Quantitative phase-field modeling of growth and coarsening in polycrystalline materials

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• Some aspects of model formulation
  • 2-phase versus multi-phase and multi-grain

• Application example
  • Slag/oxide crystallization
‘Quantitative’ phase-field models

- Physics bulk and interfaces are reproduced accurately in the simulations
  - Effect model description and parameters – Physics
  - Numerical issues

- Predictive?
  - Depends on availability and accuracy of input data
    - Requires composition and orientation dependence
  - Features on the mesoscale
Sharp – Diffuse – Thin interface models

**Sharp Interface**
- Discontinuity
- (Semi) 1-D problems
- Problem specific

**Diffuse interface**
- Complex morphologies
- Segregation, solute drag, trapping, lattice mismatch, ...
- However, $l_{\text{phys}} (<1\text{nm}) \ll l_{\text{num}} \ll R_{\text{grain}}$ (μm-mm)
- Mostly qualitative

**Thin interface**
- $l_{\text{num}}$ independent
- $l_{\text{phys}} \ll l_{\text{num}} \ll R_{\text{grain}}$
Some aspects of model formulation

- Two-phase systems: single phase-field
- Multi-grain/phase systems: multiple phase-field
2-phase systems

• Field variables: \( \phi(r, t) \) \( \rightarrow \) \( c_k(r, t) \)

• Phase \( \alpha \): \( \phi = 0 \)
• Phase \( \beta \): \( \phi = 1 \)
• Composition: \( c_B \)
2-phase systems

- Field variables: $\phi(r, t)$, $c_k(r, t)$
- Phase $\alpha$: $\phi = 0$
- Phase $\beta$: $\phi = 1$
- Composition: $c_B$
2-phase systems

- **Field variables:**
  \[ \phi(\vec{r},t), c_k(\vec{r},t) \]

- **Phase** \( \alpha \): \( \phi = 0 \)
- **Phase** \( \beta \): \( \phi = 1 \)
- **Composition:** \( c_B \)

- **Free energy**
  \[
  F = \int_V \left[ f_{chem}(c,\phi) + Wg(\phi) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right] d\vec{r}
  \]

- **Interfacial energy**

**Double well function**

\[ g(\phi) = 16\phi^2(1-\phi)^2 \]
2-phase systems

- Field variables: $\phi(r, t)$, $c_k(r, t)$

- Phase $\alpha$: $\phi = 0$
- Phase $\beta$: $\phi = 1$

- Composition: $c_B$

**Free energy**

$$F = \int_V \left[ f_{chem}(c, \phi) + W g(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] d\vec{r}$$

$$\Rightarrow \gamma = \frac{2\sqrt{2}}{3} \sqrt{W \varepsilon}, \quad \ell \propto \frac{\varepsilon}{\sqrt{2W}}$$

**Double well function**

$$g(\phi) = 16\phi^2(1-\phi)^2$$
2-phase systems

- **Field variables:** \( \phi(r, t), c_k(r, t) \)

- **Phase \( \alpha \):** \( \phi = 0 \)

- **Phase \( \beta \):** \( \phi = 1 \)

- **Composition:** \( c_B \)

- **Free energy**

\[
F = \int_V \left[ f_{\text{chem}}(c, \phi) + W_g(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] d\vec{r}
\]

- **Bulk energy**

\[
f_{\text{chem}} = h(\phi) f^\beta(c, T) + \left[ 1 - h(\phi) \right] f^\alpha(c, T)
\]

- **Interpolation function**

\[
h(\phi) = \phi^3 (10 - 15\phi + 6\phi^2)
\]
Decoupling bulk and interfacial energy

- Free energy

\[ F = \int_V \left[ f_{chem}(c, \phi) + Wg(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] d\vec{r} \]

\[ f_{chem} = h(\phi) f^\beta(c,T) + \left[ 1 - h(\phi) \right] f^\alpha(c,T) \]

\[ g(\phi) = 16\phi^2(1-\phi)^2 \]

\[ h(\phi) = \phi^3(10 - 15\phi + 6\phi^2) \]

Double well + Bulk energy with \( h(\phi) \) with zero slope at 0 and 1 = Homogeneous energy density: minima remain at 0 and 1
Decoupling bulk and interfacial energy

- Interface treated as mixture of 2 phases – KKS approach
  - c-field for each phase \( c \rightarrow c^\alpha, c^\beta \)

- Equal diffusion or chemical potential
- Bulk energy

\[ f_{\text{chem}} = h(\phi) f^\beta(c^\beta) + \left[ 1 - h(\phi) \right] f^\alpha(c^\alpha) \]

Decoupling bulk and interfacial energy

- Alternative formulation for dilute alloys

- Unified approach using a grand-canonical functional
  M. Plapp, PRE, 84 (2011) no° 031601
Kinetics -- general

- Interface movement (Allen - Cahn)

\[ \frac{\partial \phi}{\partial t} = -L \frac{\partial F}{\partial \phi} \]

\[ \frac{\partial \phi}{\partial t} = -L \left[ W \frac{\partial g}{\partial \phi} - \epsilon \nabla \phi + \frac{\partial h}{\partial \phi} \left( f^\beta - f^\alpha \right) \right] \]

Curvature driven  Bulk energy driven

- Diffusion

\[ \frac{\partial c_k}{\partial t} = \nabla \cdot \sum_{l=1}^{C-1} \left[ h(\phi) M_{kl}^\beta + [1 - h(\phi)] M_{kl}^\alpha \right] \nabla \tilde{\mu}_l \]

- Diffusion potentials:

\[ \tilde{\mu}_l = \mu_l - \mu_C \]

- Diffusion mobilities/coefficients:

\[ D^\rho = M^\rho G^\rho \]

\[ G_{kl}^\rho = \frac{\partial^2 f^\rho}{\partial c_k \partial c_l} \]

Decoupling bulk and interfacial kinetics

- Anomalous nonequilibrium effects, such as discontinuity in $\mu_i$ for $D_{\text{ineq}} \neq D_S$

$$\propto \ell, \nu_n, \vec{j}_n$$

- Non-variational anti-trapping current

$$\vec{j}_a = \alpha \sqrt{\frac{\kappa}{W}} \left(1 - \frac{D_S}{D_L}\right) \frac{\partial \phi}{\partial t} \left| \nabla \phi \right|$$

- But still ‘Kapitza’ effect for

$$\vec{j}_n \gg \nu_n$$

M. Plapp, Phil. Mat. 91 (2011) p25

Some aspects of model formulation

• Two-phase systems : single phase-field

• Multi-grain/phase systems : multiple phase-field
Multi-grain and multi-phase structures

- Single phase-field models -> Multiple phase-field models
  \[ \varphi \rightarrow \{ \varphi_1, \varphi_2, \varphi_3, \ldots, \varphi_p \} \]

- Model extension
  \[ F(\phi_1, \phi_2, \phi_3, \ldots, |\nabla \phi_1|^2, |\nabla \phi_2|^2, \ldots) \]
  - Different types of interfaces
  - Triple and higher order junctions

- Numerically
  - Homogeneous accuracy
  - Thin interface asymptotics for all interfaces
  \[ \ell_{num} = cte \]
Multi-grain and multi-phase models: major difficulties

- Third-phase contributions
  - $\sigma_{12} = \sigma_{13} = 7/10 \sigma_{12}$
  - Careful choice of multi-well function and gradient contribution

- Interpolation function
  - Zero-slope at equilibrium values of the phase fields
  - Thermodynamic consistency

$$f_{chem} = \sum_{i=1}^{p} h_i(\eta_1, \eta_2, \ldots) f^i(c, T) \Rightarrow \sum_{i=1}^{p} h_i(\eta_1, \eta_2, \ldots) = 1$$
Some aspects of model formulation

• Two-phase/grain model
• Multi-grain model
• Multi-phase multi-grain model
Anisotropic grain growth model

- **Phase fields**  \( \eta_1, \eta_2, \ldots, \eta_i(r,t), \ldots, \eta_p \)
  - With grain \( i \)
    \( (\eta_1, \eta_2, \ldots, \eta_i, \ldots, \eta_p) = (0,0,\ldots,1,\ldots,0) \)

- **Free energy**
  \[
  F_{\text{interf}} = \int \sum_{i=1}^{p} \left( \frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\nabla \eta_i)^2 dV
  \]

\[
\kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i} \kappa_{i,j} \eta_i^2 \eta_j^2 / \sum_{i=1}^{p} \sum_{j<i} \eta_i^2 \eta_j^2
\]

- For each grain boundary  \( \eta_i^2 \eta_j^2 \neq 0 \Rightarrow \kappa(\eta) = \kappa_{i,j} \)

- **Inclination dependence**
  \[
  \gamma_{i,j}(\psi_{i,j}), \kappa_{i,j}(\psi_{i,j}), L_{i,j}(\psi_{i,j}), \psi_{i,j} = \frac{\nabla \eta_i - \nabla \eta_j}{|\nabla \eta_i - \nabla \eta_j|}
  \]

A. Kazaryan et al., PRB, 61 (2000) p14275
Non-variational approach – equal interface width

- Ginzburg-Landau type equations

\[
\frac{\partial \eta_i(\vec{r},t)}{\partial t} = -L(\eta) \left[ m \left( \eta_i^3 - \eta_i + 2\eta_i \sum_{j \neq i} \gamma_{i,j} \eta_j^2 \right) - \kappa(\eta) \nabla^2 \eta_i \right]
\]

- Non-variational with respect to \( \eta \)-dependence of \( \kappa \)
- Similar to Monte Carlo Potts approach

- Definition ‘grain boundary width’

\[
l_{\text{num}} = \frac{1}{\left| \frac{d\eta_i}{dx} \right|_{\text{max}}} = \frac{1}{\left| \frac{d\eta_j}{dx} \right|_{\text{max}}}
\]

→ High controllability of numerical accuracy \((l_{\text{num}}/R < 5)\)
Grain boundary properties

- Grain boundary energy
  \[ \gamma_{gb,\theta_{i,j}} = g(\gamma_{i,j}) \sqrt{m\kappa_{i,j}} \]

- Grain boundary mobility
  \[ \mu_{gb,\theta_{i,j}} = L_{i,j} \frac{\kappa_{i,j}}{\sqrt{m(g(\gamma_{i,j}))^2}} \]

- Grain boundary width
  \[ l = \frac{4}{3} \sqrt{\frac{\kappa_{i,j}}{m(g(\gamma_{i,j}))^2}} \]

- Iterative algorithm
  \[ \ell_{gb}, [\gamma_{gb,\theta}], [\mu_{gb,\theta}] \rightarrow m, [\kappa_{i,j}], [\gamma_{i,j}], [L_{i,j}] \]

Numerical validation

- Shrinking grain:
  \[
  \frac{dA_\alpha}{dt} = -2\pi \mu_{\alpha\beta} \sigma_{\alpha\beta}
  \]

- Triple junction angles:
  \[
  \frac{dA_\alpha}{dt} = -\mu_{\alpha\gamma} \sigma_{\alpha\beta}
  \]

- Observations
  - Accuracy controlled by \( \ell_{num} / \Delta x \) for \( \ell_{num} / R \leq 5 \)
  - Diffuse interface effects for \( \ell_{num} / R \geq 5 \)
  - Angles outside [100°-140°] require larger \( \ell_{num} / \Delta x \) for same accuracy
Variational approach – interface width varies with interface energy

- Anisotropy only through $\gamma_{i,j}$, $\kappa=\text{cte}$
- Energy
  \[
  F = \int_V \left[ m \left( \sum_{i=1}^{p} \left( \frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i}^{p} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa}{2} \sum_{i=1}^{p} (\tilde{\nabla} \eta_i)^2 \right] dV
  \]
- Kinetic equations
  \[
  \frac{\partial \eta_i(\tilde{r},t)}{\partial t} = -L(\eta) \left[ m \left( \eta_i^3 - \eta_i + 2 \eta_i \sum_{j \neq i} \gamma_{i,j} \eta_j^2 \right) - \kappa \nabla^2 \eta_i \right]
  \]

$\theta = 168.5^\circ$

$\sigma_{13} = \sigma_{23} = 5\sigma_{12}$

$\eta_1$
Some aspects of model formulation

• Two-phase/grain model
• Multi-grain model
• Multi-phase multi-grain model
Extension to multi-component multi-phase alloys

- Phase field variables:
  - Grains: $\eta_{\alpha_1}, \eta_{\alpha_2}, ..., \eta_{\alpha_i}(r,t), ..., \eta_{\beta_1}, \eta_{\beta_2}, ..., \eta_{\beta_p}$
  - Composition: $x_A, x_B(r,t), ..., x_{C-1}$
Extension to multi-component multi-phase alloys

- Phase field variables:
  \[ \eta_{\alpha_1}, \eta_{\alpha_2}, \ldots, \eta_{\alpha_i}(r, t), \ldots, \]
  \[ \eta_{\beta_1}, \eta_{\beta_2}, \ldots, \eta_{\beta_i}, \eta_{\pi_1}, \ldots, \eta_{\pi_i} \]
  \[ x_A, x_B(r, t), \ldots, x_{C-1} \]

- Bulk energy:
  \[ f_{bulk}(x_k, \eta_{\rho_i}) = \sum_{\rho} \phi_{\rho} f^\rho(x^\rho_k) \]

- with
  \[ \frac{\partial f^\beta(x_k^\beta)}{\partial x_k^\beta} = \frac{\partial f^\alpha(x_k^\alpha)}{\partial x_k^\alpha} = \ldots = \tilde{\mu}_k \]
  \[ x_k = \sum_{\rho} \phi_{\rho} x_k^\rho \]

KKS approach
Interpolation function

\[ \text{and} \quad \phi_{\rho} = \frac{\sum_{i} \eta^2_{\rho i}}{\sum_{\pi=\alpha, \beta, \ldots} \sum_{i} \eta^2_{\pi i}} \]
Free energy for multi-phase systems

- **Bulk energy:**
  \[ f_{\text{bulk}}(x_k, \eta_{\rho_i}) = \sum_{\rho} h_{\rho}(\eta_{\rho_i}) f^\rho(x^\rho_k) \]

- With
  \[ h_{\rho}(\eta_{\rho_i}) = \phi_{\rho} = \frac{\sum i \eta_{\rho_i}^2}{\sum_{\pi=\alpha,\beta,...} \sum_i \eta_{\pi i}^2} \]
  and
  \[ f^\rho(x^\rho_k) = \frac{G^\rho_m(x^\rho_k)}{V_m} \]

Replaces the standard function for 2-phase systems

Interpolation function for 2-phase system

Interpolation functions for multi-phase system

Free energy for multi-phase systems

- **Interpolation function**

\[
h_\rho(\eta_{\rho_i}) = \phi_\rho = \frac{\sum_i \eta_{\rho_i}^2}{\sum_{\pi=\alpha,\beta,...} \sum_i \eta_{\pi i}^2}
\]

\[
\sum_\rho \phi_\rho = 1 \Rightarrow \text{‘phase fractions’}
\]

\[
\frac{\partial \phi_\rho}{\partial \eta} \bigg|_{\eta=0,\eta=1} = 0 \Rightarrow \text{Minima remain at (0, 0, ..., 1, ..., 0)}
\]

Interpolation functions for multi-phase system

Free energy for multi-phase systems

- Only Interfacial energy: \( f = f_0(\eta_\alpha, \eta_\beta) \)
Free energy for multi-phase systems

- Interfacial + bulk energy: \( f = f_0(\eta_\alpha, \eta_\beta) + \phi_\alpha f^\alpha + \phi_\beta f^\beta \)
Equations for interface movement

- Interface movement:
  \[ \frac{\partial \eta_{i\rho}}{\partial t} = -L \frac{\delta F(\eta_{i\rho}, x_k)}{\delta \eta_{i\rho}} \]

- Grain boundary between grain \( \rho, i \) and \( \rho, j \)
  \[ \frac{\partial \eta_{\rho i}}{\partial t} = -L \left( \frac{\partial f_{\text{interf}}}{\partial \eta_{\rho i}} - \kappa_{i,j} \nabla^2 \eta_{\rho i} \right) = -L g_{\text{int}}(\eta, \nabla \eta) \]

- Between phase \( \alpha \) and \( \beta \)
  \[ \frac{\partial \eta_{\alpha i}}{\partial t} = -L \left( g_{\text{int}}(\eta, \nabla \eta) + \nu \eta_{\alpha i} \eta_{\beta j} \frac{\nu^{\nu-1} \eta_{\beta j}^{\nu}}{(\eta_{\alpha}^{\nu} + \eta_{\beta}^{\nu})^2} \left[ f^{\alpha}(x^{\alpha}) - f^{\beta}(x^{\beta}) - (x^{\alpha} - x^{\beta}) \mu \right] \right) \]

Curvature driven  Bulk energy driven
• **Diffusion flux (of the form)**

\[ \bar{J}_k = -\sum_{l=1}^{c-1} M_{kl} \nabla (\mu_l - \mu_C) = -\sum_{l=1}^{c-1} M_{kl} \nabla \tilde{\mu}_l \]


• **E.g. for binary A-B**

\[ \bar{J}_B = -\frac{1}{V_m} \left( \sum_{\rho} \phi_{\rho} M^\rho + \sum_{\rho, i \neq \sigma, j} M_{\text{interf}} \eta^2_{\rho,i} \eta^2_{\sigma,j} \right) \nabla \tilde{\mu}_B \]

**Bulk diffusion**

**Interface diffusion**

– **Relation with interdiffusivities**

\[ M^\rho = D^\rho / \frac{\partial^2 f^\rho}{\partial x_B^2} \]

– **Relation with atomic mobilities**

\[ M^\rho = x_B (1 - x_B) (x_B \beta_A^\rho + (1 - x_A) \beta_B^\rho) \]

– **Relation with pipe interdiffusivities**

\[ M_{\text{interf}} = 3 \left( \frac{D_{\text{interf}}}{\partial^2 f^m / \partial x_B^2} \right) \left( \frac{\delta_{gb}}{\delta_{num}} \right) \]

• **Mass conservation**

\[ \frac{\partial x_B}{\partial t} = \nabla \cdot \left[ \left( \sum_{\rho} \phi_{\rho} M^\rho + \sum_{\rho, i \neq \sigma, j} M_{\rho,i} \eta^2_{\rho,i} \eta^2_{\sigma,j} \right) \nabla \tilde{\mu}_B \right] \]
Effect of diffuse interface width: Numerical validation

- **Triple junction**
- **Growing sphere**
- **Processes for which $v(t)$ decreases**
  - Accuracy controlled by $\ell_{num} / \Delta x$
    - ($\approx 1.3\%$ for 6 g.p., $<1\%$ for 10 g.p.)
  - Diffuse interface effects for $\ell_{num} / R > 5$
  - Angles outside $[100^\circ-140^\circ]$ require larger resolution for same accuracy

Model comparison

- **Multi-phase-field model**
  - Phase fields \( \varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p, \ \sum_{i=1}^{p} \varphi_i = 1 \)
  - Interfacial energy
    \[
    f_{\text{int}} = \sum_{i \neq j} \frac{4 \sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} \left| \nabla \phi_i \cdot \nabla \phi_j \right| + \phi_i \phi_j \right\} + \sum_{i \neq j} \sum_{k \neq i,j} W_{ijk} \phi_i \phi_j \phi_k
    \]
    \[0 < \phi_{i,j} < 1\]

- **Multi-order parameter models**
  - Order parameters \( \eta_1, \eta_2, \ldots, \eta_i(r,t), \ldots, \eta_p, \ \left( \sum_{i=1}^{p} \eta_i \neq 1 \right) \)
  - Interfacial energy
    \[
    f_{\text{int}} = m \left( \sum_{i=1}^{p} \left( \frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\nabla \eta_i)^2
    \]
    \[
    \kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i} \kappa_{i,j} \eta_i^2 \eta_j^2 \left/ \sum_{i=1}^{p} \sum_{j<i} \eta_i^2 \eta_j^2 \right.
    \]

For ‘equivalent’ model parameters

- Similar accuracy for 2- and 3-grain structures for grain boundary movement
- Choice $W_{ijk}$ in MPF affects triple-junction angles
- MPF can reproduce very low and high angles more accurate than the non-variational CF

Model comparison: grain assemblies

- 2 orientation variants

Model comparison: grain assemblies

- 2 orientation variants (2D)
Model Comparison: grain assemblies

- Isotropic (3D)

Model Comparison: grain assemblies

- Isotropic (3D)

\[ N. \text{ Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479} \]
Bounding Box Implementation

- **Basic elements**
  - A grain is set of connected grid points \( r \) where \( |\eta_i(r)| > \epsilon \)
  - For each grain, the corresponding bounding box is the smallest cuboid containing the grain

**Algorithm**
- Solve the equations only locally, inside bounding boxes
- Only values inside boxes are kept in memory
- Boxes grow or shrink with grain

*Object Oriented C++ implementation*

*Vanherpe et al., PRE, 76, n° 056702 (2007)*
Application example

• Solidification of oxide/silicate melts (slags, lava, magma)
Relevance of slag crystallization

- Crystallization of slags often occurs in industrial practice
  1. Slag in contact with refractory
     *Solid-liquid interaction between liquid and solid oxide material*
  2. Freeze lining due to water-cooled furnace
     *Instantaneously formed layer of crystallized slag*
  3. Tapping and cooling of slag to ambient temperature
     *Crystallization of the slag while cooling down*
Geology and pyrometallurgy

Geology

- Lava (magma)
- Oxide melt
- $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{FeO}$, $\text{Fe}_2\text{O}_3$, $\text{MgO}$ ...
- High temperature and/or pressure

Pyrometallurgy

- Slags
Specific to slag solidification

Slag solidification

- Mostly facet growth
- Strong anisotropy
- High interfacial energies
- Partial crystallization
- Glass transition
- Oxides are diffusing
- Possible redox reactions
Phase field model for slag crystallization

- Model can treat any number of phases
- Model can treat any number of components
  - CaO, Al$_2$O$_3$, FeO, Fe$_2$O$_3$, SiO$_2$, ...
- Model is coupled with thermodynamic database (FACT)
- Stoichiometric solid oxide phases
- Diffusion coefficients are taken from the literature, e.g.
  \[
  D^L = \begin{bmatrix}
  8.734 & -2.464 \\
  -3.948 & 5.977
  \end{bmatrix} \times 10^{-11}
  \]
- Dendrites and faceted crystals

J. Heulens et al., Acta Mater. 59 (2011) p2156
Equations for microstructure evolution

- System of $p$ phases and $c$ components
- Phase fields evolve by energy minimization:

$$\frac{\partial \eta_i}{\partial t} = -L(\eta) \frac{\delta}{\delta \eta_i} \left( \int_V \left( m f_0(\eta) + \frac{\kappa(\eta)}{2} \sum_{r=1}^p |\nabla \eta_r|^2 + f_{\text{chem}} \right) dV \right)$$

  - **Interfacial energy** (Double well and gradient term)
  - **Chemical energy** (Gibbs energies of phases)
- Diffusion equation for every component $k$:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left( \sum_{i=1}^p \phi_i \sum_{r=1}^{c-1} M_{rk} \nabla \tilde{\mu}_r^i \right)$$

  $$\tilde{\mu}_r^i = \mu_r^i - \mu_{SiO_2}^i$$
Coupling with FactSage databases

- KKS approach
  \[ f_{chem} = \sum_{\rho=1}^{\rho} \varphi_\rho f^\rho \left( x_k^\rho \right) \]

- Solve \( x_k^\rho \) from
  \[
  \frac{\partial f^\alpha (x_k^\alpha)}{\partial x_k^\alpha} = \frac{\partial f^\beta (x_k^\beta)}{\partial x_k^\beta} \\
  \ldots = \frac{\partial f^\rho (x_k^\rho)}{\partial x_k^\rho} = \tilde{\mu}_k \\
  x_k = \sum_\rho \phi_\rho x_k^\rho
  \]

- At discrete compositions Gibbs energy approximated with parabola

J. Heulens et al., Acta Mater. 59 (2011) p2156
Coupling with FactSage databases

- At discrete $x_k$ Gibbs energy of phase $i$ approximated by

$$\hat{f}^i = \sum_{k=1}^{c-1} \left( \frac{A_{kk}^i}{2} (x_k^i - \hat{x}_k^i)^2 + \sum_{l \neq k} A_{kl}^i (x_k^i - \hat{x}_k^i)(x_l^i - \hat{x}_l^i) + B_k^i (x_k^i - \hat{x}_k^i) \right) + C^i$$

- $A_k^i = \frac{\partial^2 f^i}{\partial x_k^i \partial x_l^i}$
- $B_k^i = \frac{\partial f^i}{\partial x_k^i} = \tilde{\mu}_k^i$
- $C^i = f^i$

- A, B and C are retrieved by ChemApp and stored in an array to load in the phase field code before start simulation

- Diffusion potentials are linear in concentrations, which greatly reduces computational effort

J. Heulens et al., Acta Mater. 59 (2011) p2156
Stoichiometric phases

- Parabola for Gibbs energy of stoichiometric phase
Anisotropic interfaces

- Dendrites -- Diffusion controlled
  - Anisotropic energy

\[ \sigma_{i,j} = \overline{\sigma}_{i,j} \left( 1 + \delta_{i,j} \cos \left( a_{i,j} \theta_{i,j} \right) \right) \]

- Facets –reaction controlled
  - Anisotropic kinetics

\[ L_{i,j} = \overline{L}_{i,j} \left( 1 - \beta_{i,j} + 2 \beta_{i,j} \tanh \left( \frac{r_{i,j}}{\tan \left( 0.5a_{i,j} \theta_{i,j} \right)} \right) \right) \]


J. Heulens et al., Acta Mater. 59 (2011) p2156
CaO-Al2O3-SiO2

Wollastonite

Gehlenite
Dissolution of Gehlenite

Parabola construction with minimal influence on results

Tie-line selection depending on diffusion kinetics in liquid

J. Heulens et al., Acta Mater. 59 (2011) p2156
Crystallization Wollastonite (1D)

- Uphill diffusion
- Automatic tie-line selection
Crystallization Wollastonite (1D)

- Uphill diffusion
- Automatic tie-line selection
Crystallization Wollastonite (2D)

Growth of wollastonite in 42CaO-10Al₂O₃-48SiO₂ at 1320°C

Confocal laser microscope

Computer cluster (100 cpu)
In situ observation

- Confocal Laser Scanning Microscope (CLSM)
- At low undercooling (1370°C) → faceted growth
- At high undercooling (1320°C) → dendrite growth with 6-fold anisotropy

Hexagonal dendrites of CaSiO$_3$ in CaO-Al$_2$O$_3$-SiO$_2$ @1320°C

Linear growth at steady-state

8.4 ± 0.3 µm s$^{-1}$

J. Heulens et al., J. Eur. Cer. Soc. 31 (2011) p1873
Crystallization Wollastonite (2D)

Experiment

Simulation

Growth of wollastonite in 42CaO-10Al₂O₃-48SiO₂ at 1320 °C

Confocal laser microscope

Computer cluster (100 cpu)
Estimation of the S-L interfacial energy

\[ \sigma_{SL} = 0.65 \pm 0.13 \text{[Jm}^{-2}\text{]} \]
Oxidation state dependent crystallization

- System: FeO-Fe$_2$O$_3$-SiO$_2$ @ 1400°C
  - Crystallization of magnetite (FeO.2Fe$_2$O$_3$)
  - Local oxidation state in liquid
  - Open system in contact with O$_2$ atmosphere (fixed $p_{O_2}$)

J. Heulens et al., Chem. Geology, 290 (2011) p156
Oxidation state dependent crystallization

- System: FeO-Fe$_2$O$_3$-SiO$_2$ @ 1400°C
  - Crystallization of magnetite (FeO·Fe$_2$O$_3$)
  - Local oxidation state in liquid
  - Open system in contact with O$_2$ atmosphere (fixed $p_{O_2}$)

- Redox reactions
  - Redox reactions in local equilibrium
  - Fe$^{3+}$/Fe$^{2+}$ direct measure for local oxygen potential (true within limited composition and $p_{O_2}$ range)
  - O$_2$ diffusion by changing the Fe$^{3+}$/Fe$^{2+}$ ratio -> diffusion of FeO and Fe$_2$O$_3$ is considered
Oxidation state dependent crystallization

- System: FeO-Fe$_2$O$_3$-SiO$_2$ @ 1400°C
  - Crystallization of magnetite (FeO·Fe$_2$O$_3$)
  - Local oxidation state in liquid
- Open system in contact with O$_2$ atmosphere (fixed $p_{O2}$)
  - Special boundary condition to preserve Fe but not O
    - Mass balance Fe
      \[
      x_{FeO}^{i=0} + 2x_{FeO}^{i=0} = x_{FeO}^{i=1} + 2x_{FeO}^{i=1}
      \]
    - Fixed $p_{O2}$
      \[
      \frac{x_{FeO}^{i=0.5}}{x_{FeO}^{i=0.5}} = cte\left(p_{O2,atm}\right)
      \]

J. Heulens et al., Chem. Geology, 290 (2011) p156
Crystallization of magnetite

- Atmosphere: $p_{O_2}=1.5 \times 10^{-3}$; Initial melt: $a_{O_2}=2.4 \times 10^{-5}$
  - Oxidation from atmosphere
  - Reduction from growth of $\text{Fe}_3\text{O}_4$
- Faceted reaction controlled growth

Contour plots $x_{\text{FeO}}$

J. Heulens et al., Chem. Geology, 290 (2011) p156
Crystallization of magnetite

- Melt is reduced
  - Faster for higher crystal density
  - Some oxidation initially for low crystal density

- Limited effect of $p_{O_2}$ atmosphere on $a_{O_2}$ melt due to crystallization
  - e.g. rhyolite lavas in Yellowstone Park

- $p_{O_2}$ atmosphere affects crystal growth

Average oxidation state at bottom of simulation domain
Conclusions

• What do we need further to improve the quantitative accuracy for polycrystalline and multi-phase systems?

  • Accurate representation of triple-junction angles outside [100°-140°] ↔ equal interface width

  • General solution for chemical potential jump across interface

  • (CALPHAD) Gibbs/free energies over full composition domain (stoichiometric phases, metastable regions)

  • Composition and orientation dependent expressions for diffusion and interfacial properties

  • Elastic and plastic effects
Acknowledgements

- OT/07/040 (Quantitative phase field modelling of coarsening in lead-free solder joints)
- IUAP Program DISCO (Dynamical Systems, Control, and Optimization)
- IWT grant SB-73163 (Phase-Field Modelling of the Solidification of Oxidic Systems)
- Research Foundation - Flanders (FWO-Vlaanderen)
- Simulations were performed on the Flemisch Super Computer (VSC)

• Thank you for your attention!! Questions?
Rotation invariance of the model

- Mathematically, the model equations are invariant to rotation, but …
- the order parameters represent orientations in a fixed reference frame.
- The precision of $\alpha$ depends on the numerical setup,
- For the model to be rotational invariant in practice, lower limit of amount of order parameters $p$:

$$p > \frac{\sqrt{2\pi L}}{n \Delta h}$$

J. Heulens and N. Moelans, Scripta Mat. (2010)
Principles of the matched asymptotic expansion

Expansion inner region:
\[ \eta(n/\varepsilon, t_1, t_2) = \eta_0(n/\varepsilon, t_1, t_2) + \varepsilon \eta_1(n/\varepsilon, t_1, t_2) + \ldots \]
\[ c(n/\varepsilon, t_1, t_2) = c_0(n/\varepsilon, t_1, t_2) + \varepsilon c_1(n/\varepsilon, t_1, t_2) + \ldots \]

Expansion outer regions:
\[ \eta^*(n, t_1, t_2) = \eta^*_0(n, t_1, t_2) + \varepsilon \eta^*_1(n, t_1, t_2) + \ldots \]
\[ c^*(n, t_1, t_2) = c^*_0(n, t_1, t_2) + \varepsilon c^*_1(n, t_1, t_2) + \ldots \]

Match inner and outer region:
\[ \lim_{n/\varepsilon \to \pm \infty} \eta_0(n/\varepsilon) = \left[ \eta^*_0 \right]^{\pm}, \quad \lim_{n/\varepsilon \to \pm \infty} \eta_1(n/\varepsilon) = \ldots \]
\[ \lim_{n/\varepsilon \to \pm \infty} c_0(n/\varepsilon) = \left[ c^*_0(0) \right]^{\pm}, \quad \lim_{n/\varepsilon \to \pm \infty} c_1(n/\varepsilon) = \ldots \]

gives sharp-interface model with corrections

Gibbs Thomson\[ \frac{c^i_{\alpha}}{c^i_{\beta}} = 1 - (1-k)\eta_0 K - (1-k)\beta \nu_n + corr(O(\varepsilon^\nu)) \]
with \[ k = \frac{c^j_{\beta}}{c^j_{\alpha}} \]

Conservation\[ (c^i_{\alpha} - c^i_{\beta})\nu_n = \left[ D \partial_n c \right]^+ + corr(O(\varepsilon^\nu)) \]
Multi-grain and multi-phase models

- Multi-phase-field model
  - Phase fields $\varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p$, $\sum_{i=1}^{p} \varphi_i = 1$
  - Interfacial energy $f_{\text{int}} = \sum_{i \neq j} \frac{4\sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} | \nabla \varphi_i \cdot \nabla \varphi_j | + \varphi_i \varphi_j \right\}$

Steinbach et al.

MICRESS phase-field code

Multi-grain and multi-phase models

• Multi-phase-field model

• Multi-order parameter models

\[ \eta_1, \eta_2, ..., \eta_i(r,t), ..., \eta_p, \quad \left( \sum_{i=1}^{p} \eta_i \neq 1 \right) \]

- Order parameters

\[ f_{\text{int}} = m \left( \sum_{i=1}^{p} \left( \frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\nabla \eta_i)^2 \]

- Interfacial energy

\[ \kappa(\eta) = \frac{\sum_{i=1}^{p} \sum_{j<i} \kappa_{i,j} \eta_i^2 \eta_j^2}{\sum_{i=1}^{p} \sum_{j<i} \eta_i^2 \eta_j^2} \]

L.-Q. Chen and W. Yang, PRB, 50 (1994) p15752

A. Kazaryan et al., PRB, 61 (2000) p14275
Multi-grain and multi-phase models

- **Multi-phase-field model**
  - Phase fields $\phi_1, \phi_2, \phi_3, \ldots \phi_p$, $\sum_{i=1}^{p} \phi_i = 1$
  - Interfacial energy $f_{\text{int}} = \sum_{i \neq j}^{p} \frac{4\sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} |\nabla \phi_i \cdot \nabla \phi_j | + \phi_i \phi_j \right\}$, $0 < \phi_{i,j} < 1$

- **Multi-order parameter models**
  - Order parameters $\eta_1, \eta_2, \ldots, \eta_i(r,t), \ldots, \eta_p$, $\sum_{i=1}^{p} \eta_i \neq 1$
  - Interfacial energy $f_{\text{int}} = m \left( \sum_{i=1}^{p} \left( \frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i}^{p} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\nabla \eta_i)^2$

$\kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i} \kappa_{i,j} \eta_i^2 \eta_j^2 / \sum_{i=1}^{p} \sum_{j<i} \eta_i^2 \eta_j^2$

Stevenbach et al. 
MICRESS phase-field code

L.-Q. Chen and W. Yang, PRB, 50 (1994) p15752

A. Kazaryan et al., PRB, 61 (2000) p14275
Multi-phase and multi-phase models

- Vector valued model
  - Orientation field ($\theta$) and phase field ($\phi$)
  - Free energy $f_{\text{int}} = f(\phi, |\nabla \phi|, |\nabla \theta|)$

- 2-phase solidification
  - Phase fields $\varphi_1, \varphi_2, \varphi_3$, $\sum_{i=1}^{3} \varphi_i = 1$
  - Free energy $f_{\text{int}} = f(\phi_1, \phi_2, \phi_3) + \frac{\kappa}{2} \sum_{i=1}^{3} (\nabla \phi_i)^2$
    - No third-phase contributions
    - Bulk energy interpolation function with 0-slope

R. Folch and M. Plapp, PRE, 72 (2005) n° 011602