Phase Field Formulation for Microstructure Evolution in Oxide Ceramics

Corning

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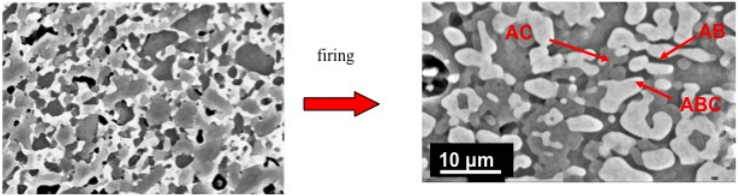
Motivation

- 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 ϕ 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

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

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

- Describes phase separation nucleation.
- $\int_{-\infty}^{\infty} cdx$ is conserved

Previous Work: Wheeler, Boettinger & McFadden 1993

- 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):

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

- WBM show that there is a conserved quantity H

$$H = Ac - f(\phi, c) + \frac{1}{2}\lambda \left(\frac{d\phi}{dx} \right)^2 + \frac{1}{2}\kappa \left(\frac{dc}{dx} \right)^2$$

Previous Work: Wheeler, Boettinger & McFadden 1993

- 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

Cogswell-Carter evolution equations

From Cogswell and Carter we have the evolution equations:

$$\frac{\partial c}{\partial t} = \frac{D}{nRT}\nabla \cdot \left(c(1-c)\nabla \left(\frac{\delta F}{\delta c} \right) \right) \qquad \text{(Cahn - Hilliard)}$$
$$\frac{\partial \phi}{\partial t} = -r_\alpha \frac{\delta F}{\delta \phi_\alpha} \qquad \text{(Allen - Cahn)}$$

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)

$$\mathcal{F}[\vec{c},\vec{\phi}] = \int_V F(\vec{c},\vec{\phi})\mathrm{d}V$$

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

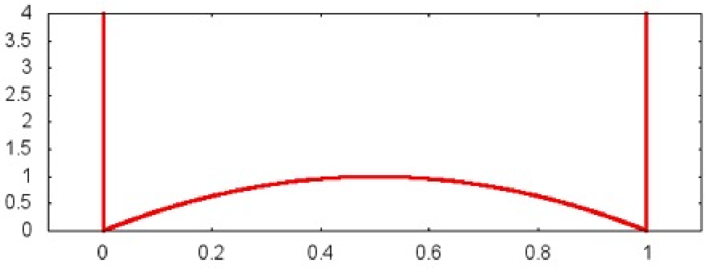
- $\vec{c}$ is a dim $N-1$ vector of mole fractions.
- Similarly, $\vec{\phi}$ is a dim $M-1$ vector of phase.
- $G_\alpha(\vec{c})$ are bulk free energy densities of the phases.
- κ and λ are gradient energy coefficients (positive definite matrices).

Phase Field Model of Cogswell and Carter

The potential $U(\vec{\phi})$ for a binary system (one independent phase) is:

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

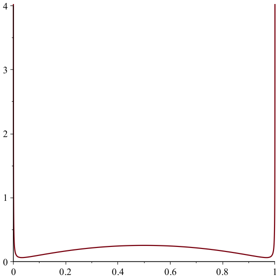
E.g. for a binary system:



The Phase Potential

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

$$\tilde{U}_\varepsilon(\phi) = \phi(1-\phi) + \frac{\varepsilon}{\phi(1-\phi)}$$



The Binary System Energy Equation (Cogswell-Carter)

- 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:

$$\phi(+\infty) = 0 \qquad \phi(-\infty) = 1.$$

- Similarly, we expect c to tend towards a constant value away from the interface

Non-dimensionalization

- 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

$$W = \frac{\tilde{W}}{\Delta \tilde{G}}, \qquad \lambda = \frac{\tilde{\lambda}}{\tilde{\kappa}}.$$

Bulk Energy

- 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:

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

Euler Lagrange Equations

- We use the calculus of variations to minimize the energy of the system.
- Resulting equilibrium equations:

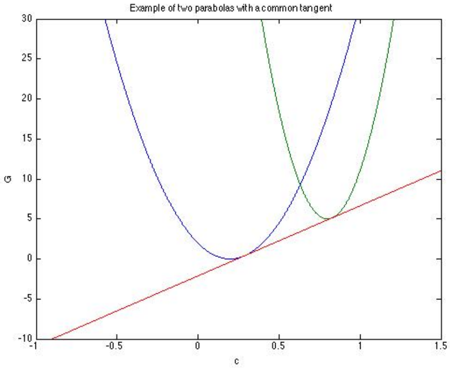
$$
\begin{aligned}
\lambda \frac{d^2\phi}{dx^2} &= G_1(c) - G_2(c) + WU'(\phi), &\qquad \lambda \frac{d\phi}{dx}(\pm\infty) = 0 \\
\frac{d^2 c}{dx^2} &= \phi G_1'(c) + (1-\phi) G_2'(c) - \mu, &\qquad \frac{dc}{dx}(\pm\infty) = 0
\end{aligned}
$$

- With $c_- = c(-\infty)$, $c_+ = c(+\infty)$.
- The parameter μ is a Lagrange multiplier that arises from the conservation of mass.

Far-field conditions

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

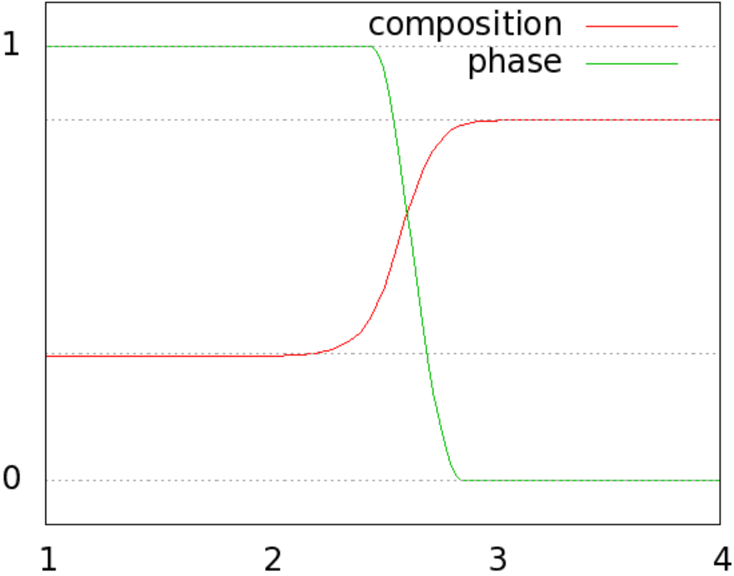
$$
\begin{aligned}
G_1(c_-) - G_2(c_-) + WU'(1) &= 0, \\
G_1(c_+) - G_2(c_+) + WU'(0) &= 0, \\
G_2'(c_-) &= \mu, \\
G_1'(c_+) &= \mu.
\end{aligned}
$$



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 ϕ 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 ϕ to find equations for c in the exclusion zones.
- Resulting equations:

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

- 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

$$\lambda \frac{d^2\phi}{dx^2} = G_1(c) - G_2(c) + WU'(\phi) \to U_0'(\phi) = 1 - 2\phi = 0$$
$$\phi = \frac{1}{2}, \qquad |x| < x_>.$$

- Introduce boundary layer, let

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

- 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 $\Phi(z = -\infty) = \phi(x = x_>^-) = 1/2$.

Asymptotics (continued)

- 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 Φ, we find a leading order solution

$$\Phi_0(z) = \frac{1}{2}\left(1 - \frac{\sin z\sqrt{2/\lambda}}{\sin z_b\sqrt{2/\lambda}}\right), \qquad |z| < z_b.$$

Asymptotics (continued)

- 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:

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

- 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: $z_b = \frac{\pi}{2}\sqrt{\frac{\lambda}{2}}$

Stability Analysis of the Cogswell-Carter model

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 idividuals phases

$$G_1(c) = 50(c - \frac{1}{5})^2 \qquad G_2(c) = 5 + 150(c - \frac{4}{5})^2$$

Stability Analysis of the Cogswell-Carter model (Governing Equations)

$$
\begin{aligned}
\frac{\partial \phi}{\partial t} &= \lambda \frac{\partial^2 \phi}{\partial x^2} + G_2(c) - G_1(c) - U'(\phi), \\
\frac{\partial c}{\partial t} &= \frac{\partial}{\partial x}\left[c(1-c) \frac{\partial}{\partial x}\left(\phi G_1'(c) + (1-\phi) G_2'(c) - \kappa \frac{\partial^2 c}{\partial x^2} \right) \right] \\
U'(\phi) &= \begin{cases} W(1-2\phi) & 0 < \phi < 1, \\ \infty & \text{else} \end{cases}
\end{aligned}
$$

Stability Analysis of the Cogswell-Carter model

- Linear perturbations to a spatially homogeneous single phase,

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

- Substituting into the PDEs and linearizing
  $\rightarrow$ determine a relation between the c and ϕ, depending on the parameter W

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

  $\rightarrow$ 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 ϕ_i's to the physically acceptable region (0,1).

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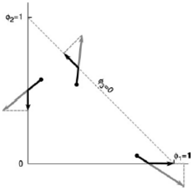

FIG. 3. The multi-obstacle projection for a three-phase system. Black points indicate initial locations in phase space, and gray arrows a possible trajectory in the absence of constraints. Constrained evolution proceeds along the bent black arrows.

Algorithm multiObstacle($\{\phi_1, \ldots \phi_{N-1}\}$)

for $\phi_i = \phi_1 \ldots \phi_{N-1}$ **do**
if $\phi_i < 0$ **then**
$\phi_i = 0$
end if
end for
$\phi_N \leftarrow 1 - \sum_{i=1}^{N-1} \phi_i$
if $\phi_N < 0$ **then**
for $\phi_i = \phi_1 \ldots \phi_{N-2}$ **do**
$\phi_i \leftarrow \phi_i + \frac{\phi_N}{N-1}$
end for
multiObstacle($\{\phi_1, \ldots \phi_{N-2}\}$)
$\phi_{N-1} \leftarrow 1 - \sum_{i=1}^{N-2} \phi_i$
end if

- 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 phase field model

Heulens et.al (2011), building on a large body of preceding work (Moelans, Eiken, Steinbach, et.al.) propose the multicomponent, multi-phase field model:

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

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

$$U(\vec{\eta}) = U_0 \left(\sum_{\alpha=1}^{M} \left(\frac{\eta_\alpha^4}{4} - \frac{\eta_\alpha^2}{2} \right) + \gamma \sum_{\alpha=1}^{M} \sum_{\beta>\alpha}^{M} \eta_\alpha^2 \eta_\beta^2 + \frac{1}{4} \right)$$

Heulens phase field model

- c_α 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 $f(\eta_1, \eta_2, c)$

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

- η_1 and η_2 are phase field variables. Phase fractions ϕ_1 and ϕ_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.