

## Last time: Particle coarsening.—II

### Elements of mean-field theory for DCC

- Growth rate of a particular particle of radius  $R_i$  from supersaturated solution

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- The particle-size distribution function  $f(r, t)$  and its associated continuity equation

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- Key result (1): Steady-state (normalized) particle-size distribution function

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- Key result (2): Functional dependence of mean particle size  $\langle R \rangle$  on time

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### Complications of real systems

- Nonzero volume fraction; particle–particle interactions

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- Coherency stresses

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- Applied stresses

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Experimental study of coarsening in semi-solid Pb–Sn alloys (Hardy and Voorhees 1988)

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## Today: Phase Transformations: Overview

Metastability, instability, and mechanisms

First-order and second-order transitions

Free energy functions; conserved and nonconserved variables

Spinodal decomposition—I.

- Diffusion within the spinodal

## 3.21 Spring 2001: Lecture 27

### Phase Transformations: Overview

#### Metastability, instability, and mechanisms

A phase transformation can occur when a system has an accessible state of lower free energy. The *mechanism* of the transformation is critically dependent on whether the starting state is metastable or unstable.

An *unstable* system can transform by making changes that are *small in degree but large in extent*. Such situations lead to mechanisms that are called *continuous transformations*. The main categories of continuous transformations in materials are *spinodal decomposition* and *continuous ordering*.

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A *metastable* system can transform by making changes that are *large in degree but small in extent*. Such situations require *nucleation* of the new phase. After nucleation takes place, a new particle can grow until it either impinges with another particle, or supersaturation of the surrounding material is depleted.

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#### First-order and second-order transitions

Ehrenfest proposed a useful scheme for classification of phase transformations based on discontinuities in derivatives of the free energy function  $F$  that are characteristic of the transformation. Simply put, the *order* of a phase transformation is the lowest order of the derivative of  $F$  that shows a discontinuity.

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Examples: melting; ordering in  $\beta$  brass

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### Decomposition into Phases: Conserved Fields

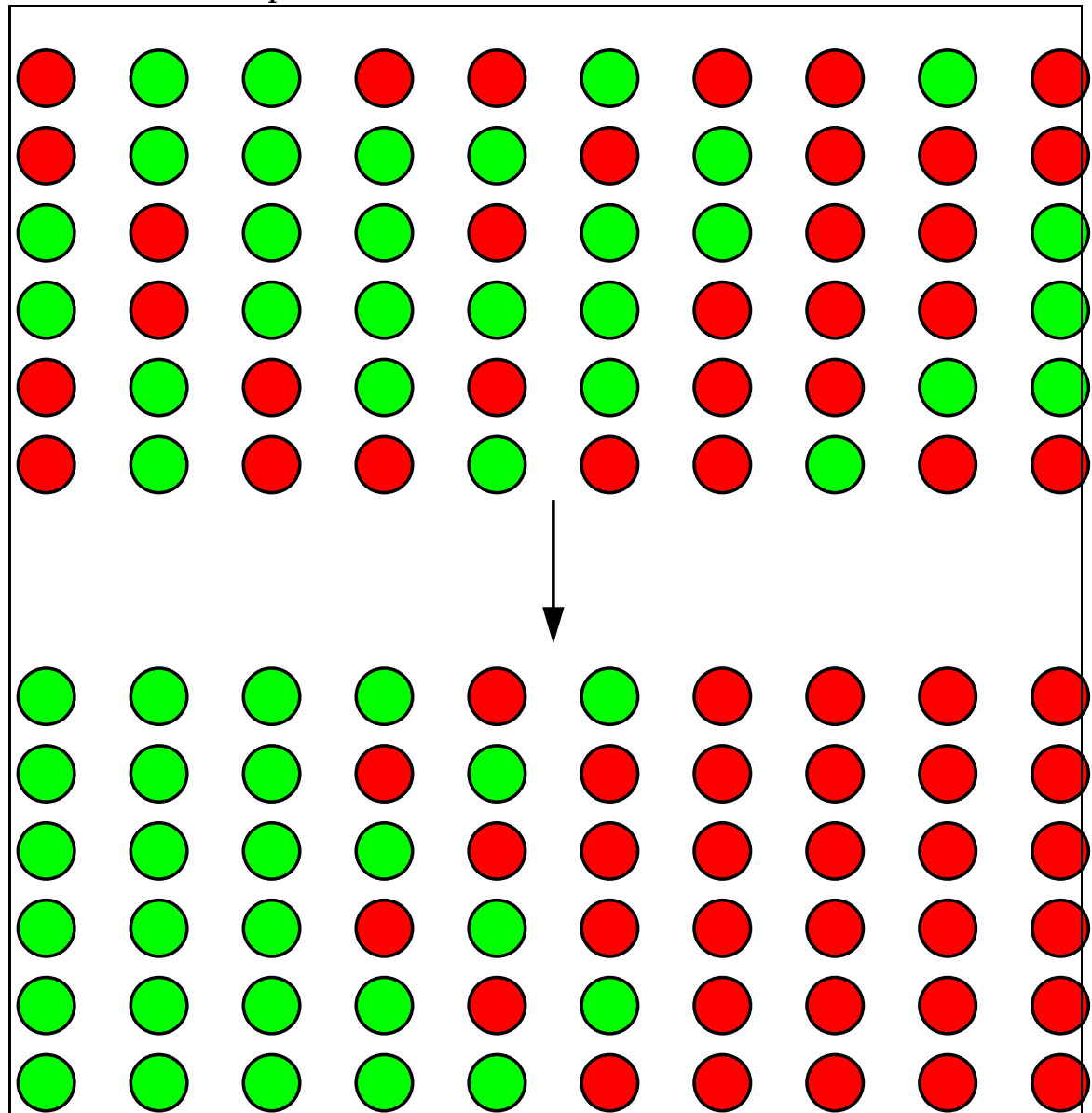


Figure 27-1: Decomposition requires long-rang diffusion. Such a transformation requires flux of a conserved field, like composition  $c(x)$ , which has an integral that is conserved for a closed system.

### Order-Disorder: Nonconserved Fields

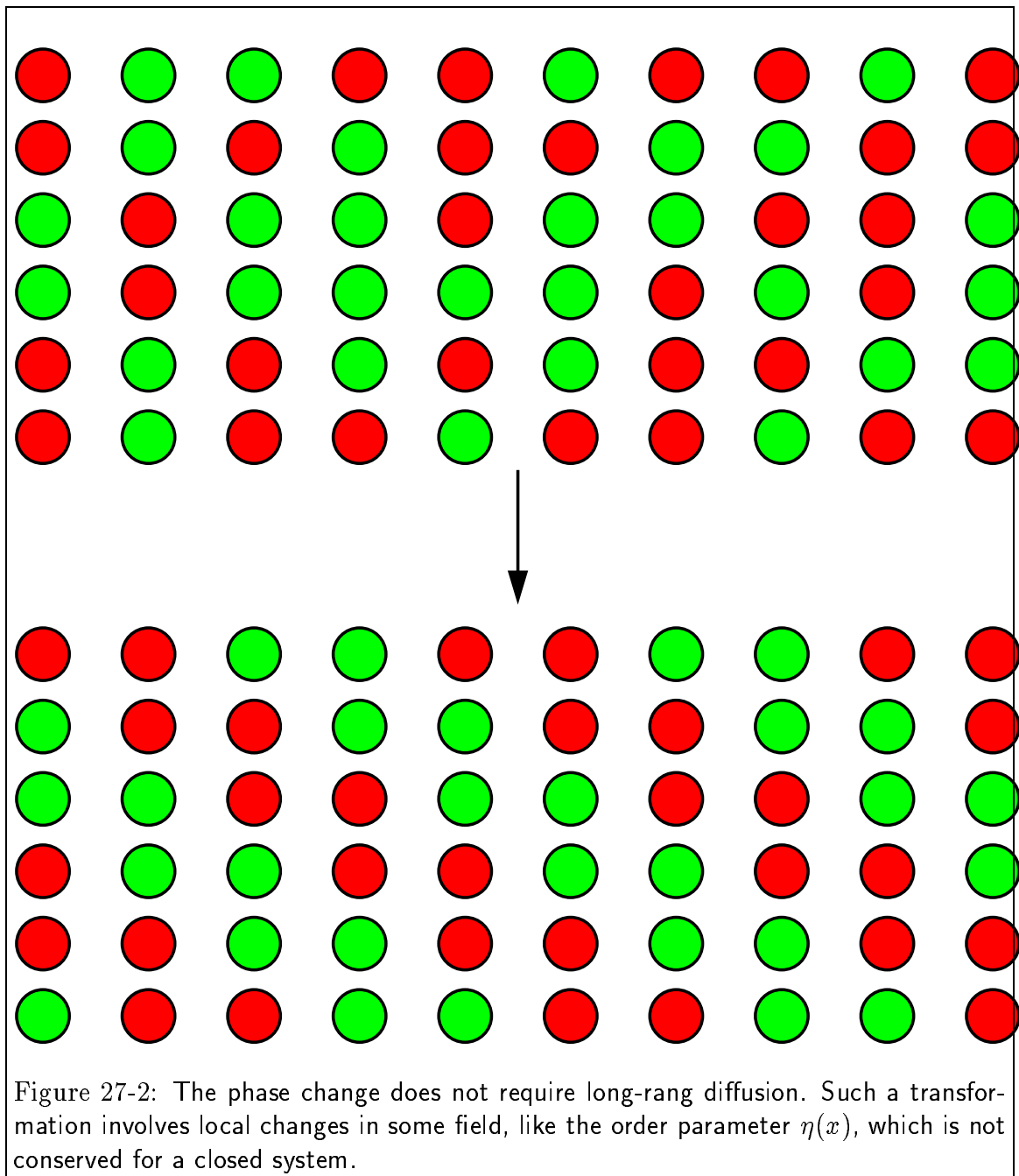


Figure 27-2: The phase change does not require long-rang diffusion. Such a transformation involves local changes in some field, like the order parameter  $\eta(x)$ , which is not conserved for a closed system.

## Order Parameters and Phase Transformations

Consider a simple one component phase transformation:

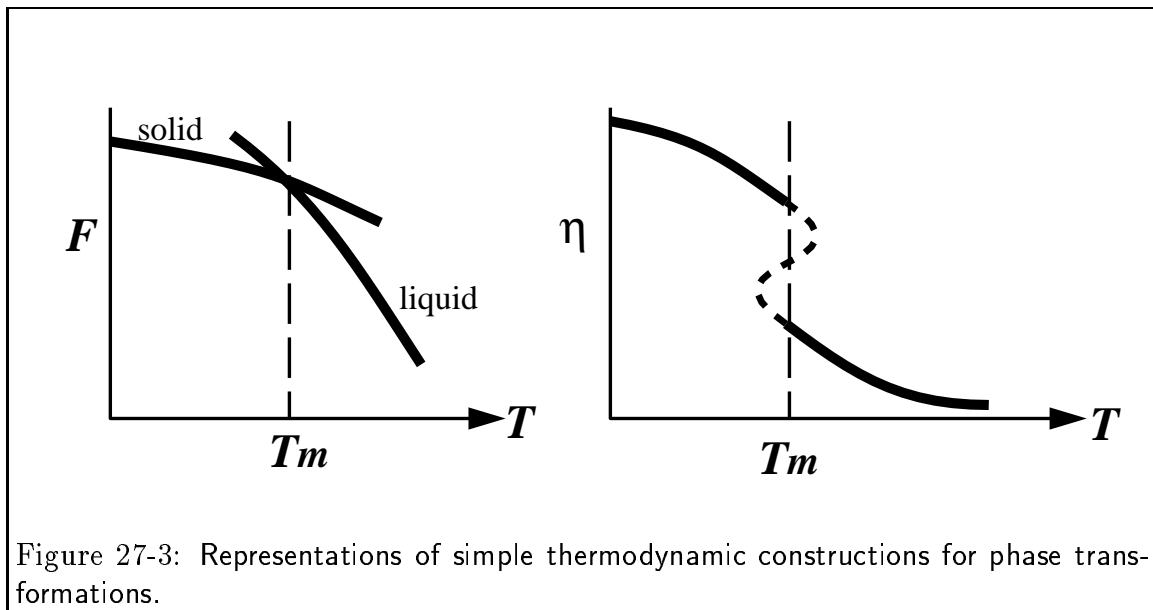


Figure 27-3: Representations of simple thermodynamic constructions for phase transformations.

We can express the transformation near the transition as a Landau expansion

$$F(T, \eta) = a_0(T) + a_1(T)\eta + a_2(T)\eta^2 + \dots \quad (27-1)$$

where  $\eta$  might be some measure of a “hidden parameter” such as the diffuseness of a peak in the atomic radial-distribution function.

The equilibrium value of  $F$  is given by

$$\frac{\partial F}{\partial \eta} = 0 \quad (27-2)$$

so the equilibrium free energy is given by  $F(T, \eta(T))$ . Whether the phase transition is first-order or second-order will depend on the relative magnitude of the coefficients of the Landau expansion.

We will use functions like  $F(T, \eta)$  to follow evolution towards equilibrium values  $F(T, \eta(T))$ .

### **Spinodal decomposition**

The chemical spinodal and “uphill diffusion”

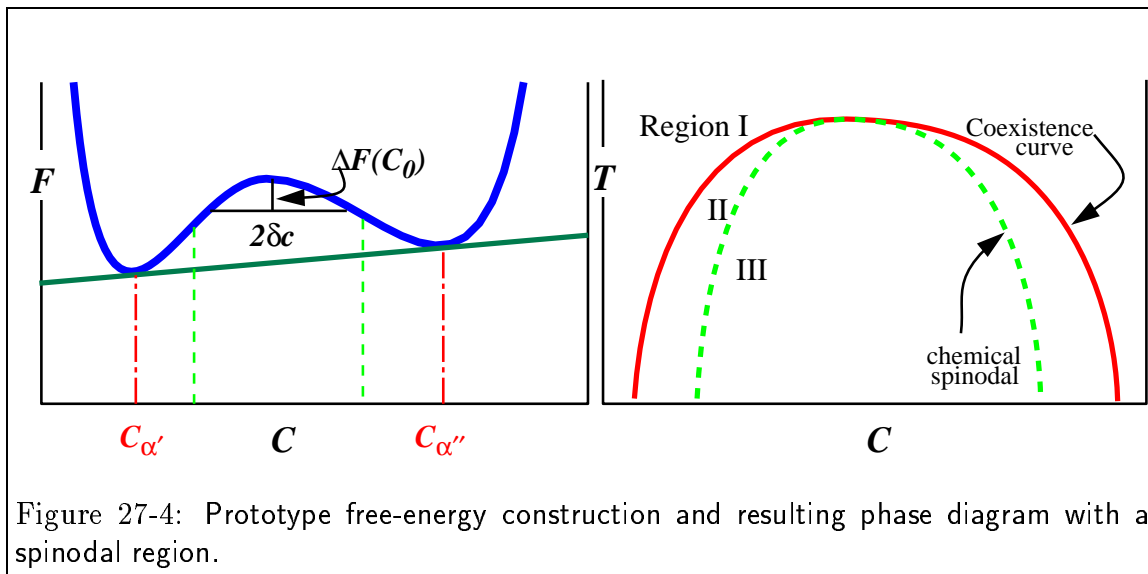
Recall that

$$\tilde{D} = (cD_A^* + (1-c)D_B^*)\left(1 + \frac{\partial \log \gamma}{\partial \log c}\right) = (cD_A^* + (1-c)D_B^*)\frac{c}{RT} \frac{\partial \mu_A}{\partial c} \quad (27-3)$$

Note that since,  $\mu \equiv \frac{\partial \bar{F}}{\partial c}$ , that the diffusivity has the same sign as the second derivative of the free energy:

$$\tilde{D} \propto \frac{\partial^2 \bar{F}}{\partial c^2} \quad (27-4)$$

Consider the following free-energy curve and resulting phase diagram:



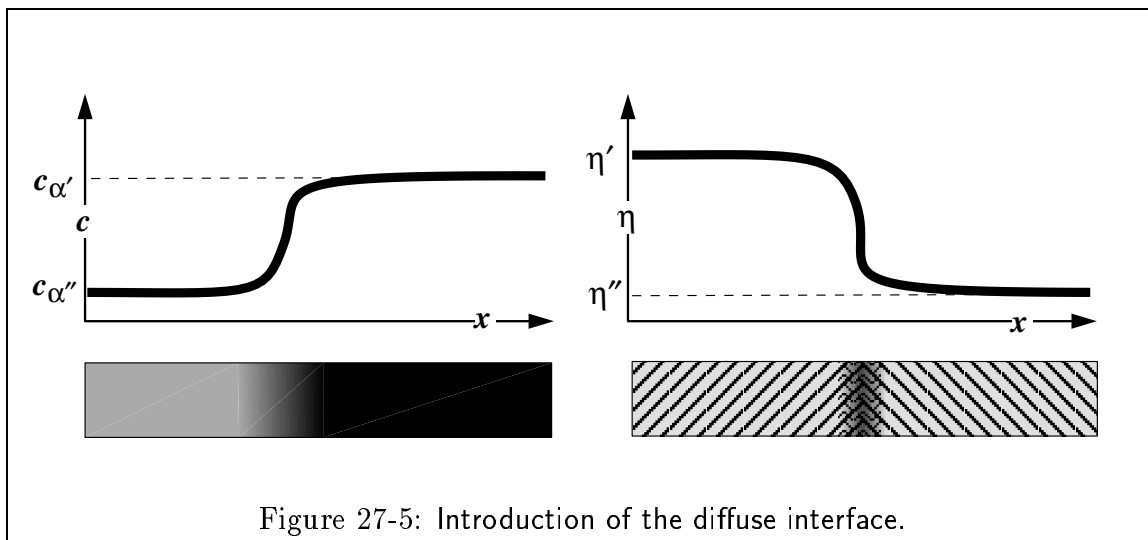
In region III,  $\tilde{D} < 0$ , how does the diffusion equation behave when  $\tilde{D} < 0$ ? Recall that for initial conditions  $c(x, t = 0) = A(t = 0) \sin \frac{2\pi i x}{\lambda}$  the diffusion equation has solution:

$$A(t) = A(0)e^{-\tilde{D}(\frac{2\pi i x}{\lambda})^2 t} \tag{27-5}$$

This will be very badly behaved for small wavelengths and give no end of trouble. It is ill-posed.

### Gradient Energy

How to fix this problem and calculate a governing equation inside the spinodal region?  
 Consider the following profile or variation in field:



What kind of penalties can be imposed that “mimic” surface energy?

Should the penalty depend on the whether the field is increasing left-to-right or increasing right-to-left?

For inhomogenous fields, expand the free energy about its homogenous value:

$$f(\vec{x}) = f_{homog}(c(\vec{x})) + \frac{K_c}{2} \nabla c \cdot \nabla c \tag{27-6}$$

$K$  is the gradient energy coefficient, it introduces surface energy into the free energy and will “regularize” the diffusion equation within (and applies outside as well) the spinodal.

For one-dimensional variations, the free energy density is:

$$f(x) = f_{homog}(c(x)) + \frac{K_c}{2} \left( \frac{\partial c}{\partial x} \right)^2 \quad (27-7)$$

### Theory of diffuse interfaces