

MSE-204 Thermodynamics for Materials Science

L8.2 MULTICOMPONENT PHASE DIAGRAMS

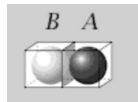
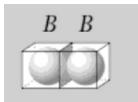
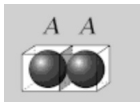
REGULAR SOLUTION MODEL | SPATIAL ARRANGEMENT OF ATOMS | MISCIBILITY GAP | INVARIANT POINTS |
INTERMEDIATE COMPOUNDS

Vaso Tileli | MXD 237

SPATIAL ARRANGEMENT UNDER THE REGULAR SOLUTION MODEL

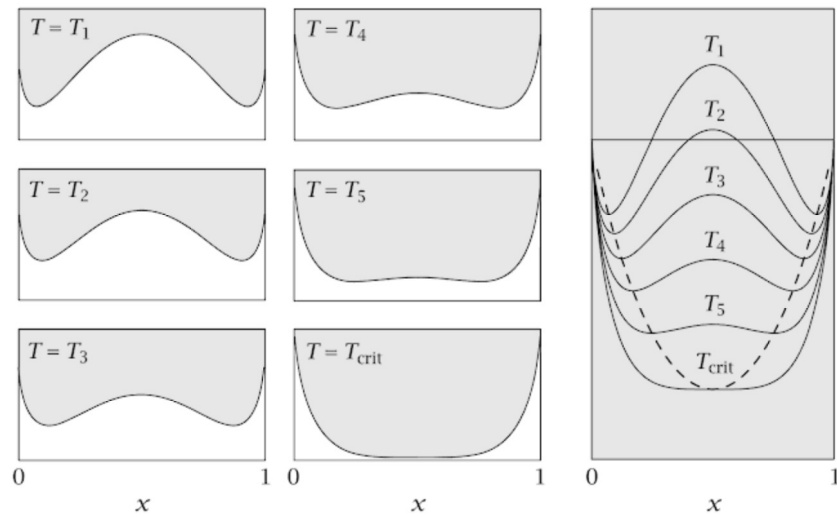
Under the **quasi-chemical model** it is assumed that the heat of mixing, $\Delta_{mix}H$, is only due to bond energies between adjacent atoms and that the volumes of pure A and pure B are equal to the final volume of the mixture.

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.

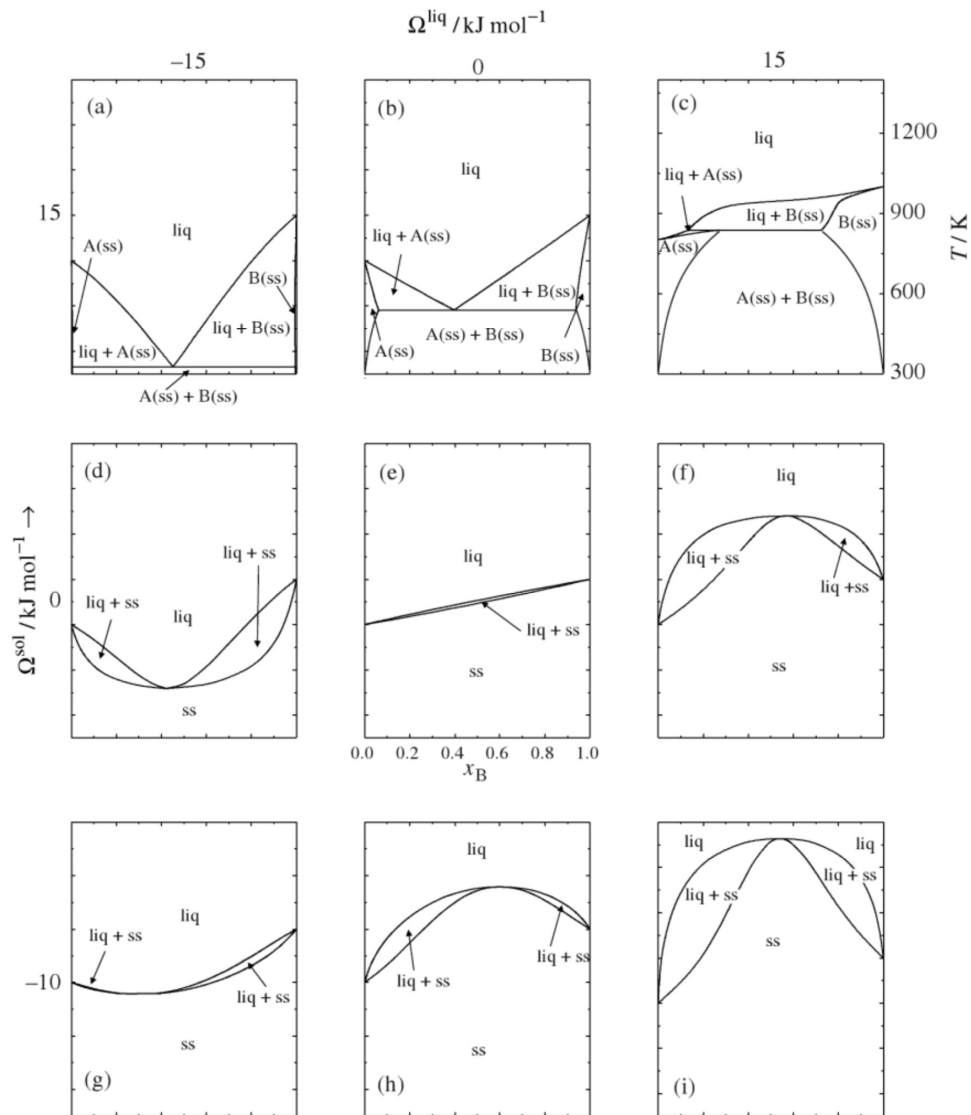


COMPOSITION DEPENDENCE OF VARIOUS THERMODYNAMIC FUNCTIONS OF A REGULAR SOLUTION

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

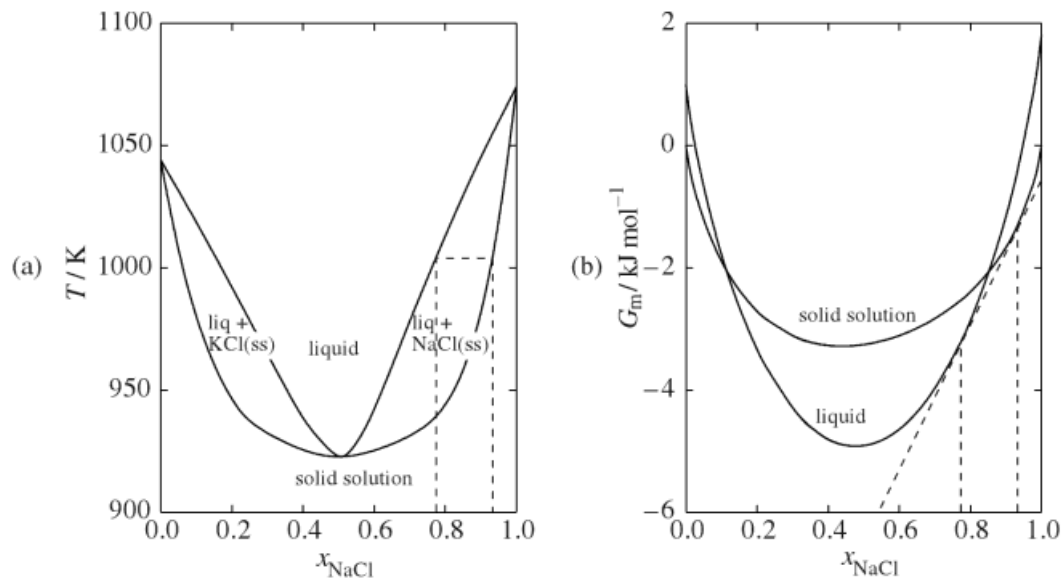


PHASE DIAGRAM OF A BINARY SYSTEM CONSISTING OF SOLID AND LIQUID SOLUTION PHASES FOR SELECTED COMBINATIONS OF Ω



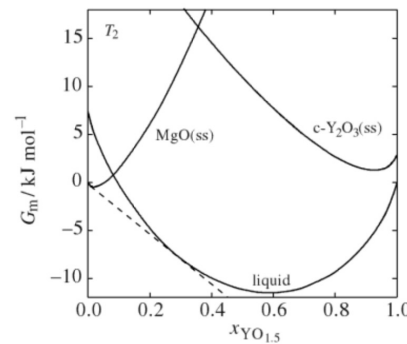
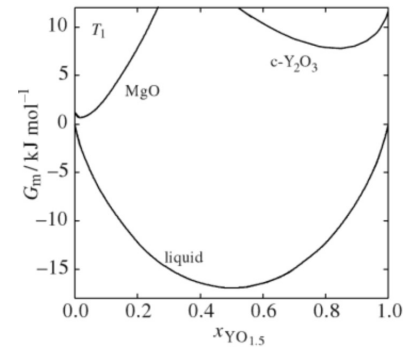
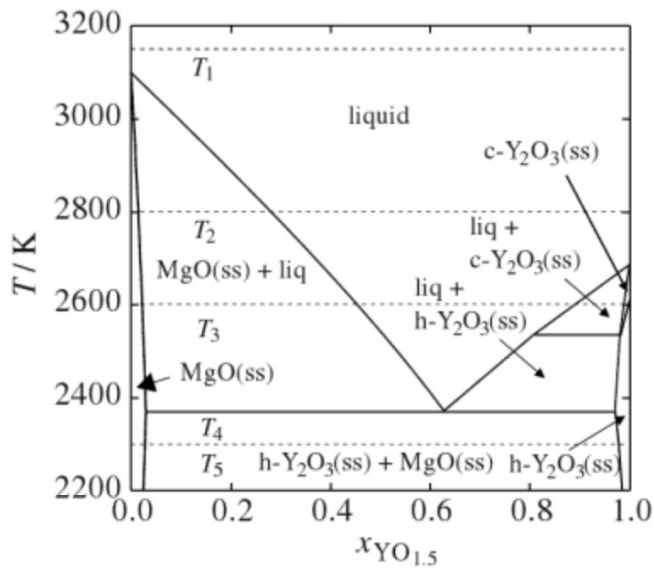
CONGRUENT PHASE DIAGRAMS

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

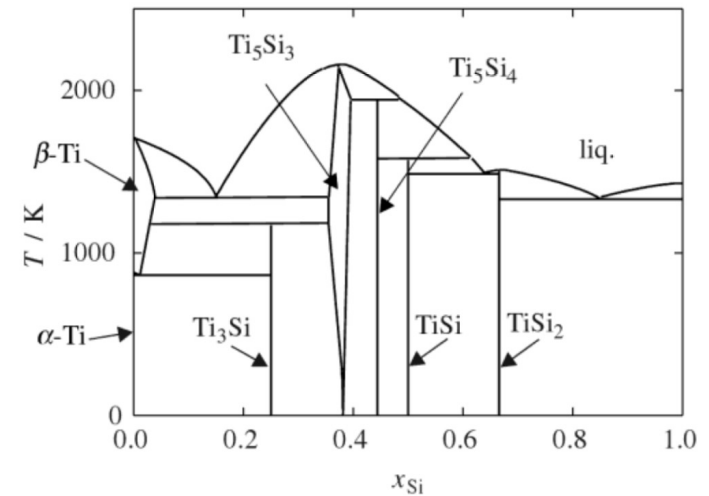
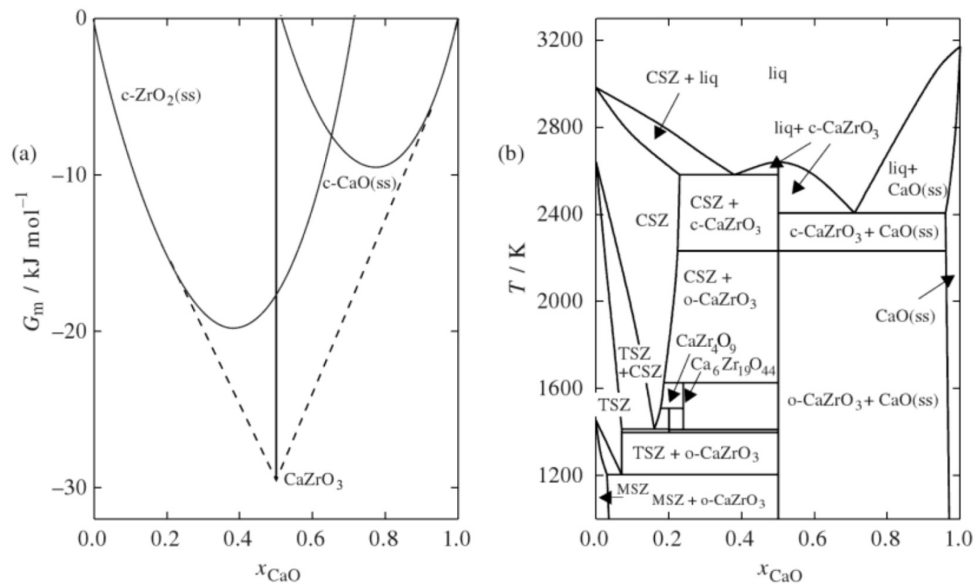
Other transformations that occur in binary systems at a fixed composition and temperature (for constant pressure) are given titles as well:

- 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

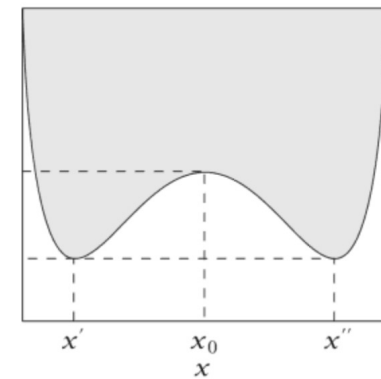
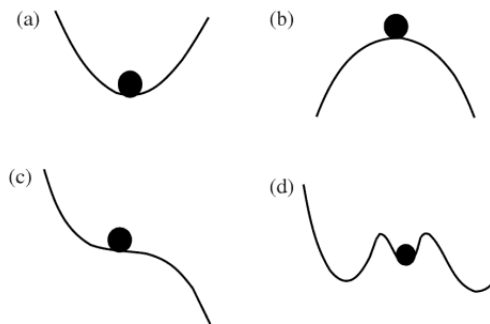
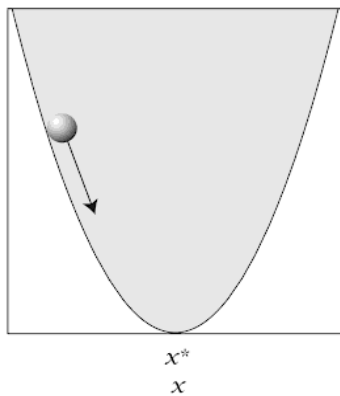
ENERGY LANDSCAPES | THE SPINODAL CURVE | METASTABILITY | NUCLEATION AND GROWTH | SPINODAL
DECOMPOSITION

Vaso Tileli | MXD 237

STABILITY WITH REGARD TO INFINITESIMAL COMPOSITIONAL VARIATIONS

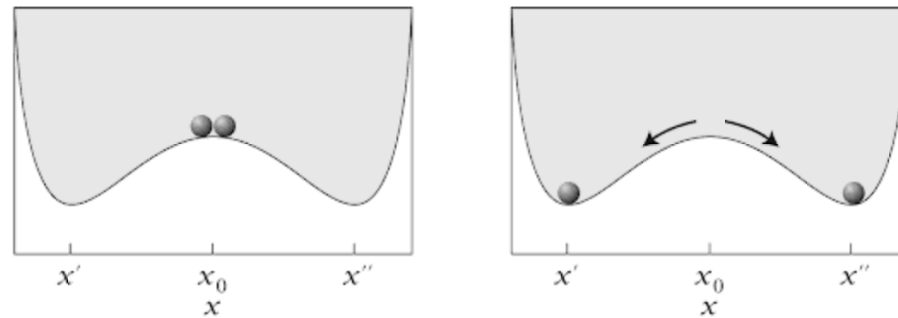
Systems at constant temperature are stable in states having minimum free energy $G(x)$.

Energy landscapes describe stabilities and phase transitions.



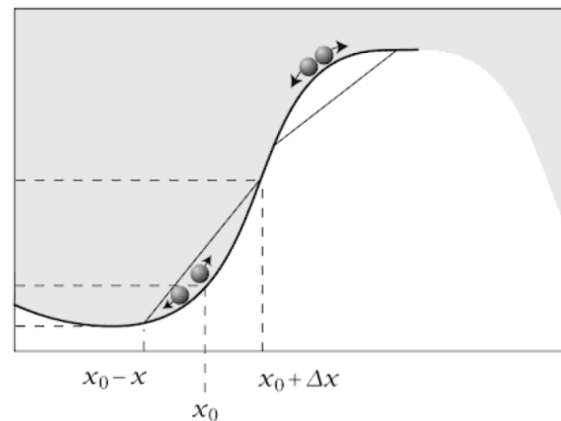
PEAKS ON ENERGY LANDSCAPES ARE POINTS OF INSTABILITY

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:

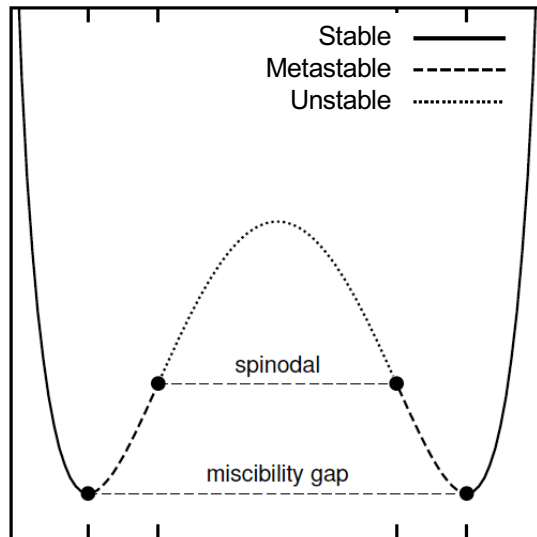


THE SPINODAL CURVE DESCRIBES THE LIMIT OF METASTABILITY

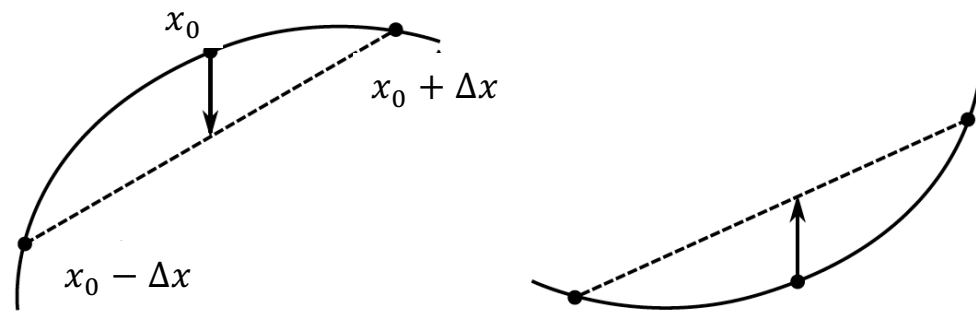
When looking at phase diagrams we described the coexistence curves (when the chemical potential of two different phases are equal). This curve is also called the binodal curve. It describes the global stability of a system against phase separation. Below, a description of metastability or local stability 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.



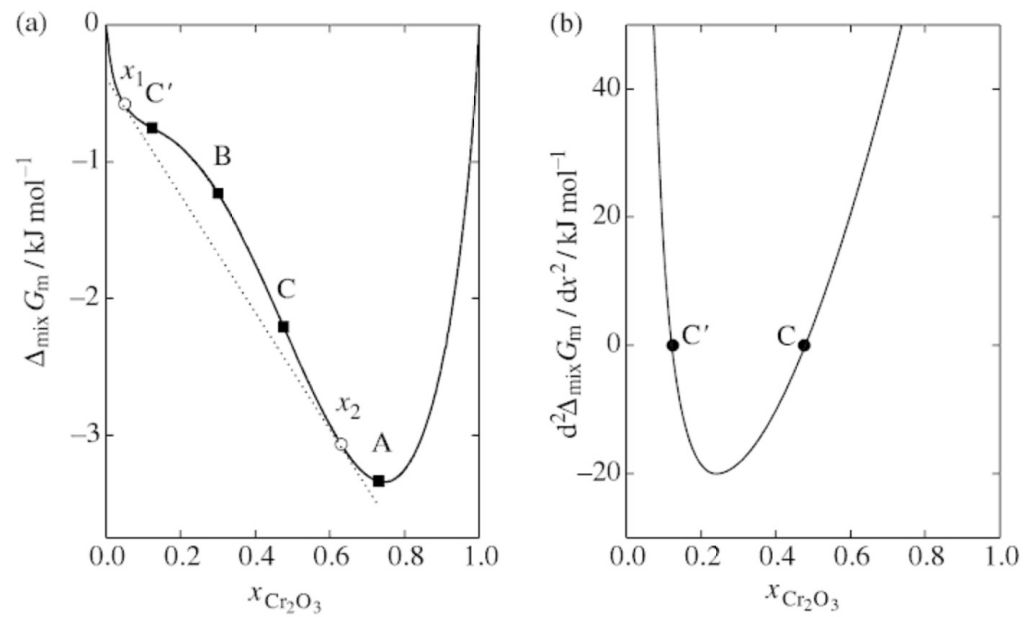
Regular solution model



STABILITY IN REGULAR SOLUTION MODEL

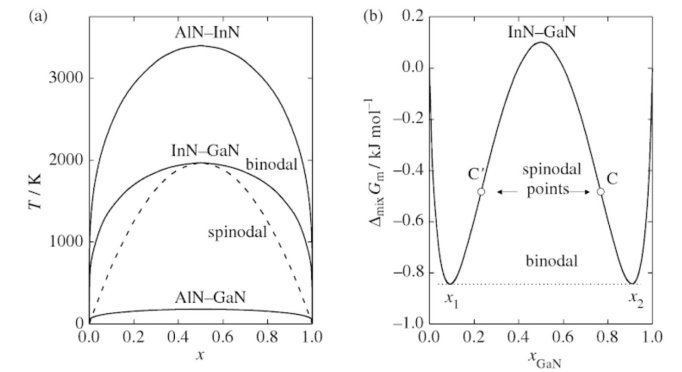


THE CRITICAL POINT



SPINODAL CURVE FOR THE CASE OF THE REGULAR SOLUTION

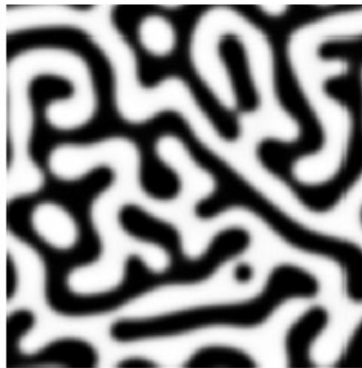
$$\bar{G}_{mix} = \Omega x_A x_B + x_A g_A^{pure} + x_B g_B^{pure} + RT(x_A \ln x_A + x_B \ln x_B)$$



B

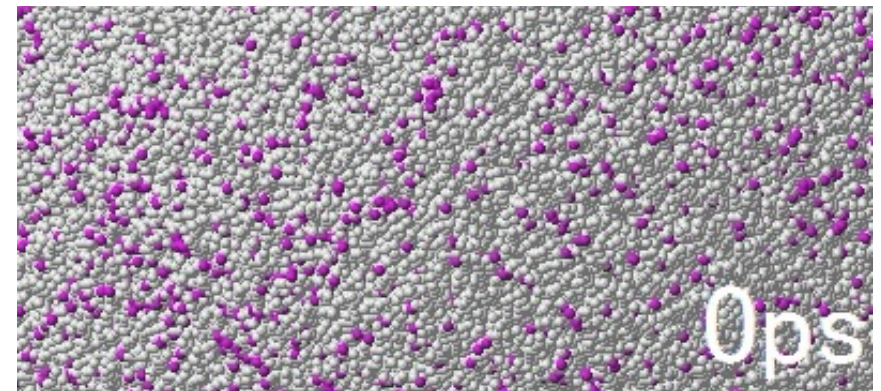
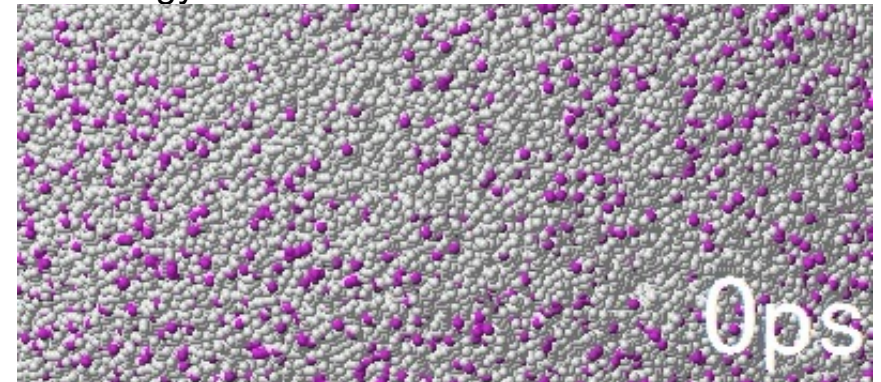
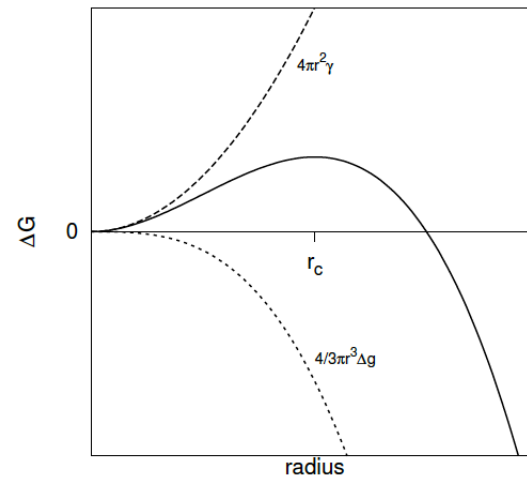
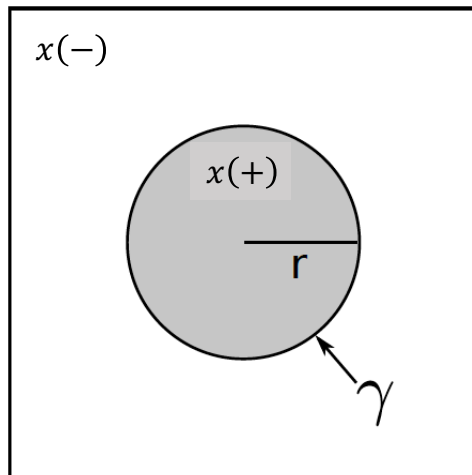
SPINODAL DECOMPOSITION

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 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)

