

MSE-204 Thermodynamics for Materials Science

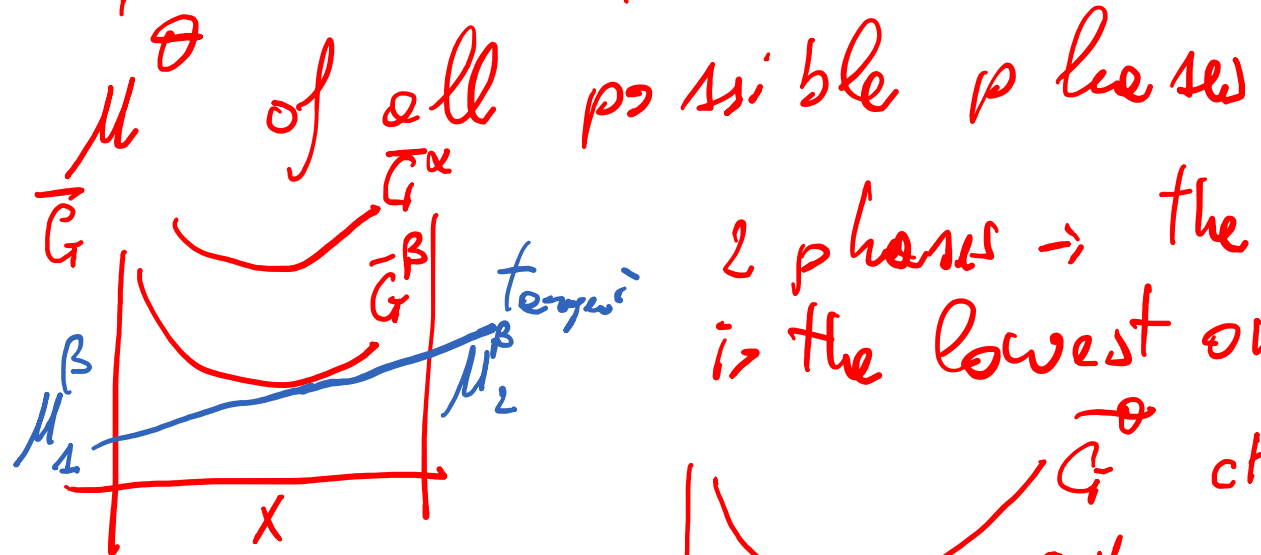
L8.2 MULTICOMPONENT PHASE DIAGRAMS

REGULAR SOLUTION MODEL | SPATIAL ARRANGEMENT OF ATOMS | MISCIBILITY GAP | INVARIANT POINTS |
INTERMEDIATE COMPOUNDS

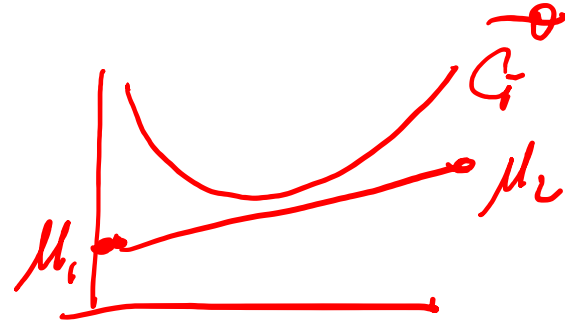
Vaso Tileli | MXD 237

REMINDER FROM LAST TIME

Equilibrium $\mu(p, T, \{x_i\})$

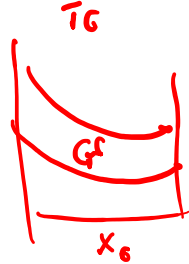
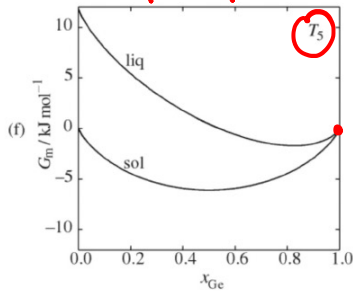
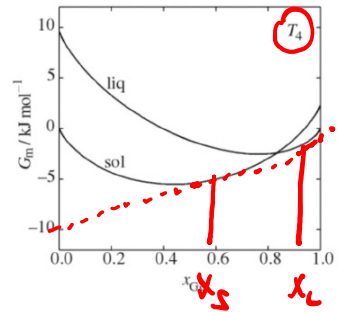
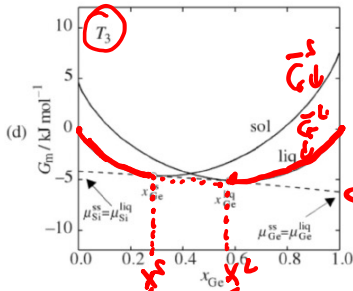
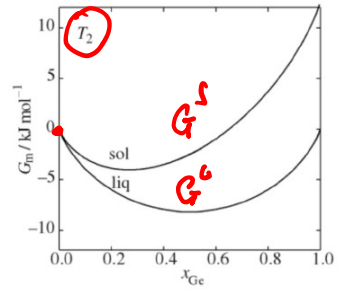
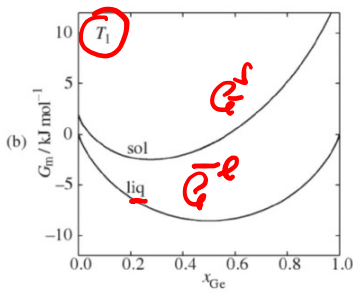
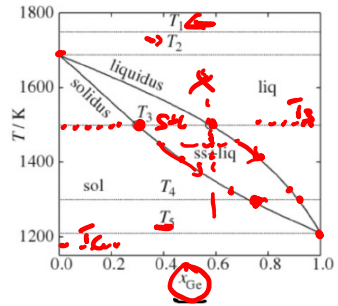


2 phases $\rightarrow$ the equilibrium phase is the lowest one



chemical mixing $\bar{G}^\theta$
 L : curve $\bar{G}^\theta$
 physical mixing (do not mix)
 L : line

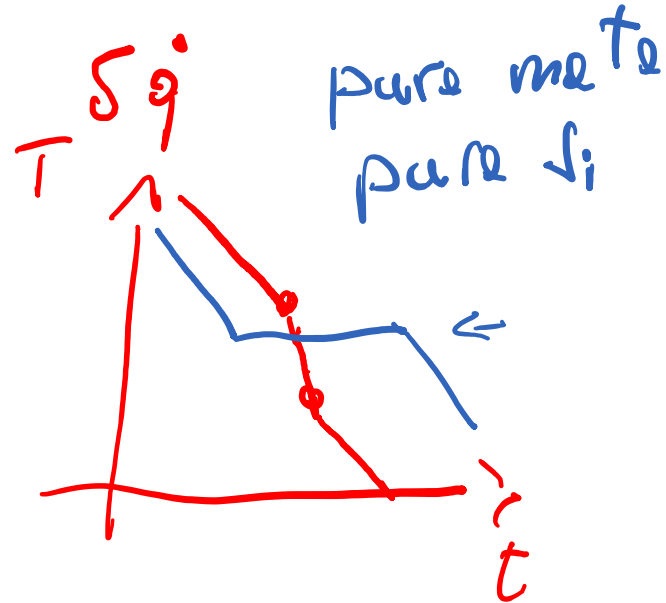
THE SI-GE PHASE DIAGRAM



IDEAL SOLUTION

$$\Delta H_{mix} = 0 \quad \Delta V_{mix} = 0$$

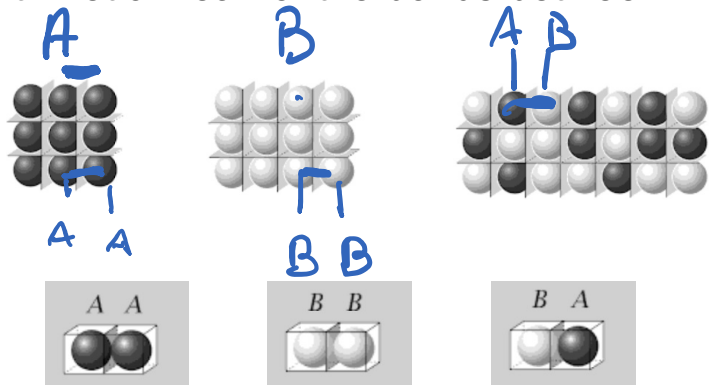
$$\bar{G} = -RT \ln(x_A \ln x_A + x_B \ln x_B)$$



SPATIAL ARRANGEMENT UNDER THE REGULAR SOLUTION MODEL

Under the **quasi-chemical model** it is assumed that the heat of mixing, $\Delta_{mix}H$, is only due to bond energies between adjacent atoms and that the volumes of pure A and pure B are equal to the final volume of the mixture.

We introduce the interaction parameter, which is defined as Ω . It quantifies the energy change due to mixing. Ω has a simple atomistic interpretation: it compares the energy of the bond between dissimilar atoms with the arithmetic mean of the bonds between like atoms.



$$\Delta_{mix} U = P_{AB} \cdot \epsilon = 2 N_A x_A x_B \cdot \epsilon$$

$$\epsilon = \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \quad \Omega = 2 N_A \epsilon$$

$$P_{AB} = N_A (2 x_A x_B)$$

$$\Delta U_{mix} = \Omega x_A x_B$$

Assumptions

- 1) $\Delta V_{mix} = 0$
- 2) same crystal structure
- 3) random mixing

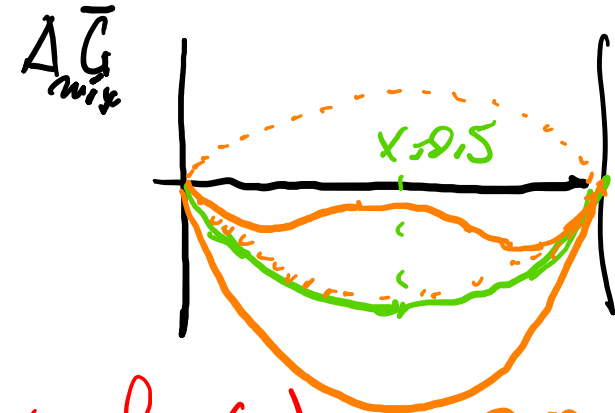
$\hookrightarrow$ no excess entropy of mixing

$$\Delta_{mix} \bar{S} = -R (x_A \ln x_A + x_B \ln x_B)$$

COMPOSITION DEPENDENCE OF VARIOUS THERMODYNAMIC FUNCTIONS OF A REGULAR SOLUTION

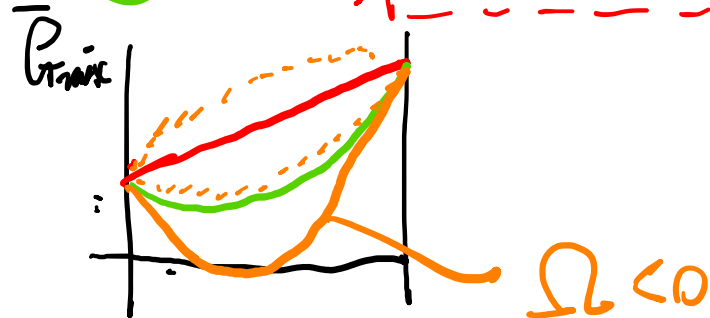
$$\Delta_{mix} \bar{H} = \Delta_{mix} \bar{U} + \Delta_{mix} (p\bar{V}) = -\Omega x_A x_B$$

$$p \Delta_{mix} \bar{V} = 0$$



$$\Delta_{mix} \bar{G} = -\Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$

$$\bar{G}_{mix} = \mu_A^* x_A + \mu_B^* x_B + \Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$

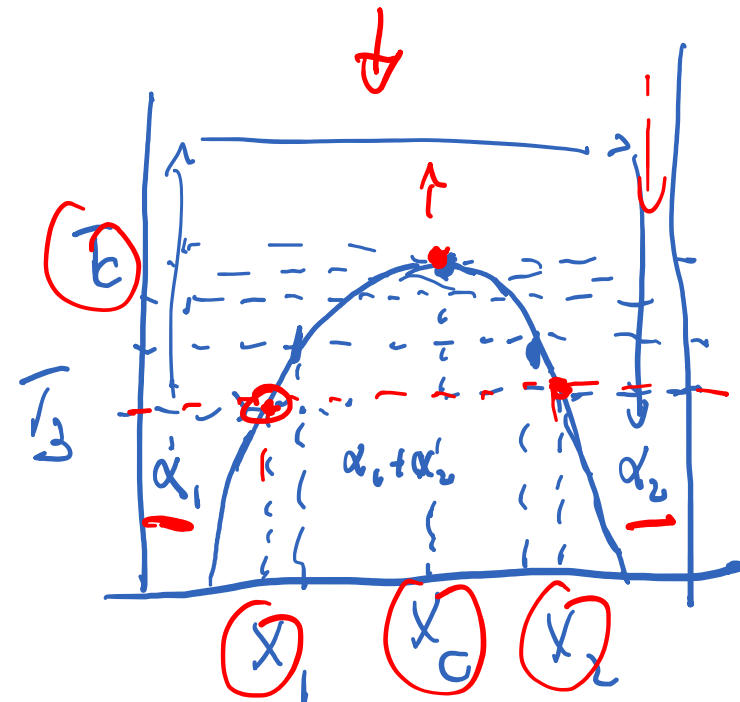
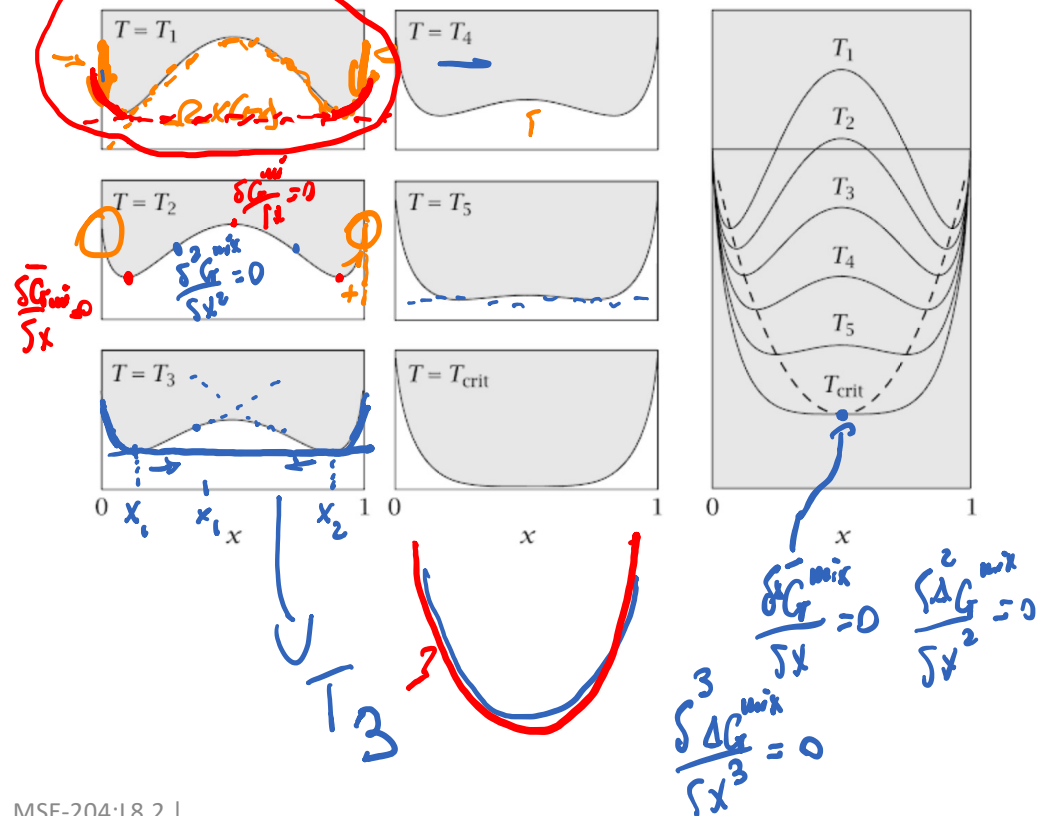


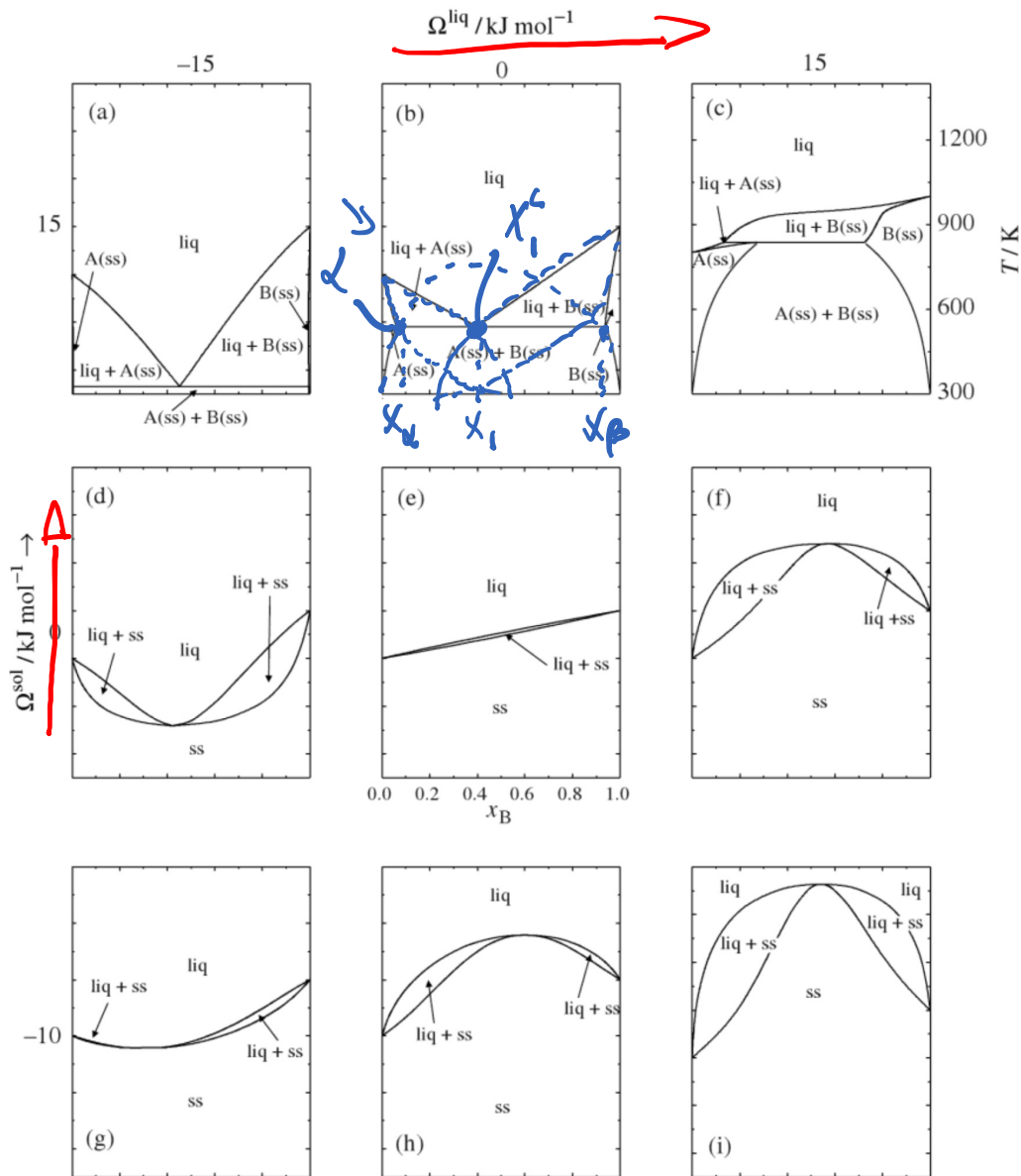
$$\begin{cases} \rightarrow \Omega < 0 \\ \rightarrow \Omega > 0 \end{cases}$$

PHASE DIAGRAM OF A REGULAR SOLUTION: MISCIBILITY GAP FOR $\Omega > 0$ AS A FUNCTION OF TEMPERATURE

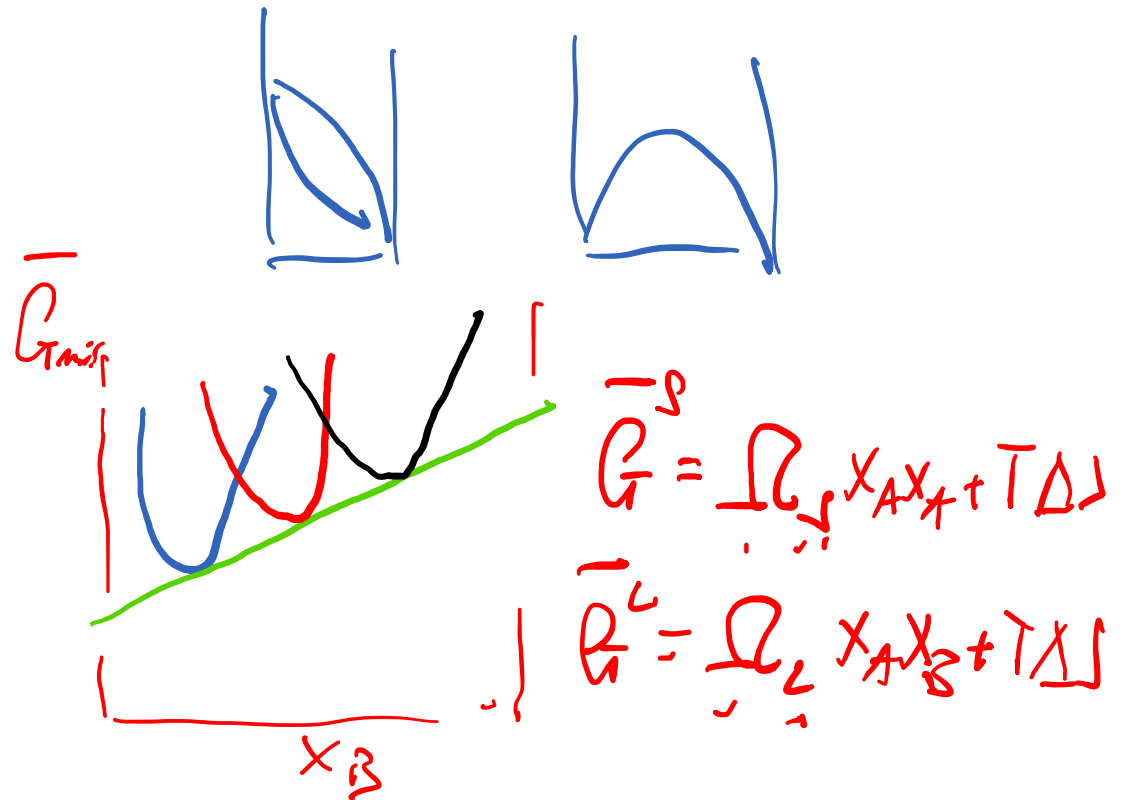
$$\Delta_{mix}G = \Omega x(1-x) + RT(x \ln x + (1-x) \ln(1-x))$$

$$d(\Delta_{mix}G) = \Omega - 2x\Omega + RT(\ln x - \ln(1-x))$$



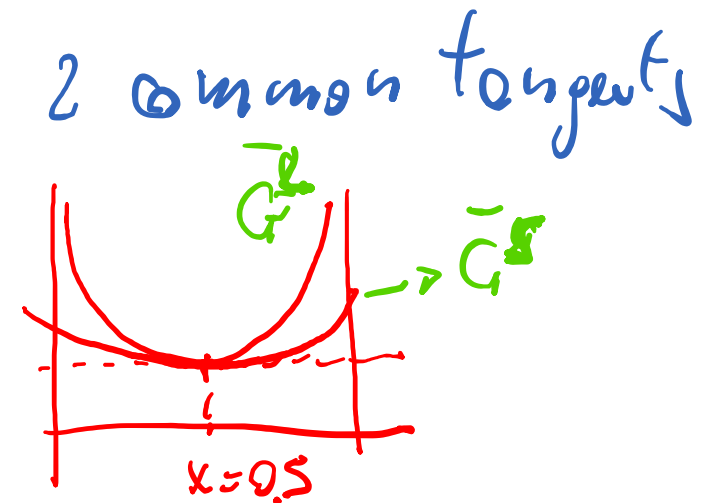
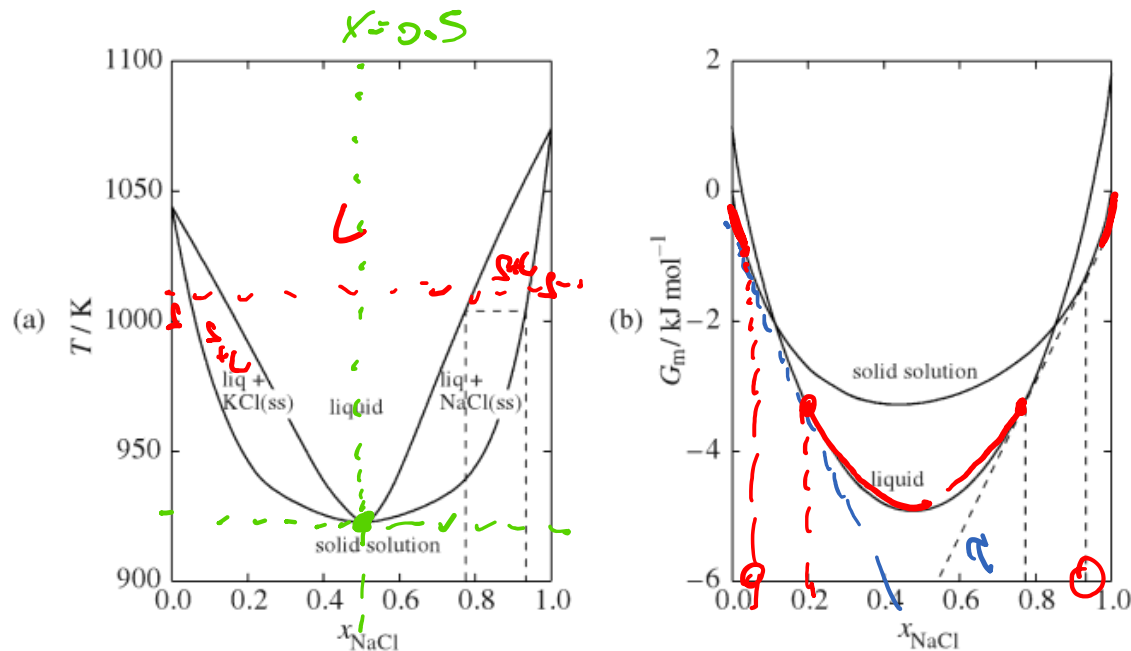


PHASE DIAGRAM OF A BINARY SYSTEM CONSISTING OF SOLID AND LIQUID SOLUTION PHASES FOR SELECTED COMBINATIONS OF Ω



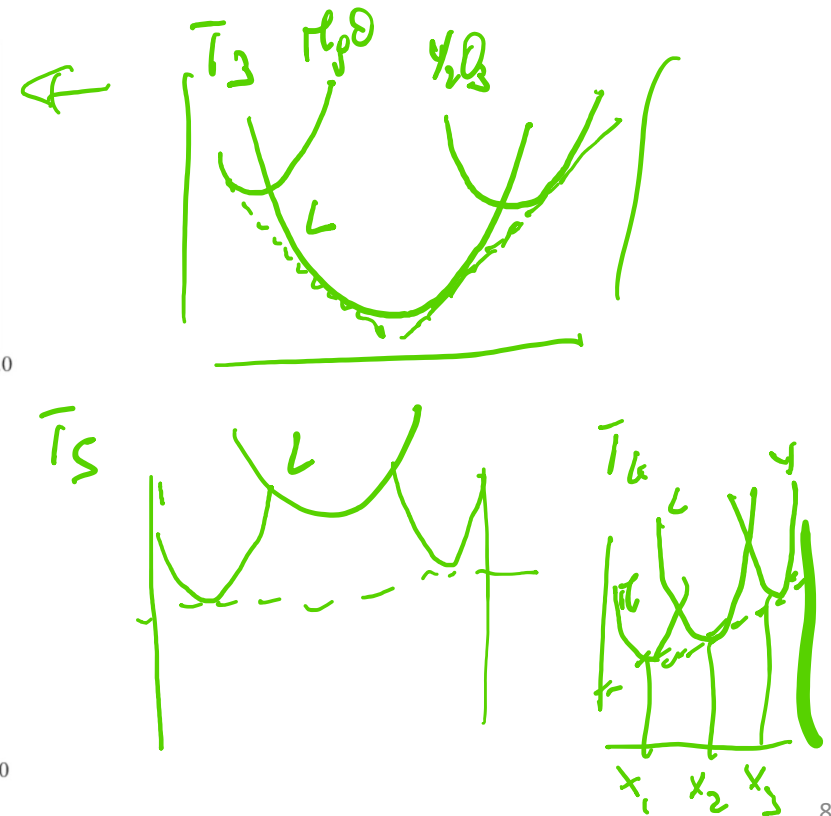
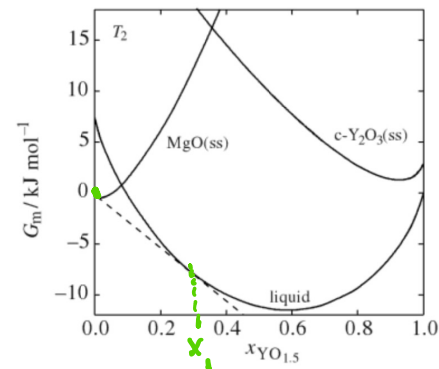
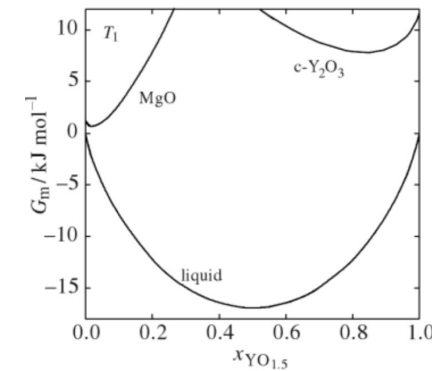
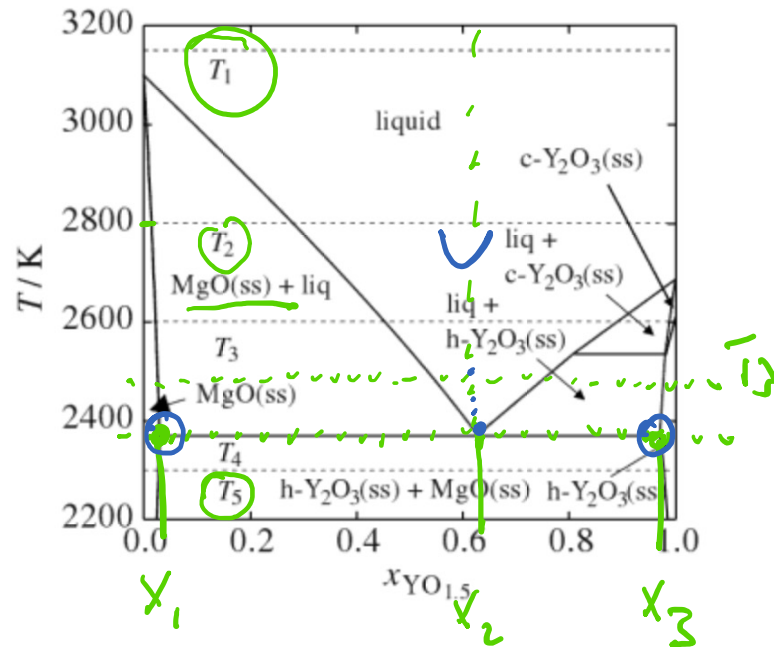
CONGRUENT PHASE DIAGRAMS

This particular system is characterized by negative deviation from the ideal behavior in the liquid state and positive deviation from ideality in the solid state. Remember that a negative Gibbs free energy of mixing corresponds to a stabilization of the solution, which manifests as a deeper curvature of the G-x curve compared to the ideal solution. Correspondingly, a positive deviation from ideal behavior destabilizes the solution and the G-x curve becomes shallower. Thus, a congruent phase transition corresponds to a complete transformation from one phase to another with no change in composition.



EUTECTIC PHASE DIAGRAMS

Most of materials are highly miscible in the liquid state, but have very limited mutual miscibility in the solid state. Thus much of the phase diagram at low temperatures is dominated by a 2-phase field of two different solid structures- one that is highly enriched in component A (the α phase) and one that is highly enriched in component B (the β phase). These binary systems, with unlimited liquid state miscibility and low or negligible solid state miscibility, are referred to as eutectic systems.



OTHER TYPES OF INVARIANT POINTS

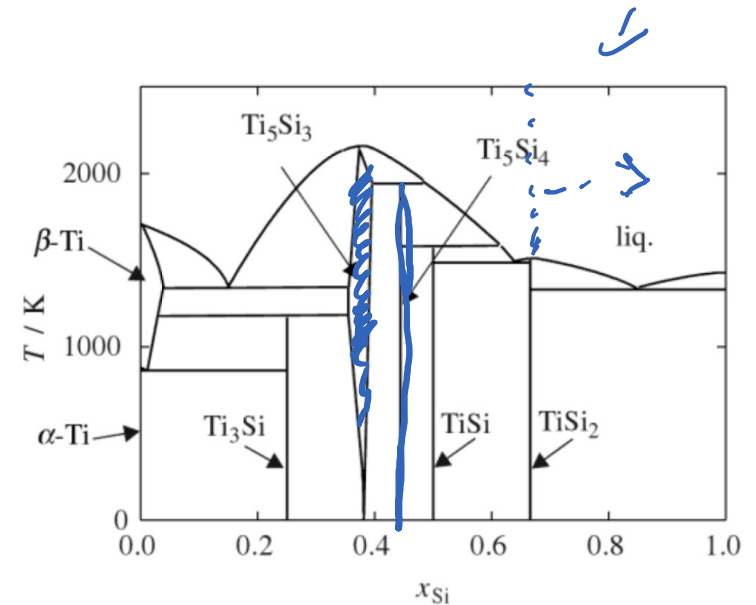
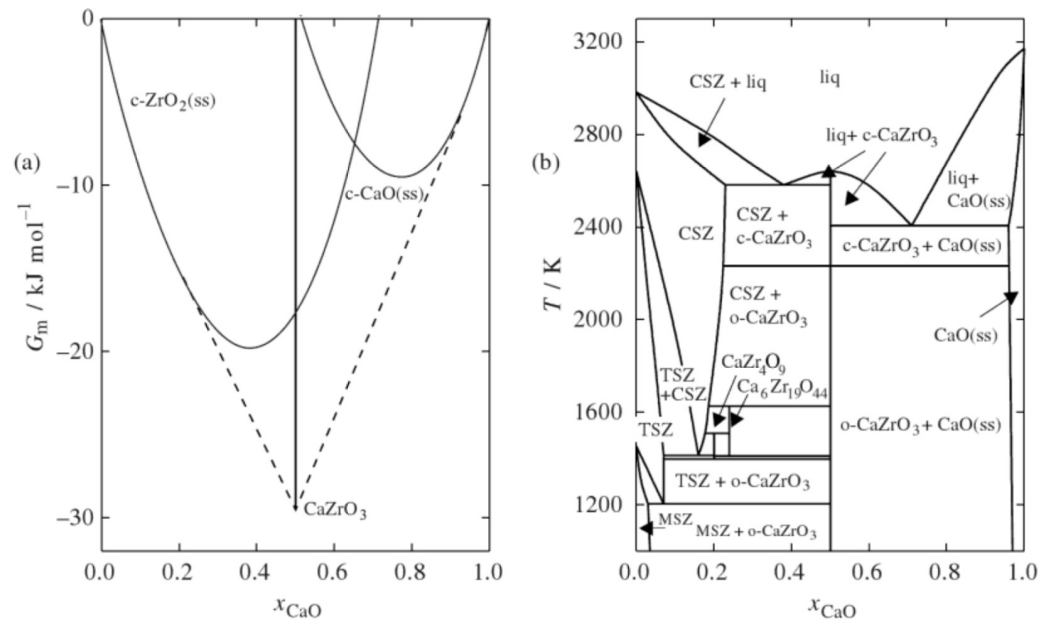
Other transformations that occur in binary systems at a fixed composition and temperature (for constant pressure) are given titles as well:

- Eutectic: $L \rightleftharpoons (\alpha + \beta)$ (upper region is liquid)
- Peritectic: $(\alpha + L) \rightleftharpoons \beta$ (upper two-phase region is solid + liquid)
- Eutectoid: $\alpha \rightleftharpoons (\beta + \gamma)$ (upper region is solid)
- Peritectoid: $(\alpha + \beta) \rightleftharpoons \gamma$ (upper two-phase region is solid + solid)

Name of reaction	Equation	Phase diagram characteristic
Eutectic	$L \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \alpha + \beta$	
Peritectic	$\alpha + L \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \beta$	
Eutectoid	$\alpha \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \beta + \gamma$	
Peritectoid	$\alpha + \beta \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \gamma$	

INTERMEDIATE COMPOUNDS IN PHASE DIAGRAMS

Stable compounds can form between the two extremes of pure component A and pure component B in binary systems, these are referred to as intermediate compounds.



When the intermediate compound melts to a liquid of the same composition as the solid, it is termed a congruently melting compound. Congruently melting intermediates subdivide the binary system into smaller binary systems with all the characteristics of typical binary systems.

MSE-204 Thermodynamics for Materials Science

L9 STABILITY OF PHASES

ENERGY LANDSCAPES | THE SPINODAL CURVE | METASTABILITY | NUCLEATION AND GROWTH | SPINODAL DECOMPOSITION

Vaso Tileli | MXD 237

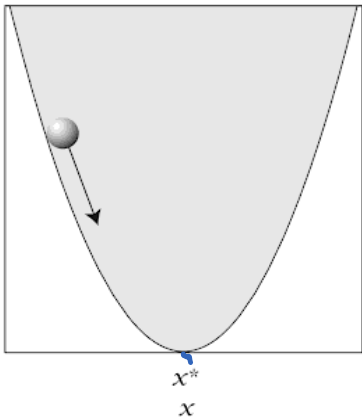
STABILITY WITH REGARD TO INFINITESIMAL COMPOSITIONAL VARIATIONS

Systems at constant temperature are stable in states having minimum free energy $G(x)$.

Energy landscapes describe stabilities and phase transitions.

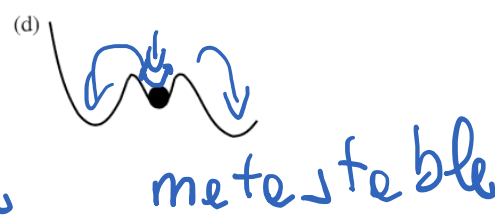
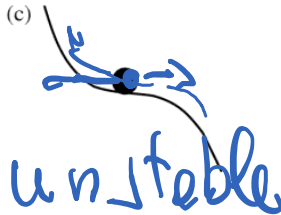
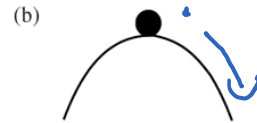
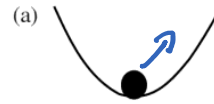
$$\Delta G = 0 \quad \frac{dG}{dx} = 0$$

$$\frac{d^2G}{dx^2} \geq 0$$

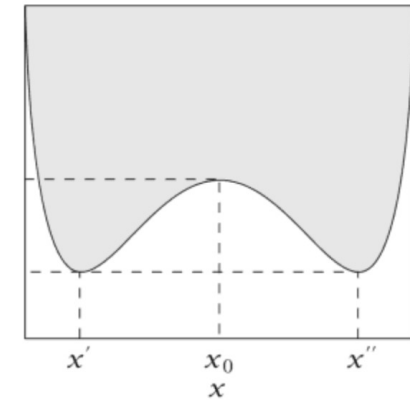


$$dU = 0$$

stable

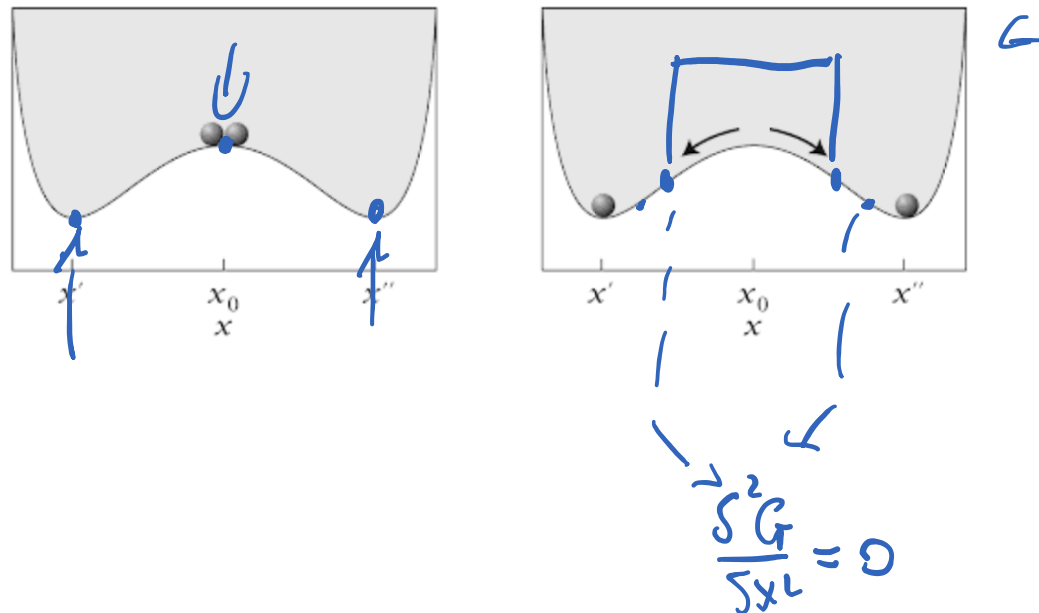


perturbation
some become stable
move away unstable



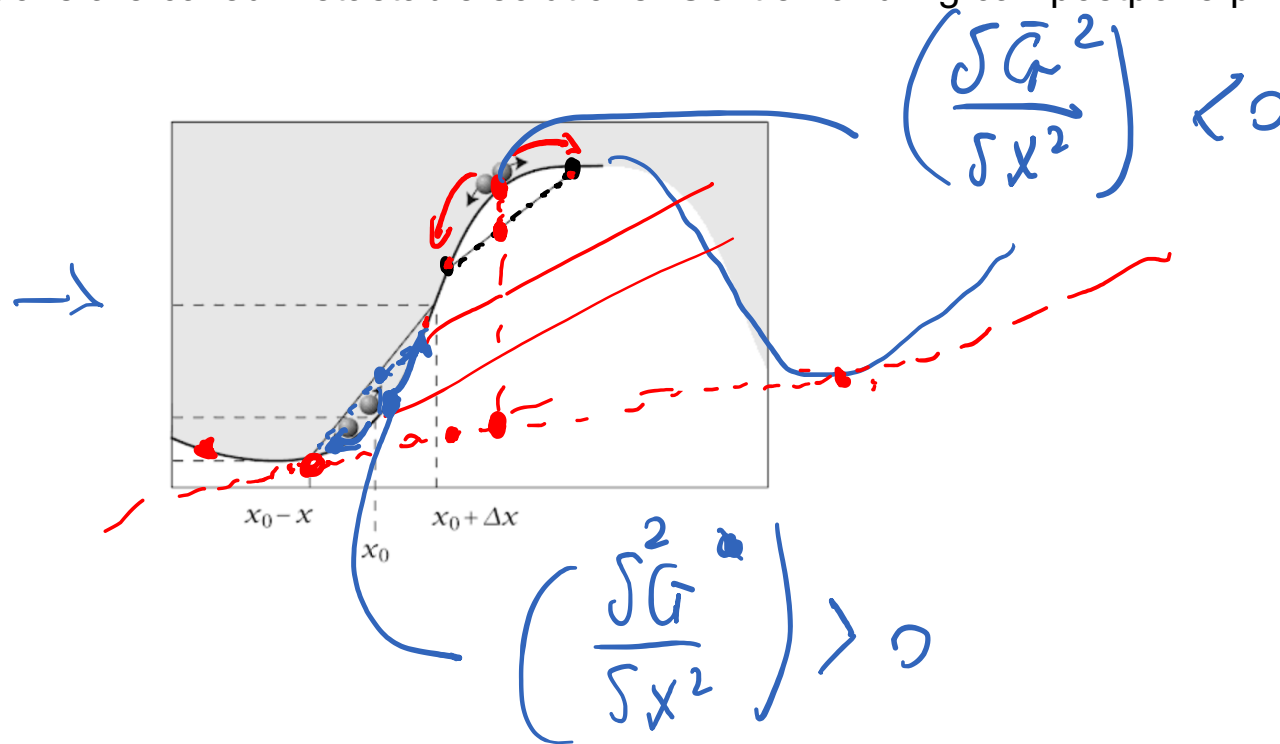
PEAKS ON ENERGY LANDSCAPES ARE POINTS OF INSTABILITY

For closed systems at constant temperature and pressure, the Gibbs free energy is minimized with respect to fluctuations in its other extensive variables. This includes fluctuations in composition. Imagine that A and B molecules in a homogeneous solution locally fluctuated and rearranged into a locally phase-separated state where A molecules preferentially gathered in one region and B molecules gathered in another region, driven by random thermal energy:

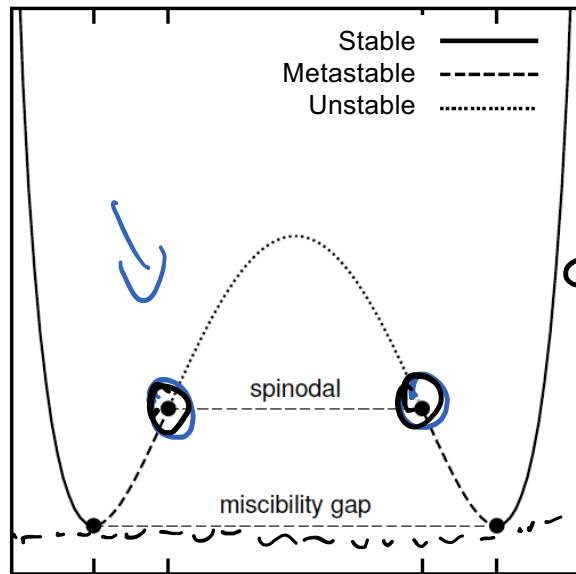


THE SPINODAL CURVE DESCRIBES THE LIMIT OF METASTABILITY

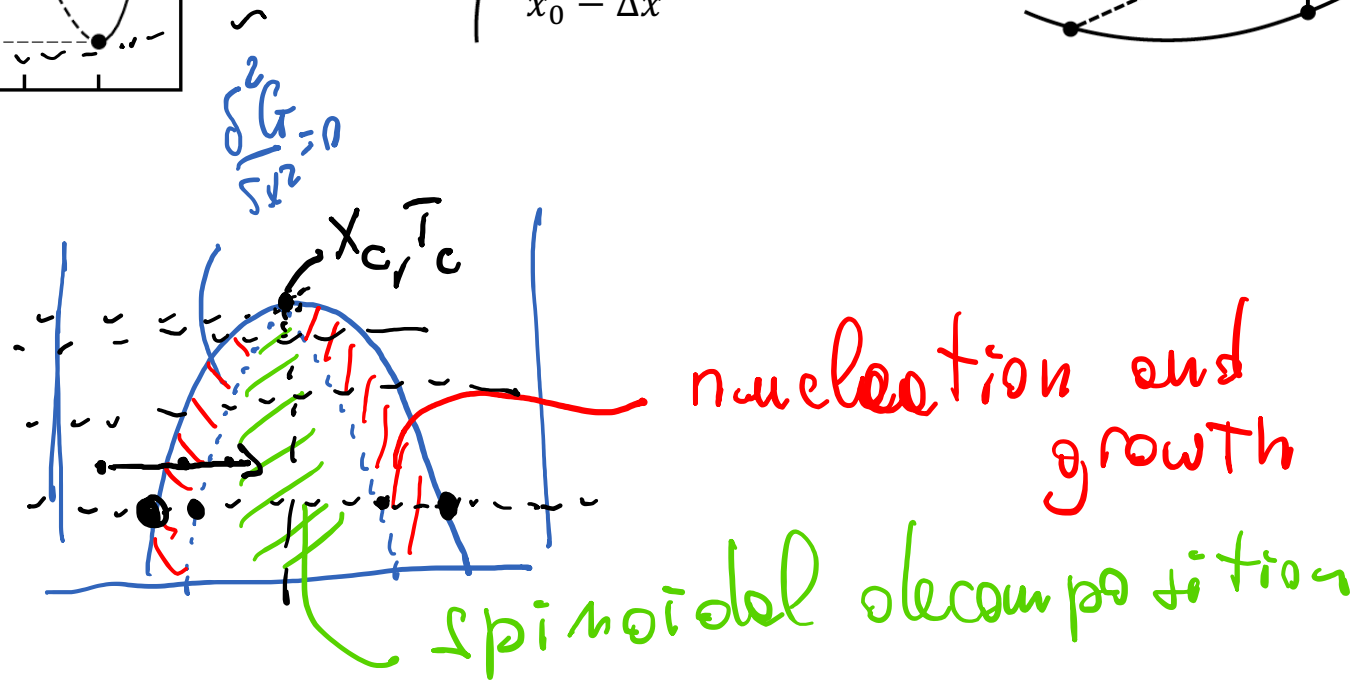
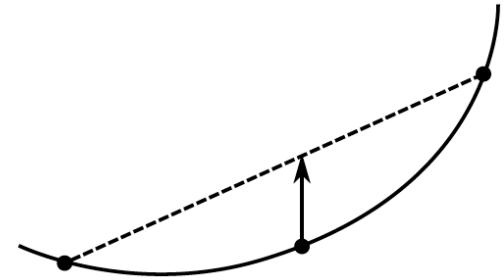
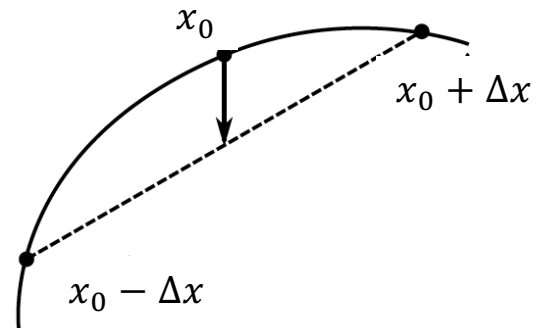
When looking at phase diagrams we described the coexistence curves (when the chemical potential of two different phases are equal). This curve is also called the binodal curve. It describes the global stability of a system against phase separation. Below, a description of metastability or local stability or spinodal curve is described. Sometimes when a system is inside a two-phase region, if handled very gently and is not shaken or stirred, it does not form separate phases. Such solutions are called metastable solutions. Gentle handling can postpone phase separation.



Regular solution model



STABILITY IN REGULAR SOLUTION MODEL



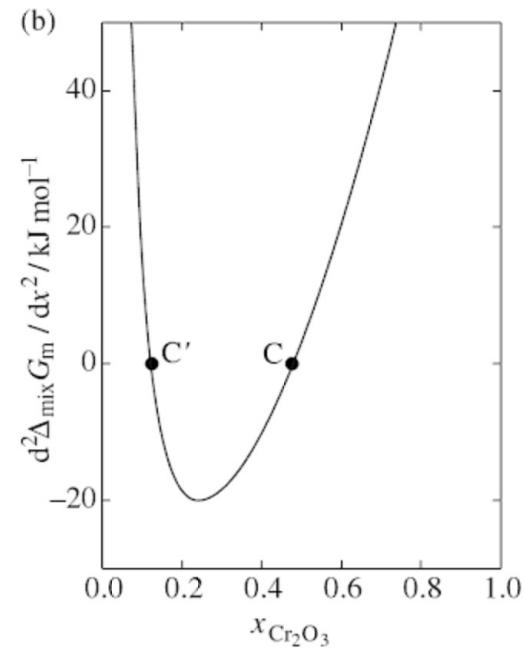
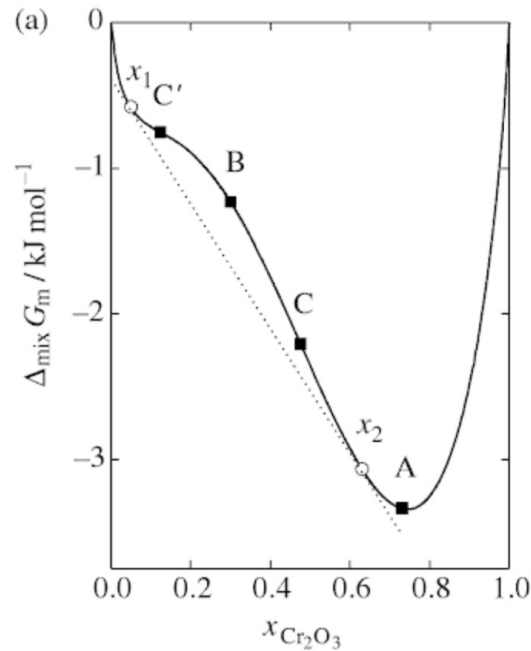
THE CRITICAL POINT

$$\frac{\partial \Delta \bar{G}_{\text{mix}}}{\partial x} = 0 \quad \leftarrow$$

$$\frac{\partial^2 \Delta \bar{G}_{\text{mix}}}{\partial x^2} = 0 \quad \rightarrow$$

$$\frac{\partial^3 \Delta \bar{G}}{\partial x^3} = 0 \quad \rightarrow$$

$$\frac{\partial^4 \Delta \bar{G}}{\partial x^4} \neq 0$$

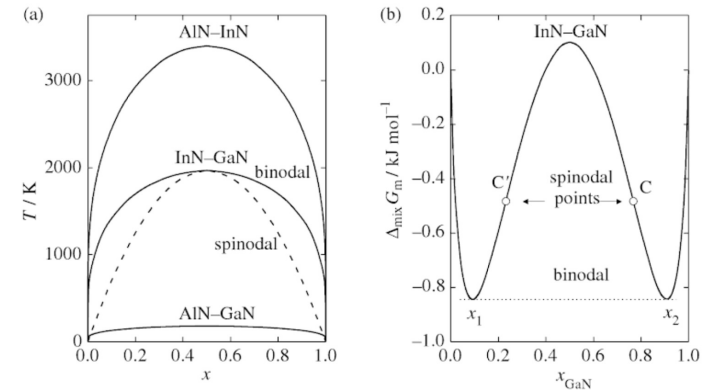


SPINODAL CURVE FOR THE CASE OF THE REGULAR SOLUTION

$$\bar{G}_{mix} = \Omega x_A x_B + x_A g_A^{pure} + x_B g_B^{pure} + RT(x_A \ln x_A + x_B \ln x_B)$$

$$\frac{\partial^2 \bar{G}_{mix}}{\partial x_A^2} = -2\Omega + RT \left(\frac{1}{x_A} + \frac{1}{x_B} \right) = 0$$

spinodal line $x_A x_B = \frac{RT}{2\Omega}$

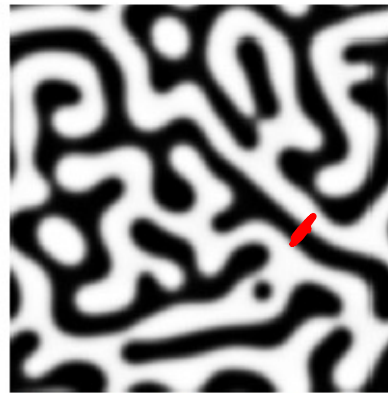
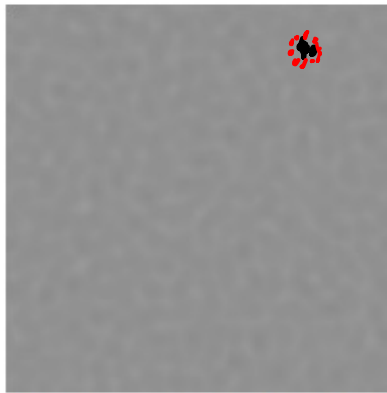


$$T_c = \frac{\Omega}{2R}$$

B

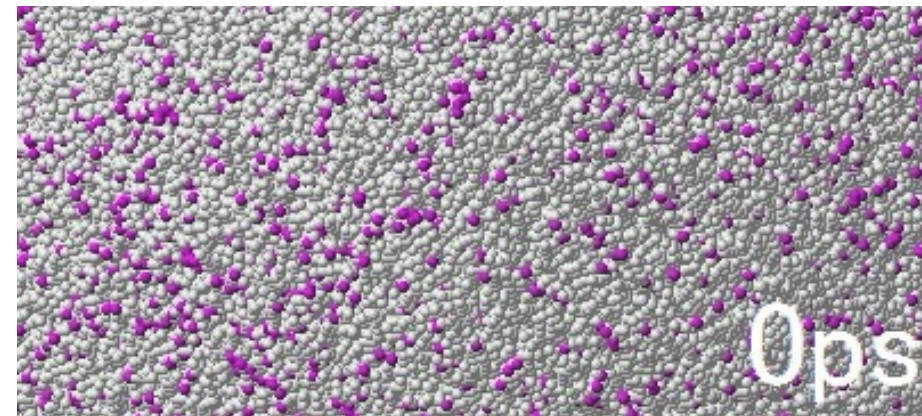
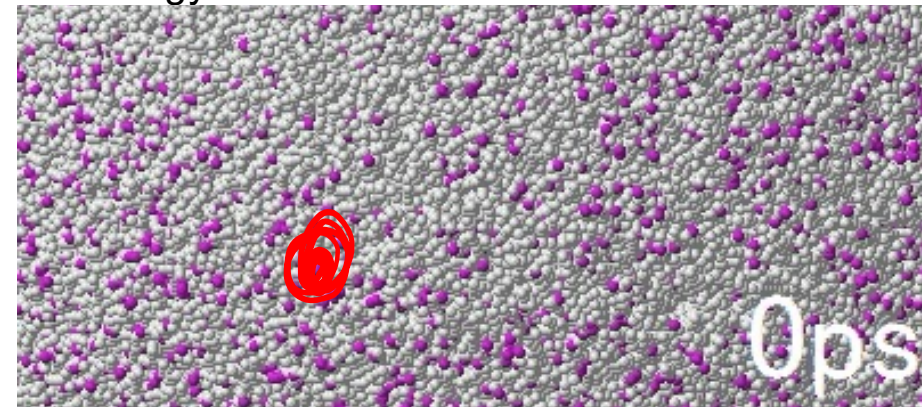
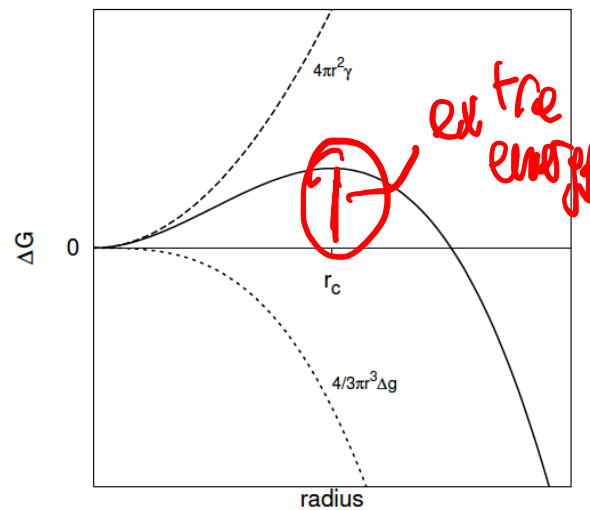
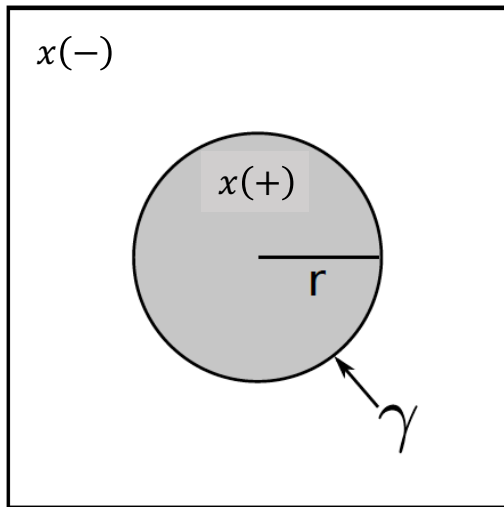
SPINODAL DECOMPOSITION

Spinodal decomposition occurs simultaneously throughout the system. For small perturbations of a uniform concentration, the interfacial tension is not the limiting factor.



NUCLEATION AND GROWTH

Nucleation and growth occurs from discrete points in the system. Nucleation is a nonlinear instability that requires the formation of a large enough nucleus of the nucleating phase. It proceeds with the creation of a nucleus of the low-energy phase with mole fraction in higher concentration form a matrix. There is a decrease in free energy associated with this conversion, and an increase in free energy due to the interfacial energy.

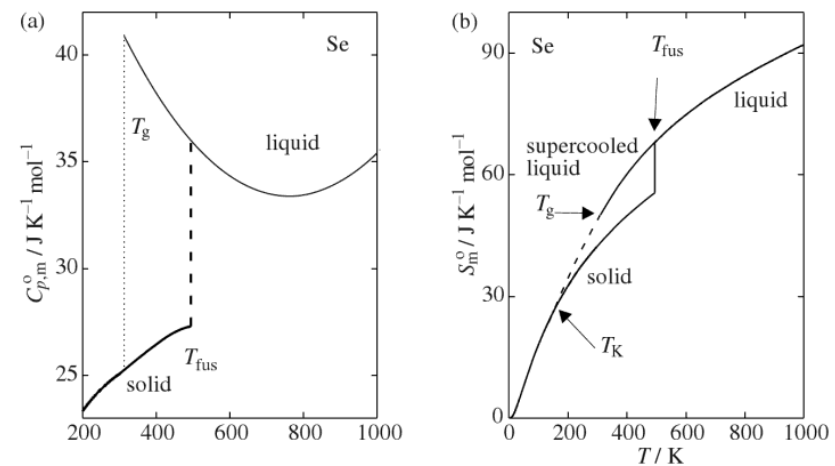


SUPERCOOLING OF LIQUIDS | SUPERHEATING OF CRYSTALS

If we use temperature as a variable for stable and metastable states, there is a limit to superheating a crystal above its melting temperature or cooling a liquid below its freezing temperature. A supercooled liquid will either crystallize or transform to a glass. Glasses are materials out of equilibrium, they cannot explore their complete phase space and some degrees of freedom are frozen in.

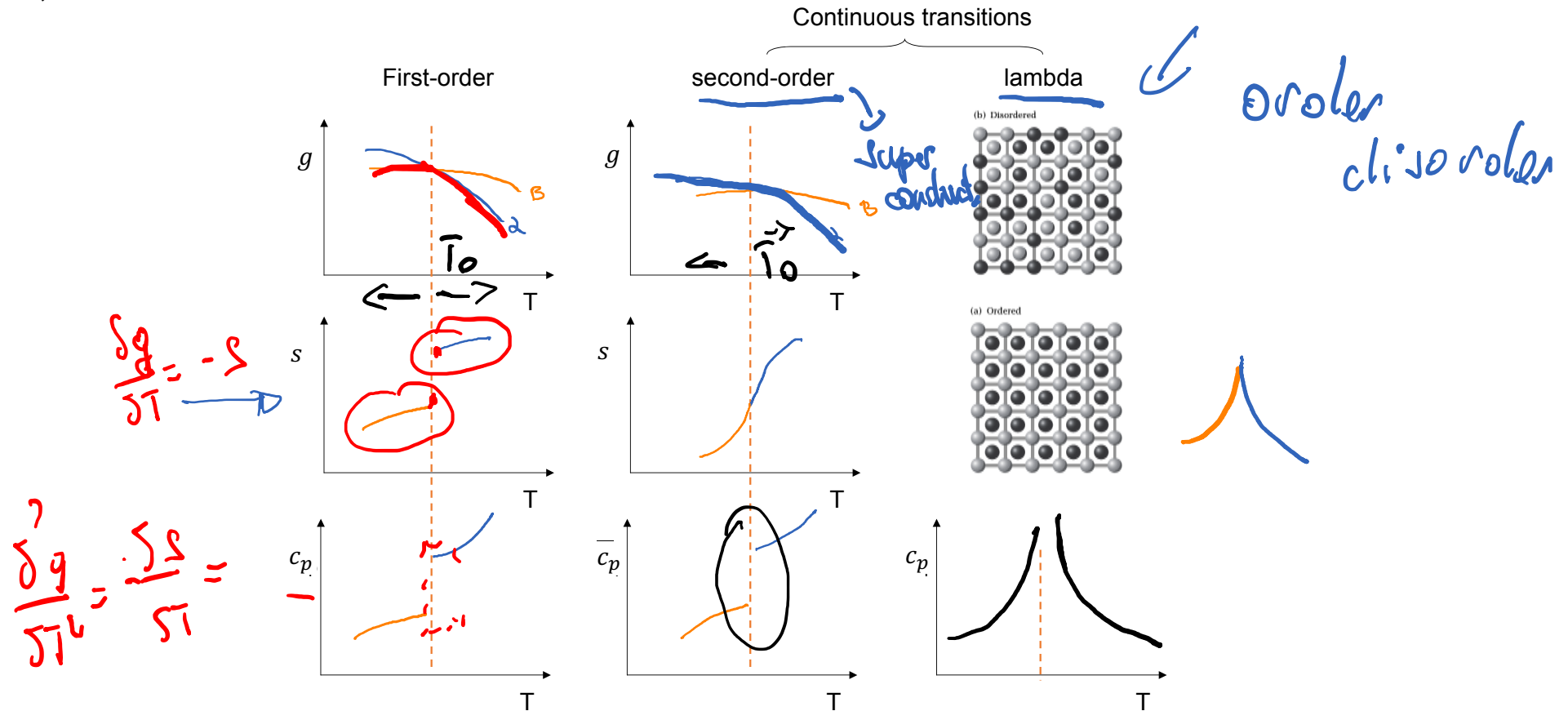


courtesy of W. Lechner (University of Innsbruck)



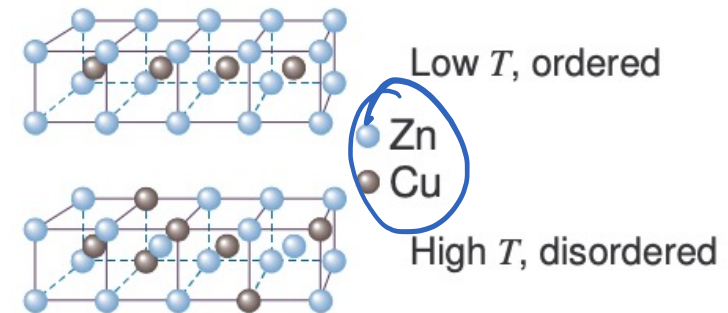
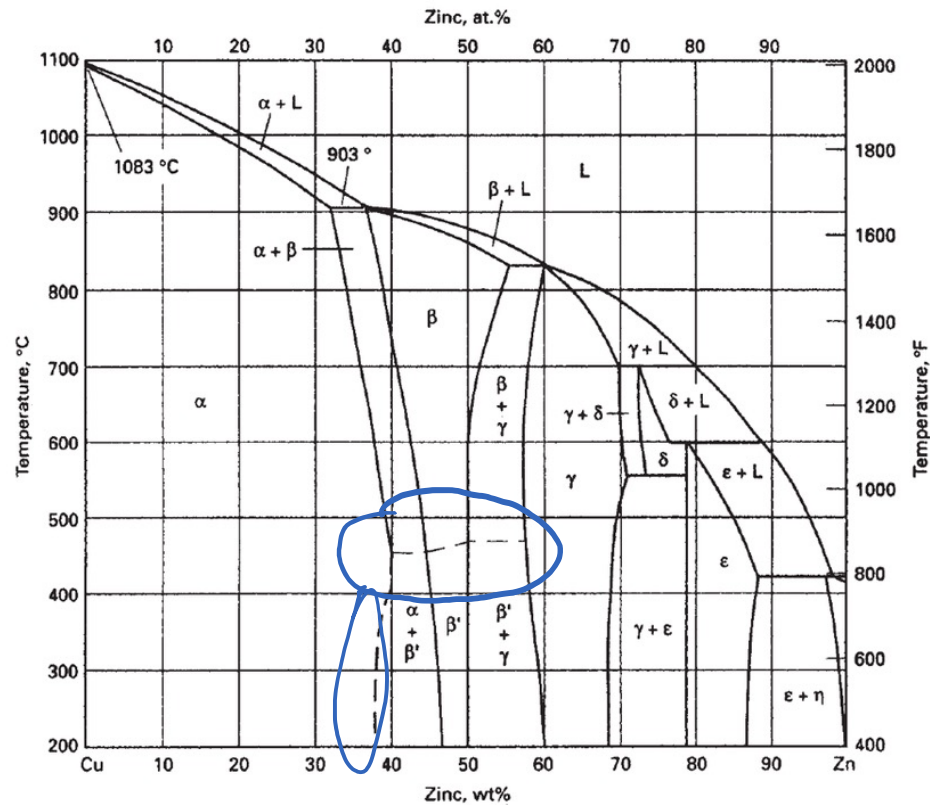
FIRST ORDER VS CONTINUOUS PHASE TRANSITIONS

Phase changes can be higher order than the ordinary ones which include melting and vaporization. In these first order phase transitions, it is the first derivatives, namely entropy and volume, which are discontinuous, whereas in the second order, discontinuities are visible in the second order derivatives..



LAMDA TRANSITION IN BETA PHASE OF BRASS

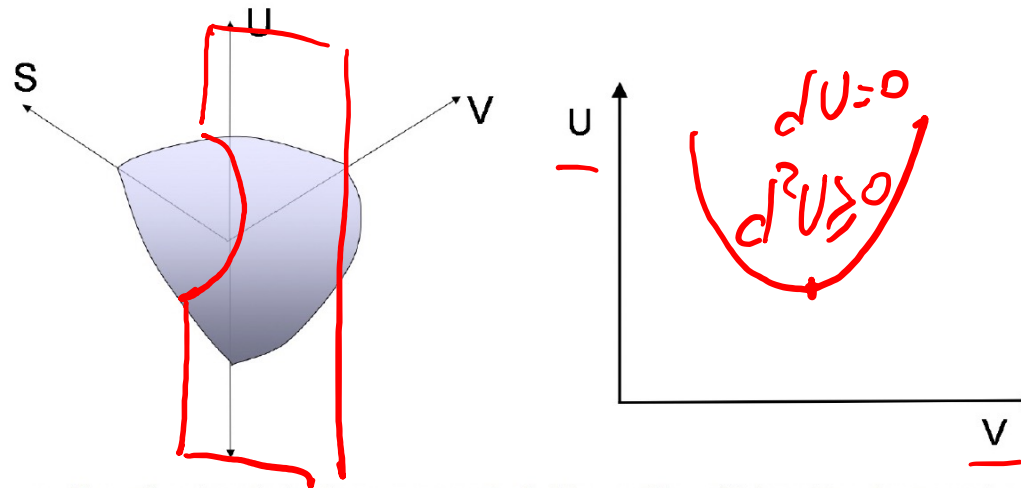
Brass is an almost 50:50, Cu:Zn alloy with a bcc structure. At low temperatures, $T < 460$ °C, the Zn and Cu atoms form an ordered structure, the Cu atoms sit in the body centred sites. As the temperature increases, the Cu and Zn atoms change places until there is a full random arrangement. Such effects are said to be cooperative.



STABILITY IN MATERIALS

Constraints on thermodynamic properties ensure stability: example of internal energy constraints

- **MAIN IDEA:** Many of the thermodynamic properties of materials can only have certain values if the material is in a stable equilibrium state.
- Recall the equilibrium condition in terms of internal energy: For conditions of fixed total entropy, the internal energy of the system is minimized. Graphically, this means:



- The surface drawn in the diagram represents all of the possible equilibrium states of some system. The mathematical requirements for a stable equilibrium are:

P, T, U, S, V

STABILITY IN MATERIALS

For equilibrium to be stable against fluctuations in S only or V only:

$$\frac{d^2U}{dS^2} \geq 0 \quad \frac{d^2U}{dV^2} \geq 0 \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

For equilibrium to be stable against coupled fluctuations in both S and V:

$$d^2U = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} dS^2 + \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} dV^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right) dS dV \geq 0 \quad \text{for stability}$$

which is equivalent to:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} dS^2 + \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} dV^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right) dS dV \geq 0$$

$$\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} dS + \left(\frac{\partial^2 U}{\partial S \partial V}\right) dV\right]^2 - \left[\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{V,n} dS + \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} dV\right]^2 \geq 0$$

This gives us a third condition for stability:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \geq 0$$

- These requirements on the shape of the internal energy surface are linked to values of thermodynamic parameters of the system:

- This is the requirement for thermal stability.* Since the absolute temperature must be > 0 the heat capacity must also be greater than 0. In addition, the entropy must increase if the temperature increases, for stability.

$$\frac{d^2U}{dS^2} \geq 0 \quad \frac{d}{dS} \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \quad T > 0 \quad C_V \geq 0$$

- Next, we have:

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_{V,n}$$

$$\frac{d^2U}{dV^2} \geq 0 \quad \frac{d}{dV} \left(\frac{\partial U}{\partial V}\right)_S = -\frac{\partial P}{\partial V} = \frac{1}{\beta_S V} \quad \beta_S \geq 0$$

$$\beta_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$$

- This is the condition for mechanical stability.*

- From this analysis, we see that *many properties of materials may only have certain values if the material is to be stable.* There are numerous other examples that can be derived using the other thermodynamic functions. In summary, one can prove that stable materials must exhibit the following trends in properties:

$$C_P \geq C_V \geq 0$$

$$\beta_T \geq \beta_S \geq 0$$

STABILITY IN MATERIALS

Requirements for the shape of free energy curves

- The relationships between the Gibbs free energy and other thermodynamic parameters tell us numerous things about how plots of G vs. various thermodynamic variables must behave in stable thermodynamic systems:

- Consider a plot of G vs. temperature:
- What should the slope of this curve be?
 - Using our differential expression for G :

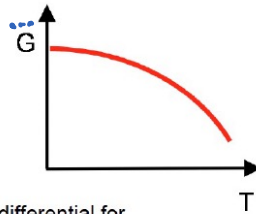
$$dG = VdP - SdT + \sum_{j=1}^P \sum_{i=1}^C \mu_i^j dn_i^j$$

- ...and combining this with the algebraic definition of the differential for $G(T, P, N)$:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, N} dT + \left(\frac{\partial G}{\partial P} \right)_{T, N} dP + \sum_{j=1}^P \sum_{i=1}^C \left(\frac{\partial G}{\partial n_i^j} \right)_{T, P, n_{j \neq i}} dn_i^j$$

$$\left(\frac{\partial G}{\partial T} \right)_{P, N} = -S$$

$$\left(\frac{\partial^2 G}{\partial T^2} \right) = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial T} \right)_{P, N} = \frac{\partial}{\partial T} (-S) = - \left(\frac{\partial S}{\partial T} \right)_{P, N} = - \frac{C_P}{T} < 0$$



- The curvature is also related to known thermodynamic quantities:

- The heat capacity and the absolute temperature must always be ≥ 0 , thus the curvature must be < 0 . **Thus plots of the free energy vs. temperature at constant pressure must always have the general shape shown at left above.**
- Similar analyses may be applied to predict the shape of other free energy curves of interest.