Computational Nanoscience

NSE C242 & Phys C203

Spring, 2008

Lecture 23:

Morphological Evolution via Phase Field Methods

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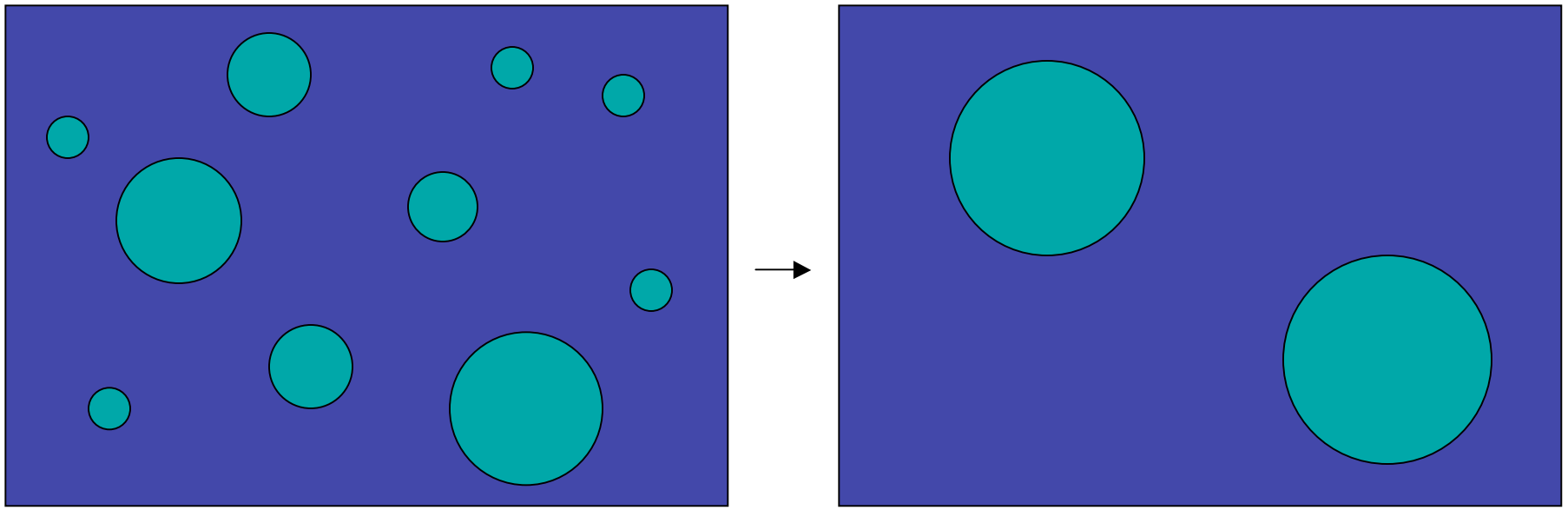
Introduction to Phase-Field Methods

- Phase field methods are a class of relatively new techniques (~20 years) for studying a variety of phenomena:
  - Phase transitions: solid-solid, solidification
  - Thin-Film growth
  - Coarsening/Ostwald Ripening processes
- Systems with multiple phases are described by the introduction of new variables ϕ, which are similar to order parameters
  - ϕ is a constant ($\phi = 0$ or $\phi = 1$, etc.) in each bulk phase
  - ϕ varies smoothly between the interface region between the phases
  - Key: rather than a sharp interface that needs to be tracked, there is a smooth transition region
- Well-suited for morphological evolutions described by nonlinear PDE's, which are solved numerically

Pre-Phase Field Modeling

Examples - Ostwald Ripening



Ostwald Ripening: large particles grow at the expense of small ones, driven by a reduction in interfacial energy

Diffusional mass transfer from regions of high to regions of low curvature

Develop a set of equations governing the evolution of the particle size distribution.

Time evolution shows a reduction in particle density and an increase in average particle size <R>

Useful for, e.g., size of precipitates in precipitation hardening, growth of nanocrystals, etc.

Examples - Ostwald Ripening

- Classical model of Ostwald Ripening is the Lifshitz-Slyozov and Wagner (LSW) approach
- Modeled the evolution of infinitely-spaced, spherical particles in a matrix
  - i.e., limit of coarsening in a zero volume fraction limit
- Found a self-similar solution as $t \rightarrow \infty$, which we call the asymptotic limit
  - Particle size distribution (PSD) is time-invariant when scaled by the time-dependent average radius

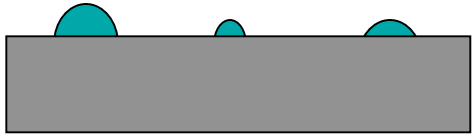
$$\langle R(t) \rangle^3 - \langle R(0) \rangle^3 = K_{LSW} t$$

- Limitations: low volume fraction limit, spherical non-touching particles, mass transport by diffusion only, no interfacial anisotropy, etc.

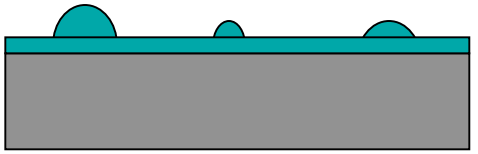
Examples - Thin Film Growth

- In lattice-mismatched heteroepitaxy, we often classify the types of thin-film growth into three categories
- The type of growth that is observed for a given system depends on the interplay between the interfacial energies and the strain energy due to lattice mismatch

Frank-van der Merwe
(layer by layer)



Volmer-Weber
(island formation)



Stranski-Krastanov

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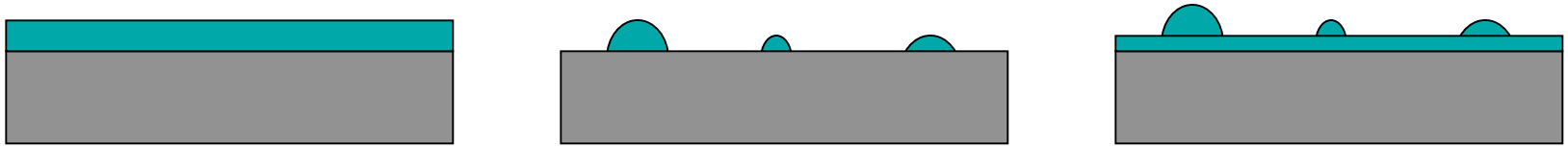

Frank-van der Merwe
(layer by layer)

Volmer-Weber
(island formation)

Stranski-Krastanov

Occurs for systems where wetting occurs (low substrate-film and film-surface energy, high substrate-surface energy) with low lattice mismatch strain

Examples - Thin Film Growth

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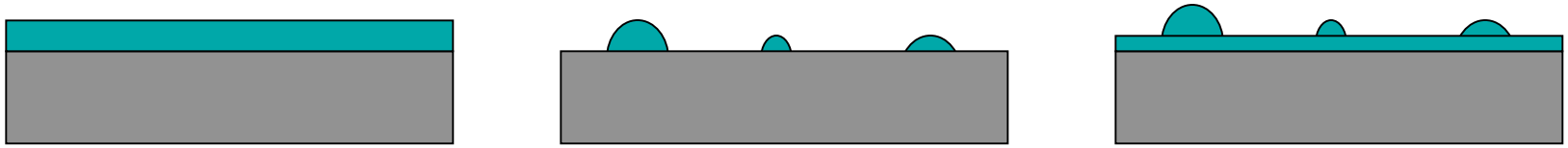

Frank-van der Merwe
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Stranski-Krastanov

In non-wetting systems (large substrate-film energy, low substrate-surface energy) results in island formation

Examples - Thin Film Growth

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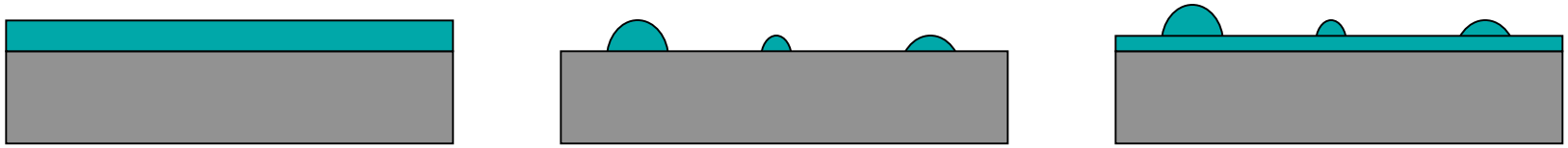


Frank-van der Merwe
(layer by layer)

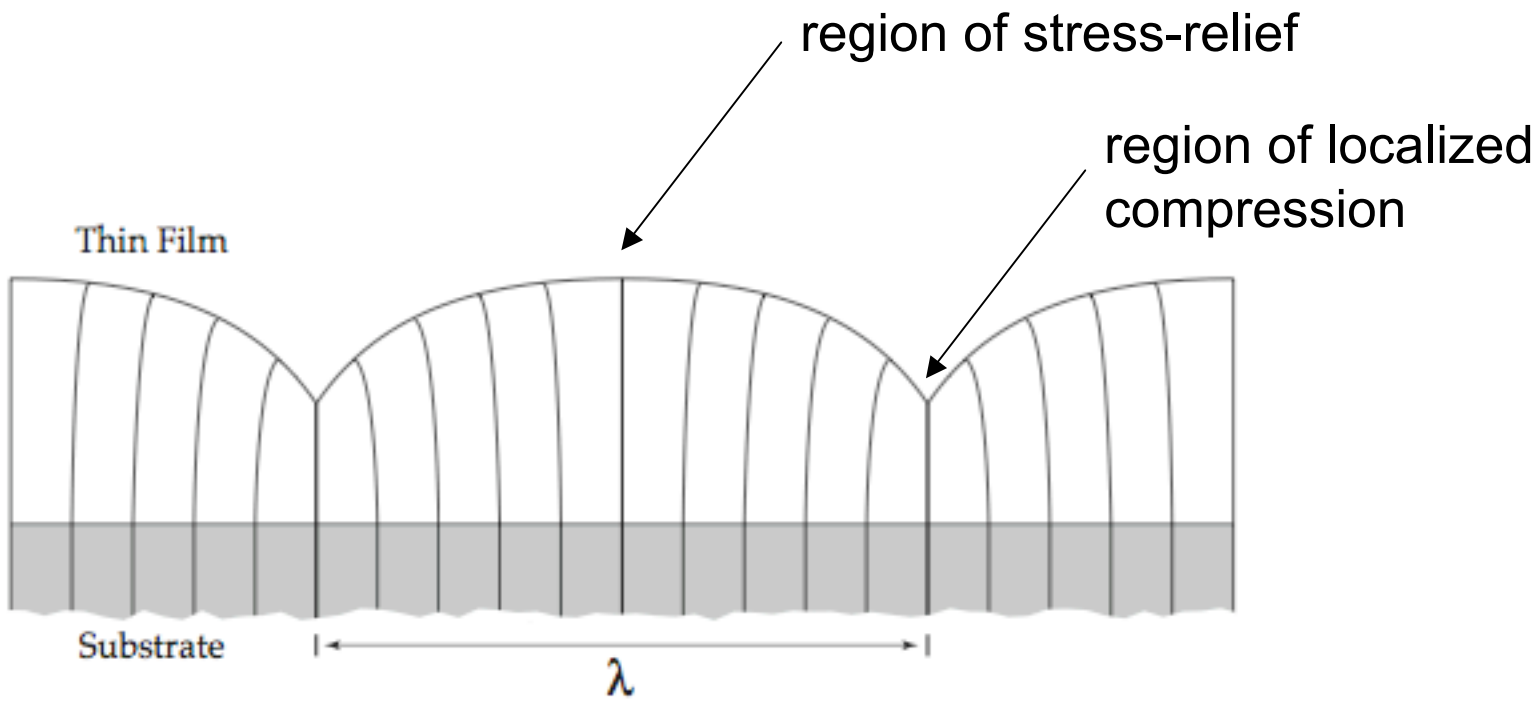
Volmer-Weber
(island formation)

Stranski-Krastanov

In wetting systems (low substrate-film energy, high substrate-surface energy) for which the lattice mismatch strain is high

Examples - Thin Film Growth

- In SK growth, a morphological instability occurs beyond some critical thickness, resulting in island growth - “surface roughening”



After Eggleston, 2001.

overall effect of distortion: relieve some strain energy

Examples - Thin Film Growth

- The critical thickness at which “surface roughening” occurs depends on energetic competition:
  - Roughening increases the surface area and hence the surface energy
  - Roughening decreases the strain energy
- Undulations of the surface occur by migration of surface atoms driven by gradients in chemical potential … hence the instability
- Roughening is usually described by a stability analysis

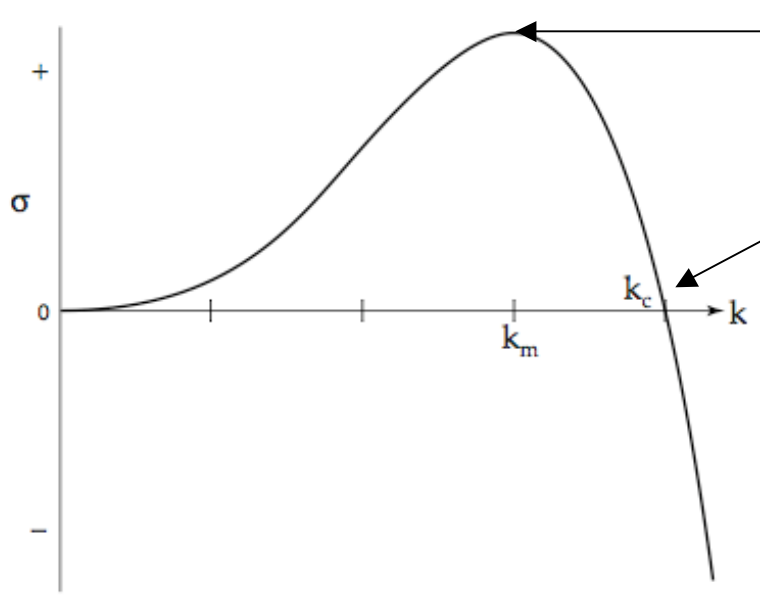
break roughening profile down into fourier components - sum of waves of different amplitudes

stability: will a given wave grow or decay? If it grows, the surface is unstable with respect to that mode. If it decays, surface is stable.

- The misfit-induced elastic strain is destabilizing for all wavelengths. However, the increase in surface energy stabilizes the small wavelength distortions … and there is a critical wavelength between these two regions

Examples - Thin Film Growth

- Two types of models:
  - Energetic: predict the stability of various wavelengths
  - Kinetic: consider the “dispersion relation”, or the relative growth rates for different wavelengths
- Kinetic models must consider mass-transport mechanisms (surface diffusion, bulk diffusion, evaporation/condensation, etc)
- Asaro-Tiller-Grinfeld: most famous kinetic model



Fastest growing mode

critical wavenumber

ATG instability for surface-diffusion dominated systems.

After Eggleston, 2001.

Classical Approach

Sharp Interface Models

Shape changes of the interface governed by an evolution equation, which gives the velocity of the interface normal to itself

$$V_n = \Omega\left(\vec{F} \bullet \vec{n} - \vec{\nabla}_s \bullet \vec{J}\right)$$

velocity normal to surface

deposition flux

surface gradient

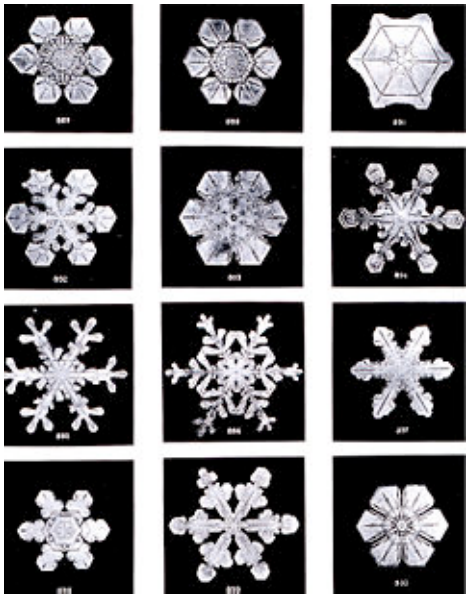
flux along surface

- track explicitly the interface
- can be tricky for growth: instabilities are prevalent
- alright for 1D, difficult for more complex microstructures

$$\vec{J} = -M\nabla_s\mu$$ M = mobility

$$\mu = \mu_o + \Omega\left(\frac{1}{2}S_{ijkl}T_{ij}T_{kl} + \gamma K\right)$$

Some Motivation



Snowflakes, Wilson Bentley, circa 1902.

might want to go beyond linear stability analysis?

Going Beyond

- Coarsening models are based on mean-field approaches at the low volume fraction limit for spherical, isotropic, non-touching particles in which diffusion is the dominant mass-transport scheme
- Thin film growth models are based on linear stability analysis - predict evolution at the onset of the instability
- We want a model for all of morphological evolution: nucleation, coarsening, coalesence that can include strain, anisotropy, etc.
- May not always be most natural to front track the interface explicitly
- Requires the solution of non-linear PDE's

The Phase Field Approach

Phase Field Basics

The phase field method is an extension of the diffuse interface models of Ginzburg and Landau, Cahn and Hilliard, and Cahn and Allen (~ 45 years old)

Basic idea: introduce a variable ϕ that is constant in bulk phases and varies smoothly across the interface

The free energy is a functional of ϕ:

$$F = \int \left[f(\phi) + \frac{1}{2}\varepsilon^2 |\nabla\phi|^2 \right] dV$$

Helmholtz free energy density

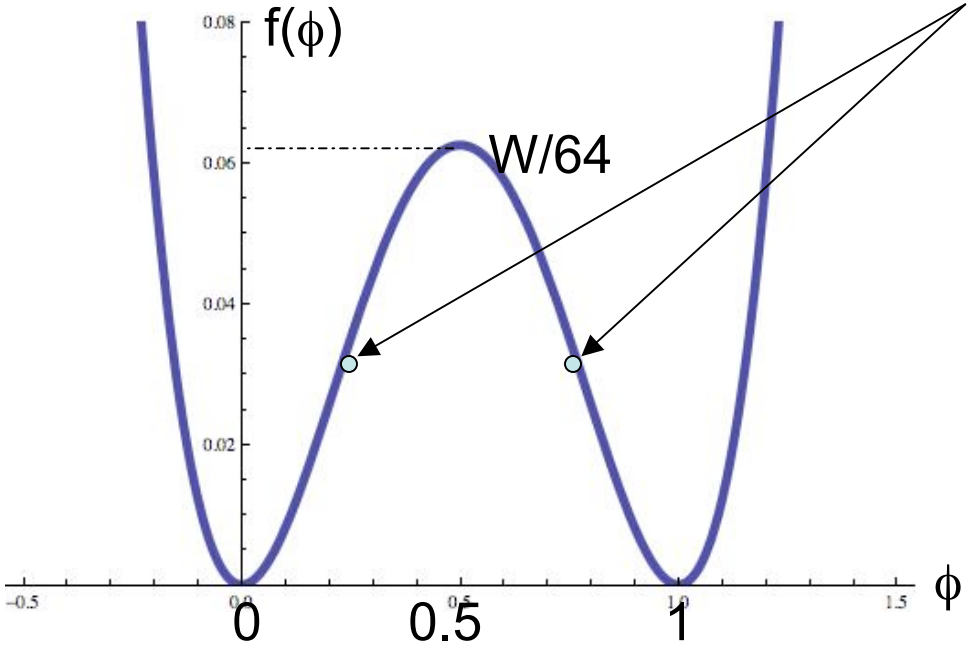
Interfacial energy terms

Phase Field Approach

The free energy is a functional of ϕ:

$$F = \int \left[f(\phi) + \frac{1}{2}\varepsilon^2 |\nabla\phi|^2 \right] dV$$

For example, $\phi = 0$ and $\phi = 1$ can correspond to two phases in equilibrium



spinodel points

f(0) = f(1) : two-phase equilibrium

at $\phi = 0$ and $\phi = 1$:

$$\frac{\partial f}{\partial \phi} = 0 \quad \text{and} \quad \frac{\partial^2 f}{\partial \phi^2} > 0$$

e.g., $f(\phi) = \frac{1}{4} W^2 \phi^2 (1-\varphi)^2$

Cahn-Hilliard Evolution Equation

Imposing the constraint that the free energy functional F decrease monotonically in time for conserved order parameter results in the Cahn-Hilliard evolution equation:

$$\frac{\partial \phi}{\partial t} = \vec{\nabla} \bullet \left(M(\varphi) \vec{\nabla} \frac{\delta F}{\delta \phi} \right)$$

mobility

functional derivative

$$\frac{\delta F}{\delta \phi} = \frac{\partial f}{\partial \phi} - \varepsilon^2 \nabla^2 \phi$$

For example, for the double well potential I described earlier and for constant M (uniform bulk diffusion), the Cahn-Hilliard evolution equation looks like:

$$\frac{\partial \phi}{\partial t} = M \nabla^2 \left\{ \frac{1}{2} W \left(2\phi^3 - 3\phi^2 + \varphi \right) - \varepsilon^2 \nabla^2 \phi \right\}$$

Basic idea: evolve the C-H equations in time. We can see phenomena such as coalescence, amplitude of decay/growth of waves, etc.

Cahn-Hilliard Evolution Equation

Generally, the C-H equation is nonlinear and we must use a numerical approach. Initially, finite difference schemes were often used.

While not particularly efficient, they were more stable to discontinuities that can arise from, e.g., highly anistropic interface energies, stress fields, etc.

Nowadays, more sophisticated approaches do exist - semi-implicit methods and adaptive mesh, for instance.

For example, for the double well potential I described earlier and for constant M (uniform bulk diffusion), the Cahn-Hilliard evolution equation looks like:

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biharmonic!

Here is a steady state solution to this equation in one-dimension:

$$\phi = \frac{1}{2}\left[1 - \tanh\left(\frac{x}{2\delta}\right)\right] \text{ with } \delta = \text{interface thickness}$$

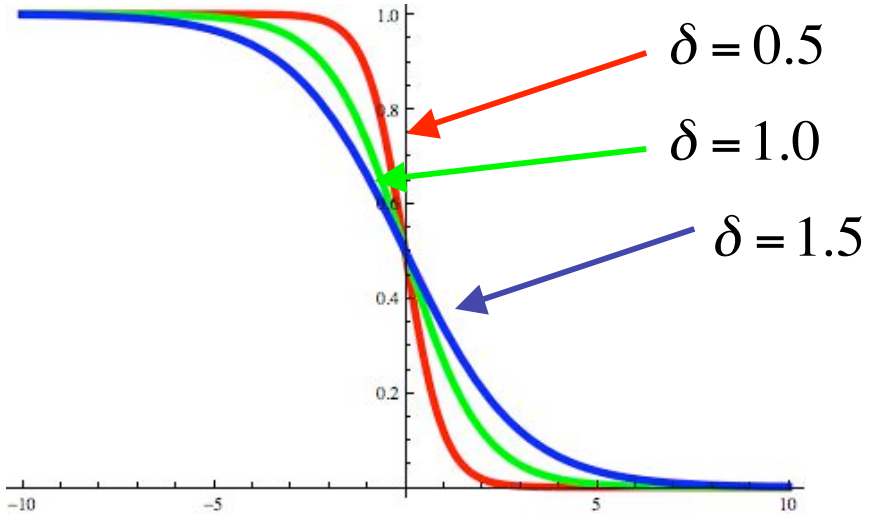
The Interfacial Solution

$$\phi = \frac{1}{2}\left[1 - \tanh\left(\frac{x}{2\delta}\right)\right] \text{ with } \delta = \text{interface thickness} \quad ; \quad \delta = \varepsilon\sqrt{\frac{2}{W}}$$

Recall our free energy functional: $F = \int \left[f(\phi) + \frac{1}{2}\varepsilon^2 |\nabla\phi|^2 \right] d\Omega$

δ is made smaller (sharpened) because f is non-zero for 0<ϕ<1 (i.e., due to W)

δ is made wider in order to reduce the interface energy from $\nabla\phi$



Summary

Phase field method is a diffuse interface approach to modeling the microstructural and morphological evolution of a multi-phase system

Microstructural evolution refers to the compositional/structural inhomogeneities that arise in order to reduce the total free energy

Can include phases and their interfaces, grains, domains (magnetic, etc), electrostatic interactions, strain effects

We use a numerical approach to evolve the (usually nonlinear) Cahn-Hilliard and Cahn-Allen (time-dependent Ginzburg Landau) equations in time.

Phase Field, More Generalized

We can generalize the free energy functional to contain many variables (conserved and non-conserved), long-range interactions, etc. Anisotropy, etc. can be accomodated

$$F = \int \left[f(c_1, c_2, \ldots, \eta_1, \eta_2, \ldots) + \sum \alpha_i (\nabla c_i)^2 + \sum\sum\sum \beta_{ij} \nabla_i \eta_k \nabla_j \eta_k \right] d^3 r + \iint G(r - r') d^3 r d^3 r'$$

free energy

Interface energy for conserved quantities

Interface energy for non-conserved quantities

Non-local part, long-range interactions (elastic, dipole-dipole, etc)

Some Cool Examples

Examples of Solidification

Movies showing solidification, dendritic growth, etc:
http://mse.mcmaster.ca/faculty/provatas/solid.html

finite element approach using an adaptive grid!

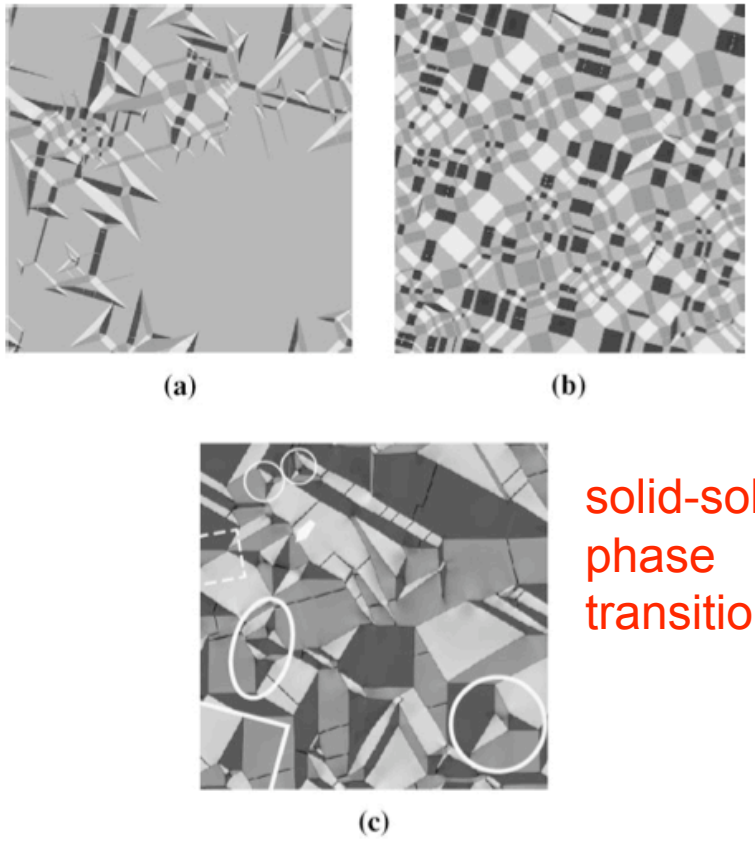
solidification in binary alloys!

More Examples

These examples are from L.-Q. Chen, “Phase Field Models for Microstructure Evolution”, Annu. Rev. Mater. Res., 2002

solidification

Figure 1 A snapshot of a three-dimensional dendrite in pure Ni with a cubic interfacial energy anisotropy obtained from a phase-field simulation with thermal noises (72) (courtesy of A. Karma). The interfacial energy and mobility anisotropies were obtained from atomistic simulations, and they are matched to the kinetic coefficients in the phase-field model using a thin-interface analysis.



solid-solid phase transition

Figure 2 Morphologies of orthorhombic precipitates in a hexagonal matrix at three representative volume fractions obtained from two-dimensional phase-field simulations (along the basal plane of the hexagonal phase) (123). (*a*) 37% volume fraction; (*b*) 67% volume fraction; (*c*) 100% volume fraction, i.e., single-phase orthorhombic domain structure. In (*a*) and (*b*), four different shades of gray correspond to variant 1, parent phase, variant 2, and variant 3, respectively, with decreasing brightness; (*c*) the three variants are presented by different gray levels.

More Examples

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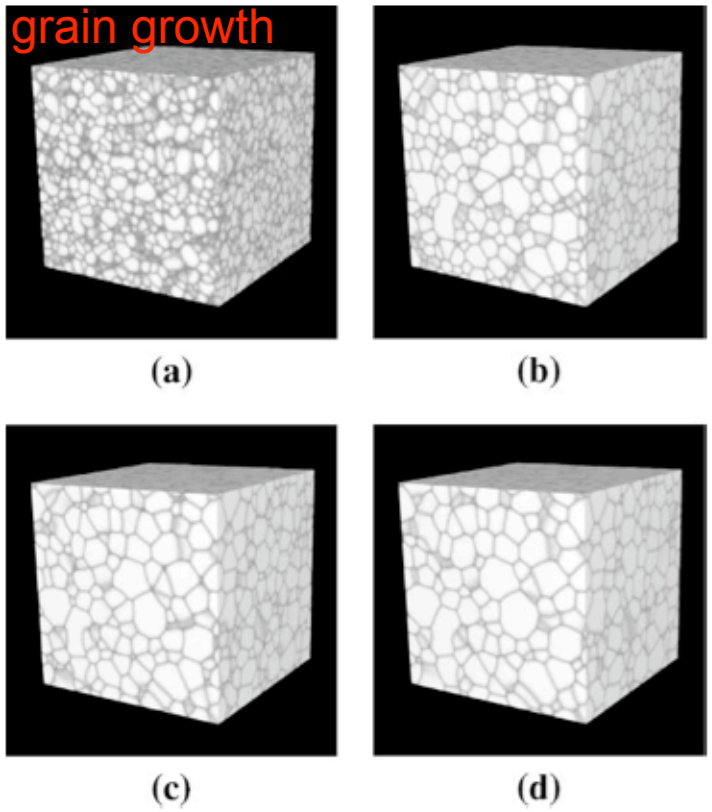

Figure 3 A typical grain evolution process obtained from a three-dimensional phase-field simulation of grain growth assuming isotropic grain boundary energy and isotropic boundary mobility (146). Twenty-five order parameters were used, and an orientation reassignment algorithm was implemented. (*a*) $t^* = 250$; (*b*) $t^* = 1000$; (*c*) $t^* = 1500$; (*d*) $t^* = 2010$, where t^* is the time in reduced unit.

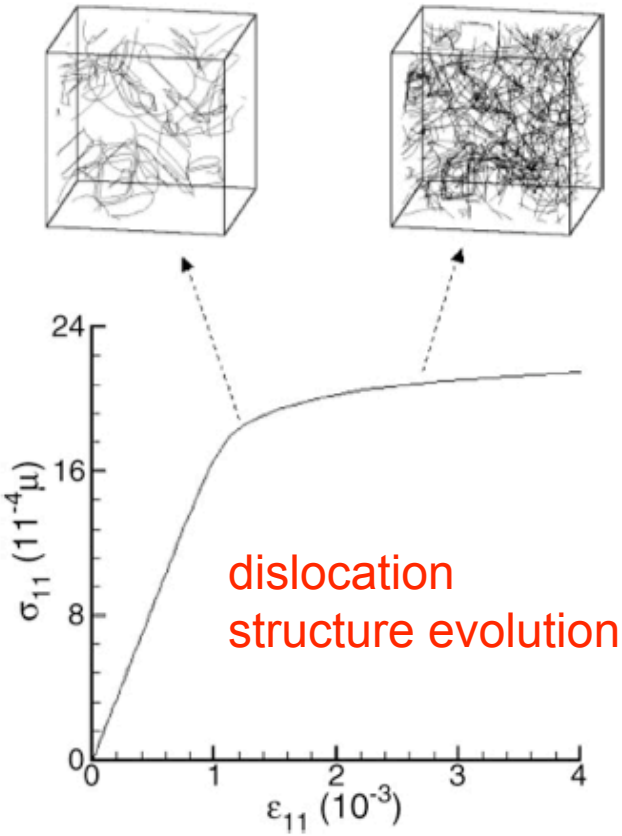

Figure 5 The stress–strain curve obtained from a three-dimensional phase-field simulation of an FCC crystal under a uniaxial loading (σ_{11}) (29, 175, 176). Plastic behavior is reproduced, and the dislocation multiplication with increasing strain (ε_{11}) is illustrated by the three-dimensional dislocation structures corresponding to different strain stages. μ is the shear modulus of the crystal (courtesy of A. Khachaturyan).