

# Phase Field Modeling of Solidification

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## Introduction

Solidification is an important step in materials processing—both during the initial processing and during fabrication steps such as welding—and remains an active area of research. A variety of complex processes can and do occur during solidification, such as the nucleation, growth, and impingement of precipitates, the segregation of solute in the solid and the melt, and the formation of complex morphologies such as eutectic segregation, columnar grains, and dendritic growth. The occurrence of such processes has implications on the subsequent processing steps (e.g., an annealing step may be necessary due to solute segregation), and, depending on the morphology of the material after solidification, subsequent mechanical working may become more difficult or costly.

Thus, understanding and, to the extent possible, predicting the solidification characteristics of an alloy system is of great interest to materials engineers. Consider a solid precipitate growing in the liquid matrix. There are three entities to consider: the solid, the liquid, and the interface between them. To describe the solidification front is to solve, at each interface, equations involving heat and solute diffusion in the solid, heat and solute diffusion in the liquid, energy conservation at the interface, total conservation of solute via transport equations across the interface, and the Gibbs-Thomson capillarity equation at the interface to account for the effect of interface curvature [1]. This assumes no convection in the liquid, and of course the location each interface must be tracked explicitly through the simulation. The computational demands of this so-called “sharp interface” model limits its applicability.

In contrast, the phase field model forgoes many of the above considerations and uses just a few equations, sacrificing some rigor for efficiency and broader applicability. The key to the approach is the “order parameter”  $\phi$ , a field variable which takes values between 0 and 1. Instead of explicitly modeling solid, liquid and interface,  $\phi$  takes on the value 0 where the system is in the solid state and 1 where the system is liquid (or vice versa, depending on convention). Where  $\phi$  changes continuously from 0 to 1 is said to be the “interface”. This results in a diffuse interface between solid and liquid, see Figure 1. Now, the interface no longer needs to be tracked explicitly, but rather  $\phi$  is allowed to evolve in time. The location of the interface in the simulation space is simply a byproduct.

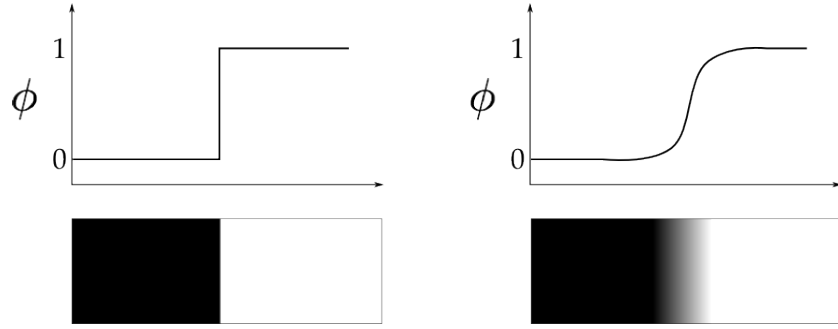


Figure 1: Contrast between the sharp interface model (left) and the phase field model. In the sharp interface model, there is a discontinuity of phase between solid (dark) and liquid (white). In the phase field model, the continuous change in  $\phi$  results in a diffuse interface between solid and liquid.

## The Phase Field Model

The treatment of the phase field model begins with the free energy functional for a pure material [2, 3],

$$F = \int_V \left[ f(\phi, T) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] dV. \quad (1)$$

$F$  here is the Gibbs free energy of the bulk,  $f(\phi, T)$  is the local free energy density, and  $\varepsilon$  is called the interfacial gradient free energy coefficient. Many other terms can be added to Eqn. (1) if they are believed to have significant effect on free energy; in particular, a composition-dependent term should be added for multi-component systems. Note that the second term on the right hand side of Eqn. (1) is only non-zero at the interface—it captures the effect of the interface on free energy, where the first term is the contribution from the solid and liquid phases individually.

To ensure that the free energy is reduced over time for this (irreversible) process, the following form for evolution of  $\phi$  is used [1]

$$\frac{\partial \phi}{\partial t} = M \left[ \varepsilon^2 \nabla^2 \phi - \frac{\partial f(\phi, T)}{\partial \phi} \right], \quad (2)$$

where  $M$  is called the interfacial mobility. This is often coupled with the heat equation for non-isothermal treatments of solidification

$$\frac{\partial u}{\partial t} = D \nabla^2 u + \frac{1}{2} \frac{\partial \phi}{\partial t} \quad (3)$$

where  $u$  is a normalized temperature defined as

$$u \equiv \frac{T - T_m}{L/c_p}.$$

where  $T_m$  is the equilibrium melting temperature,  $L$  is the latent heat of fusion, and  $c_p$  is the heat capacity.

The local free energy density  $f(\phi, T)$  is treated as an interpolation between the free energy densities of the solid and liquid phases,  $f_S$  and  $f_L$ , respectively, along with an activation energy  $Q$  to capture the fact that the liquid is metastable in this undercooled ( $T < T_m$ ) state. The energy density is written as

$$\begin{aligned} f(\phi, T) &= [1 - p(\phi)] f_S(T) + p(\phi) f_L(T) + Qg(\phi) \\ &= f_S(T) + p(\phi) [f_L(T) - f_S(T)] + Qg(\phi) \end{aligned} \quad (4)$$

The functions  $p(\phi)$  and  $g(\phi)$  are plotted in Figure 2;  $p(\phi)$  is an interpolation function and  $g(\phi)$  is a double-well function, written as

$$\begin{aligned} p(\phi) &= \phi^3 (6\phi^2 - 15\phi + 10) \\ g(\phi) &= \phi^2 (1 - \phi)^2. \end{aligned}$$

The expression for  $f(\phi, T)$  can be simplified by in two ways:

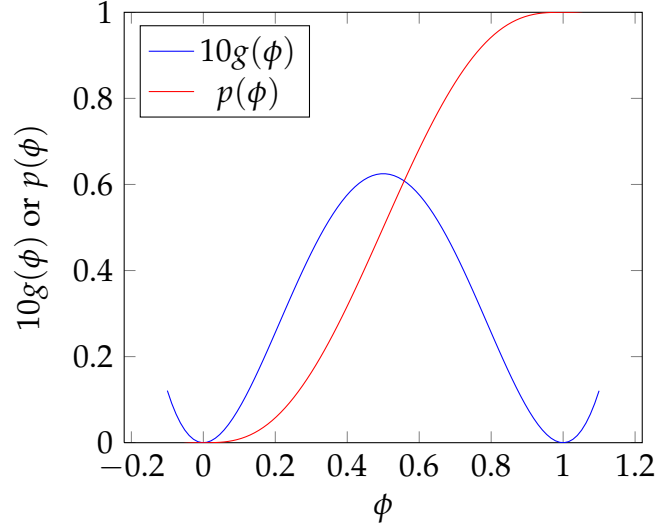


Figure 2: The functions  $p(\phi)$  and  $g(\phi)$ . The values of  $g$  have been scaled for clarity.

1. Since we only require *changes* in free energy, set solid as standard state, so that, for all  $T$

$$f_S(T) \equiv 0.$$

2. Use the common approximation for alloys at  $T \approx T_m$  [4]

$$\begin{aligned} \Delta f_{\text{melt}} = f_L(T) - f_S(T) &\approx \frac{L(T_m - T)}{T_m} \\ &= -\frac{L^2}{c_P T_m} u \\ &= -\kappa u \end{aligned}$$

where  $\kappa = L^2/(c_P T_m)$ .

Therefore, changing from  $T$  to  $u$  and substituting into (4), we have

$$f(\phi, u) = -\kappa u p(\phi) + Q g(\phi). \quad (5)$$

In one dimension, the interface thickness  $\delta$  is given by

$$\delta = \frac{\varepsilon}{\sqrt{2Q}} \quad (6)$$

and the surface free energy  $\sigma$  is

$$\sigma = \frac{\varepsilon\sqrt{Q}}{3\sqrt{2}}.$$

To introduce anisotropy, necessary for modeling, e.g., dendritic structures, let  $\varepsilon = \varepsilon(\hat{n})$ , where  $\hat{n}$  is the unit vector normal to the to the interface. Following [5],

$$\varepsilon^2(\hat{n}) = \varepsilon_0^2(1 - 3\varepsilon_c) \left[ 1 + \frac{4\varepsilon_c}{1 - 3\varepsilon_c} (n_x^4 + n_y^4 + n_z^4) \right]$$

where  $\varepsilon_c$  is a constant,  $\varepsilon$  reduces to  $\varepsilon_0$  in the isotropic case, and  $\hat{n}$  is taken as  $-\nabla\phi/|\nabla\phi|$ , so that

$$n_x^4 + n_y^4 + n_z^4 = \frac{(\partial\phi/\partial x)^4 + (\partial\phi/\partial y)^4 + (\partial\phi/\partial z)^4}{|\nabla\phi|^4}.$$

## Numerical Analysis

Finding the derivative of Eqn. (5) and substituting into (2), we have

$$\frac{\partial\phi}{\partial t} = M\varepsilon^2\nabla^2\phi + 2M\phi \left[ 15\kappa u\phi(\phi - 1)^2 - Q(1 - \phi)(1 - 2\phi) \right]$$

Let  $h(\phi, u)$  be the second term on the right hand side of the above equation, so

$$\frac{\partial\phi}{\partial t} = M\varepsilon^2\nabla^2\phi + h(\phi, u), \quad (7)$$

which is to be integrated numerically, coupled with Eqn. (3) for non-isothermal simulations.

For this work, Eqn. (7) was solved in the isothermal case for a pure system in one dimension. Attempts to extend the solution were met with difficulties in convergence which is believed to be due to the values of the coefficients ( $\varepsilon$ ,  $M$ ,  $Q$ ) coupled with the physical parameters  $T_m$ ,  $c_P$ , and  $L$ . Attempts to base these coefficients in terms of real physical quantities perhaps introduces instabilities into the solution.

Equation (7) was expanded and rewritten in terms of finite differences. A central finite difference was used for the  $\nabla^2\phi$  term. A forward difference

for  $\partial\phi/\partial t$  was first attempted (explicit scheme) but the resulting timesteps needed for convergence were vanishingly small. A fine spacial discretization is required for phase field modeling, because the interface—where  $\phi$  changes quite rapidly—is the primary feature of interest. After re-writing  $\partial\phi/\partial t$  with backward finite difference (implicit scheme), Eqn. (7) becomes a tridiagonal system of equations that must be solved at each timestep. This system was solved in different ways through the course of the project: using a LAPACK subroutine, using a Cholesky decomposition algorithm built in-house, and parallelizing the solution of the system, where each node computes on a column of the matrix and passes its results to the next node. Speedup was not detected using such a scheme.

Figures 3, 4, and 5 show the evolution of  $\phi$  with time for different choices of  $\varepsilon$  and  $M$ . Here,  $\phi = 1$  implies the solid phase. Comparing Figures 3 and 4, we see the effect that  $M$  has on the speed of the solidification process. Comparing Figures 3 and 5, we see that the energy gradient coefficient  $\varepsilon$  has not only affect the speed of the solidification process, but also the interface thickness, consistent with Eqn. (6). It is these types of parameter studies, especially when the parameters can be related to physical quantities, that can give materials engineers insight into the solidification process.

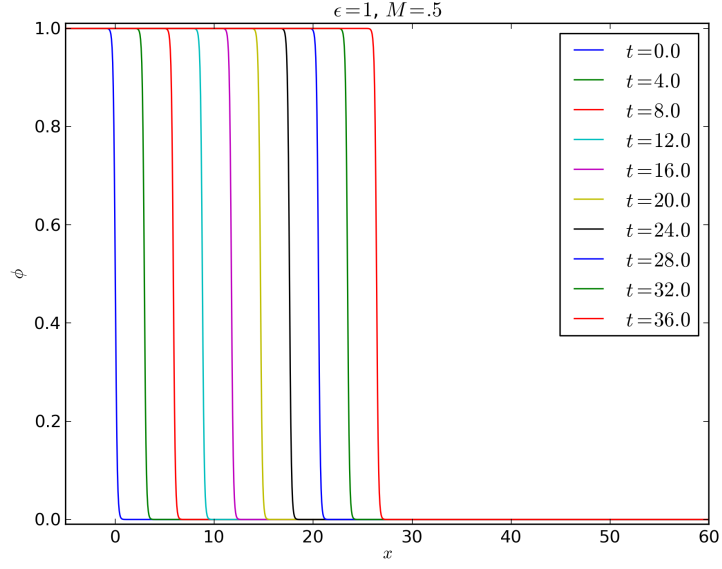


Figure 3: Evolution of  $\phi$  with time for  $\epsilon = 1$ ,  $M = 0.5$ .

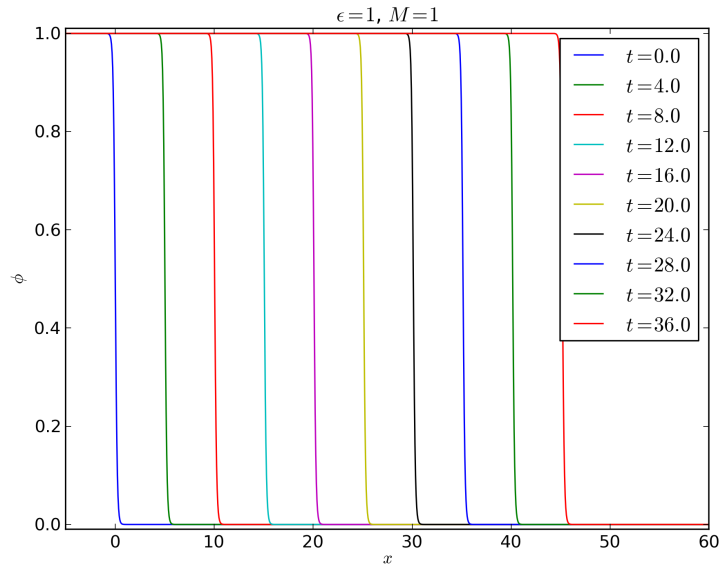


Figure 4: Evolution of  $\phi$  with time for  $\epsilon = 1$ ,  $M = 1$ .

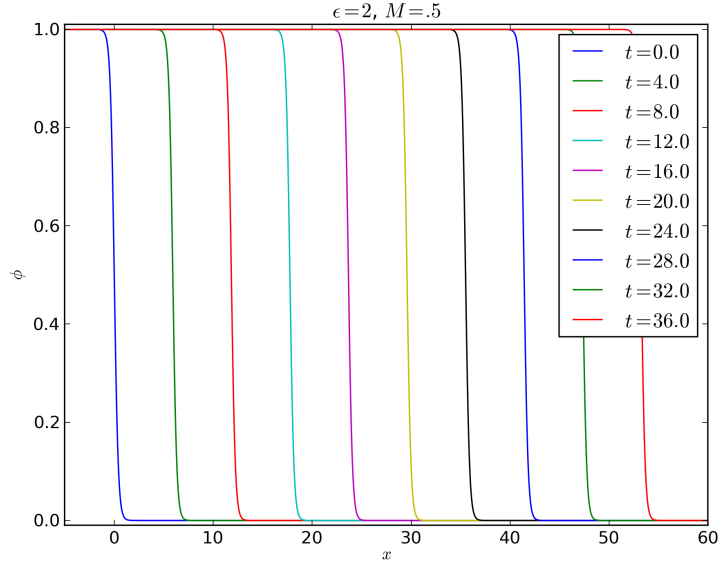


Figure 5: Evolution of  $\phi$  with time for  $\varepsilon = 2$ ,  $M = 0.5$ .

## References

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