

**Modeling Grain Boundaries
using a Phase Field Technique**

**R. Kobayashi,
J. A. Warren and W. C. Carter**

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Modeling Grain Boundaries using a Phase Field Technique

Ryo Kobayashi

Research Institute for Electronic Science

Hokkaido University

Sapporo 060, Japan

James A. Warren

Metallurgy Division and Center for

Theoretical and Computational Materials Science

National Institute of Standards and Technology

Gaithersburg, MD 20899

W. Craig Carter

Department of Materials Science and Engineering

Massachusetts Institute of Technology

Cambridge, MA, 02139-4307

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Abstract

We propose a two dimensional frame-invariant phase field model of grain impingement and coarsening. One dimensional analytical solutions for a stable grain boundary in a bicrystal are obtained, and equilibrium energies are computed. We are able to calculate the rotation rate for a free grain between two grains of fixed orientation. For a particular choice of functional dependencies in the model the grain boundary energy takes the same analytic form as the

microscopic (dislocation) model of Read and Shockley [11].

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Previously we presented a new model [1] and [2] and phase-field simulations of the simultaneous processes of solidification, impingement, and coarsening of arbitrarily oriented crystals. In earlier models of this phenomenon, a finite number of crystalline orientations are allowed with respect to the fixed coordinate reference frame. Morin et al. [3], and Lusk [4] constructed a free energy density having N minima by introducing a rotational (orientation) variable in the homogeneous free energy. Chen and Yang [5] and Steinbach et al. [6] assigned N order parameters to the N allowed orientations. In these approaches, the free energy density depends on the orientation of the crystal measured in the fixed frame—a property which is not physical.

Our previous work [1] (KWC) introduced a model invariant under rotations of the reference frame. A similarly motivated approach has also been developed by Lusk [8]. We have since determined that the one dimensional solutions obtained in [2] (WCK) are globally unstable to a lower energy solution with completely diffuse grain boundaries. Herein, we present a completely general formulation of a new class of models which allow for accurate, physical modeling of grain boundary formation by impingement and subsequent motion.

In KWC, a rotationally invariant three-parameter phase field model of solidification with subsequent impingement of grains and coarsening was proposed. The model parameters, ϕ , η , and θ , represent: a liquid-solid order parameter, a coarse-grained measure of the degree of crystalline order, and the crystalline orientation, respectively. For what follows we shall focus on the events after impingement, when the material is completely solid ($\phi = 1$), since we are interested in the construction of a physically realistic model of grain boundaries. At the close of this letter we will reintroduce solidification to complete the model.

We now more precisely define η and θ . Consider a fixed subregion of solid material. At the atomic scale we can define a discrete variable θ_i which represents the orientation of an atomic bond (lattice vector) with respect to some fixed laboratory frame. For this subregion, we define η and θ such that

$$(\eta \cos \theta, \eta \sin \theta) = \frac{1}{N} \sum_{i=1}^N (\cos \theta_i, \sin \theta_i), \quad (1)$$

where N is the number of bonds in the subregion. Then, the variable η is an order parameter for the degree of crystalline orientational order, where $\eta = 1$ signifies a completely oriented state and $\eta = 0$ a state where no meaningful value of orientation exists in the subregion, and $0 \leq \eta \leq 1$ always holds. The variable θ is an indicator of the mean orientation of the crystalline subregion. Note, that when symmetrically equivalent crystalline directions exist, θ may not be uniquely defined. However, the point group symmetry operations can be used to map each of the θ_i into a subdomain of $(0, 2\pi)$ where they are unique.

Given the order parameters η and θ we need to construct a free energy which is invariant under rotations of the reference frame. We start from the expression

$$F = \int \left[f(\eta) + s\mu(\eta)G(|\nabla\theta|) + \frac{\nu^2}{2}|\nabla\eta|^2 \right] dV, \quad (2)$$

where ν and s are constants, $f(\eta)$ is the homogeneous free energy and $G(|\nabla\theta|)$ is specified below. The function $\mu(\eta)$ should have the property $\mu(0) = 0$ and should increase monotonically with η . The constants s and ν are parameters which set the strength of the penalties for gradients in misorientation and degree of crystalline orientation, respectively. The total free energy is frame invariant since it includes the variable θ only in the form $|\nabla\theta|$. For this work we assume that only ordered phase is stable, so $f(\eta)$ has a single-well at $\eta = 1$.

In two dimensions, the equilibrium grain boundary energy is generally a function of two angles, for example, the angles of a boundary with respect to the grains on either side. We will derive the equilibrium grain boundary energy as a function of the difference of these angles (the misorientation), $\Delta\theta$, in one dimension. Effects of anisotropy (the dependence of grain boundary energy with respect to boundary orientation; i.e., the direction of $\nabla\eta$ with respect to mean crystalline orientation $\bar{\theta}$) are not currently included in our model.

Because the energy form does not include θ explicitly, no preferred values of θ are selected by the form of our equations. Therefore, values of θ are determined by Dirichlet boundary conditions, if they exist, and by gradient flow if the value of θ is not fixed at any spatial position. For a bicrystal (a single grain boundary) with Dirichlet boundary conditions, the spatial extent of the grain boundary is determined by $G(|\nabla\theta|)$ and the coupling to η . The

customary choice of square gradient, $G(|\nabla\theta|) = \nabla\theta \cdot \nabla\theta$, *cannot* be physically correct, since it leads to a diffusion equation for θ and therefore the region of misorientation spreads indefinitely. In WCK an attempt to stabilize a finite grain boundary was made by including many minima in G at different values of $|\nabla\theta|$. With this form of G , a one dimensional solution to the equations of motion can be found which has a finite grain boundary thickness. We demonstrate below that this solution has a larger energy than a completely diffuse interface, and is thus unstable.

It is useful to determine the energetic contribution of terms with the form $|\nabla\theta|^\alpha$; where α is a positive number. If the gradient is completely spread out over a one dimensional domain of length L and η is uniform, then $\nabla\theta \equiv \Delta\theta/L$, where $\Delta\theta$ is the change in angle across the domain (grain boundary misorientation). If $\eta \equiv \bar{\eta}$ where $\bar{\eta}$ gives a minimum of $f(\eta) + s\mu(\eta)|\nabla\theta|^\alpha$, and L is taken to be large, the total excess energy (associated with $\Delta\theta \neq 0$) is given by

$$\Delta F_{\alpha,L} = \int_{-\frac{L}{2}}^{\frac{L}{2}} [\Delta f(\bar{\eta}) + s\mu(\bar{\eta})|\nabla\theta|^\alpha] dx = O(L^{1-\alpha}),$$

where $\Delta f(\eta) \equiv f(\eta) - f(1)$. In particular, for $\alpha > 1$

$$\lim_{L \rightarrow \infty} \Delta F_{\alpha,L} = 0. \quad (3)$$

Thus, there is *no* form for $\alpha > 1$ leading order behavior in G which has a globally stable, non-diffuse solution, since a completely diffuse boundary has an energy which can always be made smaller than any other configuration.

However, the form of $\Delta F_{\alpha,L}$ suggests that the choice of $\alpha = 1$ may admit solutions for equilibrium grain boundaries of finite spatial extent. If $\alpha < 1$ then the derived evolution equation is completely singular in the region where $\nabla\theta = 0$. Thus, $\alpha = 1$ ($G(|\nabla\theta|) = |\nabla\theta|$ to leading order) *is the only possible choice*.

Therefore, the dimensionless energy takes the following form:

$$F = \int_{\Omega} \left[f(\eta) + \frac{\nu^2}{2} |\nabla\eta|^2 + s\mu(\eta)|\nabla\theta| \right] dV, \quad (4)$$

Here we choose for $f(\eta)$ and $\mu(\eta)$ the forms

$$f(\eta) = \frac{1}{2}(1 - \eta)^2; \quad \mu(\eta) = \eta^2. \quad (5)$$

We examine an alternative choice for $\mu(\eta)$ at the close of this letter.

We consider η and θ as a polar coordinate system on the unit disk $D = \{\eta \leq 1\}$ as Eqn.1 suggests, and introduce L^2 -norm to the functional space [13]. Then, the equations of motion are

$$\tau_\eta \eta_t = \nu^2 \nabla^2 \eta + 1 - \eta - 2s\eta |\nabla \theta|, \quad (6)$$

$$\tau_\theta \eta^2 \theta_t = s \nabla \cdot \left[\eta^2 \frac{\nabla \theta}{|\nabla \theta|} \right]. \quad (7)$$

where τ_η and τ_θ are (possibly anisotropic) inverse mobilities [1].

The form of Eqn. 7 requires careful consideration since it contains a singular diffusivity where $\nabla \theta = 0$. However, this singularity can be treated rigorously and controlled, as the work of Giga and Giga [9] and Kobayashi and Giga [10] has indicated. A complete discussion of the dynamics of this model is reserved for a longer paper, here we present equilibrium one-dimensional solutions.

The equilibrium solutions $\eta(x)$ and $\theta(x)$ must satisfy the following equations:

$$0 = \nu^2 \eta_{xx} + 1 - \eta - 2s\eta |\theta_x|, \quad (8)$$

$$0 = s \left[\eta^2 \frac{\theta_x}{|\theta_x|} \right]_x, \quad (9)$$

where the subscript x indicates differentiation with respect to x . Dirichlet boundary conditions $\theta(\pm\infty) = \theta_\pm$ are applied as well as the condition $0 \leq \eta(x) \leq 1$. Here, let us consider the equilibrium solution which corresponds to a bicrystal. Without loss of generality, the center of the grain boundary is located at $x = 0$. If $\eta(x)$ has only one minimum, it can be shown that the solution for $\theta(x)$ is a step function at the point where η takes minimum [10].

So we can take θ as

$$\theta(x) = \begin{cases} \theta_- & -\infty < x < 0; \\ \theta_+ & 0 < x < \infty. \end{cases} \quad (10)$$

Note that $|\theta_x| = \Delta\theta \delta(x)$, where $\Delta\theta = |\theta_+ - \theta_-|$ and $\delta(x)$ is the Dirac delta function. Eqn. 8 gives

$$\eta(x) = 1 - (1 - \eta_0)e^{-\frac{|x|}{\nu}} \quad (11)$$

where $\eta_0 = \eta(0)$, and should be determined by integration of Eqn. 8 through the discontinuity in θ :

$$\nu^2 [\eta_x]_{x=0^-}^{x=0^+} = 2s\eta_0\Delta\theta. \quad (12)$$

Finally, Eqns. 11 and 12 determine η_0 as

$$\eta_0 = \frac{1}{1 + \Theta}; \quad \Theta \equiv \frac{s\Delta\theta}{\nu}, \quad (13)$$

where Θ is a scaled misorientation.

We now calculate the total free energy. This quantity can be separated into two terms: the bulk contribution E_{bulk} , and the contribution from the singular core at $x = 0$, E_{core} .

$$E_{bulk} = \int_{-\infty}^{\infty} \left[\frac{\nu^2}{2} \eta_x^2 + \frac{1}{2} (1 - \eta)^2 \right] dx = \nu \left(\frac{\Theta}{1 + \Theta} \right)^2 \quad (14)$$

and

$$E_{core} = s\eta_0^2\Delta\theta = \nu\Theta \left(\frac{1}{1 + \Theta} \right)^2, \quad (15)$$

With these two energies we can find the surface excess energy

$$\gamma \equiv E_{bulk} + E_{core} = \frac{\nu\Theta}{1 + \Theta}. \quad (16)$$

Note that the energy is localized in the ν -neighborhood of the grain boundary, and the precise contribution to the energy from the region $|x| > \ell$ is $E_{bulk}e^{-\frac{2\ell}{\nu}}$.

When

$$s \gg \nu, \quad (17)$$

then, for almost all $\Delta\theta$, we have that $\Theta \gg 1$, since $\Delta\theta$ is expected to have the values of order one. Therefore, except for small values of $\Delta\theta$, we have

$$E_{bulk} \simeq \nu; \quad E_{core} \simeq \nu\Theta^{-1} \ll E_{bulk} \quad (18)$$

and

$$\gamma \simeq E_{bulk} \simeq \nu. \quad (19)$$

Also,

$$\eta_0 \simeq \Theta^{-1} \ll 1, \quad (20)$$

which means the degree of orientational order almost vanishes at the grain boundary. The typical profiles of η and θ are shown in Fig 1. Eqn. 19 implies that the grain boundary energy is independent of misorientation provided that $\Delta\theta$ is much larger than the resolution level ν/s which is very small in this particular case. Therefore, we can regard the case $s \gg \nu$ to be independent of misorientation.

So far, we have concentrated on the one grain boundary solution under Dirichlet boundary conditions. If the initial conditions had more than one boundary, the unconstrained grain(s) must rotate to lower the energy by adjusting the two boundary misorientations, until the equilibrium solution obtained above is attained. Since we are ultimately interested in the dynamics of this problem, it is useful to examine the case shown in Fig.2, where a narrow band-shaped interior grain with thickness ℓ lies between two semi-infinite grains. Like before, Dirichlet conditions are imposed as $\theta(\pm\infty) = \theta_{\pm}$.

Let the orientation of the interior grain be labeled θ_0 , and assume $\ell \gg \nu$, then the system is described by η and θ as shown in Fig.2. The system can eliminate the interior grain by two independent mechanisms: 1) by moving the boundaries towards each other at fixed misorientations; 2) by adjusting the orientation(s) of the interior grain(s) at fixed boundary spacing. Since the regions where $\eta(x)$ varies rapidly are spatially localized ($\ell \gg \nu$), variation of the boundary position has negligible effect. Therefore, we evaluate the rotation rate of the interior grain. If we assume, for example, $\theta_- < \theta_0 < \theta_+$, the following estimate holds [10]:

$$\tau_\theta \frac{\partial \theta_0}{\partial t} \simeq \frac{\nu \nu}{\ell s} \frac{2(\theta_+ - \theta_-)}{(\theta_0 - \theta_-)^2 (\theta_+ - \theta_0)^2} \left(\theta_0 - \frac{\theta_+ + \theta_-}{2} \right) \quad (21)$$

It follows from (21) that the angle θ_0 rotates to that θ_\pm which is closer to θ_0 . If τ_θ is identically 0 then the rotation rate is infinite, and a multi-grained solution would disappear instantly.

As a final point, for much of this analysis we have concerned ourselves with the case where $\Theta \gg 1$. If $\Delta\theta$ is so small that $\Theta \ll 1$ holds, Eqn.16 gives the asymptotics

$$\gamma \simeq s\Delta\theta. \quad (22)$$

The energies of low-misorientation tilt grain boundaries have been approximated by summing the energy of distribution of edge dislocations [11]. Here we discuss a method for reproducing the same energetic dependence on misorientation.

It is straightforward to repeat the one dimensional analysis given above for arbitrary $f(\eta)$ and $\mu(\eta)$. If this is done for the choice

$$\mu(\eta) = -2 \ln(1 - \eta) - 2\eta, \quad (23)$$

in Eqn. 4 and leaving $f(\eta)$ unchanged, we find η is also given by Eqn.11 and η_0 is determined by

$$(1 - \eta_0)^2 = \Theta \eta_0. \quad (24)$$

This guarantees $0 \leq \eta_0 \leq 1$ for arbitrary $\Theta \geq 0$, and gives two asymptotic expansions of η_0 :

$$\eta_0 = \Theta^{-1} - 2\Theta^{-2} + \dots \quad \text{for } \Theta \gg 1, \quad (25)$$

$$\eta_0 = 1 - \Theta^{\frac{1}{2}} + \dots \quad \text{for } \Theta \ll 1. \quad (26)$$

Thus, for $\Theta \gg 1$ we obtain the same expression as given by Eqn. 19. In addition, for the very small values of $\Delta\theta$ ($\Theta \ll 1$),

$$\gamma \simeq -s\Delta\theta \ln \Delta\theta \quad (27)$$

holds. Eqn. 27 is the Read-Shockley energy of a low angle tilt grain boundary [11]. This is a very useful result, as it allows us to mimic the physical picture of a grain boundary as a collection of dislocations using a macroscopic (coarse grained) free energy for small misorientations.

This polycrystalline model can be adopted into traditional elements of phase field modeling of solidification; the full free energy will now be of the form

$$F = \int [f(\phi, \eta, T, c_i) + \Gamma^2(\eta, \nabla\phi, \theta/\mathcal{S}) + s\mu(\eta)|\nabla\theta| + \frac{\nu^2}{2}|\nabla\eta|^2]dV. \quad (28)$$

The field ϕ is the liquid-solid order parameter, and the first two terms include the functional dependencies necessary to describe solidification with anisotropic kinetics and surface energy (see [12]). We include the temperature T , concentrations c_i , and any other thermodynamic variable which would control the state of the system. For anisotropic grain boundaries we need only reformulate $\nu^2|\nabla\eta|^2$ to be functionally similar to Γ . With this complete model, the full process of grain formation, collision and coarsening can be simulated.

To summarize, we have derived a class of models which can describe the solidification, impingement and coarsening of grains. These models are rotationally invariant, and can be modified in a straightforward manner to include a variety of physics. All of these models are analytically tractable in one dimension, which makes study of their behavior particularly direct. If we choose the coupling carefully we are able to derive a grain boundary energy identical to the Read-Shockley low misorientation tilt grain boundary energy. Following papers will explore the dynamics of this model in one and two dimensions, and include the effects of solidification, and grain boundary anisotropy.

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FIGURES

FIG. 1. Typical profiles of η and θ with one grain boundary. Simulated solution and analytic solution are both drawn, which coincide completely within the resolution of graph. Domain size = 1.0, $\nu = 0.01$, $s = 100$ and $\Delta\theta = \frac{2\pi}{3}$.

FIG. 2. A schematic plot of the order parameter η and orientation θ for a small grain with orientation θ_0 trapped between two pinned grains with orientation θ_{\pm} .

FIG. 1.

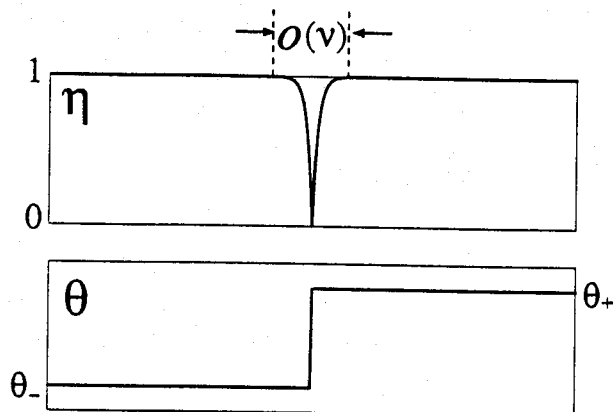


FIG. 2.

