Phase-field Prediction of Critical Nucleus Morphology in Solids

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ABSTRACT

One of the most efficient approaches to design the properties of a material is through the control of its phase transformations and microstructure evolution. The processes involved in a phase transformation are inherently multiscale. It starts with the nucleation of nanoscale nuclei of new phase particles, followed by growth and particle impingement or coarsening. In our recent works, we have developed a computational tool based on the phase-field description to predict the morphology of critical nuclei in solids under the influence of both interfacial energy anisotropy and long-range elastic interactions. Examples include cubic to cubic and cubic to tetragonal transformations. It is demonstrated that the morphology of critical nuclei in cubically anisotropic solids can be efficiently predicted without *a priori* assumptions. It is shown that strong elastic energy interactions may lead to critical nuclei with a wide variety of shapes including plates, needles, and cuboids with non-convex interfaces.

1. Nucleation

One of the most efficient approaches to design the properties of a material is through the control of its phase transformations and microstructure evolution. The processes involved in a phase transformation are inherently multiscale. It starts with the nucleation of nanoscale nuclei of new phase particles, followed by growth and particle impingement or coarsening.

Nucleation takes place when a material becomes thermodynamically meta-stable with respect to its transformation to a new state (solid, liquid and gas) or new crystal structure. Some common nucleation phenomena include formation of liquid droplets in a saturated vapor, appearance of ordered domains in a disordered solid, or nucleation of tetragonal variants in a cubic matrix, etc. Very often, it is the nucleation process that dictates the microstructure of a material. Predicting the shape of a critical nucleus in solids has been a long-standing problem in solid-state phase transformations. It is generally believed that nucleation in solid is by far the most difficult process to model and predict. Nucleation in a solid typically involves not only composition changes but also structural changes. Moreover, interfacial energy is usually anisotropic, and the elastic energy contribution arising from the lattice mismatch between nuclei and matrix plays an important role in determining the morphology of critical nuclei.

2. Existing Nucleation Theory

Early nucleation theories mostly considered phase changes in fluids, e.g. a liquid droplet in a vapor phase, and naturally assumed spherical shapes for the critical nuclei. In the classical theory of nucleation, the thermodynamic properties of a nucleus are assumed to be uniform and the same as in the corresponding bulk phase at equilibrium. The interface between a nucleus and the parent phase is considered to be sharp. The calculation of a critical nucleus size is then determined by the competition between the bulk free energy reduction and interfacial energy increase. A nucleation event takes place by overcoming the minimum energy barrier which leads to the critical size of the nucleus obtained as a stationary point of the energy. Despite the assumption of spherical shapes for critical nuclei, the same classical theories have been utilized to interpret kinetics of many phase transformations involving solids including solid to solid transformations. For some systems, the classical nucleation theory has been shown to provide a good description on the nucleation kinetics.

While it is reasonable to assume spherical shapes for nuclei during fluid-fluid phase transitions, the morphology of critical nuclei in solids is expected to be strongly influenced by anisotropic interfacial energy and anisotropic elastic interactions. For example, nuclei for γ' precipitates in Ni-alloys can be cuboidal or spherical depending the lattice mismatch between the precipitate and matrix, θ' precipitates in A1-Cu are plates, and the β' precipitates in Al-Mg-Si alloys are needle-shaped. The morphology of a critical nucleus in the presence of interfacial energy anisotropy alone can be deduced from the well-known Wulff construction. However, pre Dicting the shape of a critical nucleus in the presence of both elastic energy and surface energy anisotropy is particularly challenging since elastic energy contribution depends on the morphology of a nucleus and lattice mismatch between the nucleus and the matrix. As a result, prior applications of the classical nucleation theory to solid state transformations typically make assumptions on the shape of a nucleus as an *a priori*, and the elastic energy contribution to nucleation is included as an extra barrier for nucleation.

Another theoretical approach to nucleation is based on the diffuse-interface description, also called the non-classical nucleation theory. In this approach, the properties within a nucleus are inhomogeneous and the interface between the nucleus and parent matrix is diffuse. Following the seminal work of Cahn and Hilliard [1], the diffuse-interface approach has been previously applied to nucleation in solids (see [2] for a long list of references).

3. Phase Field Approach and Variational Calculation

In a series of recent works, we reported a computational approach for predicting the morphology of a critical nucleus as an extreme state in two dimensions by considering the presence of both interfacial energy anisotropy and elastic interactions [2-6]. The computation is based on a very general phase field framework with a diffuse interface description of the phase transformation for which the total energy incorporates the bulk energy, interfacial energy, chemical driving force and the contributions of the elastic energy.

3.1 Diffuse interface framework

The non-classical theory was pioneered by Cahn and Hilliard [1]. Since then, generalization and application to nucleation in solids have also been made. It should be pointed out that these

existing diffuse interface theories for nucleation in solids have largely ignored the anisotropic interfacial energy and anisotropic long-range elastic interactions until recently [2].

In the letter [2], we reported a computational approach for predicting the morphology of a critical nucleus as an extreme state in two dimensions by considering the presence of both interfacial energy anisotropy and elastic interactions. Two dimensional examples indicate that the morphology of a critical nucleus, or a critical fluctuation in elastically anisotropic solids can be predicted by a combination of the diffuse-interface approach and the minimax algorithm. Our calculations reveal the fascinating possibility of nuclei with non-convex shapes, as well as the phenomenon of shape-bifurcation and the formation of critical nuclei whose symmetry is lower than both the new phase and the original parent matrix.
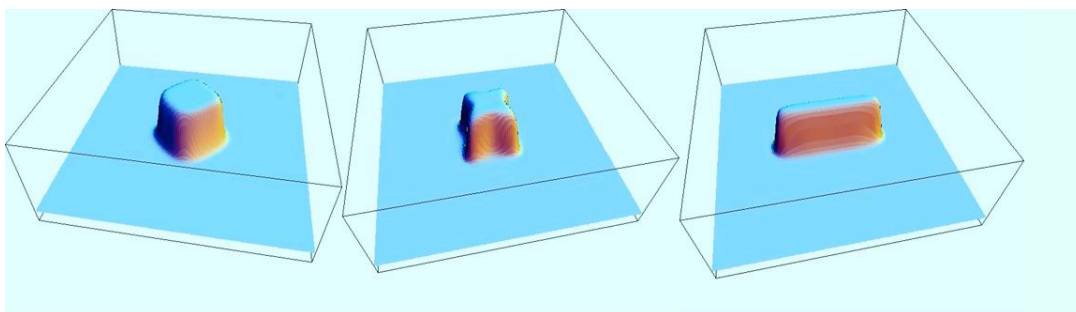

Figure 1. The change in two dimensional critical nuclei with different contributions from the anisotropic elastic energy

3.2 Rigorous mathematical theory

In a subsequent work [3], some rigorous mathematical and numerical analysis of the underlying diffuse interface framework for the nucleation in solid state phase transformations are discussed. The mathematical formulation of the diffuse-interface description of a critical nucleus is analyzed within the context of critical point theory for nonlinear variational problems [4]. In particular, the well-known Palais-Smale condition is verified which leads to the existence of saddle points for the free energy functional that includes the contributions of the anisotropic elastic energy in the form derived in [5].

In [3], we also described the numerical algorithms used to search for the saddle points of the free energy functional based on a minimax technique and the Fourier spectral implementation. A detailed presentation of the minimax algorithm based on the mountain path theorem in the calculus of variation is provided., The effect of Fourier spectral approximations is examined.

3.3 Other generalizations.

Further three dimensional computational results are reported in [6] for a particular example of cubic to cubic transformation within the homogeneous modulus approximation. Three dimensional examples are given, see Fig.2 for an illustration. In more recent works, the framework developed in [2] was extended to the case of critical nucleus in the conserved field in [7]. Following the idea giving in [9], a constrained string method is developed in [7] for the minimum energy path calculation in the conserved field case which has been shown to have

many nice approximation features. Generalizations to the case of the cubic to tetragonal transformations have been made in [8].
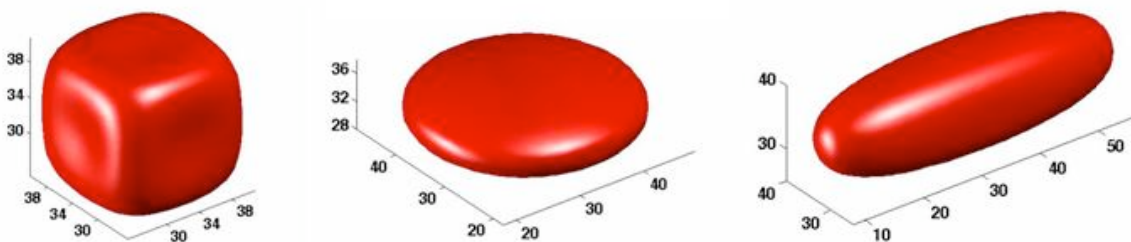

Figure 2. Three dimensional critical nuclei with non-convex, plate and needle shapes.

Acknowledgements

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