Phase Field Formulation for Microstructure Evolution in Oxide Ceramics

Corning

Problem Presenter: Leslie Button (Corning)
Problem Participants: Daniel Anderson\textsuperscript{1}, Chris Breward\textsuperscript{2}, Yanping Chen\textsuperscript{3}, Brendan DeCourcy\textsuperscript{7}, David A. Edwards\textsuperscript{5}, Joseph D. Fehribach\textsuperscript{4}, Nguyenh\textsuperscript{Ho}, Humi Mayer\textsuperscript{4}, David Nigro\textsuperscript{6}, Harrison D. Potter\textsuperscript{12}, Colin Please\textsuperscript{2}, Aminur Rahman\textsuperscript{8}, Christopher Raymond\textsuperscript{5}, Lee Safranek\textsuperscript{9}, Tianheng Wang\textsuperscript{10}, Chandara Wijeratnem\textsuperscript{11}, Tom Witelski\textsuperscript{12}, Xin Yang\textsuperscript{9}, Maxim Zyskin\textsuperscript{13}

\textsuperscript{1) George Mason University, 2) Oxford University, 3) University of Texas, Dallas, 4) Worcester Polytechnic Institute, 5) University of Delaware, 6) University of Manchester, 7) Rensselaer Polytechnic Institute, 8) New Jersey Institute of Technology, 9) Simon Fraser University, 10) North Carolina State University, 11) St. Cloud State University, 12) Duke University, 13) Rutgers University}

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Outline

I Motivation

II Background
   i Key Definitions
   ii Cahn - Hilliard equations
   iii Previous work (by Wheeler et. al.)

III Cogswell and Carter phase field model.
   i Multi-phase – multi-component model
   ii Binary system model
   iii Derivation of governing equations
   iv Asymptotics
   v Stability analysis

IV Huelens’ phase field model

V Conclusion
Corning is interested in better ceramics with better properties.

We would like to understand various phase field models that model such phenomena.
Key definitions

- In the models we looked at, the phase $\phi$ is defined to be the state of the matter.
- The component $c$ is defined to be a chemically independent constituent of a phase of a system.
- These are under the constraints:

\[
\sum_{\alpha=1}^{M} \phi_\alpha = 1 \\
\sum_{i=1}^{N} c_i = 1
\]
Cahn-Hilliard Eq. (1958)

- Order parameter \( c \)
- Two phases

\[
\frac{\partial c}{\partial t} = \frac{d^2}{dx^2} \left( f'(c) - \kappa \frac{\partial^2 c}{\partial x^2} \right)
\]

\[
f(c) = c^2(1 - c)^2, \quad \mathcal{F}[c] = \int_{-\infty}^{\infty} \left( f(c) + \frac{1}{2} \kappa \left( \frac{dc}{dx} \right)^2 \right) dx
\]

- Describes phase separation nucleation.
- \( \int_{-\infty}^{\infty} cdx \) is conserved
Free energy for a two-phase binary alloy, smooth function $f(\phi, c)$

$$
\mathcal{F}[\phi, c] = \int_{-\infty}^{+\infty} \left[ f(\phi, c) + \frac{1}{2} \kappa \left( \frac{dc}{dx} \right)^2 + \frac{1}{2} \lambda \left( \frac{d\phi}{dx} \right)^2 \right] dx
$$

Calculus of Variations for Equilibrium: (conserved $c$):

$$
\frac{\partial f}{\partial \phi} - \lambda \frac{d^2 \phi}{dx^2} = 0, \quad \frac{\partial f}{\partial c} - \kappa \frac{d^2 c}{dx^2} = A \quad (A = \text{Lagrange Multiplier})
$$

WBM show that there is a conserved quantity $H$

$$
H = Ac - f(\phi, c) + \frac{1}{2} \lambda \left( \frac{d\phi}{dx} \right)^2 + \frac{1}{2} \kappa \left( \frac{dc}{dx} \right)^2
$$
Far-field conditions: $x \to -\infty$ [$\phi \to 1$, $c \to c_{-\infty}$] and $x \to \infty$ [$\phi \to 0$, $c \to c_{\infty}$] lead to three conditions that correspond to the common tangent construction

$$A = \frac{\partial f}{\partial c}(0, c_{\infty}) = \frac{\partial f}{\partial c}(1, c_{-\infty}) = \frac{f(0, c_{\infty}) - f(1, c_{-\infty})}{c_{\infty} - c_{-\infty}},$$

AND two other conditions satisfied by careful construction of $f(\phi, c)$.

Key point of interest to Corning: This careful construction does not generalize well to multi-phase/multi-species systems.
From Cogswell and Carter we have the evolution equations:

\[
\begin{align*}
\frac{\partial c}{\partial t} &= \frac{D}{nRT} \nabla \cdot \left( c(1 - c) \nabla \left( \frac{\delta F}{\delta c} \right) \right) \quad \text{(Cahn - Hilliard)} \\
\frac{\partial \phi}{\partial t} &= -r_\alpha \frac{\delta F}{\delta \phi_\alpha} \quad \text{(Allen - Cahn)}
\end{align*}
\]

Where $D$ is diffusivity, $R$ is gas constant, and $T$ is temperature. These come from Nernst - Einstein relation.
Phase Field Model of Cogswell and Carter

- Model has a non-smooth free energy functional (multiple obstacle in the phase fields) (Cogswell and Carter 2011)

\[
F[\vec{c}, \vec{\phi}] = \int_V F(\vec{c}, \vec{\phi})dV
\]

\[
F(\vec{c}, \vec{\phi}) = \sum_{\alpha=1}^{M} \phi_\alpha G_\alpha(\vec{c}) + U(\vec{\phi}) + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \kappa_{ij} \nabla c_i \cdot \nabla c_j
\]

\[
+ \frac{1}{2} \sum_{\alpha=1}^{M-1} \sum_{\beta=1}^{M-1} \lambda_{\alpha\beta} \nabla \phi_\alpha \cdot \nabla \phi_\beta
\]

- $\vec{c}$ is a dim $N - 1$ vector of mole fractions.
- Similarly, $\vec{\phi}$ is a dim $M - 1$ vector of phase.
- $G_\alpha(\vec{c})$ are bulk free energy densities of the phases.
- $\kappa$ and $\lambda$ are gradient energy coefficients (positive definite matrices).
The potential $U(\vec{\phi})$ for a binary system (one independent phase) is:

\[
\begin{cases}
U(\vec{\phi}) = \phi(1 - \phi), & 0 < \phi < 1 \\
U(\vec{\phi}) = +\infty, & \text{otherwise}
\end{cases}
\]

E.g. for a binary system:
The Phase Potential

- The infinite barrier potential can cause issues at the boundaries due to discontinuity.
- Introduce a smooth function instead.
- Example:

\[ \tilde{U}_\varepsilon(\phi) = \phi(1 - \phi) + \frac{\varepsilon}{\phi(1 - \phi)} \]
For the two phase, two component system, the function \( \tilde{F} \) simplifies to

\[
\tilde{F} \left( c, \phi, \frac{dc}{d\tilde{x}}, \frac{d\phi}{d\tilde{x}} \right) = \phi \tilde{G}_1(c) + (1 - \phi) \tilde{G}_2(c) + \tilde{U}(\phi) \\
+ \frac{\tilde{\kappa}}{2} \left( \frac{dc}{d\tilde{x}} \right)^2 + \frac{\tilde{\lambda}}{2} \left( \frac{d\phi}{d\tilde{x}} \right)^2.
\]

In the far-field, we want to satisfy the pure phase assumption:

\[
\phi(+\infty) = 0 \quad \phi(-\infty) = 1.
\]

Similarly, we expect \( c \) to tend towards a constant value away from the interface.
After non-dimensionalizing the energy equation, we have

\[
F \left( c, \phi, \frac{dc}{dx}, \frac{d\phi}{dx} \right) = \phi G_1(c) + (1 - \phi) G_2(c) + WU(\phi)
\]

\[
+ \frac{1}{2} \left( \frac{dc}{dx} \right)^2 + \frac{\lambda}{2} \left( \frac{d\phi}{dx} \right)^2.
\]

with the parameters

\[
W = \frac{\tilde{W}}{\Delta \tilde{G}}, \quad \lambda = \frac{\tilde{\lambda}}{\tilde{\kappa}}.
\]
In the energy equation, $G_1(c)$ and $G_2(c)$ represent the bulk free energy density.

Can be complicated functions, but the relevant parts can be approximated as quadratic:

$$G_\alpha(c) = G_{\alpha,0} + \frac{1}{2} G_{\alpha,2} (c - c_\alpha^*)^2, \quad G_{\alpha,2} > 0.$$
Euler Lagrange Equations

- We use the calculus of variations to minimize the energy of the system.

- Resulting equilibrium equations:

\[
\lambda \frac{d^2 \phi}{dx^2} = G_1(c) - G_2(c) + WU'(\phi), \quad \lambda \frac{d \phi}{dx}(\pm \infty) = 0
\]

\[
\frac{d^2 c}{dx^2} = \phi G'_1(c) + (1 - \phi) G'_2(c) - \mu, \quad \frac{dc}{dx}(\pm \infty) = 0
\]

- With \( c_- = c(-\infty), \ c_+ = c(+\infty) \).

- The parameter \( \mu \) is a Lagrange multiplier that arises from the conservation of mass.
Far-field conditions

From the Euler-Lagrange equations we have the following conditions:

\[ G_1(c_-) - G_2(c_-) + WU'(1) = 0, \]
\[ G_1(c_+) - G_2(c_+) + WU'(0) = 0, \]
\[ G_2'(c_-) = \mu, \]
\[ G_1'(c_+) = \mu. \]
One component - two phase simulation via finite differences
Time evolution run via finite differences
In case the movie doesn’t work
The Exclusion Zones

- We expect $\phi$ to tend towards pure phase at infinity.
- Boundary conditions:

$$\phi(x) = \begin{cases} 
1, & x \leq x_-, \\
0, & x \geq x_+.
\end{cases}$$

- We use these values for $\phi$ to find equations for $c$ in the exclusion zones.
- Resulting equations:

$$c_<(x) = c_- + A_- \exp(G_{1,2}(x - x_-))$$
$$c_>(x) = c_+ - A_+ \exp(-G_{2,2}(x - x_+)).$$

- The $c$’s tend towards $c_-$ and $c_+$, and decay slightly towards the barrier.
Asymptotics with Large $W$

- Taking $W \to \infty$, we find the discontinuous leading order equation

$$
\lambda \frac{d^2 \phi}{dx^2} = G_1(c) - G_2(c) + WU'(\phi) \to U'_0(\phi) = 1 - 2\phi = 0
$$

$$
\phi = \frac{1}{2}, \quad |x| < x_>.
$$

- Introduce boundary layer, let

$$
z = W^{1/2}(x - x_>) , \quad \Phi(z) = \phi(x).
$$

- Resulting equation:

$$
\lambda \frac{d^2 \Phi}{dz^2} + 2\Phi = 1.
$$

- The solutions to the above equation oscillate, which cannot match the matching condition that $\Phi(z = -\infty) = \phi(x = x_<) = 1/2$. 
We expect $\Phi(z)$ to vary only in some interval $(-z_b, z_b)$, with boundary conditions:

$$
\Phi(z) = \begin{cases} 
1, & z \leq -z_b, \\
0, & z \geq z_b.
\end{cases}
$$

From the boundary conditions on $\Phi$, we find a leading order solution

$$
\Phi_0(z) = \frac{1}{2} \left(1 - \frac{\sin z \sqrt{2/\lambda}}{\sin z_b \sqrt{2/\lambda}}\right), \quad |z| < z_b.
$$
We use the nondimensional version of the evolution equation from Cogswell and Carter for large $W$:

$$\frac{\partial \Phi}{\partial t} = -r \frac{\delta \mathcal{F}}{\delta \phi} = -r \left[ 1 - 2\Phi - \lambda \frac{\partial^2 \Phi}{\partial z^2} \right].$$

Introduce small perturbation with exponential decay:

$$\Phi(z, t) = \Phi_0(z) + \varepsilon e^{At} \cos \left( \frac{(2n + 1)\pi z}{2z_b} \right), \quad n \geq 0.$$

Using the time evolution equation, we find

$$A = r \left[ 2 - \lambda \frac{(2n + 1)^2 \pi^2}{4z_b^2} \right].$$

We must require $A < 0$ for decay, for all $n$.

Using the same kind of analysis one would use on the Fisher equation, we get: $z_b = \frac{\pi}{2} \sqrt{\frac{\lambda}{2}}$. 
Consider the following simple case for the stability analysis

- Two-phase, two-component system in one-dimension
- \( c = c_1 \) with \( c_2 = 1 - c \) where \( 0 < c < 1 \)
- \( \phi = \phi_1 \) with \( \phi_2 = 1 - \phi_1 \) where \( 0 < \phi < 1 \)
- Simple quadratic functions for the free energies for the individuals phases

\[
G_1(c) = 50(c - \frac{1}{5})^2 \quad G_2(c) = 5 + 150(c - \frac{4}{5})^2
\]
Stability Analysis of the Cogswell-Carter model (Governing Equations)

\[ \frac{\partial \phi}{\partial t} = \lambda \frac{\partial^2 \phi}{\partial x^2} + G_2(c) - G_1(c) - U'(\phi), \]

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ c(1 - c) \frac{\partial}{\partial x} \left( \phi G_1'(c) + (1 - \phi) G_2'(c) - \kappa \frac{\partial^2 c}{\partial x^2} \right) \right] \]

\[ U'(\phi) = \begin{cases} 
W(1 - 2\phi) & 0 < \phi < 1, \\
\infty & \text{else}
\end{cases} \]
Linear perturbations to a spatially homogeneous single phase,

\[ c(x, t) \sim \bar{c} + \varepsilon A \cos(kx)e^{\sigma t} \quad \phi(x, t) \sim \bar{\phi} + \varepsilon B \cos(kx)e^{\sigma t} \]

Substituting into the PDEs and linearizing
→ determine a relation between the \( c \) and \( \phi \), depending on the parameter \( W \)

\[ \bar{\phi} = \frac{1}{2} - \frac{100\bar{c}^2 - 220\bar{c} + 99}{2W} \]

→ For \( k = 0 \): \( \sigma_1 = 0 \): neutrally stable mode, \( \sigma_2 = 2W > 0 \): an unstable mode.
Criticism of the Cogswell-Carter model

- Numerically, if $\phi \leq 0 \rightarrow \phi = 0$ and if $\phi \geq 1 \rightarrow \phi = 1$
- Cogswell and Carter proposed the algorithm which should restrict the set of $\phi_i$’s to the physically acceptable region (0,1).

However,... the algorithm can be shown to be flawed for two reasons
  - If $\phi_N < 0$ is violated, its value does not end corrected.
  - The output algorithm is not invariant under cyclic permutations for relabeling the phases.
Heulens et.al (2011), building on a large body of preceding work (Moelans, Eiken, Steinbach, et.al.) propose the multicomponent, multi-phase field model:

\[
F = \sum_{\alpha=1}^{M} \phi_\alpha G_\alpha(\bar{c}_\alpha) + U(\bar{\eta}) + \frac{\lambda}{2} \sum_{\alpha=1}^{M} |\nabla \eta_\alpha|^2
\]

\[
\phi_\alpha = \frac{\eta_\alpha^2}{\sum_\beta \eta_\beta^2}
\]

\[
U(\bar{\eta}) = U_0 \left( \sum_{\alpha=1}^{M} \left( \frac{\eta_\alpha^4}{4} - \frac{\eta_\alpha^2}{2} \right) + \gamma \sum_{\alpha=1}^{M} \sum_{\beta>\alpha} \eta_\alpha^2 \eta_\beta^2 + \frac{1}{4} \right)
\]
c_\alpha \text{ is determined by a constrained minimization problem.}

For the binary two-phase case

$$\min\{\phi_1 G_1(c_1) + \phi_2 G_2(c_2)\}.$$ 

subject to the constraint

$$c = \phi_1 c_1 + \phi_2 c_2.$$
Heulens phase field model (equilibrium)

- Free energy for a two-phase binary alloy, smooth function \( f(\eta_1, \eta_2, c) \)

\[
\mathcal{F}[\eta_1, \eta_2, c] = \int_{-\infty}^{\infty} \left[ f(\eta_1, \eta_2, c) + \frac{1}{2} \kappa \left( \frac{dc}{dx} \right)^2 + \frac{1}{2} \lambda_1 \left( \frac{d\eta_1}{dx} \right)^2 + \frac{1}{2} \lambda_2 \left( \frac{d\eta_2}{dx} \right)^2 \right] dx
\]

- \( \eta_1 \) and \( \eta_2 \) are phase field variables. Phase fractions \( \phi_1 \) and \( \phi_2 \) are

\[
\phi_1 = \frac{\eta_1^2}{\eta_1^2 + \eta_2^2}, \quad \phi_2 = \frac{\eta_2^2}{\eta_1^2 + \eta_2^2}
\]

- We demonstrated that, as in WBM, this model recovers the common tangent construction and meets all other equilibrium conditions using the careful construction for \( f(\eta_1, \eta_2, c) \) by Heulens et al.

- Key point of interest to Corning: This careful construction does generalize well to multi-phase/multi-species systems
Conclusion

- We analyzed the Cogswell-Carter and Heulens et al. models.
- Asymptotic analysis was used to understand the behavior of the phase and component in certain regions for the Cogswell-Carter model.
- However, while the Cogswell-Carter model can be generalized to multi-phase – multi-component systems, the potential $U$ caused problems with the numerics.
- The Heulens et al. model may be able to remedy this.