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Form of critical nuclei at homo-phase boundaries

Rongpei Shi *[,1], Chen Shen [2], Suliman A. Dregia, Yunzhi Wang *

Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA

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ABSTRACT

Even though more than six decades have passed since the first theory on heterogeneous nucleation at grain boundaries (GBs) was established in the 1950s, the *concurrent shape variation* (co-deformation) of both the nucleus and the GB was still not captured by existing models. By using a fully *variational* approach, we demonstrate for the first time that a nucleus with low-energy facet(s) is highly deformable in response to its interaction with the GB along the triple junction line and, consequently, its energy of formation can be reduced by orders of magnitude relative to predictions by previous methods.

Since nucleation is the first step in all first-order phase transformations that are ubiquitous in nature (such as formation of dew drops on a spider's web) and widely utilized in many technologies (such as environmental science and technology, chemical and metallurgical engineering, materials design and synthesis, food science and processing, etc.) [1], the ability to control the process is of tremendous scientific and practical significance. For example, people have been using dislocations, internal interfaces, and patterned templates or substrate surfaces to direct nucleation and tune the number density, size, shape, orientation and spatial distribution of desired phases [2–10].

However, nucleation is still one of the toughest nuts to crack, in particular for solid state processes, and heterogeneous nucleation (HN), even though much more common, appears to be even more difficult to deal with as compared to homogeneous nucleation. Consider, for example, the most classical problem of HN of a new phase at a pre-existing homo-phase interface such as grain boundaries (GBs). Existing studies [11–14] suggest that the process is often complicated by the necessity to account simultaneously for orientation relationships between the nucleus and the parent crystals, formation of low-energy facets on the nucleus (see schematic drawings in Fig. 1(c) and (d)), and the interaction between the facets and the GB planes that leads to their concurrent shape variation (*co-deformation*). Moreover, the properties of a critical nucleus (including its size, shape, and activation energy barrier for nucleation) depend sensitively on the GB characteristics (i.e., misorientation and inclination).

Because of these challenges, the existing models for HN at GBs, both classical [15] and non-classical [16,17], considered only a limited number of degrees of freedom for the nucleus and GB to relax their shapes and hence are not able to provide a complete sampling over all possible configurations, except for a few simple cases. For example, the work by Clemm and Fisher [18] and its extension by Cahn and Hoffman [19] considered a double-spherical-cap as the equilibrium shape of a critical nucleus (Fig. 1(a)). Latter Lee and Aaronson [20,21] and Carter et al. [22,23] considered faceted nucleus by using respectively a modified Wulff construction (Fig. 1(b)) and a double-winterbottom method [22,24]. By assuming that the shape of a nucleus derived from the graphical methods is the shape that a critical nucleus will take and, correspondingly, the adjoining GB takes either a non-puckered (planar) [20] (Fig. 1(c)) or puckered (curved with a zero mean curvature) shape (Fig. 1(d)), they are able to consider simultaneously the dependence of critical nucleus shape on GB energy and interfacial energy and its anisotropy (see Fig. S3 in Supplementary material (SM)). However, both the criticla nucleus and the GB may change their shapes in response to their mutual interactions [13,14]. Furthermore, the torque term [26] (Fig. 1(b)), originated from interfacial energy anisotropy and reflecting the resistance of an interface to rotation, is not considered in these approaches, which is, however, a prerequisite to achieve a complete force balance at the interface junction where the low-energy facet of a nucleus intersects the GB. Thus the shape of a critical nuclei predicted in these approaches may not be the true equilibrium shape (unconstrained).

Recent molecular dynamics studies of HN at GBs [13,14,25] have shown that, in the case of low-energy facet(s) in contact with a GB, the nucleus shape deviates significantly from its counterpart derived by the graphical methods. On the other hand, experimental study of HN of ferrite at austenite GBs has suggested that the total free energy increase associated with the formation of a critical nucleus (will be

* Corresponding authors.
E-mail addresses: shi7@llnl.gov (R. Shi), wang.363@osu.edu (Y. Wang).
[1] Present address: Computational Materials Science Group, Materials Science Division, Lawrence Livermore National Laboratory, 7000 East Avenue, L-367, Livermore, CA 94550 USA.
[2] Present address: GE Global Research, 1 Research Circle, Niskayuna, NY 12309 USA.

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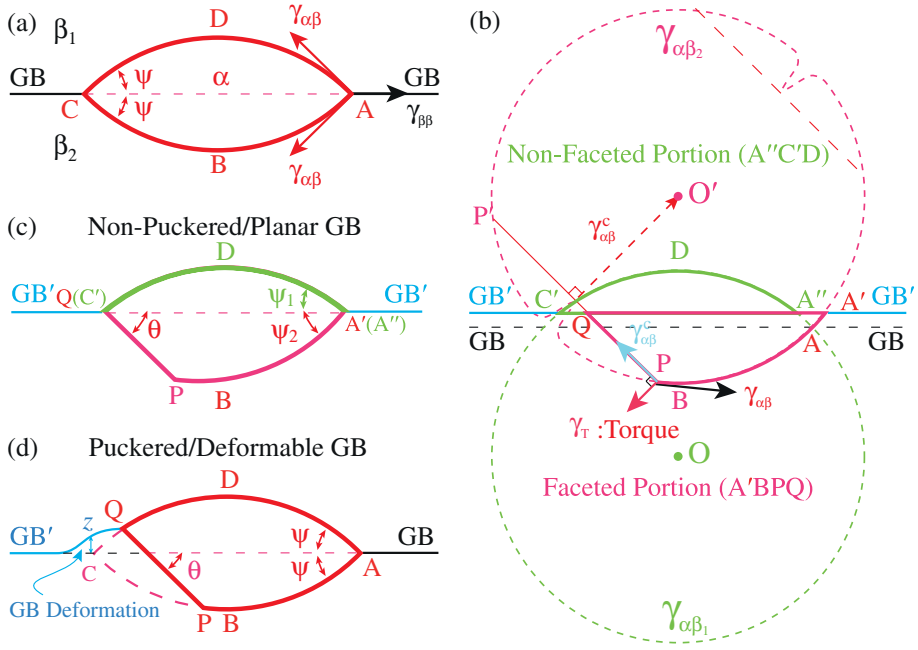

Fig. 1. Schematic illustration of various critical nucleus shapes at a grain boundary (GB). (a) A symmetrical double-spherical-cap α nucleus at a GB between β_1 and β_2 with an isotropic GB energy $\gamma_{\beta\beta}$ and interface energy $\gamma_{\alpha\beta} = \gamma_{\alpha\beta_2} = \gamma_{\alpha\beta_1}$. ψ is the equilibrium contact angle; (b) A graphical construction of the nucleus shape in the presence of a low-energy facet. O(O′) is the center of the γ-plot for the $\alpha/\beta_1(\beta_2)$ interfacial energy with a radius of $\gamma_{\alpha\beta_1}(\gamma_{\alpha\beta_2})$. O and O′ is separated along the normal of the GB plane (GBP) with the distance of $\gamma_{\beta\beta}$. A cusp orients at a distance $\gamma^c_{\alpha\beta}$ from O′ and an angle θ with respect to the GBP. (c) The nucleus shape at a planar (non-puckered) GB. (d) The nucleus shape at a deformable (puckered) GB that is a truncated double spherical cap by the plane $\overline{PP'}$ in (b). The geometry of the GB adjacent to the nucleus is approximated by a catenoid that has a zero mean curvature. In (b) a schematic for forces acting at the junction P is given, showing that a torque term, γ_T, is necessary for force balance (see Figs. S1–S2 in SM for more details).

referred as activation energy for nucleation hereafter) determined by the experiment could be orders of magnitude smaller than that predicted by the existing models [27]. These studies prompt the need to investigate how *co-deformation* of a nucleus and the hosting GB in respond to their mutual interactions affect their equilibrium shapes and, more importantly, the activation energy barrier for nucleation (ΔG^*) without any *a prior* assumptions on their shapes. Here by *deformation* we refer to simultaneous shape change of both nucleus and GB through atomic diffusion rather than elastic or plastic deformation.

Since a critical nucleus is defined by the saddle point along the minimum energy path (MEP) on the total free energy surface in a high-dimensional phase space (including all degrees of freedom, structural, compositional and geometrical), interface forces and torques must be balanced at junctions and everywhere else. Thus both the nucleus and GB plane involved have to be able to relax their shapes simultaneously and freely (i.e. *co-deformable*) in order to achieve equilibrium, which requires a *fully variational* approach. In this study we formulate such an approach using a combination of a multi-phase field model (MPFM) [28] and a free-end nudged elastic band (FE-NEB) method [29,30]. The former allows us to formulate the total free energy in the high-dimensional phase space mentioned above, while the latter allows us to search effectively the saddle point along the MEP on the free energy surface. With the nucleus and GB being treated as a whole and forces (including torque terms) being balanced naturally at junctions, and without any a priori assumptions and constraints about the shape of the critical nucleus and the corresponding geometry of the GB plane, the approach allows us, for the first time, to remove all the simplifying assumptions involved in previous graphical approaches mentioned earlier. The calculation results show that a nucleus is highly deformable in response to its interaction with the GB along the triple-junction (TJ) line. Its shape deviates significantly from those derived using the geometrical methods, and the same is true for the GB surface geometry and the GB area removed by the nucleation event. As a consequence, the activation energy barrier for nucleation can be reduced by orders of magnitude relative to predictions by previous methods.

For a system with $\alpha = 1, \ldots, N$ phases and $i = 1, \ldots, M$ components, the total free energy functional is defined as the integral of interfacial energy density f^{intf} and bulk chemical free energy density f^{chem} over a finite size [28]:

$$F(\{\phi_\alpha\}, \{\boldsymbol{c}_\alpha\}) = \int d\boldsymbol{x} \left\{ f^{intf}(\{\phi_\alpha\}) + f^{chem}(\{\phi_\alpha\}, \{\boldsymbol{c}_\alpha\}) \right\} \quad (1)$$

where the phase fields, $\{\phi_\alpha\}$, define the local fractions of all phases present, with their phase composition fields given by $\{\boldsymbol{c}_\alpha\}$. The brackets denote the ensemble of all phases. $\{\phi_\alpha\}$ follow an additional constraint $\sum_{\alpha=1}^{N} \phi_\alpha = 1$ according to its definition. The phase concentration vector $\boldsymbol{c}_\alpha = (c_\alpha^{i=1}, \ldots, c_\alpha^M)$ is used to describe a generic multi-component nature of a specific phase.

According to the gradient thermodynamics [31], the interfacial free energy density is defined by the gradients of the phase-fields and the potential function [32]:

$$f^{intf}(\{\phi_\alpha\}) = \sum_{\alpha=1}^{N} \sum_{\beta>\alpha}^{N} \left[-\frac{\kappa_{\alpha\beta}\, \Gamma(\boldsymbol{n}_{\alpha\beta})}{2} \nabla\phi_\alpha \cdot \nabla\phi_\beta + \omega_{\alpha\beta}\, \Gamma(\boldsymbol{n}_{\alpha\beta}) \left| \phi_\alpha \phi_\beta \right| \right] \quad (2)$$

where $\kappa_{\alpha\beta}$ and $\omega_{\alpha\beta}$ are related to interface energy $\gamma_{\alpha\beta}$ and width $\Lambda_{\alpha\beta}$. To capture interface energy anisotropy and thus the formation of low-energy facet, both $\kappa_{\alpha\beta}$ and $\omega_{\alpha\beta}$ are further multiplied by $\Gamma(\hat{\boldsymbol{n}}_{\alpha\beta})$, a function of the local interface inclination characterized by a unit vector $\hat{\boldsymbol{n}}_{\alpha\beta}$ normal to the interface.

A necessary condition for a saddle point is given by a vanishing functional variation of the grand potential Ω, i.e., $\delta\Omega = 0$, where $\Omega \equiv F - \lambda \boldsymbol{C}$, $\boldsymbol{C} = \boldsymbol{C}[\{\phi_\alpha\}, \{\boldsymbol{c}_\alpha\}]$ stands for additional physical constraints on the phase fields [28,32], and λ is the Lagrange multipler. The saddle point in such a high-dimensional space can be located by the NEB method [33] that has been used widely for calculating reaction pathways of atomic-scale processes in chemical reactions and phase transformations. (For more details, one can refer to the section Method in SM).