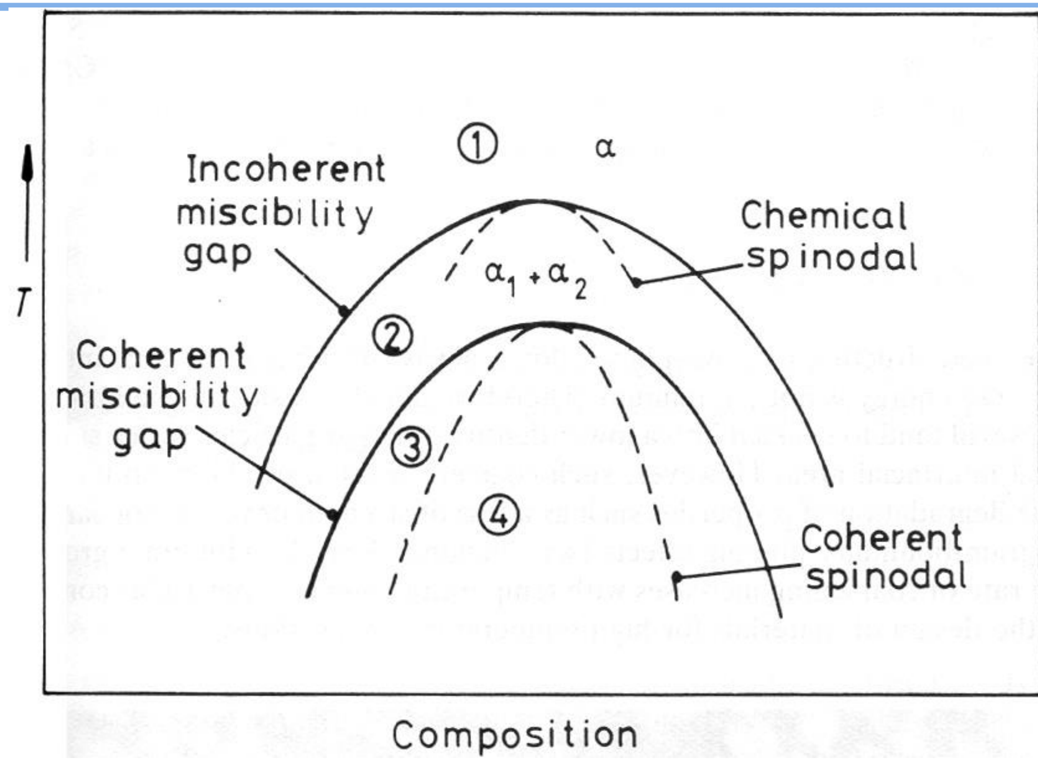


$$\lambda^2 > -2K / \left(\frac{d^2 G}{dX^2} + 2\eta^2 E' V_m \right)$$

for coherent Spinodal

The min. possible wavelength ↓ with ΔT↑ below the coherent spinodal

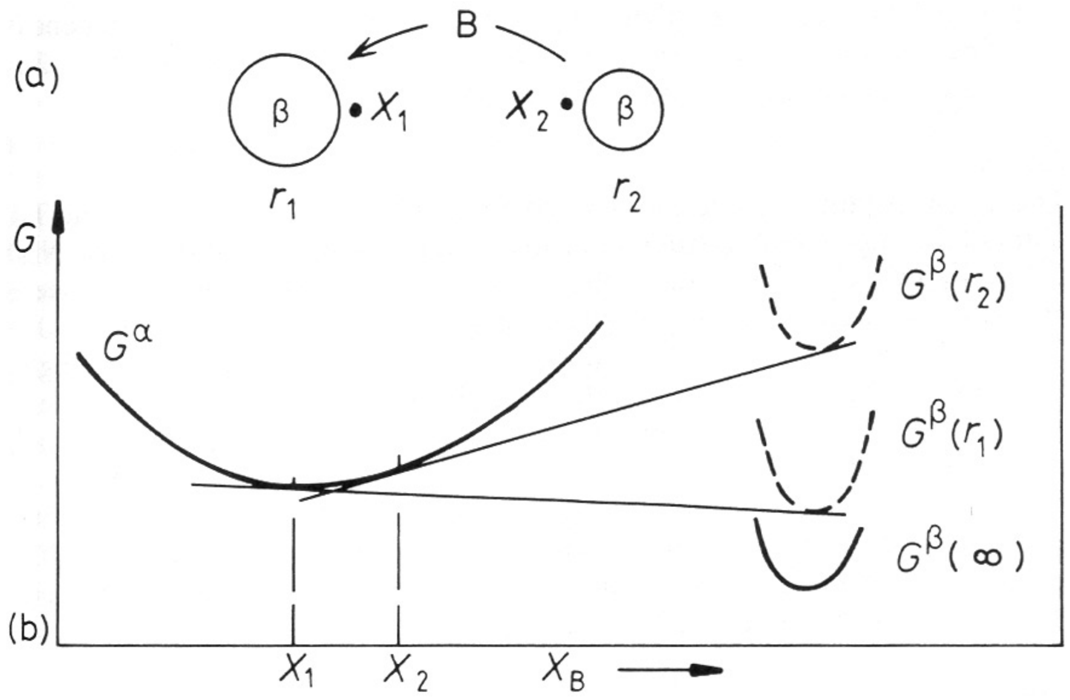
5.5.5 Spinodal Decomposition



1. Homogenous *a* stable
2. Homogenorus *a* metastable, only incoherent phases can nucleation
3. Homogenorus *a* metastable, coherent phase can nucleate
4. Homogenorus *a* unstable, no nucleation barrier,
   spinodal decomposion occur

5.5 Precipitation in Age-Hardening Alloys

5.5.6 Particle Coarsening



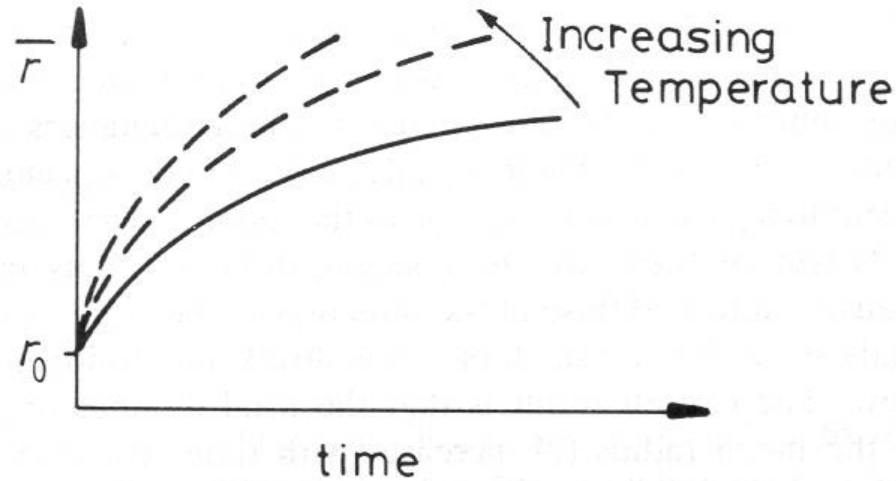
$$(\bar{r})^3 - r_0^{\ 3} = kt$$

where $k \propto D\gamma X_e$

r_o : mean radius at time t=0

5.5 Precipitation in Age-Hardening Alloys

$D = D_0 \exp(-\frac{Q}{RT})$, $X_e = X_0 \exp(-\frac{Q}{kT})$ $\therefore \frac{d\bar{r}}{dt}$ ↑ rapidly with temp.



$$\boxed{\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}}$$ Rate of coarsening

Meaning : distribution of small ppts coarsen most rapidly.

3.5 Interface Migraiton

- Growth can be categorized into diffusion-controlled growth and interface-controlled growth

3.5 Interface Migration

✓ Phase transformation occurs by nucleation growth process.

✓ β forms at a certain sites within α (parent) during nucleation (interface created) then the α/β interface "migrate" into the parent phase during growth.

- **Types of interfaces**
  1. Glissile: by ⊥ glide → results in the shearing of parent lattice into the product (β), motion (glide) insensitive to temperature (athermal)
  2. Non glissile (most of cases): migration by random jump of individual atoms across the interface (similar to high angle grain boundary migration)

3.5 Interface Migration

A. Heterogeneous Transformation

- Classifying nucleation and growth transformation (=heterogeneous transformation)
  - ✓ Transformation by the migration of a glissile interface
    → Military transformation
  - ✓ Uncoordinated transfer of atoms across non-glissile interface
    → Civilian transformation

- Military transformation
  - ✓ The nearest neighbors of any atom are unchanged.
  - ✓ The parent product phases – the same composition, no diffusion involved
    (martensite transformation , mechanical twins)