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

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Abstract

This paper demonstrates that the standard approach to the modeling of multi-phase field dynamics for the solidification of alloys has three major defects and offers an alternative approach.

The phase field formulation of solidification for alloys with multiple solid phases is formed by relating time derivatives of each variable of the system (e.g. phases and alloy concentration), to the variational derivative of free energy with respect to that variable, in such a way as to ensure positive local entropy production. Contributions to the free energy include the free energy density, which drives the system, and a penalty term for the phase field gradients, which ensures continuity in the variables. The phase field equations are supplemented by a constraint guaranteeing that at any point in space and time the phases sum to unity. How this constraint enters the formulation is the subject of this paper, which postulates and justifies an alternative to current methods.

Keywords:
Multi-phase, Phase field, Lagrange multiplier, Solidification, Crystal growth, Eutectic, Peritectic, Gibbs free energy

1. Introduction

In recent years the importance of phase-field simulation as a tool to understanding microstructure formation during solidification has grown significantly, (e.g.[1],[2],[3],[4] and [5]). As a result, phase-field modelling is now the technique of choice for simulating solidification microstructures, with numerous notable examples of its success. These include the inclusion of flow effects, [6] and electric currents [7] in the solidifying melt, elucidating the

mechanisms behind long-standing problems in solidification such as spontaneous grain refinement, [8], and predicting the effect of external oscillating fields on dendrites [9]. 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. This generally represented either the thermally controlled growth of a pure substances (e.g. [10]), or the isothermal solidification of an ideal binary solid-solution [11]. 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 [12]. 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 independently, an additional condition must be applied to ensure that the sum of the phases remains everywhere constant.

There are two main ways in which this can be achieved, either by the use of a Lagrange undetermined multiplier (e.g. [13], [14],[15],[16]) or by specifying explicitly how the phases vary with respect to one another (e.g [17],[18] and [19]). In this latter case a common assumption is that phase transformations within a multiphase system are governed solely by interactions at two-phase interfaces (but there are exceptions: see [22] for example, which uses a higher order multipole exapnsion). Consequently, at a triple point, where three phases meet, the dynamics of the system would be governed by the three, two-phase interfaces stretching out from the triple point. This allows for any terms within the derivation which depend upon three phases to be ignored in favour of terms dependent upon only two phases.

[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

Both approaches have potential drawbacks. The use of a Lagrange undetermined multiplier has been found to lead to the formation of spurious phases local to the interface region: "... in the interface, the phase fields $\theta_k, k \neq i, j$, can be different from zero" [20], which goes on to state: "... if computations are to remain feasible, we have to accept the presence of additional phases in the interfaces". Conversely it has been shown that models assuming all interactions occur at two-phase interfaces may produce incorrect triple point morphologies (see [17]). Of these the Lagrange multiplier approach has generally received greater attention.

By examining the consequences of the Lagrange multiplier approach in section 2, we demonstrate some critical weaknesses with this formulation. In order to remedy this, we show that underlying the Lagrange multiplier method is an assumption that the *independent* phase variables ϕ_i form the coordinates of a flat surface (of dimension $N-1$ embedded in $\mathbf{R}^N$). In section 3, we relax this condition, taking care in section 3.1 to use the correct (symmetric) transformation between the two different types of vector spaces that the unconstrained phase field equations represent. We then postulate a set of criteria that a reasonable alternative must possess leading, in sections 3.4 and 3.5, to the presentation of alternative formulations.

We end the paper with some numerical results in section 4.1, showing the effect of N in growth rates, for the different formulations. For the Lagrange multiplier approach, results show dependence on N, spurious phase growth and less stability than the proposed formulations, which avoid these defects.

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. [14]

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

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 [14] (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

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

We now demonstrate that the standard Lagrange multiplier treatment of multi-phase field dynamics, e.g. [14], does not reduce to the equivalent single phase form [2]. 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

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

[2] This is a well known by many in the phase field community but has not, to our knowledge, been explicitly stated in the literature.

The single phase equation is

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

This is equivalent, in the multi-phase (binary 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[3]

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

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.

We now explore whether the discrepancy between the single and $N = 2$ multi-phase formulation is symptomatic of a more general problem. The Lagrange multiplier treatment of the N phase free energy can be written

$$\dot{\boldsymbol{\theta}} = \mathbf{P}_{(N)}\frac{\delta F}{\delta \boldsymbol{\theta}},$$

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

where $\mathbf{P}_{(N)} = \mathbf{I} - \frac{1}{N}\mathbf{U}$ where the $N \times N$ matrix $\mathbf{U}$ has unit entries in all components. For example,

$$\mathbf{P}_{(2)} = \begin{bmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{bmatrix}, \quad \mathbf{P}_{(3)} = \begin{bmatrix} 2/3 & -1/3 & -1/3 \\ -1/3 & 2/3 & -1/3 \\ -1/3 & -1/3 & 2/3 \end{bmatrix},$$
$$\mathbf{P}_{(4)} = \begin{bmatrix} 3/4 & -1/4 & -1/4 & -1/4 \\ -1/4 & 3/4 & -1/4 & -1/4 \\ -1/4 & -1/4 & 3/4 & -1/4 \\ -1/4 & -1/4 & -1/4 & 3/4 \end{bmatrix}. \tag{7}$$

Hence for $N = 3$, for example, the equation for θ_1 is

$$\dot{\theta}_1 = \tfrac{2}{3}\frac{\delta F}{\delta \theta_1} - \tfrac{1}{3}\left(\frac{\delta F}{\delta \theta_2} + \frac{\delta F}{\delta \theta_3}\right)$$

and for $N = 4$, the equation for θ_1 is

$$\dot{\theta}_1 = \tfrac{3}{4}\frac{\delta F}{\delta \theta_1} - \tfrac{1}{4}\left(\frac{\delta F}{\delta \theta_2} + \frac{\delta F}{\delta \theta_3} + \frac{\delta F}{\delta \theta_4}\right).$$

More generally, if we replace one of the phase variables, say $\theta_N = 1 - \sum_{j=1}^{N-1} \theta_j$ and write

$$\phi_i = \theta_i, i \in [1, N-1], \tag{8}$$

in the free energy, then the system

$$-\tau \dot{\phi}_i = \frac{\delta F}{\delta \phi_i} \tag{9}$$

is a different system of equations to those resulting from the Lagrange multiplier approach. However, the mapping (8) is not unique and the system (9) should more correctly be written

$$-\sum_{j=1}^{N}\sum_{k=1}^{N-1} \tau J_{ji} J_{jk} \dot{\phi}_k = \frac{\delta F}{\delta \phi_i}, \quad i \in [1, N-1], \quad \left(\text{or } -\tau \mathbf{J}^T \mathbf{J} \dot{\boldsymbol{\phi}} = \frac{\delta F}{\delta \boldsymbol{\phi}}\right) \tag{10}$$

where

$$J_{ij} = \frac{\partial \theta_i}{\partial \phi_j} \quad \left(\text{or } \mathbf{J} = \frac{\partial \boldsymbol{\theta}}{\partial \boldsymbol{\phi}}\right).$$

This comes about because

$$\frac{\delta F}{\delta \phi_i} = \sum_{j=1}^{N} \frac{\partial \theta_j}{\partial \phi_i} \frac{\delta F}{\delta \theta_j}, \quad i \in [1, N-1] \quad \left(\text{or } \frac{\delta F}{\delta \boldsymbol{\phi}} = \mathbf{J}^T \frac{\delta F}{\delta \boldsymbol{\theta}} \right)$$

and

$$\dot{\theta}_j = \sum_{k=1}^{N-1} \frac{\partial \theta_j}{\partial \phi_k} \dot{\phi}_k, \quad j \in [1, N] \quad \left(\text{or } \dot{\boldsymbol{\theta}} = \mathbf{J} \dot{\boldsymbol{\phi}} \right)$$

giving the constrained version of (3) as (10).

Note that the above argument allows for any smooth mapping

$$\begin{aligned} R^N &\to R^{N-1} \\ \boldsymbol{\theta} &\mapsto \boldsymbol{\theta}(\boldsymbol{\phi}). \end{aligned}$$

Indeed in Appendix A we show that system (10) is identical to the Lagrange multiplier approach (this is seen most easily when $N = 2$ where we have $J_i^j J_k^j = J_1^1 J_1^1 + J_1^2 J_1^2 = 2$). This observation might appear to indicate that the single phase formulation formally requires a factor of $\frac{1}{2}$ on the right-hand side to be in general agreement with the Lagrange multiplier method for $N = 2$. However, there is another difficulty with the Lagrange multiplier method, which suggests that it is the Lagrange multiplier formulation of the multi-phase field that is in error and consequently that the single phase formulation may be assumed correct.

2.1. Spurious extra phases and N dependence

This section shows that the formulation in [14], 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 $i > 2$. In cases where an additional phase is actually required, for example, to correct an ill-spaced eutectic growth, it is possibly preferable to introduce this by numerical noise rather than through the formulation. Moreover, even in this case the additional phase would be restricted at the liquid-solid interface and not at the solid-solid interface.

The Lagrange multiplier formulation in [14] 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 (see Appendix B)

$$\frac{\delta F}{\delta \theta_i} = \sum_{j\neq i}^{N} \Gamma^{ij}\{2(\theta_i \nabla\theta_j - \theta_j\nabla\theta_i)\cdot\nabla\theta_j + (\theta_i\nabla^2\theta_j - \theta_j\nabla^2\theta_i)\theta_j\} + \sum_{j\neq i}^{N} 2W_{ij}\theta_i\theta_j^2 - 30m_i\theta_i^2(1-\theta_i)^2. \tag{11}$$

Considering the Lagrange multiplier formulation for $N = 3$, with $\theta_3 = 0$, we find

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

so that

$$\tau\dot{\theta}_3 = \tfrac{1}{3}\left(\frac{\delta F}{\delta\theta_1} + \frac{\delta F}{\delta\theta_2}\right).$$

Thus the growth of θ_3 is zero if

$$\frac{\delta F}{\delta \theta_1} + \frac{\delta F}{\delta \theta_2} = 0.$$

However, the left-hand side is non-vanishing at a $(1,2)$ interface and can give rise to spurious unwanted phases, see Fig. 1. It should be added that with careful choice of potential, see [5], spurious growth can be mitigated (see Appendix C). However, this only holds for $N = 3$ and the generalisation to $N > 3$ is not clear within the Lagrange multiplier formulation.

More generally, 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

$$\begin{aligned} -\tau\dot{\theta}_1 &= (1-\tfrac{1}{N})\frac{\delta F}{\delta\theta_1} - \tfrac{1}{N}\frac{\delta F}{\delta\theta_2} \\ -\tau\dot{\theta}_2 &= (1-\tfrac{1}{N})\frac{\delta F}{\delta\theta_2} - \tfrac{1}{N}\frac{\delta F}{\delta\theta_1} \\ -\tau\dot{\theta}_{i>2} &= -\tfrac{1}{N}\left(\frac{\delta F}{\delta\theta_1} + \frac{\delta F}{\delta\theta_2}\right), \end{aligned} \tag{12}$$

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).

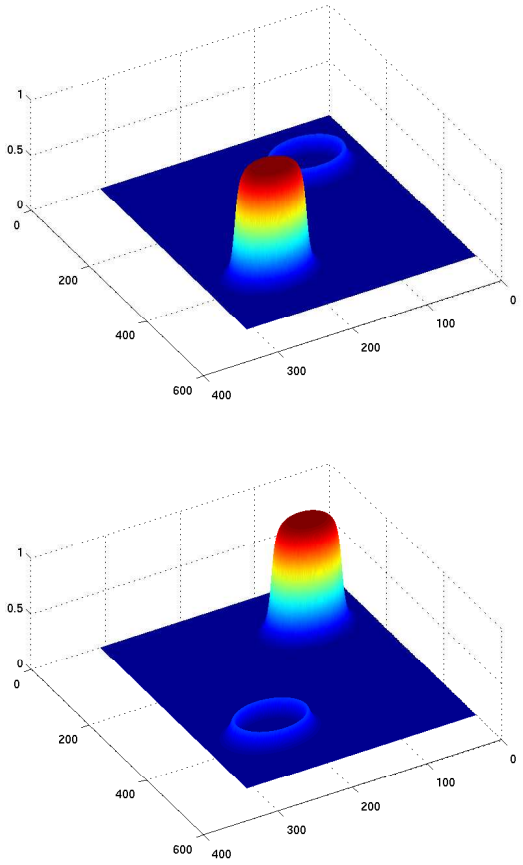

Figure 1: The growth from two separated solid seeds of θ_2 and θ_3, in a melt θ_1, using the Lagrange multiplier model. The left shows θ_2 and the right θ_3. Surrounding each growth is a significant amount of the other phase. This effect is not present in the model developed in this paper — see section 3.

3. Development of a new formulation

Having identified at least three defects in the Lagrange multiplier approach (non-reduction to single phase, spurious growth of additional phases and N dependence) this section develops a new formulation that addresses these issues. Specifically an N independent formulation with consistent reduction to single phase at any (pure) binary phase interface.

The matrix transformation, $\mathbf{P}$, illustrated in (7), can be also looked at as a projection (hence the nomenclature)

$$\mathbf{P} = \mathbf{I} - \mathbf{n}\mathbf{n}^T \tag{13}$$

where, for $N = 2$,

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

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.

An alternative to the constant Lagrange multiplier was introduced by [21] in order to eliminate N dependence. It is shown in the appendix that this method is equivalent to a numerical implementation of the constraint used currently, for example, in [22] and [27].

It uses a Lagrange multiplier vector Λ_i

$$-\tau\dot{\theta}_i = \frac{\delta F}{\delta \theta_i} + \Lambda_i$$

where

$$\Lambda_i = -\theta_i \sum_{j=1}^{N} \frac{\delta F}{\delta \theta_j}.$$

This is equivalent to the projection

$$\mathbf{P}_{(N)} = \mathbf{I}_{(N)} - [\boldsymbol{\theta}, \boldsymbol{\theta}, \ldots, \boldsymbol{\theta}]$$

For example, when $N = 2$,

$$\mathbf{P}_{(2)} = \begin{bmatrix} 1 - \theta_1 & \theta_1 \\ -\theta_2 & 1 - \theta_2 \end{bmatrix}. \tag{14}$$

We now show that this projection adopted and used in [21] is unacceptable and that the projection must be a symmetric matrix.

3.1. Consistency of form in the phase equations

Here, and in subsequent sections, we make use of the equivalence between differential operators and vector bases (e.g. $\frac{\partial}{\partial x} \equiv \mathbf{i}, \frac{\partial}{\partial y} \equiv \mathbf{j}$ etc). Any linear combination of these bases is termed a contravariant vector. We also use the concept of covariant vectors, which are equivalent to linear combinations of differentials, e.g. $\mathrm{d}x$, $\mathrm{d}\theta_i$ etc. Transformations of these objects induced by maps then follow the chain rule and are equivalent to the perhaps more familiar Jacobian matrices (see for discussion [23]).

Consider the system

$$-\tau \frac{\partial \theta_i}{\partial t} = \frac{\delta F}{\delta \theta_i}. \tag{15}$$

In the language of differential geometry, the left-hand side may be written as the push forward (linear map) of the tangent vector on the time line to the phase variable space

$$\frac{\partial}{\partial t} = \frac{\partial \theta_i}{\partial t} \frac{\partial}{\partial \theta_i}.$$

The left-hand side of (15) is thus a contravariant vector. On the other hand, the right-hand side of equation (15) is a covariant vector

$$\delta F = \frac{\delta F}{\delta \theta_j} \, \mathrm{d}\theta_j$$

(see the book, [23], in the earlier chapters, for a discussion for the necessity of the two types of vectors and Chapter 6 for discussion of Calculus of variations and their connection with covariant vectors).

By equating the two objects in (15) we are saying something about the metric, i.e. drawing an equivalence between the covariant vector basis, $\mathrm{d}\theta_i$, and contravariant vector basis $\frac{\partial}{\partial \theta_i}$. By making this equivalence we assume the metric on the phase space is flat and the coordinates, Cartesian. For other coordinates contravariant and covariant vectors are not (automatically) equivalent, e.g. in polar coordinates, the angle, $\frac{\partial}{\partial \varphi}$, is not equivalent to $\mathrm{d}\varphi$ [4]. To change a covariant vector to a physically equivalent contravariant vector requires a metric $\mathbf{g}$. The system (15) is more correctly written

$$\tau \frac{\partial \theta_i}{\partial t} = g^{ij} \frac{\delta F}{\delta \theta^j} \tag{16}$$

[4] On the other hand $(1/r)\frac{\partial}{\partial \varphi}$ is considered physically equivalent to $r \, \mathrm{d}\varphi$

where $\mathbf{g}$ is positive definite and symmetric. For Cartesian coordinates $g^{ij} = \delta^{ij}$, so the metric is redundant and we can write (15). For an $N-1$ dimensional surface, the metric is represented by a rank $N-1$ matrix and consequently is singular if, as in the Lagrange multiplier treatment, there are N coordinates, θ_i, $i \in [1, N]$ (or non-singular if the unconstrained variables, ϕ_i, $i \in [1, N-1]$ are used).

The constant Lagrange multiplier with metric $\mathbf{P}_{(N)}$ is acceptable in this respect, since it represents the metric of an $N-1$ dimensional (flat) space embedded in an N dimensional flat space with coordinates θ_i, but the *vector* Lagrange multiplier, Λ_i, which gives rise to the matrix (14), is not symmetric and therefore cannot be formally correct. This is because a projection is a mapping from a contravariant vector to a contravariant vector implying $\mathbf{P}$ has components $P^i{}_j$. So the correct way of projecting (16) is

$$\tau \frac{\partial \theta_i}{\partial t} = P^i{}_j g^{jk} \frac{\delta F}{\delta \theta^k} \tag{17}$$

and we find that the object

$$P^{ik} \equiv P^i{}_j g^{jk} = (\delta^i{}_j - n^i n_j) g^{jk} = g^{ik} - n^i n^k$$

is symmetric. From hereon we assume $\mathbf{P}$ with components P^{ik} is an $N \times N$ symmetric matrix with eigenvalues ≥ 0. In passing, it is interesting to note the similarity between P in (17) and a projection operator, (denoted π_P), found in [24]

As we have noted, the g^{ij} in equation (16) is necessary to balance the covariant and contravariant vectors. Other tensors, e.g. T^{ij}, can do this, but a metric transformation retains the physical significance of the object — in this case $\frac{\delta F}{\delta \theta^j}$ — and can be constructed from a given specified, smooth, $N-1$ dimensional surface in an N dimensional Cartesian space. We give an example of this in Sec. 3.3 where we construct a metric of a line embedded in two dimensional flat space.

3.2. Properties that the mapping must possess

We are now able to lay down a set properties that the matrix (metric) $\mathbf{P}$ must possess

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

2. The projection must never be zero at any point, as this will inhibit growth from a pure phase.
3. 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: the vector Lagrange multiplier (14) of [21] fails this test.
4. The metric should be degenerate and continuous: that is, it must map from dimension N to dimension $n < N$ smoothly.
5. Triple points should be active parts of the system: this excludes the model proposed by Steinbach [17].

Possibly the most difficult test to satisfy is the first one. The model [14] fails this, but models such as Steinbach [17] are consistent with this test.

3.3. Mapping for correct reduction to single phase

This section introduces, for $N = 2$, a mapping from θ_1, θ_2 to a unit circular arc which induces a metric which reproduces the single phase reduction. This is used in the following section to build a more general mapping for arbitrary N.

Consider the mapping

$$\begin{aligned} r &= \theta_1 + \theta_2, \\ \phi &= \frac{\theta_1}{r} \end{aligned}$$

where r and ϕ are polar coordinates in a plane. The angle, ϕ, physically representing the single phase variable and r physically representing the total quantity so that the constraint (5) is represented in this scheme as the restriction in the plane to a unit circular arc. Rearranging we have

$$\begin{aligned} \theta_1 &= r\phi, \\ \theta_2 &= r(1 - \phi), \end{aligned}$$

which implies

$$\frac{\partial}{\partial \phi} = r \left(\frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_2} \right)$$

The Euclidean metric in polar coordinates is[5]

$$\mathbf{g} = \frac{\partial}{\partial r} \otimes \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial \phi} \otimes \frac{\partial}{\partial \phi}$$

and so the projected metric on to a circular arc of radius r is

$$\begin{aligned} \mathbf{g} - \frac{\partial}{\partial r} \otimes \frac{\partial}{\partial r} &= \frac{1}{r^2} \frac{\partial}{\partial \phi} \otimes \frac{\partial}{\partial \phi} \\ &= \left(\frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_2} \right) \otimes \left(\frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_2} \right) \end{aligned}$$

and since the tensor, $\mathbf{P} = P^{ij} \frac{\partial}{\partial \theta_i} \otimes \frac{\partial}{\partial \theta_j}$ we have that the components are given by the matrix

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

and in particular when $r = \theta_1 + \theta_2 = 1$ the parameter ϕ is arc length. This agrees with the single phase formulation (6).

There are other mappings, however, that do this. Consider the mapping in Cartesian coordinates x, y

$$x = \frac{1}{\sqrt{2}} \theta_1, \quad y = \frac{1}{\sqrt{2}} \theta_2$$

then by a similar process the metric on the surface, $\theta_1 + \theta_2 = 1$ (or $x + y = 1/\sqrt{2}$), is also

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

since a unit Cartesian basis on the surface is

$$\frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) = \frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_2}.$$

The common feature of both mappings is that the resultant curve has unit length. This suggests a generalisation to $N = 3$ (and beyond), where the simplex lies on a hypersurface with the property that the edges have unit length and, to avoid N dependence, the surface degenerates to a line for a

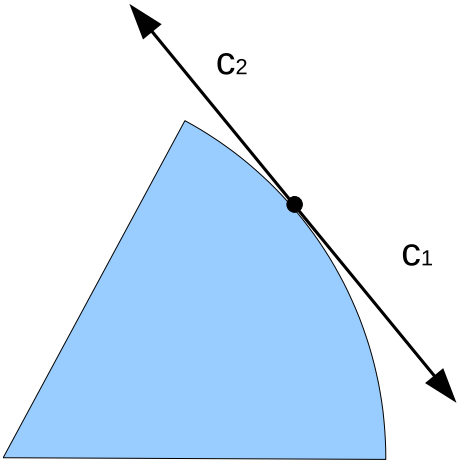

Figure 2: On the unit length circular arc we show two unit length (not to scale) vectors defined at one point. A metric of the arc may be formed from a tensor combination of either or both vectors.

pure interface. To this end we first write the above in a form that may be generalised.

Let us define two unit vectors on the arc (see Fig. 2)

$$\mathbf{c}_1 \equiv \frac{\partial}{\partial\theta_1} - \frac{\partial}{\partial\theta_2}, \quad \mathbf{c}_2 \equiv \frac{\partial}{\partial\theta_2} - \frac{\partial}{\partial\theta_1}.$$

Then we find that we can trivially write the metric on the arc as

$$\mathbf{P} = \alpha\mathbf{c}_1 \otimes \mathbf{c}_1 + (1-\alpha)\mathbf{c}_2 \otimes \mathbf{c}_2$$

for any α. In particular we may write

$$\begin{aligned}\mathbf{P} &= \theta_1\mathbf{c}_1 \otimes \mathbf{c}_1 + \theta_2\mathbf{c}_2 \otimes \mathbf{c}_2 \\ &= \sum_{i=1}^{2} \theta_i\mathbf{c}_i \otimes \mathbf{c}_i \end{aligned} \tag{18}$$

We can also trivially write

$$\mathbf{P} = \frac{\theta_1\theta_2}{(1-\theta_1)(1-\theta_2)} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \tag{19}$$

[5]In Cartesian coodinates x, y the metric of a flat plane is $\mathbf{g} = \frac{\partial}{\partial x} \otimes \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \otimes \frac{\partial}{\partial y}$, so that using $x = r\cos\phi, y = r\sin\phi$ and the chain rule we obtain the form given here.

Generalisations to $N > 2$ of these two equivalent formulations, (18) and (19) for $N = 2$ are exploited in the following subsections.

3.4. Proposed multi-phase formulation A

We now develop a natural generalisation of the $N = 2$ case, (18), to $N > 2$. For $N = 2$ we could interpret the construction as a mapping from the (straight) line segment $\theta_1 + \theta_2 = 1$ to a circular arc to induce a metric. Extending this approach to $N = 3$ we consider a mapping from the 2 dimensional simplex $\theta_1 + \theta_2 + \theta_3 = 1$ to a 2 dimensional non flat surface – in particular a sphere. In this way, under the constraint, θ_i form barycentric coordinates on the simplex and map to spherical barycentric coordinates on a sphere [6]. We then modify the result so that the metric reduces to that of $N = 2$ for a pure binary interface.

We first aim to establish a geodesic coordinate system on a spherical triangular simplex. Consider first longitude and latitude on a sphere- θ, φ respectively. Then θ parametrises a set of geodesics labelled by φ, and conversely the curves parametrised by φ intersect these curves at constant values of θ. Limiting the domain to an eighth sphere (positive x, y, z) with $\theta, \varphi \in [0, \pi/2]$, we have an equilateral spherical triangle with three poles $\mathbf{x} = (1, 0, 0), (0, 1, 0), (0, 0, 1)$ in Cartesian coordinates, where each geodesic of constant φ conventionally begins at the pole $(0, 0, 1)$ and ends at $(\cos\varphi, \sin\varphi, 0)$. We can equally well choose the other two poles as the origin of the geodesics. Let us label these three coordinates systems $(\theta_1, \varphi_1), (\theta_2, \varphi_2), (\theta_3, \varphi_3)$. Note that the duplicate use here of the symbol θ_i for angle as well as for the phase field is no coincidence. The three sets of geodesics $\mathbf{C}_1(\theta_1, \varphi_1), \mathbf{C}_2(\theta_2, \varphi_2), \mathbf{C}_3(\theta_3, \varphi_3)$ are generated by and are integral curves of three vector fields, $\mathbf{c}_1, \mathbf{c}_2$ and $\mathbf{c}_3$ respectively. Considering the spherical equilateral triangle as a mapping from a flat equilateral triangle, then the straight lines emanating from the vertices of the flat triangle map to geodesics on the spherical triangle. The barycentric coordinates of a point on the flat triangle, say $(\lambda_1, \lambda_2, \lambda_3)$, correspond exactly to geodesic distances $(\pi/2 - \theta_1, \pi/2 - \theta_2, \pi/2 - \theta_3)$ to each respective vertex. If we reverse the direction of the parameter θ_i so that the integral curves begin at the equator and move towards the poles then the relation is $\theta_i = (\pi/2)\lambda_i$.

[6] However, we still interpret the vector fields $\frac{\partial}{\partial\theta_i}$ as existing in the N dimensional space.

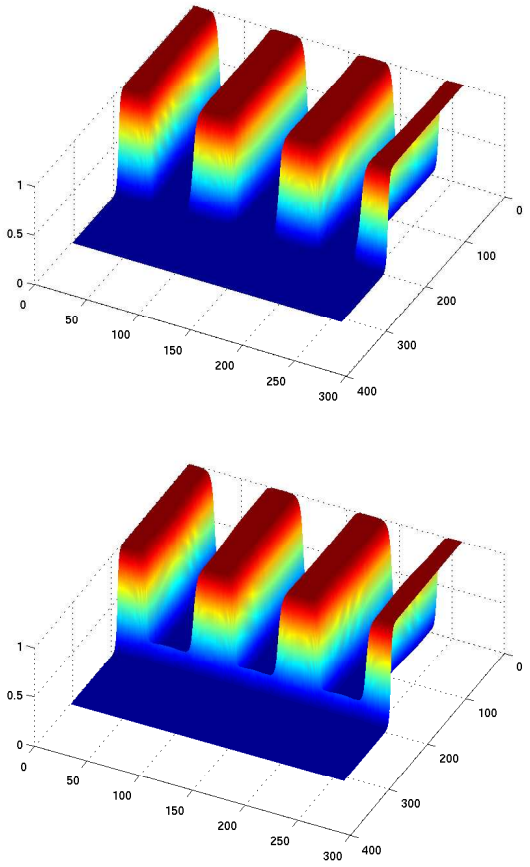

Figure 3: Eutectic growth of solid θ_2 for the proposed model (left) and the Lagrange multiplier (right). We see on the right that there is spurious growth of solid θ_2 at the interface between solid θ_3 and the liquid θ_1. This is not present at all in the proposed model.

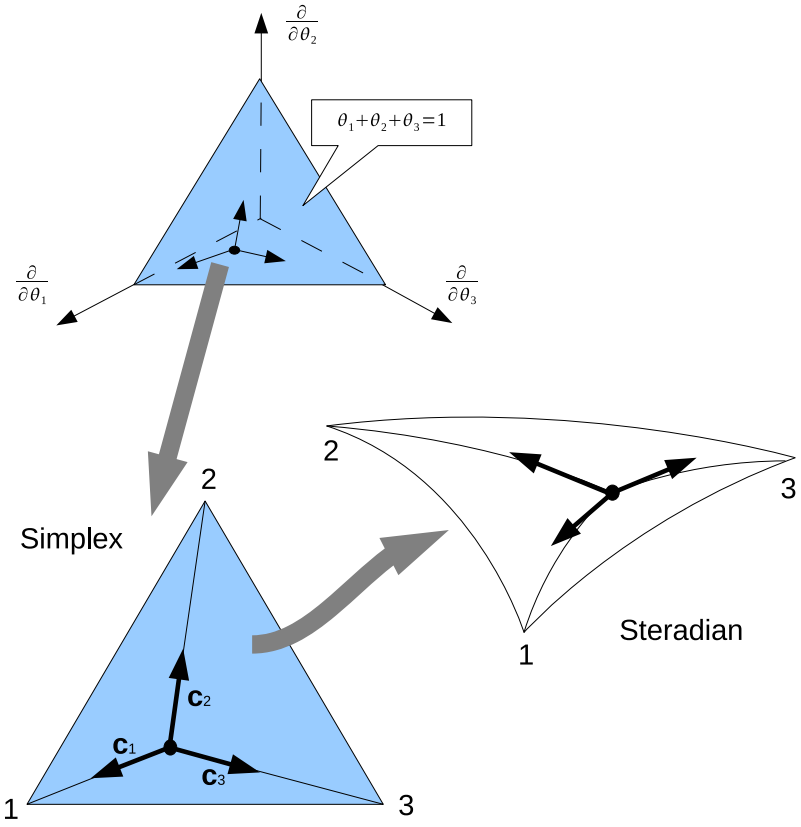

Figure 4: Mapping from the $N = 3$ dimensional space to the flat simplex (implementing the constraint) to the steradian (implementing the metric). The unit vectors $\mathbf{c}_i$ point along the line to the respective vertices, i. The distance between a vertex, $\mathbf{x}_i$ and a point, $\mathbf{x}$, is given by the distance on the steradian, $1 - \theta_i$. As a point approaches an edge, say $\theta_2 \to 0$, two of the vectors become colinear and a metric formed from just these two vectors gives a metric of a curve.

Moving on to the spherical triangle with unit geodesic edges (a steradian) and with the reversed direction of parametrisation the correspondence becomes $\lambda_i = \theta_i$. This implies that the distance from a vertex i to a general point is given by $1 - \theta_i$. Interestingly, the *distances* to a point in the *flat* triangle from the vertices do not have such a neat relation to the barycentric coordinates as the spherical barycentric coordinates do. See [25] for issues on creating spherical barycentric coordinates, in particular the 'coordinate' system we have created does not have all the properties that a true barycentric coordinate system has, e.g. lines of constant θ_1 are not geodesics and therefore not parametrised by θ_2 or θ_3.

The three unit geodesic vector fields on the unit spherical triangle correspond to

$$\mathbf{c}_i = \frac{\mathbf{x}_i - \mathbf{x}}{1 - \theta_i}$$

on the flat triangle, where the barycentric position,

$$\mathbf{x} = \sum \theta_i \mathbf{x}_i,$$

with each pure phase given by

$$\mathbf{x}_1 = [1, 0, 0]^T, \mathbf{x}_2 = [0, 1, 0]^T, \mathbf{x}_3 = [0, 0, 1]^T.$$

In component form $\mathbf{c}_i$ is thus

$$(\mathbf{c}_i)_j \equiv c_{ij} = \frac{\delta_{ij} - \theta_j}{1 - \theta_i}, \tag{20}$$

We know this because the geodesics from any point to any vertex on the spherical triangle map to straight lines from $\mathbf{x}$ to each vertex $\mathbf{x}_i$ on the flat triangle. So a tangent to each geodesic maps to a tangent to each straight line – see Fig. 4. To make this tangent vector unit length we divide by the geodesic distance of the point *on the spherical triangle*, corresponding to $\mathbf{x}$ on the flat triangle, from the vertices, i.e. $1 - \theta_i$. The relation between the vectors on the $N - 1$ simplex $\mathbf{c}_i$ and the N dimensional space is

$$\mathbf{c}_i = c_{ij} \frac{\partial}{\partial \theta_j}.$$

We note that as a point approaches an edge, say $\theta_2 \to 0$ two of the vectors ($\mathbf{c}_1$ and $\mathbf{c}_3$) become colinear. A metric formed from just these two vectors

will give a metric for a curve. With this in mind we construct a metric from the three vector fields, for an arbitrary point on the simplex, as follows:

$$\mathbf{P} = \sum_{j}^{N} \theta_j \mathbf{c}_j \otimes \mathbf{c}_j \tag{21}$$

where the coefficients, θ_i of $\mathbf{P}$, amount to a postulate, without which we would have no degeneracy to local regions $n < N$, where n is the number of phases present in a local region. In component form the metric is

$$P^{ij} = \sum_{k}^{N} \theta_k c_{ki} c_{kj} \tag{22}$$

Note that, for $N = 3$, by construction when say $\theta_2 = 0$, so that $\theta_1 + \theta_3 = 1$ and $\mathbf{c}_3 = -\mathbf{c}_1$, then the metric degenerates to

$$\begin{aligned} \mathbf{P}|_{\theta_2=0} &= \theta_1 \mathbf{c}_1 \otimes \mathbf{c}_1 + \theta_3 \mathbf{c}_3 \otimes \mathbf{c}_3 \\ &= (\theta_1 + \theta_3)\mathbf{c}_1 \otimes \mathbf{c}_1 \\ &= \mathbf{c}_1 \otimes \mathbf{c}_1 \\ &= \left(\frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_3} \right) \otimes \left(\frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_3} \right). \end{aligned} \tag{23}$$

We can see that even though we have restricted the argument to $N = 3$, the more general case is immediately found simply by allowing any $N > 1$. For example, for $N = 4$ with only two phases present in a region the formulation exactly reproduces $N = 2$ behaviour, which itself exactly reproduces the

single phase formulation. To illustrate this we give $\mathbf{P}$ for this case explicitly

$$\mathbf{P}_{(4)} = \frac{\theta_1}{(1-\theta_1)^2}\begin{bmatrix} (1-\theta_1)^2 & -(1-\theta_1)\theta_2 & -(1-\theta_1)\theta_3 & -(1-\theta_1)\theta_4 \\ -(1-\theta_1)\theta_2 & {\theta_2}^2 & \theta_2\theta_3 & \theta_2\theta_4 \\ -(1-\theta_1)\theta_3 & \theta_2\theta_3 & {\theta_3}^2 & \theta_3\theta_4 \\ -(1-\theta_1)\theta_4 & \theta_2\theta_4 & \theta_3\theta_4 & {\theta_4}^2 \end{bmatrix}$$
$$+ \frac{\theta_2}{(1-\theta_2)^2}\begin{bmatrix} {\theta_1}^2 & -(1-\theta_2)\theta_1 & \theta_3\theta_1 & \theta_4\theta_1 \\ -(1-\theta_2)\theta_1 & (1-\theta_2)^2 & -(1-\theta_2)\theta_3 & -(1-\theta_2)\theta_4 \\ \theta_3\theta_1 & -(1-\theta_2)\theta_3 & {\theta_3}^2 & \theta_3\theta_4 \\ \theta_4\theta_1 & -(1-\theta_2)\theta_4 & \theta_3\theta_4 & {\theta_4}^2 \end{bmatrix}$$
$$+ \frac{\theta_3}{(1-\theta_3)^2}\begin{bmatrix} {\theta_1}^2 & \theta_1\theta_2 & -(1-\theta_3)\theta_1 & \theta_4\theta_1 \\ \theta_1\theta_2 & {\theta_2}^2 & -(1-\theta_3)\theta_2 & \theta_2\theta_4 \\ -(1-\theta_3)\theta_1 & -(1-\theta_3)\theta_2 & (1-\theta_3)^2 & -(1-\theta_3)\theta_4 \\ \theta_4\theta_1 & \theta_2\theta_4 & -(1-\theta_3)\theta_4 & {\theta_4}^2 \end{bmatrix}$$
$$+ \frac{\theta_4}{(1-\theta_4)^2}\begin{bmatrix} {\theta_1}^2 & \theta_1\theta_2 & \theta_3\theta_1 & -(1-\theta_4)\theta_1 \\ \theta_1\theta_2 & {\theta_2}^2 & \theta_2\theta_3 & -(1-\theta_4)\theta_2 \\ \theta_3\theta_1 & \theta_2\theta_3 & {\theta_3}^2 & -(1-\theta_4)\theta_3 \\ -(1-\theta_4)\theta_1 & -(1-\theta_4)\theta_2 & -(1-\theta_4)\theta_3 & (1-\theta_4)^2 \end{bmatrix} \tag{24}$$

which indeed reduces to

$$\begin{bmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

for $\theta_3 = \theta_4 = 0$ when we impose $\sum_j \theta_j = 1$. For a triple point $\theta_1 = \theta_2 = \theta_3 =$

1/3 we obtain

$$\begin{bmatrix} 1/2 & -1/4 & -1/4 & 0 \\ -1/4 & 1/2 & -1/4 & 0 \\ -1/4 & -1/4 & 1/2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}.$$

This matrix has a singularity when any phase equals unity. There are a number of ways of resolving this which are discussed in Section 3.6 after we introduce an alternative formulation (model B).

3.5. Proposed multi-phase formulation B

It is not suggested that the proposed mapping and resulting projection, Sec. 3.4, is the only acceptable approach to constraining the phase variables. Further examples that do not reduce to single phase are given in Appendix D. We give another example here which generalises the $N = 2$ case via equation (19). For $N = 3$, we can construct $\mathbf{P}$ as follows:

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

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

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

where $\mathbf{x}_i$ are the barycentric coordinates of each vertex, i.e. $(\mathbf{x}_i)_j = \delta_{ij}$, so that in components, (a, b)

$$P_{ab} = \sum_{j=2}^{N} \sum_{i=1}^{j-1} \frac{\theta_i\theta_j}{(1-\theta_i)(1-\theta_j)} (\delta_{ai} - \delta_{aj})(\delta_{bi} - \delta_{bj}). \tag{25}$$

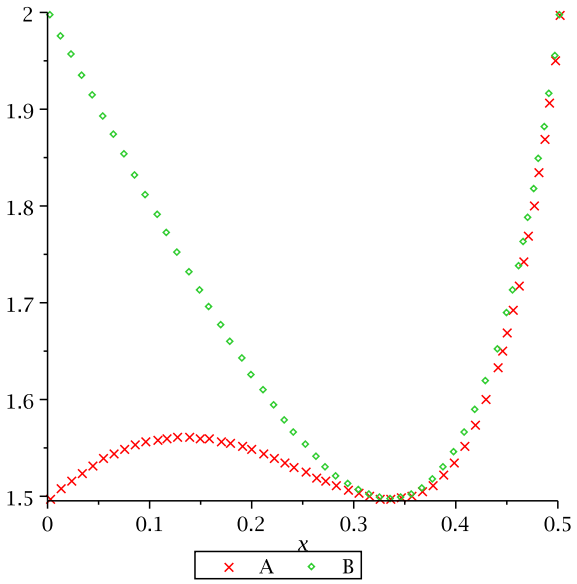

Figure 5: Red crosses show the value of tr($\mathbf{P}$) for a path joining vertex $\theta_3 = 1$ to the middle of the interface opposite. The trace at the vertex differs from the value of 2 for model A on this path even though it equals two on the adjoining edges ($\theta_1 = 0$ and $\theta_2 = 0$). Formulation B has constant and therefore defined tr($\mathbf{P}$) for any path from a vertex.

This formulation (B) has the advantage of being lower order in θ_i than that of formulation A of Sec. 3.4. The behaviour on an interface and at a triple point is identical, but otherwise they differ.

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

Models A and B, as they stand, both suffer 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 $\theta_2 = 0$:

$$\mathbf{P}|_{\theta_3=0} = \begin{bmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \mathbf{P}|_{\theta_2=0} = \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{bmatrix}. \tag{26}$$

Thus we require, in addition to the definition (21), 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

$$\mathbf{P}_{\text{vertex}} = 2\mathbf{I} - \mathbf{U}, \text{ if } 1 - \theta_i < \delta, \text{ for any } i, \tag{27}$$

where the small parameter, $\delta \ll 1$, did not significantly alter results[7]. 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,

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

[7]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

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

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

has a right hand side which is non-zero in general. In fact, from (11) 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, (27), easily follows.

3.7. Some properties of models A and B

This section considers the models 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

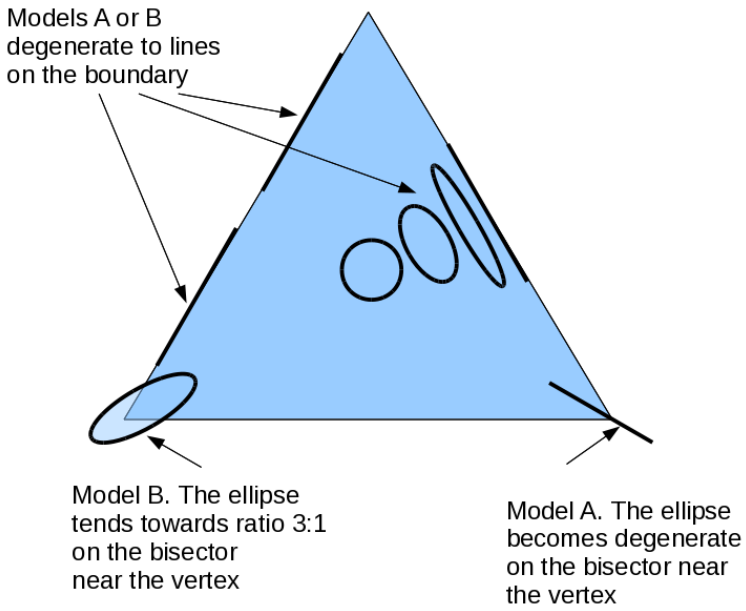

Figure 6: Eigen values and vectors displayed as ellipses as a function of position on the triangular simplex. As a point approaches the boundary the ellipse degenrates to a line. The main difference between the two models shows itself as a point approaches a vertex along a bisector. Model A degenerates to a line whereas Model B remains elliptical.

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. 6).

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

$$\mathbf{x}(t) = [\theta_1 = t, \theta_2, \theta_3 = 1 - 2t], \quad t \in [0, \tfrac{1}{2}]. \tag{28}$$

We are interested in the property of $\mathbf{P}$ as we approach the vertex $\theta_3 = 1$ as t tends to zero. We find, for formulation A that, in the limit, the effect of $\mathbf{P}$ once again degenerates to a line (this time of length 3/2) pointing along the path defined by (28). However, in formulation B 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. We find this type behaviour along all paths approaching the vertices.

By inspecting the trace, $\mathrm{tr}(\mathbf{P}) = \sum_i^N P_{ii}$,for both models we find for formulation A that $\mathrm{tr}(\mathbf{P})$ is path dependent at a vertex. This is illustrated in Fig. 5, which shows $\mathrm{tr}(\mathbf{P})$ for both models for a path $\theta_1 = x, \theta_2 = x, \theta_3 = 1 - 2x$, i.e. from vertex $\theta_3 = 1$ to a point on the interface opposite (where $\mathrm{tr}(\mathbf{P}) = 2$) via the triple point (where $\mathrm{tr}(\mathbf{P}) = 3/2$).

A constant value of 2 for the trace of $\mathbf{P}$ *throughout* the simplex may be enforced for both models by the transformation

$$\mathbf{P} \to \hat{\mathbf{P}} = 2\frac{\mathbf{P}}{\mathrm{tr}(\mathbf{P})}.$$

This modification of either model was found to make no significant change to eutectic or single phase growth.

4. A numerical comparison of models

4.1. Growth velocity comparison for a single seed

In this section we study the growth of one solid phase, θ_2, in a multi-phase system $N = 3$ and $N = 4$ to measure and compare growth rates for the two models. We stress that in this preliminary treatment we do not include anisotropy and thus the growth from a circular seed grows as a circle, which has no steady state velocity.

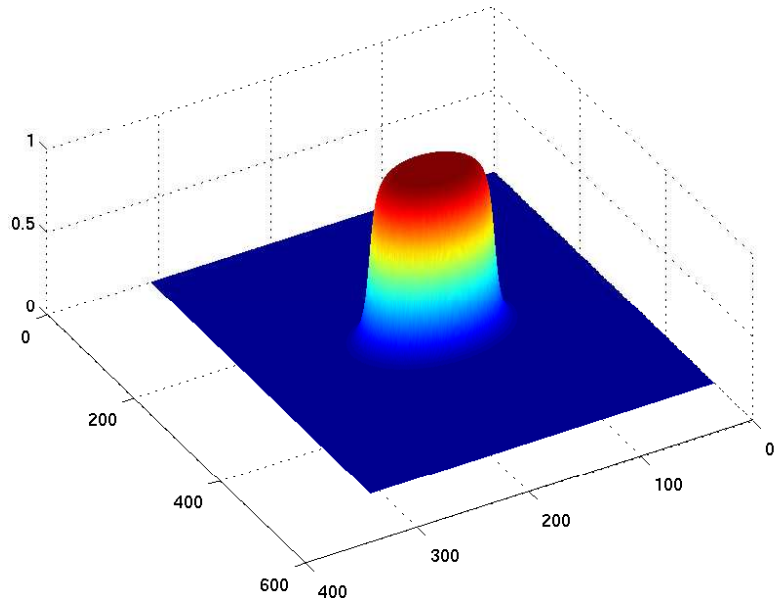

Figure 7: Growth from a single seed θ_2 in the melt, θ_1 in a multi-phase $N = 3, 4$ model.

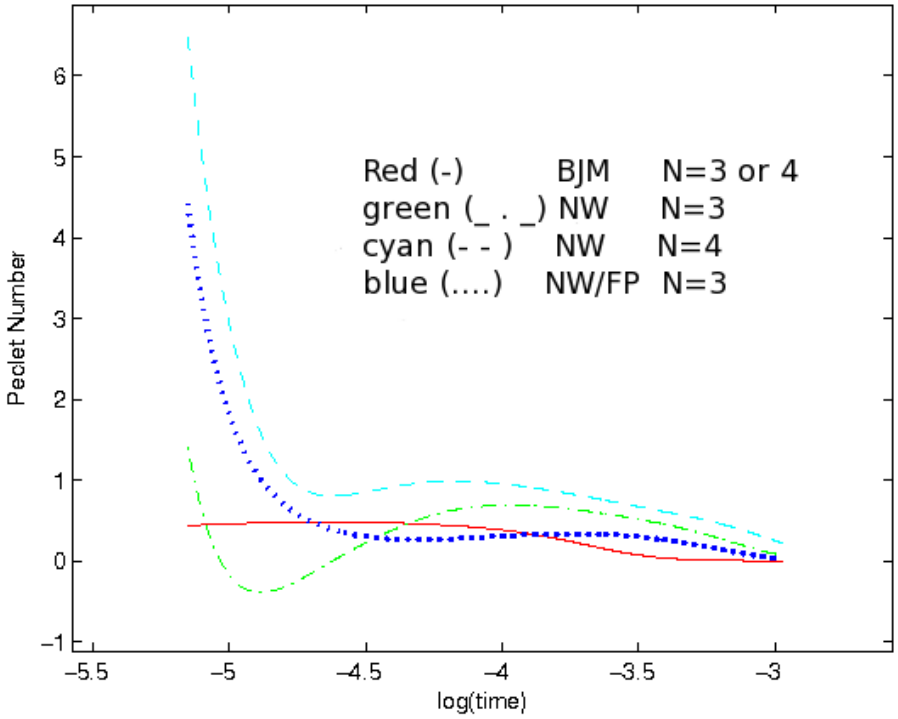

Figure 8: Péclet number, $\frac{1}{2}\times$ Velocity $\times$ Radius/Diffusivity of liquid $(1 \times 10^{-9})m^2/s$ against $\log_{10}(t)$, for: The proposed model (A or B with $N = 3$ or $N = 4$ are all identical in this test), Lagrange multiplier model used in Nestler-Wheeler (NW) $N = 3$ and (NW) $N = 4$. We also include the Lagrange multiplier model with Folch-Plapp type change to the potential (NW/FP) $N = 3$ which avoids spurious phase growth. The first 2000 time steps (with $\Delta t = 3.5 \times 10^{-9}$) are suppressed because of extreme transient behaviour in the Lagrange multiplier models. The proposed model (BJM, continuous red line) clearly exhibits more stable behaviour throughout the simulation.

In the new models A or B (BJM) there is no difference in growth velocity, whatever the value of N. On the other hand the Lagrange multiplier model (NW) behaves differently, as expected, depending on N. We also include a modified potential into the NW model to make the potential have a maximum in the middle of the simplex in the manner of [5] (FP).

To calculate the interface velocity we use the formulation

$$v_n = \frac{x_n - x_{n-1}}{\Delta t}$$

where the x position of the interface at time t_n is given by

$$x_n = \frac{\int_O^\infty x h(\theta_1(x, t_n))\,\mathrm{d}x}{\int_O^\infty h(\theta_1(x, t_n))\,\mathrm{d}x}$$

where O is the origin of the seed, $\theta_1(x, t_n)$ is the amount of liquid at the point x at time t_n, and the function (interface selector)

$$h(\theta) \equiv 16\theta^2(1-\theta)^2$$

is used to isolate the interface.

A snap shot of θ_2 in the simulation is illustrated in Fig. 7. Fig. 8 illustrates the differing growth rates using the Péclet number, $\frac{1}{2}\times$ Velocity $\times$ Radius/Diffusivity, for the models and also, detrimentally for the NW model, we find differing growth rates for $N = 3$ and 4 cases. In BJM there is no difference between $N = 3$ and $N = 4$ the growth rates being identical. The simulation reveals that BJM is also more stable than the Lagrange multiplier model(s). We also ran a simulation for the Lagrange multiplier formulation with a modified potential (NW/FP) to eliminate spurious phases, but even in this case there is significant difference in growth rate between this model and the proposed model (BJM). We did not run a simulation for $N = 4$ with the modified potential NW/FP because as commented in [12]: *... a special type of a potential function that guarantees the stability of dual interfaces is constructed* (in [5]). *This formulation, however, is restricted to triple junctions and will be difficult to generalize.*

4.2. Eutectic growth differences between models A and B

There is a relationship (given for example in [26]) which relates the growth velocity, v, and the width, λ, of the eutectic for a small under-cooling. Below a certain width, $\lambda = \lambda^*$, the eutectic seed will melt. Conversely, above λ^*

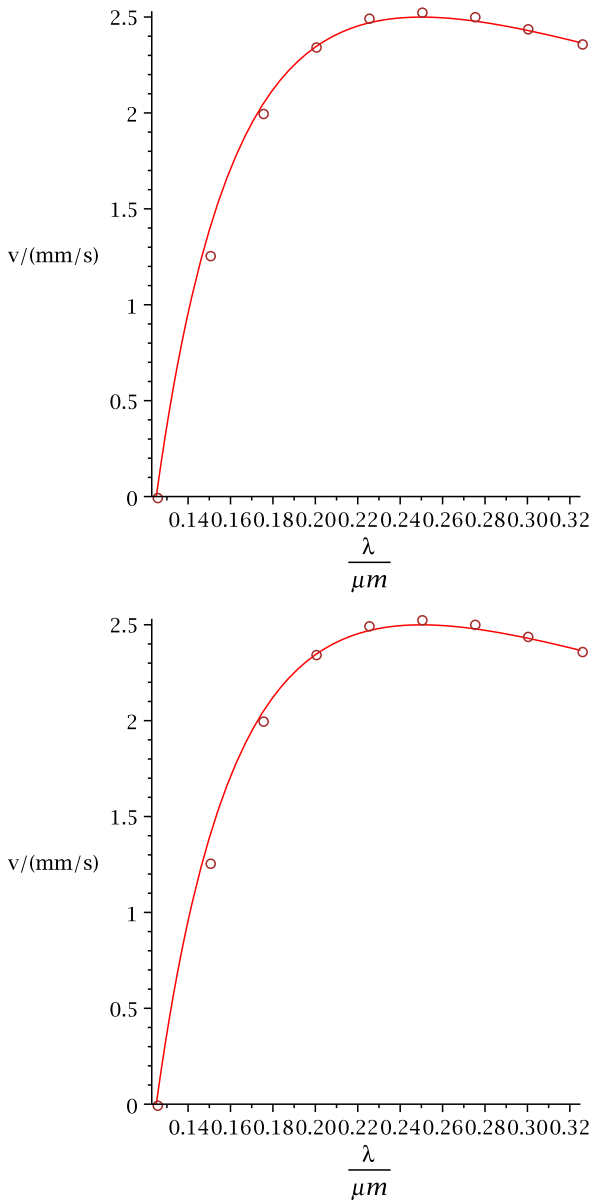

Figure 9: Velocity as a function of eutectic width (circles A(left) B(right)) against the solid line, $\frac{1}{\lambda}(1-\frac{\lambda^*}{\lambda})$.

the eutectic solidifies more rapidly with increased width until a maximum, $\lambda = 2\lambda^*$, is reached. This "velocity scaling law" can be shown to be:

$$v \propto \frac{1}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right).$$

Fig. 9 shows the analytical relation (solid line) against the data for different λ, for an undercooling of 6.9K. Both models A and B fit well through the range from 1 to 3 times the minimum spacing $\lambda \to \lambda^*$. Modifying the models to ensure trace 2 does not have any significant effect and there is no significant observed difference between models A and B in this test. It has been shown in [21] that the constant Lagrange multiplier model and vector Lagrange multiplier do not reproduce this scaling correctly, whereas the model of [19] does successful reproduce the law.

5. Conclusion

We have proposed two multi-phase formulations that reduce to standard single phase, have no N dependence, do not generate spurious additional phases at binary interfaces and fit the velocity scaling law well. Moreover, they use a simple potential for general N, given in [14].

Towards these formulations we first explored properties of the Lagrange multiplier method for multi-phase fields and identified the unphysical aspects: non reduction to single phase, the generation of additional spurious phases and N dependence. In particular we have shown that the Lagrange multiplier method is equivalent to a projection with a specified normal which assumes a Cartesian metric on the phase variables. By relaxing this assumption we exploit the extra freedom to construct a projection that allows growth of a pure seed into the melt without influence of the remaining phases.

Reduction to single phase is achieved by the introduction of a symmetric matrix, which degenerates to a single non-zero eigenvalue when only two phases are present. Thus the form of the potential is not critical at a pure interface. However, reduction to single phase and N independence are conditions that necessarily create an ambiguity when the phase is pure. For example, a point of pure melt $\theta_1 = 1$ cannot simultaneously be a single phase formultion for more than one solid growth. This reveals itself in the proposed formulation as being ill-defined at these points. We resolved this by specifying a particular matrix, $\mathbf{P}_{\text{vertex}}$, at these points consistent with the value of $\mathbf{P}$ nearby.

Because the new formulation reduces exactly to the single phase formulation at a pure binary interface more elaborate treatment of the latter, e.g. solute anti trapping, may be imported into multi-phase field modelling. This is a subject for future research.

5.1. Summary of the proposed multi-phase field models A and B

For the convenience of the reader we finish with a summary of the proposed model.

- We use free energy in equation (1) with the potential, equation (2)
- The evolution of concentration is given by (4)
- The constraint (5) is applied to unconstrained phase field equations, (3), by

$$-\tau\dot{\boldsymbol{\theta}} = \mathbf{P}\frac{\delta F}{\delta \boldsymbol{\theta}}$$

- where $\mathbf{P}$ is an $N \times N$ symmetric matrix given in component form by two proposed formulations:
  - Model A: (22) with c_{ij} given by (20);
  - Model B: (25)
- Because these formulations are ill-defined at pure phases (vertices $\theta_i = 1$) we specify a matrix (27) if any of the phases approaches unity.

Both models A and B perform equally well in simulations and far better than with the Lagrange multiplier approach for general N [8].

Appendix A. Proof of the equivalence of (10) and the Lagrange multiplier approach

This section shows the equivalence between the Lagrange multiplier method of constraining the N equations and that of using any mapping $\boldsymbol{\theta} = \boldsymbol{\theta}(\boldsymbol{\phi})$

[8] However, for the special case of $N = 3$ the use of a potential obstacle (see Appendix C) can eliminate spurious phases for the Lagrange multiplier formulation

that automatically preserves the constraint $\sum_i \theta_i = 1$. Since the Lagrange multiplier pe se is traditionally used in pure minimisation problems (i.e. no time dependence) it is not necessarily obvious that the two approaches are identical, although the identification of the Lagrange multiplier as a projection (equation (13)) strongly suggests that they are.

We need to show that[9]

$$\mathbf{J}^T\mathbf{J}\dot{\boldsymbol{\phi}} = \frac{\delta F}{\delta \boldsymbol{\phi}}, \tag{A.1}$$

where the entries

$$\sum_{i=1}^{N} J_{ij} = 0, \quad j \in [1, N-1],$$

is equivalent to

$$\dot{\boldsymbol{\theta}} = \mathbf{P}\frac{\delta F}{\delta \boldsymbol{\theta}}$$

with $\mathbf{P}$ given by

$$\mathbf{P} \equiv \mathbf{I} - \frac{1}{N}\mathbf{U},$$

and $\mathbf{U}$ defined as an $N \times N$ matrix with unit entries.

First we note that

$$\dot{\theta}_i = \frac{\partial \theta_i}{\partial \phi_j}\dot{\phi}_j \Rightarrow \dot{\boldsymbol{\theta}} = \mathbf{J}\dot{\boldsymbol{\phi}} \tag{A.2}$$

and similarly

$$\frac{\delta F}{\delta \boldsymbol{\phi}} = \mathbf{J}^T\frac{\delta F}{\delta \boldsymbol{\theta}}. \tag{A.3}$$

So that constraining the system of N equations

$$\dot{\boldsymbol{\theta}} = \frac{\delta F}{\delta \boldsymbol{\theta}}$$

[9]For the purpose of the proof we drop the constant, $-\tau$

to an $N-1$ system by writing $\boldsymbol{\theta} = \boldsymbol{\theta}(\boldsymbol{\phi})$ and using (A.2) and (A.3) results in the $N-1$ independent equations (A.1)

$$\mathbf{J}^T\mathbf{J}\dot{\boldsymbol{\phi}} = \frac{\delta F}{\delta \boldsymbol{\phi}}.$$

Using (A.2) and (A.3), we can rearrange this as the N *dependent* equations

$$\dot{\boldsymbol{\theta}} = \mathbf{Q}\frac{\delta F}{\delta \boldsymbol{\theta}}.$$

where we define

$$\mathbf{Q} \equiv \mathbf{J}(\mathbf{J}^T\mathbf{J})^{-1}\mathbf{J}^T \tag{A.4}$$

Hence, we need to show that $\mathbf{P} \equiv \mathbf{I} - \mathbf{U}/N = \mathbf{J}(\mathbf{J}^T\mathbf{J})^{-1}\mathbf{J}^T \equiv \mathbf{Q}$. To prove this result it is sufficient to prove the equality for the symmetric $(N-1)\times(N-1)$ matrix, $\hat{\mathbf{P}}$, formed from the independent rows and columns of $\mathbf{P}$. We choose, without loss of generality, that row and column N are deleted to form $\hat{\mathbf{P}}$ and similarly the Nth row of $\mathbf{J}$ to form $\hat{\mathbf{J}}$ etc—note that unlike $\mathbf{J}$ and $\mathbf{P}$, the rank $N-1$ matrices $\hat{\mathbf{J}}$ and $\hat{\mathbf{P}}$ are invertible.

Using

$$\begin{aligned}
(\mathbf{J}^T\mathbf{J})_{ij} &= \sum_{k=1}^{N} J_{ki}J_{kj} \\
&= \sum_{k=1}^{N-1} J_{ki}J_{kj} + J_{Ni}J_{Nj} \\
&= \sum_{k=1}^{N-1} J_{ki}J_{kj} + \left(\sum_{m=1}^{N-1} J_{mi}\right)\left(\sum_{n=1}^{N-1} J_{nj}\right) \\
&= \left(\hat{\mathbf{J}}^T\hat{\mathbf{J}} + \hat{\mathbf{J}}^T\hat{\mathbf{U}}\hat{\mathbf{J}}\right)_{ij}
\end{aligned}$$

we find from (A.4)

$$\hat{\mathbf{Q}} \equiv \hat{\mathbf{J}}(\hat{\mathbf{J}}^T\hat{\mathbf{J}} + \hat{\mathbf{J}}^T\hat{\mathbf{U}}\hat{\mathbf{J}})^{-1}\hat{\mathbf{J}}^T.$$

Using the notation $\hat{\mathbf{J}}^{-T} \equiv (\hat{\mathbf{J}}^T)^{-1}$ we find

$$(\hat{\mathbf{J}}^T\hat{\mathbf{J}} + \hat{\mathbf{J}}^T\hat{\mathbf{U}}\hat{\mathbf{J}})^{-1} = \mathbf{J}^{-1}\hat{\mathbf{Q}}\hat{\mathbf{J}}^{-T}.$$

so that

$$\begin{aligned}\hat{\mathbf{I}} &= (\hat{\mathbf{J}^T}\hat{\mathbf{J}} + \hat{\mathbf{J}^T}\hat{\mathbf{U}}\hat{\mathbf{J}})\mathbf{J}^{-1}\hat{\mathbf{Q}}\hat{\mathbf{J}}^{-T} \\ &= \hat{\mathbf{J}^T}\hat{\mathbf{Q}}\hat{\mathbf{J}}^{-T} + \hat{\mathbf{J}^T}\hat{\mathbf{U}}\hat{\mathbf{Q}}\hat{\mathbf{J}}^{-T} \\ &= \hat{\mathbf{Q}} + \hat{\mathbf{U}}\hat{\mathbf{Q}} \\ &= (\hat{\mathbf{I}} + \hat{\mathbf{U}})\hat{\mathbf{Q}}\end{aligned}$$

implying

$$\hat{\mathbf{Q}} = (\hat{\mathbf{I}} + \hat{\mathbf{U}})^{-1}$$

Now

$$\begin{aligned}(\hat{\mathbf{I}} - \frac{1}{N}\hat{\mathbf{U}})(\hat{\mathbf{I}} + \hat{\mathbf{U}}) &= \hat{\mathbf{I}} + \hat{\mathbf{U}} - \frac{1}{N}\hat{\mathbf{U}} - \frac{1}{N}\hat{\mathbf{U}}\hat{\mathbf{U}} \\ &= \hat{\mathbf{I}} + \hat{\mathbf{U}} - \frac{1}{N}\hat{\mathbf{U}} - \frac{N-1}{N}\hat{\mathbf{U}} \\ &= \hat{\mathbf{I}}\end{aligned}$$

implying

$$\hat{\mathbf{I}} - \frac{1}{N}\hat{\mathbf{U}} = (\hat{\mathbf{I}} + \hat{\mathbf{U}})^{-1}$$

and so

$$\hat{\mathbf{Q}} = \hat{\mathbf{I}} - \frac{1}{N}\hat{\mathbf{U}} = \hat{\mathbf{P}}$$

giving $\mathbf{P} = \mathbf{Q}$ as required.

Appendix B. Variational derivative calculations

The purpose of this appendix is to show how the variational derivative of the gradient contribution enter the giverning equations (11).

We wish to find $\frac{\delta G}{\delta \theta_k}$ where

$$G = \int_\Omega h(\boldsymbol{\theta}, \nabla\boldsymbol{\theta})\,\mathrm{d}^3\mathbf{x}$$

with

$$h = \tfrac{1}{2}\sum_{j=2}^{N}\sum_{i=1}^{j-1}\Gamma^{ij}|\theta_i\nabla\theta_j - \theta_j\nabla\theta_i|^2$$

Then

$$\frac{\delta G}{\delta\theta_k} = \frac{\partial h}{\partial\theta_k} - \nabla\cdot\frac{\partial h}{\partial\nabla\theta_k}$$

Writing

$$\mathbf{r}_{ij} \equiv \theta_i\nabla\theta_j - \theta_j\nabla\theta_i$$

we find

$$\begin{aligned}
\frac{\partial h}{\partial\theta_k} &= \sum_{j=2}^{N}\sum_{i=1}^{j-1}\Gamma^{ij}\mathbf{r}_{ij}\cdot\frac{\partial r_{ij}}{\partial\theta_k} \\
&= \sum_{j=2}^{N}\sum_{i=1}^{j-1}\Gamma^{ij}\mathbf{r}_{ij}\cdot(\delta_{ik}\nabla\theta_j - \delta_{jk}\nabla\theta_i) \\
&= \sum_{j=2}^{N}\Gamma^{kj}r_{kj}\cdot(\nabla\theta_j - \delta_{jk}\nabla\theta_k) \\
&= \sum_{j\neq k}^{N}\Gamma^{kj}\mathbf{r}_{kj}\cdot\nabla\theta_j.
\end{aligned}$$

A similar calculation gives

$$\begin{aligned}
\frac{\partial h}{\partial\nabla\theta_k} &= \sum_{j=2}^{N}\sum_{i=1}^{j-1}\Gamma^{ij}\mathbf{r}_{ij}\frac{\partial\mathbf{r}_{ij}}{\partial\nabla\theta_k} \\
&= -\sum_{j\neq k}^{N}\Gamma^{kj}\mathbf{r}_{kj}\theta_j.
\end{aligned}$$

and thus

$$-\nabla\cdot\frac{\partial h}{\partial\nabla\theta_k} = \sum_{j\neq k}^{N}\Gamma^{kj}\left(\theta_j\nabla\cdot\mathbf{r}_{kj} + \mathbf{r}_{kj}\cdot\nabla\theta_j\right).$$

Hence

$$\frac{\delta G}{\delta \theta_k} = \sum_{j \neq k}^{N} \Gamma^{kj} \left(2\mathbf{r}_{kj} \cdot \nabla\theta_j + \theta_j \nabla \cdot \mathbf{r}_{kj}\right)$$
$$= \sum_{j \neq k}^{N} \Gamma^{kj} \{2(\theta_k \nabla\theta_j - \theta_j \nabla\theta_k) \cdot \nabla\theta_j + (\theta_k \nabla^2\theta_j - \theta_j \nabla^2\theta_k)\theta_j\}$$

Appendix C. A modified potential to suppress spurious growth in the Lagrange multiplier model

This section examines a modification to the potential that mitigates spurious phases in the Lagrange multiplier approach.

See Fig. C.10 showing the Nestler Wheeler potential on the left and the Folch-Plapp potential on the right. The drawback for the NW potential is that there is a gradient away from an interface (an edge of the simplex) towards the centre. The Folch Plapp potential avoids this, whilst taking care not to create a gradient out of the simplex.

The barrier contribution to the potential for $N = 3$ is

$$f_{\text{barrier}} = \sum_{k=2}^{3} \sum_{j=1}^{k-1} W_{jk} \theta_j^2 \theta_k^2$$

if we modify this potential

$$f_{\text{barrier}} = \sum_{k=2}^{3} \sum_{j=1}^{k-1} W_{jk} (\theta_j^2 \theta_k^2 + \alpha\theta_1\theta_2\theta_3) \tag{C.1}$$

where α is a new parameter. We find for $\theta_3 = 0$

$$\frac{\partial f_{\text{barrier}}}{\partial \theta_1} = 2W_{12}\theta_1\theta_2^2$$
$$\frac{\partial f_{\text{barrier}}}{\partial \theta_2} = 2W_{12}\theta_2\theta_1^2$$
$$\frac{\partial f_{\text{barrier}}}{\partial \theta_3} = \alpha W_{12}\theta_1\theta_2 \tag{C.2}$$

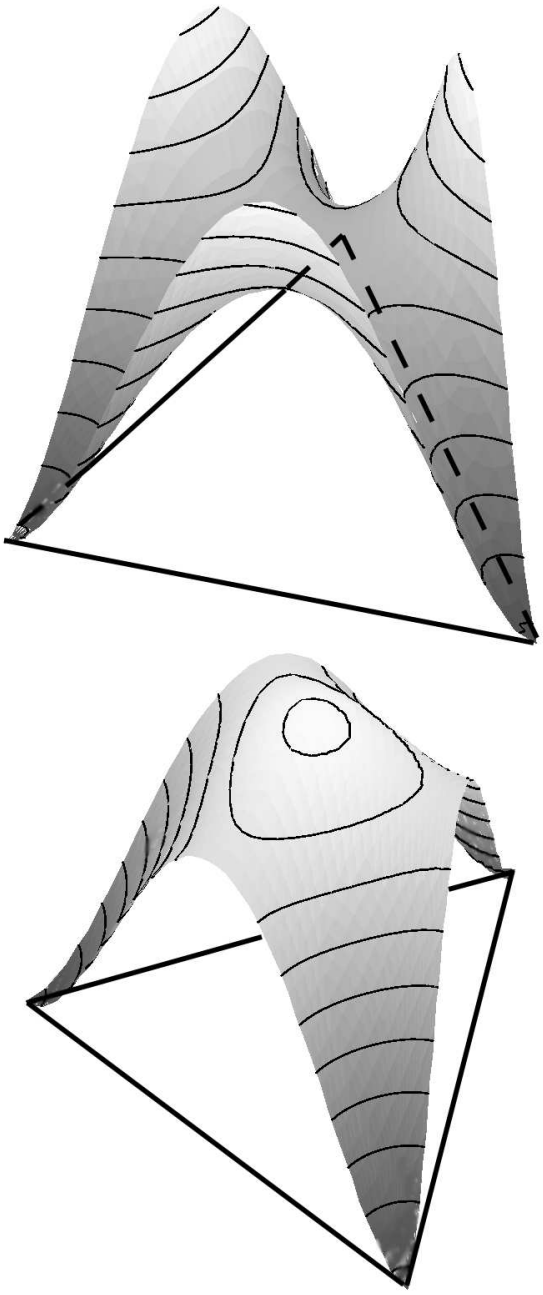

Figure C.10: Two potential for multi-phase potentials for $N = 3$ as a function of $\boldsymbol{\theta}$ on the simplex (bold triangle). The Nestler-Wheeler potential has a saddle point at the centre of the simplex, which is avoided in the Folch/Plapp potential (left) thus mitigating against the system wandering away from an interface (edge of the simplex).

so that, for $\alpha = 1$, with the Lagrange multiplier this contribution to the growth of phase 3 is

$$\tfrac{2}{3}\frac{\partial f_{\text{barrier}}}{\partial \theta_3} - \tfrac{1}{3}\left(\frac{\partial f_{\text{barrier}}}{\partial \theta_1} + \frac{\partial f_{\text{barrier}}}{\partial \theta_2}\right) = 0$$

since $\theta_1 + \theta_2 = 1$. So the addition of the 'hump' into the potential negates its contribution to the growth of θ_3, but there still remains contributions to spurious growth due to the non-potential term. However, this can be mitigated by choosing $\alpha > 1$ and sufficiently large, relying on an infinite well at the simplex boundary.

Appendix D. Alternative formulations for P

We state without comment or justification two possible forms for $\mathbf{P}$ which, though they do not reduce correctly to the standard single phase formulation, do demonstrate alternative approaches to implementing the constraint that avoid N dependence and spurious phase generation:

1.
$$P_{ij} = \theta_i \delta_{ij} - \theta_i \theta_j;$$

2.
$$P_{ij} = d^2 \nabla\theta_i \cdot \nabla\theta_j,$$

with d a parameter of dimension length commensurate with phase width.

Appendix E. Numerical implementation of the constraint

Following a suggestion by the reviewers of this article we were asked to comment on the method of [22] who in turn use the method of [27] for implementing the constraint. Consider the equations with constants assumed unity for simplicity:

$$\dot{\theta}_i = \frac{\delta F}{\delta \theta_j}.$$

Using explicit Euler for time stepping for illustration, Hirouchi et al implement the constraint as follows:

At time step $t = t^{n+1}$ the equation is computed first without the constraint

$$\theta_i^{n+1} \leftarrow \theta_i^n + \Delta t \frac{\delta F}{\delta \theta_i^n}$$

The constraint is then imposed by

$$\theta_i^{n+1} \leftarrow \frac{\theta_i^{n+1}}{\sum_j \theta_j^{n+1}}.$$

To analyse this let us rewrite this process into one line

$$\begin{aligned}\theta_i^{n+1} &= \frac{\theta_i^n + \Delta t \frac{\delta F}{\delta \theta_i^n}}{\sum_j \theta_j^n + \Delta t \sum_j \frac{\delta F}{\delta \theta_j^n}} \\ &= \frac{\theta_i^n + \Delta t \frac{\delta F}{\delta \theta_i^n}}{1 + \Delta t \sum_j \frac{\delta F}{\delta \theta_j^n}}\end{aligned}$$

which for small Δt can be written

$$\frac{\theta_i^{n+1} - \theta_i^n}{\Delta t} \approx \frac{\delta F}{\delta \theta_i^n} - \theta_i^n \sum_j \frac{\delta F}{\delta \theta_j^n}.$$

We now see that this is the numerical approximation to

$$\dot{\theta}_i = \frac{\delta F}{\delta \theta_i} - \theta_i \sum_j \frac{\delta F}{\delta \theta_j}$$

which is the vector Lagrange multiplier approach mentioned in [21].

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