Phase Field Formulation for Microstructure Evolution in Oxide Ceramics

Problem Presenter

Leslie Button, Corning

Report Editor

David A. Edwards, University of Delaware

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Preface

At the 29th Annual Workshop on Mathematical Problems in Industry (MPI), Leslie Button of Corning presented a problem concerning microstructure evolution in oxide ceramics. The problem consisted of two parts, both involving phase field models. In particular, each part addressed the issue of how to maintain the phase variables in the range $[0, 1]$.

The first problem concerned the analysis of the *Cogswell model*, which uses an obstacle potential (infinite barrier) to keep the phase variables in the proper range. The second was the analysis of the more complicated *Heulens model*, which introduces secondary variables into the analysis to keep the phase variables in the proper range.

This manuscript is really a collection of reports from teams in the group working on one or both aspects of the problem. Here is a brief summary of each:

1. Anderson *et al.* outline the general problem with discussions of both models and some asymptotic results for the Cogswell model.
2. Fehribach discusses some subtleties of the infinite barrier, in particular the subderivative.
3. Zyskin discusses the well-posedness of the Cogswell system (number of conditions matching number of unknown constants) and gives an algorithm for finding the energy minimizer.
4. Witelski performs some linear stability analysis for both models.
5. Potter performs a careful derivation of the Cogswell model and performs numerical simulations for some simple cases.
6. DeCourcy analyzes the Heulens model and looks at some asymptotic limits.
7. Nigro and Rahman use shooting and finite-difference methods to analyze the Cogswell model.
8. Chen and Wang also use shooting methods to analyze the Cogswell model.
9. Ho and Witelski point out some shortcomings of the published algorithm to solve the 3-phase Cogswell model.
10. Safranek *et al.* perform numerical simulations of the time-dependent Cogswell and Heulens models.

In addition to the authors of these reports, the following people participated in the group discussions:

- Chris Breward, Oxford University
- Humi Mayer, Worcester Polytechnic Institute
- Colin Please, Oxford University
- Chandana Wijeratne, St. Cloud State University

Special recognition is due to Nguyenho Ho, Lee Safranek, Brendan DeCourcy, and Aminur Rahman for contributing to the group's oral presentations throughout the week.

Asymptotic Results for a Barrier Potential Model; Discussion of Additional Models in the Literature

Daniel Anderson, George Mason University
David A. Edwards, University of Delaware
Christopher S. Raymond, University of Delaware

Section 1: Governing Equations

When formulating oxide ceramics, one wishes to keep track of the *composition* and the *phase distribution* of the resulting structures. Though not precise definitions, for the purposes of this manuscript, we consider the composition at position $\tilde{x}$ to be the ensemble of *neutral moieties* at $\tilde{x}$. (Here and throughout, variables with tildes have dimensions.) For instance, such a ceramic may be composed of silicon dioxide (SiO_2) and alumina (Al_2O_3). We denote the molar fraction of component i by

$$c_i(\tilde{x}), \quad i = 1, 2, \ldots, N. \tag{1.1}$$

(Note that we will index components by Roman symbols.) As these are all molar fractions, we have that

$$\sum_{i=1}^{N} c_i(\tilde{x}) = 1, \tag{1.2}$$

and hence we need consider only $N-1$ independent variables c_i for any problem, since c_N can trivially be obtained by (1.2).

We consider the phase distribution at position x to be the ensemble of different phases at position x. Here phases can represent states of matter (melt, solid) or types of crystalline structure (quartz and crystalobite for silicon dioxide, for instance). Each phase α is tracked through an order parameter

$$\phi_\alpha(\tilde{x}), \quad \alpha = 1, 2, \ldots, M; \qquad 0 \leq \phi_\alpha \leq 1, \tag{1.3}$$

which represents the fraction of the ceramic that is in phase α. (Note that we will index phases by Greek symbols.) For this reason, an equation analogous to (1.2) holds:

$$\sum_{\alpha=1}^{M} \phi_\alpha(\tilde{x}) = 1, \tag{1.4}$$

and so similarly we need to consider only $M-1$ phase variables.

Therefore, at any position $\tilde{x}$ there are N different values of the compositions and M different values of the phases. To obtain the molar fraction of composition i in phase α, we just take the product $\phi_\alpha c_i$. However, in a general system there will be MN such combinations, while the present model has only $M+N$ variables. The paradox can be explained by noting that since there is a single value of ϕ_α for the *entire* system, this model implies that each component has the same division between phases. In practice, that is not true: under certain conditions, silicon dioxide may be much more likely to be in the crystal form than alumina. Other more complicated models [1] address this discrepancy.

The equilibrium configuration of the ceramic must minimize the free energy of the system, which consists of the following parts (for more details, see [2]):

1. A term
$$\sum_{\alpha=1}^{M} \phi_\alpha \tilde{G}_\alpha(\vec{c}), \qquad \vec{c} = (c_1, c_2, \dots c_{N-1}) \tag{1.5}$$
which is the sum of the "bulk" free energy density $G_\alpha(\vec{c})$ of phase α, weighted by the order parameter ϕ_α. Here the tilde indicates that the quantity has units. (Again, recall that one of the ϕ_α and c_i may be neglected, as we can use (1.2) and (1.4) to write them in terms of the other variables.)
2. A term
$$\tilde{U}(\vec{\phi}), \qquad \vec{\phi} = (\phi_1, \phi_2, \dots \phi_{M-1}) \tag{1.6}$$
which measures the potential associated with the phase.
3. A term
$$\frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \tilde{\kappa}_{ij} (\tilde{\nabla} c_i) \cdot (\tilde{\nabla} c_j) \tag{1.7}$$
which penalizes gradients in the compositions. Here the $\tilde{\kappa}_{ij}$ are the gradient energy coefficients associated with the compositions, and they form the entries of a positive definite matrix.
4. A term
$$\frac{1}{2} \sum_{\alpha=1}^{M-1} \sum_{\beta=1}^{M-1} \tilde{\lambda}_{\alpha\beta} (\tilde{\nabla} \phi_\alpha) \cdot (\tilde{\nabla} \phi_\beta) \tag{1.8}$$
which plays a similar role, but penalizes gradients in the phases. Here the $\tilde{\lambda}_{\alpha\beta}$ are the gradient energy coefficients associated with the phases, and they form the entries of a positive definite matrix.

Summing each of these terms and integrating over the volume under consideration, we have that the total free energy is given by

$$\tilde{\mathcal{F}}[\vec{c}, \vec{\phi}] = \int_V \sum_{\alpha=1}^{M} \phi_\alpha \tilde{G}_\alpha(\vec{c}) + \tilde{U}(\vec{\phi}) + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \tilde{\kappa}_{ij} (\tilde{\nabla} c_i) \cdot (\tilde{\nabla} c_j) + \frac{1}{2} \sum_{\alpha=1}^{M-1} \sum_{\beta=1}^{M-1} \tilde{\lambda}_{ij} (\tilde{\nabla} \phi_\alpha) \cdot (\tilde{\nabla} \phi_\beta) \, dV. \tag{1.9}$$

We specialize to the case of a one-dimensional infinite domain with $M = N = 2$. Then (1.9) reduces to

$$\tilde{\mathcal{F}}[c, \phi] = \int_{-\infty}^{\infty} \tilde{F} \left(c, \phi, \frac{dc}{d\tilde{x}}, \frac{d\phi}{d\tilde{x}} \right) d\tilde{x}, \tag{1.10a}$$

$$\tilde{F} \left(c, \phi, \frac{dc}{d\tilde{x}}, \frac{d\phi}{d\tilde{x}} \right) = \phi \tilde{G}_1(c) + (1 - \phi) \tilde{G}_2(c) + \tilde{U}(\phi) + \frac{\tilde{\kappa}}{2} \left(\frac{dc}{d\tilde{x}} \right)^2 + \frac{\tilde{\lambda}}{2} \left(\frac{d\phi}{d\tilde{x}} \right)^2. \tag{1.10b}$$

The true forms of the $\tilde{G}_\alpha$ can be quite complicated, but for our purposes they can be approximated as quadratics:

$$\tilde{G}_\alpha(c) = \tilde{G}_{\alpha,0} + \frac{\tilde{G}_{\alpha,2}^2(c - c_\alpha^*)^2}{2}, \qquad \tilde{G}_{\alpha,2} > 0, \tag{1.11}$$

where c_α^* is the minimum value for the bulk free energy density for phase α. The squared notation on $\tilde{G}_{\alpha,2}$ is used for two reasons. First, it reminds us that this coefficient should be positive for a reasonable potential. Moreover, it simplifies the algebra later on.

Typically, away from a thin interface one would normally see the phases in pure form; hence, $U(\phi)$ should have the values $\phi = 0$ and $\phi = 1$ as minima. However, since ϕ must be bounded between 0 and 1, one approach is to put an infinite barrier at those values to keep ϕ trapped in that range:

$$\tilde{U}(\phi) = \tilde{W} U_0(\phi), \qquad U_0(\phi) = \begin{cases} \phi(1-\phi), & 0 \le \phi \le 1, \\ \infty, & \text{else}, \end{cases} \tag{1.12}$$

where the W measures the size of the internal hump in the potential.

Note from (1.11) and (1.12) that the sum of the first three terms in $\tilde{F}$ will be nonzero as $\tilde{x} \to \pm\infty$. Therefore, the free energy as defined in (1.10a) will be unbounded. Hence we redefine the free energy density as an average:

$$\tilde{\mathcal{F}}[c, \phi] = \lim_{\tilde{L}\to\infty} \frac{1}{2\tilde{L}} \int_{-\tilde{L}}^{\tilde{L}} \tilde{F}\left(c, \phi, \frac{dc}{d\tilde{x}}, \frac{d\phi}{d\tilde{x}}\right) d\tilde{x}. \tag{1.13}$$

We now scale our problem to introduce dimensionless variables and parameters. We scale the bulk free energy densities as follows:

$$G_\alpha(c) = \frac{\tilde{G}_\alpha(c) - \tilde{G}_{1,0}}{\Delta\tilde{G}}, \qquad \Delta\tilde{G} = \tilde{G}_{2,0} - \tilde{G}_{1,0}, \tag{1.14}$$

which produces the functional forms

$$G_1(c) = \frac{G_{1,2}^2(c - c_1^*)^2}{2}, \qquad G_{1,2}^2 = \frac{\tilde{G}_{1,2}^2}{\Delta\tilde{G}}, \tag{1.15a}$$

$$G_2(c) = 1 + \frac{G_{2,2}^2(c - c_2^*)^2}{2}, \qquad G_{2,2}^2 = \frac{\tilde{G}_{2,2}^2}{\Delta\tilde{G}}. \tag{1.15b}$$

Motivated by (1.12), we let

$$U(\phi) = \frac{\tilde{U}(\phi)}{\tilde{W}}. \tag{1.16}$$

For the length scale, we may choose a scale including $\tilde{\kappa}$, $\tilde{W}$, or $\tilde{\lambda}$. We choose the last:

$$x = \tilde{x}\sqrt{\frac{\Delta\tilde{G}}{\tilde{\kappa}}}. \tag{1.17}$$

Substituting (1.14), (1.16), and (1.17) into (1.13), we have the following:

$$\mathcal{F}[c,\phi] = \lim_{L\to\infty} \frac{1}{2L}\int_{-L}^{L} F(c,\phi)\,dx, \tag{1.18a}$$

$$\mathcal{F}[c,\phi] = \frac{\tilde{\mathcal{F}}[c,\phi]}{\Delta\tilde{G}}, \qquad F\left(c,\phi,\frac{dc}{dx},\frac{d\phi}{dx}\right) = \frac{1}{\Delta\tilde{G}}\tilde{F}\left(c,\phi,\frac{dc}{d\tilde{x}},\frac{d\phi}{d\tilde{x}}\right), \qquad L = \tilde{L}\sqrt{\frac{\Delta\tilde{G}}{\kappa}}. \tag{1.18b}$$

Then normalizing $\tilde{F}$, we have

$$\begin{aligned} F\left(c,\phi,\frac{dc}{dx},\frac{d\phi}{dx}\right) &= \frac{1}{\Delta\tilde{G}}\Big\{\phi[\Delta\tilde{G}G_1(c)+\tilde{G}_{1,0}] + (1-\phi)[\Delta\tilde{G}G_2(c)+\tilde{G}_{1,0}] + \tilde{W}U(\phi) \\ &\qquad + \frac{\tilde{\kappa}}{2}\left(\frac{\Delta\tilde{G}}{\tilde{\kappa}}\right)\left(\frac{dc}{dx}\right)^2 + \frac{\tilde{\lambda}}{2}\left(\frac{\Delta\tilde{G}}{\tilde{\kappa}}\right)\left(\frac{d\phi}{dx}\right)^2\Big\} \\ &= \phi G_1(c) + (1-\phi)G_2(c) + WU(\phi) + \frac{1}{2}\left(\frac{dc}{dx}\right)^2 + \frac{\lambda}{2}\left(\frac{d\phi}{dx}\right)^2 + \frac{\tilde{G}_{1,0}}{\Delta\tilde{G}}, \end{aligned} \tag{1.19a}$$

$$W = \frac{\tilde{W}}{\Delta\tilde{G}}, \qquad \lambda = \frac{\tilde{\lambda}}{\tilde{\kappa}}. \tag{1.19b}$$

The last term in (1.19a) represents a shift in the total energy, and will drop out of the problem once we perform optimization.

Section 2: The Minimization Problem

We begin by considering a standard calculus of variations problem to minimize $\mathcal{F}$, with no boundary conditions given. Hence performing the standard analysis, we obtain

$$\begin{aligned}\frac{\delta\mathcal{F}}{\delta c} &= \lim_{L\to\infty}\frac{1}{2L}\int_{-L}^{L} h\frac{\partial F}{\partial c} + h'\frac{\partial F}{\partial c'}\,dx \\ &= \lim_{L\to\infty}\frac{1}{2L}\left\{\left[h\frac{\partial F}{\partial c'}\right]_{-L}^{L} + \int_{-L}^{L} h\left[\frac{\partial F}{\partial c} - \frac{d}{dx}\frac{\partial F}{\partial c'}\right]\,dx\right\} = 0,\end{aligned}$$

where h is a test function and we use the prime notation for derivatives. This must be true for all h, so we have

$$\begin{aligned}\frac{\partial F}{\partial c} - \frac{d}{dx}\frac{\partial F}{\partial c'} &= 0 \\ \frac{\partial F}{\partial c} - \frac{d^2 c}{dx^2} &= 0 \qquad (2.1a)\\ \frac{\partial F}{\partial c'}(\pm\infty) &= 0 \\ \frac{dc}{dx}(\pm\infty) &= 0. \qquad (2.1b)\end{aligned}$$

Equation (2.1b) requires some further discussion. Note that given the form of $\mathcal{F}$, a suitable test function can approach a nonzero constant as $|x|$ gets large. Hence $\partial F/\partial c'$ must vanish as x gets large.

We may consider $\delta\mathcal{F}/\delta\phi$ similarly, but with an appropriate caveat. **IF** all the derivatives are smooth, to find the minimum we set $\delta\mathcal{F}/\delta\phi = 0$, yielding

$$\begin{aligned}\frac{\partial F}{\partial \phi} - \frac{d}{dx}\frac{\partial F}{\partial \phi'} &= 0 \\ \frac{\partial F}{\partial \phi} - \lambda\frac{d^2\phi}{dx^2} &= 0 \qquad (2.2a)\\ G_1(c) - G_2(c) + WU'(\phi) - \lambda\frac{d^2\phi}{dx^2} &= 0, \qquad (2.2b)\\ \frac{\partial F}{\partial \phi'}(\pm\infty) &= 0 \\ \lambda\frac{d\phi}{dx}(\pm\infty) &= 0, \qquad (2.3)\end{aligned}$$

analogous to (2.1). However, a critical point of the functional also occurs where the derivative does not exist. For $U_0(\phi)$, this occurs at $\phi = 0$ and $\phi = 1$, so these are also critical points that must be tested.

However, upon adapting the analysis by the paper by Cogswell and Carter [2] to the case of two compositions, they have that

$$\frac{\delta \mathcal{F}}{\delta c} = \mu, \tag{2.4}$$

where μ is related to a normalized version of the difference of the chemical potentials corresponding to each composition. At least schematically, this is equivalent to minimizing $\mathcal{F}$ subject to the constraint

$$\lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} c\, dx = \bar{c}, \tag{2.5}$$

where $\bar{c}$ is an average value of c determined at the beginning of the experiment. Minimizing subject to this constraint is equivalent to minimizing

$$\lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} F - \mu c\, dx$$

and treating μ as a Lagrange multiplier. In this case, μ becomes a parameter that comes out of the analysis. However, it is unclear whether the derivation in [2], which is related to the difference in derivatives with respect to c and actual molar values, implies that μ can be considered to be known *a priori*.

In the Lagrange multiplier context, (2.1a) is replaced by

$$\frac{\partial (F - \mu c)}{\partial c} - \frac{d^2 c}{dx^2} = 0, \tag{2.6a}$$

$$\phi G_1'(c) + (1-\phi) G_2'(c) - \frac{d^2 c}{dx^2} = \mu, \tag{2.6b}$$

as required by (2.4).

From (2.1b) and (2.3), we have that c and ϕ must be constant as $x \to \pm\infty$, as expected from our physical intuition. Let

$$c_- = c(-\infty), \qquad c_+ = c(\infty), \tag{2.7}$$

and similarly for ϕ. An important consideration throughout this report will be whether we have an appropriate number of conditions to solve the problem. We note that by evaluating (2.2b) and (2.6b) at $x = \pm\infty$, we have the following four conditions:

$$G_1(c_-) - G_2(c_-) + WU'(\phi_-) = 0, \tag{2.8a}$$

$$G_1(c_+) - G_2(c_+) + WU'(\phi_+) = 0, \tag{2.8b}$$

$$\phi_- G_1'(c_-) + (1-\phi_-) G_2'(c_-) = \mu, \tag{2.9a}$$

$$\phi_+ G_1'(c_+) + (1-\phi_+) G_2'(c_+) = \mu. \tag{2.9b}$$

With the addition of (2.5), we now have five conditions for the five unknowns $\{c_\pm, \phi_\pm, \mu\}$. In theory, we can then solve for the five unknowns, **if** $U'(\phi)$ **is smooth**, which in our case means that ϕ_+ and ϕ_- are in $(0,1)$.

Multiplying (2.2a) by $d\phi/dx$ and (2.6a) by dc/dx and adding, we obtain

$$\frac{\partial F}{\partial \phi}\frac{d\phi}{dx} - \lambda \frac{d\phi}{dx}\frac{d^2\phi}{dx^2} + \frac{\partial (F-\mu c)}{\partial c}\frac{dc}{dx} - \frac{dc}{dx}\frac{d^2c}{dx^2} = 0$$
$$\frac{d(F-\mu c)}{dx} - \frac{1}{2}\frac{d}{dx}\left[\lambda\left(\frac{d\phi}{dx}\right)^2 + \left(\frac{dc}{dx}\right)^2\right] = 0.$$

Integrating this expression from $x = -\infty$ to $x = \infty$, we have

$$F(c_+, \phi_+, 0, 0) - \mu c_+ - [F(c_-, \phi_-, 0, 0) - \mu c_-] = 0,$$

where we have used (2.1b), (2.3), and (2.7). This expression is clearly true for all smooth x (see the analysis in [3] and §6). Hence if ϕ_+ and ϕ_- are in $(0, 1)$, we obtain the following:

$$[\phi_+ G_1(c_+) + (1-\phi_+)G_2(c_+) + W(U(\phi_+))] \\ - [\phi_- G_1(c_-) + (1-\phi_-)G_2(c_-) + W(U(\phi_-))] = \mu(c_+ - c_-). \quad (2.10)$$

In the experimental systems under consideration, in the bulk the phases will be pure; hence we take

$$\phi_- = 1, \quad \phi_+ = 0. \quad (2.11)$$

(Note that the choice of phase is arbitrary, so we could have just as easily taken $\phi_- = 0$, $\phi_+ = 1$.) Now we turn our attention to the number of constants. Substituting our choices of $\phi_\pm$ into (2.8) and (2.9), we obtain

$$G_1(c_-) - G_2(c_-) + WU'(1) = 0, \quad (2.12a)$$
$$G_1(c_+) - G_2(c_+) + WU'(0) = 0, \quad (2.12b)$$
$$G_1'(c_-) = \mu, \quad (2.13a)$$
$$G_2'(c_+) = \mu. \quad (2.13b)$$

Note that if U' is smooth, (2.12) and (2.13) form an overdetermined system. This is because (2.1b) and (2.3) imply that we are trying to find a heteroclinic orbit in the phase plane between $(c_-, 0, \phi_-, 0)$ and $(c_+, 0, \phi_+, 0)$. The values of $c_\pm$ and $\phi_\pm$ are obtained by finding the fixed points in the phase plane, not imposed *a priori*. However, this argument assumes that U' exists at 0 and 1, a property which the original U_0 does not have.

How do we resolve the overdetermination in (2.12) and (2.13)? Consider a solution that approaches 0 given the potential in (1.12). As $\phi \to 0^+$, $U'(\phi) \to 1$, not zero. Hence the solution may not have $\phi' \to 0$ as $\phi \to 0^+$, since $\phi = 0$ is a steady state due only to the barrier at $\phi = 0$, which the solution has not yet seen. Hence we expect that the solutions to the system with U_0 may not have $\phi' = 0$ when $\phi = 0$; in other words, they will have compact support (see Fig. 2.1). However, note from (2.6b) that c can still continue to evolve in those regions, so c will not have compact support.

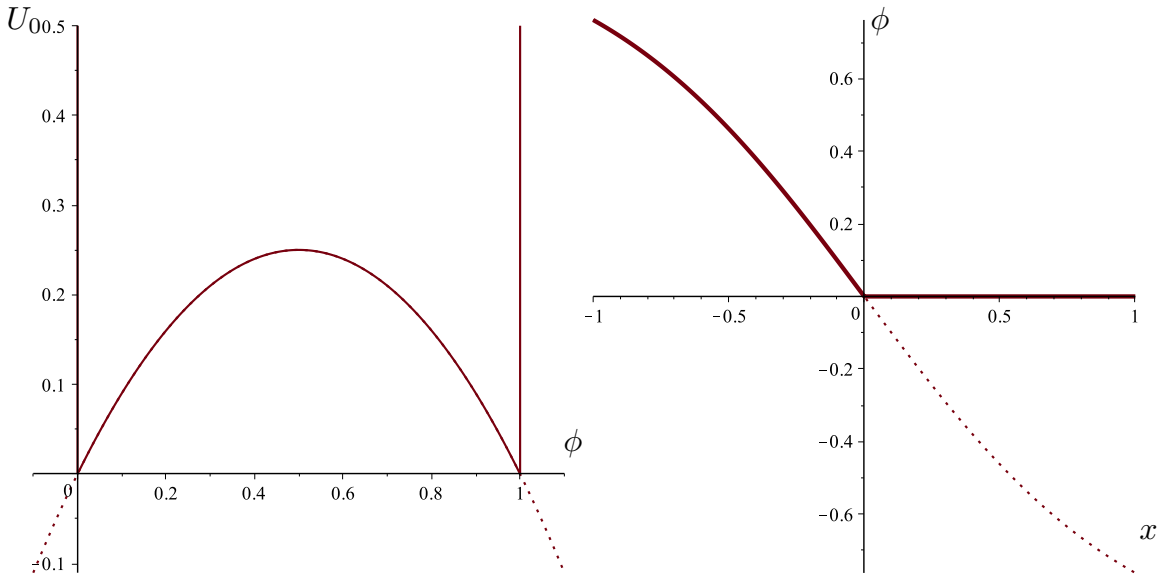

Figure 2.1. Left: U_0 with (solid) and without (dotted) barrier. Right: ϕ with (solid) and without (dotted) barrier.

Another simple way to see this is through the toy system

$$\frac{d\phi}{dx} = y, \tag{2.14a}$$

$$\frac{dy}{dx} = U_0'(\phi). \tag{2.14b}$$

A phase plane is shown in Fig. 2.2. Note that for $0 < \phi < 1$, $U_0'(\phi) = 1 - 2\phi$ and the trajectories are portions of closed orbits about $(1/2, 0)$. Since we are minimizing a functional and hence get x-derivatives, the behavior is exactly the opposite of what we would expect if we had a potential as in (1.12) in a time-dependent problem, where we would expect $(1/2, 0)$ to be a saddle.

When the trajectories hit the barriers at $\phi = 0$ and $\phi = 1$, they stop. Hence again we see that ϕ' may not equal 0 when ϕ goes to 0 or 1, so the solutions have compact support. (Here the full orbit shown is forbidden.) However, there is one solution (the one that goes through the origin) that does have $\phi' = 0$ when ϕ goes to 0 or 1. This trajectory will prove to be critically important.

The question is then to determine which of the infinite number of trajectories is stable. Also, note that in the full problem, the G terms vary with x, which is equivalent to moving between different trajectories as $x \to \pm\infty$. But the basic principle should still hold.

Due to the form of the barrier function, ϕ can be equal to these extremal values over various regions; therefore, we define $x_<$ and $x_>$ as follows:

$$\phi(x) = \begin{cases} 1, & x \le x_<, \\ 0, & x \ge x_>. \end{cases} \tag{2.15}$$

Note that $x_<$ and $x_>$ are unknown constants which will have to be determined in the analysis. Note that when $x > x_>$ or $x < x_<$, the U term in (1.19a) doesn't vary, and

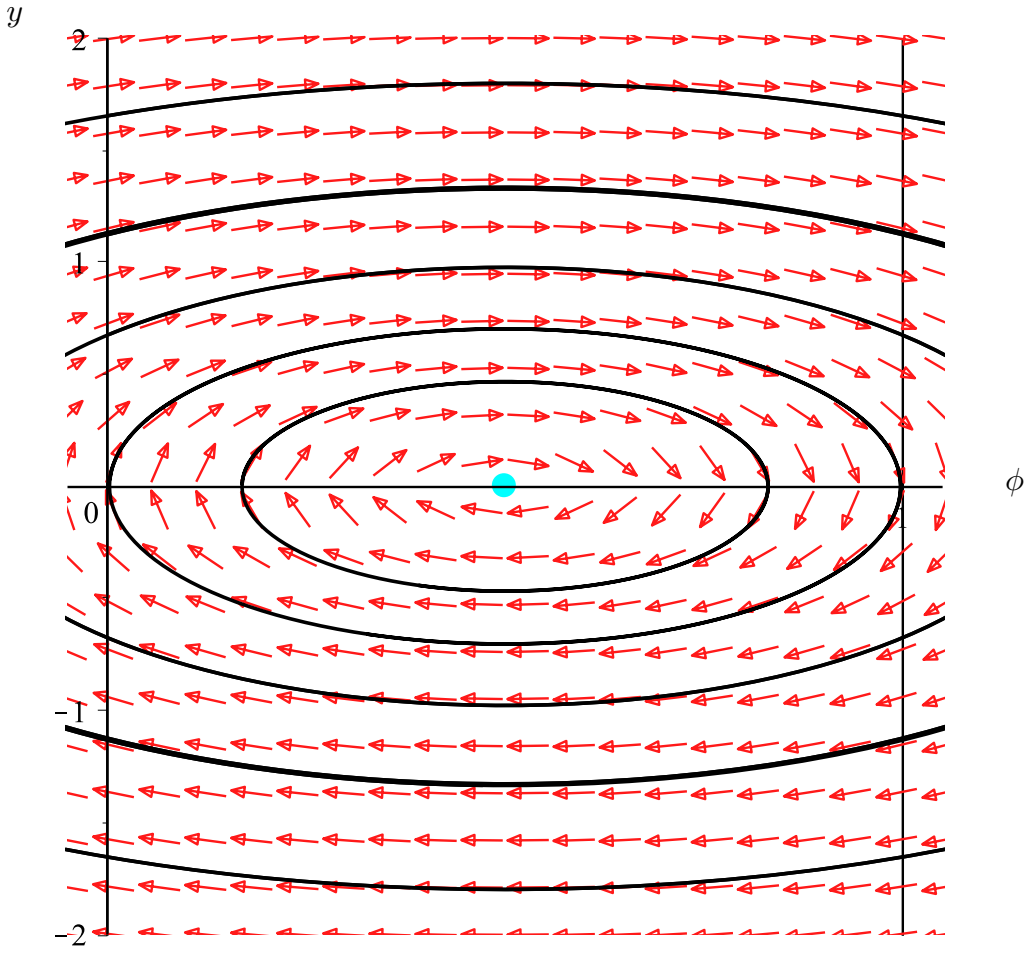

Figure 2.2. Phase plane for toy system (2.14).

the $d\phi/dx$ term is zero. Hence in these regions the functional minimization is done only over c. We call the region $x > x_>$ the *right exclusion zone*, and the region $x < x_<$ the *left exclusion zone*, where the terminology reminds us that ϕ will be excluded from the analysis in this region.

Therefore, when performing the analysis in the exclusion zones that leads to (2.10), we can eliminate U from the analysis. The other terms are bounded, and so we have

$$\begin{aligned} G_2(c_+) - G_1(c_-) &= \mu(c_+ - c_-) \\ \frac{G_2(c_+) - G_1(c_-)}{c_+ - c_-} &= \mu. \end{aligned} \tag{2.16}$$

One can also obtain this heuristically by noting that U is even about $\phi = 1/2$, so $U(1)$ "equals" $U(0)$.

Equations (2.13) and (2.16) define the *common tangent* constraint, namely that the far-field values c_+ and c_- are chosen such that the secant line through $G_2(c_+)$ and $G_1(c_-)$ is tangent to both curves at the point of intersection (see Figure 2.3).

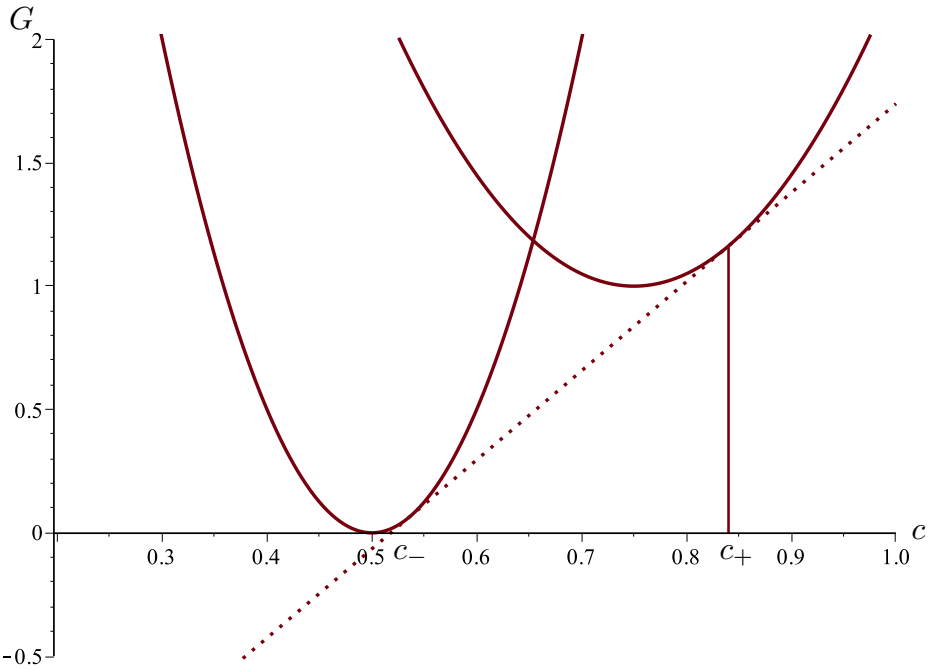

Figure 2.3. Two quadratic potentials (solid) and the common tangent (dotted).

Section 3: Dividing the Domain

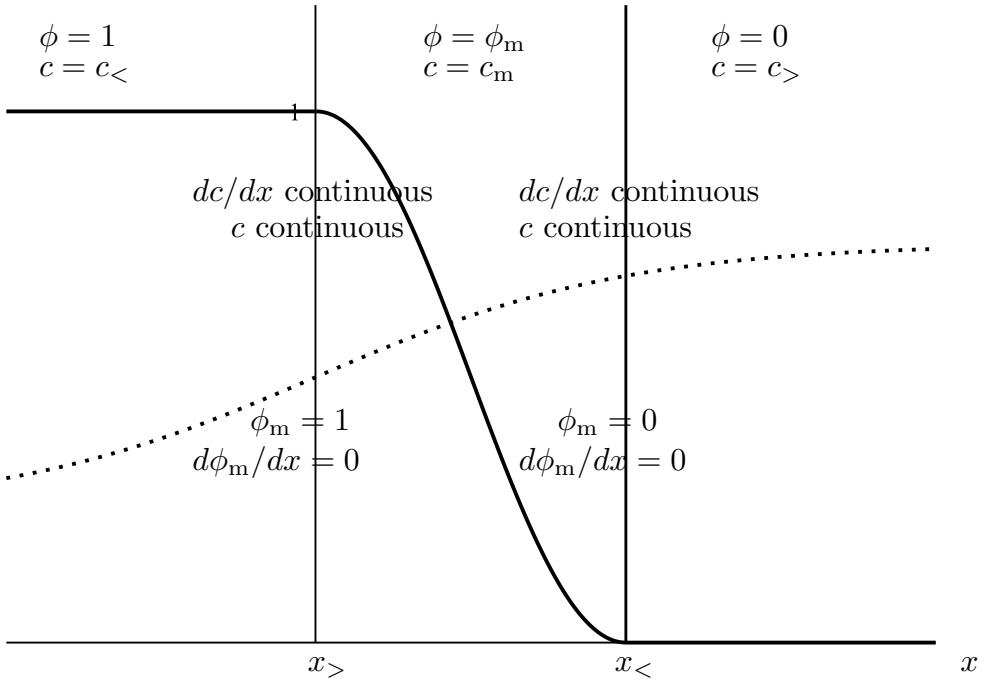

Figure 3.1. Schematic of subdivided diagram and characteristic sketches of ϕ (solid) and c (dotted).

Given the existence of the exclusion zones, we provide a schematic of the diagram above. There are two ways to consider a system with such an exclusion zone. The first (which we shall pursue here) is to treat the system as a free-boundary problem and derive (or define) appropriate boundary conditions at $x = x_<$ and $x = x_>$. The second is to use the principle of linear complementarity, as in [4]. A further discussion of linear complementarity for a moving boundary-value problem (though in the context of the American option in the Black-Scholes model) can be found in §7.6 of [5].

In the left exclusion zone, the only governing equation is (2.6b) with $\phi = 1$:

$$
\begin{aligned}
G_1'(c_<) - \frac{d^2 c_<}{dx^2} &= \mu, \qquad x < x_< \\
\frac{d^2 c_<}{dx^2} - G_{1,2}^2 (c_< - c_1^*) &= -\mu \\
\frac{d^2 c_<}{dx^2} - G_{1,2}^2 c_< &= -(G_{1,2}^2 c_1^* + \mu) \\
c_<(x) &= c_1^* + \frac{\mu}{G_{1,2}^2} + A_< \exp(G_{1,2}(x - x_<)), \qquad x < x_<, \quad \text{(3.1a)}
\end{aligned}
$$

where the subscript $<$ indicates that we are in the left exclusion zone. Note from (3.1a) that

$$c_- = c_1^* + \frac{\mu}{G_{1,2}^2}, \tag{3.1b}$$

and that $A_<$ must be determined later.

Similarly, using (2.6b) with $\phi = 0$ gives us the solution in the right exclusion zone:

$$\begin{aligned} G_2'(c_>) - \frac{d^2 c_>}{dx^2} &= \mu, \qquad x > x_>, \\ \frac{d^2 c_>}{dx^2} - G_{2,2}^2 c_> &= -(G_{2,2}^2 c_2^* + \mu) \\ c_>(x) &= c_+ - A_> \exp(-G_{2,2}(x - x_>)), \qquad x > x_>, \qquad (3.2a) \\ c_+ &= c_2^* + \frac{\mu}{G_{2,2}^2}. \qquad (3.2b) \end{aligned}$$

Here we have chosen the minus sign so that $A_> > 0$, as will be shown below.

Now we turn our attention to the mass constraint, rewritten in this context:

$$\lim_{L\to\infty} \frac{1}{2L} \left[\int_{-L}^{x_<} c_<(x)\,dx + \int_{x_<}^{x_>} c_{\mathrm{m}}(x)\,dx + \int_{x_>}^{L} c_>(x)\,dx \right] = \bar{c}, \tag{3.3}$$

where we denote the solution in the middle by c_{m}. Note that the only terms that will contribute to the first and third integrals will be the constant terms in (3.1a) and (3.2a). But in that case the $x_<$ and $x_>$ terms would drop out, which is unreasonable since we expect their positions (and hence how much of each composition is in the solution) to matter.

To resolve the paradox, consider a finite domain of length $2L$. For a given value of L, we would expect particular values of $x_<$ and $x_>$ to characterize what fraction of the total mass comes from $c_<$, and what fraction comes from $c_>$. Now double the length of the box. Then to maintain the same fraction, we would have to double each of $x_<$ and $x_>$. This suggests taking

$$x_< = \xi_< L, \quad x_> = \xi_> L; \qquad -1 \le \xi_< \le \xi_> \le 1, \tag{3.4}$$

where the ξs are constant. Making these substitution into (3.3), we have

$$\begin{aligned} \lim_{L\to\infty} \frac{1}{2L} \left[\int_{-L}^{\xi_< L} c_<(x)\,dx + \int_{\xi_< L}^{\xi_> L} c_{\mathrm{m}}(x)\,dx + \int_{\xi_>}^{L} c_>(x)\,dx \right] &= \bar{c} \\ \lim_{L\to\infty} \frac{1}{2L} \left[\int_{-L}^{\xi_< L} c_-\,dx + \int_{\xi_< L}^{\xi_> L} c_{\mathrm{m}}(x)\,dx + \int_{\xi_> L}^{L} c_+\,dx \right] &= \bar{c}, \end{aligned}$$

where we have used the fact that only the constant terms in $c_<$ and $c_>$ will contribute to the expression once we divide by L and take the limit. Continuing to simplify, we obtain

$$\begin{aligned} \lim_{L\to\infty} \frac{1}{2L} \left[c_-(\xi_< L + L) + \int_{\xi_< L}^{\xi_> L} c_{\mathrm{m}}(x)\,dx + c_+(L - \xi_> L) \right] &= \bar{c} \\ \frac{c_-(\xi_< + 1) + c_+(1 - \xi_>)}{2} + \lim_{L\to\infty} \frac{1}{2L} \int_{\xi_< L}^{\xi_> L} c_{\mathrm{m}}(x)\,dx &= \bar{c}. \qquad (3.5) \end{aligned}$$

Note that the ξs are related to what fraction of the domain is in a particular phase in a finite-domain problem, and they retain that character as we take the domain to be an infinite. Note also that the remaining integral is related to the average of c_{m} over the domain.

Again, we count up the constants and make sure we have the proper number of constraints. We have one constant from each of the exclusion zones ($A_<$ and $A_>$). We have two constants from the free boundaries of the exclusion zones ($\xi_<$ and $\xi_>$). The Lagrange multiplier μ is undetermined, and we have two second-order ODEs in the middle region, which provide four other constants. Hence there are nine constants to be determined.

Equation (2.6b) is smooth, so c and dc/dx must be continuous at $x = x_<$ and $x = x_>$, which yields four conditions. The constraint (3.5) provides another condition. The question then is the proper boundary conditions on ϕ.

Given that the energies in the exclusion zones must be minimized, we could pose a new optimization problem just for $x_< < x < x_>$, ignoring how those boundaries are determined. In that case, we would know nothing about ϕ on the boundaries *a priori*, and hence using the same techinques as in §2, we would have the natural boundary conditions

$$\frac{d\phi_{\mathrm{m}}}{dx}(x_<) = 0, \tag{3.6a}$$

$$\frac{d\phi_{\mathrm{m}}}{dx}(x_>) = 0, \tag{3.6b}$$

analogous to (2.3). However, consider how the free boundaries $x_<$ and $x_>$ are defined: namely, that

$$\phi_{\mathrm{m}}(x_<) = 1, \tag{3.7a}$$

$$\phi_{\mathrm{m}}(x_>) = 0. \tag{3.7b}$$

Equations (3.6) and (3.7) provide the remaining four conditions to close the system.

There are several reasons to argue why (3.6) is the proper condition for the derivative. It appears in Blowey and Elliott [4], but there they explicitly say that they are looking for solutions that are continuously differentiable, which isn't immediately obvious by integrating (2.2b) across the jump, given the unusual nature of the singularity in $U'(\phi)$.

There may be another way to impose that condition, as in the Black-Scholes analysis (principle of no arbitrage), or from the principle of linear complementarity.

Section 4: Large W Asymptotics

The system is substantially more complicated in $(x_<, x_>)$, since both (2.2b) and (2.6b) must be solved. Therefore, we begin by considering the case where $W \to \infty$. In this section we track only the leading-order terms, so we don't write our dependent variables in formal perturbation series.

Taking $W \to \infty$, (2.2b) becomes, to leading order,

$$\begin{aligned} U_0'(\phi_\mathrm{m}) = 1 - 2\phi_\mathrm{m} &= 0 \\ \phi_\mathrm{m} &= \frac{1}{2}, \qquad x_< < x < x_<. \end{aligned} \tag{4.1}$$

The solution for ϕ_m has a discontinuity at $x = x_>$ which we will resolve with the use of a boundary layer. Inserting the boundary layer, we let

$$X = W^{1/2}(x - x_>), \qquad \Phi(X) = \phi_\mathrm{m}(x). \tag{4.2}$$

Note that this definition is equivalent to taking the characteristic length scale to be that associated with $\tilde{W}$ instead of the one in (1.17). This makes sense, because the original length scale in (1.17) is associated with $\tilde{\kappa}$, which characterizes variations in c. In contrast, $\tilde{W}$ is associated with the potential for ϕ_m. Assuming that $W \to \infty$ is equivalent to saying the two processes occur on distinct length scales, and hence the equations decouple.

Substituting (4.2) into (2.2b), we obtain, to leading order,

$$G_1(c_\mathrm{m}) - G_2(c_\mathrm{m}) + W(1 - 2\Phi) - W\lambda\frac{d^2\Phi}{dX^2} = 0, \tag{4.3a}$$

$$\begin{aligned} \lambda\frac{d^2\Phi}{dX^2} + 2\Phi &= 1 \\ \Phi(X) = \frac{1}{2} + B_\mathrm{s}\sin X\sqrt{\frac{2}{\lambda}} &+ B_\mathrm{c}\cos X\sqrt{\frac{2}{\lambda}}. \end{aligned} \tag{4.3b}$$

But the solutions to the above equation oscillate, which cannot satisfy the matching condition

$$\Phi(X = -\infty) = \phi_\mathrm{m}(x = x_>^-) = \frac{1}{2}.$$

These oscillations reflect the fact that $\phi_\mathrm{m} = 1/2$ is an unstable steady state due to the form of the potential.

Hence we must conclude that there is no $O(1)$ region $(x_<, x_>)$ where (4.1) holds. Therefore $x_< = x_>$, and we call the point x_b. Hence we must insert an interior layer to smooth the jump in ϕ between 0 and 1.

We begin by continuing with the outer solution for c. Note that because the scales separate, ϕ totally drops out of the system on this time scale. Instead, we have two

solutions $c_<$ and $c_>$ which hold on two sides of some value $x = x_\mathrm{b}$. It might seem that x_b is arbitrary by translation invariance, but that is not correct.

First, we note from (2.6b) that only the second derivative of c jumps when ϕ jumps. Hence both c and dc/dx will be continuous at $x = x_\mathrm{b}$. Therefore, using (3.1a) and (3.2a), we obtain

$$\frac{dc}{dx}(x_\mathrm{b}) = G_{1,2}A_< = G_{2,2}A_>.$$

So we let $A_< = G_{2,2}A$, $A_> = G_{1,2}A$ for some unknown constant A. Then we have

$$\begin{aligned} c(x_\mathrm{b}) = c_- + G_{2,2}A &= c_+ - G_{1,2}A \\ A(G_{2,2} + G_{1,2}) &= c_+ - c_- \\ c_<(x) &= c_- + \frac{G_{2,2}(c_+ - c_-)}{G_{2,2} + G_{1,2}} \exp(G_{1,2}(x - x_\mathrm{b})), \qquad (4.4a) \\ c_>(x) &= c_+ - \frac{G_{1,2}(c_+ - c_-)}{G_{2,2} + G_{1,2}} \exp(-G_{2,2}(x - x_\mathrm{b})). \qquad (4.4b) \end{aligned}$$

To find the value of ξ_b, we use the fact that the middle region is negligible in (3.5) to find

$$\frac{c_-(\xi_\mathrm{b} + 1) + c_+(1 - \xi_\mathrm{b})}{2} = \bar{c}, \qquad (4.5)$$

which is the same as the bulk phase system. Equation (4.5) is called the *lever rule*.

Note that ξ_b is then directly related to the fraction of the ceramic in each phase. $\xi_\mathrm{b} = -1$ corresponds to all $c_<$, as expected. Similarly, all $c_>$ corresponds to $\xi_\mathrm{b} = 1$, and if $c_+ = c_-$, then $c_+ = c_- = \bar{c}$.

We now consider the solution in the boundary layer. For the reasons discussed in §3, we expect that $\Phi(X)$ will have compact support. Since the X problem is invariant under translation, we expect that $\Phi(X)$ will vary only in $(-X_\mathrm{b}, X_\mathrm{b})$, where X_b is as yet undetermined. In particular we have that the analog to (3.6) and (3.7) holds:

$$\begin{aligned} \frac{d\Phi}{dX}(-X_\mathrm{b}) &= 0, \qquad (4.6a) \\ \frac{d\Phi}{dX}(X_\mathrm{b}) &= 0, \qquad (4.6b) \\ \Phi(-X_\mathrm{b}) &= 1, \qquad (4.7a) \\ \Phi(X_\mathrm{b}) &= 0. \qquad (4.7b) \end{aligned}$$

Equation (4.3a) holds no matter the value of $x_>$, so (4.3b) still holds. Given that Φ is continuous at $X = \pm X_\mathrm{b}$, (4.6) and (4.7) provide the boundary conditions on Φ needed to find the constants B. In particular, satisfying (4.7), we have

$$\Phi(X) = \frac{1}{2}\left(1 - \frac{\sin X\sqrt{2/\lambda}}{\sin X_\mathrm{b}\sqrt{2/\lambda}}\right), \qquad |X| < X_\mathrm{b}. \qquad (4.8)$$

Note from (4.8) that $\Phi(X)$ is odd about $X = 0$, $\Phi = 1/2$, so the equations in (4.6) are redundant. Hence we need satisfy only (4.6b), yielding

$$-\sqrt{\frac{2}{\lambda}}\cot X_{\rm b}\sqrt{\frac{2}{\lambda}} = 0,$$

$$X_{\rm b} = \pi(n+1/2)\sqrt{\frac{\lambda}{2}}, \qquad n \geq 0, \tag{4.9}$$

as shown in Fig. 4.1.

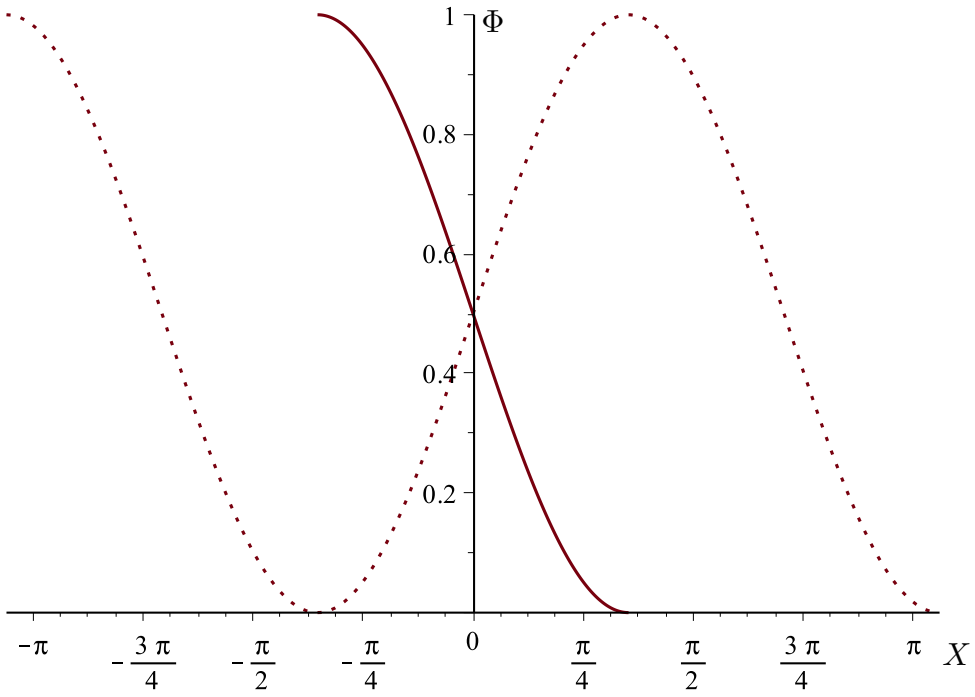

Figure 4.1. Graph of $\Phi(X)$ *vs.* X with $\lambda = 1$ and $n = 0$ (solid, acceptable case), and $n = 1$ (dotted, showing unphysical oscillation).

Note that the acceptable case has $n = 0$, since once the solution hits $\phi = 0$ or $\phi = 1$, it must stop there. Hence we have that

$$X_{\rm b} = \frac{\pi}{2}\sqrt{\frac{\lambda}{2}} \tag{4.10a}$$

$$\Phi(X) = \frac{1}{2}\left(1 - \sin X\sqrt{\frac{2}{\lambda}}\right), \qquad |X| < \frac{\pi}{2}\sqrt{\frac{\lambda}{2}}. \tag{4.10b}$$

Section 5: Large G Asymptotics

Another asymptotic case of interest is when $G_{2,2}^2 \to \infty$. This corresponds to one component whose surface energy has high curvature, so it takes a lot of energy to displace c from c_2^*.

In this limit, our solution process in the exclusion zone is the same. Hence $c_<$ is still given by (3.1a), while $c_>$ is given by (3.2a) in the limit of large $G_{2,2}$:

$$c_>(x) = c_+ = c_2^*, \qquad x > x_>, \tag{5.1}$$

as one could expect physically from the high-curvature argument.

In the middle region, (2.6b) becomes

$$\phi_{\mathrm{m}} G_1'(c_{\mathrm{m}}) + (1-\phi_{\mathrm{m}}) G_{2,2}^2 (c_{\mathrm{m}} - c_2^*) - \frac{d^2 c_{\mathrm{m}}}{dx^2} = \mu, \tag{5.2}$$

where we have used (1.15b). The leading order of this equation for large $G_{2,2}$ is

$$c_{\mathrm{m}} = c_2^*. \tag{5.3}$$

Hence $c_{\mathrm{m}}(x_<) = c_2^*$, and continuity of composition gives us

$$\begin{aligned} c_<(x_<) &= c_- + A_< = c_2^*, \\ c_<(x) &= c_- + (c_2^* - c_-)\exp(G_{1,2}(x - x_<)). \end{aligned} \tag{5.4}$$

Moreover, substituting (5.1) and (5.3) into (3.5), we have

$$\begin{aligned} \frac{c_-(\xi_< + 1) + c_2^*(1-\xi_>)}{2} + \lim_{L\to\infty} \frac{1}{2L} \int_{\xi_< L}^{\xi_> L} c_2^* \, dx &= \bar{c} \\ \frac{c_-(\xi_< + 1) + c_2^*(1-\xi_>)}{2} + \frac{c_2^*(\xi_> - \xi_<)}{2} \, dx &= \bar{c} \\ \frac{c_-(\xi_< + 1) + c_2^*(1-\xi_<)}{2} &= \bar{c}, \end{aligned} \tag{5.5}$$

which is (4.5) with ξ_{b} replaced by $\xi_<$ and c_+ replaced by c_2^*.

We note that we cannot satisfy the derivative condition at $x = x_<$, since the derivative on the right is zero, which cannot match to the exponential on the left. Therefore, we will need a corner layer near $x = x_<$. Why does this happen? Note that as $x \to x_<$, $\phi_{\mathrm{m}} \to 1^-$. Hence the $(1-\phi_{\mathrm{m}})$ term in (5.2) becomes small enough that it balances the $G_{2,2}^2$ term, allowing c_{m} to move away from c_2^*.

Before inserting the corner layer, we examine the behavior of ϕ_{m}. Substituting (5.3) into (2.2b), we obtain the following:

$$\begin{aligned} G_1(c_2^*) - G_2(c_2^*) + W(1-2\phi_{\mathrm{m}}) - \lambda \frac{d^2\phi}{dx^2} &= 0, \\ \lambda \frac{d^2\phi_{\mathrm{m}}}{dx^2} + 2W\phi_{\mathrm{m}} &= W - G_1(c_2^*) + 1, \end{aligned} \tag{5.6a}$$

where we have used (1.15). Solving (5.6a), we have

$$\phi_{\mathrm{m}}(x) = \frac{1+A_*}{2} + B_{\mathrm{s}} \sin x\sqrt{\frac{2W}{\lambda}} + B_{\mathrm{c}} \cos x\sqrt{\frac{2W}{\lambda}}, \qquad A_* = \frac{G_1(c_2^*)-1}{W}, \tag{5.6b}$$

analogous to (4.3b). Note that the solution will oscillate about the constant term; hence we require that

$$\begin{aligned} 0 \le \frac{1+A_*}{2} &\le 1 \\ |A_*| &\le 1. \end{aligned} \tag{5.7}$$

The physical significance of this bound isn't completely clear, though we were told that $\tilde{W}$ should be larger than $\Delta\tilde{G}$. We should also note that this bound comes from the Dirichlet conditions only; another bound comes from the flux conditions below.

In order to strengthen the analogy with the work in the previous section, we define the following quantities:

$$\bar{x} = \frac{x_< + x_>}{2}, \qquad \Delta x = \frac{x_> - x_<}{2}, \qquad x_{\mathrm{m}} = x - \bar{x}. \tag{5.8}$$

Then our solution may be written as

$$\phi_{\mathrm{m}}(x_{\mathrm{m}}) = \frac{1+A_*}{2} + B_{\mathrm{s}} \sin x_{\mathrm{m}}\sqrt{\frac{2W}{\lambda}} + B_{\mathrm{c}} \cos x_{\mathrm{m}}\sqrt{\frac{2W}{\lambda}}, \tag{5.9}$$

where we have redefined the constants in (5.6b). Moreover, the interval becomes $-\Delta x \le x_{\mathrm{m}} \le \Delta x$. Hence we may solve as in §4 with X replaced by x_{m} and X_{b} replaced by Δx. Thus we have

$$\phi_{\mathrm{m}} = \frac{1}{2}\left(1 - \frac{\sin x_{\mathrm{m}}\sqrt{2W/\lambda}}{\sin \Delta x\sqrt{2W/\lambda}}\right) + \frac{A_*}{2}\left(1 - \frac{\cos x_{\mathrm{m}}\sqrt{2W/\lambda}}{\cos \Delta x\sqrt{2W/\lambda}}\right), \qquad |x_{\mathrm{m}}| < \Delta x, \tag{5.10}$$

which satisfies (3.7).

In §4, the forcing constant was 1/2, the mean of the matching values for ϕ, and hence we were able to satisfy both derivative conditions simultaneously. Here we can satisfy only one of the conditions. Since we already expect a corner layer about $x = x_<$, we choose to satisfy the condition at $x = x_>$ ($x_{\mathrm{m}} = \Delta x$) instead, yielding

$$\frac{d\phi_{\mathrm{m}}}{dx_{\mathrm{m}}}(\Delta x) = -\frac{1}{2}\sqrt{\frac{2W}{\lambda}} \cot\left(\Delta x\sqrt{\frac{2W}{\lambda}}\right) + \frac{A_*}{2}\sqrt{\frac{2W}{\lambda}} \tan\left(\Delta x\sqrt{\frac{2W}{\lambda}}\right) = 0, \tag{5.11a}$$

$$\cot^2\left(\Delta x\sqrt{\frac{2W}{\lambda}}\right) = A_*. \tag{5.11b}$$

Therefore, in order to satisfy the condition at $x_{\rm m} = \Delta x$, we must have that

$$0 \le A_* \le 1. \tag{5.12}$$

Note that $A_* > 0$ corresponds to the case shown in Fig. 2.3. (Otherwise, c_1 always has a lower energy.) If (5.12) is satisfied, then Δx is defined by (5.11b) and the outer solutions are complete.

There still remains a problematic issue. To wit, recall from our previous definitions in (3.4) that

$$\Delta x = \frac{x_> - x_<}{2} = \frac{L(\xi_> - \xi_<)}{2},$$

where $\xi_>$ and $\xi_<$ are $O(1)$ constants. Before we were able to deal with this issue by taking limits, but there are no corresponding limits for the ϕ equation. Hence with a finite Δx, it seems as if we are driving $\xi_<$ and $\xi_>$ together again, making a sharp interface.

The solution may be to choose the ratio of bulk phases to be the same as $L \to \infty$. This allows the two bulk phases to become infinitely large in the same proportion, while allowing the interface width to be finite.

These computations are enough to determine our solutions except for a small corner layer near $x = x_<$, *i.e.*, enough to determine the solution on a macroscopic scale. For mathematical completeness, we write down the equations in the corner layer. We let

$$X = G_{2,2}^A(x - x_<), \quad X > 0; \qquad \phi_{\rm m}(x_{\rm m}) = 1 - G_{2,2}^{-A}\Phi(X), \qquad c_{\rm m}(x_{\rm m}) = c_2^* + G_{2,2}^{-A}C(X), \tag{5.13}$$

where A is a constant that has to be chosen the same in each expression in order to make the derivatives match. Note that $X = 0$ corresponds to $x = x_<$, or $x_{\rm m} = -\Delta$.

Hence for the boundary conditions, we see that at $X = 0$, the derivative of Φ must vanish:

$$-\frac{d\Phi}{dX}(0) = 0, \tag{5.14a}$$

while as $X \to \infty$, the derivative of C must vanish:

$$\frac{dC}{dX}(\infty) = \frac{dc_{\rm m}}{dx_{\rm m}}(-\Delta x) = 0. \tag{5.14b}$$

Similarly, at $X = 0$, the derivative of C must match:

$$\frac{dC}{dX}(0) = \frac{dc_<}{dx}(x_<) = G_{1,2}(c_2^* - c_-), \tag{5.15}$$

where we have used (5.4). As $X \to \infty$, the derivative of Φ must match:

$$\begin{aligned} -\frac{d\Phi}{dX}(\infty) &= \frac{d\phi_{\rm m}}{dx_{\rm m}}(-\Delta x) \\ &= -\frac{1}{2}\sqrt{\frac{2W}{\lambda}}\cot\left(\Delta x\sqrt{\frac{2W}{\lambda}}\right) - \frac{A_*}{2}\sqrt{\frac{2W}{\lambda}}\tan\left(\Delta x\sqrt{\frac{2W}{\lambda}}\right) \end{aligned} \tag{5.16a}$$

$$\frac{d\Phi}{dX}(\infty) = \frac{1}{2}\sqrt{\frac{2W}{\lambda}}\sqrt{A_*} + \frac{A_*}{2}\sqrt{\frac{2W}{\lambda}}\frac{1}{\sqrt{A_*}} = \sqrt{\frac{2WA_*}{\lambda}}, \tag{5.16b}$$

where we have used (5.10) and (5.11b).

Substituting (5.13) into (2.6b), we have, to leading order,

$$G_1'(c_2^*) + G_{2,2}^{-A}\Phi G_{2,2}^2(G_{2,2}^{-A}C) - G_{2,2}^A\frac{d^2C}{dX^2} = \mu,$$

which implies that $A = 2/3$ and the leading order is given by

$$\Phi C - \frac{d^2C}{dX^2} = 0. \tag{5.17}$$

Substituting (5.13) with $A = 2/3$ into (2.2b), we obtain

$$G_1(c_2^*) - \left[1 - \frac{G_{2,2}^2(G_{2,2}^{-2/3}C)^2}{2}\right] + W[1 - 2(1)] - \lambda G_{2,2}^{2/3}\frac{d^2\Phi}{dX^2} = 0$$

$$\frac{C^2}{2} - \lambda\frac{d^2\Phi}{dX^2} = 0. \tag{5.18}$$

Equations (5.17) and (5.18) form a nonlinear system which can be solved numerically for the solutions in the boundary layer.

Section 6: Literature Review

Notes on Wheeler, Boettinger & McFadden, Phys Rev. E 1993

Another view of the two phase binary alloy problem follows from the work of Wheeler, Boettinger & McFadden [3, 6]. In [3] a free energy functional of the form (given here in one dimension for simplicity)

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

is considered. The specific form of the bulk energy term $f(\phi, c)$ must be specified and will be discussed later. In their earlier work, Wheeler *et al.* [6], proposed a similar free energy functional that did not include the gradient energy term in composition c (i.e. $\tilde{\kappa} = 0$). They argued in [3] that inclusion of the gradient energy in composition is appropriate, especially for the case of rapid solidification where the length scale of the solute boundary layers at a moving interface may approach atomic dimensions.

In [3] the authors examine a stationary interface scenario in which bulk phases with $\phi \to 0$ and $c \to c_\infty$ $(x \to \infty)$ and $\phi \to 1$ and $c \to c_{-\infty}$ $(x \to -\infty)$ with the compositional values c_∞ and $c_{-\infty}$ to be determined. (Hence $c_{\pm\infty}$ in [3] correspond to our earlier $c_\pm$.)

As outlined in §3, equilibrium conditions for the above system can be identified via standard calculus of variations techniques. Minimization with respect to ϕ leads to $\delta\mathcal{F}/\delta\phi = 0$ so that

$$\frac{\partial f}{\partial \phi} - \tilde{\lambda}\frac{d^2\phi}{dx^2} = 0. \tag{6.1}$$

Minimization with respect to c, keeping in mind that the total concentration is a conserved quantity gives $\delta\mathcal{F}/\delta c = A$, where A is a constant Lagrange multiplier whose value is to be determined. (Hence A in [3] correspond to our earlier μ.) This condition gives

$$\frac{\partial f}{\partial c} - \tilde{\kappa}\frac{d^2c}{dx^2} = A. \tag{6.2}$$

An underlying conserved quantity can be identified by multiplying equation (6.1) by $d\phi/dx$, equation (6.2) by dc/dx and adding the two results. This leads to

$$\frac{d}{dx}\left[f(\phi, c) - cA - \frac{1}{2}\tilde{\lambda}\left(\frac{d\phi}{dx}\right)^2 - \frac{1}{2}\tilde{\kappa}\left(\frac{dc}{dx}\right)^2 \right] = 0,$$

which reveals the conserved quantity

$$Ac - f(\phi, c) + \frac{1}{2}\tilde{\lambda}\left(\frac{d\phi}{dx}\right)^2 + \frac{1}{2}\tilde{\kappa}\left(\frac{dc}{dx}\right)^2 = H, \tag{6.3}$$

where H is a constant.

In [3] the authors then examine these results in the far-field limit where they expect $d\phi/dx$ and dc/dx vanish. From equation (6.3) it follows that

$$Ac_{-\infty} - f(1, c_{-\infty}) = Ac_{\infty} - f(0, c_{\infty}). \tag{6.4}$$

Additionally, from equations (6.1) and (6.2) the far-field conditions imply

$$\frac{\partial f}{\partial \phi}(0, c_{\infty}) = 0, \tag{6.5}$$

$$\frac{\partial f}{\partial \phi}(1, c_{-\infty}) = 0, \tag{6.6}$$

$$\frac{\partial f}{\partial c}(0, c_{\infty}) = A, \tag{6.7}$$

$$\frac{\partial f}{\partial c}(1, c_{-\infty}) = A. \tag{6.8}$$

Equations (6.4), (6.7) and (6.8) can be used to determine A, c_{∞} and $c_{-\infty}$. These three conditions can be expressed as

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

which is the common tangent construction that generalizes (2.13) and (2.16). The remaining two equations (6.5) and (6.6) remain to be satisfied. In [3] the form of $f(\phi, c)$ was chosen in such a way that these two conditions were satisfied automatically. Their particular choice for $f(\phi, c)$, which we do not outline here, is difficult to generalize to the case of multiple phases and multiple species.

Notes on Heulens et al., 2011

One way to address the difficulties in generalizing a model such as the one outlined above to multiphase/multispecies scenarios is to take the approach used by Heulens *et al.* [1]. Here a set of phase field variables for the M phases are introduced:

$$\eta_1, \eta_2, \ldots, \eta_M.$$

The local phase fractions are defined in terms of these phase field variables using

$$\phi_{\alpha} = \frac{\eta_{\alpha}^2}{\sum_{\alpha=1}^{M} \eta_{\alpha}^2}.$$

Notice that, by definition, we have that

$$\sum_{\alpha=1}^{M} \phi_{\alpha} = 1,$$

but that the same property does not necessarily hold for the η_α variables. A free energy functional could then be defined in terms of the phase field variables η_α and a set of compositional variables (*e.g.*, mole fractions) c_i for the N species of interest.

For the present discussion we shall simplify to the scenario with a two-phase binary system. We introduce a free energy functional of the form

$$\mathcal{F}[\eta_1, \eta_2, c] = \int_{-\infty}^{\infty} \left[f(\eta_1, \eta_2, c) + \frac{1}{2}\tilde{\kappa}\left(\frac{dc}{dx}\right)^2 + \frac{1}{2}\tilde{\lambda}_1\left(\frac{d\eta_1}{dx}\right)^2 + \frac{1}{2}\tilde{\lambda}_2\left(\frac{d\eta_2}{dx}\right)^2 \right] dx,$$

where the function $f(\eta_1, \eta_2, c)$ will be specified below. Following Heulens *et al.* [1] we suppose

$$f(\eta_1, \eta_2, c) = \phi_1 f_1(c) + \phi_2 f_2(c) + U(\eta_1, \eta_2), \tag{6.9}$$

where

$$U(\eta_1, \eta_2) = \left(\frac{\eta_1^4}{4} - \frac{\eta_1^2}{2}\right) + \left(\frac{\eta_2^4}{4} - \frac{\eta_2^2}{2}\right) + \gamma\eta_1^2\eta_2^2 + \frac{1}{4}.$$

This function has minima when $(\eta_1, \eta_2) = (0, 1)$ and $(1, 0)$. Note that

$$\phi_1 = \frac{\eta_1^2}{\eta_1^2 + \eta_2^2}, \quad \phi_2 = \frac{\eta_2^2}{\eta_1^2 + \eta_2^2}.$$

Minimizing as before but now noting that there are three variables η_1, η_2 and c we find the following. Minimizing with respect to η_1 leads to $\delta\mathcal{F}/\delta\eta_1 = 0$ so that

$$\frac{\partial f}{\partial \eta_1} - \tilde{\lambda}_1 \frac{d^2\eta_1}{dx^2} = 0. \tag{6.10}$$

Minimizing with respect to η_2 leads to $\delta\mathcal{F}/\delta\eta_2 = 0$ so that

$$\frac{\partial f}{\partial \eta_2} - \tilde{\lambda}_2 \frac{d^2\eta_2}{dx^2} = 0. \tag{6.11}$$

Minimizing with respect to c, keeping in mind the conservation of total species, leads to $\delta\mathcal{F}/\delta c = A$ so that

$$\frac{\partial f}{\partial c} - \tilde{\kappa} \frac{d^2 c}{dx^2} = A. \tag{6.12}$$

In a similar manner to the previous section we can identify the conserved quantity

$$H = f - cA - \frac{1}{2}\tilde{\kappa}\left(\frac{dc}{dx}\right)^2 - \frac{1}{2}\tilde{\lambda}_1\left(\frac{d\eta_1}{dx}\right)^2 - \frac{1}{2}\tilde{\lambda}_2\left(\frac{d\eta_2}{dx}\right)^2.$$

We now examine the far-field conditions where we expect $c \to c_{-\infty}$, $\phi_1 \to 1$ [along with $(\eta_1, \eta_2) \to (1, 0)$] as $x \to -\infty$ and $c \to c_\infty$, $\phi_1 \to 0$ [along with $(\eta_1, \eta_2) \to (0, 1)$] as $x \to \infty$. First, from the conservation of H we find

$$f(1, 0, c_{-\infty}) - c_{-\infty}A = f(0, 1, c_\infty) - c_\infty A. \tag{6.13}$$

From the η_1 equation (6.10)

$$\frac{\partial f}{\partial \eta_1}(1, 0, c_{-\infty}) = 0, \tag{6.14}$$

$$\frac{\partial f}{\partial \eta_1}(0, 1, c_{\infty}) = 0. \tag{6.15}$$

From the η_2 equation (6.11)

$$\frac{\partial f}{\partial \eta_2}(1, 0, c_{-\infty}) = 0, \tag{6.16}$$

$$\frac{\partial f}{\partial \eta_2}(0, 1, c_{\infty}) = 0. \tag{6.17}$$

From the c equation (6.12)

$$\frac{\partial f}{\partial c}(1, 0, c_{-\infty}) = A, \tag{6.18}$$

$$\frac{\partial f}{\partial c}(0, 1, c_{\infty}) = A. \tag{6.19}$$

We find that equations (6.14)–(6.17) are automatically satisfied by the choice of $f(\eta_1, \eta_2, c)$ shown above in equation (6.9). The remaining equations (6.13), (6.18) and (6.19) can be combined to obtain the required conditions

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

which again can be recognized as the common tangent construction.

Section 7: Notes on Computing the Functional Derivative for the Quasi-equilibrium Model: Ternary Case

Here we examine the free energy for the Heulens *et al.* [1] for M phases and N components. For brevity and for the purposes of interest here we write this as

$$\mathcal{F} = \int_{-\infty}^{+\infty} \left[\sum_{\alpha=1}^{M} \phi_\alpha G_\alpha(\vec{c}_\alpha(\vec{c}, \vec{\phi})) + \sum_{\alpha,\beta=1}^{M} \lambda_{\alpha,\beta} \nabla\eta_\alpha \cdot \nabla\eta_\beta + U(\eta_\alpha) \right] dx,$$

where ϕ_α represent the phase fractions for $\alpha = 1, \ldots, M$ and $\vec{c}_\alpha = [c_\alpha^1, \ldots, c_\alpha^{N-1}]$ are compositions specifically associated with phase α and $\vec{c} = [c_1, \ldots, c_{N-1}]$ are the total concentrations at a given point in space and time. For the particular calculation under consideration here the gradient energy terms will not play a role, nor will the potential $U(\eta_\alpha)$. Note that the quantity $\vec{c}$ is related to the ϕ_α and $\vec{c}_\alpha$ terms by

$$\vec{c} = \sum_{\alpha=1}^{M} \phi_\alpha \vec{c}_\alpha. \tag{7.1}$$

In the quasi-equilbrium state we determine each c_α by minimizing

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

over the $\vec{c}_\alpha$ subject to the constraint (7.1). Introducing Lagrange multipliers Λ^j for $j = 1, ..., N-1$ leads to the following linear system for the $M \times N$ unknowns c_α^j and Λ^j:

$$c_j = \sum_{\alpha=1}^{M} \phi_\alpha c_\alpha^j, \qquad \text{for } j = 1, .., N-1, \tag{7.2}$$

$$0 = -\phi_\alpha \frac{\partial G_\alpha}{\partial c_\alpha^j} + \phi_\alpha \Lambda^j, \qquad \text{for } j = 1, ..., N-1 \text{ and } \alpha = 1, ..., M. \tag{7.3}$$

We comment that the $-\phi_\alpha$ could be factored out but is left in place to give rise to a symmetric matrix in a later stage of the calculation.

Here we think about the ternary case with three phases so that $\vec{\phi} = (\phi_A, \phi_B, \phi_C)$, $\vec{c} = (c_1, c_2)$ and $\vec{c}_\alpha = (c_\alpha^1, c_\alpha^2)$ for $\alpha = A, B, C$. For a formal derivation of governing

equations, the particular aspect of that calculation of interest here is examining variations of $\mathcal{F}$ with respect to c_j:

$$\phi_A \left[\frac{\partial G_A}{\partial c_A^1} \frac{\partial c_A^1}{\partial c_j} + \frac{\partial G_A}{\partial c_A^2} \frac{\partial c_A^2}{\partial c_j} \right] + \phi_B \left[\frac{\partial G_B}{\partial c_B^1} \frac{\partial c_B^1}{\partial c_j} + \frac{\partial G_B}{\partial c_B^2} \frac{\partial c_B^2}{\partial c_j} \right] + \phi_C \left[\frac{\partial G_C}{\partial c_C^1} \frac{\partial c_C^1}{\partial c_j} + \frac{\partial G_C}{\partial c_C^2} \frac{\partial c_C^2}{\partial c_j} \right],$$

for $j = 1, 2$. There are twelve derivatives $\partial c_\alpha^i / \partial c_j$ to be determined. A linear system can be obtained by differentiating the equations (7.2) and (7.3) that determine $\vec{c}_\alpha$ with respect to c_1 and c_2. Doing so leads to a 16×16 symmetric linear system of the form $M\vec{x} = \vec{b}$ where

$$M = \begin{bmatrix} M_A & 0 & 0 & \Phi_A \\ 0 & M_B & 0 & \Phi_B \\ 0 & 0 & M_C & \Phi_C \\ \Phi_A & \Phi_B & \Phi_C & 0 \end{bmatrix},$$

$$M_\alpha = -\phi_\alpha \begin{bmatrix} \frac{\partial^2 G_\alpha}{\partial {c_\alpha^1}^2} & 0 & \frac{\partial^2 G_\alpha}{\partial c_\alpha^1 \partial c_\alpha^2} & 0 \\ 0 & \frac{\partial^2 G_\alpha}{\partial {c_\alpha^1}^2} & 0 & \frac{\partial^2 G_\alpha}{\partial c_\alpha^1 \partial c_\alpha^2} \\ \frac{\partial^2 G_\alpha}{\partial c_\alpha^1 \partial c_\alpha^2} & 0 & \frac{\partial^2 G_\alpha}{\partial {c_\alpha^2}^2} & 0 \\ 0 & \frac{\partial^2 G_\alpha}{\partial c_\alpha^1 \partial c_\alpha^2} & 0 & \frac{\partial^2 G_\alpha}{\partial {c_\alpha^2}^2} \end{bmatrix},$$

and

$$\Phi_\alpha = \begin{bmatrix} \phi_\alpha & 0 & 0 & 0 \\ 0 & \phi_\alpha & 0 & 0 \\ 0 & 0 & \phi_\alpha & 0 \\ 0 & 0 & 0 & \phi_\alpha \end{bmatrix}$$

for $\alpha = A, B, C$. The vector $\vec{x}$ has the form

$$\vec{x} = \begin{bmatrix} \vec{x}_A \\ \vec{x}_B \\ \vec{x}_C \\ \vec{x}_\Lambda \end{bmatrix},$$

where

$$\vec{x}_\alpha = \begin{bmatrix} \frac{\partial c_\alpha^1}{\partial c_1} \\ \frac{\partial c_\alpha^1}{\partial c_2} \\ \frac{\partial c_\alpha^2}{\partial c_1} \\ \frac{\partial c_\alpha^2}{\partial c_2} \end{bmatrix}$$

for $\alpha = A, B, C$ and

$$\vec{x}_\Lambda = \begin{bmatrix} \frac{\partial \Lambda^1}{\partial c_1} \\ \frac{\partial \Lambda^1}{\partial c_2} \\ \frac{\partial \Lambda^2}{\partial c_1} \\ \frac{\partial \Lambda^2}{\partial c_2} \end{bmatrix}.$$

Finally, $\vec{b}$ is the zero vector everywhere except in the last 4×1 block which takes the form

$$\begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}.$$

It appears that at least some progress can be made analytically towards a solution of the problem $Mx = b$ under the conditions that

$$\frac{\partial^2 G_\alpha}{(\partial c_\alpha^1)^2} \frac{\partial^2 G_\alpha}{(\partial c_\alpha^1)^2} - \left(\frac{\partial^2 G_\alpha}{\partial c_\alpha^1 \partial c_\alpha^2} \right)^2 \neq 0,$$

for $\alpha = A, B, C$. This would allow the block matrices M_α to be inverted.

Section 8: Further Discussion of U

As we have seen, the discontinuity in (1.12) causes analytical problems, since we would like U to be as differentiable as possible. Therefore, we may wish to consider $U_0(\phi)$ as the limit of a smooth function, such as these alternatives:

$$U_\epsilon(\phi) = \phi(1-\phi) + \frac{\epsilon}{\phi(1-\phi)}, \tag{8.1a}$$

$$U_\epsilon(\phi) = \phi(1-\phi) - \log(\phi(1-\phi)/\epsilon), \tag{8.1b}$$

$$U_\epsilon(\phi) = \phi(1-\phi) + \exp\left(\frac{\epsilon}{\phi(1-\phi)}\right). \tag{8.1c}$$

Graphs of some of these approximations are shown below. Note that all the functional forms are even about $\phi = 1/2$, which we would expect given the definition of the order parameter.

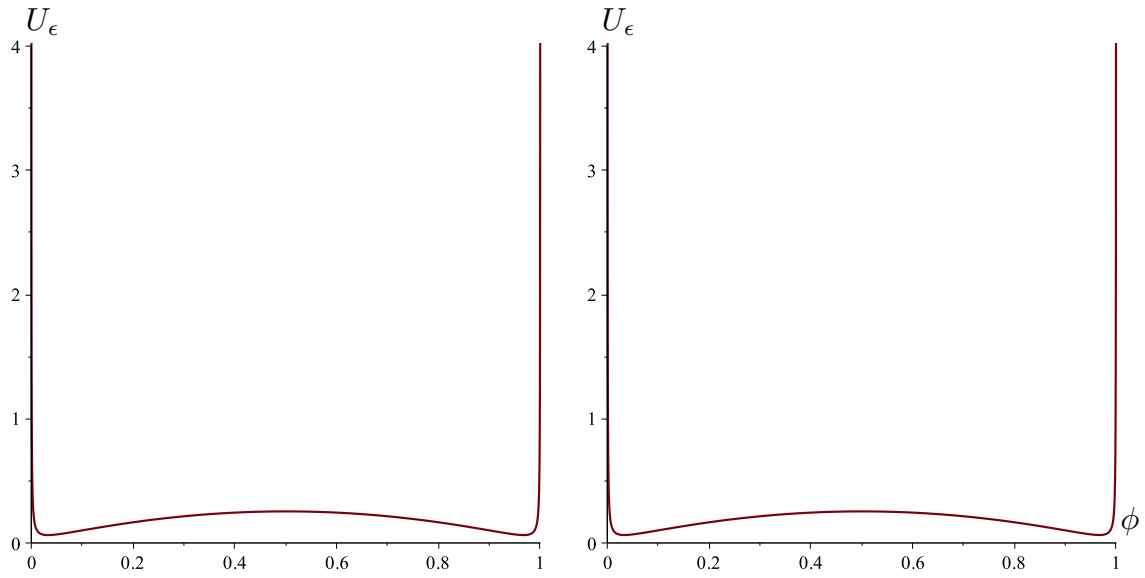

Figure 8.1. Left: (8.1a) with $\epsilon = 10^{-3}$. Right: (8.1c) with $\epsilon = 10^{-3}$.

However, further investigation suggests that these regularized forms would simply smooth ϕ near 0 and 1, rather than fundamentally change the behavior.

The overdetermined nature of the system (2.12) and (2.13) may be why U_0 was defined as sharp as it was. Consider a simpler case, where U is just given by the quartic $U = \phi^2(1-\phi)^2$, as shown in Fig. 8.2. Here 0 and 1 are the local minima of the potential, and hence the fixed points. Note that the G terms in (2.2b) essentially perturb the potential, which in most cases would shift the minima. As a toy problem, let's perturb the potential in Fig. 8.2 by a small linear potential, as shown in Fig. 8.3.

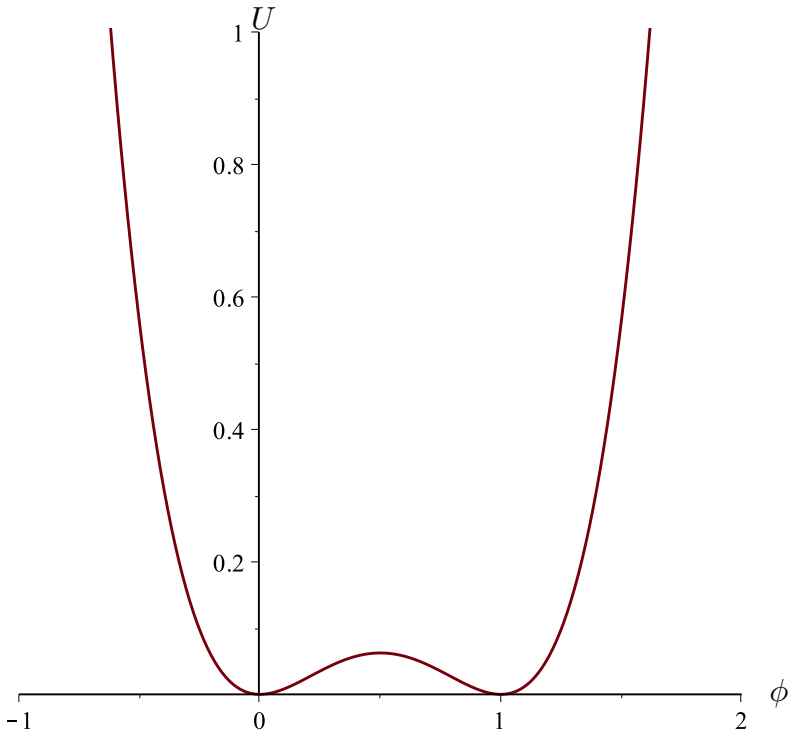

Figure 8.2. Unperturbed quartic potential.

Note that the minima have shifted, and in particular the second minimum is negative. This is unphysical, and hence must be suppressed by the choice of U.

Now let's look at the same situation with the potential given by U_0 in (1.12), as shown in Fig. 8.3. Note that even though the *value* of the second minimum has changed, the *position* has not. This will be true for any perturbation, given the infinite barrier, which is unchangeably high and pins any minima at $\phi = 0$ and 1.

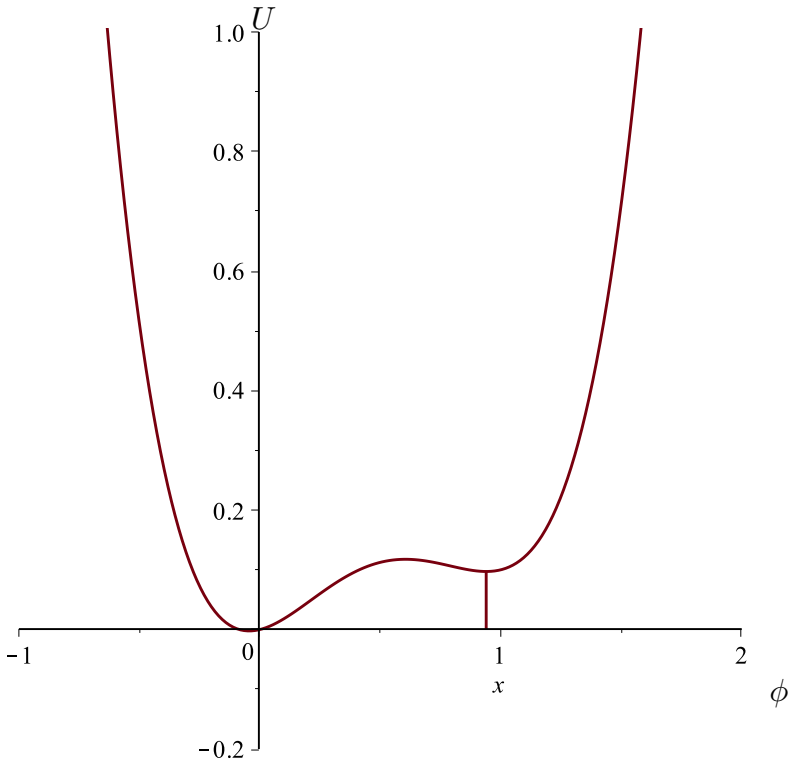

Figure 8.3. Quartic potential perturbed by 0.01ϕ with larger minimum marked.

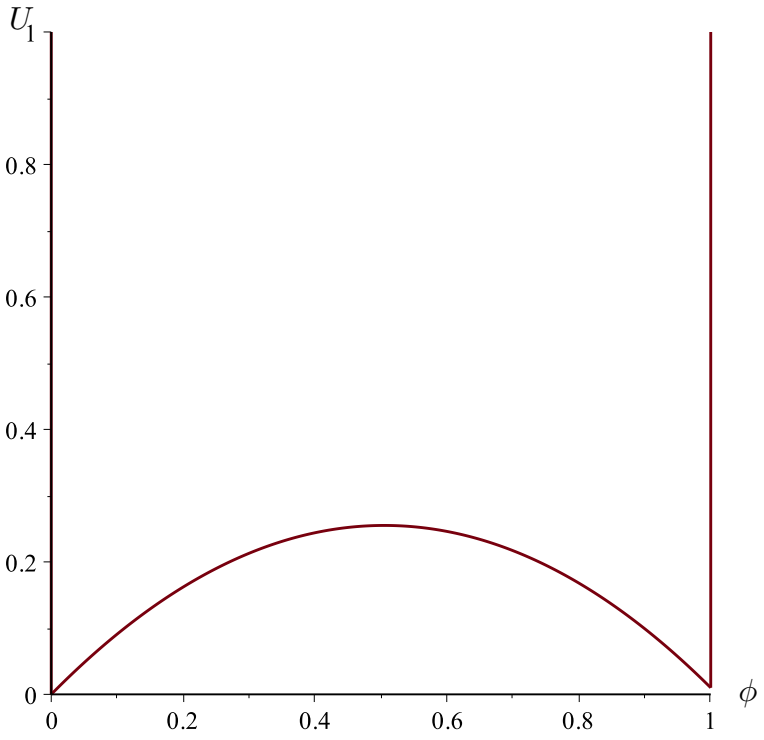

Figure 8.3. $U_0(\phi)$ in (1.12) perturbed by 0.01ϕ.

Nomenclature

Units are listed in terms of mass (M), moles (N), length (L), and time (T). If a symbol appears both with and without tildes, the symbol with tildes has units, while the one without is dimensionless. Equation numbers where a variable is first defined is listed, if appropriate.

A: arbitrary constant, variously defined.
B: arbitrary constant, variously defined.
$\vec{b}$: vector in the Heulens model.
$C(\cdot)$: corner-layer variable (5.13).
$c(\tilde{x})$: composition fraction at position $\tilde{x}$ (1.1).
$\tilde{\mathcal{F}}[\vec{c},\vec{\phi}]$: free energy, units ML^2/T^2 (1.9).
$\tilde{F}$: free energy density, units ML/T^2 (1.10b).
f: free energy density in literature review section.
$\tilde{G}_\alpha(\vec{c})$: "bulk" free energy density of phase α, units ML/T^2 (1.5).
H: conserved constant (6.3).
h: test function for variational problem.
i: integer used to index composition (1.1).
j: integer used to index composition (1.7).
$\tilde{L}$: dummy length used to normalize $\mathcal{F}$, units L (1.13).
M: number of phases (1.3) or matrix in the Heulens model.
N: number of compositions (1.1).
$\tilde{U}(\vec{\phi})$: phase potential, units ML/T^2 (1.6).
V: arbitrary volume (1.9).
$\tilde{W}$: constant characterizing the potential, units ML/T^2 (1.12).
X: boundary-layer variable, variously defined (4.2).
$\tilde{x}$: distance along ceramic, units L (1.1).
$\vec{x}$: vector in the Heulens model.
y: phase plane variable, variously defined (2.14).
α: integer used to index composition (1.3).
β: integer used to index composition (1.8).
$\Delta\tilde{G}$: difference between energy minima of phases (1.14).
Δx: width of transtion region (5.8).
η: phase field variable in Heulens [1].
$\tilde{\kappa}$: gradient energy coefficient associated with the compositions, units ML^3/T^2 (1.7).
Λ: Lagrange multiplier in Heulens model.
$\tilde{\lambda}$: gradient energy coefficient associated with the phases, units ML^3/T^2 (1.8).
μ: variable related to the chemical potential (2.4).
ξ: scaling factor for subdomains (3.4).
Φ: phase fraction in the boundary layer (4.2) or matrix in the Heulens model.

$\phi(\tilde{x})$: phase fraction at position $\tilde{x}$ (1.3).

Other Notation

0: as a subscript on U, used to indicate the infinite-barrier potential (1.12).
A: as a subscript, used to indicate one of the phases in the ternary phase problem.
B: as a subscript, used to indicate one of the phases in the ternary phase problem.
b: as a subscript, used to indicate the shared boundary of the exclusion zones.
C: as a subscript, used to indicate one of the phases in the ternary phase problem.
m: as a subscript, used to indicate the solution in the middle (not in the exclusion zones) (3.3).
ϵ: as a subscript on U, used to indicate the smoothed potentials (8.1).
$>$: as a subscript, used to indicate the right exclusion zone (2.15).
$<$: as a subscript, used to indicate the left exclusion zone (2.15).
$-$: as a subscript, used to indicate a value as $x \to -\infty$ (2.7).
$+$: as a subscript, used to indicate a value as $x \to \infty$ (2.7).
$*$: used to indicate a minimum in the bulk free energy density (1.11).
$\bar{}$: used to indicate a spatial average (2.5).

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[1] J. Heulens, B. Blanpain, and N. Moelans, "A phase field model for isothermal crystallization of oxide melts," *Acta Mater.*, vol. 59, pp. 2156–2165, 2011.

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Comments on Blowey & Elliott

Joseph D. Fehribach
Worcester Polytechnic Institute

Editor's Note: All references to sections, etc. refer to [1], the paper listed in the title.

1 Subderivative of the indicator function

The most important detail in understanding the concept of the subderivative of the indicator function as discussed in the Introduction is that the indicator function here is *not* the same as the characteristic function.

Definition 1.1 *Suppose X is some superset (the union over some collection of sets). The* **indicator function** *for a set $A \subset X$ is $I_A : X \to \mathbb{R}^\infty$ where*

$$I_A(x) = \begin{cases} 0 & x \in A \\ +\infty & x \notin A \end{cases}$$

The subderivative is then the *set* of all slopes which lie below the convex function being considered. For a classically differentiable function, the subderivative is the singleton set containing the value of the derivative of the function.

Definition 1.2 *Suppose F is a convex function from some subset Ω of the real line into the extended reals: $F : \Omega \to \mathbb{R}^\infty$. Let u be a point in the domain where the function is finite: $F(u) < +\infty$. The slope m is in the* **subderivative** *of F at u ($m \in \partial F(u)$) if and only if $m(v-u) + F(u) \leq F(v)\ \forall\, v \in \Omega$.*

Example. Suppose $A = [-1, 1]$ and consider the indicator function of A. Notice that I_A is convex. For $u \in (-1, 1)$, I_A is differentiable (indeed constant), and thus $\partial F(u) = \{0\}$. For $u \notin [-1, 1]$, I_A is not finite, so either $\partial F(u)$ is undefined, or alternatively, $\partial F(u) = \emptyset$. Hence the two interesting points are the endpoints of the interval: $u = \pm 1$. Consider $u = 1$; since $F(1) = 0$, $F(v) = 0\ \forall\, v \in [-1, 1]$, and $F(v) = +\infty\ \forall\, v > 1$, the inequality in the definition of *subderivative* is satisfied if and only if $m \geq 0$. For $u = -1$, the result is that $m \leq 0$.

2 The one-dimensional problem

The problem in section 3.2 is the one-dimensional version of the stationary problem $(\mathbf{S}_\gamma)$ introduced at the beginning of section 3. Lemma 3.2 is used to translate the variational formulation of $(\mathbf{S}_\gamma)$ given in (3.1) to the more traditional formulation of the problem in one dimension as stated in (3.14). Here the domain is $\Omega = (0, \ell)$, *i.e.*, an interval of length ℓ. So $u(x) = \pm 1 \; \forall \, x \in \Omega - \Omega_0$ and

$$\gamma u''(x) + u(x) + \lambda = 0 \qquad\qquad \forall \, x \in \Omega_0 \tag{1}$$

where Ω_0 is the subset of Ω where $-1 < u < 1$. From basic real analysis, any open subset of the real line (or of $(0, \ell)$) can be written as the countable union of disjoint open intervals. So $\Omega_0 = \cup_{i=1}^{\infty} \Omega_0^i$ where $\Omega_0^i = (x_L^i, x_R^i)$[1]. Now the derivatives must match in the stationary problem at each interface point between $\Omega - \Omega_0$ and Ω_0, so $u'(x) = 0 \; \forall \, x \in \partial\Omega_0$ (a jump in the first derivative at an interface point would imply that the second derivative is delta function). Since $u = \pm 1$ on $\Omega - \Omega_0$, this no-flux condition implies that $u \in C^{1,1}(\Omega)$. This means that u and its first derivative are both Lipschitz continuous.

Suppose that we consider the transition from a $u = +1$ phase to a $u = -1$ phase. Consider one of the subintervals of Ω_0 (the i-th subinterval), and without loss of generality, assume that $u(x_L^i) = 1$ and $u(x_R^i) = -1$. This is the *Type 1* possibility of Blowey & Elliott. As we are interested in a transitional solution and not an oscillatory one, the unique solution satisfying all of the boundary conditions is

$$u(x) = \cos((x - x_L^i)/\sqrt{\gamma}) \qquad\qquad \forall \, x \in \Omega_0^i = (x_L^i, x_R^i) \tag{2}$$

where $x_L^i - x_R^i = \sqrt{\gamma}\pi$. So for this system, at least in one dimension, the parameter γ controls the width of the transition layer between the phases. The other types (*Type 2* and *Type 3*) deal with the cases where there is a transition between two portions of the same phase (say $u = +1$ at both endpoints), solutions involving the overall interval endpoints ($x = 0$ or $x = \ell$), and finally the case where $\Omega_0 = (0, \ell)$, the transition region being the entire domain interval.

The rest of the section is a meticulous piecing together of the various solution types to reach and overall solution. Finally Theorem 3.6 states that provided the parameter γ is small enough to allow at least one transition layer, *i.e.*, $\gamma < \ell^2/\pi^2$, the minimizers of $(\mathbf{M}_\gamma)$ are the steady state solutions with the narrowest transition layer(s), *i.e.*, smallest $|\Omega_0|$. The non-uniqueness of the minimizing solution is due at least in part to location of the transition layers being arbitrary when the overall boundary conditions require two transitions.

References

[1] J. Blowey and C. Elliott, "The Cahn-Hilliard gradient theory for phase separation with non-smooth free energy. Part I: Mathematical analysis," *European J. Appl. Math*, vol. 2, pp. 233–280, 1991.

[1] Blowey & Elliott did not place a naught subscript on these subintervals, but they should have!

Interface solution in 2 phases, 2 concentrations problem

Maxim Zyskin
Rutgers University

Our 2-phase, 2-concentrations problem is described by fields $c_1(x) \equiv c(x)$, $c_2(x) = 1 - c_1(x), x \in \mathbb{R}$ (concentrations), $\varphi_1(x) \equiv \varphi(x), \varphi_2(x) = 1 - \varphi(x)$, (phases), with the range for all fields being $[0, 1]$.

The free energy for the 2-phase, 2-concentrations problem is given by

$$F[\varphi, c] = \int \left\{ \varphi G_1(c) + (1-\varphi) G_2(c) + \frac{\lambda}{2} |\nabla c|^2 + \frac{\kappa}{2} |\nabla \varphi|^2 + W(\varphi) - Kc \right\} dx, \tag{1}$$

where K is the chemical potential, G_i are quadratic,

$$G_i(c) = g_i + \tfrac{1}{2}\Omega_i (c - c_i)^2, \quad i = 1, 2, \tag{2}$$

and

$$W(\varphi) = \begin{cases} w\varphi(1-\varphi), & 0 \le \varphi \le 1 \\ +\infty, & \varphi \notin [0,1] \end{cases} \tag{3}$$

We can think that the integral defining the free energy is taken over a sufficiently large interval $x \in [-L, L]$.

We are seeking a solution which is "well-behaved" as $L \to \infty$ (solution we describe below does not depend on L, provided L is large enough).

The Euler-Lagrange equations, taking into the account the constraint $0 \le \varphi \le 1$, are:

$$\begin{array}{l} -\kappa\varphi'' + G_1(c) - G_2(c) + W'(\varphi) \quad \begin{cases} = 0, & 0 < \varphi < 1; \\ \le 0, & \varphi = 1; \\ \ge 0, & \varphi = 0; \end{cases} \\ -\lambda c'' + \varphi G_1'(c) + (1-\varphi) G_2'(c) - K = 0, \\ 0 \le \varphi \le 1. \end{array} \tag{4}$$

(Sign of inequalities in (4) ensures that the free energy cannot be *lowered* by varying the fields, without *violating the constraint.* We assume that only phase fields may take 0 or 1 values, while concentrations happen to stay away from 0 or 1.)

It can be checked that in general there is no solution with φ approaching values 0, 1 respectively from above (below) as $x \to -\infty$ ($x \to \infty$), and c approaching a constant value. However, there may be an interface solution, with φ exactly 0 or 1 outside of a finite interval.

Thus we are seeking an interface solution of (4) with

$$\begin{array}{l}\varphi = \left\{ \begin{array}{ll} 0 & x < a \\ 1 & x > b \end{array} \right. , \\ c' \to 0, |x| \to \infty \text{ (or, equivalently, } c \text{ is bounded at infinity).}\end{array} \tag{5}$$

for some $a < b$,and such that φ, φ', c, c' are continuous at $x = a, b$.

From (4), (5) it follows that

$$c(x) = \left\{ \begin{array}{ll} A_1 + B_1 \exp\left(-\sqrt{\frac{\Omega_1}{\lambda}}x\right), & A_1 = c_1 + \frac{K}{\Omega_1}, \quad x > b \\ A_2 + B_2 \exp\left(\sqrt{\frac{\Omega_2}{\lambda}}x\right), & A_2 = c_2 + \frac{K}{\Omega_2}, \quad x < a \end{array} \right. , \tag{6}$$

with arbitrary B_1, B_2. This implies a condition relating c and c',

$$\begin{array}{rl} c' = -\sqrt{\frac{\Omega_1}{\lambda}}(c - A_1), & x \geq b \\ c' = \sqrt{\frac{\Omega_2}{\lambda}}(c - A_2), & x \leq a \end{array} . \tag{7}$$

At first it appears that such a solution in general will not exist. Indeed, by shifting x by a we may assume that $a = 0$. A general solution of (4) will involve 4 arbitrary constants, and b gives another free parameter; however for this 5 parameters, there are 6 conditions to satisfy: conditions (7) at $x = a, b$, and continuity of φ, φ' at the endpoints.

However, there is a conserved quantity

$$H = \varphi G_1(c) + (1 - \varphi) G_2(c) - \tfrac{\lambda}{2} |\nabla c|^2 - \tfrac{\kappa}{2} |\nabla \varphi|^2 + W(\phi) - Kc, \tag{8}$$

the "Hamiltonian" for the action (1). It is immediate to check by differentiation that if (4) are satisfied than $\frac{dH}{dx} = 0$. Therefore, H is constant, on $x < a$, $x > b$, and $a < x < b$. Continuity of φ, φ', c, c' at the endpoints will imply that H is continuous at $x = a$, $x = b$, therefore H is the same constant for all x. Comparing H at $x \to \pm\infty$ yields

$$G_1(A_1) - KA_1 = G_2(A_2) - KA_2 = H, \tag{9}$$

thus

$$K = \frac{G_2(A_2) - G_1(A_1)}{A_2 - A_1}. \tag{10}$$

Note that since $A_i = c_i + \frac{K}{\Omega_i}$, differentiation of (2) gives

$$G_i'(A_i) = K, i = 1, 2. \tag{11}$$

Thus K must be the slope of a common tangent to parabolas $G_1(c), G_2(c)$. Note that (9) is a quadratic equation for K, with coefficients determined by coefficients in G_1, G_2. Thus for interface solution as described above to exist, the chemical potential should be fixed by the

common tangent condition (9). Let us now assume that K is such that the tangent condition is satisfied. It is easy to check that conservation of H implies that

$$(c(a) - A_2)^2 - \tfrac{\lambda}{\Omega_2} (c'(a))^2 = (c(b) - A_1)^2 - \tfrac{\lambda}{\Omega_1} (c'(b))^2 , \tag{12}$$

thus if the conditions (7) is satisfied at $x = a$, it is satisfied (up to $\pm$ sign) at $x = b$ automatically.

WLOG, let's take $a = 0$. To find a solution, we perform the following steps:

1. Pick a $c_0 \in [0, 1]$ and set conditions at $x = 0$ to be $\varphi(0) = \varphi'(0) = 0$, $c(0) = c_0$ $c'(0) = \sqrt{\frac{\Omega_2}{\lambda}}(c_0 - A_2)$ (so $c'(0)$ satisfies (7)).

2. Solve (4) with such conditions to get $c(x), \varphi(x)$ for $x \geq 0$.

3. Find the smallest $b > 0$ such that $\varphi'(b) = 0$. Such b will depend on a choice of c_0. Constants c_0 for which $\varphi(x)$ or $c(x) \notin [0, 1], 0 \leq x \leq b$, can be disregarded.

4. Now vary admissible c_0, and try to find c_0 such that $\varphi(b) = \varphi'(b) = 0$. (That can be achieved for example by spotting two values of c_0 with $\varphi(b) - 1$ of opposite sign, and than using the secant method).

5. Verify that the condition (7) is satisfied at $x = b$ (it should be satisfied automatically up to a sign from the conservation of H, within numerical accuracy). Disregard solutions which give the wrong sign for $c'(b)$.

For illustration, we have performed this computation in the case

$$\begin{aligned} &G_1(c) = \tfrac{1}{2}(c - 0.2)^2, \\ &G_2(c) = 0.03 + \tfrac{3}{2}(c - 0.6)^2, \\ &\lambda = \kappa = 1 \end{aligned} \tag{13}$$

We have taken $K \approx 0.0804$, which satisfies the common tangent condition, as illustrated in Fig. 1 We have found an interface solution with $c_0 \approx 0.604$. This solution is shown in Fig. 2.

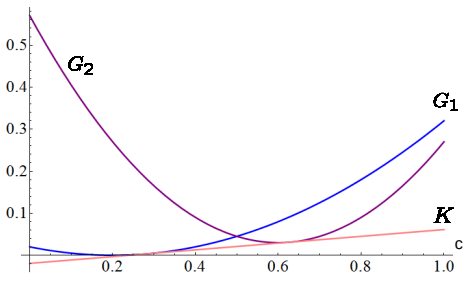


Figure 1: Common tangent construction

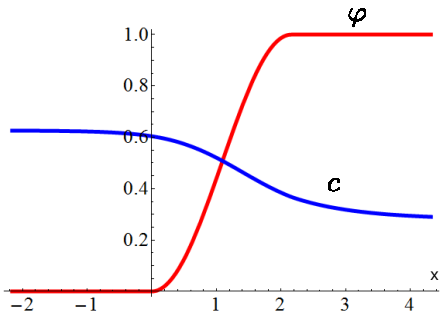


Figure 2: Interface solution

Linear stability analysis of phase field models

Thomas Witelski
Duke University

Linear stability analysis can provide helpful predictions on stability of equilibrium states and rates of growth/decay of infinitesimal perturbations of those states. While these results are limited to short-time predictions of near-equilibrium behavior[1], they can be used at a basic level to help understand and compare fundamental properties of different phase field models being considered.

1 Cahn-Hilliard equation

$$\frac{\partial c}{\partial t} = \frac{\partial^2}{\partial x^2}\left(f'(c) - \kappa \frac{\partial^2 c}{\partial x^2}\right) \qquad f(c) = \frac{1}{2}c^2(1-c)^2 \tag{1}$$

Consider small perturbations to constant (spatially homogeneous) states,

$$c(x,t) \sim \bar{c} + \epsilon \cos(kx) e^{\sigma t} \tag{2}$$

Because of the conservation of the composition parameter, the value $\bar{c}$ is determined by the average of the initial condition,

$$\bar{c} = \frac{1}{L}\int_0^L c_0(x)\, dx \tag{3}$$

Then, substituting the ansatz for $c(x,t)$ into the PDE and linearizing (keeping up to $O(\epsilon)$ terms), yields the dispersion relation

$$\sigma(k;\bar{c}) = -k^2(1 - 6\bar{c} + 6\bar{c}^2 + \kappa\, k^2) \tag{4}$$

A consequence of the conservation of c for linear stability is that the $k = 0$ 'bulk mode' must be neutrally stable, $\sigma(0) = 0$, which is consistent with the above result. The dispersion relation also shows that ranges around each pure component-phase, $\bar{c} = 0, \bar{c} = 1$ are also stable with $\sigma < 0$ for $k > 0$ – namely for initial conditions corresponding to large or small $\bar{c}$ averages, perturbations will decay and the solution will equilibrate to the constant $\bar{c}$.

In contrast, in the spinodal range $\frac{1}{2} - \sqrt{3}/6 < \bar{c} < \frac{1}{2} - \sqrt{3}/6$ (i.e. the marginal case, where $1 - 6\bar{c} + 6\bar{c}^2 = 0$, $0.211 < \bar{c} < 0.788$) exhibits instabilities ($\sigma > 0$ for some range of k) and perturbed near-constant compositions will break-up into phase-separated states with interfaces between regions with $c = 0$ and $c = 1$.

[1] and can be done analytically only for simple states

2 Cogswell-Carter model

Consider a two-phase, two-component system in one-dimension. This system is governed by two PDE evolution equations, one for the composition fraction ($c = c_1$ with $c_2 = 1 - c$) and one for the phase fraction ($\phi = \phi_1$ with $\phi_2 = 1 - \phi_1$),

$$\frac{\partial \phi}{\partial t} = \lambda \frac{\partial^2 \phi}{\partial x^2} + G_2(c) - G_1(c) - U'(\phi), \tag{5a}$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[c(1-c)\frac{\partial}{\partial x}\left(\phi G_1'(c) + (1-\phi)G_2'(c) - \kappa \frac{\partial^2 c}{\partial x^2}\right)\right] \tag{5b}$$

$$G_1(c) = 50(c - \tfrac{1}{5})^2 \qquad G_2(c) = 5 + 150(c - \tfrac{4}{5})^2 \tag{6}$$

$$U'(\phi) = \begin{cases} W(1-2\phi) & 0 < \phi < 1, \\ \infty & \text{else} \end{cases} \tag{7}$$

While any homogeneous values for c, ϕ are equilibrium solutions of the composition equation, because of the reaction terms in the phase equation, the overall system only has steady solutions for specific values of c, ϕ. Depending on the value of the W parameter, these may not lie in the physically acceptable range ($0 \le c, \phi \le 1$).

Consider linear perturbations to a spatially homogeneous single phase,

$$c(x,t) \sim \bar{c} + \epsilon A \cos(kx) e^{\sigma t} \qquad \phi(x,t) \sim \bar{\phi} + \epsilon B \cos(kx) e^{\sigma t} \tag{8}$$

Substituting into the PDEs and linearizing, at $O(\epsilon^0)$ we determine a necessary relation between the composition and the phase, depending on the parameter W,

$$\bar{\phi} = \frac{1}{2} - \frac{100\bar{c}^2 - 220\bar{c} + 99}{2W}. \tag{9}$$

For general values of $W > 0$ this relation does not correspond to either expected pure phase (i.e. neither $\phi = 1$ for $c = \frac{1}{5}$ nor $\phi = 0$ for $c = \frac{4}{5}$). At $O(\epsilon)$, the growth rate of instabilities, $\sigma(k)$ follows from solving a 2×2 matrix eigenvalue problem for the coefficient eigenvector $(A, B)^T$. This problem is somewhat messy for general wavenumber $k > 0$, but it simplifies a lot for $k = 0$ (spatially uniform perturbations) and yields $\sigma_1 = 0$ (the neutrally stable mode for mass conservation) and $\sigma_2 = 2W > 0$ an unstable spatially uniform phase change mode. This solution does not seem physically acceptable.

3 Moelans/Heulens model

The corresponding two-phase, two-component version of the model by Heulens takes the form

$$\frac{\partial \eta_1}{\partial t} = \lambda \frac{\partial^2 \eta_1}{\partial x^2} - \eta_1^3 + \eta_1 - 2\eta_1\eta_2^2 - \left([G_1(c_1) - G_1'(c_1)c_1] - [G_2(c_2) - G_2'(c_2)c_2]\right) \frac{\partial \phi_1}{\partial \eta_1} \tag{10a}$$

$$\frac{\partial \eta_2}{\partial t} = \lambda \frac{\partial^2 \eta_2}{\partial x^2} - \eta_2^3 + \eta_2 - 2\eta_2\eta_1^2 - \left([G_2(c_2) - G_2'(c_2)c_2] - [G_1(c_1) - G_1'(c_1)c_1]\right) \frac{\partial \phi_2}{\partial \eta_2} \quad (10b)$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\phi_1 \frac{\partial c_1}{\partial x} + (1-\phi_2)\frac{\partial c_2}{\partial x}\right) \quad (10c)$$

$$\phi_1 = \frac{\eta_1^2}{\eta_1^2+\eta_2^2} \qquad \phi_2 = \frac{\eta_2^2}{\eta_1^2+\eta_2^2} \quad (10d)$$

$$c_1 = \tfrac{1}{5} - \tfrac{\alpha}{100} \qquad c_2 = \tfrac{4}{5} - \tfrac{\alpha}{300} \qquad \alpha = \frac{\frac{1}{5}\phi_1 + \frac{4}{5}(1-\phi_1) - c}{\frac{1}{100}\phi_1 + \frac{1}{300}(1-\phi_1)}. \quad (10e)$$

The stability analysis for this system follows similar lines to the approach used for the Cogswell-Carter model: assume perturbed solutions

$$c(x,t) \sim \bar{c} + \epsilon A\cos(kx)e^{\sigma t} \qquad \eta_1(x,t) \sim \bar{\eta}_1 + \epsilon B\cos(kx)e^{\sigma t} \qquad \eta_2(x,t) \sim \bar{\eta}_2 + \epsilon C\cos(kx)e^{\sigma t} \quad (11)$$

At $O(\epsilon^0)$ there is a complicated relation between $\bar{c}, \bar{\eta}_1, \bar{\eta}_2$. At $O(\epsilon)$, there is a 3×3 matrix eigenvalue problem for the growth rates ($\sigma(k=0)=0$ must be one solution by the mass constraint). Further work is needed to analyze these resulting equations.

MPI 2013 Contributions

Harrison Potter
Duke University

I worked through the derivation given in the paper "Thermodynamics phase-field model for microstructure with multiple components and phases: the possibility of metastable phases" by Daniel A. Cogswell and W. Craig Carter. I then used my formulation of their equations to determine the PDE governing the mole fractions c_i and phase fractions ϕ_α for 2 components / 1 phase, 1 component / 2 phases, and 2 components / 2 phases and implemented each of these cases numerically using the method of finite differences with Newton's method to handle the nonlinearity and a Backward-Time Centered-Space implicit difference scheme.

1 General Equations

Let our system have M components indexed by α, N phases indexed by i, and d dimensions, where $d \in \{1, 2, 3\}$. We will here consider only the $d = 1$ case.

The Cahn-Hilliard equations are derived from energy considerations, in particular by considering the free energy $f(\vec{c}, \vec{\phi}, \vec{\nabla}\vec{c}, \vec{\nabla}\vec{\phi}, \ldots)$. A full expression for the free energy is totally unknown, but we can approximate it by linearizing it about the homogeneous free energy $f_0(\vec{c}, \vec{\phi}, 0, 0, \ldots)$ in a Taylor expansion to get the leading order correction terms. If we then postulate the form of f_0 we will have an approximate expression for f.

This linearization yields the following quadratic form:

$$\frac{1}{2}\begin{bmatrix}\vec{\nabla}\vec{c} & \vec{\nabla}\vec{\phi}\end{bmatrix}\begin{bmatrix}\kappa_{ij} & \xi_{i\alpha} \\ \xi_{\alpha i} & \lambda_{\alpha\beta}\end{bmatrix}\begin{bmatrix}(\vec{\nabla}\vec{c})^T \\ (\vec{\nabla}\vec{\phi})^T\end{bmatrix} \tag{1.1}$$

where $\vec{c}$ is a row vector with $M-1$ entries and $\vec{\phi}$ is a row vector with $N-1$ entries since we set

$$c_M := 1 - \sum_{i=1}^{M-1} c_i \qquad \text{and} \qquad \phi_N := 1 - \sum_{\alpha=1}^{N-1} \phi_\alpha. \tag{1.2}$$

The three matrices above are $d\times(M+N-2)$, $(M+N-2)\times(M+N-2)$, and $(M+N-2)\times d$. Our free energy functional is then

$$F[\vec{c}, \vec{\phi}] = \int_V \left(f_0 + \frac{1}{2}\begin{bmatrix}\vec{\nabla}\vec{c} & \vec{\nabla}\vec{\phi}\end{bmatrix}\begin{bmatrix}\kappa_{ij} & \xi_{i\alpha} \\ \xi_{\alpha i} & \lambda_{\alpha\beta}\end{bmatrix}\begin{bmatrix}(\vec{\nabla}\vec{c})^T \\ (\vec{\nabla}\vec{\phi})^T\end{bmatrix} \right) dV \tag{1.3}$$

We model the homogeneous free energy f_0 as a linear combination of paraboloid potential wells in mole fractions, one for each phase; i.e. each phase has an instrinsic composition c^*_α according to its preferred composition of components, and deviations from this composition lead to more energetically costly states. Each such potential well we shall denote by $G_\alpha(\vec{c})$. We also introduce a potential barrier that separates each phase from its competitors, which we denote by $U(\vec{\phi})$. Thus we postulate that

$$f_0 = \sum_{\alpha=1}^{N} \phi_\alpha G_\alpha(\vec{c}) + U(\vec{\phi}) \tag{1.4}$$

where

$$G_\alpha(\vec{c}) = E_\alpha + S_\alpha \sum_{i=1}^{M-1} (c_i - c^*_{i,\alpha})^2 \tag{1.5}$$

and

$$U(\phi) = \frac{1}{2}\vec{\phi} W \vec{\phi}^T. \tag{1.6}$$

Several parameters here enter our model. E_α is the energy level of phase α, S_α is the steepness of the potential well for phase α, and W is a symmetric matrix with 0 entries on its diagonal and positive entries off the diagonal. The entry $W_{\alpha,\beta}$ gives the magnitude of the potential barrier between phase α and phase β.

This completes our specification of the energy functional:

$$F[\vec{c}, \vec{\phi}] = \int_V \left(\sum_{\alpha=1}^{N} \phi_\alpha \left(E_\alpha + S_\alpha \sum_{i=1}^{M-1} (c_i - c^*_{i,\alpha})^2 \right) + \frac{1}{2}\vec{\phi} W \vec{\phi}^T \right. \tag{1.7}$$

$$\left. + \frac{1}{2} \begin{bmatrix} \vec{\nabla}\vec{c} & \vec{\nabla}\vec{\phi} \end{bmatrix} \begin{bmatrix} \kappa_{ij} & \xi_{i\alpha} \\ \xi_{\alpha i} & \lambda_{\alpha\beta} \end{bmatrix} \begin{bmatrix} (\vec{\nabla}\vec{c})^T \\ (\vec{\nabla}\vec{\phi})^T \end{bmatrix} \right) dV \tag{1.8}$$

The PDE equations governing $\vec{c}$ and $\vec{\phi}$ are then given as follows. The mole fractions evolve according to a generalization of Ficksian diffusion, i.e. instead of evolving with flux

$$\vec{q}_{Ficks,i} = -D_i \vec{\nabla} c_i \tag{1.9}$$

the mole fractions evolve with flux

$$\vec{q}_{CH,i} = -M_i \vec{\nabla} \mu_i = -\frac{D_i}{RT} c_i \vec{\nabla} \mu_i \tag{1.10}$$

where D_i is the diffusivity of component i, M_i is the mobility of component i, R is the universal gas constant, T is temperature, and μ_i is the chemical potential associated with component i. This chemical potential is defined to be a functional derivative of our free energy functional from above:

$$\mu_i := \frac{1}{n} \frac{\delta F}{\delta c_i}. \tag{1.11}$$

We are then left with the PDE

$$\frac{\partial c_i}{\partial t} = \vec{\nabla} \cdot \left(\frac{D_i}{nRT} c_i \vec{\nabla} \frac{\delta F}{\delta c_i} \right). \tag{1.12}$$

The PDE governing the phases is a gradient flow of the free energy functional:

$$\frac{\partial \phi_\alpha}{\partial t} = -\frac{r_\alpha}{n} \frac{\delta F}{\delta \phi_\alpha} \tag{1.13}$$

where the parameters r_α give a measure of how rapidly each phase progresses along its path of steepest descent.

2 2 Components, 1 Phase

In this case $\phi_1 \equiv 1$ with $c_2 := 1 - c_1$ so that c_1 is our only variable. Our energy functional is

$$F[c_1] = \int_V \left(E_1 + S_1 (c_1 - c_{1,1}^*)^2 + \frac{1}{2} \kappa_{11} (c_{1,x})^2 \right) dV \tag{2.1}$$

so that our PDE here is

$$\frac{\partial c_1}{\partial t} = \frac{D_1}{nRT} \left(-\kappa_{11} \left(c_1 c_{1,xxx} \right)_x + \left(c_1 \left(2 S_1 (c_1 - c_{1,1}^*) \right)_x \right)_x \right). \tag{2.2}$$

This case is incredibly boring: numerical simulations lead to solutions that demonstrate nothing more than fourth order diffusion. As there is no competition between phases for components the components simply level off and you are left with a terribly boring uniform solution.

3 1 Component, 2 Phases

In this case $c_1 \equiv 1$ with $\phi_2 := 1 - \phi_1$ so that ϕ_1 is our only variable. Our energy functional is then

$$F[\phi_1] = \int_V \left(\phi_1 E_1 + (1 - \phi_1) E_2 + W_{12} \phi_1 (1 - \phi_1) + \frac{1}{2} \lambda_{11} (\phi_{1,x})^2 \right) dV \tag{3.1}$$

so that our PDE here is

$$\phi_{1,t} = -\frac{r_1}{n} \left(E_1 - E_2 + W_{12} (1 - 2\phi_1) - \lambda_{11} \phi_{1,xx} \right). \tag{3.2}$$

This case is much more interesting. If $E_1 < E_2$, then this dominates long-term behavior of the system: as phase 1 is in this case a lower energy phase in the long run everything converts into phase 1 so that $\phi_1 \equiv 1$ as $t \to \infty$. This progression towards a uniform solution takes the form of a front separating the phase 1 and phase 2 regions that propogates towards the boundary. If $E_1 = E_2$ then this front does not progress towards the boundary, but rather remains stationary in the center of the computational domain and develops a steady state solution. The steepness of this interface between phase 1 and phase 2 regions is determined by the magnitude of W_{12}: as W_{12} gets larger the interface becomes sharper, i.e. there is a more rapid transition from phase 1 to phase 2. This is shown in Figure 1 below.

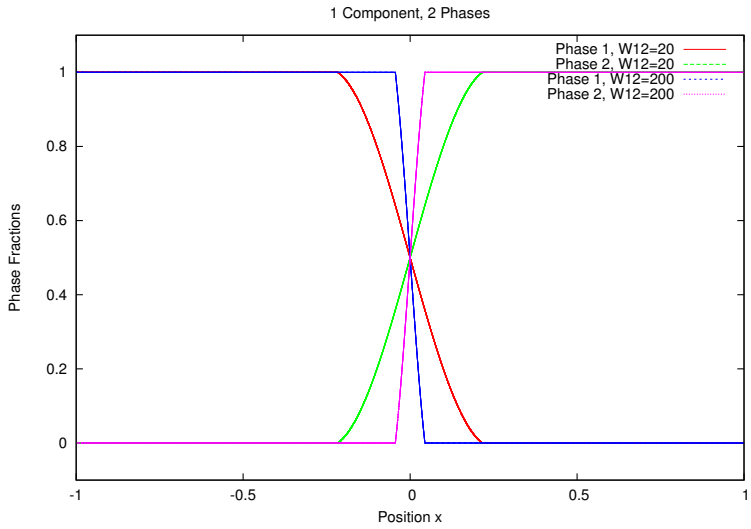


Figure 1: Evolution of PDE yields steady state interface between phases. Interface is steeper as W_{12} increases.

4 2 Components, 2 Phases

In this case we have that $c_2 := 1 - c_1$ and $\phi_2 := 1 - \phi_1$ so that we are left with the two variables c_1 and ϕ_1. Our energy functional is then

$$F[c_1, \phi_1] = \int_V \big(\phi_1 E_1 + \phi_1 S_1 (c_1 - c_{1,1}^*)^2 \tag{4.1}$$

$$+ (1-\phi_1) E_2 + (1-\phi_1) S_2 (c_1 - c_{1,2}^*)^2 \tag{4.2}$$

$$+ W_{12}\phi_1(1-\phi_1) + \frac{1}{2}\kappa_{11}(c_{1,x})^2 + \frac{1}{2}\lambda_{11}(\phi_{1,x})^2 + \xi_{12}\phi_x c_x \Big)\, dV \tag{4.3}$$

so that our system of PDE here is

$$c_{1,t} = \frac{D_1}{nRT}\left[-\xi_{12}\left(c_1\phi_{1,xxx}\right)_x - \kappa_{11}\left(c_1 c_{1,xxx}\right)_x \right. \tag{4.4}$$

$$\left. + \Big(c_1\left[2\phi_1 S_1(c_1 - c_{1,1}^*) + 2(1-\phi_1)S_2(c_1 - c_{1,2}^*)\right]_x\Big)_x\right] \tag{4.5}$$

and

$$\phi_{1,t} = \frac{-r_1}{n}\left(E_1 - E_2 + S_1(c_1 - c_{1,1}^*)^2 - S_2(c_1 - c_{1,2}^*)^2 \right. \tag{4.6}$$

$$\left. + W_{12}(1-2\phi_1) - \xi_{12}c_{1,xx} - \lambda_{11}\phi_{1,xx}\right). \tag{4.7}$$

My simulations in this case were deemed undesirable as they seemed to show behavior that was not consistent with the expectations of the industrial presenter; specifically, even if the energy levels of the two phases were set equal to one another the front that developed

from step-function in phase and uniform in component initial conditions propagated past the computational domain, leaving only one phase remaining in the entire domain, and uniform component mole fractions throughout the entire domain.

Minimizing Energy in the Quasi-Equilibrium Phase Field Approach

Brendan DeCourcy
Rensselær Polytechnic Institute

1 The Two-phase Energy Equation, Heulens et. al. (2011)

One of the difficult intricacies of the Cogswell and Carter model is the infinite barriers of the phase potential, which restricts the phase to a domain of $\phi \in [0, 1]$. A method that eliminates this problem is described by Heulens, Blanpain, and Moelans [1]. For a two phase system, the energy functional is

$$\tilde{\mathcal{F}}[\vec{\eta}, c] = \int_{-\infty}^{\infty} \tilde{F}\left(\eta_1, \eta_2, \frac{\partial \eta_1}{\partial \tilde{x}}, \frac{\partial \eta_2}{\partial \tilde{x}}, c\right) d\tilde{x}, \tag{1}$$

with

$$\tilde{F}\left(\eta_1, \eta_2, \frac{\partial \eta_1}{\partial \tilde{x}}, \frac{\partial \eta_2}{\partial \tilde{x}}, c\right) = \tag{2}$$
$$\phi_1 \tilde{G}_1(c) + \tilde{G}_2(c) + \tilde{U}(\vec{\eta}) + \frac{\tilde{\lambda_1}}{2}\left(\frac{\partial \eta_1}{\partial \tilde{x}}\right)^2 + \frac{\tilde{\lambda_2}}{2}\left(\frac{\partial \eta_2}{\partial \tilde{x}}\right)^2,$$

where

$$\tilde{U}(\vec{\eta}) = \tilde{U}_0\left(\frac{\eta_1^4}{4} - \frac{\eta_1^2}{2} + \frac{\eta_2^4}{4} - \frac{\eta_2^2}{2} + \gamma\eta_1^2\eta_2^2 + \frac{1}{4}\right), \tag{3}$$

$$\phi_1 = \frac{\eta_1^2}{\eta_1^2 + \eta_2^2}, \qquad \phi_2 = \frac{\eta_2^2}{\eta_1^2 + \eta_2^2}, \tag{4}$$

for constants $\tilde{U}_0$ and γ, and where the $\tilde{}$ represent dimensional values. With these definitions for ϕ, the need for the infinite potential barrier is eliminated, as $\phi_1 + \phi_2 = 1$ by construction.

To find the minimal energy state, we use calculus of variations to find the following

equations for η_1, η_2, and c:

$$\frac{\delta \tilde{F}}{\delta \eta_1} = 0, \tag{5}$$

$$\frac{\delta \tilde{F}}{\delta \eta_2} = 0, \tag{6}$$

$$\frac{\delta \tilde{F}}{\delta c} = \tilde{\mu}, \tag{7}$$

where $\tilde{\mu}$ is a Lagrange multiplier that arises from conservation of mass. The corresponding Euler-Lagrange equations are:

$$\lambda_1 \eta_1'' = \frac{2\eta_1\eta_2^2}{(\eta_1^2+\eta_2^2)^2}[\tilde{G}_1(c) - \tilde{G}_2(c)] + \tilde{U}_0[\eta_1^3 + \eta_1(2\gamma\eta_2^2 - 1)] \tag{8}$$

$$\lambda_2 \eta_2'' = -\frac{2\eta_1^2\eta_2}{(\eta_1^2+\eta_2^2)^2}[\tilde{G}_1(c) - \tilde{G}_2(c)] + \tilde{U}_0[\eta_2^3 + \eta_2(2\gamma\eta_1^2 - 1)] \tag{9}$$

$$0 = \eta_1^2[\tilde{G}_1'(c) + \tilde{\mu}] + \eta_2^2[\tilde{G}_2'(c) + \tilde{\mu}]. \tag{10}$$

We also have the natural boundary conditions,

$$\left.\frac{\partial \eta_1}{\partial \tilde{x}}\right|_{\pm\infty} = \left.\frac{\partial \eta_2}{\partial \tilde{x}}\right|_{\pm\infty}. \tag{11}$$

To analyze these equations, it will be beneficial to simplify their form by defining the following functions from (8), (9), and (10):

$$P(c) \equiv \frac{\tilde{G}_1'(c) + \tilde{\mu}}{\tilde{G}_2'(c) + \tilde{\mu}}, \qquad \tilde{G}(c) \equiv \tilde{G}_1(c) - \tilde{G}_2(c). \tag{12}$$

Substituting these into (8), (9), and (10) yields

$$\tilde{\lambda_1}\eta_1'' = -\frac{2P(c)\tilde{G}(c)}{(1-P(c))^2}\frac{1}{\eta_1} + \tilde{U_0}[(1-2\gamma P(c))\eta_1^3 - 1] \tag{13}$$

$$\tilde{\lambda_2}\eta_2'' = \frac{2P(c)\tilde{G}(c)}{(P(c)-1)^2}\frac{1}{\eta_2} + \tilde{U_0}[(1-2\gamma P(c)^{-1})\eta_2^3 - 1] \tag{14}$$

$$\eta_2^2 = -P(c)\eta_1^2. \tag{15}$$

One last function will be defined to make these equations more compact before analyzing them:

$$\tilde{J}(c) \equiv \frac{2P(c)\tilde{G}(c)}{(1-P(c))^2}. \tag{16}$$

And thus, the simplified dimensional versions of equations (14) and (15) are:

$$\tilde{\lambda_1}\eta_1'' = -\tilde{J}(c)\eta_1^{-1} + \tilde{U_0}[(1-2\gamma P(c))\eta_1^3 - 1] \tag{17}$$
$$\tilde{\lambda_2}\eta_2'' = \tilde{J}(c)\eta_2^{-1} + \tilde{U_0}[(1-2\gamma P(c)^{-1})\eta_2^3 - 1]. \tag{18}$$

2 Non-dimensionalization of the Minimum Energy Equations

The next step in solving for η_1, η_2, and c is to non-dimensionalize the equations.

Recall the quadratic form used for the bulk free energy equations:

$$\tilde{G}_\alpha(c) = \tilde{G}_{\alpha,0} + \frac{1}{2}\tilde{G}_{\alpha,2}^2(c - c_\alpha^*)^2$$

We non-dimensionalize:

$$G_1(c) = \frac{\tilde{G}_1(c) - \tilde{G}_{2,0}}{\Delta\tilde{G}}, \qquad G_2(c) = \frac{\tilde{G}_2(c) - \tilde{G}_{1,0}}{\Delta\tilde{G}}, \qquad \Delta\tilde{G} = \tilde{G}_{1,0} - \tilde{G}_{2,0} \tag{19}$$

such that

$$\tilde{G}(c) = \Delta\tilde{G}[G_1(c) - G_2(c) - 1] \equiv \Delta\tilde{G}G(c), \tag{20}$$

and

$$\tilde{J}(c) = \Delta\tilde{G}\frac{2P(c)G(c)}{(1-P(c))^2} \equiv \Delta\tilde{G}J(c) \tag{21}$$
$$P(c) = \frac{G_1'(c) + \mu}{G_2'(c) + \mu}, \tag{22}$$

with $\mu = \tilde{\mu}/\Delta\tilde{G}$.

If we use the scaling $x = \tilde{x}\sqrt{\tilde{\lambda_1}/\Delta\tilde{G}}$, we can reduce our equations to non-dimensional form:

$$\eta_1'' = -J(c)\eta_1^{-1} + U_0[(1-2\gamma P(c))\eta_1^3 - 1] \tag{23}$$
$$\lambda\eta_2'' = J(c)\eta_2^{-1} + U_0[(1-2\gamma P(c)^{-1})\eta_2^3 - 1], \tag{24}$$

where the dimensionless constants are defined as follows:

$$\lambda = \frac{\tilde{\lambda_2}}{\tilde{\lambda_1}}, \qquad U_0 = \frac{\tilde{U_0}}{\Delta\tilde{G}}.$$

3 Examining Extreme Values of the Parameters

The next step we will take is to examine how large or small parameter values affect the behavior of the equations, and to see what physical meaning can be found in the results.

3.1 Small U_0

First we examine what happens when U_0 is small. This will occur when the potential energy scale is much smaller than the bulk free energy scale. In this case, the equations simplify to the following:

$$\eta_1'' = -J(c)\eta_1^{-1}, \tag{25}$$
$$\lambda\eta_2'' = J(c)\eta_2^{-1}, \tag{26}$$

with the addition of the natural boundary conditions (11). We can rearrange these equations to eliminate $J(c)$, and thus the dependence on c, and integrate over the domain $x \in (-\infty, \infty)$:

$$\int_{-\infty}^{\infty} (\eta_1''\eta_1 + \lambda\eta_2''\eta_2)dx = 0.$$

By integrating by parts and applying (11), we find

$$\int_{-\infty}^{\infty} [(\eta_1')^2 + \lambda(\eta_2')^2]dx = 0, \quad \Rightarrow \quad (\eta_1')^2 + \lambda(\eta_2')^2 = 0. \tag{27}$$

We can justify this by the fact that in order to 'penalize' the energy gradients associated with η_1 and η_2, we must take $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$ to be positive. Thus, the integrand in (27) is greater than or equal to zero at all values $x \in (-\infty, \infty)$. Since $\lambda > 0$ and we require that the phases are purely real values, we must conclude that

$$\eta_1 = \text{constant}, \tag{28}$$
$$\eta_2 = \text{constant}, \tag{29}$$

and accordingly, both ϕ_1 and ϕ_2 are constant. This implies the existance of an infinitesmally small interface where a sharp transition between phases occur.

3.2 Large U_0

In the case of large potential energy and small scale bulk free energy, we can look at what happens when U_0 is large. The equations become:

$$\eta_1^3 = \frac{1}{1 - 2\gamma P(c)}, \qquad \eta_2^3 = \frac{P(c)}{P(c) - 2\gamma}. \tag{30}$$

In this case, we can solve for η_1 and η_2 explicitly in terms of $c(x)$, and with the inclusion of the non-dimensional version of (8), we have a system of three equations and three unknowns which can be solved. These equations were not explored in further detail.

References

[1] J. Heulens, B. Blanpain, and N. Moelans, "A phase field model for isothermal crystallization of oxide melts," *Acta Mater.*, vol. 59, pp. 2156-2165, 2011.

Numerical Schemes for the Cogswell-Carter Model

David Nigro
University of Manchester

Aminur Rahman
New Jersey Institute of Technology

1 Shooting method

Consider the Gibbs free energy functional for a binary system,

$$F\left(c,\phi,\frac{dc}{dx},\frac{d\phi}{dx}\right)=\phi G_1(c)+(1-\phi)G_2(c)+W(1-2\phi)+\frac{\kappa}{2}\left(\frac{dc}{dx}\right)^2+\frac{\lambda}{2}\left(\frac{d\phi}{dx}\right)^2, \quad (1)$$

with the usual far-field conditions, as $x\to-\infty$, $\phi\to 1$, $c\to c_1$, and as $x\to\infty$, $\phi\to 0$, $c\to c_2$. Taking $\delta F/\delta c=K$ and $\delta F/\delta\phi=0$, where K is the Lagrange multiplier, gives the following system of ordinary differential equations,

$$\phi G_1'(c)+(1-\phi)G_2'(c)-\kappa c''=K, \quad (2)$$
$$G_1(c)-G_2(c)-\lambda\phi''+W(1-2\phi)=0. \quad (3)$$

For the numerics we consider the following functions for the Gibbs free energies,

$$G_1(c)=0+\frac{1}{2}(100)(c-0.2)^2, \quad (4)$$
$$G_2(c)=5+\frac{1}{2}(300)(c-0.8)^2. \quad (5)$$

To find the common tangent, we solve the equations,

$$G_1'(c_1)=G_2'(c_2), \quad (6)$$
$$(c_2-c_1)K=G_2(c_2)-G_1(c_1), \quad (7)$$

to get $K=8.75699$, $c_1=.294098$, and $c_2=.831366$.

We write a shooting method code using bisection and `ode45` to solve the system of differential equations. In Figure 1, we see that while we could match the boundaries we artificially provided, we could not avoid having discontinuous derivatives. Also, further analysis shows that c is a negative exponential for a region, $(-\infty,-z_b)\cup(c_b,\infty)$, for some z_b, which contradicts our assumption that c is constant in this region.

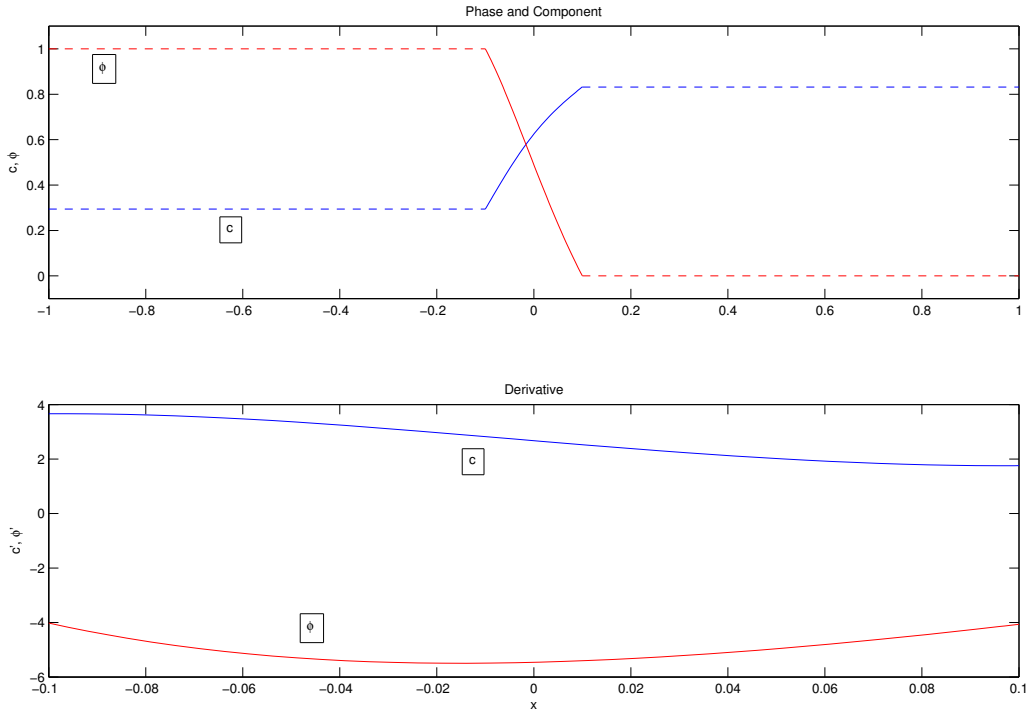


Figure 1: Plot of the phase and component graphs found using shooting method.

2 Finite differences

Consider the full Cogswell and Carter evolution equations [1],

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

We attempt to solve this *via* finite differences, using a standard forward in time – centered in space scheme. However we get peculiar results, as can be seen in Figure 2. Changing the time step and spacial discretization either gives similar results or crashes the code. Finite differences may not be the best way to numerically solve the Cogswell-Carter evolution equations.

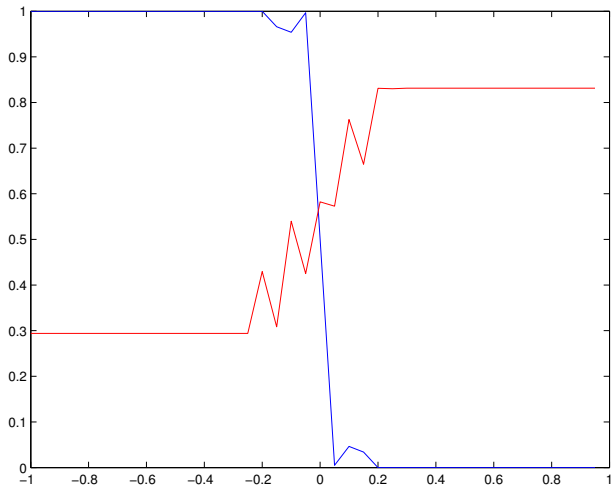


Figure 2: Plot of phase and component graphs found using a forward in time and centered in space scheme.

References

[1] D.A. Cogswell and W.C. Carter (2011). Thermodynamic phase-field model for microstructure with multiple components and phases: The posibility of metastable phases. *Phys. Rev. E* **83**, 061602.

Shooting Method for the Cogswell Model

Yanping Chen
University of Texas, Dallas

Tianheng Wang
North Carolina State University

Here is an example with two phases and two components. The energy is given as

$$F[c,\phi] = \int_{-\infty}^{\infty} \phi G_A(c) + (1-\phi)G_B(c) + \frac{\kappa}{2}(\frac{dc}{dx})^2 + \frac{\lambda}{2}(\frac{d\phi}{dx})^2 + U(\phi)\ dx \tag{1}$$

The equilibrium conditions, which can be obtained from calculus of variations, are the following ODEs:

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

$$\kappa\frac{d^2c}{dx^2} = \phi G'_A(c) + (1-\phi)G'_B(c) - K \tag{3}$$

where G_A, G_B are the quadratic potentials for the two phases, given as

$$G_A(c) = \frac{G''_A}{2}(c-c_A^0)^2 + G_A^0, \quad G_B(c) = \frac{G''_B}{2}(c-c_B^0)^2 + G_B^0, \quad 0 < c < 1.$$

With the expressions of $G_A(c)$ and $G_B(c)$, we can solve for the values of c_A^*, c_B^* and K which satisfy the common tangent condition, *i.e.*,

$$K = G'_A(c_A^*) = G'_B(c_B^*) = \frac{G_A(c_A^*) - G_B(c_B^*)}{c_A^* - c_B^*}.$$

Since we know ϕ becomes one at some position "to the left" and zero at another position "to the right", we can solve the composition equation (3) in the "far field" regions analytically. Let's do the left side. (3) turns into

$$\kappa\frac{d^2c}{dx^2} = G''_A(c-c_A^0) - K. \tag{4}$$

The general solution to (4) is

$$c(x) = Ce^{\sqrt{\frac{G''_A}{\kappa}}x} + De^{-\sqrt{\frac{G''_A}{\kappa}}x} + \frac{G''_Ac_A^0 + K}{G''_A}, \tag{5}$$

where C, D are to be determined. It is clear to see $D = 0$ since $c(x)$ should be bounded when $x < 0$. Substituting $K = G'_A(c^*_A) = G''_A(c^*_A - c^0_A)$ into (5), we get

$$c(x) = Ce^{\sqrt{\frac{G''_A}{\kappa}}x} + c^0_A + \frac{G''_A(c^*_A - c^0_A)}{G''_A} = Ce^{\sqrt{\frac{G''_A}{\kappa}}x} + c^*_A.$$

Thus we have the expression for $c(x)$ at far field (beyond the interface):

$$c(x) = c_1 e^{\zeta_A x} + c^*_A, \quad \zeta_A = \sqrt{\frac{G''_A}{\kappa}}, \quad x < 0, \tag{6}$$

$$c(x) = c_2 e^{-\zeta_B x} + c^*_B, \quad \zeta_B = \sqrt{\frac{G''_B}{\kappa}}, \quad x > l, \tag{7}$$

where c_1 and c_2 are to be determined, and l is the length of interface. It is easy to verify that

$$c'(0) - \zeta_A(c(0) - c^*_A) = 0, \tag{8}$$

$$c'(l) + \zeta_B(c(l) - c^*_B) = 0. \tag{9}$$

Now we apply the shooting method. Guess value for $\phi'(x = 0)$ and $c(x = 0)$; integrate the ODE system (2),(3) until $\phi = 1$ (implicitly defining the length of interface l); refine the guess for the initial value until boundary condition (9) is satisfied. We will dump the guess if c grows beyond [0,1] when integrating the ODE system.

We could see this shooting method is underdetermined, meaning there is a family of initial guesses $\{\phi'(0), c(0)\}$ (parameterized by $\phi'(0)$), which will satisfy the boundary condition (9). Our interest is to find the pair $(\phi'(0), c(0))$, which will minimize the energy integral.

Let's take a closer look at the energy integral. ϕ' and $U(\phi)$ vanish at far field; $c(x)$ decreases exponentially, and is thus integrable; however

$$\lim_{x\to-\infty} \phi G_A(c) = G_A(c^*_A);$$
$$\lim_{x\to\infty} \phi G_A(c) = 0;$$
$$\lim_{x\to-\infty} (1-\phi) G_B(c) = 0;$$
$$\lim_{x\to\infty} (1-\phi) G_B(c) = G_B(c^*_B);$$

which implies the energy integral will go to infinity. How can we do minimization?

Let's separate the energy integral into three parts.

$$F[c,\phi] = I_1 + I_2 + I_3 = \int_{-\infty}^{0} + \int_0^L + \int_L^{\infty} \phi G_A(c) + (1-\phi) G_B(c) + \frac{\kappa}{2}(c')^2 + \frac{\lambda}{2}(\phi')^2 + U(\phi)\, dx. \tag{10}$$

Here L is a sufficiently large number which is greater than the length of interface l for any pair $(\phi'(0), c(0))$ satisfying (9). Then

$$I_1 = \int_{-\infty}^{0} \frac{G''_A c_1^2}{2} e^{2\zeta_A x} + G''_A c_1 (c_A^* - c_A^0) e^{\zeta_A x} + \frac{\kappa}{2}(c')^2 + \frac{G''_A (c_A^* - c_A^0)^2}{2}\, dx, \tag{11}$$

$$I_3 = \int_{L}^{\infty} \frac{G''_B c_2^2}{2} e^{-2\zeta_B x} + G''_B c_2 (c_B^* - c_B^0) e^{-\zeta_B x} + \frac{\kappa}{2}(c')^2 + \frac{G''_B (c_B^* - c_B^0)^2}{2}\, dx. \tag{12}$$

If we drop the constant terms which have nothing to do with the shooting, then the integral is finite! So we can compare the energy integral for different guesses $(\phi'(0), c(0))$.

We didn't prove the existance of the L, which bounds the length of interface l. Here we can show the graph "l v.s. $\phi'(0)$" as a small evidence that such large L exists. We should have written "l v.s. $(\phi'(0), c(0))$", notice that $c(0)$ is determined by $\phi'(0)$ from shooting method.

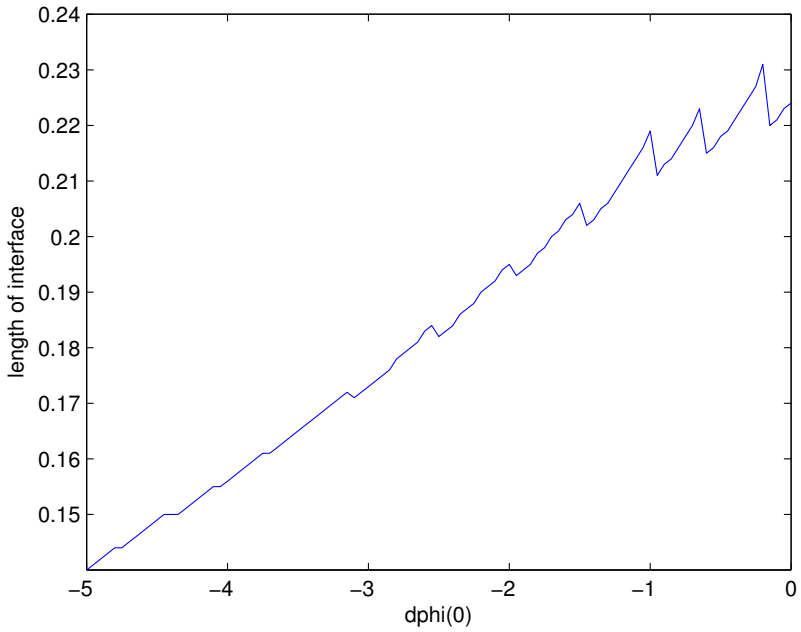


Figure 1: l v.s. $\phi'(0)$

One Example

Given $G_A(c) = 50(c - 0.2)^2$, $G_B(c) = 150(c - 0.8)^2 + 5$, $\kappa = 5, \lambda = 1, W = 80$.

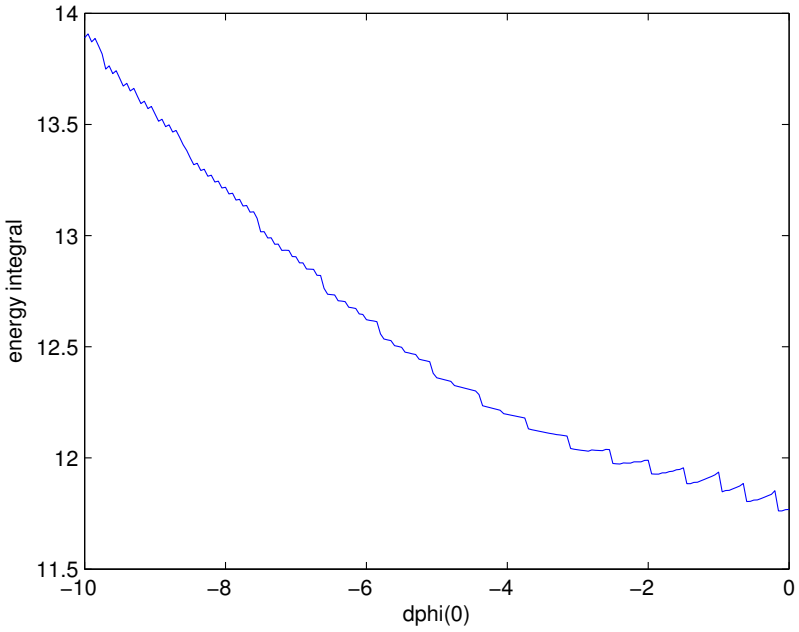


Figure 2: energy v.s. $\phi'(0)$

The figure above indicates that the guess $\phi'(0) \approx 0$ will lead to minimal energy. Now we choose the pair $(\phi'(0), c(0))$ that minimize the energy, solve the ODE system (2), (3) as IVP, thus obtaining the behavior of $\phi(x)$ and $c(x)$ at the interface.

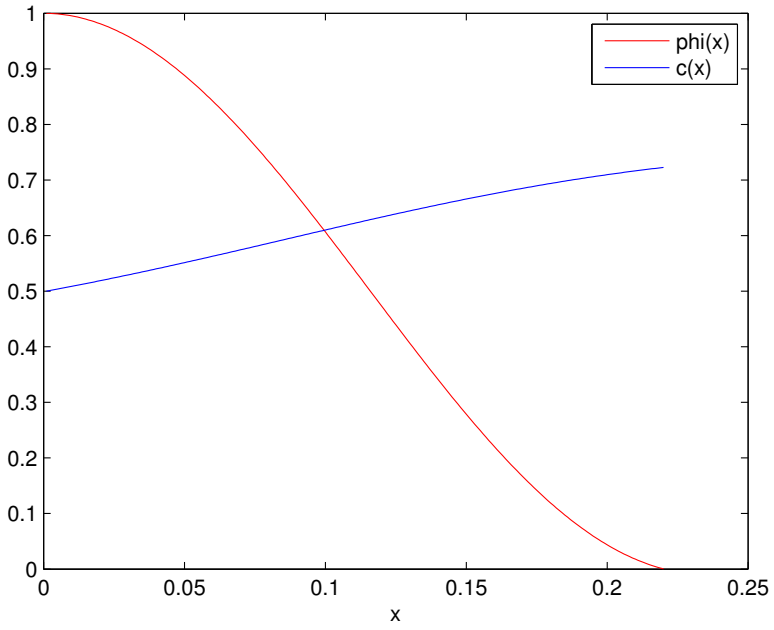


Figure 3: behavior of $\phi(x)$ and $c(x)$ at the interface

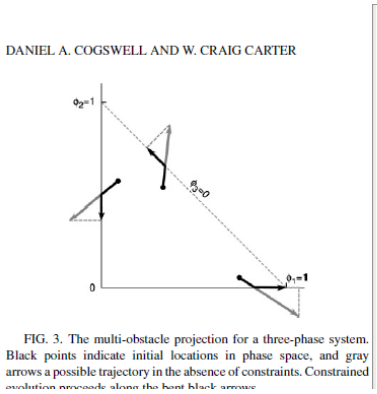
Examination of the Cogswell-Carter multiObstacle algorithm

Nguyenho Ho
Worcester Polytechnic Institute

Thomas Witelski
Duke University

In the Physical Review E paper published in 2011, Daniel A. Cogswell provided a pseudo-code algorithm to enforce constraints on phase evolution in their phase-field model [1]. The phase-field model uses ϕ_α as the phase fractions where index α distinguishes between different phases, $\alpha = 1, 2, ..., N$ in the system. Their energy is unbounded if any of the phases go outside the region of physically admissible solutions. Therefore, there is a need for a process that projects all ϕ_α onto the set of admissible solutions. As described in [1, 2] admissible phases must satisfy: the individual phase fraction is between zero and one, and the sum of all the ϕ must add up to one. In other words, the phase fractions must satisfy the following constraints

1. $0 < \phi_\alpha < 1$ for each $\alpha = 1, 2, ..., N$
2. $\sum_{\alpha=1}^{N} \phi_\alpha = 1.$



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

Figure 1: The algorithm proposed in Cogswell and Carter [1].

The algorithm `multiObstacle` proposed in [1], see Fig. 1 claims to carry this out. Their algorithm appears to be flawed for two reasons:

(i) If positivity of the final phase ($\phi_N = 1 - \sum_{\alpha=1}^{N-1} \phi_\alpha$), $\phi_N < 0$ is violated, its value is not truncated to $\phi_N = 0$ in the algorithm, and

(ii) The output algorithm is not invariant under cyclic permutations for relabeling the phases. namely, considering a four-phase system with $\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1$, if input values for the 'raw' phase values are given as the ordered set $\{\phi_A, \phi_B, \phi_C, \phi_D\}$ and the algorithm produces the truncated output values $\{\tilde{\phi}_A, \tilde{\phi}_B, \tilde{\phi}_C, \tilde{\phi}_D\}$ then inputting $\{\phi_B, \phi_C, \phi_D, \phi_A\}$ should produce $\{\tilde{\phi}_B, \tilde{\phi}_C, \tilde{\phi}_D, \tilde{\phi}_A\}$ and similarly for other permutations of the values since the results should be independent of the arbitrary labeling/ordering of the phases.

The simplest case is with two phases, $N = 2$, *i.e.*, $\phi_1 + \phi_2 = 1$, where the system can be reduced to a single phase parameter, ϕ, with $\phi_1 = \phi, \phi_2 = 1 - \phi$ that will satisfy both constraints if $0 \le \phi \le 1$. If ϕ is not in this range, then it must be truncated back into the range $0 \le \phi \le 1$, *i.e.*, if $\phi < 0$ then $\phi := 0$ and if $\phi > 1$ then $\phi := 1$, respectively. Cogswell's `cutoffBarrier2D` algorithm [2, section 2.3, p. 55] correctly implements this:

```
function cutoffBarrier2D(phi1)
if phi1<0
    phi1=0;
elseif 1-phi1<0
    phi1=1;
end
end
```

In his thesis, Cogswell also gives the algorithm for the $N = 3$ case [2, section 2.3, p. 57]

```
function phi=cutoffBarrier3D(phi1,phi2)
if phi1<0
    phi1=0;
end
if phi2<0
    phi2=0;
end
phi3=1-phi1-phi2;
if phi3<0
    phi1=phi1+phi3/2;
    cutoffBarrier2D(phi1);
    phi2=1-phi1;
end
phi=[phi1;phi2;phi3];
sum(phi(1:end))
end
```

This algorithm is flawed in that it does not correct the value of ϕ_3 if the $\phi_3 < 0$ case is active, but this can be fixed by adding the command $\phi_3 = 1 - \phi_1 - \phi_2$ after "$\phi_2 = 1 - \phi_1$". This routine satisfies the condition on permutations of the phases in terms of the interchange of $\phi_1 \leftrightarrow \phi_2$, namely the results from `cutoffBarrier3D(0.5,0.6)` map onto those from `cutoffBarrier3D(0.6,0.5)`. But if all three phases had been provided, for example consider $\{\phi_1 = 0.5, \phi_2 = 0.6, \phi_3 = -0.1\}$, then different permutations of which two phases are used in `cutoffBarrier3D` will produce different results.

The algorithm called `multiObstacle` in [1] is the general version of the algorithm from Cogswell's thesis [2, section 2.3, p. 58], and makes use of the recursive structure suggested by `cutoffBarrier3D`,

```
function phi=cutoffBarrier(N,phi)
sum1=0;
for i=1:N-1
    if phi(i)<0
        phi(i)=0;
    end
    sum1=sum1+phi(i);
end
phi(N)=1-sum1;
sum2=0;
 if phi(N)<0
     for i=1:N-2
         phi(i)=phi(i)+phi(N)/(N-1);
         sum2=sum2+phi(i);
     end
     cutoffBarrier(N-1,phi(1:N-2));
     phi(N-1)=1-sum2;
end
```

It can be shown that this routine has the same problems identified above for `cutoffBarrier3D`.

For instance, we implemented a code for the case $N = 4$ with produced from random values for the phases, $\{\phi_1, \phi_2, \phi_3, \phi_4\} = \{0.278498218867048, 0.546881519204984, 0.957506835434298, 0.964888535199277\}$, respectively. Each individual phase was generated as a uniformly distributed random number between zero and one, which immediately satisfies the first constraint, the sum of them is 2.747775108705607 violating the second constraint. Therefore, the proposed algorithm in [1] has is not correct in stated form and needs some corrections.

```
clear;
clc;
format long
N=4;
phi=rand(N,1);
sum=sum(phi(1:N));
cutoffBarrier(N,phi(1:N-1));
sum2=0;
if phi(N)<0
```

```
    for i=1:N-2
        phi(i)=phi(i)+phi(N)/(N-1);
        sum2=sum2+phi(i);
    end
    cutoffBarrier(N-1,phi(1:N-2));
    phi(N-1)=1-sum2;
end
phi
```

When running the code, the proposed algorithm was still not consistent with the two basic constraints stated above. In order words, there were cases that either the results would satisfy both constraints or failed to accompany with either of them. We present some further examples for $N = 3$ in the table below to show the inconsistency of the troublesome algorithm.

Table 1: The results for 3D algorithm, N=3

Cases	ϕ_1	ϕ_2	ϕ_3	Summation
1	0.255095115459269	0.505957051665142	0.238947832875589	1
2	0.129906208473730	0.568823660872193	0.301270130654077	1
3	0.469390641058206	0.011902069501241	0.518707289440553	1
4	0.741534749319551	0.258465250680449	-0.105499582728712	0.894500417271288
5	0.482432297668387	0.517567702331613	-0.343293601616790	0.656706398383210

References

[1] D. A. Cogswell and W. C. Carter, "Thermodynamic phase-field model for microstructure with multiple components and phases: The possibility of metastable phases," Phys. Rev. E, vol. 83, 061602, 2011

[2] D. A. Cogswell, A phase-field study of ternary multiphase microstructures, Ph.D. thesis, Materials Science and Engineering, Massachusetts Institute of Technology, 2010

Time-dependent numerical simulations of the phase field models

Lee Safranek
Simon Fraser University

Thomas P. Witelski
Duke University

Xin Yang
Simon Fraser University

As an approach to gaining a better understanding of the dynamics in the phase field models, we implemented numerical simulations of the time-dependent model equations in the simplest cases. All of the computations made use of finite-difference schemes with second-order accuracy in space, first-order accurate implicit (backward Euler) or explicit (forward Euler) time-stepping. Some were written in C, others were done in MATLAB. Below we outline the specific simulations that were carried out.

1 Cahn-Hilliard equation

This 'sub-model' has one conserved composition parameter, $c(x,t)$ and simulations were considered only in one dimension,

$$\frac{\partial c}{\partial t} = \frac{\partial^2}{\partial x^2}\left(f'(c) - \kappa\frac{\partial^2 c}{\partial x^2}\right), \qquad f(c) = \frac{1}{2}c^2(1-c)^2 \tag{1}$$

on $0 \le x \le L$ with no-flux boundary conditions

$$\partial_x c = \partial_{xxx} c = 0 \qquad \text{at } x = 0, L. \tag{2}$$

Both implicit and explicit codes were written. Because the governing equation is fourth order in x, the explicit code has a strong constraint on its timestep for stability, $\Delta t < O(\Delta x^4)$. The implicit code uses a backward Euler discretization that is solved at each time step using Newton's method.

Numerical computations confirmed that initial conditions starting with either uniformly high or low c would converge to spatially constant values while initial conditions resembling step profiles would evolve to steady interface solutions connecting $c = 0$ to $c = 1$.

These simulations mainly served as validations for the more complicated later models.

2 Cogswell-Carter two-phase model

For this model we considered a two-phase, two-component system in one-dimension. This problem is governed by two PDE evolution equations, one for the composition fraction ($c = c_1$ with $c_2 = 1 - c$) and one for the phase fraction ($\phi = \phi_1$ with $\phi_2 = 1 - \phi_1$):

$$\frac{\partial \phi}{\partial t} = \lambda \frac{\partial^2 \phi}{\partial x^2} + G_2(c) - G_1(c) - U'(\phi), \tag{3a}$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[c(1-c)\frac{\partial}{\partial x}\left(\phi G_1'(c) + (1-\phi)G_2'(c) - \kappa \frac{\partial^2 c}{\partial x^2}\right)\right] \tag{3b}$$

We used simple quadratic functions for the free energies for the individual phases given by

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

and the phase potential function,

$$U'(\phi) = \begin{cases} W(1-2\phi) & 0 \le \phi \le 1, \\ \infty & \text{else}, \end{cases} \tag{5}$$

where $W > 0$ is a positive constant. Cogswell and Carter selected this singular form for $U'(\phi)$ to effectively impose an infinite energy-penalty to prevent the phase from going outside of the physically acceptable range $0 \le \phi \le 1$. At an operational level, the meaning of the "else" case is that in numerical simulations of the system, if $\phi \ge 1$, then it is truncated to $\phi = 1$ and if $\phi \le 0$ then it is set to $\phi = 0$.

Both implicit and explicit codes were written for this model, with the explicit code having the same constraint on Δt as the Cahn-Hilliard equation.

Fig. 1 shows the smooth steady state interface starting from the Heaviside step functions for ϕ, c using the explicit code. The dash lines are the compositions which satisfy the common tangent condition (equations (2.13) and (2.16) in the report by Anderson *et al.*). Due to the time-step restriction, we could only run the explicit code for a short time, however, from Fig 1 it is clear that transients were very fast as the solution converged to the equilibrium values for the composition away from the phase interface.

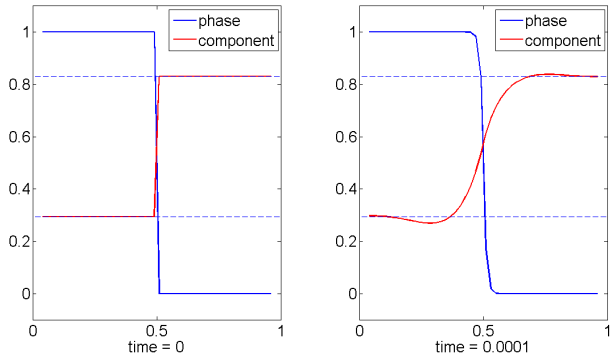


Figure 1: The simulation of Cogswell-Carter model using explicit time stepping: (left) initial condition for ϕ, c, (right) the solution having evolved towards a steady-state after a short time.

3 Moelans/Heulens model

The corresponding two-phase, two-component version of the model by Heulens and Moelans takes the form

$$\frac{\partial \eta_1}{\partial t} = \lambda \frac{\partial^2 \eta_1}{\partial x^2} - \eta_1^3 + \eta_1 - 2\eta_1\eta_2^2 - \left([G_1(c_1) - G_1'(c_1)c_1] - [G_2(c_2) - G_2'(c_2)c_2]\right) \frac{\partial \phi_1}{\partial \eta_1}, \tag{6a}$$

$$\frac{\partial \eta_2}{\partial t} = \lambda \frac{\partial^2 \eta_2}{\partial x^2} - \eta_2^3 + \eta_2 - 2\eta_2\eta_1^2 - \left([G_2(c_2) - G_2'(c_2)c_2] - [G_1(c_1) - G_1'(c_1)c_1]\right) \frac{\partial \phi_2}{\partial \eta_2}, \tag{6b}$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\phi_1 \frac{\partial c_1}{\partial x} + (1-\phi_2)\frac{\partial c_2}{\partial x}\right), \tag{6c}$$

where the phases ϕ_1, ϕ_2 automatically satisfy $\phi_1 + \phi_2 = 1$ since they are given in terms of η_1, η_2 by

$$\phi_1 = \frac{\eta_1^2}{\eta_1^2 + \eta_2^2} \qquad \phi_2 = \frac{\eta_2^2}{\eta_1^2 + \eta_2^2}, \tag{6d}$$

so each ϕ necessarily lies in the range $0 \le \phi \le 1$.

The c_1, c_2 are intermediate variables that describe the portion of each component involved in the various phases present. These values satisfy the condition[1]

$$c(x,t) = \phi_1(x,t)c_1 + \phi_2(x,t)c_2$$

and are selected to minimize the total homogeneous free energy

$$\min_{c_1,c_2} \phi_1 G_1(c_1) + \phi_2 G_2(c_2)$$

[1] where $c(x,t), \phi_1(x,t), \phi_2 = 1 - \phi_1$ are assumed given at each x, t for this calculation

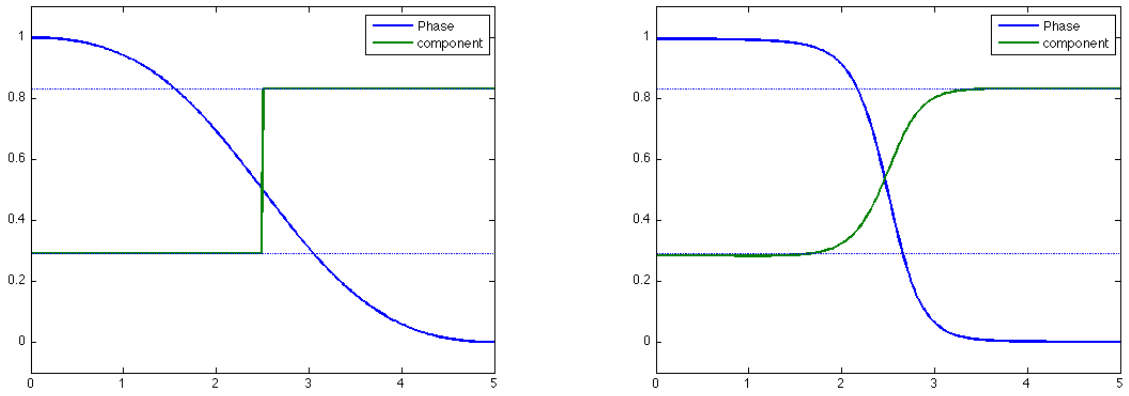


Figure 2: Evolution of the composition and phase in Heulens model in one dimension: (left) the initial conditions and (right) near-steady solution computed after a finite time. Dashed blue lines represent the common-tangent values, c_+ and c_-.

This can be worked out explicitly as a constrained optimization problem, using the Lagrangian objective function

$$\mathcal{L} = \phi_1 G_1(c_1) + \phi_2 G_2(c_2) - \alpha(\phi_1 c_1 + \phi_2 c_2 - c)$$

where α is a Lagrange multiplier. This yields $G_1'(c_1) = G_2'(c_2) = \alpha$ for the Lagrange multiplier, and then from our choices of G_1, G_2 we obtain c_1, c_2 in terms of ϕ_1, c:

$$c_1 = \tfrac{1}{5} - \tfrac{\alpha}{100} \qquad c_2 = \tfrac{4}{5} - \tfrac{\alpha}{300} \qquad \alpha = \frac{\frac{1}{5}\phi_1 + \frac{4}{5}(1-\phi_1) - c}{\frac{1}{100}\phi_1 + \frac{1}{300}(1-\phi_1)}, \tag{6e}$$

namely c_1, c_2 are nonlinear algebraic functions of η_1, η_2, c.

Substituting the later algebraic relations yields a closed system of three PDEs for c, η_1, η_2 that is solved with Neumann no-flux boundary conditions. Note that each equation in this system is only second-order with respect to x derivatives, and hence an explicit code can have $\Delta t = O(\Delta x^2)$, a much less restrictive condition on the timestep.

Explicit codes were written for this model in 1-D and 2-D (with the natural generalizations of $\partial_x \to \nabla$ for $c(x,t) \to c(x,y,t)$ and similarly for η_1, η_2 in the PDE's). Figure 2 shows the evolution of the phase and composition fields in the Heulens model starting from a single 1-D phase/composition interface. Very similarly to the Cogswell-Carter model, transients decay quickly and the structure of the equilibrium interface can be obtained to good accuracy.

As in the Cahn-Hilliard equation, starting from an initial condition in the unstable range of compositions, leads to spinodal decomposition, marked by the formation of several interfaces, see Figure 3. Similar evolution in two-dimensions is shown in Figure 4.

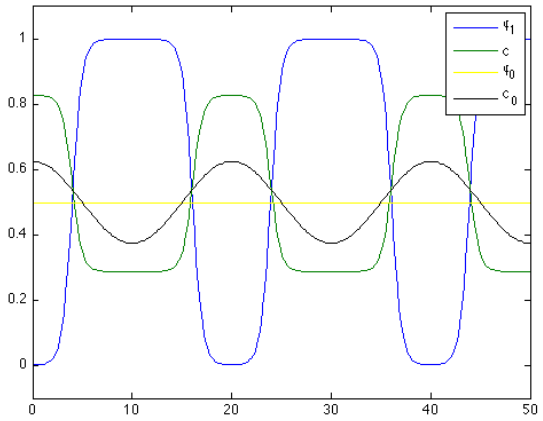


Figure 3: Small perturbations lead to development of sharp interfaces

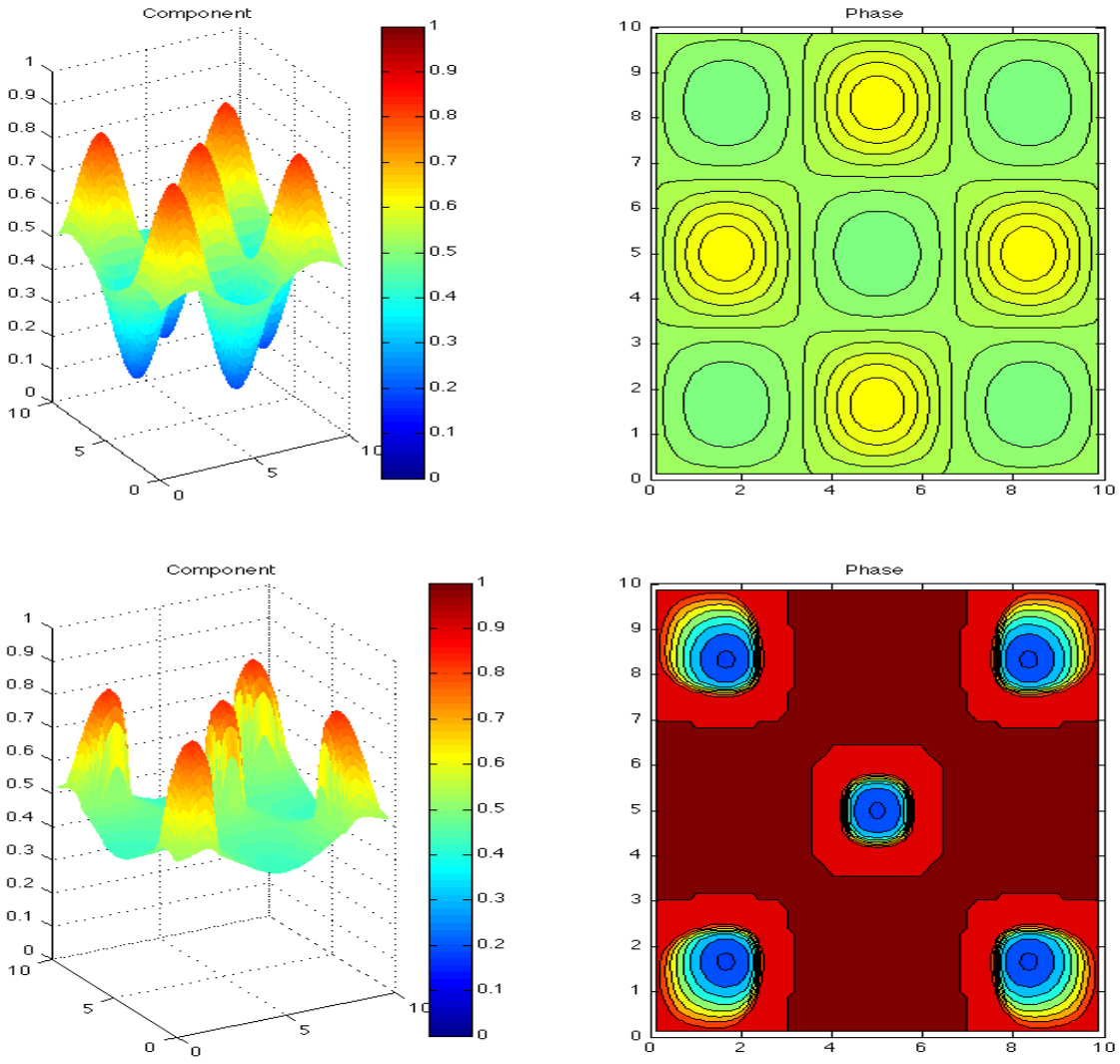


Figure 4: Simulation of Heulens' model in two dimensions: (top) 3-d/contour plots of the initial conditions for the composition and phase, (bottom) the development of sharp interfaces in both composition and phase.