Phase Field Crystals

Binary Alloy Model and Solute Drag

Michael Greenwood et al...





So....Why PFC?

1. To develop better Phase Field Models for larger scale simulation (Amplitude Space)



2. To Simulate Diffusive time Problems at the atomic level (defects, nanocrystals, thin films)

Or....

Phase Fields can't easily capture the physics and Molecular Dynamics is too slow

1 - Better Phase Field Models for larger scale simulation

Distill "new" phase field models from PFC model.



[B. Athreya, N. Goldenfeld, J. Dantzig, *M. Greenwood,* N. Provatas, Phys. Rev. E (2007)]

2 - To simulate diffusive time problems at the atomic level (defects, nanocrystals, thin films) Dislocation melting - BCC

Grain boundaries are naturally made up of arrays of defects in low angle tilts.

Elasticity also emerges and dislocations glide under applied strains.

Dislocation Glide



Stefanovic 2007, Berry 2006



Berry 2008

Conceptualizing a Phase Field Crystal

Probability is coarse grained over time:

The phase field crystal model represents lattice positions by a probability density field. These probability structures can be viewed as a coarse graining of the atomic vibrations over a time scale greater than the atomic vibration time and less than the diffusive time scale of the atoms.

$\rho_m(r)$ occord occord

Instantaneous Atomic Field



Probability Number Density Field

Swift-Hohenberg Model and Periodic Structures

$$F = \int d\vec{r} \left(\phi \mathbf{G} \, \phi + \frac{\phi^4}{4} \right) \quad \text{Double Well}$$

Originally developed to study Rayleigh-Bénard convection





$$\Delta F = \frac{\Delta \mathbf{F}}{k_B T} = \frac{1}{k_B T} (\Delta F_{ID} + \Delta F_{Ext} + \Delta F_{ex})$$

Interacting Energy
External Energy Source
Non Interacting Energy

Expansion of CDFT energy

$$\Delta F_{ID} = \int dr \left[\rho \ln\left(\frac{\rho}{\rho_r}\right) - \delta\rho \right] \cong \int dr \left[\frac{n^2}{2} - \xi \frac{n^3}{6} + \chi \frac{n^4}{12}\right]$$



The density is normalized relative to a reference density

$$n = \frac{\rho - \rho_r}{\rho_r}$$

Particle Correlations

The correlative energy is truncated in an expansion of particle correlations. In the PFC model this expansion is truncated to 2nd order. (ie. Only two particle correlations are considered.)

$$F_{Corr} = \int dr \left[-\frac{n}{2} \int_{space} (\rho_r C_2(|r-r|)) n dr \right]$$

The simplest form for a two particle correlation function that produces beriodic structures
$$C_2(k) = -(r + (1 - k^2)^2)$$







The structure factor is constructed by summing over the fourier transforms of the gaussian peaks at their lattice positions. $1 \sigma^2 \vec{k}^2$

$$\rho_j(k) = \exp(i\vec{k}r_j)e^{-\frac{1}{2}(2\pi)^2}$$

The direct correlation function:

$$C_2(\vec{k}) = 1 - \frac{1}{S(\vec{k})}$$





The reciprocal lattice for a square arrangement is also a square lattice. Using the square lattice Kernel produces a square lattice structure but is limited to a particular orientation.







Spectral Bragg Peaks and Relation to Correlation Function

$$\Delta F = \Delta F_{ID} - \int dr \left[\frac{n}{2} \int_{space} dr' \left(\rho_r C_2(|r-r'|)n' \right) \right]$$



Non Interacting Energy



Temperature and Debye-Waller Effect

Temperature enters the model through the correlation peak heights. The heights of the peaks are modulated by a Debye-Waller effect.

Higher frequency peaks are hit harder at higher temperatures.







Liquid-BCC-FCC Phase Diagram For a PURE material

Phase diagram construction is constructed by double tangent construction from the energy curves for liquid, FCC and BCC states.





Greenwood et al, PRL2010

Linear Elastic Coefficients

Linear Elastic coefficients can be calculated by the second derivative of the free energy for small strains

$$\Delta F \cong F_o + m_1 \delta^2 + \dots$$
$$\Delta F \cong F_o + m_2 \delta^2 + \dots$$
$$\Delta F \cong F_o + m_3 \delta^2 + \dots$$





Energy is proportional to the convolution of the correlation function value with the mode the density field exists at.

$$\Delta F_{ex} \approx \hat{C}_2(k)\hat{n}(k)$$

Greenwood et al, PRE2011

Multiple Components - Binary Model

Free Energy is written in terms of the sum of the individual energies and interacting energies between the two components

$$\Delta F = \frac{1}{\rho_l} \int \Delta F_{AA} + \Delta F_{BB} + \Delta F_{AB}$$

The individual energies can be written as the pure model and correspondingly dimensionalized

$$\Delta F_{ii} = \rho_i \ln \left(\frac{\rho_i}{\rho_i^o} \right) - (\rho_i - \rho_i^o) - \frac{1}{2} (\rho_i - \rho_i^o) \int C_2^{ii} (|r - r'|) (\rho_i - \rho_i^o)$$

$$\approx \frac{n_i^2}{2} - \xi \frac{n_i^3}{6} + \chi \frac{n_i^4}{12} - \frac{1}{2} n_i \int C_2^{ii} (|r - r'|) n'_i$$

The interaction term contains information about inter-particle correlations and mixing energies.

Let's leave the math of this out

Simplified Binary Model

Instead, lets make some definitions:

Fractional composition:
$$c = \frac{\rho_B}{\rho_A + \rho_B}$$
 Dimensionless
Occupancy Probability: $n = \frac{\rho_A + \rho_B}{\rho_A^o + \rho_B^o} - 1$

In addition, we assume that the composition varies on length scales longer than the density.

Binary Model :
$$\Delta F = \int \frac{n^2}{2} - \xi \frac{n^3}{6} + \chi \frac{n^4}{12} - \frac{1}{2} n \int C_{eff} (|r - r'|) n' + (n+1) \Delta F_{mix} + \omega |\vec{\nabla}c|^2$$

Pure Model : $\Delta F = \int \frac{n^2}{2} - \xi \frac{n^3}{6} + \chi \frac{n^4}{12} - \frac{1}{2} n \int C_2 (|r - r'|) n'$

Mixing Energy :

rgy:

$$\Delta F_{mix} = c \ln\left(\frac{c}{c_o}\right) + (1-c) \ln\left(\frac{1-c}{1-c_o}\right)$$

Effective Correlation Function :

$$C_{eff}(|r-r'|) = X_1(c)C_2^{AA} + X_2(c)C_2^{BB}$$



Phase Diagrams

A number of factors Influence the phase diagram in this model.

Choice of interpolation functions : $X_1 X_2$

Elastic Moduli of the two phases :

Lattice Spacings and Structure :





Parameter Summary

$$\Delta F = \int \frac{n^2}{2} - \xi \frac{n^3}{6} + \chi \frac{n^4}{12} - \frac{1}{2} n \int C_{eff} (|r - r'|) n' + (n+1) \Delta F_{mix} + \omega |\vec{\nabla}c|^2$$



Two phase Lamella Growth – Eutectic

Solute saturation and short circuit diffusion ahead of the interface.
Growth rate decreases with increase in lamella spacing.



Blue (element A) – Square structure Red (element B) – Triangle structure

Lamella and triple junction structure

Surface energy due to crystalline symmetries naturally emerge from the model and lead to force balancing at the triple junctions between lamella and the liquid phases.



Composition segregation to Boundaries and Defects

Two crystals are misoriented with a uniform composition everywhere. Solute diffuses to the <u>defects and the interfaces</u>



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Increasing Elastic Anisotropy

Composition segregation to Boundaries and Defects

ncreasing Elastic Stiffness





Reciprocal lattice peaks of a square symmetry phase



Orientation biased kernel



Orientation Bias

Inserting an orientation bias in this fashion has a non-linear relationship with the resultant applied driving force. However at the low driving force values we want to study it is a roughly linear relationship.





Zener Pinning

Introduce a fictitious field which turns off one correlation function and turns on another.

Misorient two square lattices and drive one across the particle.

If the driving force is not great enough the lattice symmetries can trap the interface on the particle at a misorientation between the two lattices.

Solute Drag



interface and can influence the overall velocity of the interface. This is dependent upon the driving force and the ability of the solute to diffuse.

Solute Drag

At constant driving pressure the diffusion constant of the composition field slows the movement of the interface.



At different diffusivities the compositional profile (line) around the interface (dots) becomes asymmetrical due the driving pressure and the resistance to move by the solute.



Position



Composition Profile of Low Driving Force



Composition Profile of the stepwise motion of the interface

Solute diffuses across the interface until the interface can advance.





Summary

- Phase Field models can incorporate many solid state characteristics in the model. However, as the atomistic effects become increasingly dominant over the bulk properties it becomes difficult to construct phase field models.
- The PFC formalism can be used to either:
 - Construct new phase field models with some of the atomic information built in more naturally.
 - Simulate the atomic structures directly at a coarse grained probability level.
- We have shown how to systematically include additional Correlation Peaks to stabilize relevant metallurgical structures of interest, such as bcc, fcc, hcp and sc.
- In addition, the introduction of these peaks allows for a simple method to tune the anisotropic properties of the crystal structure.
- The model shows promise on being able to simulate solute drag for a variety of structurally different phases and for various misorientations.

fcc – bcc transformation

The domain is seeded with a stripe each of bcc and fcc and quenched into the fcc portion of the phase diagram.

