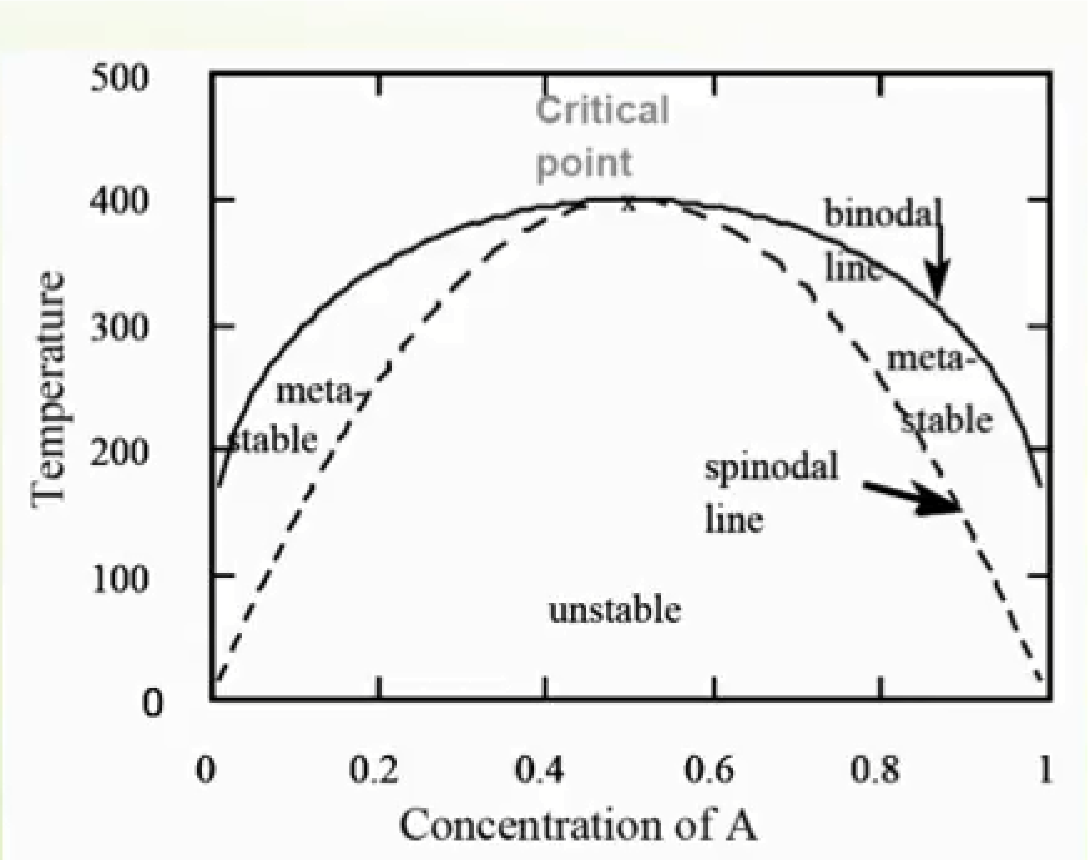
University of Babylon/ College of Materials Engineering

Department of Ceramic Engineering and Building Materials

Phase Transformations in Materials

- **Spinodal Decomposition**



check
Lec. 3EL solid solution

Spinodal Decomposition

- Spinodal decomposition is a mechanism by which a solution of two or more components can separate into distinct phases with distinctly different chemical compositions and physical properties. This mechanism differs from the classical nucleation : the phase separation due to spinodal decomposition is much more defined, and occurs uniformly throughout the material—not just at discrete nucleation sites. dynamics of phase changes in materials, which are caused by transferring the material into an initial state that is not thermodynamically stable (e.g. by rapid cooling ("quenching") or, occasionally, rapid heating; in fluids the system may also be prepared by a rapid pressure change).

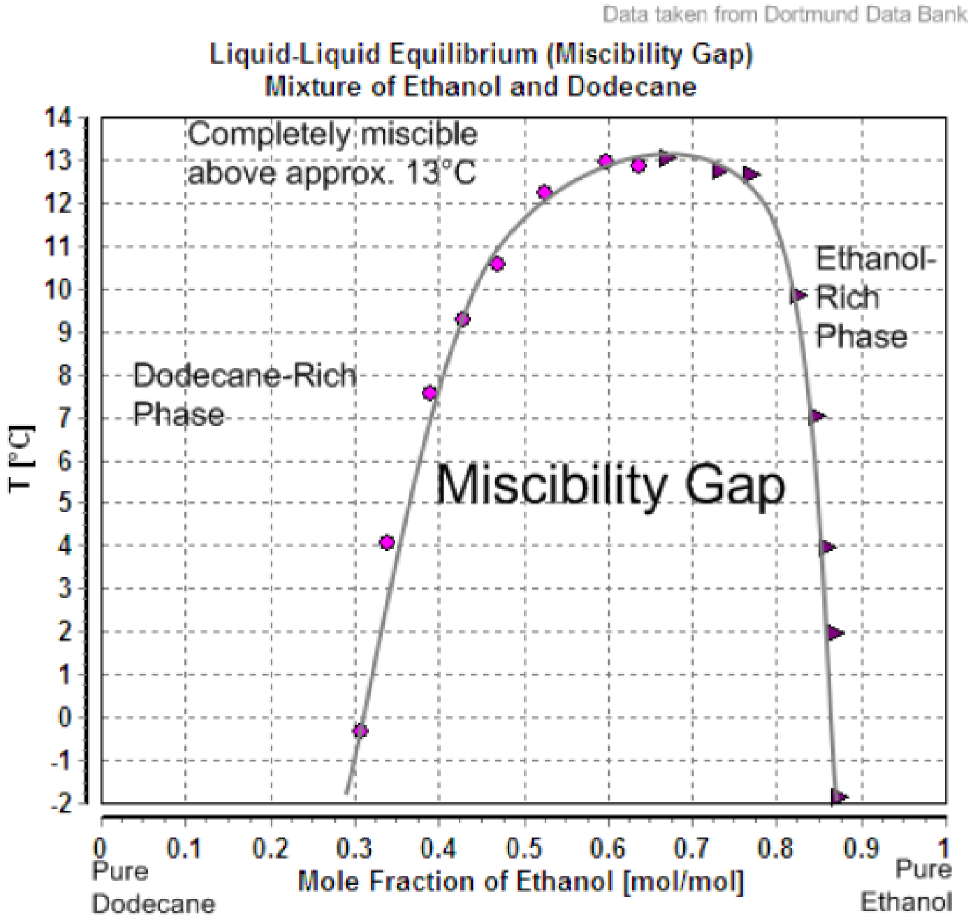
- Spinodal decomposition is of interest primarily due to its inherent simplicity, and thus represents one of the few phase transformations in solids for which there is any *plausible quantitative theory*. Since there is no thermodynamic barrier to the reaction inside of the spinodal region, the decomposition is determined solely by *diffusion*. Thus, the process can be treated purely as a diffusion problem, and many of the characteristics of the decomposition can be described by an *approximate analytical solution* to the general diffusion equation. In contrast, theories of nucleation and growth have to invoke the thermodynamics of fluctuations, and the diffusion problem involved in the growth of the nucleus is far more difficult to solve, because it is unrealistic to linearize the diffusion equation.

Spinodal Decomposition

- Spinodal decomposition is also of interest from a more practical standpoint, as it provides a means of producing a very finely dispersed microstructure that can significantly enhance the physical properties of the material. A lot of examples of materials in real practice require such defined phase segregation.

Several Important Terms:

- **Miscibility Gap**: Area within the coexistence curve of an isobaric phase diagram (temperature vs composition) or an isothermal phase diagram (pressure vs. composition). A miscibility gap is observed at temperatures below an upper critical solution temperature (UCST) or above the lower critical solution temperature (LCST). Its location depends on pressure. In the miscibility gap, there are at least two phases coexisting. Below is an example of “Liquid-Liquid Equilibrium (Miscibility Gap) Mixture of Ethanol and Dodecane.”

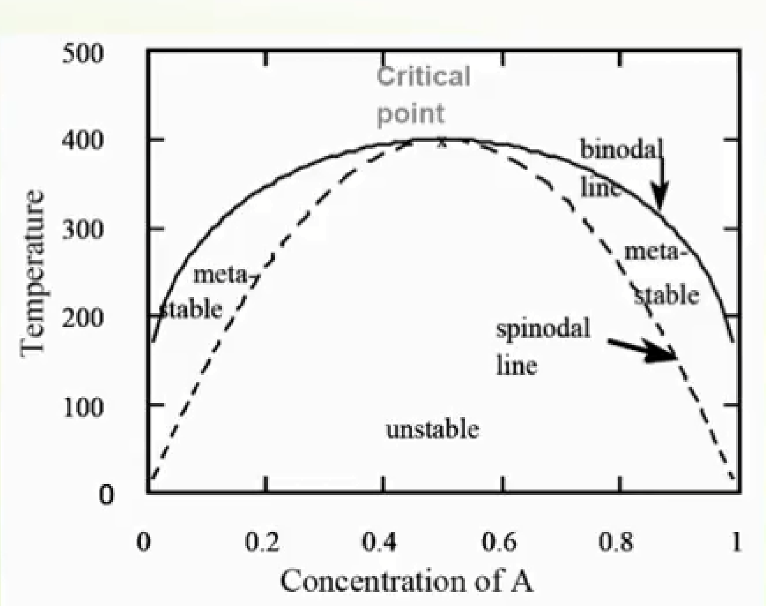


Data taken from Dortmund Data Bank

Liquid-Liquid Equilibrium (Miscibility Gap)
Mixture of Ethanol and Dodecane

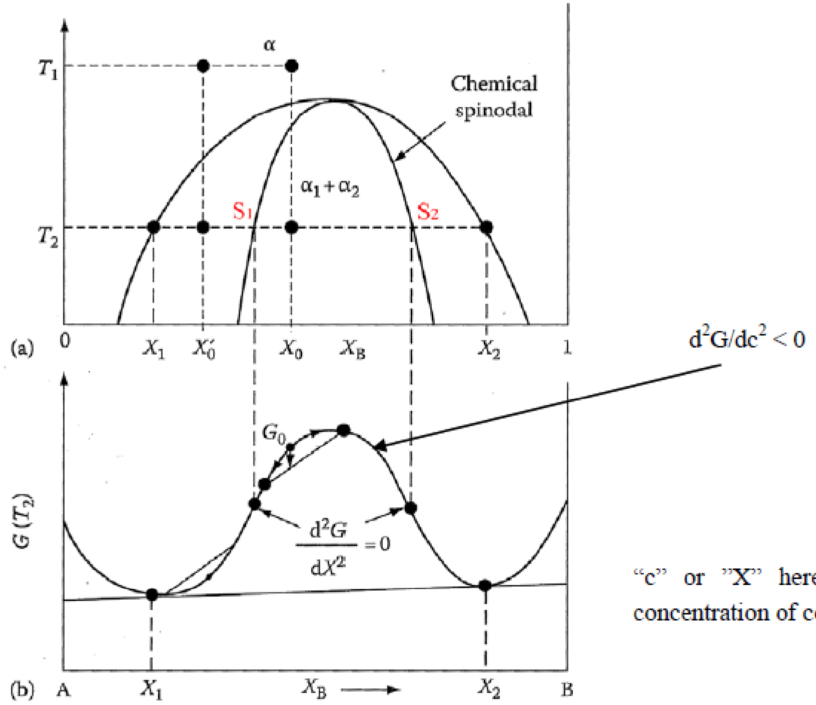
- **Binodal Curve or Coexistence Curve**: It is a curve (like the bell-like one shown above) defining the region of composition and temperature in a phase diagram for a binary mixture across which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable or unstable. Binodal compositions are defined by pairs of points on the curve of Gibbs energy of mixing vs composition that have common tangents, corresponding to compositions of equal chemical potentials of each of the two components in two phases.

- **Spinodal Curve**: A curve that separates a metastable region from an unstable region in the coexistence region of a binary mixture. Above the spinodal curve the process of moving towards equilibrium occurs by droplet nucleation, while below the spinodal curve there are periodic modulations of the order parameter, which have a small amplitude at first (i.e., spinodal decomposition). Spinodal curve is not a sharp boundary in real systems as a result of fluctuations.



Phase Diagram and Free-energy Diagram of spinodal decomposition:

- As a special case of phase transformation, **spinodal decomposition** can be illustrated on a phase diagram exhibiting a miscibility gap (see the diagram below). Thus, phase separation occurs whenever a material transitions into the unstable region of the phase diagram. The boundary of the unstable region, sometimes referred to as the binodal or coexistence curve, is found by performing a common tangent construction of the free-energy diagram. Inside the binodal is a region called the spinodal, which is found by determining, where the curvature of the free-energy curve is negative. The binodal and spinodal meet at the critical point. It is when a material is moved into the spinodal region of the phase diagram that spinodal decomposition can occur.

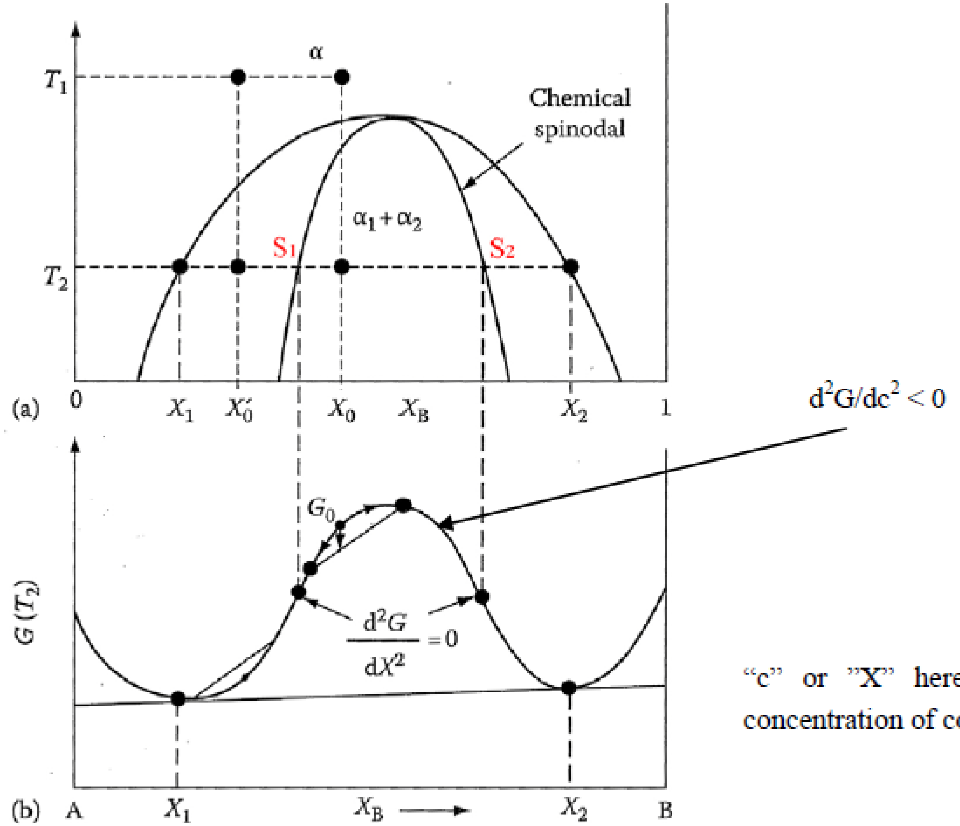


"c" or "X" here refers to the concentration of components.

adapted from the Book "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E. Easterling and M. Y. Sherif, CRC Press, third edition.

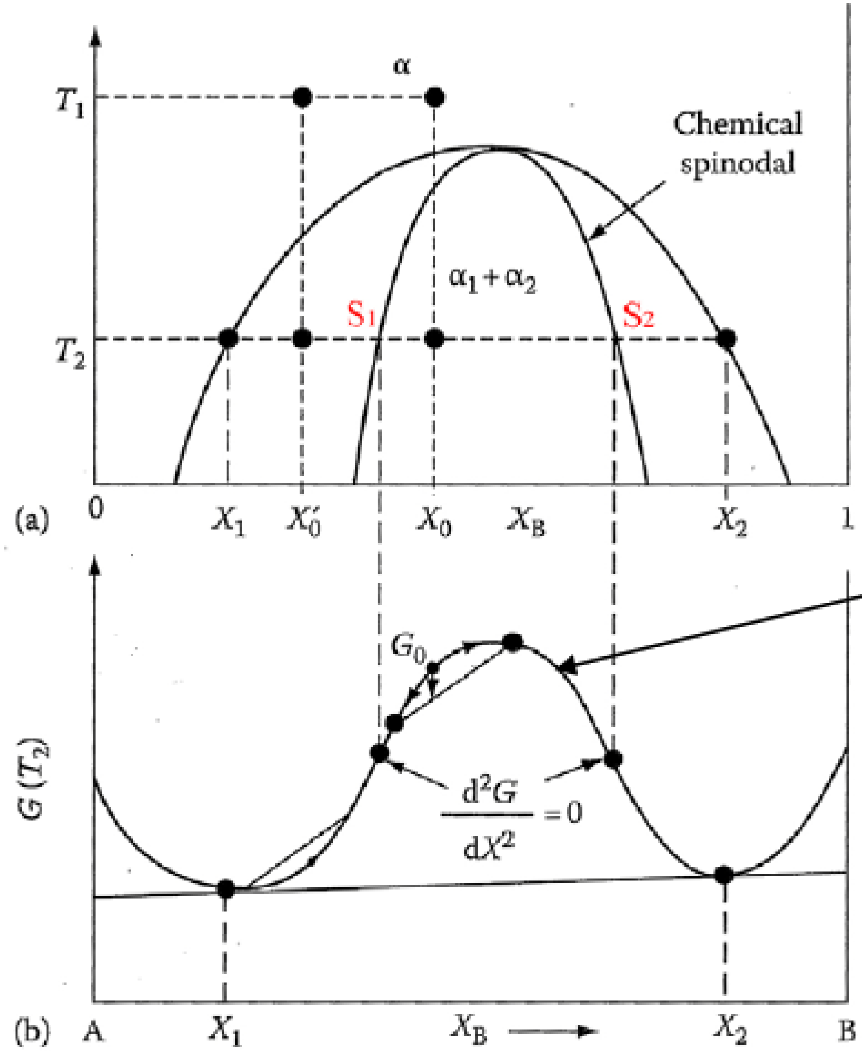
Phase Diagram and Free-energy Diagram of spinodal decomposition:

- In comparison, if an alloy lies outside the spinodal (i.e., with composition of X_0' as shown) is solution treated at a high temperature T_1, and then quenched to a lower temperature T_2, small variations in composition lead to an increase in free energy (as shown), and the alloy is therefore metastable. The free energy of the system cam only be decreased in this case if nuclei are formed with a composition very different from the matrix. Therefore outside the spinodal the transformation must proceed by a process of nucleation and growth



"c" or "X" here refers to the concentration of components.

adapted from the Book "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E. Easterling and M. Y. Sherif, CRC Press, third edition.

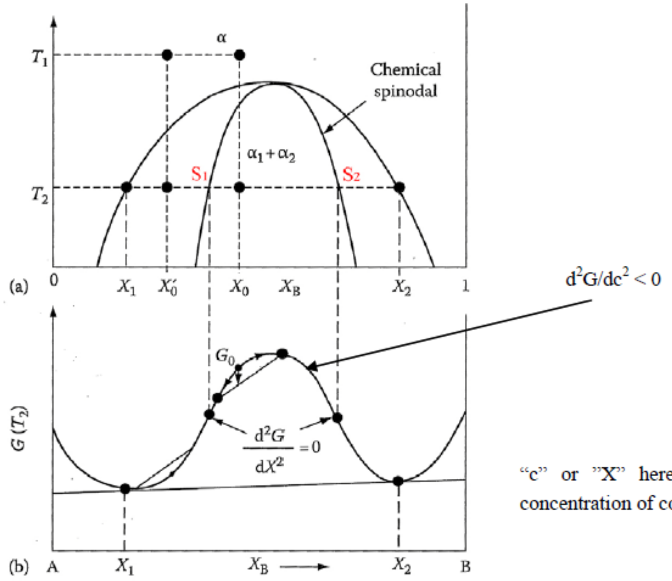


$d^2G/dc^2 < 0$

“c” or ”X” here refers to the concentration of components.

adapted from the Book "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E. Easterling and M. Y. Sherif, CRC Press, third edition.

- The free energy curve is plotted as a function of composition for the phase separation temperature T_2. Equilibrium phase compositions are those corresponding to the free energy minima. Regions of negative curvature ($d^2G/dc^2 < 0$) lie within the inflection points of the curve ($d^2G/dc^2 = 0$) which are called the spinodes (as marked as S_1 and S_2 in the diagram above). For compositions within the spinodal, a homogeneous solution ***is unstable against microscopic fluctuations in density or composition, and there is no thermodynamic barrier to the growth of a new phase, i.e., the phase transformation is solely diffusion controlled.***
- To reach the spinodal region of the phase diagram, a transition must take the material through the binodal region or the critical point. Often phase separation will occur via nucleation during this transition, and spinodal decomposition will not be observed. To observe spinodal decomposition, a very fast transition, often called a *quench*, is required to move from the stable to the spinodally unstable region of the phase diagram.



“c” or ”X” here refers to the concentration of components.

adapted from the Book "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E. Easterling and M. Y. Sherif, CRC Press, third edition.