



EMA5001 Lecture 19

Spinodal Decomposition



Introduction

❑ Certain solid-state transformation does not have (significant) barrier to nucleation

- Spinodal decomposition

❑ Topics

- Basics and unique features
- Driving force

❑ Features

- Simplicity and more precise mathematical description
- Transformation kinetics determined purely by diffusion



Composition & Temperature Range for Spinodal Decomposition

□ Binary system with a miscibility gap

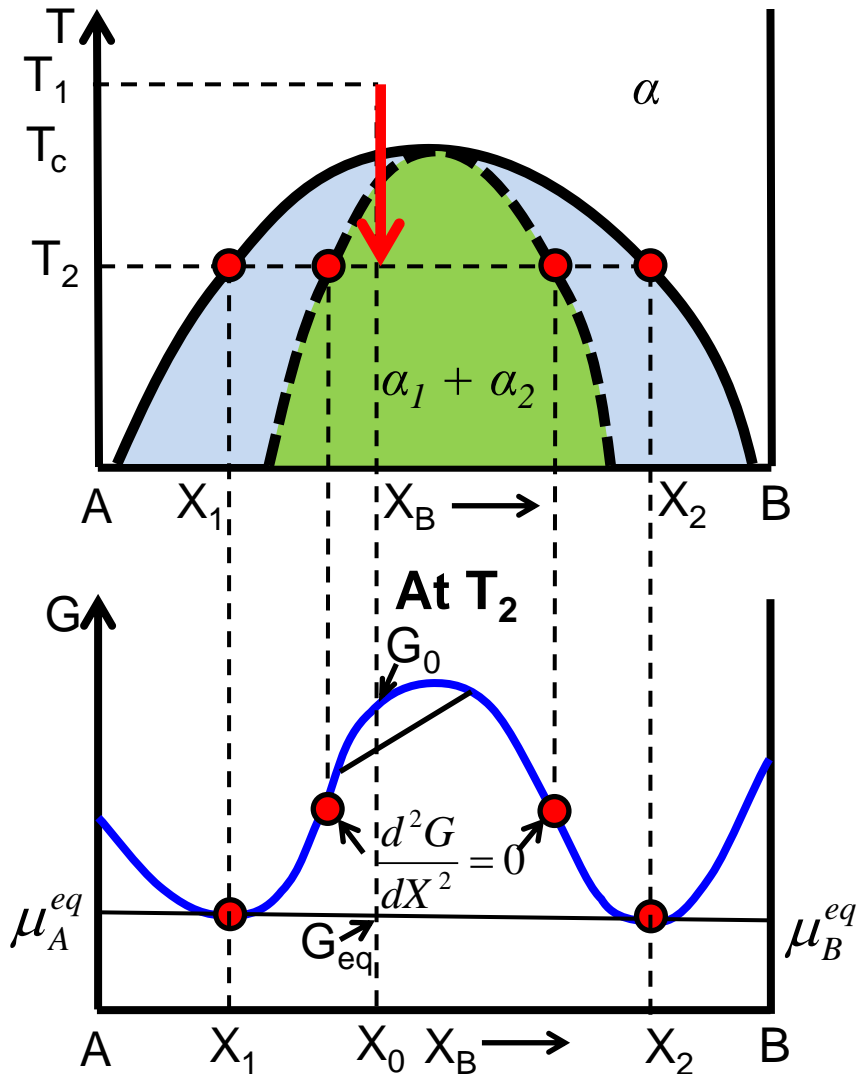
- Gibbs free energy – composition curve at a given temperature below T_c

Cooling from $T_1 (> T_c)$ to $T_2 (< T_c)$

For certain composition X_0

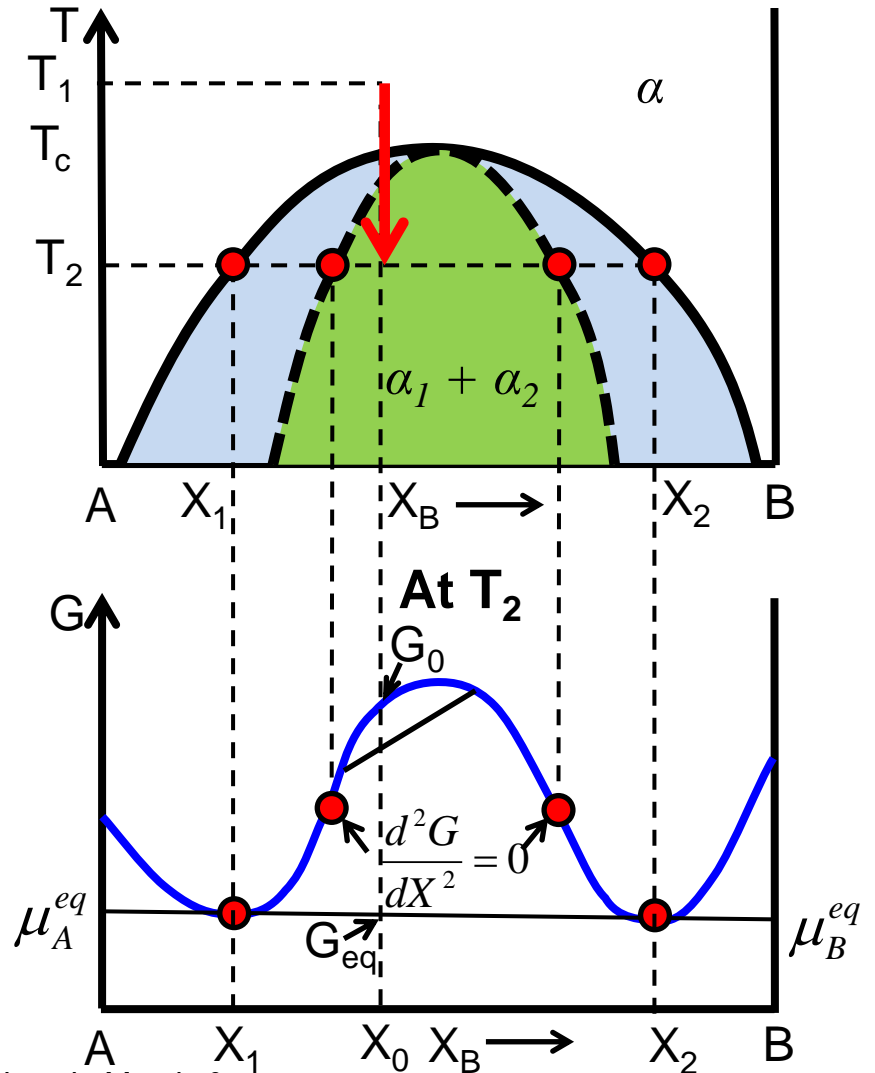
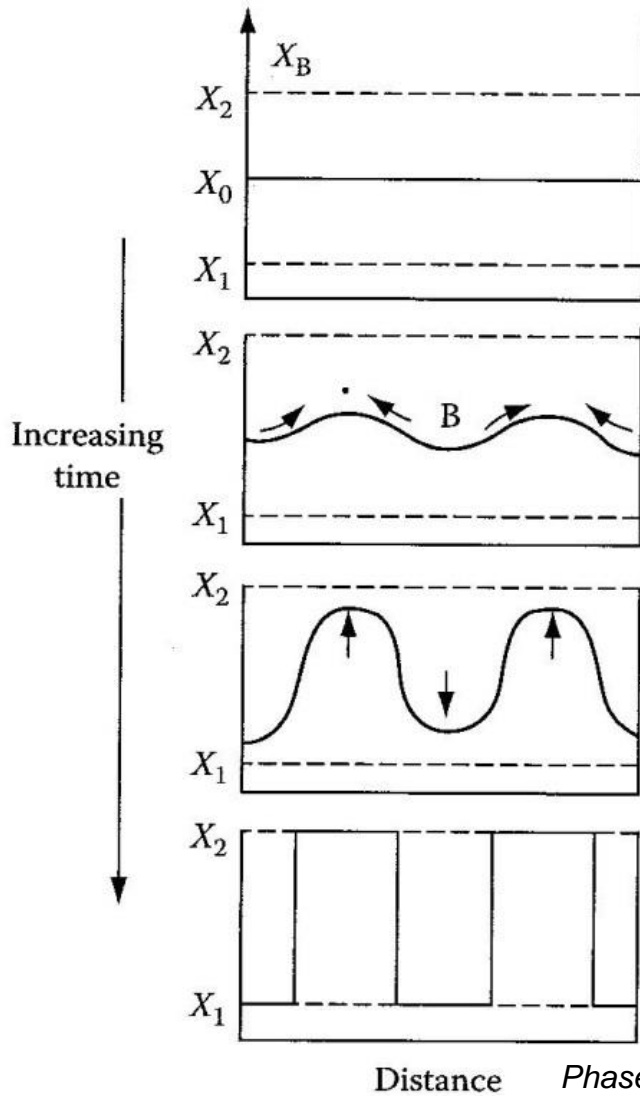
- Initial free energy G_0 higher than equilibrium
- Slight composition variation near X_0 leads to lowering of system energy
 - **Spontaneous decomposition**
 - **“Uphill” diffusion**
 - **Will always reach equilibrium**
- Condition for such transformation or unstable region

$$\frac{d^2G}{dX^2} < 0$$





Composition Change with Time for Spinodal Decomposition



Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 305



Transformation Outside Spinodal Decomposition Range

□ Outside (chemical) spinodal

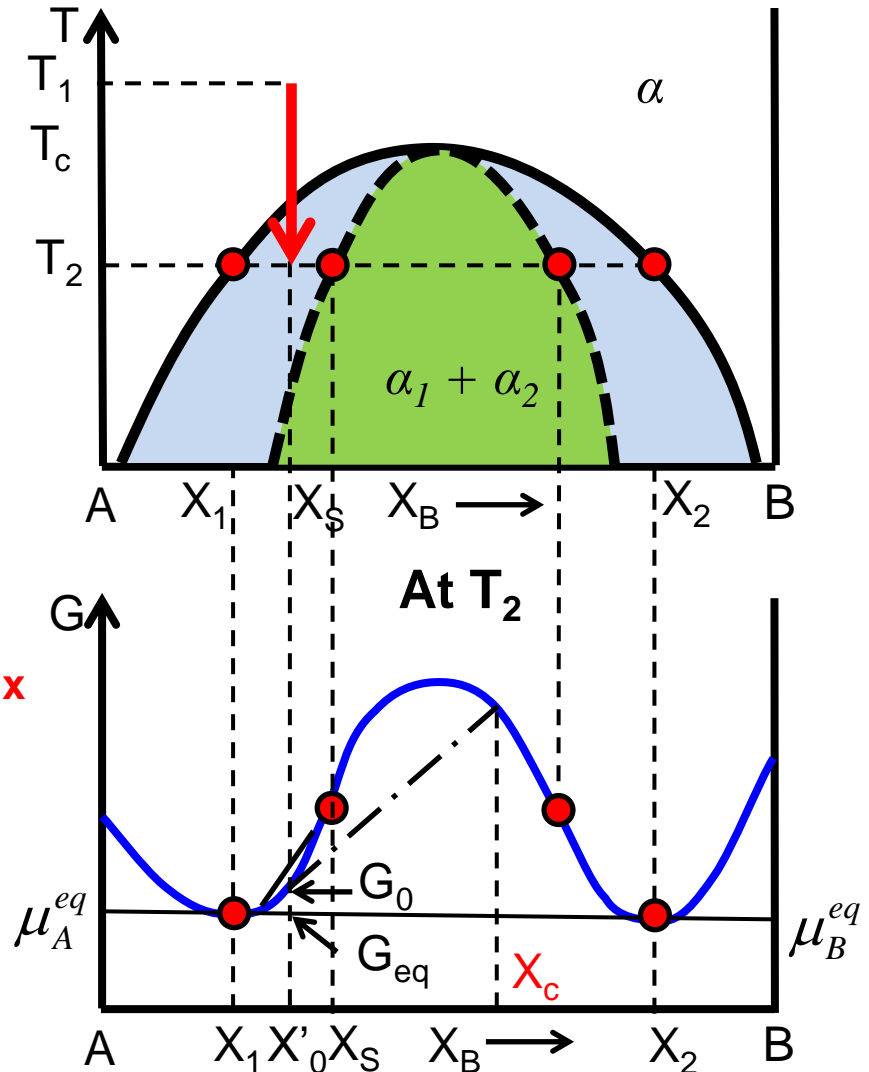
Same system as before

Cooling from $T_1 (> T_c)$ to $T_2 (< T_c)$

For certain composition X'_0

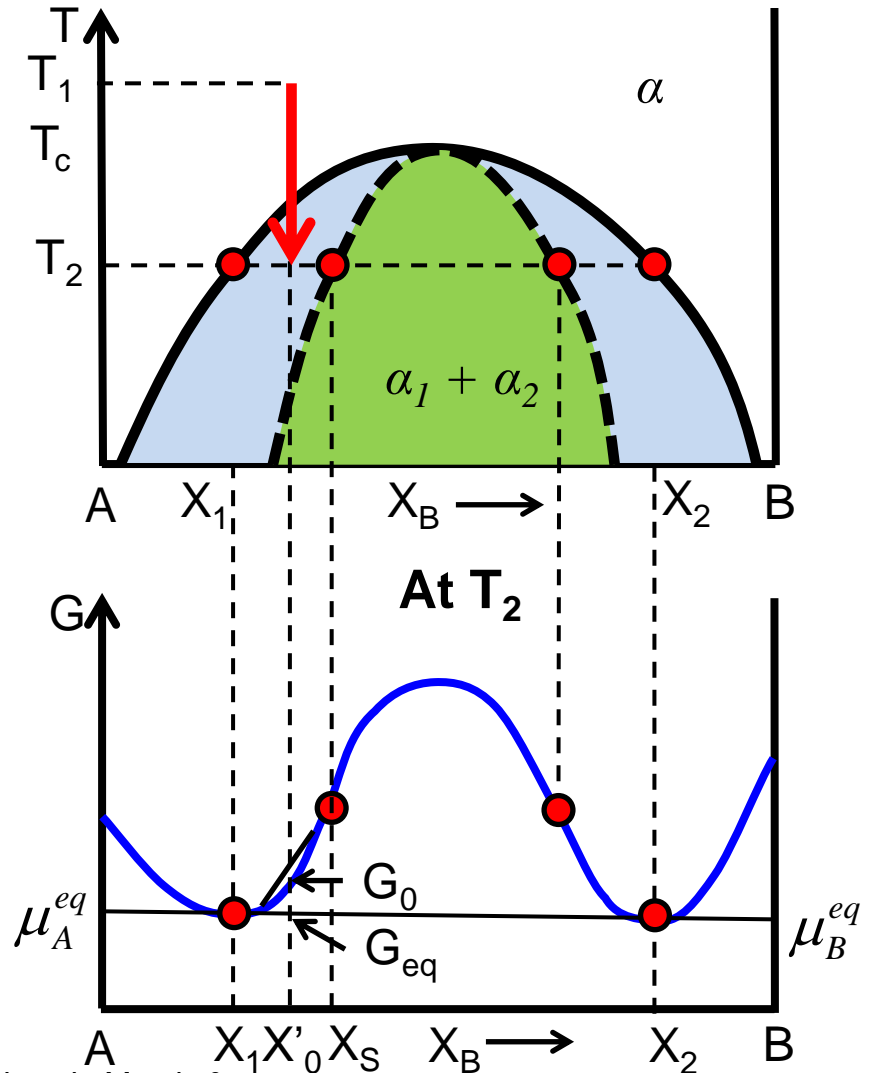
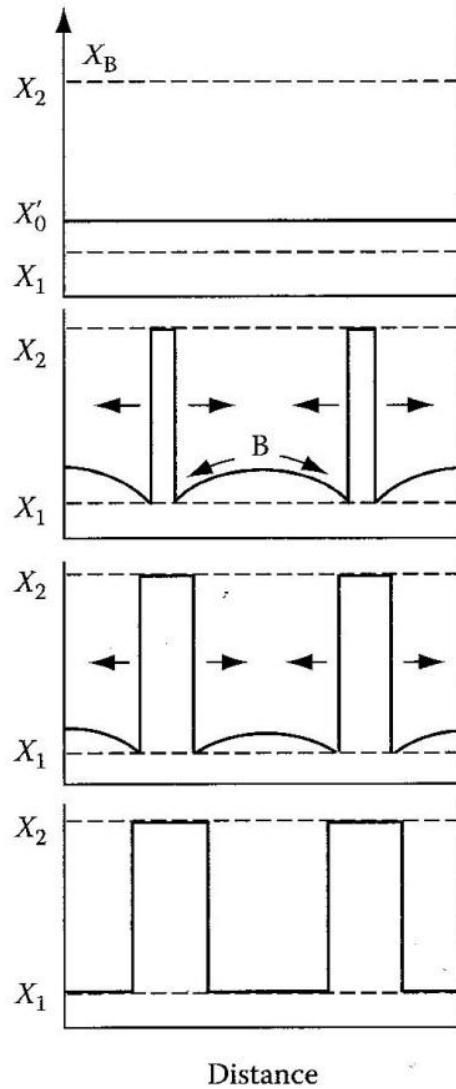
- Initial free energy higher than equilibrium
- **Small** composition fluctuation near original composition (X'_0) leads to increase in system free energy
 - **Need nucleation process with nuclei composition very different from matrix ($> X_c$)**
 - **“Down-hill” diffusion**
 - **May stay at meta-stable condition**
- Condition for such transformation or unstable region

$$\frac{d^2G}{dX^2} > 0 \quad X_1 < X'_0 < X_s$$





Transformation Outside Spinodal Decomposition Range



Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 306



Spinodal Decomposition vs. Nucleation & Growth

Type of precipitation	Nucleation & Growth	Spinodal Decomposition
Free energy – composition curve	$\frac{d^2G}{dX^2} > 0$	$\frac{d^2G}{dX^2} < 0$
Condition	Critical supercooling	Composition fluctuation
Nucleus formation?	Yes	No
Composition change from matrix to new phase	Very large	Small
Structure change from matrix to new phase	Typically large	Essentially no change
Interface	Distinct	Diffuse and not well defined
Direction of diffusion	Down-hill	Uphill
Rate of transformation	Slow	Fast
Precipitate size and distribution	Small number of precipitates with large size	Large number of precipitates with small size



Driving Force for Spinodal Decomposition (1)

Assuming initial matrix composition of X_0

For simplicity, assume it locally experiences compositional fluctuation of $\pm\delta X$

Local sys. free energy before fluctuation G_0

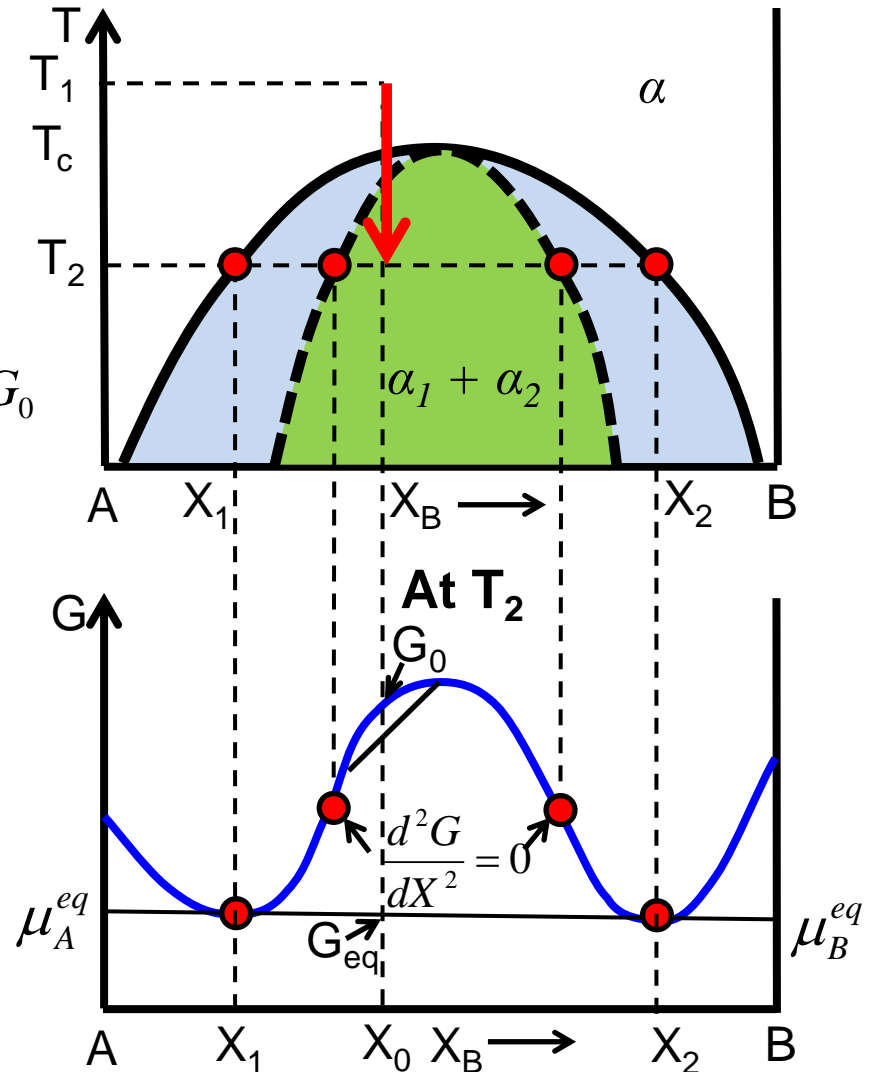
Local sys. free energy after fluctuation (omitting 3rd order and higher terms)

$$G_0' = \frac{1}{2} \left[G_0 + \frac{dG}{dX} \delta X + \frac{1}{2} \frac{d^2G}{dX^2} (\delta X)^2 \right] +$$

$$\frac{1}{2} \left[G_0 - \frac{dG}{dX} \delta X + \frac{1}{2} \frac{d^2G}{dX^2} (\delta X)^2 \right]$$

Local system free energy change:

$$\Delta G_v = G_0' - G_0$$





Driving Force for Spinodal Decomposition (2)

□ Continue from p.8

Assuming system interface energy and straining energy can be neglected
System free energy change for such local composition fluctuation is

$$\Delta G_v = G_0' - G_0$$

$$\text{Since } G_0' = \frac{1}{2} \left[G_0 + \frac{dG}{dX} \delta X + \frac{1}{2} \frac{d^2G}{dX^2} (\delta X)^2 \right] + \frac{1}{2} \left[G_0 - \frac{dG}{dX} \delta X + \frac{1}{2} \frac{d^2G}{dX^2} (\delta X)^2 \right]$$

$$\text{We have } \Delta G_v = \frac{1}{2} \cdot \frac{d^2G}{dX^2} (\delta X)^2$$

$$\text{Therefore, only when } \frac{d^2G}{dX^2} < 0$$

$$\text{we have } \Delta G_v = \frac{1}{2} \cdot \frac{d^2G}{dX^2} (\delta X)^2 < 0$$

The phase separation/transformation will be **spontaneous**



Up-Hill Diffusion in Spinodal Decomposition (1)

□ Describing diffusive flux of atoms from chemical potential gradient

Net drift velocity v **superimposed on random jumping** due to a driving force/potential

Intrinsic diffusive flux of B (with respect to a lattice plane) is related to drift velocity as

$$J_B = v_B C_B$$

Drift velocity is proportional to local gradient of chemical potential, i.e.,

$$v_B = -M_B \frac{\partial \mu_B}{\partial x'} = -M_B \frac{\partial \mu_B}{\partial x}$$

Where M_B is the atomic mobility

Therefore, flux of B due to the driving force is

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$



Up-Hill Diffusion in Spinodal Decomposition (2)

□ Continue from p. 10

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

Consider: $C_B = X_B / V_m$

$$\text{We have } J_B = -M_B (X_B / V_m) \cdot \frac{\partial \mu_B}{\partial (X_B / V_m)} \cdot \frac{\partial C_B}{\partial x} = - \left(M_B X_B \cdot \frac{\partial \mu_B}{\partial X_B} \right) \frac{\partial C_B}{\partial x}$$

For binary alloy, $G = X_A \mu_A + X_B \mu_B$

Under constant temperature and pressure, Gibbs-Duham equation gives

$$X_A d\mu_A + X_B d\mu_B = -SdT + VdP = 0$$

On the other hand, $dG = [X_A d\mu_A + X_B d\mu_B] + [\mu_A dX_A + \mu_B dX_B]$

We have $dG = \mu_A dX_A + \mu_B dX_B$



Up-Hill Diffusion in Spinodal Decomposition (3)

□ Continue from p.11

$$dG = \mu_A dX_A + \mu_B dX_B$$

Therefore,
$$\frac{dG}{dX_B} = \mu_A \frac{dX_A}{dX_B} + \mu_B = \mu_B - \mu_A$$

$$\frac{d^2G}{dX_B^2} = \frac{d\mu_B}{dX_B} - \frac{d\mu_A}{dX_A} \cdot \frac{dX_A}{dX_B} = \frac{d\mu_B}{dX_B} + \frac{d\mu_A}{dX_A}$$

For regular solution
$$\mu_B = \mu_B^0 + RT \ln a_B = \mu_B^0 + RT \ln(\gamma_B X_B)$$

$$\frac{d\mu_B}{dX_B} = RT \left(\frac{1}{X_B} + \frac{d \ln \gamma_B}{dX_B} \right) = \frac{RT}{X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$$

Similarly,

$$\frac{d\mu_A}{dX_A} = \frac{RT}{X_A} \left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right)$$



Up-Hill Diffusion in Spinodal Decomposition (4)

□ Continue from p.12

$$\frac{d\mu_A}{dX_A} = \frac{RT}{X_A} \left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right) \quad \frac{d\mu_B}{dX_B} = \frac{RT}{X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$$

Again, remember $X_A d\mu_A + X_B d\mu_B = 0$ and $X_A + X_B = 1$

We have

$$X_A \cdot \frac{RT}{X_A} \left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right) dX_A + X_B \cdot \frac{RT}{X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right) dX_B = 0$$

Or

$$\left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right) (-dX_B) + \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right) dX_B = 0$$

Therefore,

$$\left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right) = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$$

Therefore,

$$\frac{d^2 G}{dX_B^2} = \frac{d\mu_B}{dX_B} + \frac{d\mu_A}{dX_A} = RT \left(\frac{1}{X_A} + \frac{1}{X_B} \right) \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right) = \frac{RT}{X_A X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$$



Up-Hill Diffusion in Spinodal Decomposition (5)

□ Continue from p.13

$$\frac{d^2G}{dX_B^2} = \frac{RT}{X_A X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$$

On the other hand, $\frac{d\mu_B}{dX_B} = \frac{RT}{X_B} \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right)$ and $\frac{d\mu_A}{dX_A} = \frac{RT}{X_A} \left(1 + \frac{d \ln \gamma_A}{d \ln X_A} \right)$

Therefore, $X_A X_B \frac{d^2G}{dX_B^2} = RT \left(1 + \frac{d \ln \gamma_B}{d \ln X_B} \right) = X_B \frac{d\mu_B}{dX_B} = X_A \frac{d\mu_A}{dX_A}$

Diffusion coefficient $J_B = - \left(M_B X_B \cdot \frac{\partial \mu_B}{\partial X_B} \right) \frac{\partial C_B}{\partial x}$

Therefore, diffusion coefficient $D = M_B X_B \cdot \frac{\partial \mu_B}{\partial X_B} = M_B X_A X_B \frac{d^2G}{dX_B^2}$

When $\frac{d^2G}{dX^2} < 0$ $D < 0$



Interfacial Energy & Strain Energy Effects on Spinodal Decomposition

□ If interfacial energy and strain energy could NOT be neglected

- Interfacial energy / gradient energy term
 - Origin from bonding energy difference between A-B versus A-A and B-B types of bonding

- Value

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

K proportional constant

λ Wavelength of composition variation

- Strain energy term

- Origin from size difference in atoms

- Value
$$\Delta G_s = \eta^2 (\Delta X)^2 \frac{E}{1-\nu} V_m = \eta^2 (\Delta X)^2 E' V_m$$

η Defined as
$$\eta = \frac{1}{a} \cdot \frac{da}{dX}$$

ν Poisson's ratio



Interfacial Energy & Strain Energy Effects on Spinodal Decomposition

□ Total free energy change has three contributions

$$\Delta G_v = \frac{1}{2} \cdot \frac{d^2G}{dX^2} (\delta X)^2 \quad \Delta G_\gamma = K \left(\frac{\Delta X}{\lambda} \right)^2 \quad \Delta G_s = \eta^2 (\Delta X)^2 \frac{E}{1-\nu} V_m$$

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

- For Spinodal decomposition to occur $\frac{d^2G}{dX^2} + \frac{2K}{\lambda^2} + 2\eta^2 E' V_m < 0$
- At a given temperature, the limiting composition for Spinodal decomposition to occur (i.e., when $\lambda \rightarrow \infty$) satisfies

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

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