CORNING

Science & Technology

Phase field formulation for microstructure evolution in oxide ceramics*

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Motivation

- Corning makes cellular ceramic monoliths for environmental remediation (catalytic converters, diesel particulate filters)
- Microstructure governs material properties
- Can we develop models that capture key trends in reactive batch firing processes *at the microstructure level*?
  - Diffusional transport and solid state reactions driving chemical and phase transformations
  - Consumption of reactant phases; growth of product and transient phases
  - Nucleation of new phases
  - Effects of grain boundary liquids
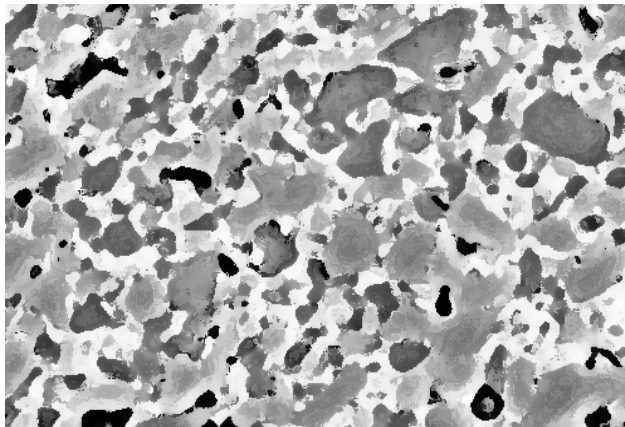
firing
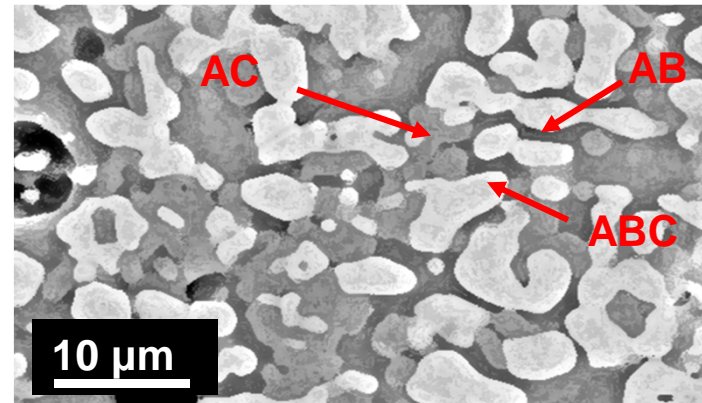
Warm-up: Phase Field Model of Cogswell & Carter

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

- Free energy functional for *N* components and *M* phases is

$$F \;=\; \int_V \left(\sum_{\alpha=1}^{M} \phi_\alpha G_\alpha(\vec{c}) + U(\vec{\phi}) \right.$$

$$\left. + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \kappa_{ij} \nabla c_i \cdot \nabla c_j + \frac{1}{2} \sum_{\alpha=1}^{M-1} \sum_{\beta=1}^{M-1} \lambda_{\alpha\beta} \nabla \phi_\alpha \cdot \nabla \phi_\beta \right) dV$$

- $\vec{c}$ is a dim *N*-1 vector of mole fractions (component *N* defined implicitly by $\sum_i c_i = 1$), and is a conserved order parameter

- Similarly $\vec{\phi}$ is a dim *M*-1 vector, and is a non-conserved order parameter

- $G_\alpha(\vec{c})$ are "bulk" free energy densities of the phases

- $\boldsymbol{\kappa}$ and $\boldsymbol{\lambda}$ are gradient energy coefficients (positive definite matrices)
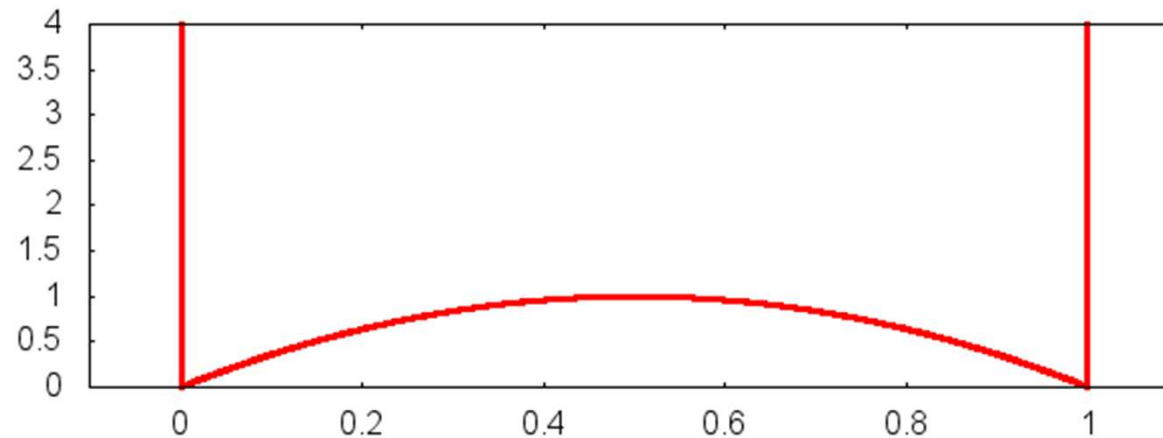
The "phase potential"

- The potential $U(\vec{\phi})$ is

$$U(\vec{\phi}) = \sum_{\alpha=1}^{M} \sum_{\beta=1}^{\alpha-1} W_{\alpha\beta}\, \phi_\alpha\, \phi_\beta,\; 0 \le \phi_\alpha \le 1 \text{ for all } \alpha = 1, \dots, M$$

$$U(\vec{\phi}) = +\infty, \text{ otherwise}$$

- E.g. for a binary system (one independent phase)

Cogswell-Carter transient evolution

- Follows standard formal development for conserved and non-conserved order parameters
  - (After making some special assumptions on compositional dependence of the Onsager transport coefficients)
- Get a "generalized diffusion equation" for the composition fields $\vec{c}$, with gradients of chemical potential replaced by gradients of $\delta F/\delta c$
  - Standard Cahn-Hilliard development, get terms of the form $\kappa \nabla^2 c$ as part of the composition fluxes
- Gradient flow ($\partial \phi_\alpha / \partial t = -M_\phi \, \delta F/\delta \phi_\alpha$) assumed for the phase field variables, i.e. Allen-Cahn type dynamics

Analysis of a single interface at equilibrium

- Wanted to do a standard thing: understand the nature of a simple planar equilibrium interface
  - If nothing else, for parameter identification: how do coefficients relate interface energies, diffuse thickness?
- Start with the simplest possible situation: binary composition space, interface between only two phases
- Equilibrium: "generalized diffusion potential" is uniform in space, and zero time derivative for phase variable

$$\frac{\delta F}{\delta c} = K,$$

$$\frac{\delta F}{\delta \phi} = 0,$$

- For some K to be determined

Governing equations

- Let "A" and "B" be labels for the phases
- In 1D planar interface context, equilibrium conditions are

$$\lambda \frac{d^2\phi}{dx^2} = G_A(c) - G_B(c) + W(1 - 2\phi),$$

$$\kappa \frac{d^2 c}{dx^2} = \phi G'_A(c) + (1 - \phi)G'_B(c) - K.$$

- Boundary conditions: far from interface, expect uniform compositions (at values consistent with the two-phase equilibrium, say c_A^*, c_B^*)
- Also uniform phase (zero and one)

Composition equation

- No problem: far from interface, where $\phi \to 0$ or $\phi \to 1$, and where spatial derivatives presumably vanish, we get two conditions

$$
\begin{aligned}
G'_A(c^*_A) &= K, \\
G'_B(c^*_B) &= K.
\end{aligned}
$$

- Consistent with usual "common tangent" condition for thermodynamic equilibrium

Phase equation

- The putative (barrier free) "right hand side" for the phase equilibrium equation takes on *non-zero values* far from the interface:

$$G_A(c_A^*) - G_B(c_A^*) + W, \qquad \text{for } \phi \to 0, c \to c_A^*$$
$$G_A(c_B^*) - G_B(c_B^*) - W, \qquad \text{for } \phi \to 1, c \to c_B^*.$$

- No way a single *W* value can make both of these limits zero. Conclusion: generically, the phase field "*must hit the barrier*": it does not have an asymptotic decay to infinity
- Conclusion supported by analysis of Blowey & Elliott (1990)

Failed attempt to establish a solution

- Assume quadratic free energies for simplicity
- Since we know ϕ becomes *strictly* zero at some position "to the left" of the interface, and *strictly* one at another position "to the right", we can solve the composition equation in the "far field" regions analytically (get exponential functions)
- Let the point where ϕ "leaves the barrier" be $x = 0$ and the point where it first "reenters the barrier" be $x = \ell$. The analytical solution for the composition outside $0 < x < \ell$ gives us two boundary conditions

$$c'(0) - \zeta_A(c(0) - c_A^*) = 0,$$
$$c'(\ell) + \zeta_B(c(\ell) - c_B^*) = 0,$$
$$\zeta_A = \sqrt{\frac{G_A''}{\kappa}}, \quad \zeta_B = \sqrt{\frac{G_B''}{\kappa}}.$$

Failure (completed)

- But what are the boundary conditions on ϕ (or more properly, on $d\phi/dx$) at $x = 0, \ell$?!
- If "arbitrary" values for $d\phi/dx$ at the boundaries of the "phase interface region" are used…
  - Let $\phi(x = 0) = 0$; assume some value for $\phi'(x = 0)$
  - Guess $c(x = 0)$; integrate ODE's until $\phi = 1$ (implicitly defining the value of ℓ); refine guess for initial composition until boundary conditions at $x = \ell$ are satisfied
  - Not unique? Get solution family parameterized by $\phi'(x = 0)$
- Is there a way to describe true "energy minimization" for a problem like this? What conditions assure it is well-defined?
- Blowey & Elliot (1990) say this is a "differential inclusion problem"

Natural followup questions

- *Most important:* what if far-field boundary conditions on the composition field "c" don't correspond to final phase equilibrium?
  - The case of practical interest: transient evolution of the phase domain(s)
  - What is the velocity of the interface? How does interface mobility b depend on model parameters (λ, κ, W), and what is the natural "driving force" F in the relationship $v = b \cdot F$?
- Ternary, quaternary, general N composition spaces?
- Can we say anything meaningful about the role of "off-diagonal" terms in the gradient energy coefficients?

Main Event: "Quasi-equilibrium" phase field approach

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

- Free energy functional:

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

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

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

Observations

- The "eta trick" means that phase variables *automatically* are in the [0,1] range, and sum to 1. (No infinite barrier needed to impose that constraint ☺)

- The potential function U has degenerate minima at "pure phases", saddle points between (exhaustive discussion in Moelans et.al. 2008).

- U_0 and λ are not constants, but instead are taken as "phase weighted averages" of values assigned to *each binary interface*, according to desired surface energy and diffuse thicknesses for those interfaces:
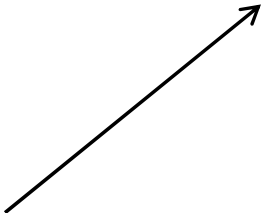
$$U_0 = \frac{\sum_{\alpha,\beta} U_{\alpha\beta} \eta_\alpha^2 \eta_\beta^2}{\sum_{\alpha,\beta} \eta_\alpha^2 \eta_\beta^2},$$

$$\lambda = \frac{\sum_{\alpha,\beta} \lambda_{\alpha\beta} \eta_\alpha^2 \eta_\beta^2}{\sum_{\alpha,\beta} \eta_\alpha^2 \eta_\beta^2}.$$

$$\sigma_{\alpha\beta} = \frac{\sqrt{4 U_{\alpha\beta} \lambda_{\alpha\beta}}}{3},$$

$$\ell_{\alpha\beta} = \sqrt{\frac{8 \lambda_{\alpha\beta}}{U_{\alpha\beta}}}.$$

Key construction in this family of models

- The "compositional energy density" is written as a sum over phases, weighted by phase fractions, as one might expect

$$f_{\text{composition}} = \sum_{\alpha=1}^{M} \phi_\alpha G_\alpha(\vec{c}_\alpha)$$

But notice that each phase gets its own composition!

Argument for the quasi-equilibrium conditions

- What determines the phase compositions $\vec{c}_\alpha$?
- First condition: $\sum_\alpha \phi_\alpha \vec{c}_\alpha = \vec{c}$
- Second condition: argue that
  - these variables are "non-conserved", so follow a gradient flow,
  - within spatially small region ("the interface"), equilibrium *of phase compositions* is established "quickly" compared to overall evolution of the phase variable (which requires interface to *move*, i.e. collective rearrangement of lots of atoms)
- Use Lagrange multiplier(s) for first condition(s), then the second condition yields the so-called "quasi-equilibrium" conditions for the phase compositions

The quasi-equilibrium conditions

$$
c^i = \sum_{\alpha=1}^{M} c_\alpha^i, \quad i = 1, \ldots, N-1,
$$

$$
P^i = \frac{\partial G_\alpha}{\partial c_\alpha^i}, \quad i = 1, \ldots, N-1, \ \alpha = 1, \ldots, M.
$$

- $(M+1)*(N-1)$ equations
- Same number of unknowns (phase compositions plus the Lagrange multipliers P)
- Further analysis shows that
  - Lagrange multipliers are chemical potential differences, $P^i = \mu_\alpha^i - \mu_\alpha^N$
  - The same compositions are obtained no matter which component we choose as "number N"
- *This is not equilibrium*: "phase fractions" are held fixed!

Evolution equations

- For completeness, the model's time evolution (as we prefer to write it) is governed by

$$\frac{\partial c^i}{\partial t} = -\nabla \cdot J^i,$$

$$J^i = -\sum_{\alpha=1}^{M} \phi_\alpha D_\alpha^{ij} \nabla c_\alpha^j,$$

Inter-diffusivities often poorly known, but that's a problem for another day

$$\frac{\partial \eta_\alpha}{\partial t} = -M \frac{\delta F}{\delta \eta_\alpha}$$

$$= -M \left\{ U_0 \left(\eta_\alpha^3 - \eta_\alpha + 2\gamma \eta_\alpha \sum_{\beta \neq \alpha} \eta_\beta^2 \right) - \lambda \nabla^2 \eta_\alpha \right.$$

$$\left. + \sum_{\beta=1}^{M} \frac{\partial \phi_\beta}{\partial \eta_\alpha} \left(G_\alpha - \sum_{i=1}^{N-1} P^i c_\alpha^i \right) \right\}$$

"Parallel tangent planes" between phases; at equilibrium, get "common tangent planes"

Solution of the quasi-equilibrium equations

- If free energies can be (locally) described by quadratic functions, then the quasi-equilibrium equations turn into a bunch of linear equations

- Not much further theoretical analysis done to figure out when the equations "make sense"

  - Starting from arbitrary initial conditions, e.g. a "sharp interface", phase compositions apparently can be driven to unphysical values ($c<0$, $c>1$) during the "very early transient".

  - But in general, all works out in practice (e.g. in COMSOL)

- More importantly, apparently free energy *curvature* makes a huge difference

- And we have systems where phases are almost perfectly stoichiometric!

Treatment of stoichiometric phases

- What is a good strategy for dealing with stoichiometric phases? How can we make the quasi-equilibrium conditions more "numerically tractable" for high curvature phases?
  - Could an asymptotic analysis for the "large $G''(\vec{c})$ limit" be fruitful?
  - Could we describe certain phases as "dead"? Instead of having an overwhelming influence on the compositions of the other phases, make that influence negligible… but then have a way to describe such phases as "donors" or "acceptors" of mass flux only at their interfaces?
  - Other approaches?

References

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