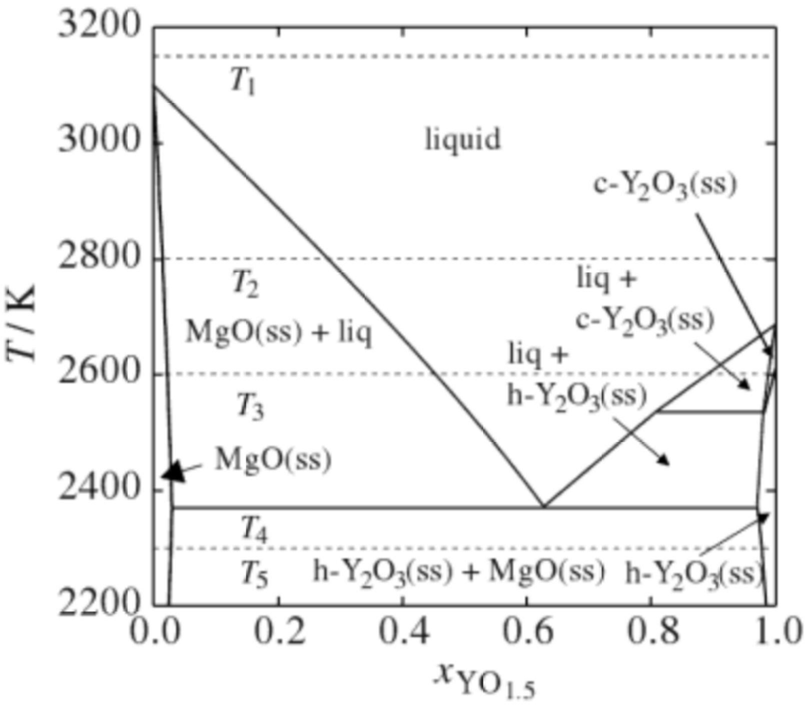
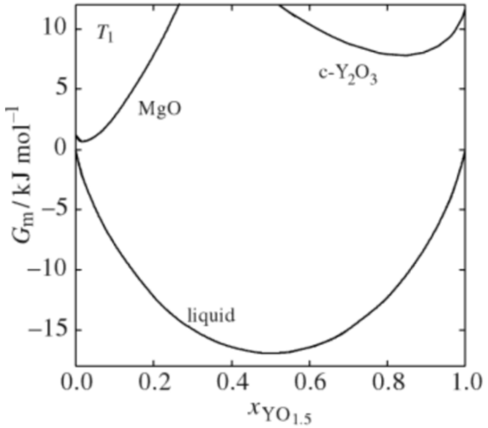
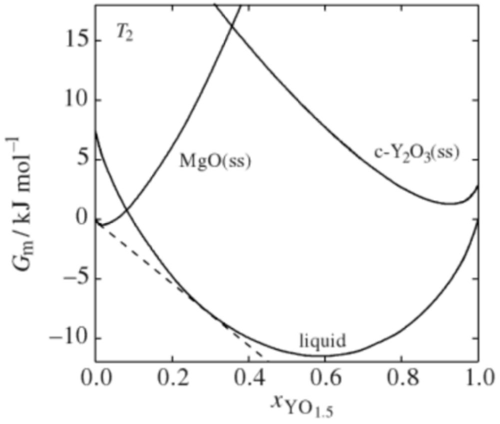
EUTECTIC PHASE DIAGRAMS

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). <u>These binary systems, with unlimited liquid state miscibility and low or negligible solid state miscibility, are referred to as eutectic systems.</u>





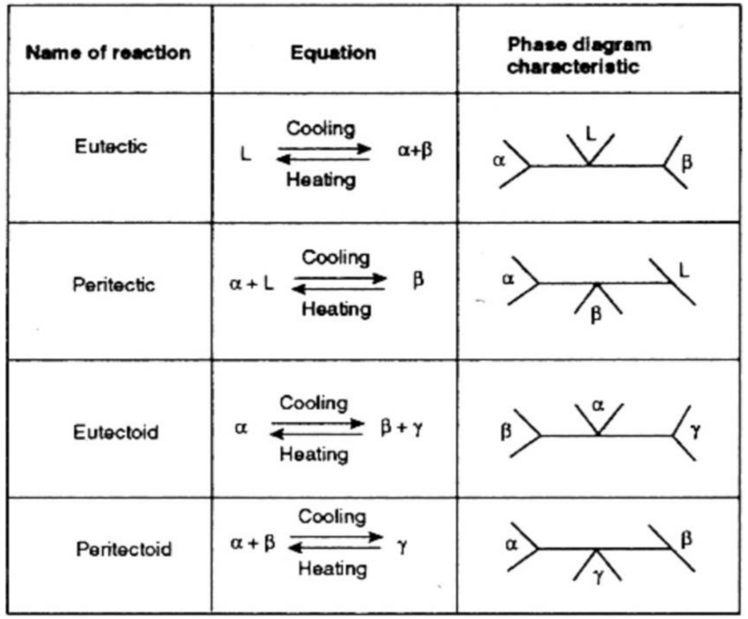


OTHER TYPES OF INVARIANT POINTS

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

- Eutectic: **$L \rightleftarrows (\alpha + \beta)$** (upper region is liquid)
- Peritectic: **$(\alpha + L) \rightleftarrows \beta$** (upper two-phase region is solid + liquid)

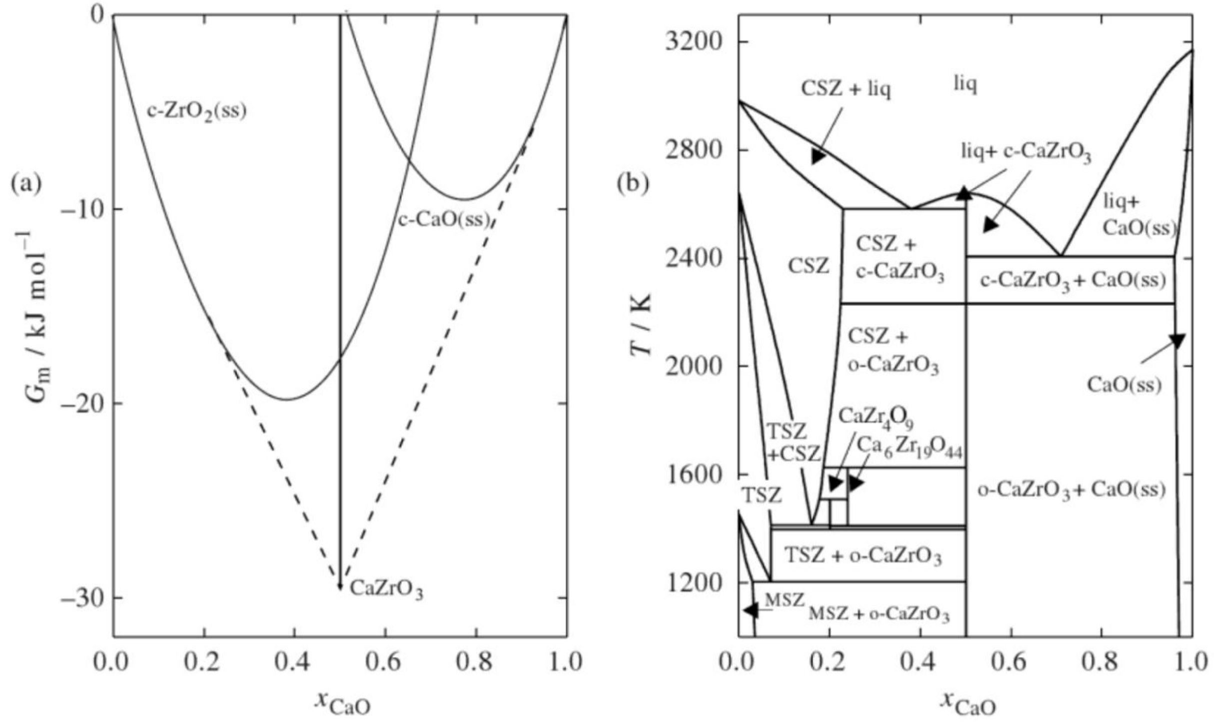
- Eutectoid: **α ⇄ (β + ©)** (upper region is solid)
- Peritectoid: **$(\alpha + \beta) \rightleftarrows \gamma$** (upper two-phase region is solid + solid)

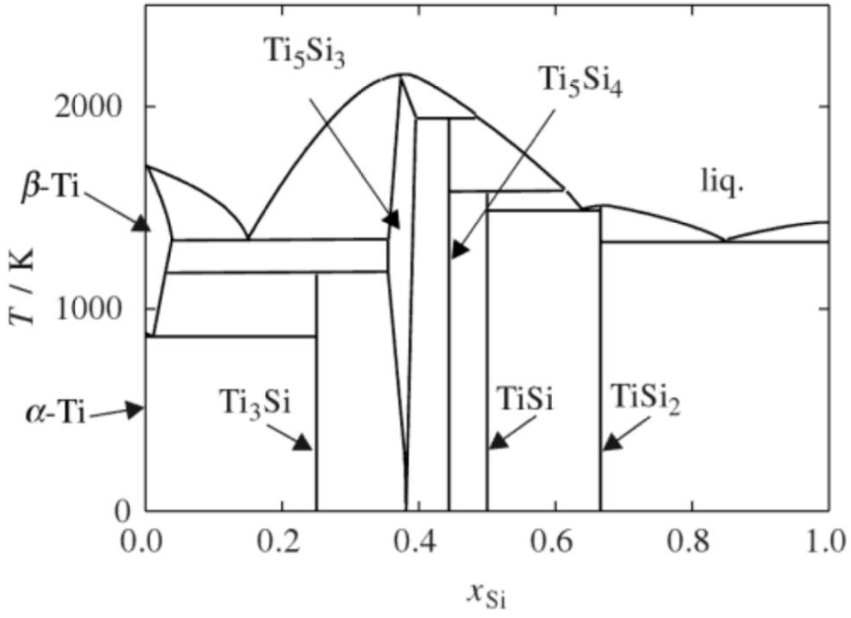


Name of reaction	Equation	Phase diagram characteristic
Eutectic	$L \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \alpha+\beta$	α L β
Peritectic	$\alpha + L \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \beta$	α L β
Eutectoid	$\alpha \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \beta + \gamma$	β α γ
Peritectoid	$\alpha + \beta \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \gamma$	α β γ

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

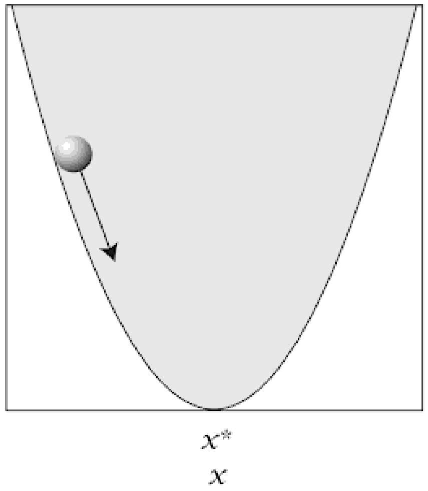
ENERGY LANDSCAPES | THE SPINODAL CURVE | METASTABILITY | NUCLEATION AND GROWTH | SPINODAL DECOMPOSITION

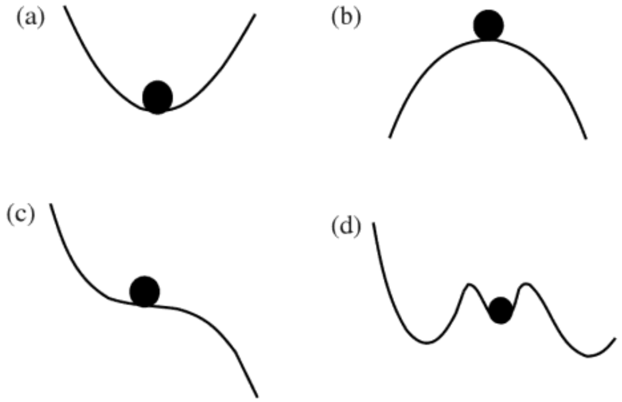
Vaso Tileli | MXD 237

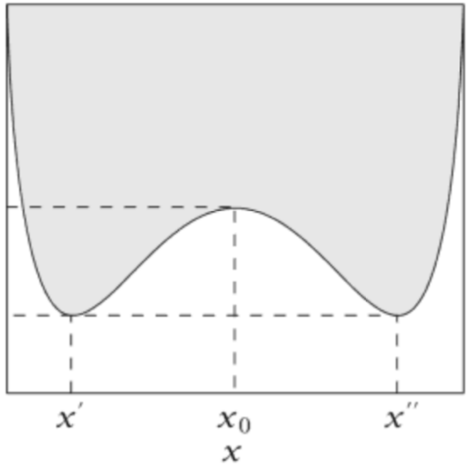
Stability with Regard to Infinitesimal Compositional Variations

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

Energy landscapes describe stabilities and phase transitions.

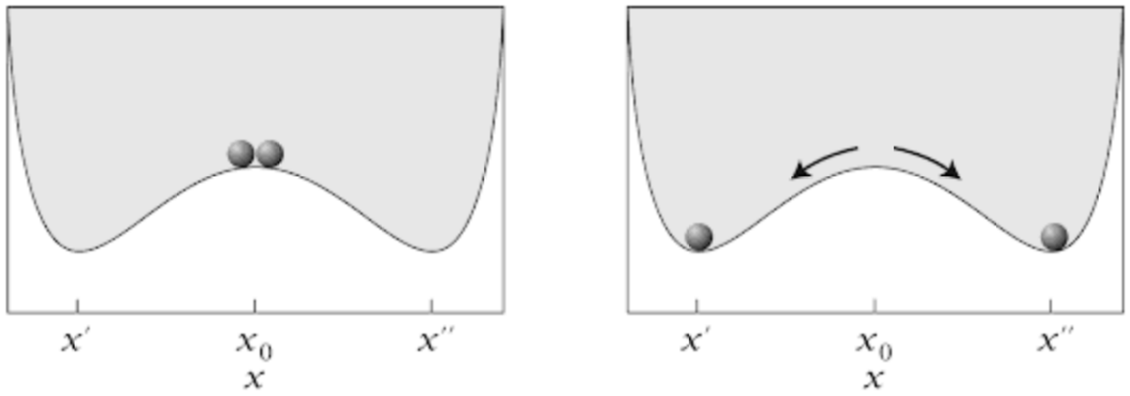






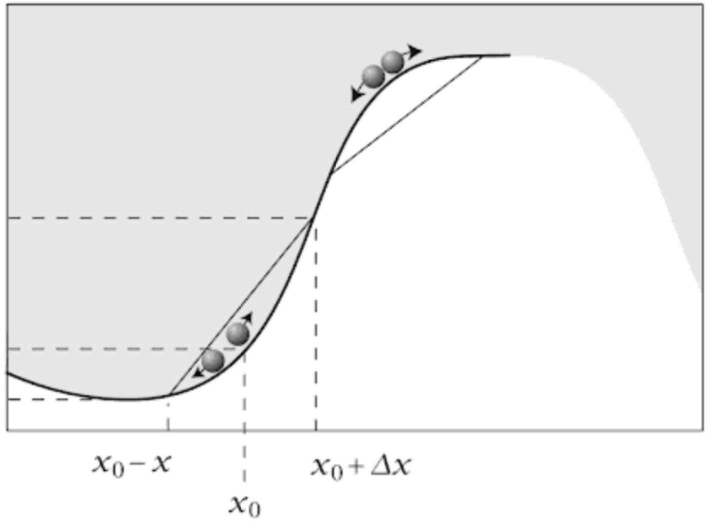
PEAKS ON ENERGY LANDSCAPES ARE POINTS OF INSTABILITY

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:

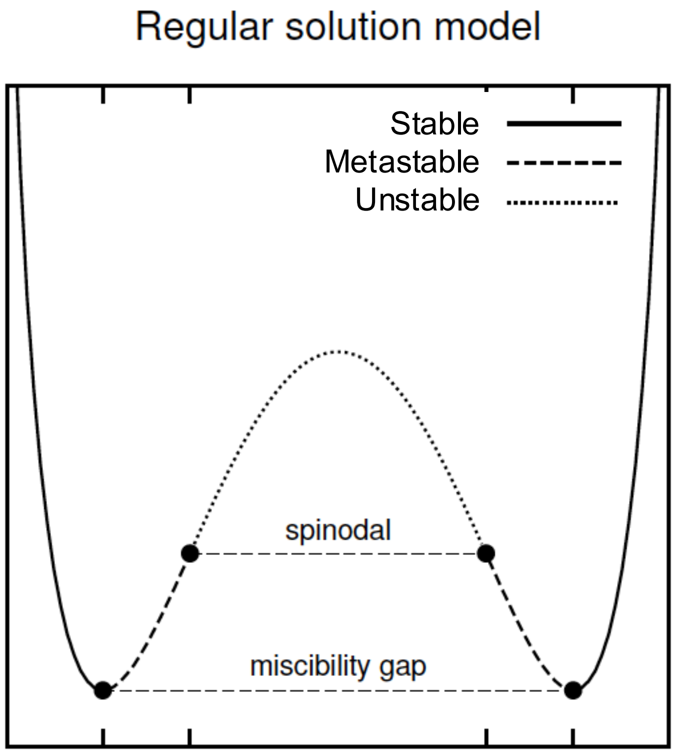


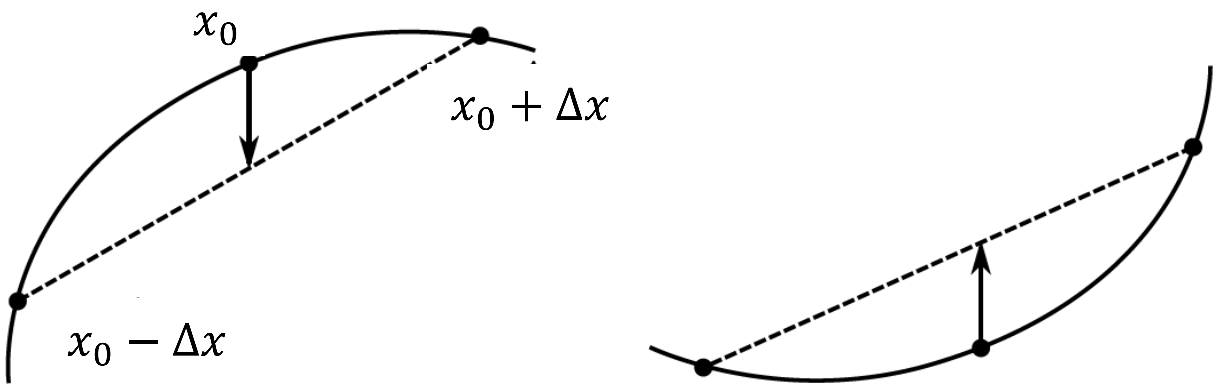
THE SPINODAL CURVE DESCRIBES THE LIMIT OF METASTABILITY

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.

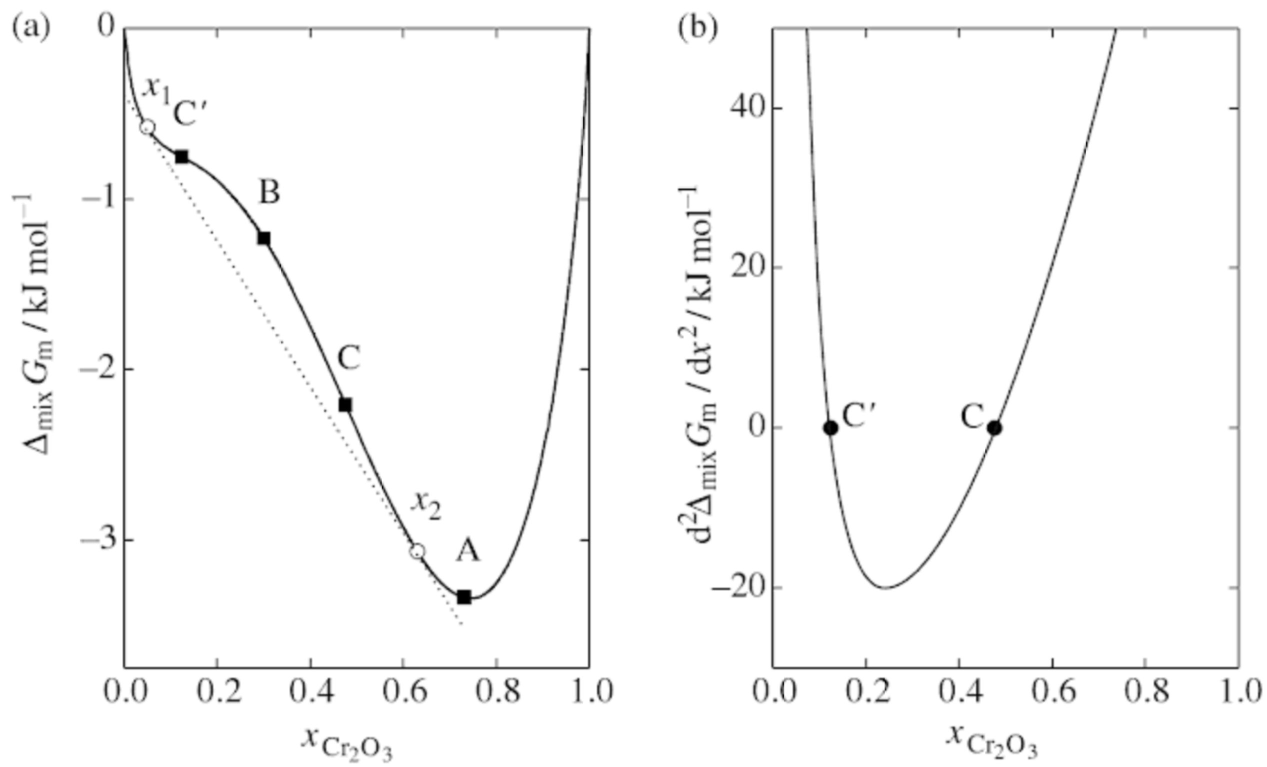


Stability in Regular Solution Model



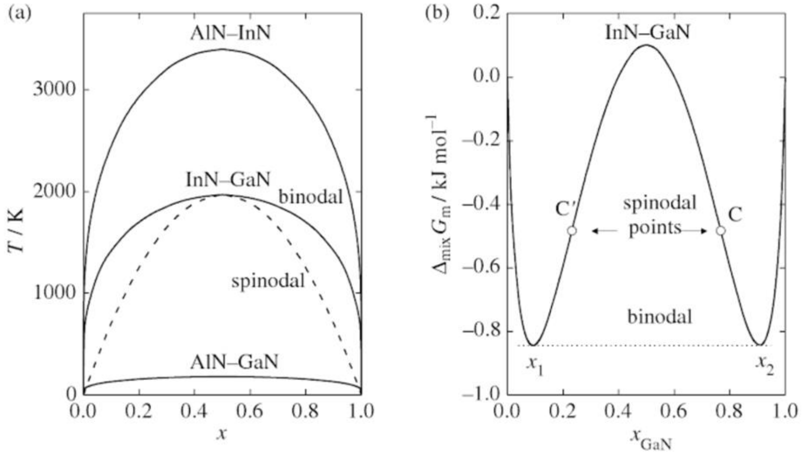


The Critical Point of the Miscibility Gap under the Regular Solution Model



ANALYTICAL EXPRESSIONS FOR THE CURVES UNDER THE REGULAR SOLUTION MODEL

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



For the binodal curve:

$$\frac{\partial \Delta_{mix}\bar{G}}{\partial x_B} = 0 \qquad \Rightarrow \qquad \ln\frac{x_B}{x_A} = \frac{\Omega}{RT}(x_B - x_A)$$

For the spinodal curve:

$$\frac{\partial^2 \Delta_{mix}\bar{G}}{\partial x_B^2} = 0 \qquad \Rightarrow \qquad x_A\, x_B = \frac{RT}{2\Omega}$$

For the critical point:

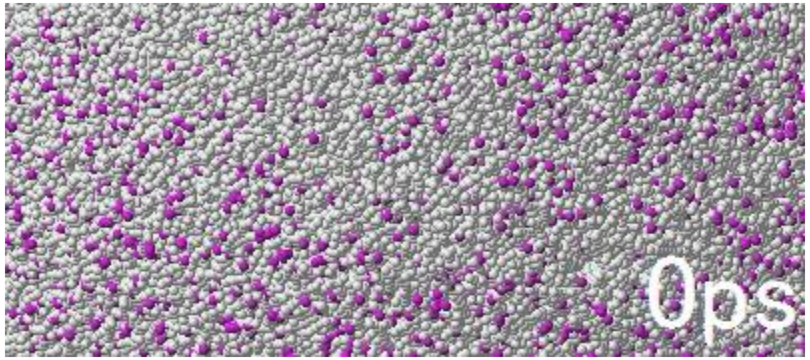
$$\left[\frac{\partial^3 \Delta_{mix}\bar{G}}{\partial x_B^3}\right]_{x_B = x_C = 0.5} = 0 \qquad \Rightarrow \qquad T_C = \frac{\Omega}{2R}$$

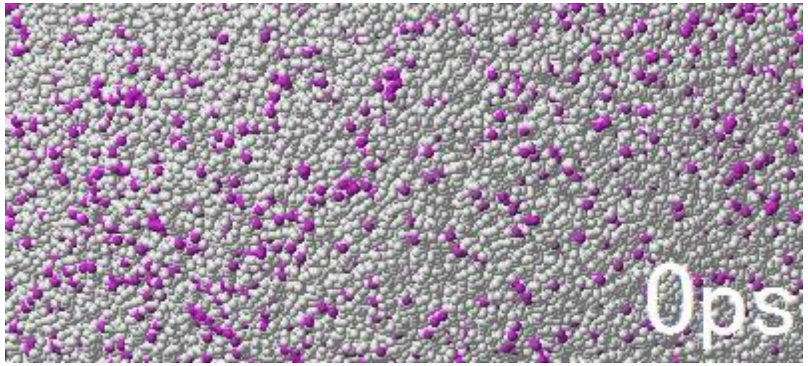
SPINODAL DECOMPOSITION

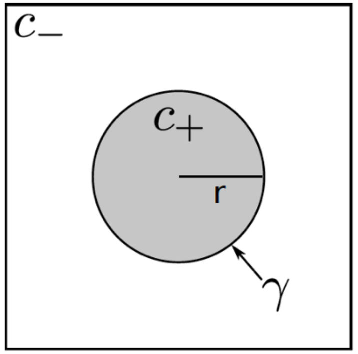
Spinodal decomposition occurs simultaneously throughout the system for small compositional perturbations of a uniform concentration, forming a continuous network

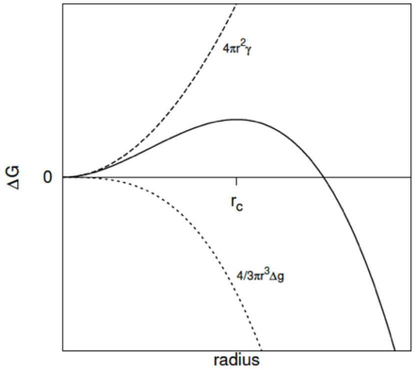
NUCLEATION AND GROWTH

Nucleation and growth occurs from discrete points in the system. It proceeds with the creation of a nucleus of a phase with mole fraction in higher concentration from a matrix. There is a decrease in free energy associated with this conversion, and an increase in free energy due to the interfacial energy.





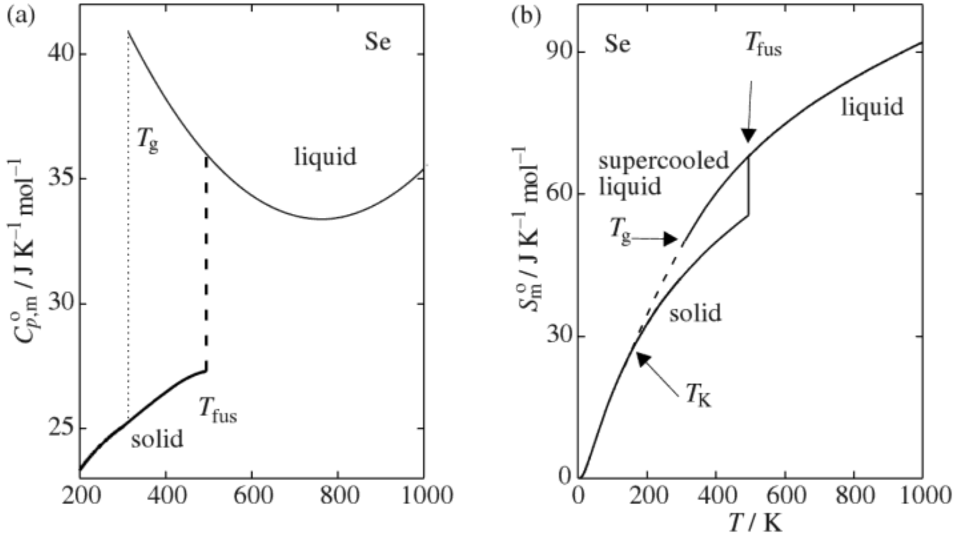




SUPERCOOLING OF LIQUIDS | SUPERHEATING OF CRYSTALS

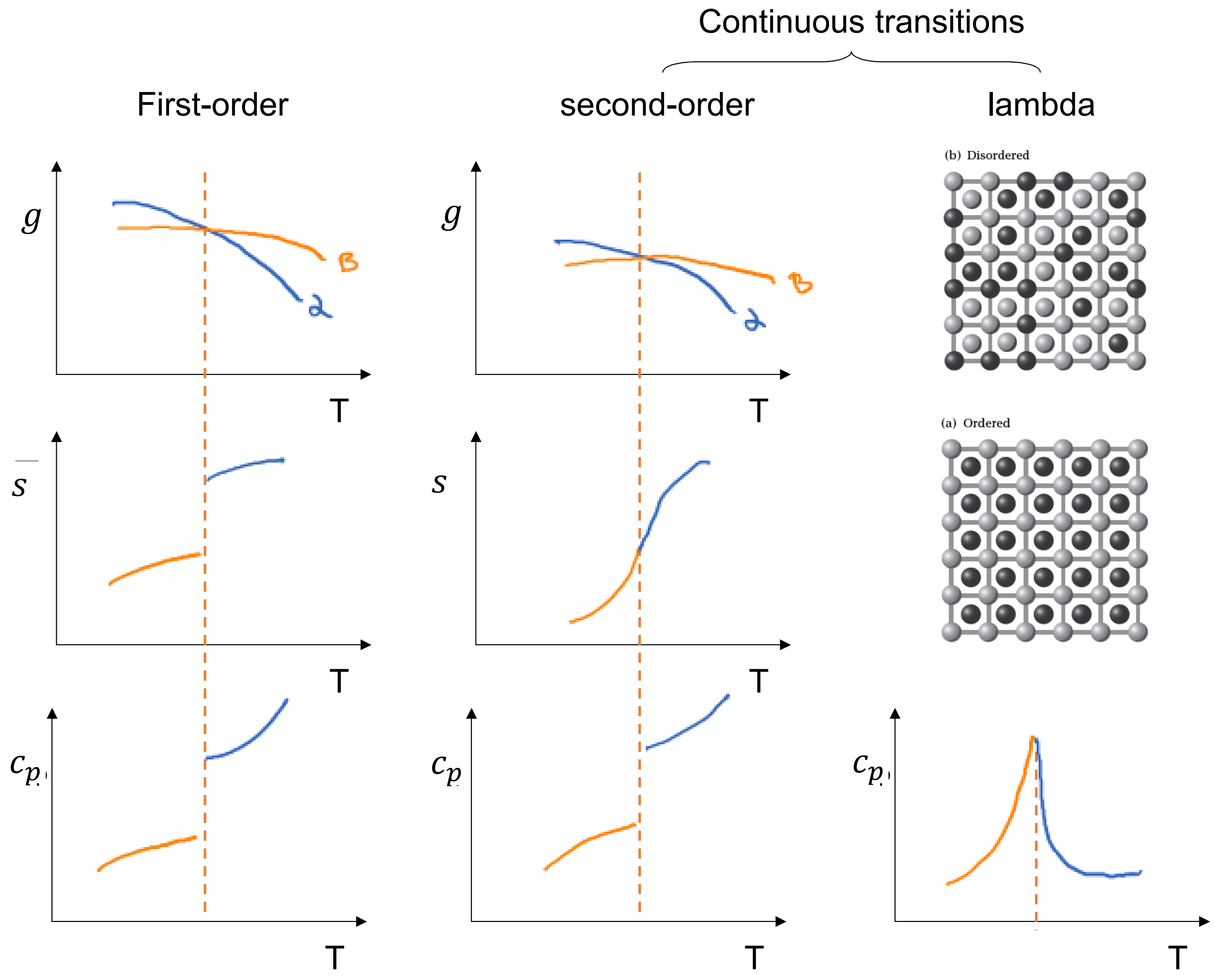
If we use temperature as a variable for stable and metastable states, there is a limit to superheating a crystal above its melting temperature or cooling a liquid below its freezing temperature. A supercooled liquid with either crystallize or transform to a glass. Glasses are materials out of equilibrium, 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 HIGHER ORDER 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 ºC, 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.