Phase field modeling of complex microstructure
I. Fundamentals

Anter El-Azab
School of Nuclear Engineering, School of Materials Engineering
Purdue University

CAMS Summer School on
University of Florida, Gainesville
May 19-24, 2013
Acknowledgements

- Karim Ahmed, Ph.D. student, CMSG, Purdue
- Dr Srujan Rokkam, Advanced Cooling Technologies, Inc.
- Prof Santosh Dubey, University of Petroleum and Energy Studies, India
- Prof Thomas Hochrainer, Bremen University, Germany
Acknowledgements

- Dr. Jim Belak, Lawrence Livermore National Laboratory (solidification example)
- Dr. Hui-Chia Yu, University of Michigan
- Professor Yunzhi Wang, Materials Science, Ohio State University
- Professor Marisol Koslowski, Mechanical Engineering, Purdue
- Professor Long-Qing Chen, Penn State University

Dr Jim Belak

Prof L-Q Chen

Prof Yunzhi Wang

Prof Marisol Koslowski

Dr Hui-Chia Yu
Objectives of this lecture

- This lecture covers the fundamentals and applications of phase field modeling in materials science.
- Phase field is a theory and simulation approach for micro chemical and microstructure evolution in materials.
- Fundamentals include basic concepts, governing equations, numerical methods and connection to atomic scale models.
- Applications include virtually all diffusional, phase transformation and interfacial dynamical processes in materials (i.e., chemical or compositional evolution and microstructure evolution). Applications include (but are not limited to): dislocation dynamics, solid state phase changes, solidification, grain growth and radiation effects.
Outline

Part I

➢ Basic Concepts
  – Introduction to microstructure and composition evolution in materials
  – Interfaces and diffuse interfaces in materials
  – Free energy of heterogeneous materials systems
  – Non-equilibrium thermodynamics and evolution
  – The phase field method, phase field equations and numerical solution

Part II:

➢ Two example problems
  – Grain growth
  – Void formation under irradiation

➢ A survey of applications
Why is phase field modeling important?

- Materials Science and Engineering is the science field that focuses on the structure and properties of materials.

- Structure of materials
  - *Atomic/molecular structure* (domain of all scientists → chemists, physicists, materials scientists, biologist, …)
  - *Mesoscale* (hierarchical) structure of materials (mostly the domain of materials scientists)

- Microstructure science is the part of materials science that focuses on understanding the hierarchical structure of materials and its influence on materials performance.
Why is phase field modeling important?

- Microstructure is important in two contexts:
  - Making materials (solidification, heat treatment, sintering, metal forming, atomic and molecular deposition, plasma spray, …)
  - Using materials (structural, chemical, physical, thermal, biological … applications)

- Microstructure changes during materials processing and utilization

- Because microstructure dictates properties and because we care to know properties all the time, we care about microstructure evolution.

- Phase field approach is currently the most commonly used modeling approach for microstructure evolution studies.
Microstructure science is mesoscale science

- In the context of modeling, the term *mesoscale* is often used to refer to the microstructure scale.
- And it implies models that capture details and the effects of microstructure and composition fields, or
  
  … *models that tackle materials heterogeneity.*
Outline

Part I

➢ Basic Concepts
  – Introduction to microstructure and composition evolution in materials
  – Interfaces and diffuse interfaces in materials
  – Free energy of heterogeneous materials systems
  – Non-equilibrium thermodynamics and evolution
  – The phase field method, phase field equations and numerical solution

Part II:

➢ Two example problems
  – Grain growth
  – Void formation under irradiation

➢ A survey of applications
Microstructure and heterogeneity of materials

- Grain structure of materials is the first example we encounter when we look closer into the hierarchical structure of materials.
Microstructure and heterogeneity of materials

- The feature we see are grain boundary as *interfaces* between *misoriented* single grains.
- Boundaries are associated with an *energy* penalty; a rise in the energy of the material.
- The material would prefer to turn itself into a single grain if possible, and, when possible, the material undergoes *transitions* to come to a more preferred state.
The term *misorientation* implies that there is some sort of a *long range order* in the material, which if interrupted (changed) the material forms domains separated by interfaces.

- The grain structure of the material is nothing but one example of such partitioning of materials by interfaces.
- Other types of interfaces include ferroelectric domain boundaries, ferromagnetic domain boundaries, order-disorder domain boundaries, etc.

- Interfaces appear in materials when they undergo phase transitions.
- Interfaces are deliberately introduced into materials when we make structure of dissimilar materials.
Domain: a region of the material in which polarization is the same;

Domain boundaries are thin regions over which the polarization direction changes

Ferroelectric domains and domain boundaries

Amorphous/crystalline ceria interfaces

Left: Sol-gel processed ceria.

Right: Fast ion induced amorphization
Microstructure and heterogeneity of materials

Oxide super-lattice structure (hetero structure) produced by OPA-MBE

Oxide quantum dots, Copper oxide on STO, contain interfaces between dissimilar materials

Interfaces appear in materials spontaneously during phase changes, such as in superalloys

Picture provided by Yunzhi Wang
Grain boundaries are **sharp interfaces**.

Tilt boundary and twist boundary
There is a step change of order and properties across the interface.

Ferro electric domain boundaries are **diffuse interfaces**

Gradual change in order and properties across the interfaces
Interfaces carry energy

- Interfaces have energy associated with them
  - grain boundary energy
  - surface energy
  - hetero-phase interface energy (soli-solid interface, solid-liquid interface)
  - domain boundary energy
- The energy of interfaces is often sensitive to chemical, mechanical or physical state of the interface.
What are transitions?

- A transition is a process by which the material changes its energy state.

- Transitions are thermally activated.

- Transitions that are continuous in time are called kinetic processes.
Outline

Part I

- Basic Concepts
  - Introduction to microstructure and composition evolution in materials
  - Interfaces and diffuse interfaces in materials
  - Free energy of heterogeneous materials systems
  - Non-equilibrium thermodynamics and evolution
  - The phase field method, phase field equations and numerical solution

Part II:

- Two example problems
  - Grain growth
  - Void formation under irradiation

- A survey of applications
Microstructure and micro chemical evolution

- Microstructure change is a morphological evolution process that occurs in order to lower the free energy of the material.
- Micro chemical evolution is a composition change that occurs to also lower the free energy.
- Microstructure and micro chemical changes can be coupled in certain material systems.

- Sometimes, these changes occur while the free energy is not decreasing – case of driven materials acted upon by external forces of mechanical, thermal, chemical or physical nature.
The energy (or, in general, the thermodynamic) state of the material is fixed by the thermodynamic state variables and the material configuration.

The collection of energy states is called the energy landscape. Evolution is *motion over this energy landscape* under the action of thermodynamic forces.
Evolution is a configuration (structural) change

Evolution of quantum dots on a surface

Evolution of dendrites during solidification

Grain growth in a ceramic material
Micro chemical evolution

Evolution of composition field in Cu-Au alloy under irradiation

This is also an example of a driven material system.
Phase transformation versus interface motion

Phase Transformations

- Nucleation and growth of new phases.
- Continuous transformation (spinodal instabilities, order-disorder transition)
- Nucleation and growth involve interface motion, coupled with diffusion (atomic/defect fluxes throughout the system)
- Not all phase changes involve diffusion

Interface motion

- Motion of interfaces by atomic or molecular rearrangement locally (spin, polarization, …) or by short range diffusion
- Motion of a grain boundary
- Motion of a free surface
- Etc
What makes things happen in a material?

The thermodynamic state

Current state = Equilibrium state

- Current state is an equilibrium state → Nothing happens
- Current state is not an equilibrium state → Something will happen

Phase transformation and microstructure evolution occurs to bring material from non-equilibrium states to equilibrium states.
An equilibrium state is characterized by a minimum free energy. This energy depends on the imposed physical, chemical, mechanical constraints (state variables)

Gibbs free energy,  
\[ G = U - TS + PV \]
\[ = F + PV \]
\[ \equiv H - TS \]

\( U, H, S \) and \( F \) are internal energy, enthalpy, entropy and Helmholtz free energy.

If \( G \) can be made smaller by an internal change in the material keeping \( T, P \) fixed, then the material is in an unstable state.

If \( G \) cannot be made smaller, then it is at its global free energy minimum and it is stable.
Studying a material undergoing transformation or evolution is partly about finding the free energy changes as evolution takes place.

(chemical, elastic, interfacial, electrostatic, ... energy changes)

It is also about relating the energy changes to the underlying speed of transformation (kinetic mechanisms) or microstructure change.

Diagram:
- **Cause**
  - forces
    - (Thermodynamic)
- **Effect**
  - fluxes, motion
    - (Kinetics)
Modeling phase changes starts out by defining the appropriate order parameters that describe the thermodynamic state of the material, and by developing equations for the time and space evolution (kinetic equations) of the order parameters.

The analysis is thus about the “temporal evolution of a materials initiated by variations in order parameters from equilibrium states”.
- Small variations
  - Long wave fluctuations with small amplitude
  - Localized fluctuations of large amplitude

- This classification, which was introduced by Gibbs a century ago, helps us distinguish continuous and discontinuous phase transformations
We consider the molar free energy $F$ and an internal variable $\xi$ for a one-component system at fixed volume. $\xi$ is an internal thermodynamic variable that cannot be controlled directly, and it is thus a characteristic of the transformation process.

- Molar free energy as a function of $T$ for a melting transition
- Temperature-dependent order parameter $\xi$
For fixed $V$, the equilibrium value of $F$ depends only on $T$.

$$F(T, \xi) = a_o(T) + a_1(T)\xi + a_2(T)\xi^2 + \cdots$$

(Landau expansion)

The equilibrium value of $\xi$, $\xi_{eq}(T)$ can be found from: $\frac{\partial F}{\partial \xi}|_T = 0$

At equilibrium, $F_{eq}(T, \xi_{eq}(T))$

$(\xi(x) - \xi_{eq}(T))$ is a local measure of departure from equilibrium.
Other types of order parameters

- Order parameters may refer to the underlying crystal structure or symmetry properties.
- In a ferroelectric material, an ion is always displaced in some direction or its opposite relative to center of the unit cell (both directions are energetically equivalent). If we choose an order parameter $\eta$ to describe this, the expression of the free energy (molar Gibbs energy) will only include even powers of $\eta$,

$$G(T, P, \eta) = G_o(T, P) + a(P)(T - T_c)\eta^2 + B(P)\eta^4 + \cdots$$
\( \eta \) determines the polarization

Equilibrium state found from the condition:

\[
\left( \frac{\partial G}{\partial \eta} \right)_T = 0
\]

Thus

\[
G^{eq}, \eta^{eq} \rightarrow \text{depend on } T, P
\]

\[
\eta^{eq} = \begin{cases} 
\pm \sqrt{-a(P)(T - T_c)/2B(P)} & T < T_c \\
0 & T \geq T_c
\end{cases}
\]

\[
G^{eq}(T, P) - G_o(T, P) = \begin{cases} 
-\left[a(P)(T - T_c)\right]^2/4B(P) & T < T_c \\
0 & T \geq T_c
\end{cases}
\]

\( T_c \): transition temperature

\[
\eta = \begin{cases} 
\pm \xi^{eq} & \text{piezoelectric state} \\
0 & \text{non-piezoelectric state}
\end{cases}
\]
The previous two examples refer to equilibrium of \textit{homogeneous} systems $\rightarrow$ we worked with molar free energy functions.

In a \textit{heterogeneous} system, we work with the corresponding free energy functionals (the total free energy of the heterogeneous system).

Spatial dependence comes into the picture.
Outline

Part I

➢ Basic Concepts
  – Introduction to microstructure and composition evolution in materials
  – Interfaces and diffuse interfaces in materials
  – Free energy of heterogeneous materials systems
  – Non-equilibrium thermodynamics and evolution
  – The phase field method, phase field equations and numerical solution

Part II:

➢ Two example problems
  – Grain growth
  – Void formation under irradiation

➢ A survey of applications
The phase field approach

- Phase field is an approach for modeling evolution in heterogeneous materials.

- The concept evolved from early work by theoretical physicists on thermodynamics of heterogeneous systems (1950-70s).

- Original name: *field theoretic approach*.

- The approach focuses on the thermodynamics and kinetics of heterogeneous systems, with a connection to the statistical mechanical description of the underlying atomic systems.
Phase field ‘cont.’

- Field theoretic models start with a representation of the free energy functional of the heterogeneous material system in terms of order parameters

\[ G[c, \eta] = \int_{\Omega} g_b(c, \eta) \, d\Omega + \int_{\partial\Omega} g_i(c, \eta) \, d\Omega \]

- We do two things with free energy
  - Either minimize it to find the ‘shape’ of fields over a domain
    \[ \min_{c,\eta} G[c,\eta] \]
  - Or use non-equilibrium thermodynamics and develop kinetic equations, with driving forces defined from the free energy.

- We thus have variational and evolutionary phase field formalisms.
Conserved and non-conserved order parameters

- Order parameters may be derived from *extensive variables* such as mass or composition.
  - Kinetic equations that apply to such order parameters must satisfy the conservation principles that the extensive variables satisfy.

- Ferroelectric polarization, magnetic spin, crystal lattice orientation, etc., are not subject to conservation principles.
  - We call the corresponding variables non-conserved order parameters.
Order parameters in two component solids

- Random solid solutions:
  - Use conserved order parameters (concentrations).
  - Kinetic equations are generalized diffusion equations.

- Solid solution that can developed ordered phases:
  - Use conserved order parameters for concentrations and non-conserved order parameters for long-range order.
  - Two types of evolution equations.
Energy changes

- In a binary alloy A-B in equilibrium at a molar concentrations \( X_B \), a small fluctuation of composition, \( \delta X_B = X'_B - X^o_B \), results in a change in the free energy \( G(X_B) \), which we write in terms of \( \delta X_B \) as follows:

\[
G(X'_B) = G_B(X^o_B) + \delta X_B \frac{\partial G}{\partial X_B} \bigg|_{X_B=X^o_B} + \frac{1}{2} \left( \delta X_B \right)^2 \frac{\partial^2 G}{\partial X^2_B} \bigg|_{X_B=X^o_B} + \ldots
\]

- First order term is trivial (by equilibrium requirement), and the free energy change is given by

\[
\Delta G(X'_B) = \frac{1}{2} \left( \delta X_B \right)^2 \frac{\partial^2 G}{\partial X^2_B} \bigg|_{X_B=X^o_B} + \ldots
\]

- The variation in molar free energy is proportional to \( (\delta X_B)^2 \), for conserved species.

- If \( \frac{\partial^2 G}{\partial X^2_B} \) is positive, a barrier exists for the growth of localized fluctuations (nucleation). Otherwise, transformation is barrierless.
For non-conserved order parameters, the lowest-order term for change in molar free energy is,

\[ \Delta G = \delta \xi \left. \frac{\partial G}{\partial \xi} \right|_{\xi = \xi^0} \]
Continuous versus non-continuous phase transformations

➢ Consider a typical molar free energy versus composition curve of a homogeneous alloy

\[ \Delta G \]

\[ \frac{\partial^2 \Delta G}{\partial x^2} > 0 \]

\[ \frac{\partial^2 \Delta G}{\partial x^2} < 0 \]

Two phases stable (miscibility gap)

\[ x_B^{'}, x_B^{''} \]

Molar Free Energy curve

➢ There exist different regions corresponding to different signs for leading to different type of evolution.

\[ \frac{\partial^2 \Delta G}{\partial x^2} \]
Spinodal instability

- Consider a part of free energy where curvature is negative and suppose we have spatial fluctuations in composition.

- Free energy change is negative for small fluctuation change. The system is thus inherently unstable and phase separation proceeds.

- **Condition** for spinodal decomposition:

  \[ \frac{\partial^2 \Delta G^{\text{mixing}}}{\partial X_B^2} < 0 \]

- Uphill diffusion.
Nucleation and growth

- Consider a region of free energy in which curvature is positive.

- The system is stable (“meta-stable”) with respect to small fluctuations in composition.

- And a large (localized) composition fluctuation is required to decrease the free energy.

- The system separates as illustrated through a process of nucleation.

- Note: the new phase must initiate with a composition that is not near that of the parent phase.
<table>
<thead>
<tr>
<th>Continuous transformations</th>
<th>Discontinuous transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>➢ System is initially unstable.</td>
<td>➢ System is initially metastable.</td>
</tr>
<tr>
<td>➢ Infinitesimal variation initiate transformation and decrease bulk free energy.</td>
<td>➢ There is a <strong>free energy barrier</strong> to infinitesimal variations. A sufficiently large variation is required.</td>
</tr>
<tr>
<td>➢ Transformations can begin over <strong>large regions</strong> and over entire volume.</td>
<td>➢ Transformations is over a <strong>small region</strong> and the surrounding volume of sub-system do not transform</td>
</tr>
<tr>
<td>➢ Examples,</td>
<td>➢ Examples,</td>
</tr>
<tr>
<td>- Spinodal decomposition</td>
<td>- Nucleation (formation of an A-rich precipitate)</td>
</tr>
<tr>
<td>- Order-disorder transformation</td>
<td></td>
</tr>
</tbody>
</table>
Kinetics of a conserved order parameter

- Cahn-Hilliard (generalized diffusion) equation applies. It accounts for concentration gradients in free energy construction.

\[
\frac{\partial c_i(r,t)}{\partial t} = \nabla \cdot M_{ij} \nabla \frac{\delta F}{\delta c_j(r,t)} + \xi_{\text{fluct}}^{c_i}
\]

- \(M_{ij}\) is a matrix of mobility's of the conserved species

- \(\frac{\delta F}{\delta c_j} = \mu_j\) is the chemical potential of the species

- The gradient energy coefficients \(\kappa^c_i\) account for inhomogeneities in the concentration field.

- Substituting variational derivative, we get the kinetic equation,

\[
\frac{\partial c_i(r,t)}{\partial t} = \nabla \cdot M_{ij} \nabla \left( \frac{\partial f(r,t)}{\partial c_j} - \kappa^c_i \nabla^2 c(r,t) \right)
\]
For formalism, see:

Kinetics of a non-conserved order parameter

- Allen-Cahn (Ginsburg-Landau) equation applies to kinetics of nonconserved order parameters.

\[
\frac{\partial \eta_p(r,t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_q(r,t)}
\]

- $L_{pq}$ is the interfacial mobility matrix; it is related to microscopic rearrangement kinetics. The K.E. can be rewritten in the form:

\[
\frac{\partial \eta_p(r,t)}{\partial t} = -L_{pq} \left( \frac{\partial f(r,t)}{\partial \eta_q} - \kappa^\eta \nabla^2 \eta(r,t) \right)
\]

- $\kappa^\eta$ is the gradient energy coefficient which accounts for the gradients in nonconserved field.

- Depending on initial variations in $\eta$, a system may seek minima such that $\eta$ will be attracted to local minima of $f^{\text{hom}}$. 

Bad notation; $F$ is used for $G$ from now on.
The phase field approach is based on the kinetic equations for the conserved and non-conserved order parameters.

Cahn-Hilliard Eq.
\[ \frac{\partial c}{\partial t} = \nabla \cdot M \nabla \frac{\delta F}{\delta c} + \xi(x,t) \]

Allen-Cahn (G.L.) Eq.
\[ \frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta} + \xi(x,t) \]

Formally, \( \eta \) is the variable called the phase field but nowadays the approach itself is called phase field …
A classification by physicists

- **Type A models**: evolution of non-conserved order parameters or a phase field

  \[
  \frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta} + \zeta(x, t)
  \]

- **Type B models**: evolution of conserved order parameters

  \[
  \frac{\partial c}{\partial t} = \nabla \cdot M \nabla \frac{\delta F}{\delta c} + \xi(x, t)
  \]

- **Type C models**: coupled conserved and non-conserved order parameter problems

  \[
  \frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta} + \zeta(x, t)
  \]

  \[
  \frac{\partial c}{\partial t} = \nabla \cdot M \nabla \frac{\delta F}{\delta c} + \xi(x, t)
  \]
Engineers model sharp interfaces by equiv. diffuse ones

- Example: GB evolution is now modeled in the same way ferroelectric domains are modeled.

- Phase field here is more a mathematical framework than physical. As such, there is some flexibility in model development so long as the model can reproduce the sharp-interface dynamics.

- Asymptotic analysis need to ensure equivalence with sharp interface limit and fix model parameters.
Numerical solution

- Phase field equations are often non-linear and strongly coupled.

- They are also often spatially and temporally stiff.

- All numerical machinery for PDE solution can work.

- Methods used:
  - Spatial discretization: FD, FEM, FV, spectral
  - Time discretization: first order and higher order, explicit and implicit
Constructing a phase field model

- Determine phase field variables that fit the problem at hand
- Develop a form for the free energy of the system in terms of these variables
- Determine the energy and kinetic parameters
- Write the kinetic evolution equations and solve them
Summary

- Basic concepts of microstructure and micro chemical evolution in materials were given.
- The underlying thermodynamics concepts were reviewed.
- Application to heterogeneous materials led to the development of phase field approach.
References


- J W Cahn and J E Hilliard, Free energy of a nonuniform system. I. Interface free energy, J Chem Phys, 28 (1957) 258


- Nikolas Provatas and Ken Elder, Phase field methods in materials science and engineering, Wiley-VCH