

Finding Critical Nuclei in Phase Transformations by Shrinking Dimer Dynamics and its Variants

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Received 25 September 2013; Accepted (in revised version) 24 March 2014

Communicated by Long-Qing Chen

Available online 4 July 2014

Abstract. We investigate the critical nuclei morphology in phase transformation by combining two effective ingredients, with the first being the phase field modeling of the relevant energetics which has been a popular approach for phase transitions and the second being shrinking dimer dynamics and its variants for computing saddle points and transition states. In particular, the newly formulated generalized shrinking dimer dynamics is proposed by adopting the Cahn-Hilliard dynamics for the generalized gradient system. As illustrations, a couple of typical cases are considered, including a generic system modeling heterogeneous nucleation and a specific material system modeling the precipitate nucleation in FeCr alloys. While the standard shrinking dimer dynamics can be applied to study the non-conserved case of generic heterogeneous nucleation directly, the generalized shrinking dimer dynamics is efficient to compute precipitate nucleation in FeCr alloys due to the conservation of concentration. Numerical simulations are provided to demonstrate both the complex morphology associated with nucleation events and the effectiveness of generalized shrinking dimer dynamics based on phase field models.

AMS subject classifications: 37M05, 49K35, 37N30, 34K28, 65P99

Key words: Critical nucleus, phase field models, saddle point, shrinking dimer dynamics, heterogeneous nucleation, precipitate nucleation, phase transformation.

1 Introduction

Many material processes start with the nucleation of nanoscale nuclei of new phase particles, and followed by growth and particle impingement or coarsening. Nucleation in

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phase transformations is often viewed as a difficult process to study experimentally since the nucleation process is a rare event and the critical nucleus only appears transiently. It also poses a modeling challenge given the complex energy landscape and material heterogeneities. Finding critical nucleus configuration computationally has attracted much attention in recent years [1–6]. There have been much studies on the homogeneous nucleation through both classical nucleation theory and non-classical diffuse interface theory [1, 4, 6] which utilizes the phase field approach to model the nucleation and microstructure evolution.

Nucleation of a new phase requires overcoming a minimum thermodynamic barrier. A critical nucleus is defined as the order parameter or composition fluctuation having the minimum free energy increase among all fluctuations which lead to nucleation, i.e., the saddle point configuration along the minimum energy path between the initial metastable phase and the final equilibrium phase. Thus, finding saddle points (transition states) of an energy landscape is critical to the study of rare thermally-activated transitions between different equilibria and metastable states associated with the total free energy landscape. There have been extensive studies of numerical algorithms for computing saddle point including chain-of-state methods such as nudged elastic band [7] and string method [8, 9] which provides the minimum energy path containing the desired saddle point and surface-walking methods such as gentlest ascent method [10, 11], dimer method [12] and shrinking dimer dynamics [13], and so on [14]. During the phase transformation, the computation of saddle points is often subject to one or more constraints, such as precipitation in a supersaturated solid or liquid solution. It is thus necessary to develop algorithms to compute constrained saddle point by overcoming difficulties caused by both the unstable nature of saddle points and the complications due to constraints. To complement unconstrained algorithms, constrained string method was developed as a chain-of-state method to find constrained minimum energy path [15] and constrained shrinking dimer dynamics has also been proposed recently as a surface-walking method to search index-1 saddle point on a constrained manifold [16].

In terms of applying saddle point search algorithms to the nucleation problem, much of the focus has so far been on the homogeneous nucleation and the corresponding morphology of critical nuclei. For instance, the phase field approach and the minimax algorithm have been used to predict the morphology of critical nucleus in solids by taking into account both interfacial anisotropy and long range elastic interactions [4, 17, 18]. Other successful applications include finding both critical nucleus and equilibrium precipitate simultaneously in solids [6, 19], incorporating diffuse-interface critical nuclei in phase field simulation [20], using phase-field-crystal model to find critical nuclei for homogeneous nucleation [21] and finding the transition pathway of ordered phases in block copolymers [5]. As most of the nucleation events in practice are not homogeneous due to the presence of grain boundaries or crystal lattice defects, heterogeneous nucleation often occurs at preferential sites [22, 23], thus leading to further complications to the critical nuclei morphology.

In this paper, we illustrate the effectiveness of coupling the shrinking dimer dynamics