A Physically Consistent Multiphase-Field Theory of First Order Phase Transitions

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1. ABSTRACT

A multiphase-field theory is presented that describes interface driven multi-domain dynamics. The free energy functional and the dynamic equations are constructed on the basis of criteria of mathematical and physical consistency. First, it is demonstrated that the most widely used multiphase theories are physically inconsistent, therefore, a new theory has to be developed. Combining elements of the investigated models with a new multivariate generalization of the free energy surface results in a general multiphase / multi-component theory, which keeps the variational formalism, reduces / extends naturally on the level of both the free energy functional and the dynamic equations, utilizes arbitrary pairwise equilibrium interfacial properties, features equilibrium ≡ stationary equivalency, and avoids the appearance of spurious phases.

2. INTRODUCTION

Despite advances in atomic scale continuum modeling of crystalline solidification, phase-field methods based on the multiphase-field (MPF) concept remain the method of choice, when addressing complex multiphase problems. Therefore, it is desirable to compare these models, and identify possible advantages / disadvantages they have relative to each other, to see whether a more general formulation unifying the advantageous features can be constructed.

In attempting to develop a consistent MPF description, the criteria of consistency are formulated first. These are: (i) The multiphase-field descriptions view the employed fields $u_i(\boldsymbol{r},t)$ as local and temporal (mass/volume) *fractions*, prescribing thus $\sum_{i=1}^{N} u_i(\boldsymbol{r},t) = 1$. (ii) The physical results should be independent of the labeling of the variables. (iii) The solution of the dynamic equations should evolve towards the equilibrium solution, which minimizes the free energy functional. (iv) The free energy of the system should decrease monotonically with time. (v) It should be possible to recover the respective models from each other, when adding or removing a new phase / component / grain. (vi.a) The two-phase planar interfaces should represent a (stable) equilibrium, and should be free of additional phases. (vi.b) The dynamic extension of this requirement reads as follows: if a phase is not present, it should not appear deterministically at any time. (vii) Finally, the model should allow the choice of independent interfacial properties and the kinetic coefficients for the individual phase pairs.

3. ANALYSIS OF PREVIOUS MULTIPHASE DESCRIPTIONS

While most of the criteria of Section 2 formulate natural / self-evident requirements, some of them were neglected, when developing previous MPF models, which might result in physical inconsistencies / numerical difficulties. Therefore, we analyzed these models against all the consistency criteria listed in Section 2 (the results of the analysis are summarized in Table I). It has been found, that none of the MPF models investigated here satisfy all the consistency criteria specified above.

Table I. Properties of different multiphase-field models from the viewpoint of the criteria defined in Section 2.

model \ criterion	i	ii	Iii	iv	v	vi.a	vi.b	vii
Steinbach et al.	x	x					x	x
Steinbach / Pezzola	x	x					x	x
Nestler / Wheeler	x	x					x	x
Kim et al.	x	x		x	x		x	x
Bollada / Jimack/Mullis	x	x		x	x		x	x
Ankit et al.	x	x	x	x				x
Folch / Plapp	x	x	x	x		x	x	

4. CONSISTENT MULTIPHASE FORMALISM

We derived a multiphase description that satisfies criteria (i) to (vii). The general dynamic equations read as

$$-\frac{\partial u_i}{\partial t} = \sum_{j\neq i} \alpha_{ij}\left(\frac{\delta F}{\delta u_i} - \frac{\delta F}{\delta u_j}\right),$$

where $\delta F/\delta u_i$ is the functional derivative of the free energy functional with respect to $u_i(\boldsymbol{r},t)$, while the mobility matrix $L_{ii} := \sum_{j\neq i}\alpha_{ij}$, $L_{ij} := -\alpha_{ij}$ must be positive semi-definite. From the no labeling condition $\alpha_{ij} = \alpha_{ji}$ also follows, and we propose the field-dependent mobilities $\alpha_{ij} = \alpha_{ij}^0 \left|\frac{u_i}{1-u_i}\right| \left|\frac{u_j}{1-u_j}\right|$, where α_{ij}^0 is a positive constant. The *interface* contribution of the free energy functional reads

$$F = \int dV \left\{ \frac{\varepsilon^2(\boldsymbol{u},\nabla\boldsymbol{u})}{2} \sum_{i=1}^{N} (\nabla u_i)^2 + w(\boldsymbol{u}) g(\boldsymbol{u}) + A_3 f_3(\boldsymbol{u}) \right\}.$$

The coefficients $\varepsilon^2(\boldsymbol{u},\nabla\boldsymbol{u})$ and $w(\boldsymbol{u})$ are multivariate polynomials constructed following Kazaryan:

$$\varepsilon^2(\boldsymbol{u},\nabla\boldsymbol{u}) = \frac{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \varepsilon_{ij}^2(\mathbf{n}_{ij}) u_i^2 u_j^2}{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_i^2 u_j^2}; \qquad w(\boldsymbol{u}) = \frac{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} w_{ij} u_i^2 u_j^2}{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_i^2 u_j^2},$$

where $\varepsilon_{ij}^2(\mathbf{n}_{ij}) = \varepsilon_{ij,0}^2 h_{ij}(\mathbf{n}_{ij})$ contains the anisotropy of the *(i,j)* interface via the anisotropy function $h_{ij}(\mathbf{n}_{ij})$, where $\mathbf{n}_{ij} := \frac{\nabla u_i - \nabla u_j}{|\nabla u_i - \nabla u_j|}$. Note that the pairwise interfacial properties are defined independently by $\varepsilon_{ij,0}^2$ and w_{ij}. Furthermore, the free energy landscape is based on the function

$$g(\boldsymbol{u}) = \frac{1}{12} + \sum_{i=1}^{N}\left(\frac{u_i^4}{4} - \frac{u_i^3}{3}\right) + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_i^2 u_j^2 .$$

It is important to mention that the natural extensions of the two-phase planar interfaces $u_i(x) = 1 - u_j(x) = \left[1 + \tanh(x/\delta_{ij})\right]/2$, $u_k(x) = 0$ are always equilibrium solutions of the *N*-phase model, while their stability can be established by choosing a suitable amplitude A_3 for the triplet term

$$f_3(\boldsymbol{u}) = \sum_{i=1}^{N-2}\sum_{j=i+1}^{N-1}\sum_{k=j+1}^{N} |u_i||u_j|\,|u_k| .$$

5. RESULTS

5.1. Validation of the model

We tested the present model extensively against criteria (i)-(vii) defined in Section 2. We found that all these criteria are satisfied (for details, see Ref. [1]). For example, Fig 1 shows that, even if anisotropy is combined with asymmetric pairwise interface thicknesses and interfacial free energies, no recognizable amount of the third phase appears at the (otherwise curved) equilibrium interfaces.

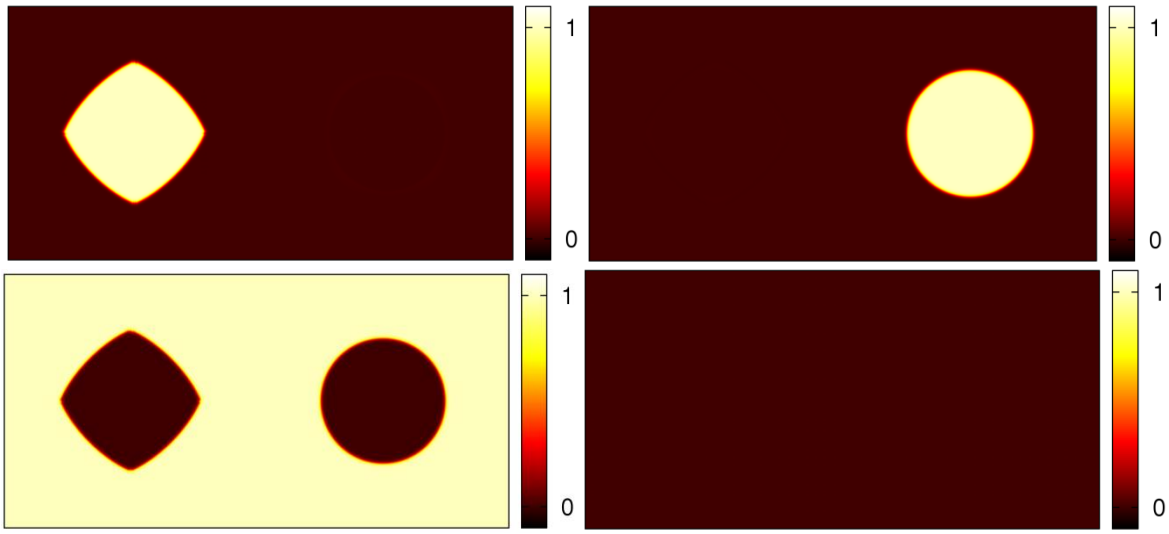

Fig 1. Equilibrium in a 4-phase system (for conserved fields). The panels show the individual fields, indicating no spurious phases at the two-phase interfaces. In the initial condition phase 4 was set to 0, and, due to the special choice of the mobility matrix, it never appears.

5.2. Grain coarsening

We've used our model to address the grain coarsening process. Here the fields represent different crystallographic orientations. We've found a limiting grain size distribution (LGSD) that appears better than the results from previous MPF models (see Fig 2). While the LGSD fits the experimental data well for large sizes, there are differences for small sizes. A possible reason for this could be that some sort of a microscopic mechanism, which accelerates the evolution of small grains (e.g., grain rotation), is yet missing from the model.

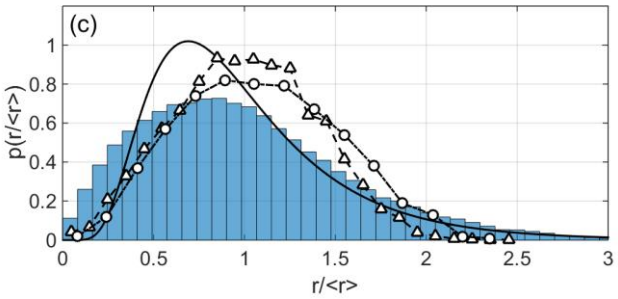

Fig 2. Limiting grain size distribution during grain coarsening. The simulation data (blue bars) fit well the experimental values (solid line) on large sizes. For comparison, results of previous multiphase descriptions are also displayed (triangles and circles).

5.3. Multicomponent Cahn-Hilliard liquid

To address phase-separation in multicomponent liquids, we start from the Navier-Stokes equation, the equation of motion for the velocity field $\boldsymbol{v}(\boldsymbol{r},t)$:

$$\rho\frac{d\boldsymbol{v}}{dt}=\nabla\cdot(\boldsymbol{R}+\boldsymbol{D})\,,$$

Here ρ is the (constant) density of the system, while $\boldsymbol{R}$ and $\boldsymbol{D}$ are the reversible and dissipative stresses, respectively (for details, see Ref. [2]). Since the fields are now associated with the local mass fractions, conserved dynamics must be set up for them:

$$\frac{du_i}{dt}=\nabla\cdot\left[\sum_{j\neq i}\alpha_{ij}\left(\nabla\frac{\delta F}{\delta u_i}-\nabla\frac{\delta F}{\delta u_j}\right)\right]\,,$$

where $\frac{du_i}{dt}=\frac{\partial u_i}{\partial t}+\boldsymbol{v}\cdot\nabla u_i$ is the material derivative. The multiphase model creates equilibrium planar binary interfaces without the appearance of a third phase, while the contact angle measurements resulted in less than 1.5% relative error compared to the theoretical values (see Fig 3). The time dependence of the multicomponent system has also been studied. As it is shown in Fig 4, asymmetric interfacial data, diffusion constants and viscosities lead to the formation of patterns known in microfluidics, while the third phases appeared dynamically indeed tend to vanish yielding eventually binary interfaces. Deeper understanding of the underlying microscopic phenomena may offer new routes for designing novel materials, and generate knowledge that might play a crucial role in various fields ranging from advanced drug delivery to combined crude oil recovery / CO2 storage.

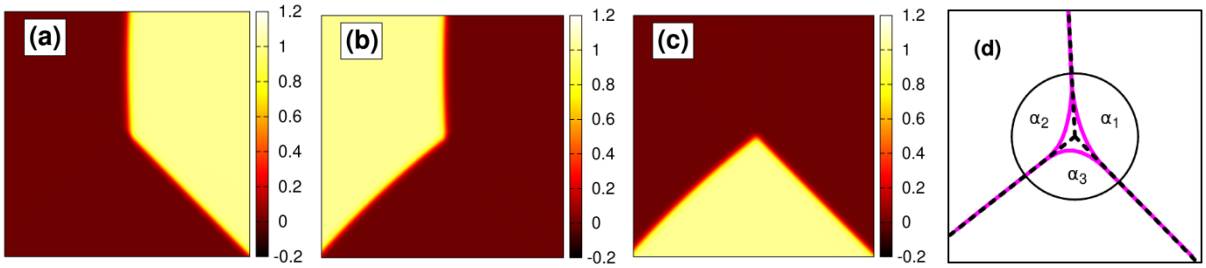

Fig 3. Equilibrium trijunction in a slightly asymmetric ternary system. Besides the individual fields (panels a-c) the $\mathrm{u_i}=1/2$ isolines are also presented (a magnification of the trijunction's small vicinity is shown in panel d).

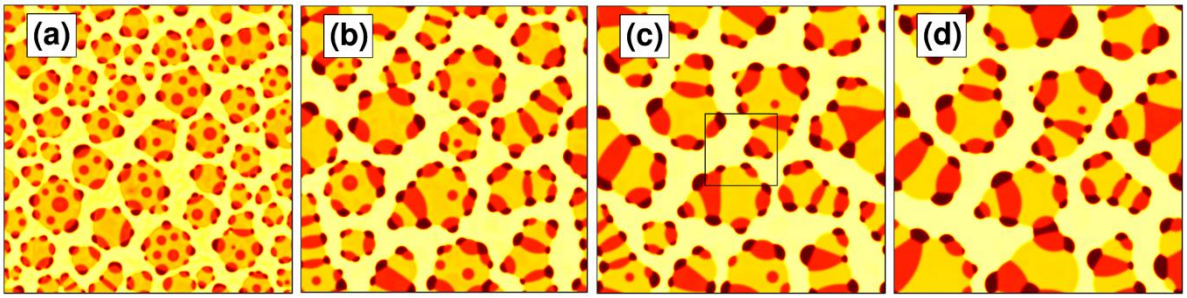

Fig 4. Phase separation in a strongly asymmetric 4-component incompressible Cahn-Hilliard liquid. Snapshots of the simulation are shown.

REFERENCES

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[2] G. I. Tóth and B. Kvamme, submitted to Phys. Rev. E. (2015).