MATE 664 Lecture 13

Phase Diagram and Phase Transformation

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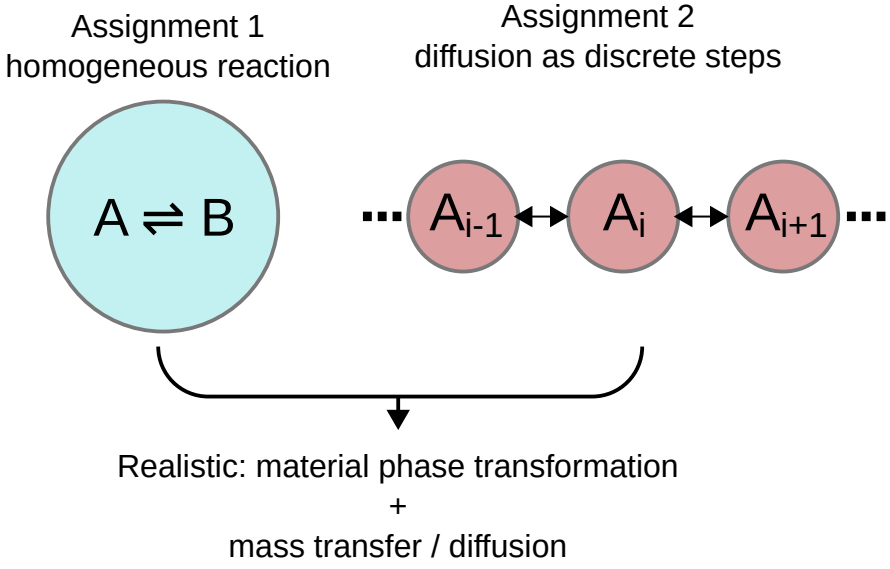
Kinetics of Materials Part II

What topics have we learned so far?

- How to describe kinetic process: **irreversible thermodynamics**
- What causes nonequilibrium mass transfer: **chemical potential** as driving force
- Diffusion in materials: **Fick's equations**
- Determine diffusivity D: **Macroscopic** and **Microscopic** models

What do we study in Part II?

Insights from assignments 1 and 2



Topic 1: phase transformation

Key question: how do materials evolve when chemical potentials are not at equilibrium?

- In-depth study of **phase diagrams**
- Continuous phase transformation: **spinodal decomposition**
- Phase transformation with barrier: **nucleation**

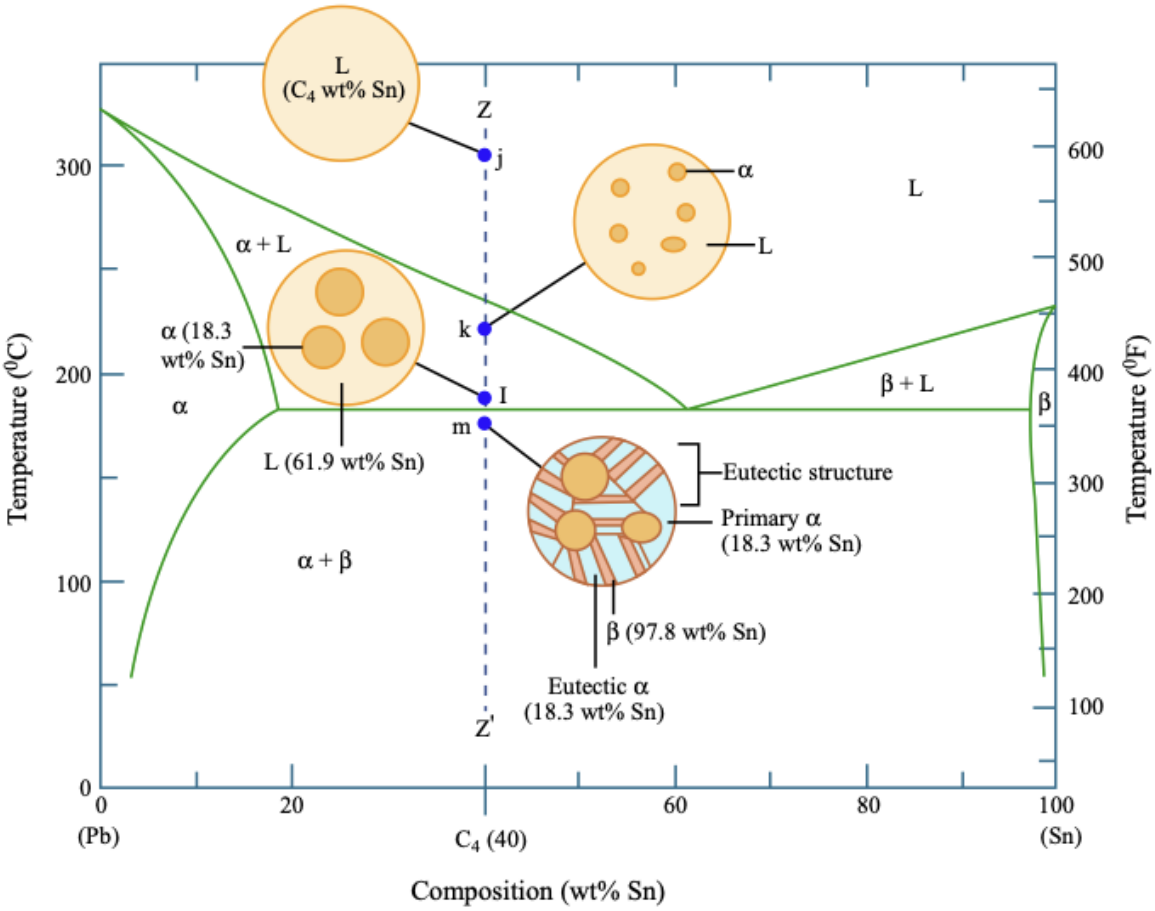


Figure 1: MIT course *Fundamentals of Materials Sciece*

Topic 2: interfacial phenomena

Key question: how do material interfaces change in non-equilibrium process?

- **Solidification**: heat / mass-transfer at interfaces:
- **Sintering**: surface-energy-mediated transformation:

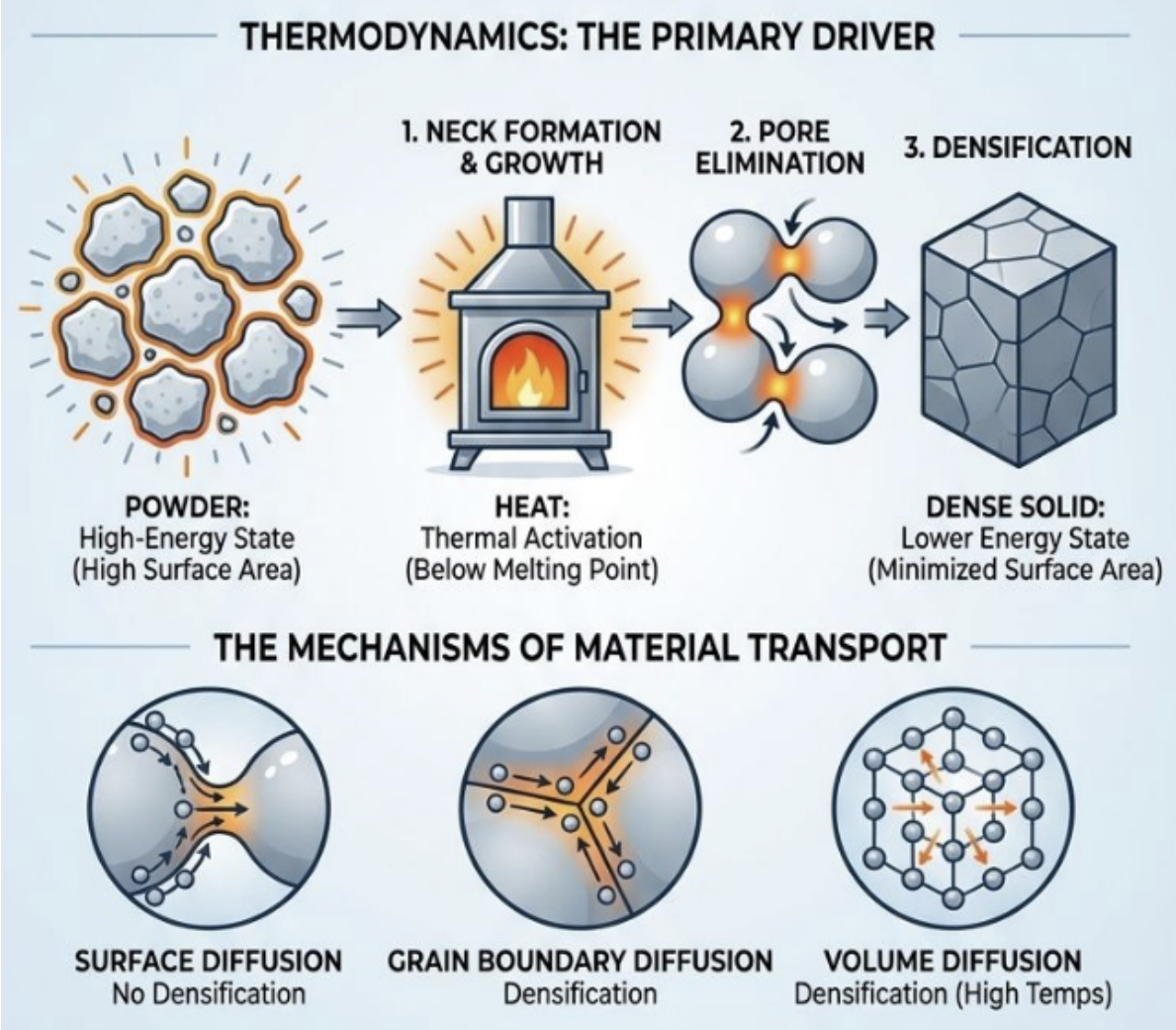


Figure 2: Copyright: kintek.com

Topic 3: analysis of kinetic process in materials

Key question: how do the competition between different effects change the material behaviour?

- **Aggregation phenomena**: diffusion & reaction of soft materials
- **Dendrite formation**: morphological control in battery electrodes
- **Carrier transport**: designing optical materials

Topic 4: simulating kinetic problems

Key question: what methods can we use to simulate kinetic systems, and how good are they?

- Macroscopic transport: **phase-field method**
- Kinetic Monte-Carlo (**KMC**)
- Molecular dynamics (**MD**)
- Thermodynamic parameters from **first principles** and **machine learning**

Introduction to phase transformation

Learning outcomes

After this lecture, you will be able to:

- **Recall** key components of a phase diagram
- **Distinguish** the meaning of axes in a phase diagram
- **Identify** key thermodynamic relations from a phase diagram
- **Analyze** phase transformation regions in a phase diagram

This lecture is adapted from Porter et al. *Phase Transformations in Metals and Alloys*

What is phase transformation?

Before introducing any fancy terminologies, let's define a few concepts:

- **Phase**:
  - a region with uniform structure and properties
- **Transformation**
  - a kinetic process to reduce total free energy by turning phases –>
- **Interface**
  - a boundary separating two phases

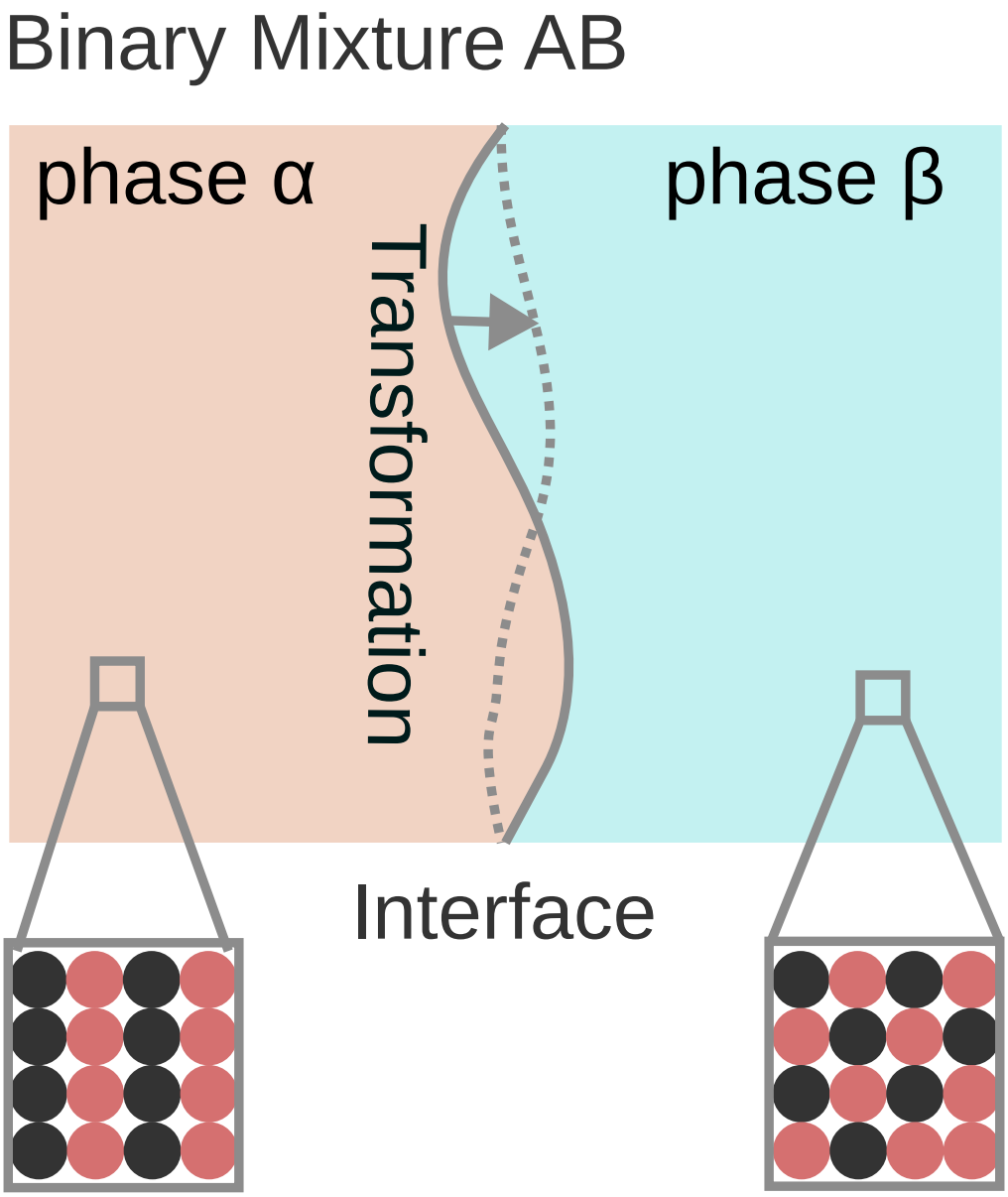


Figure 3: Phase transformation scheme

What can be considered as a phase?

- Mathematically (Landau & Lifshitz 1963), different phases are distinguished by *order parameter* ξ
- The molar free energy $F(T, \xi)$ can be written as a series expansion of ξ
- F can be Helmholtz or Gibbs free energy

$$F(T,\xi) = a_0(T) + a_1(T)\xi + a_2(T)\xi^2 + \cdots \tag{1}$$

- **1st order** phase transition
  - F is continuous at phase interfaces,
  - ξ has abrupt jump

General picture of phase transformation (1st-order)

- Example of solid-liquid transformation (KOM book)
- Order parameter ξ can be arbitrary
- ξ always lower on the high-T phase

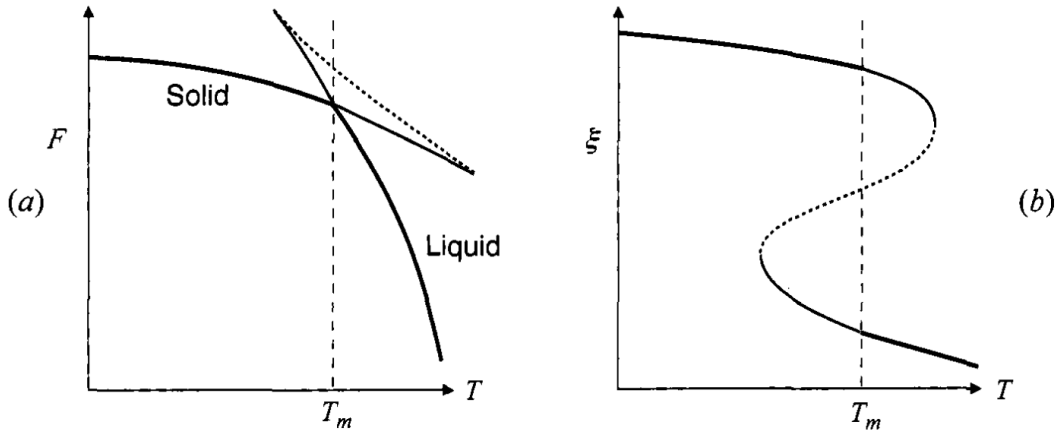


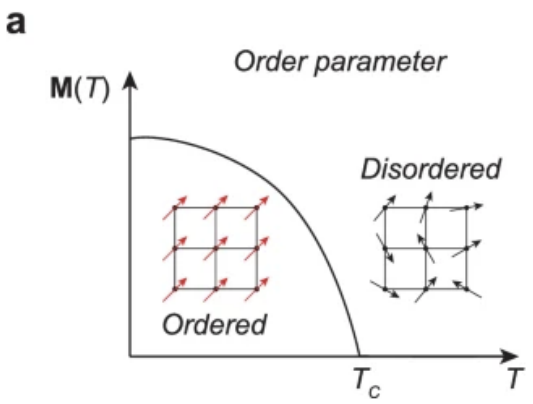
Figure 17.1: **(a)** Molar free energy as a function of temperature for a melting transition. **(b)** Temperature dependence of an order parameter ξ for the transition in (a).

What quantity can be an order parameter?

Examples of order parameters ξ (what changes across a phase boundary)

- **structure**: e.g., fcc $\leftrightarrow$ bcc
- **molar volume** V_m: liquid $\leftrightarrow$ solid
- **magnetization** M: paramagnetic $\leftrightarrow$ ferromagnetic
- **superconducting** order parameter ψ: normal $\leftrightarrow$ superconducting

Fig. 1: Introduction of re-order parameter.



a Classical order parameter in thermal equilibrium. As tem
state transitions into an ordered state through the alignme
namely magnetization **M**(*T*) for ferromagnets. The order p
transition at the critical temperature T_c, which can be effe
curve. **b** Dynamic re-order parameter in nonequilibrium. A
re-ordering at the re-ordering temperature T_{RO}, accompan
order parameter, denoted as d**M**(*T*)/d*t*. This re-order para
magnetization in magnets, demonstrates a high sensitivity

Magnetization as order parameter (second-order transition)

Dissecting the solid-liquid free energy diagram

- Typical H and G diagrams for the single-component system
- G is continuous while H is discontinuous
- Difference in liquid-solid enthalpy: latent heat L

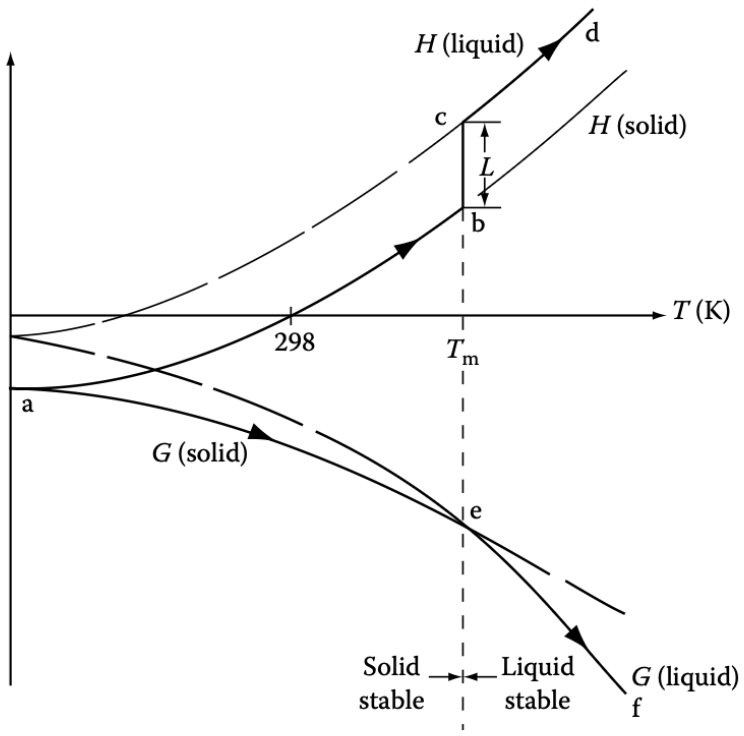


FIGURE 1.4
Variation of enthalpy (H) and free energy (G) with temperature for the solid and liquid phases of a pure metal. L is the latent heat of melting, T_m the equilibrium melting temperature.

How do we get here?

- Enthalpy from specific heat C_p: $C_p = \left(\frac{\partial H}{\partial T}\right)|_p$
- Entropy from specific heat: $\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)|_p$

Single-component system: including pressure

- Left to right: increasing T (melting / evaporation)
- Lower to upper: increasing p (condensation)
- How do free energy profile look like?

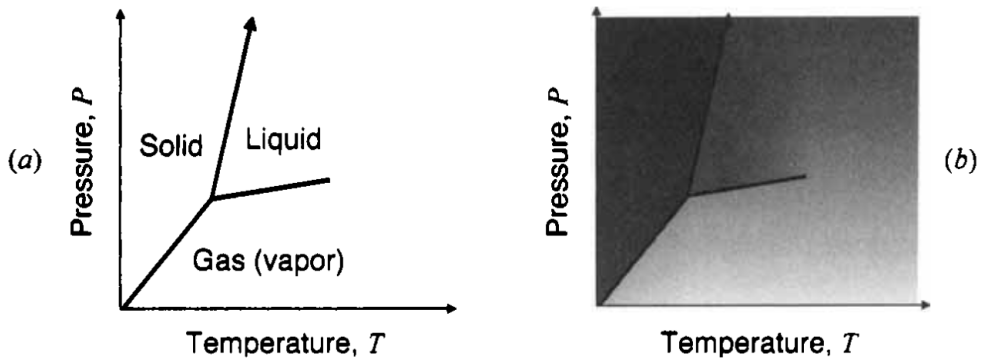


Figure 17.2: **(a)** Single-component phase diagram. **(b)** Shading represents the equilibrium value of a molar extensive quantity such as molar volume V (i.e., light gray represents a large value and dark gray a small value) that apply to each phase at that particular P and T. For phase transitions, the grayscale (or V) could be used as an order parameter indicating phase.

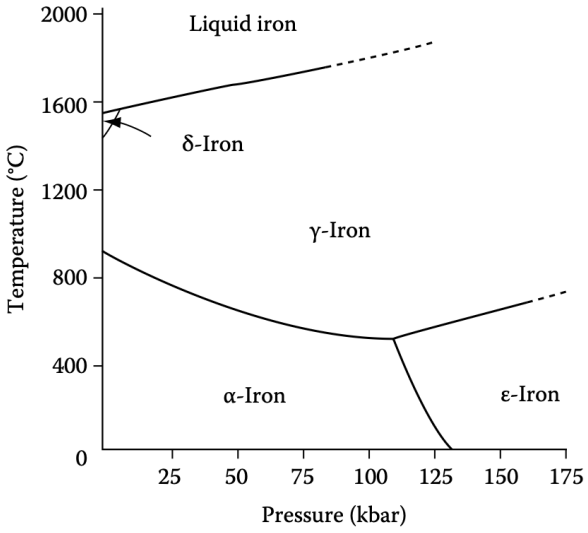
Single-component system: slope of phase boundary

- Phase boundary equilibrium $G^{\alpha} = G^{\beta}$
- Slope of $p - T$ diagram: Clausius-Clapeyron equation

$$\left(\frac{\partial p}{\partial T}\right)|_{\text{eq}} = \frac{\Delta H}{T_{\text{eq}} \Delta V_m} \tag{2}$$

Reading single-component phase diagram (Fe)

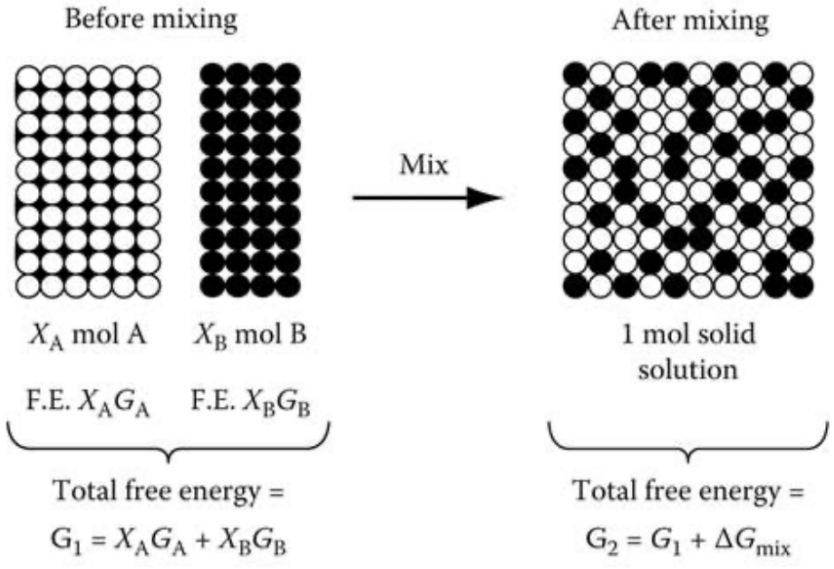
- What can we say about the lattice structure about Fe allotropes?



Free energy diagrams of binary mixture

- Mixing of two materials A and B causes free energy to change
- Before mixing, **molar** free energies G_A, G_B
- After mixing, molar free energy becomes

$$G = X_A G_A + X_B G_B + \Delta G_{\text{mix}} \tag{3}$$



Ideal solution: mixing entropy

- In ideal solution $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$
- Ideal mixing entropy

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$$

Chemical potential on molar free energy diagram

- Chemical potential from G: $\mu_A = \left(\frac{\partial G}{\partial X_A}\right)|_{T,p,X_B}$
- Ideal solution: $\mu_A = G_A + RT \ln X_A$

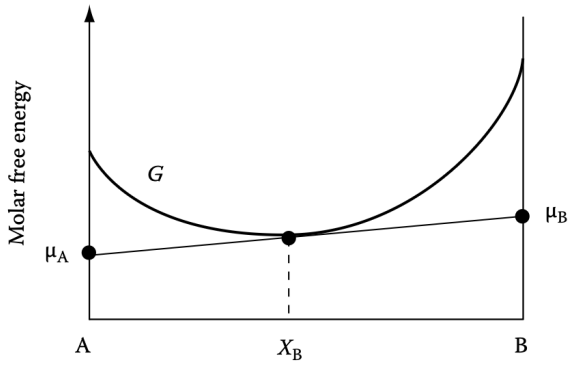


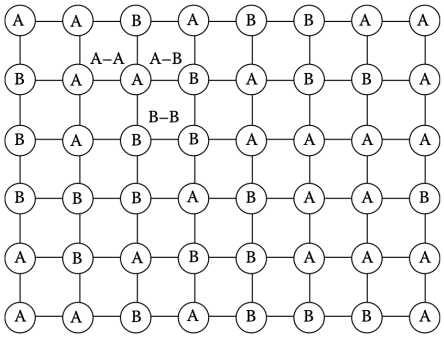
Figure 4: Graphical explanation of chemical potential

Regular solution: mixing enthalpy

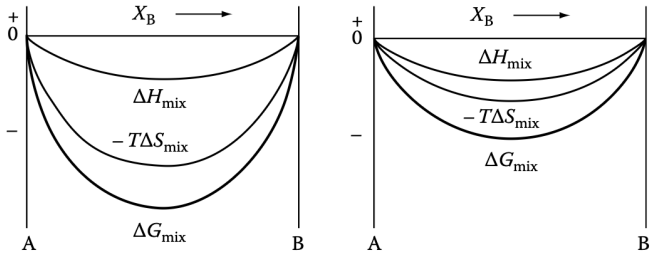
- Generally $\Delta H_{\text{mix}} \neq 0$
- Can be expressed by "likeliness" between A-B

$$\Delta H_{\text{mix}} = N_A z(\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}))X_A X_B$$

1. A—A bonds each with an energy ϵ_{AA},
2. B—B bonds each with an energy ϵ_{BB},
3. A—B bonds each with an energy ϵ_{AB}.

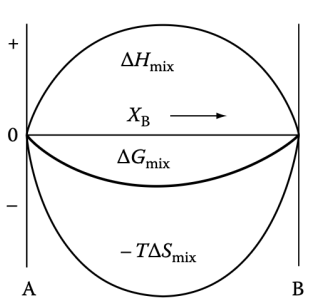


Enthalpic and entropic contributions to mixing

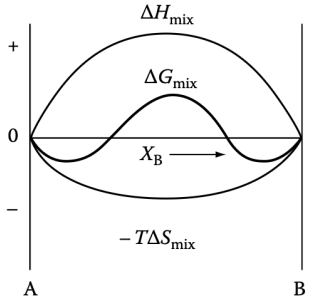


(a) Ω < O, high T

(b) Ω < O, low T



(c) Ω > O, high T



(d) Ω > O, low T

Heterogeneous phase diagram

- At each T, molar free energy of 2 phases are calculated separately
- Imaginary "unstable lattice" for incompatible crystals
- What is the most stable phase at each X?

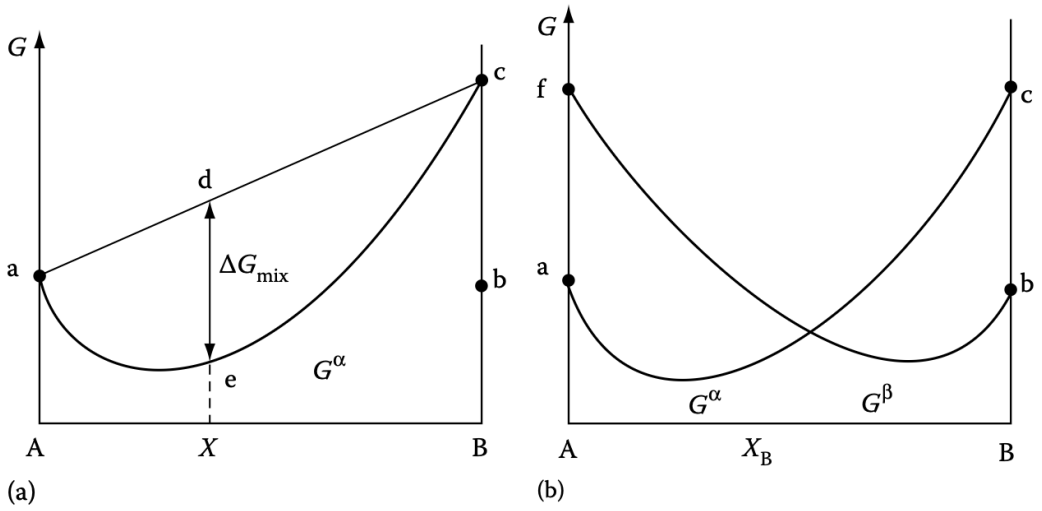


FIGURE 1.25
(a) The molar free energy curve for the α phase, (b) Molar free energy curves for α and β phases.

Heterogeneous system: equilibrium

- Equilibrium condition (common tangent): $\mu_A^\alpha = \mu_A^\beta$ & $\mu_B^\alpha = \mu_B^\beta$
- Lever rule: graphical explanation

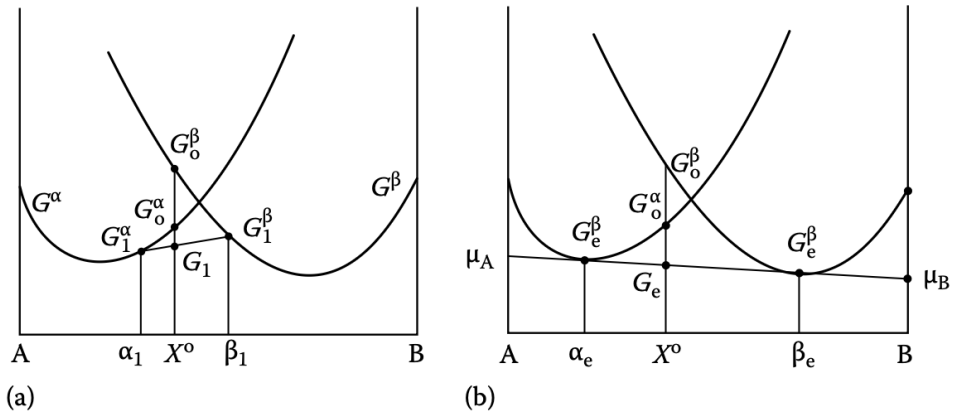
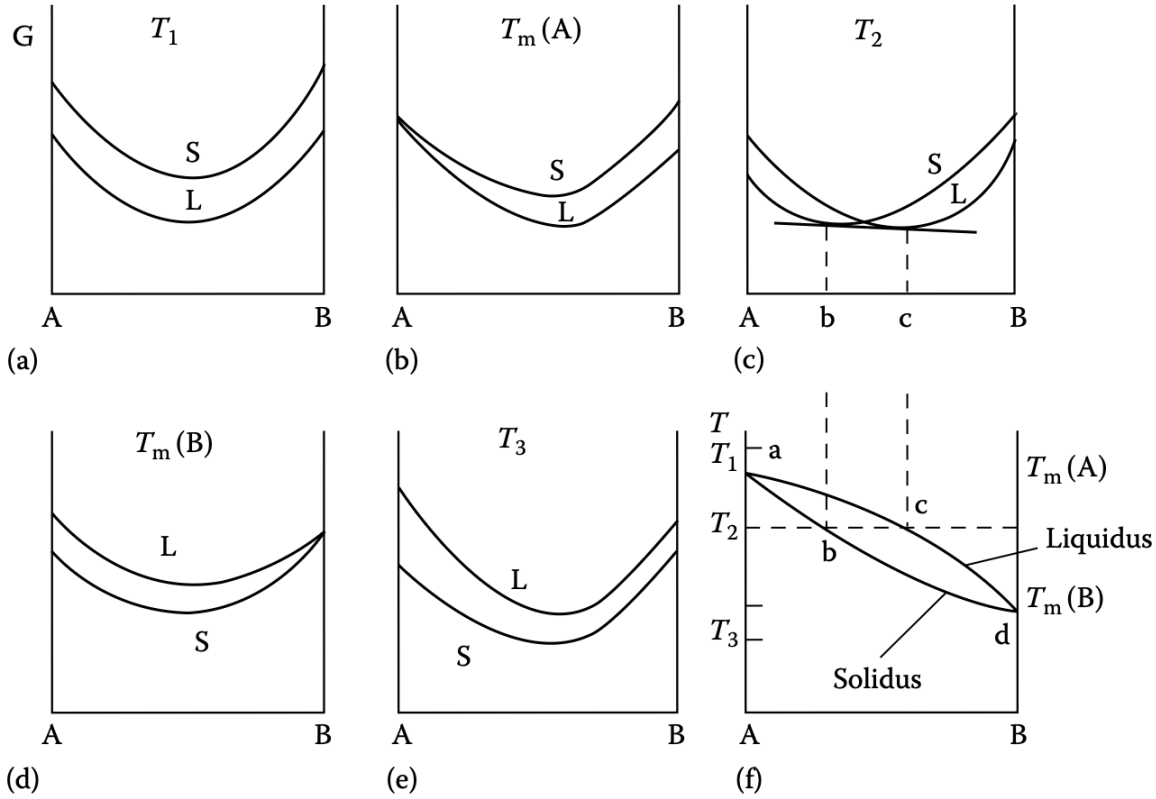


FIGURE 1.27
(a) Alloy X^0 has a free energy G_1 as a mixture of $\alpha_1 + \beta_1$. (b) At equilibrium, alloy X^0 has a minimum free energy G_e when it is a mixture of $\alpha_e + \beta_e$.

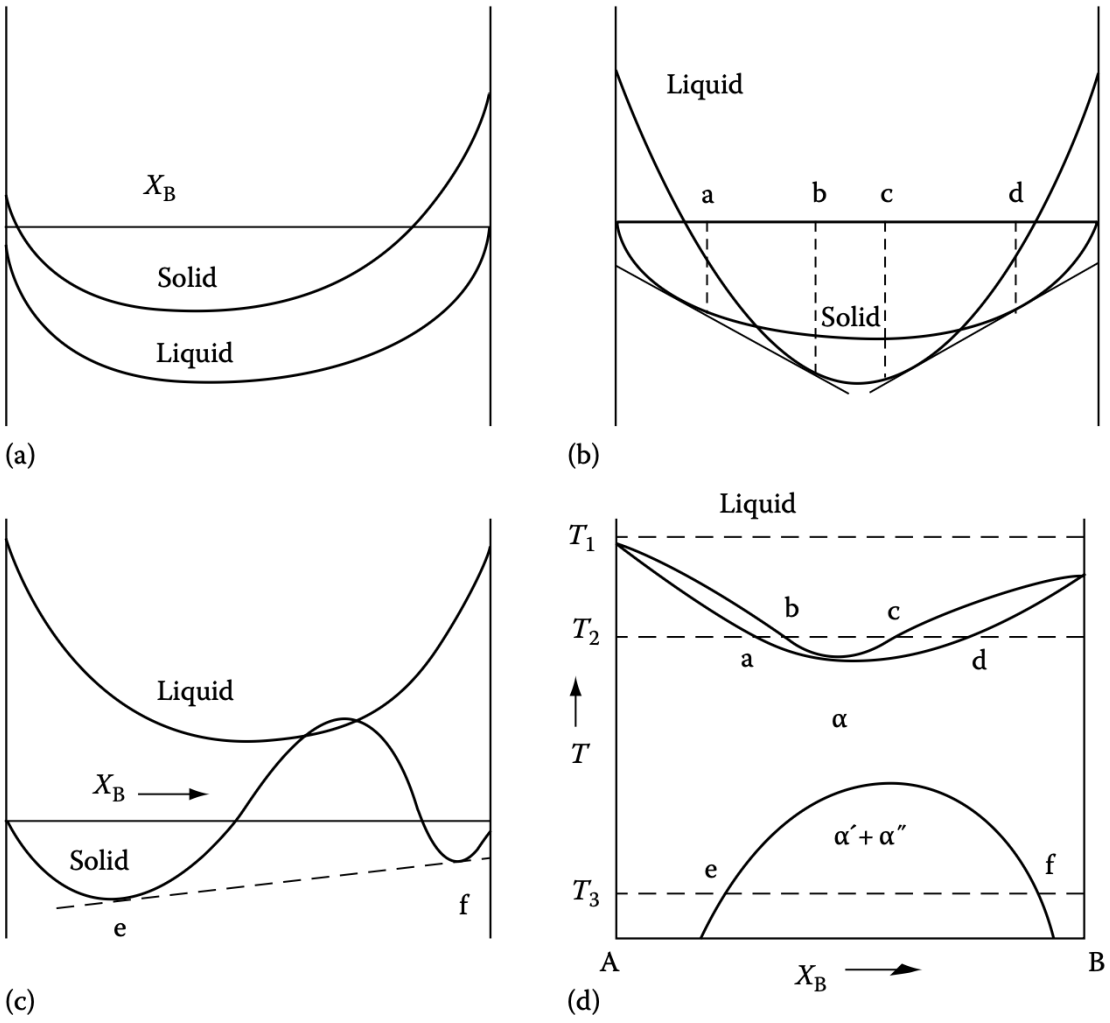
Phase diagram example 1: completely miscible solid & liquid

- E.g. Cu–Ni alloy (fcc)



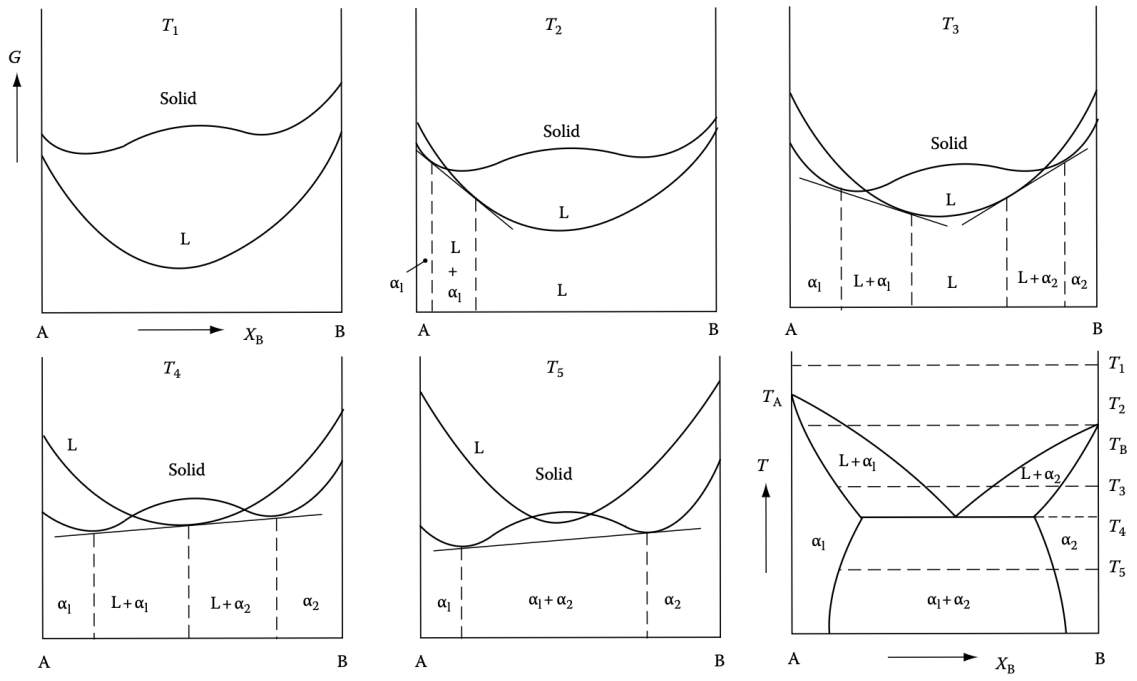
Phase diagram example 2: miscibility gap

- Solid state $\Delta H_{\text{mix}} > 0$
- Will be our example for spinodal decomposition



Phase diagram example 3: eutectic alloy (same lattice)

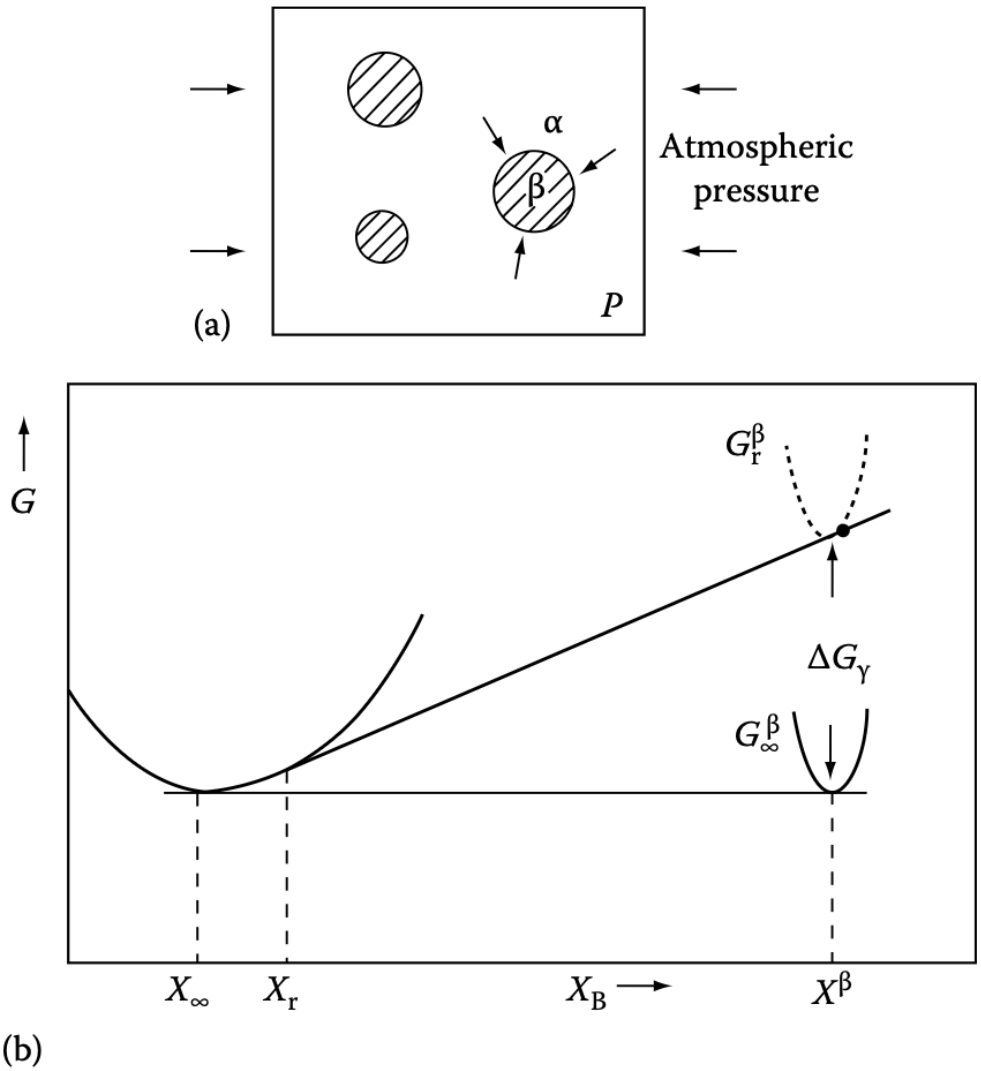
- Eutetic formation due to dominant solid-phase



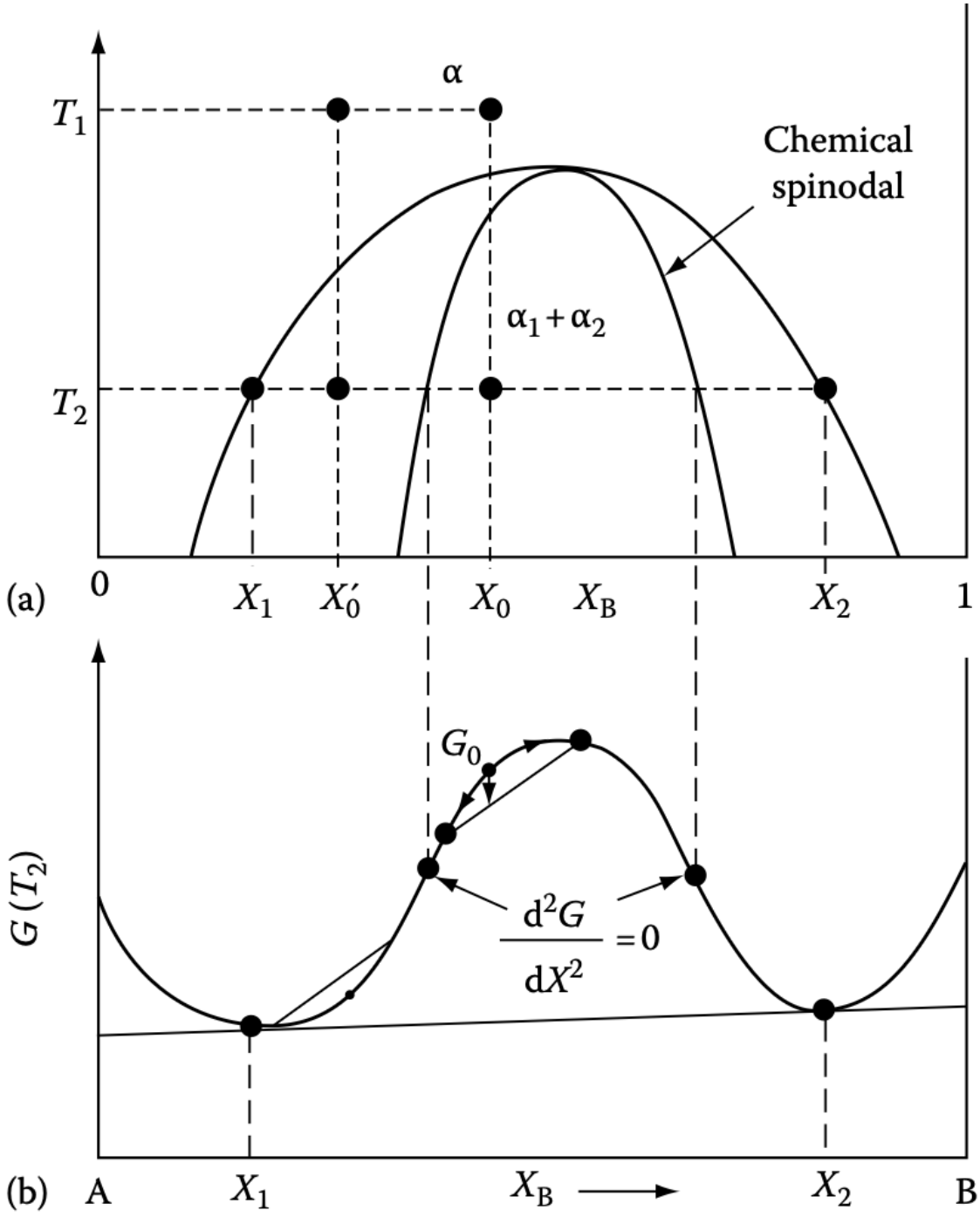
Additional effects for phase stability

- Phase diagram does not tell everything!
- Stability of a phase depends on
  - Molar free energy (what phase diagram tell)
  - Interfacial energy (extra work to stablize interface)
  - Kinetic stability (metastable & unstable regions)
- Actual important issue for kinetic course
  - Interface influence: **nucleation theory**
  - Kinetic stability: **spinodal decomposition**

Preview: influence of interfacial energy



Preview: second-order stability in spinodal decomposition



Summary

In today's lecture, we overviewed the origin of phase transformation and phase diagram.

- Phase transformation can be described by free energy as function of an ordered parameter
- Equilibrium phase diagram is constructed by the lowest free energy phase
- Free energy of mixing –> chemical potential –> constructing phase diagram
- Basic literacy in phase diagram reading!