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A New Approach to Multi-Phase field for the Solidification of Alloys

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Abstract. We show that the standard approach to the modeling of multi-phase field dynamics for the solidification of alloys has three major defects and offer an alternative more successful formulation. The model contains an action made up of a free energy functional of the temperature, concentration and the phase variables. In addition there is a penalty functional for the gradients of the phase variables, which keeps all field variables continuous — the phase field method. A variation of this action is related to time derivatives of the variables in the field. At any physical point there exists up to N phases, ϕ_i, each of which represent the proportion of each phase at that point, thus implying the constraint, $\sum_{i=1}^{N} \phi_i = 1$. The standard Lagrange multiplier treatment for imposing this constraint has three major defects: non-reduction to standard single phase formulation; a dependence on the value of N; generation of unphysical additional phases. We demonstrate a multi-phase formulation that avoids these two defects and, partly as a consequence, does not generate spurious additional phases. Moreover, this aim is achieved without losing the active part that three non-zero phases should play if present at any point.

1. Introduction

In recent years the importance of phase-field simulation as a tool to understanding microstructure formation during solidification has grown significantly. The key advantage of such models is that by introducing a continuous (differentiable) phase variable, ϕ, the value of which represents the phase of the material, the need to explicitly track the solid-liquid interface is removed. Instead, the mathematically sharp interface is replaced by a diffuse interface of finite width, the motion of which may be tracked using standard techniques for partial differential equations.

Early phase-field models of solidification concentrated on single-phase systems, in which there was the liquid and only a single solid phase present. However, the phase-field concept may be extended to systems where there is more than one solid phase present, resulting in multi-phase field models. For a topical review of multi-phase field modelling in material science see [1]. In multi-phase field models the scalar variable, ϕ, is replaced by a vector, $\boldsymbol{\theta}$, where the ith element θ_i, is the amount of phase i present[1]. This extension has, though, yielded variations in the derivation techniques used to obtain the equations of motion for the interface from the starting equations, with consequent differences in the properties of the resulting models. One of the main issues to arise in multi-phase field models is that because the phases, θ_i, can act

[1] We use the notation $\theta_i, i \in [1, N]$ for the linearly dependent physical variable and $\phi_i, i \in [1, N-1]$ for the independent variables

independently, an additional condition must be applied to ensure that the sum of the phases remains everywhere constant.

2. Standard Lagrange multiplier treatment

Most phase field models of solidification (both single and multi-phase) have a common starting point, this being the definition of a free energy functional, F, of the phase variables, θ_i, concentration, c and temperature, T. The appropriate form of F for the multi-phase problem has been adapted from several sources in the literature, e.g. [2]

$$F \equiv \int_\Omega \tfrac{1}{2} \sum_{i=1}^{j-1} \sum_{j=2}^{N} \Gamma^{ij} |\theta_i \nabla\theta_j - \theta_j \nabla\theta_i|^2 \, \mathrm{d}^3\mathbf{x} + \int_\Omega f(\boldsymbol{\theta}, c, T) \, \mathrm{d}^3\mathbf{x} \tag{1}$$

where: Ω is an arbitrary volume; Γ^{ij} includes the gradient energy coefficients and the anisotropy between phases i and j necessary, for example, for dendritic growth; and f is the free energy density. A particularly simple example of the latter, sufficient for this paper, is given by a minor modification to the formulation of [2] (though the arguments to be presented here are independent of the precise form assumed for f):

$$f \equiv \sum_{i=1}^{j-1} \sum_{j=2}^{N} W_{ij} \theta_i^2 \theta_j^2 - \sum_j m_j \theta_j^3 (6\theta_j^2 - 15\theta_j + 10) + \frac{RT}{v_m} \left[c \ln(c) + (1-c) \ln(c) \right], \tag{2}$$

with the coefficients governing the concentration-dependent double-well potential extended to N phases given by

$$W_{ij} = W_{ij}^A c + (1-c) W_{ij}^B$$
$$m_j = m_j^A c + (1-c) m_j^B.$$

Here R is the universal gas constant, v_m the molar mass (assumed constant), the constants W_{ij}^A and W_{ij}^B are entries of symmetric matrices whose values are dependent upon the double-well potential barrier between phases i and j and the constants m_i^A and m_i^B relate to the Gibbs energy of phase i, for either pure component A or B. Specifically, this formulation omits any enthalpy of mixing terms, which restricts the type of solid phases that can result to ideal binary solid solutions.

The equations governing the evolution of the phase and solute profiles can be given as

$$-\tau \frac{\partial \theta_i}{\partial t} = \frac{\delta F}{\delta \theta_i}, \quad i \in [1, N] \tag{3}$$

and

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D(\boldsymbol{\theta}) c(1-c) \nabla \frac{\delta F}{\delta c} \right) \tag{4}$$

together with the constraint

$$\sum_{j=1}^{N} \theta_j = 1, \tag{5}$$

where: τ is a characteristic time equivalent to inverse mobility, which is here assumed constant; D is a function defining the local diffusivity, which is a sum of the diffusivities for each phase weighted by the amount of each phase present.

The constraint (5) implies a linear dependence of the variables indicating that the system can be represented by $N-1$ independent variables, which we denote by $\phi_i, i \in [1, N-1]$. In particular, when $N = 2$ the multi-phase system is related to a single phase system with variable ϕ. This may be set to, say, $\phi = \theta_1$, but there are other equally valid alternatives.

The Lagrange multiplier method for ensuring the constraint (5) expresses (3) as

$$-\tau \frac{\partial \theta_i}{\partial t} = \frac{\delta F}{\delta \theta_i} + \Lambda, \quad i \in [1, N]$$

where, to guarantee $\sum_{j=1}^{N} \dot{\theta}_j = 0$, we must have

$$\Lambda = -\frac{1}{N} \sum_{j=1}^{N} \theta_j.$$

2.1. Non-reduction of the multiphase formulation to single phase

We now demonstrate that the standard Lagrange multiplier treatment of multi-phase field dynamics, e.g. [2], does not reduce to the equivalent single phase form. Let $F(\theta_1, \theta_2, c)$ be the free energy for an $N = 2$ phase system dependent on liquid phase, θ_1 and solid phase, θ_2 and concentration, c. Then $\theta_1 + \theta_2 = 1$ and we choose a single variable ϕ so that

$$\theta_1 = \phi$$

and

$$\theta_2 = 1 - \phi.$$

The multi-phase gradient contribution for $N = 2$, for example, is

$$G(\theta_1, \theta_2) = \int_\Omega \tfrac{1}{2} \Gamma^{12} |\theta_1 \nabla \theta_2 - \theta_2 \nabla \theta_1|^2 \, \mathrm{d}^3\mathbf{x}$$

which reduces to

$$G(\phi, 1-\phi) = \int_\Omega \tfrac{1}{2} \Gamma^{12} |\nabla \phi|^2 \, \mathrm{d}^3\mathbf{x}$$

The single phase equation is

$$-\tau \dot{\phi} = \frac{\delta F}{\delta \phi}$$

This is equivalent, in the multi-phase (two phase) variables to

$$\begin{aligned} -\tau \dot{\theta}_1 &= \frac{\delta F}{\delta \theta_1} - \frac{\delta F}{\delta \theta_2} \\ -\tau \dot{\theta}_2 &= \frac{\delta F}{\delta \theta_2} - \frac{\delta F}{\delta \theta_1} \end{aligned} \tag{6}$$

since[2]

$$\begin{aligned} \frac{\delta F}{\delta \phi} &= \frac{\partial \theta_i}{\partial \phi} \frac{\delta F}{\delta \theta_i} \\ &= \frac{\delta F}{\delta \theta_1} - \frac{\delta F}{\delta \theta_2}. \end{aligned}$$

[2] Note that throughout this paper repeated sufficies will imply summation, unless they appear on both sides of the equation.

Whereas in the multi-phase formulation the Lagrange multiplier gives

$$-\tau\dot{\theta}_i = \frac{\delta F}{\delta\theta_i} - \frac{1}{N}\sum_j^N \frac{\delta F}{\delta\theta_j},$$

which for $N = 2$ gives

$$\begin{aligned} -\tau\dot{\theta}_1 &= \tfrac{1}{2}\frac{\delta F}{\delta\theta_1} - \tfrac{1}{2}\frac{\delta F}{\delta\theta_2} \\ -\tau\dot{\theta}_2 &= \tfrac{1}{2}\frac{\delta F}{\delta\theta_2} - \tfrac{1}{2}\frac{\delta F}{\delta\theta_1}. \end{aligned}$$

Thus the Lagrange multiplier approach does not reduce to the single phase formulation and in the particular case for $N = 2$ gives precisely half that of the single phase formulation.

2.2. Spurious extra phases and N dependence

This section shows that the formulation in [2], when used with solidification from a pure seed, say θ_2 growing into melt θ_1, leads to the unphysical formation of the other phase(s), θ_i for $i > 2$. This is illustrated in Fig. 2 (left) for $N = 3$). See also [5] p301. A new alternative model that does not exhibit spurious growth, see Fig. 2 (right), is presented in Section 3. The Lagrange multiplier formulation in [2] is

$$-\tau\dot{\theta}_i = \frac{\delta F}{\delta\theta_i} - \frac{1}{N}\sum_{j=1}^N \frac{\delta F}{\delta\theta_j}$$

where for isotropy (Γ^{ij} independent of $\boldsymbol{\theta}$) we have

$$\begin{aligned} \frac{\delta F}{\delta\theta_i} = &\sum_{j\neq i}^N \Gamma^{ij}\{2(\theta_i\nabla\theta_j - \theta_j\nabla\theta_i)\cdot\nabla\theta_j + (\theta_i\nabla^2\theta_j - \theta_j\nabla^2\theta_i)\theta_j\} \\ &+ \sum_{j\neq i}^N 2W_{ij}\theta_i\theta_j^2 - 30m_i\theta_i^2(1-\theta_i)^2. \end{aligned} \tag{7}$$

Consider a system of N phases but only two phases θ_1, θ_2 present in some region with no interaction with other phases. With $\theta_{i>2} = 0$ the Lagrange multiplier gives

$$\begin{aligned} -\tau\dot{\theta}_1 &= (1-\tfrac{1}{N})\frac{\delta F}{\delta\theta_1} - \tfrac{1}{N}\frac{\delta F}{\delta\theta_2} \\ -\tau\dot{\theta}_2 &= (1-\tfrac{1}{N})\frac{\delta F}{\delta\theta_2} - \tfrac{1}{N}\frac{\delta F}{\delta\theta_1} \\ -\tau\dot{\theta}_{i>2} &= -\tfrac{1}{N}\left(\frac{\delta F}{\delta\theta_1} + \frac{\delta F}{\delta\theta_2}\right), \end{aligned} \tag{8}$$

and clearly the growth depends on N. Moreover, it is only for $N = 2$ that a pure phase grows as single phase growth (up to a factor of two).

It should be added that with careful choice of potential, see [3], spurious growth can be mitigated. However, this only holds for $N = 3$ and the generalisation to $N > 3$ is not clear within the Lagrange multiplier formulation.

The Lagrange multiplier approach may be viewed as an $N \times N$ matrix projection, $\mathbf{P}$,

$$-\tau\dot{\boldsymbol{\theta}} = \mathbf{P}_{(N)}\frac{\delta F}{\delta \boldsymbol{\theta}}, \quad -\tau\dot{\theta}^i = P^{ij}_{(N)}\frac{\delta F}{\delta \theta^j}$$

where the projection equivalent to the Larange multiplier is given by

$$\mathbf{P}_{(N)} = \mathbf{I} - \mathbf{n}\mathbf{n}^T. \tag{9}$$

For example with $N = 2$, we have

$$\mathbf{n} = \frac{1}{\sqrt{2}}[1, 1]^T$$

is the outward normal to the line $\theta_2 = 1 - \theta_1$. If we consider the phase variables, θ_1 and θ_2 to be Cartesian coordinates, then $\mathbf{n}$ has unit length.

3. A new formulation

The essence of the new formulation is to alter the projection matrix, $\mathbf{P}$, in such a way as to eliminate the defects we have highlighted with the Lagrange multiplier approach. To this end we propose a set of properties that the matrix (metric) $\mathbf{P}$ must possess (like the Lagrange multiplier specification of $\mathbf{P}$ does not affect material properties of the model):

(i) Reduces to $n < N$ case when only n phases are present locally in a N phase system.

(ii) The projection must never be zero at any point, as this will inhibit growth from a pure phase.

(iii) The projection must be symmetric with positive or zero eigenvalues as a result of the consistency requirement between the left-hand and right-hand side components.

(iv) The metric should be degenerate and continuous: that is, it must map from dimension N to dimension $n < N$ smoothly.

(v) Triple points should be active parts of the system: this excludes the model proposed by Steinbach [4].

These criteria do not fix a unique value for $\mathbf{P}$. We now give a form for $\mathbf{P}$ which satisfies most (but not all at this stage) of the criteria.

By inspecting (6) we see that for $N = 2$ we must have

$$\mathbf{P} = \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

In order to generalise this result we note that we may trivially write this

$$\mathbf{P} = \frac{\theta_1\theta_2}{(1-\theta_1)(1-\theta_2)}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \tag{10}$$

since $\theta_1 = 1 - \theta_2$. This suggests a more general form for $\mathbf{P}$ given by

$$\mathbf{P} = \sum_{j=2}^{N}\sum_{i=1}^{j-1}\frac{\theta_i\theta_j}{(1-\theta_i)(1-\theta_j)}(\mathbf{x}_i - \mathbf{x}_j)\otimes(\mathbf{x}_i - \mathbf{x}_j),$$

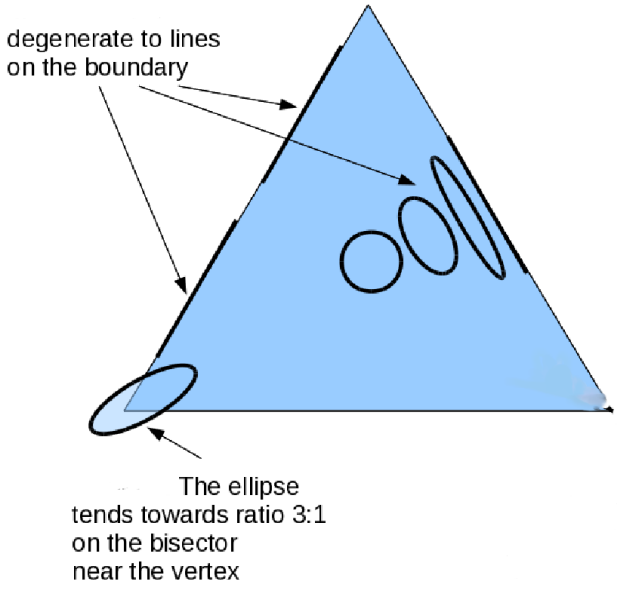

Figure 1. Eigen values and vectors displayed as ellipses as a function of position on the triangular simplex. As a point approaches the boundary the ellipse degenerates to a line, but as we approach a vertex from the centre the circle becomes elliptical.

where $\mathbf{x}_i$ are the barycentric coordinates of each vertex of the simplex representing the multiphase field, e.g. a triangle for $N = 3$, tetrahedran for $N = 4$ etc. The vertices are thus, $(\mathbf{x}_i)_j = \delta_{ij}$, so that in components, P^{kl}

$$P^{kl} = \sum_{j=2}^{N} \sum_{i=1}^{j-1} \frac{\theta_i \theta_j}{(1-\theta_i)(1-\theta_j)} (\delta_{ki} - \delta_{kj})(\delta_{li} - \delta_{lj}). \tag{11}$$

The $N = 3$ case follows as

$$\mathbf{P} = \frac{\theta_1\theta_2}{(1-\theta_1)(1-\theta_2)} \begin{bmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\theta_2\theta_3}{(1-\theta_2)(1-\theta_3)} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{bmatrix} + \frac{\theta_3\theta_1}{(1-\theta_3)(1-\theta_1)} \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{bmatrix}.$$

where we note that if, say, $\theta_3 = 0$ we obtain the $N = 2$ case.

3.1. Some properties of $\mathbf{P}$

This section considers the new model from the perspective of eigenvectors and eigenvalues of the matrix $\mathbf{P}$ in order to see the effect on the system. The interface defined by $\theta_3 = 0$ gives the matrix

$$\mathbf{P} = \begin{bmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

This has one positive eigenvalue, 2, with corresponding eigenvector $[1, -1, 0]$, which aligns with the the interface. On the other hand, in the centre of the simplex, $\boldsymbol{\theta} = [1/3, 1/3, 1/3]$, we find one eigenvalue of $3/4$ corresponding to any vector lying on the simplex. So in the centre

the matrix, $\mathbf{P}$, simply projects out the term normal to the simplex and multiplies by 3/4. On the other hand, on the interface, $\mathbf{P}$ has the effect of also projecting out the term normal to the interface. In general $\mathbf{P}$ has the double effect of projecting out the normal component and rescaling the components of the vector along the two eigenvectors. Representing $\mathbf{P}$ at any point on the simplex by an ellipse with major and minor axes of lengths and direction given by the eigenvalues and eigenvectors, we can view the action of $\mathbf{P}$ in the centre as a circle and at an interface a degenerate ellipse — a line (see Fig. 1).

Consider a typical path on an $N = 3$ simplex given by

$$\mathbf{x}(t) = [\theta_1 = t, \theta_2, \theta_3 = 1 - 2t], \quad t \in [0, \tfrac{1}{2}]. \tag{12}$$

We are interested in the property of $\mathbf{P}$ as we approach the vertex $\theta_3 = 1$ as t tends to zero. We find that $\mathbf{P}$ is an ellipse with major axis of length 3/2 pointing along the line and minor axis of length 1/2.

In contrast, for the Lagrange multiplier, $\mathbf{P}$ is represented as a circle throughout the triangle.

3.2. Ill-defined $\mathbf{P}$ *for a pure phase*

The model as it stands suffers from being ill-defined at any vertex, $\theta_i = 1$. This is due to a feature of our construction that, at the vertices, $\mathbf{P}$ depends on the path. For example, with $N = 3$, and $\theta_1 = 1$ we find $\mathbf{P}$ degenerates to two matrices for paths along the two adjoining edges $\theta_3 = 0$ and $\theta_2 = 0$:

$$\mathbf{P}|_{\theta_3=0} = \begin{bmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \mathbf{P}|_{\theta_2=0} = \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{bmatrix}. \tag{13}$$

Thus we require, in addition to the definition (11), to define unique matrices at each vertex. Alternatives such as enforcing $\theta_i < 1$ via the initial condition, the use of a small parameter in local averaging, or modifying the potential are all problematic.

Many candidates for the value of $\mathbf{P}$ at the vertices fail, including: $\mathbf{P} = \mathbf{0}$, which inhibits growth; and $\mathbf{P} = \mathbf{I} - \mathbf{U}/N$, which introduces spurious growth. However, we found

$$\mathbf{P}_{\text{vertex}} = 2\mathbf{I} - \mathbf{U}, \text{ if } 1 - \theta_i < \delta, \text{ for any } i, \tag{14}$$

where the small parameter, $\delta \ll 1$, did not significantly alter results[3]. To discuss this we write this out for $N = 3$

$$\mathbf{P}_{\text{vertex}} \equiv \begin{bmatrix} 1 & -1 & -1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \end{bmatrix}$$

and assume that θ_3 and its gradients vanish. Thus,

$$\frac{\delta F}{\delta \theta_3} = 0$$

Consequently the third column plays no role and $\dot{\theta}_1$ and $\dot{\theta}_2$ reduce correctly to a two phase formulation. On the other hand

$$\tau \dot{\theta}_3 = \frac{\delta F}{\delta \theta_1} + \frac{\delta F}{\delta \theta_2}$$

[3] For a range of 10^{-10} to 10^{-14} in δ we found the steady state growth rate was effectively unaltered in eutectic or pure phase simulation

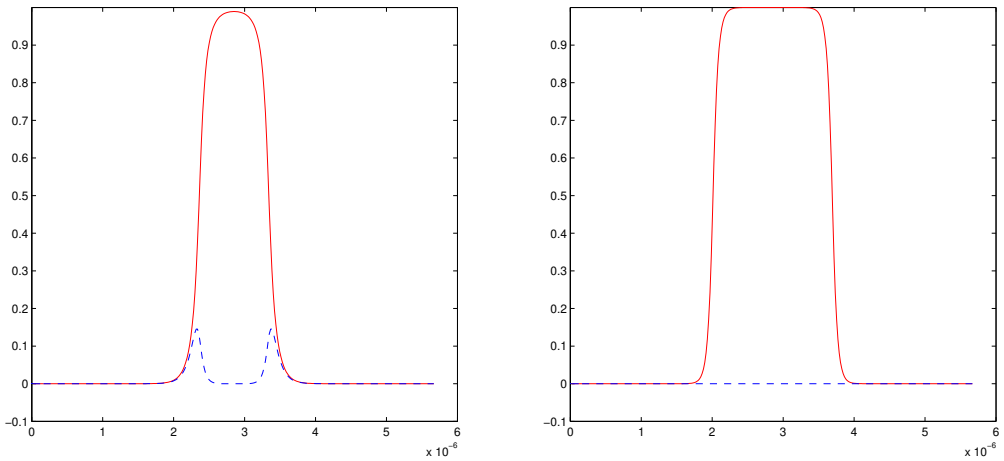

Figure 2. Comparison of the growth of a pure phase, $\theta_2 = 1$ (red continuous line), for the Lagrange multiplier model (left) and an alternative new model presented in section 3 (right). A cross section of the growing seed, θ_2 is superimposed with the cross section of phase θ_3 (blue dashed line). The liquid phase, $\theta_1 = 1 - \theta_2 - \theta_3$, is not shown. The Lagrange multiplier (left) introduces spurious growth of phase θ_3 at the growing boundary, which is completely absent using the new model (right) presented in Section 3. This also effects the speed of growth: the new model grows at a greater rate.

has a right hand side which is non-zero in general. In fact, from (7) we see that the contribution from the potential is zero leaving, for $\theta_1 = 1$:

$$\tau\dot{\theta}_3 = 2(\nabla\theta_1 \cdot \nabla\theta_1) + \nabla^2\theta_1.$$

Now, since $\theta_1 = 1$ we must have $\nabla\theta_1 = 0$ and $\nabla^2\theta_1 \leq 0$ implying $\tau\dot{\theta}_3 \leq 0$. Assuming negative contributions are trapped numerically (if $\theta_i < 0$ then $\theta_i = 0$) this contribution is effectively ignored.

Hence, we have shown that when θ_3 and all its gradients are vanishing, then at one of the other vertices, we find that

$$\mathbf{P}_{\text{vertex}} \equiv \begin{bmatrix} 1 & -1 & -1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \end{bmatrix} \text{ is indistinguishable from } \begin{bmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The general case, (14), easily follows.

Using this model we obtained the result given in right of Fig. 2. The model also eliminates spurious growth in eutectic solidification.

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