Lecture 22: Spinodal Decomposition: *Part 1: general description and practical implications*

Today's topics

- basics and unique features of spinodal decomposition and its practical implications.
- The relationship between the phase diagram and the free energy (ΔG) vs. composition plot.
- Initial understanding of spinodal decomposition from the Cahn-Hilliard Equation.

About 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 (as we went through in previous Lectures #10-14): the phase separation due to spinodal decomposition is much more defined, and occurs *uniformly* throughout the material—not just at discrete nucleation sites.

  (see an animation for the microstructural evolution under the Cahn–Hilliard equation, demonstrating distinctive coarsening and phase separation through spinodal decomposition: http://www.eng.utah.edu/~lzang/images/cahn-hilliard-anim.gif; and also a movie clip simulating the phase separation due to spinodal decomposition on a hexagonal lattice (from Oono, Y. and Puri, S., Study of phase-separation dynamics by use of cell dynamical systems. I. Modeling, Physical Review A (General Physics), Volume 38, Issue 1, July 1, 1988, pp.434-453): http://www.eng.utah.edu/~lzang/images/spinodal.wmv)

- 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 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. One example is the plastic solar cells

(see picture below), where the C60 and polymer phase should be well separated to provide separate charge carrier transport thus minimizing the charge recombination, but meanwhile still maintaining the large interface contact to maximize the photoinduced charge separation to produce the free charge carriers (electrons and holes), which in turn demands uniform, very finely dispersed micro- or even nanoscale structured phases of the n-type and p-type materials. To this end, the smaller the segregation (the wavelength, λ, as to be described below), the large the interface, and thus the more the n-p contact, and thus the more efficient for the photoinduced charge separation.
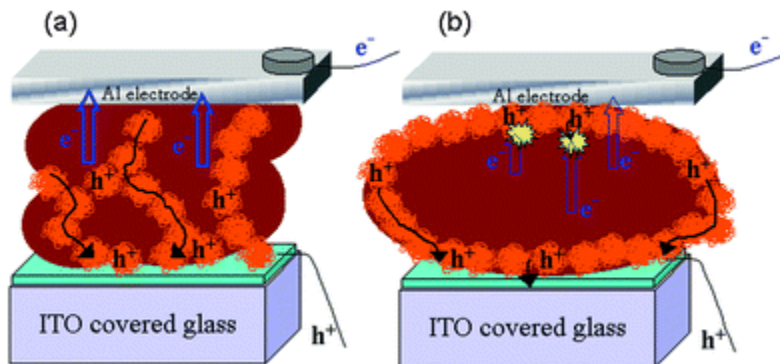
Plastic solar cell device based on a sanwiched compsoiteds of conducting polymer and C60: In (a) both the polymer nanospheres as well as the fullerene phase offer percolated pathways for the transport of holes and electrons, respectively. In (b) electrons and holes suffer recombination, as the percolation is not sufficient.
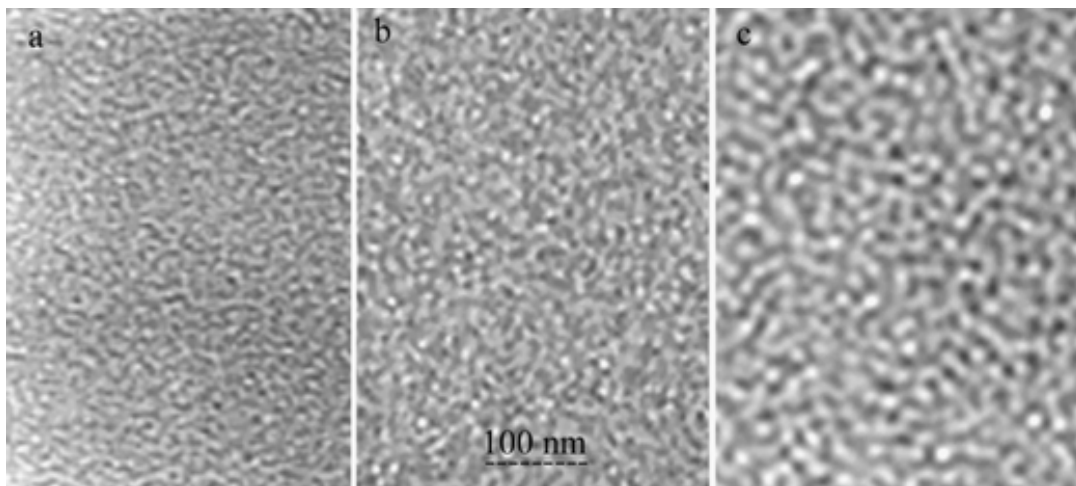

High resolution TEM images of regioregular polymer:C60 (P3HT:PCBM 1:0.8) blend films cast from chlorobenzene, (a) as cast, (b) annealed at 150 °C for 30 min and (c) for 2 hours. Clearly visible are the spherical P3HT nanostructures with a size on the order of 10 nm.

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."
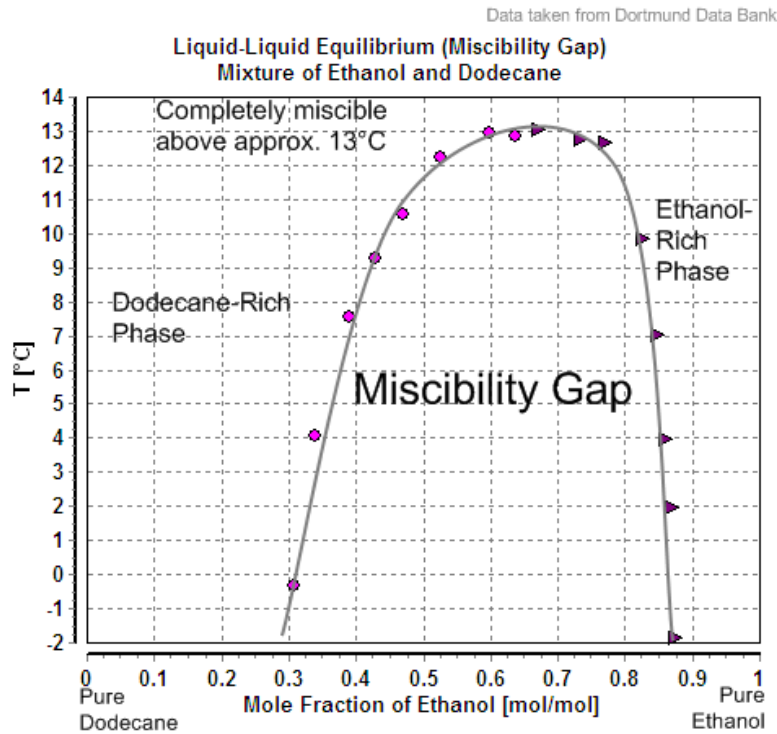
Binodal Curve or Coexistence Curve: It is a curve (like the bell-like one shown above) defining the region of composition and temperature in a phase diagram for a binary mixture across which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable 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.
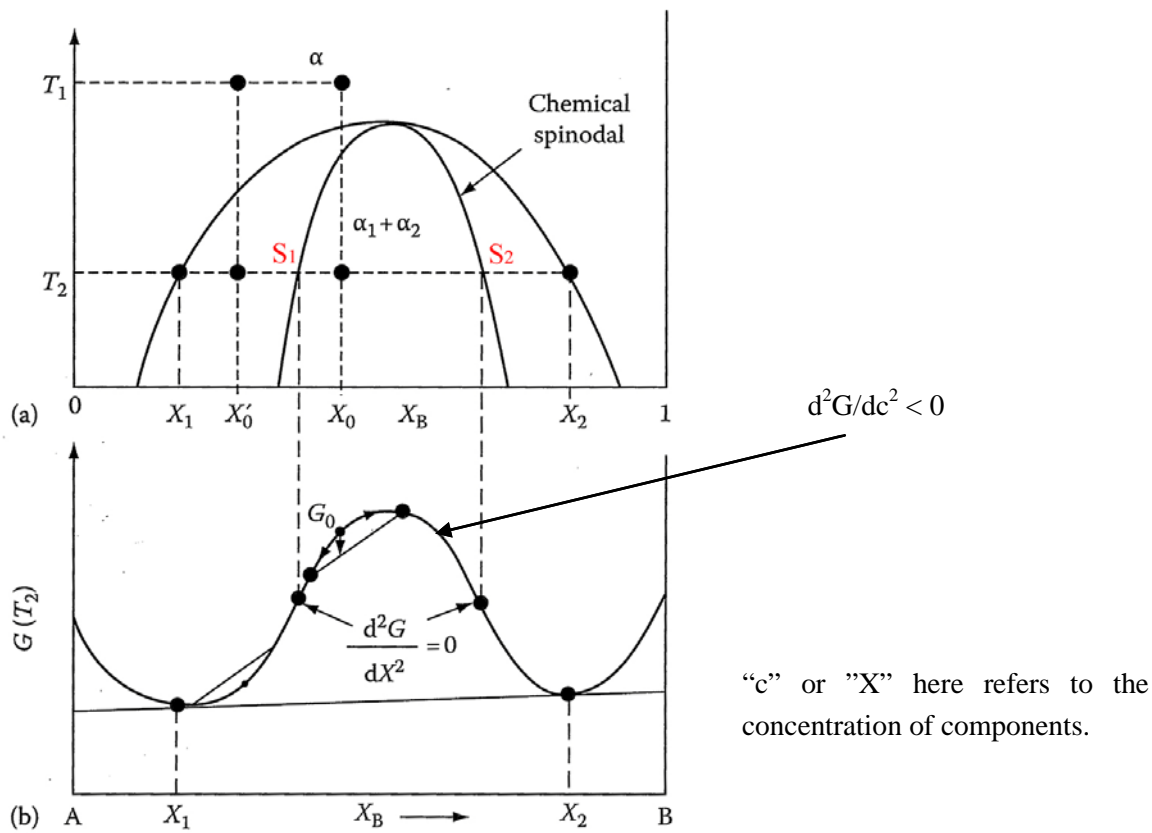
Spinodal Curve: A curve that separates a metastable region from an unstable region in the coexistence region of a binary mixture. Above the spinodal curve the process of moving towards equilibrium occurs by droplet nucleation, while below the spinodal curve there are periodic modulations of the order 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.

- If an alloy with composition of X_0 is solution treated at a high temperature T_1, and then quenched (rapidly cooled) to a lower temperature T_2, the composition will initially be the same everywhere and its free energy will be G_0 on the G curve in the following diagram. However, the alloy will be immediately unstable, because small fluctuation in composition that produces A-rich and B-rich regions will cause the total free energy to decrease. Therefore, "up-hill" diffusion (see the illustration at the end of this lecture) takes place until the equilibrium compositions X_1 and X_2 are reached. *How such small composition fluctuation leads to the spinodal phase separation is today's and next two lectures' topics.*

- 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 as we learned in the past Lectures 9-14.

"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.

Brief description of Spinodal Decomposition following the Free-energy Diagram

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Early Background of Spinodal Decomposition:
- In the early 1940s, Bradley reported the observation of sidebands around the Bragg peaks of the x-ray diffraction pattern from a Cu-Ni-Fe alloy that had been quenched and then annealed inside the miscibility gap. Further observations on the same alloy were made by Daniel and Lipson, who demonstrated that the sidebands could be explained by a <u>periodic modulation of composition</u> in the <100> directions. From the spacing of the sidebands they were able to determine the wavelength of the modulation, which was of the order of 100 Å.

- The growth of a composition modulation in an initially homogeneous alloy implies <u>uphill diffusion</u> (see the illustration at the end of this lecture), or a <u>negative diffusion coefficient</u> (see Lecture 5). Becker and Dehlinger had already predicted a *negative diffusivity inside the spinodal region of a binary system*. But their treatments could not account for the growth of a modulation of particular wavelength (λ), such as was observed in the Cu-Ni-Fe alloy. In fact, *any model based on <u>Fick's law</u> yields a physically unacceptable solution when the diffusion coefficient is negative* (see Lecture 5).

- The first explanation of the periodicity was given by Mats Hillert in his 1955 Doctoral Dissertation at MIT. Starting with a regular solution model, he derived a flux equation for *one-dimensional diffusion* on a discrete lattice. This equation differed from the usual one by the inclusion of a term which allowed for the effect on the driving force of the interfacial energy between adjacent inter-atomic planes that differed in composition. Hillert solved the flux equation numerically and found that i*nside the spinodal it yielded a periodic variation of composition with distance*. Furthermore, the wavelength of the modulation was of the same order as that observed in the Cu-Ni-Fe alloys.
- A more *flexible continuum model* was subsequently developed by John W. Cahn, who included the effects of <u>coherency strains</u> as well as the <u>gradient energy term</u>. The strains are significant in that they dictate the ultimate morphology of the decomposition in anisotropic materials.

About Mats Hillert:
- **Mats Hillert**, born November 28, 1924 in Gothenburg, is a Swedish metallurgist who is an emeritus professor in metallography (physical

metallurgy) at the Royal Institute of Technology (KTH).

- Hillert has made contribution to many areas of metals research, including thermodynamics and phase transitions.
- In 1973, he was elected a member of the Royal Swedish Academy of Engineering Sciences, and in 1982 a member of the Royal Swedish Academy of Sciences.

About John W. Cahn:

- John Werner Cahn (born 1928) is an American scientist and winner of the National Medal of Science in 1998. Since 1977, he has held a position at the National Institute of Standards and Technolog.
- Cahn received a bachelor's degree in Chemistry in 1949 from the University of Michigan. He later earned a Ph.D in Physical Chemistry in 1953 from the University of California at Berkeley.
- 1973 Member, National Academy of Sciences.
- 1998 Member, National Academy of Engineering

Comparison between Spinodal Decomposition and Nucleation and Growth

- An initially homogeneous solution develops fluctuations of chemical composition when supercooled into the spinodal region. These fluctuations are at first small in amplitude but grow with time until there are identifiable precipitates of equilibrium composition (vide infra).
- In contrast, during nucleation and growth, there is a sharp interface between the parent and product crystals; furthermore, the precipitate at all stages of its existence has the required equilibrium composition (vide infra).
- Spinodal decomposition involves *uphill diffusion*, whereas diffusion is always down a concentration gradient for nucleation and growth of the type illustrated below.

*Spinodal decomposition refers to a mechanism of phase transformation inside a miscibility gap. It is characterized by the occurrence of diffusion up against a concentration gradient (see Lecture 5), often referred as "uphill" diffusion (*see the illustration at the end of this lecture), *leading to formation of a uniform-sized, periodic fine microstructure.*
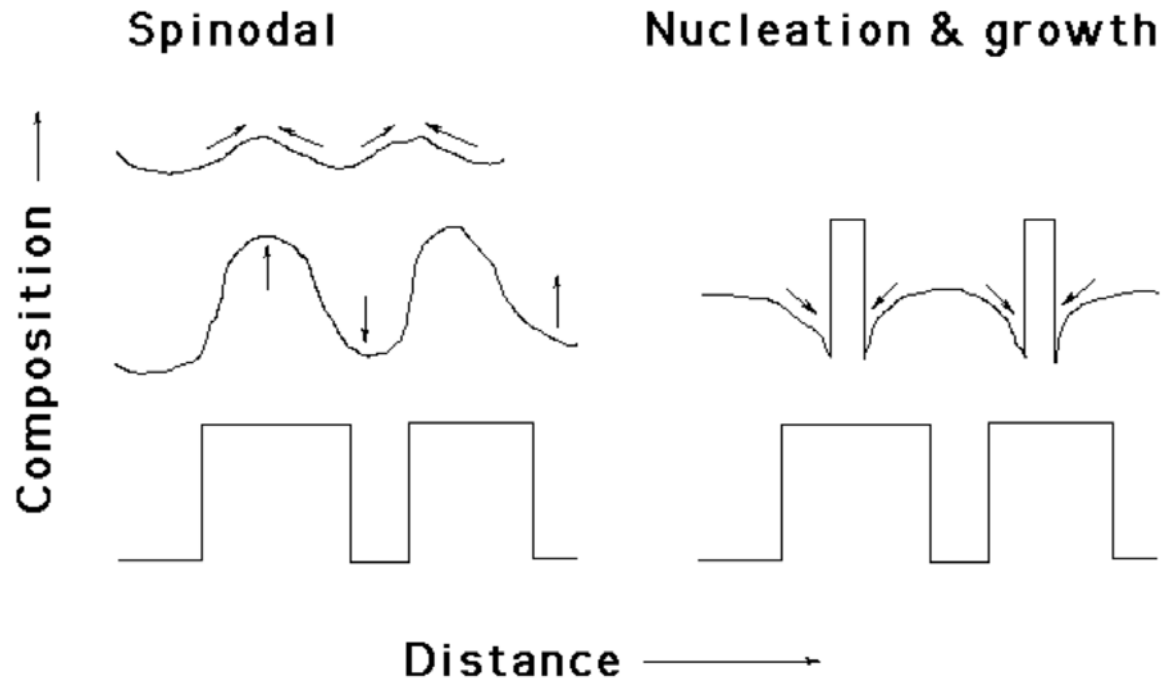
Illustration: Evolution of phase separation in spinodal decomposition and during nucleation and growth. The arrows indicate the direction of diffusion.

--- from "Kinetics and Microstructure Modelling", H. K. D. H. Bhadeshia, Cambridge U.