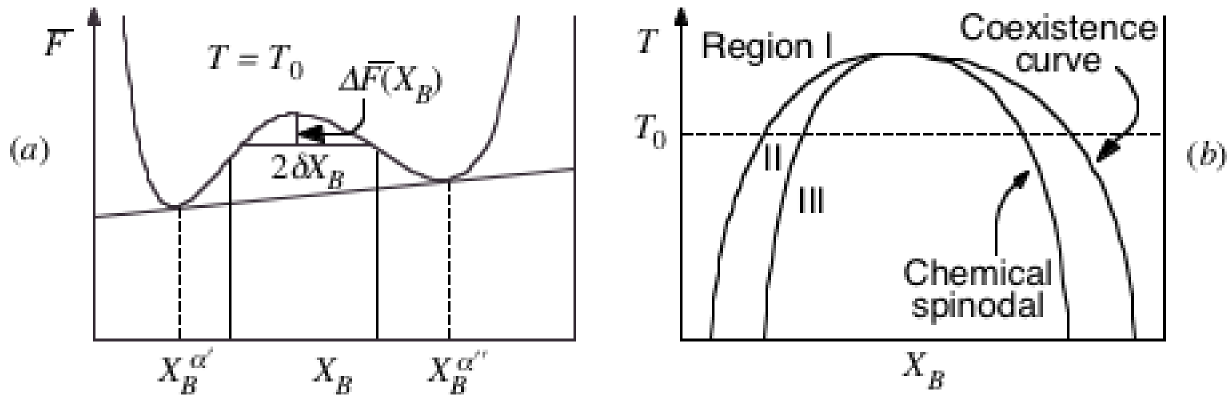
Phase Transformations: Spinodal Decomposition

Today’s topics:

- **A phase diagram with a spinodal region**
- **The free energy of a compositionally inhomogenous solution**
- **Interdiffusion within the spinodal region**
- **The kinetics of spinodal decomposition**
- **Spinodal microstructures**

A phase diagram with a spinodal region

- **The chemical spinodal is defined by** $\dfrac{\partial^2 F}{\partial {X_B}^2} = 0$ **and it coincides with the limit to metastability with respect to infinitesimal fluctuations of composition.**



Spinodal decompositon becomes possible in region III where $\dfrac{\partial^2 F}{\partial {X_B}^2} < 0$

Free energy of inhomogeneous system

- **Thermodynamics of solutions normally describes systems which are compositionally homogeneous, at least on a local scale.**
- **Real materials often contain composition gradients or composition discontinuities (e.g., consider a binary alloy in a two-phase equilibrium state).**
- **It is possible to develop a description for the free energy of a phase in which there is an arbitrary compositional variation $c(x)$.**

Free energy of inhomogeneous system...

- **Cahn and Hilliard (1958) used a variational approach to formulate a general expression for $F[c(x)]$ in a system of cross sectional area A with a one-dimensional compositional variation**

$$F\left[c(x)\right] = A\int_{-\infty}^{\infty}\left[f(c) + K\left(\frac{dc}{dx}\right)^2\right]dx$$

K is a positive materials constant called the *gradient-energy coefficient* and $f(c)$ is the free energy for a homogeneous system.

Interdiffusion in the spinodal region

- In *any* system with composition gradients, gradient energy will modify the local driving force for diffusion. Practically speaking, gradient-energy effects are only important when the material contains a high density of regions with gradients (thin-film multilayers!).
- When gradient-energy effects are considered, the diffusion equation in 1-D becomes

$$\frac{\partial c}{\partial t} = \tilde{D}\left\{\frac{\partial^2 c}{\partial x^2} - \left(2K \bigg/ \frac{\partial^2 f}{\partial c^2}\right)\frac{\partial^4 c}{\partial x^4}\right\}$$

Solution to modified diffusion equation

- **The interdiffusivity is negative in the spinodal region**

$$\tilde{D} = M_c \frac{\partial^2 f}{\partial c^2}$$

(M_c **is a mobility and is inherently positive).**

- **In the spinodal region the solution to the diffusion equation has the form**

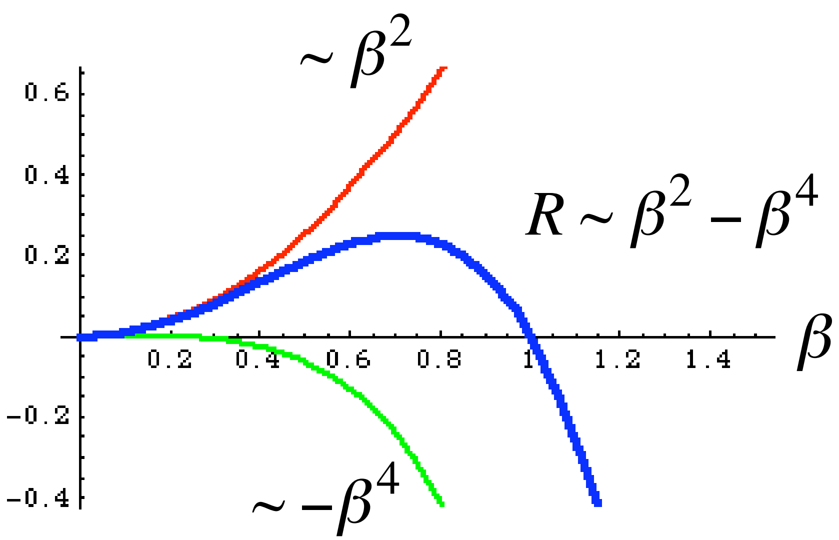
$$c = c_0 + e^{R(\beta)t} \cos(\beta x)$$

with

$$R(\beta) = -\tilde{D}\beta^2 \left[1 + \left(\frac{2K}{\partial^2 f / \partial c^2} \right) \beta^2 \right]$$

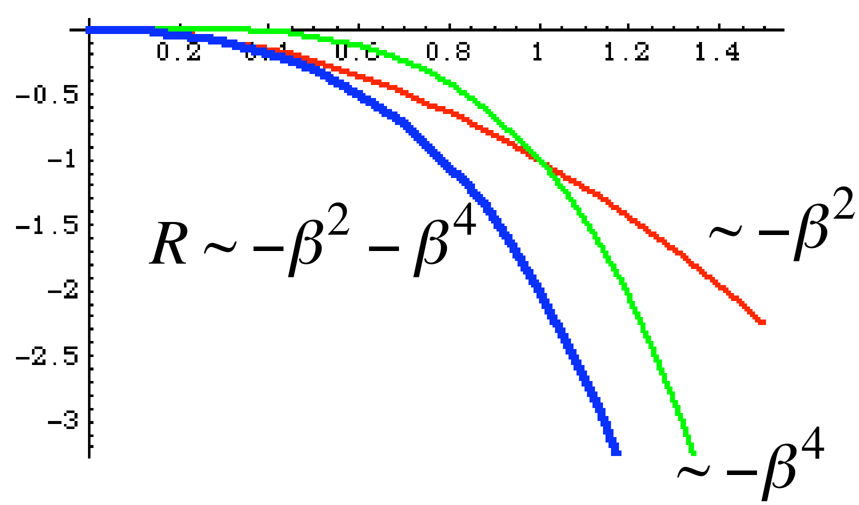
Solution to modified diffusion equation…

- **The amplification factor $R(\beta)$ is a fourth-order polynomial with this form**



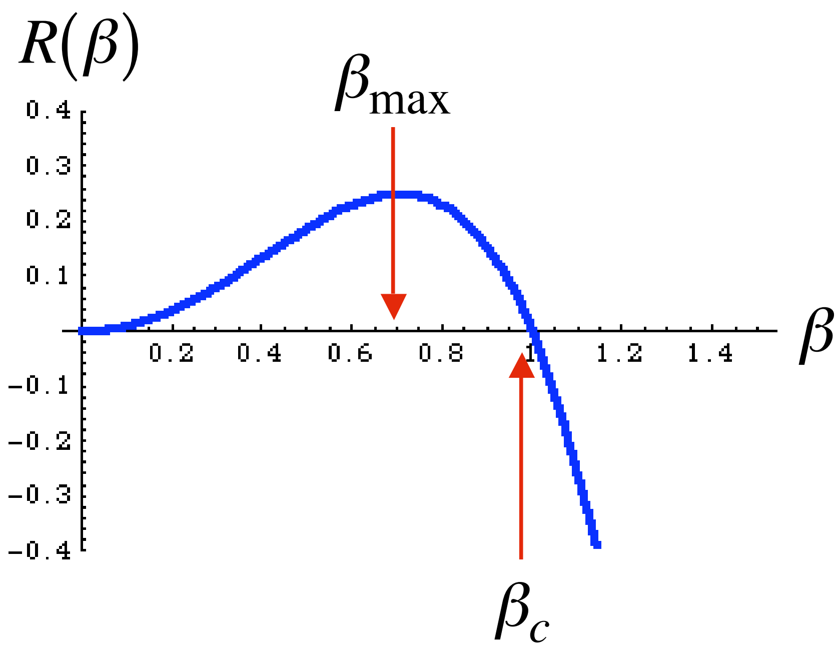
Inside **spinodal**
unstable waves grow

Outside **spinodal**
all waves decay



Solution to modified diffusion equation…

- **Inside the spinodal, for small β, $R(\beta)$ is positive and it has a maximum at $\beta_{\max}$.**



- **Microstructure of developing structure is *periodic* with wavelength determined by**

$$\lambda_{\max} = \frac{2\pi}{\beta_{\max}}$$

Solution to modified diffusion equation...

- $\beta_{\max}$ **is determined from the condition**

$$\frac{dR(\beta)}{d\beta} = 0 \quad \text{and thus} \quad 2\beta_{\max} + 8\frac{K}{\partial^2 f / \partial c^2}\beta_{\max}^3 = 0$$

$$\text{so} \quad \beta_{\max} = \sqrt{-\frac{\partial^2 f / \partial c^2}{4K}}$$

β_c **is determined from the condition**

$$R(\beta) = 0 \quad \text{and thus} \quad 1 + 2\frac{K}{\partial^2 f / \partial c^2}\beta_c^2 = 0$$

$$\text{so} \quad \beta_c = \sqrt{-\frac{\partial^2 f / \partial c^2}{2K}} \quad \text{and thus} \quad \beta_c = \sqrt{2}\,\beta_{\max}$$

Spinodal microstructures

- **The spinodal instability and the rapid growth of waves at β_{max} leads to periodic modulations of composition. In elastically anisotropic alloys, the spinodal structure tends to be aligned along elastically soft directions.**

Figures removed due to copyright restrictions.
See Figures 18.16 and 18.17 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Spinodal microstructures, cont'd

- **The wavelength of spinodal decomposition depends strongly on temperature because** $\partial^2 f/\partial c^2$ **is to first approximation a linearly decreasing function of temperature (becoming increasingly negative deeper inside the spinodal).**
- **As** $\partial^2 f/\partial c^2$ **becomes more negative, the wavelength of the spinodal structure gets smaller.**