

Last time: Phase Transformations: Overview

Metastability, instability, and mechanisms

First-order and second-order transitions

Free energy functions; conserved and nonconserved variables

Today: Spinodal decomposition—I.

Background

- Diffusion within the spinodal
 - Free energy of an inhomogeneous system
 - An improved diffusion equation
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Spinodal decomposition—I.

Diffusion within the spinodal (see notes from Lecture 27)

Free energy of an inhomogeneous system

Cahn and Hilliard 1958 laid important groundwork for the theory of spinodal decomposition by working out a theory for the "gradient-energy" contribution to the free energy of a solution that has composition gradients. The usual free energy vs. composition curves that we draw plot the free energy per unit volume $f(c)$ for a *homogeneous* solution in which the composition is uniform. When there are compositional inhomogeneities, there is an extra contribution to the total free energy that is proportional to the square of the gradient of composition.

This is readily extended to develop an expression for the free energy of equilibrium, diffuse interfaces between coexisting phases.

An improved diffusion equation

The diffusion potential for classical diffusion (in which the gradient-energy contribution to f can be ignored) is modified by gradient-energy effects. This introduces additional terms into the flux and continuity equations for diffusion (Fick's first and second laws). It's important to note that the modified diffusion equation is an improvement over Fick's second law because it includes additional physical phenomena. The modified equation differs from Fick's second law only when the spatial scale in which the composition variations take place is very small—in most materials this involves compositional modulations on the order of 1–50 nm. For larger length scales, the traditional Fick's second law is generally adequate.
