Continuum Models for Intergranular Films in Silicon Nitride and Comparison to Atomistic Simulations

by

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Abstract

A continuum thermodynamic model is developed for the treatment of interfaces in materials. This phase-field model includes energetic contributions from chemical, structural and electrostatic effects. A small parameter set is introduced in the model. These parameters should be adjusted based on the relation of equilibrated phase-field structures to atomistic simulations and experimental observations. To compare the continuum fields to discrete data sets, coarse-graining methods are proposed. Two methods of measuring local atomic structure are developed, one based on Voronoi tessellations and the other based on bond-angle distribution functions. A coarse-graining method based on volume averaging over Voronoi tessellations is employed to continuize both structure and composition information. These fields give insight into the local atomic environment that is necessary for devising continuum models.

The stability of intergranular films in CaO-doped Si$_3$N$_4$ is examined. A modified associate model that incorporates bulk-thermodynamic Gibbs free energy functions and treats non-bulk equilibrium compositions is developed. Kinetic equations are derived to solve for the equilibrium fields. While the simulations do not reach equilibrium, some trends can be observed. Locally charged domains are kinetically stable near the film. Non-uniform calcium distributions in the doped films indicate that calcium is preferentially located near the film-grain interface. The structural width of the film can be tuned by altering appropriate model parameters.

Future avenues of research suggested by this thesis include: developing algorithms for measuring local structure and orientation in multi-component systems and devising atomistic simulations of intergranular pockets that couple experimental information with interatomic potentials.

Thesis Supervisor: W. Craig Carter
Title: Lord Foundation Associate Professor of Materials Science and Engineering
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In three dimensions, it is possible to rotate the system of planes to look along the edges of a section. The planes of constant charge, $P_{q}$ and $P_{0}$, are parallel and intersect $P_{n}$ at an angle $\phi$. The translation vector has a direction $\hat{v}$ and a length $l$. The Euclidean distance between the charged planes is $q/|\hat{v}|$.

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Chapter 1

Introduction

1.1 Motivation

As a class of materials, ceramics generally display higher thermal stability, higher wear resistance, and better corrosion resistance than metals. The use of ceramics in certain applications, for example in engines where the efficiency of the engine cycle increases with increasing operating temperature, is limited, in part, by low fracture toughness and high creep rate. The mechanical properties of a polycrystalline ceramic are influenced by grain size and shape, distribution of bulk-stable second phases, and the character of the grain or interphase boundaries. With respect to the last of these, many relatively simple ceramic materials such as doped and undoped Si$_3$N$_4$, Al$_2$O$_3$, and SiC exhibit intergranular films (IGFs) [6]. Engineering the microstructure, including the chemistry and thickness of the IGF, will allow later optimization of material properties and performance.

The thermodynamic stability of IGFs, including the coupling between the chemistry, structure, and electrostatics, is not well understood. In addition to exploring the thermodynamic basis for IGFs in CaO-doped Si$_3$N$_4$, this work aims to develop the general understanding of the interaction between competing thermodynamic effects in non-bulk equilibrium systems.
1.2 Organization of Introduction

The work in this thesis draws on a disparate set of previous work. Therefore, the introduction section contains an overview of published work in several fields. After a review of experimental observations and atomistic simulations results on intergranular films, Section 1.5 contains a discussion of relevant fields necessary for modeling intergranular films. Theoretical tools for continuum modeling based on diffuse interface theory are presented in Section 1.6. Diffuse interface theory is the basis for many of the previous models of intergranular films in the literature. The phase-field model, which derives from diffuse interface theory, is implicitly used in many models of IGFs and is the basis for the model derived in this thesis. Several simple diffuse interface theory based models of IGFs are presented in Section 1.7. The major features of two phase-field models that capture adsorption at interphase boundaries and the geometric properties of grain boundaries, respectively, are discussed in Section 1.8. A brief discussion of methods to incorporate physical information from other length-scales into phase-field models is presented in Section 1.9. This Chapter concludes with an overview of the structure of the rest of this thesis.

1.3 Experimental Observations

1.3.1 Silicon Nitride

In air, the surface of Si₃N₄ particles is covered with a film of SiO₂ that can introduce on the order of 2 wt% oxygen into bulk ceramics [7]. Upon sintering, oxygen, sintering aides, and impurities segregate to the grain boundaries. Silicon nitride is also liquid-phase sintered using a silicious liquid that leaves these same species at grain boundaries. Intergranular glassy films with thickness on the order of 1–2nm are observed at many grain boundaries in silicon nitride. This section discusses important experimental observations on those IGFs.
Figure 1-1: TEM image of intergranular film in Si₃N₄. The lattice fringes from a low-index plane in each of the two grains are visible as horizontal lines in the lower grain and near-vertical lines in the upper grain. The film thickness is identified from the region over which the lattice fringes cannot be imaged. Reproduced from Pan [1].

Grain boundary films can be imaged and characterized in transmission electron microscopes (TEMs), Fig. 1-1. The structural film thickness is often measured from high resolution images of the lattice planes in the grains.¹ The chemical film thickness is measured by identifying the region over which the composition differs from that in the grains. These two film thickness determination techniques give different values, suggesting that there may be variable physical widths of the intergranular film.

Observations of silicon nitride show that low angle and special boundaries are free of the IGF, while all general boundaries, faceted and rough, exhibit a film [8]. For general high-angle boundaries, the structural thickness of the film is insensitive to misorientation across the grain boundary.

In high purity silicon nitride with only SiO₂ additions, the film thickness remains constant with additions of SiO₂ above approximately 3 vol%, Fig. 1-2 (a) [9]. Additional SiO₂ increases the size of the intergranular pockets. This suggests that at the cutoff the thickness of the IGF has reached its equilibrium value.

Experimental evidence shows that in silicon nitride ceramics doped with calcia, the calcia segregates to the IGF and pockets at multi-grain junctions [10]. Tanaka

¹In order to image the boundary, some low index direction must be parallel in each of the two grains.
et al. found that the film thickness in silicon nitride with no added calcium was 1.0 ± 0.1nm [11]. This thickness decreased with calcium additions up to 80ppm then increased upon further additions up to 500ppm, Fig. 1-2 (b).

Gu et al. used EELS to examine the distribution of Ca dopant in HIP-ed silicon nitride [12]. They found that calcium was evenly distributed along the grain boundaries but was sometimes expelled from the large multi-grain pockets to collect at the intersection of the grain boundaries with these pockets for the highest Ca level. The statistical distribution of IGF calcium is bimodal with a higher excess measured for rough compared to faceted boundaries. This implies a relation between grain structure, orientation, and calcium adsorption.

Unpublished work by Gu suggests that the IGF thickness with 1000ppm Ca additions is statistically the same as that with 500ppm Ca [13]. Additionally, as Ca is added to Si$_3$N$_4$, excess accumulates at the intergranular pockets. Evidence indicates that the Ca composition near the edges of the pockets and especially near the boundary of the pockets and intergranular films is higher than in the center of the intergranular pockets. The samples with Ca additions at and above 500ppm exhibit phase separation within the intergranular pockets. These phases have different Ca concentrations. The phase with higher Ca content appears to nearly wet the Si$_3$N$_4$. 
grains and so collects near the interface between the intergranular pocket and film. These observations are based on a few difficult TEM measurements where samples are prone to damage.

The IGFs were studied in a series of samples made with rare earth-aluminum silicate glasses, where different rare earths were used [9, 14]. The equilibrium IGF thickness in Si$_3$N$_4$ increases with the addition of rare earth dopants with increasing ionic radii. Analytical TEM revealed that the level of rare earth adsorption in the film in equilibrium with glasses was much higher with La than with Yb [15]. This trend suggests that the strain effects in the glassy film may be important.

Post-processing heat treatments can crystallize the phase at multi-grain pockets but not the IGF in Si$_3$N$_4$. This indicates that the grain boundary phase is thermodynamically, not just kinetically, stable in this ceramic [9].

### 1.3.2 Other Simple Ceramics

Observations of other simple ceramic systems indicate IGF behavior similar to that in Si$_3$N$_4$. In thick-film resistor ruthenates, the thickness of the IGF increases with additions of TiO$_2$ [16]. Observations of doped Al$_2$O$_3$ show that impurities segregate within the glassy intergranular phase and that although the intergranular pockets can be crystallized the intergranular films remain glassy [17, 18].

In addition, experiments on bismuth-doped zinc oxide indicate that the intergranular films are equilibrium features of the materials [19]. Wang and Chiang prepared samples by a number of processing methods, including routes where the sample remained below the eutectic temperature. In each case, intergranular films were observed with compositions different from the eutectic and thicknesses in the range of 1.0-1.5nm. This study shows that these films are thermodynamically stable and not just kinetically frozen eutectic liquid.

Intergranular films are also observed at heterophase interfaces. A model experiment by Ackler and Chiang found an intergranular film at a quartz SiO$_2$-TiO$_2$ bound-
ary [20]. The experiment was devised so that residual stresses and capillary effects were minimized. The authors showed that in the absence of such potential nucleation barriers, the intergranular film was the stable structure.

While it is noted that the stability and behavior of IGFs is a general phenomenon, this thesis focuses on the thermodynamics of IGFs in CaO-doped Si$_3$N$_4$.

1.4 Atomistic Simulations

Atomistic simulation methods, such as molecular dynamics (MD) and Monte Carlo (MC), allow relatively small systems of atoms to be explored. MD is a deterministic technique where the motion of atomic species is governed by the force on each atom as a result of the interatomic potential. In contrast, MC methods are based on energy minimization using probabilities. Both result in an equilibrium description of a small system of atoms given some boundary or subsidiary conditions, e.g. constant pressure or constant composition. However, these methods are limited to data sets on the order of 10$^6$ atoms due to the computationally intensive calculation of the interatomic interactions.

Litton et al. examined calcium aluminosilicate intergranular films on alumina facets using MD with multi-body potentials [21]. The authors examined different terminations of Al$_2$O$_3$ basal (0001) planes abutting a film. They found that the calcium ions occupy sites in cage-like structures at the edges of the film near the alumina grains. The authors suggest that this configuration is driven by charge compensation. Simulations show that after the cage sites are saturated, additional Ca is located in the middle of the film.

Yoshia et al. examined the energetics of silicon nitride grain boundaries with and without a silicon oxynitride film using MD with pair-wise potentials [22]. The simulations confirm that the energy of a clean 0$^\circ$ twist boundary is lower than that of the boundary with equilibrated film. Further, the energy of the 180$^\circ$ twist boundary
is lower with than without a film.

Recent MD simulations by Garofalini have examined silicon nitride grain boundaries with SiO$_2$ and CaO-based films [23]. The simulations examine pure SiO$_2$ and 0.12 mole fraction CaO films with thicknesses of approximately 1 and 2 nm. Preliminary results indicate that, unlike the Ca atoms in the aluminosilicate films between Al$_2$O$_3$ grains, the Ca atoms are preferentially located in the center of the film. In addition, density modulations for Si and O are observed in the film. Section 2.4 introduces an analysis method for comparing segregation behaviors in IGFs through continuum fields.

1.5 Discussion of Physical Important Effects

The experimental and computational literature suggests that the stability of intergranular films is dictated by the couplings between structure, chemistry, and electrostatics. In order to devise a model to examine the stability of IGFs, these effects must be quantified.

There are five macroscopic degrees of freedom that describe the geometry of a grain boundary. Three of these describe the misorientation and two the inclination of the boundary. These macroscopic measures can be related to the microscopic fields that describe the system in the model. To do so, it is necessary to have a field that describes the local orientation of the material and a field that gives the location the grain boundary.

In the simplest grain boundaries in binary metallic systems, adsorption of the minority component is observed at grain boundaries. Therefore, even in simple systems, the composition in the vicinity of the grain boundary is a non-bulk equilibrium composition, it is interface-stabilized. It is necessary for the composition fields in the model to allow the description of non-bulk equilibrium compositions.

In ionic systems, defects such as cation vacancies and anion interstitials carry
charge. While macroscopic thermodynamics requires a bulk sample to be net-charge neutral, this does not preclude the existence of locally charged regions, especially near a grain boundary. Therefore, a grain boundary model should be able to describe local charge density and its response to electrostatic potential.

A continuum model must be constructed from fields that describe the physical system at the microscopic level and also can be related to macroscopic measures of a grain boundary. These fields should include measures of composition (in a way that does not assume local charge neutrality), charge density, electrostatic potential, local orientation, and local deviations from a crystalline environment.

Once the fields are identified, an appropriate thermodynamic functional is constructed. The potential should reproduce bulk thermodynamic relations in the macroscopic limit and also include elements of microscopic physics in a physically consistent manner.

1.6 Diffuse Interface Theory

1.6.1 Theory

Diffuse interface theory is central to many of the published models of IGF stability. The concept of a spatially diffuse interface originates with Gibbs, but the modern development in alloys was by Cahn and Hilliard, Fig. 1-3 [24].

Cahn and Hilliard, in the treatment of the free energy of non-uniform systems and spinodal decomposition, and Allen and Cahn, in the context of anti-phase domains utilize the diffuse interface idea [24, 25]. The order parameter in Cahn and Hilliard’s derivation is composition in a binary system, \( c \). The sharp interface in Fig 1-3 results from minimizing the homogeneous free energy of the system, \( f(c) \), or, equivalently, by applying the common tangent rule to the homogeneous free energy for a fixed composition. However in a non-uniform system, the free energy should depend on both the composition of the immediate environment, \( f(c) \), and on the surrounding envi-
Figure 1-3: Here the $\phi(x)$ represents, for example, the density profile in a system of a one-component liquid and gas where $\phi^\alpha$ and $\phi^\beta$ are the equilibrium densities of the gas and liquid, respectively. (a) A sharp interface between states $\phi^\alpha$ and $\phi^\beta$. There is an infinite gradient in $\phi(x)$ at the interface. (b) A diffuse interface between states $\phi^\alpha$ and $\phi^\beta$, for example, near the critical point. The profile has finite gradients across the interface.

The environment through additional terms that treat heterogeneity or first-order departures from equilibrium. This is accomplished by expanding the homogeneous free energy, $f_0(c)$, the energy per particle in a uniform system of composition $c$, in a Taylor series for small deviations from uniformity in composition.

$$ f(c, \nabla c, \nabla^2 c) = f_0(c) + \sum_i L_i(\partial c/\partial x_i) + \sum_{ij} \kappa^{(1)}_{ij}(\partial^2 c/\partial x_i \partial x_j) + (1/2) \sum_{ij} \kappa^{(2)}_{ij}[(\partial c/\partial x_i)(\partial c/\partial x_j)] + \ldots $$

This treatment assumes that $f(c, \nabla c, \nabla^2 c)$ has continuous derivatives. In the above, $L$ is a polarization vector, and $\kappa^{(1)}$ and $\kappa^{(2)}$ are tensors. By symmetry constraints, for a cubic crystal or any crystal with a center of symmetry, Eq. 1.1 reduces to the following.

$$ f(c, \nabla c, \nabla^2 c) = f_0(c) + \kappa_1 \nabla^2 c + \kappa_2(\nabla c)^2 + \ldots $$

The total free energy, $F$, of the volume, $V$, is given by the integral of Eq. 1.2 after application of the divergence theorem assuming $\nabla c \cdot \hat{n} = 0$ where $\hat{n}$ is the unit normal
at the boundary and \( N_V \) is the number of sites per unit volume.

\[
F = N_V \int_V f dV = N_V \int_V [f_0 + \kappa(\nabla c)^2 + \ldots] dV
\]  

(1.3)

The gradient energy coefficient is \( \kappa \).

\[
\kappa = -d\kappa_1/dc + \kappa_2 = -[\partial^2 f/\partial c\partial \nabla^2 c]_0 + [\partial^2 f/(\partial |\nabla c|)^2]_0
\]  

(1.4)

The total free energy of the system is given by a functional of the function, \( c(x) \). A positive gradient energy coefficient contributes an energetic penalty for non-zero gradients in composition. There is also an energetic penalty for non-bulk equilibrium values of composition when there is an interface between stable phases. The energetic minimum for the system is a compromise between reducing the infinite gradients of the step function and minimizing the homogeneous contribution to the energy. This results in a smooth profile across the interphase boundary from one stable phase to the next. A consequence of including a gradient energy term in the total energy of the system is that compositions that are not predicted from the equilibrium phase diagram are stabilized near the interface.

In the vicinity of the consolute point within the spinodes, the composition profile takes the form of

\[
c(x) = c_c + (c_\alpha - c_\beta) \tanh \left( \frac{\beta(T - T_c)}{2\kappa} \right)^{\frac{1}{2}} x
\]  

(1.5)

The composition at the consolute point is \( c_c \), \( c_\alpha \) and \( c_\beta \) are the compositions of the bulk equilibrium phases, \( T_c \) is the temperature at the consolute point, \( \kappa \) is the gradient energy coefficient defined in Eq. 1.4, and \( \beta = (\partial^3 f_0/\partial T\partial c^2)/2 \) is evaluated at \( T_c \) and \( c_c \).

Cahn derives the conditions for stable perturbations of small amplitude in solutions that are unstable with respect to decomposition. In addition to examining
systems where the chemical effects dominate, he also treats simple binary systems with significant strain effects upon decomposition and magnetic materials decomposing in an applied field [26, 27].

The wavenumber of the largest stable perturbation in the chemical system is \( \beta_{chem} = \left( \frac{2\kappa}{\tilde{f}} \right)^{\frac{1}{2}} \), where \( \kappa \) is the gradient energy coefficient and \( \tilde{f} \) is the magnitude of the curvature of the homogeneous free energy at the consolute point. In decomposing binary systems, the elastic energy serves to depress the spinodal and decrease the maximum stable wavenumber. The principal result for magnetically-aged systems is that at low undercoolings only small wavenumber perturbations parallel to the applied field are stable. While at larger undercoolings, perturbations both parallel and perpendicular to the applied field are stable for small wavenumbers.

1.6.2 Phase-Field Model

The phase-field model is based on diffuse interface theory. It has been used to treat many kinds of phase transitions [28]. Not only has it been shown to be mathematically rigorous in the asymptotic limit of sharp interfaces, but it also provides a simple algorithm for tracking interfaces with complex geometries compared to other techniques that require the position of the interface to be known at all times. This algorithm uses level sets to locate interfaces. The model has been applied to a variety of problems including solidification of alloys, grain growth, and dendritic growth [29, 30, 31]. It can capture segregation and the instabilities that lead to dendritic branching.

In a simple phase-field model, the phase field, \( \phi(\vec{x}) \), represents the state or phase of the material. The field is continuous and varies smoothly over the volume of the system. For example, in a model for the solidification of a one-component system, \( \phi(\vec{x}) = 1 \) represents the solid and \( \phi(\vec{x}) = 0 \) represents the liquid, for \( 0 \leq \phi(\vec{x}) \leq 1 \). The total energy of the system is then formulated as a functional, \( F \), where the integrand is the free energy density for the heterogeneous system. The homogeneous contribution to the energy is \( f_0(\phi) \) and the gradient energy penalty that intrinsically
incorporates interfacial energy is $\frac{1}{2} \kappa^2 (\nabla \phi)^2$.

$$F[\phi] = \int_{-\infty}^{\infty} \left[ f_0(\phi) + \frac{1}{2} \kappa^2 (\nabla \phi)^2 \right] dx$$  \hspace{1cm} (1.6)

The calculus of variations can be used to determine the equilibrium states of functionals [32]. A necessary condition for equilibrium, Eq. 1.7, is that the Euler-Lagrange equation be satisfied by $\phi(\vec{x})$ where $\frac{\delta F}{\delta \phi}$ is the variational derivative of $F$ with respect to $\phi$.

$$\frac{\delta F}{\delta \phi} = 0 = \frac{df_0}{d\phi} - \kappa^2 \nabla^2 \phi$$  \hspace{1cm} (1.7)

1.6.3 Kinetics

The microstructural evolution is determined by the evolving phase field. The kinetics of the field guarantee that the total free energy of the system decreases monotonically in time as the field evolves. There are two kinds of fields each with a different norm and rule for calculating the path of fastest descent for the free energy functional. A general field, $\phi(\vec{x})$, is conserved or non-conserved [33]. Conserved fields, such as composition, have the property that there are no sources or sinks of the field quantity and zero flux boundary conditions with $\Omega$ the extent of the system, $\int_{\Omega} \phi(\vec{x}) dV$ is a constant. Whereas for a non-conserved field, such as magnetic moment or electric polarization, there are sources and sinks and the value of the integral may change over time with zero flux boundary conditions.

For a conserved field, the appropriate norm is $H^{-1}$. The time rate of change of the field is given by minus the divergence of the flux of the field, Eq. 1.8. Assuming linear kinetics, the flux of the field is proportional to the negative of the gradient of the variational derivative with respect to the field, $\frac{\delta F}{\delta \phi}$. The additional divergence term ensures local conservation of the quantity associated with the flux. The gradient of the variational derivative is the thermodynamic driving force in the same way that
the gradient of the chemical potential is in Fick's First Law.

\[
\frac{\partial \phi}{\partial t} = -\nabla \cdot \left[ -M_\phi \nabla \frac{\delta F}{\delta \phi} \right]
\]  

(1.8)

Here, \(M_\phi\) is a mobility and may depend on position. When applied to diffuse interface theory, as described above, this equation is called the Cahn-Hilliard equation or Model B Ginsberg-Landau equation [24].

For a non-conserved field, the appropriate norm is \(L^2\). The kinetics are such that the total free energy decreases monotonically without restrictions on the flux. In other words, for linear kinetics, the time rate of change of the field is proportional to the negative of the variational derivative of the energy with respect to the field, \(\frac{\delta F}{\delta \phi}\).

\[
\frac{\partial \phi}{\partial t} = -\frac{1}{\tau_\phi} \frac{\delta F}{\delta \phi}
\]  

(1.9)

The relaxation time or inverse mobility is \(\tau_\phi\) and may be a function of the field. When applied to diffuse interface theory, Eq. 1.9 is called the Allen-Cahn or Model A Ginsberg-Landau equation [25].

1.7 Simple Models of Intergranular Glassy Films in Ceramics

Diffuse interface theory has been applied to models of intergranular films. Previous work has examined many important aspects of the thermodynamics but no single work has examined the multiple couplings presented in this thesis.

David Clarke made the first attempt to explain the equilibrium thickness of silicate-based IGFs in silicon nitride using a force balance across the boundary [34]. The crystals are misoriented by 180° with respect to each other and separated by a liquid phase which is assumed to wet both crystals. The net normal force on the
boundary must be zero.

\[ P + P_c + \Pi = 0 \] (1.10)

Here \( P \) is the applied pressure, \( P_c \) is the capillary pressure, and \( \Pi \) is the disjoining pressure. The disjoining pressure is the sum of the pressures due to all interfacial forces.

\[ \Pi = \Pi_{\text{DISP}} + \Pi_{\text{EDL}} + \Pi_{\text{ADS}} + \Pi_{\text{HB}} + \Pi_{\text{ST}} \] (1.11)

The contributions to \( \Pi \) are from \( \Pi_{\text{DISP}} \), the van der Waals dispersion forces; \( \Pi_{\text{EDL}} \), electrical double layer forces; \( \Pi_{\text{ADS}} \), interactions due to solute adsorption at the grain walls; \( \Pi_{\text{HB}} \), hydrogen-bonding forces; and \( \Pi_{\text{ST}} \), steric or structural forces. He simplified the problem to one of finding a force balance, and thus the equilibrium separation, between two planar crystal interfaces.

He considers a balance of two disjoining forces, a long-range attractive force and a short-range repulsive one. The attractive force is the van der Waals dispersion force between two planar interfaces separated by another medium, \( \Pi_{\text{DISP}} \). The repulsive force is the steric force resulting from ordering induced in the glass near each grain, \( \Pi_{\text{ST}} \). Clarke derives the form for the steric force using diffuse interface theory [24]. The resulting force balance, assuming reasonable material properties such as dielectric constants and gradient energy coefficients, yields an equilibrium thickness of approximately 2nm.

In another paper, Clarke et al. consider the effect of electrical double layer forces on the above described force balance [35]. Ceramics are ionic materials, so defects and disruption of order can introduce charge. The authors assume that the liquid IGF acts like an electrolyte between the two flat, parallel grain faces and consider the resultant repulsive force of the entropic electrical double layer interaction. The problem is solved for the balance in Eq. 1.12 using the same symbols as Eqs. 1.10 and 1.11.
\[ 0 = P_c + \Pi_{\text{DISP}} + \Pi_{\text{EDL}} \] (1.12)

First the electric double layer is treated with DLVO theory. The double layers are assumed to be independent. Therefore, the magnitude of the surface potential determines the double layer force and the concentration of ions in solution determines the Debye screening length. The equation is evaluated assuming that ions in solution dissociate to give a surface charge on the grains. The profile of the counterions in solution produces the repulsive force. For each of these cases, Eq. 1.12 is evaluated with material properties appropriate for Al$_2$O$_3$ grains separated by a SiO$_2$ liquid film. The analysis showed that it is reasonable for the electric double layer force to contribute to the disjoining pressure in order to stabilize a film of thickness 2nm.

Ackler analyzes the problem with a balance of steric and van der Waals effects using a thermodynamic approach [36]. Unlike Clarke, no \textit{a priori} relation for the profile of the order parameter across the film region is assumed [34]. The IGF is treated as a liquid with some induced order near the misoriented grain faces. The interfacial energy of a system is written as the sum of the structural energy from diffuse interface theory and a contribution from the van der Waals interaction across the film.

\[ \sigma(h) = \int_{h_1}^{h_2} \left[ \nu \phi(x)^2 + \epsilon^2 |\nabla \phi(x)|^2 \right] dx + \frac{A_{121}}{12\pi h^2} \] (1.13)

The phase field, $\phi(x)$, represents two microscopic quantities: first, the local order or disorder in the material where $\phi = 1$ is a perfect crystal and $\phi = 0$ is a liquid, and, second, the local orientation such that it is a projection of the orientation onto an arbitrary reference direction in two dimensions. There is an ambiguity when $\phi = 0$. \nu is a measure of the curvature of the homogeneous free energy contribution, $\epsilon$ is the gradient energy coefficient, $h = h_2 - h_1$ is the thickness of the film, and $A_{121}$ is the Hamaker constant for plate-like bodies of material 1 separated by material 2. Minimization is performed on the structural contribution to find the profile of $\phi$ across the
IGF. Stable and unstable regions of parameter space are defined for a non-dimensional Hamaker constant, non-dimensional width, and measure of misorientation. However, it has since been shown that the homogeneous free energy must be reference-frame invariant and therefore \( \phi \) as an orientation is unphysical in Eq. 1.13. Also, the form of the gradient term in the integral leads to a completely flat interface in the limit of large thickness [37].

Clarke also put forth a theory for the stability of intergranular films based on composition gradients across the film [38]. He suggests that for a binary system the profile of concentration across a single interface between phases \( \alpha \) and \( \beta \) varies as a \( \tanh \left( \frac{x}{\xi} \right) \), where \( x = 0 \) is the center of the film and \( \xi \) is a correlation length. The thin film is then modeled as a region with two independent liquid-solid diffuse interfaces. As the film thickness decreases the two interfaces are no longer independent and the two tanh profiles overlap. The equilibrium liquid composition is not reached in the center of the film and so the energy of the system increases. Clarke likens this effect to an osmotic pressure that tends to thicken the film in opposition to the attractive van der Waals dispersion force between the two grain faces.

Bobeth et al. performed numerical simulations with a composition-based diffuse interface model in periodic systems [39]. They concluded that, based on chemical effects, a film is unstable without additional repulsive forces such as those derived from structural and electrostatic interactions.

Choi et al. refine Clarke’s original model to include the effects of cation network modifiers on silicate-based glassy films in silicon nitride [40]. The authors examine the force balance in Eq. 1.14 as a function of the amount and type of additive.

\[
\Pi_{\text{disp}} + \Pi_{\text{st}} + \sigma = 0
\]  

(1.14)

Here, the dispersion force, \( \Pi_{\text{disp}} \), steric force, \( \Pi_{\text{st}} \), and the local compressive stress, \( \sigma \), scale with the Hamaker constant, \( H_{\beta\beta} \), film thickness, \( h \), structural correlation length, \( \xi \), degree of epitaxy at the film-boundary interface, \( \eta_{\Omega} \), latent heat of the
film material, $a$, applied pressure, $\sigma_a$, and the angle between the grain boundary and applied pressure, $\theta$, as described in Eqs. 1.15, 1.16, 1.17.

\[
\Pi_{disp} = \frac{H_{\beta \bar{\beta}}}{6\pi h^3} \tag{1.15}
\]
\[
\Pi_{st} = -4a\bar{\eta}_0^2 \exp \left( -\frac{h}{\zeta} \right) \tag{1.16}
\]
\[
\sigma = \sigma_a \left( \frac{1}{2} - \cos 2\theta \right) \tag{1.17}
\]

The authors use the concept of a bond strength which depends on the ionic radius and valence of the cation additive to modify the Hamaker constant and latent heat. The concentration of cation modifier is introduced with a rule of mixing that allows an energy balance at difference doping levels to yield a corresponding equilibrium thickness. This simple model predicts both the general trend of increasing IGF thickness with increasing cation radius for the lanthanides and also the form of the dependence of the IGF thickness on calcium doping level. However, this analysis does not consider entropic or electrostatic effects and uses several broad simplifications, such as setting the dependence of the structural contributions to the free energy as a parabolic function of epitaxy at the film-boundary interface.

The models presented in this section make assumptions about the single or two dominant effects in stabilizing an IGF. Each of these models lacks coupling between structure and chemistry. The model derived in this thesis addresses the couplings of chemistry, structure, and electrostatics.

### 1.8 Other Grain Boundary Models

Phase-field models in the areas of microstructural evolution and phase transformations offer instructional perspectives. While these models treat single component systems and structure-less systems, Sections 1.8.1 and 1.8.2, respectively, elements of each are essential for treating intergranular films.
1.8.1 Grain Growth

Kobayashi, Warren, and Carter (KWC) use a phase-field model with two fields to investigate grain growth in one-component systems. The first field is a measure of the degree of crystalline order, \( \eta(\vec{x}) \), where \( \eta(\vec{x}) = 1 \) is defined as perfect crystalline order and \( \eta(\vec{x}) < 1 \) represents the degree of disordered solid. The second field, \( \theta(\vec{x}) \), is a local measure of crystallographic orientation that represents a rotation with respect to a particular laboratory reference-frame in two-dimensions [37].

The total energy of a system is formulated as an integral over the volume, \( \Omega \), of a free energy density for a heterogeneous system, Eq. 1.18. Here \( f(\eta) \) is the homogeneous free energy that captures the bulk equilibrium states of the system, and \( s, \epsilon, \) and \( \nu_0 \) are parameters that, in addition to \( f(\eta) \), control the interfacial width and energy.

\[
F[\eta, \theta] = \int_{\Omega} \left[ f(\eta) + s \eta^2 |\nabla \theta| + \frac{1}{2} \epsilon^2 (\nabla \theta)^2 + \frac{1}{2} \nu_0^2 (\nabla \eta)^2 \right] dV \tag{1.18}
\]

The homogeneous energy density is correctly reference-frame invariant. Also, the leading order energy penalty for gradients in \( \theta \) is \( |\nabla \theta| \) rather than the typical square gradient. The \( |\nabla \theta| \) is necessary in order to stabilize finite interfacial widths, and it also ensures cusps in the grain boundary energy as a function of misorientation.

An analytic solution is obtainable for a grain boundary profile with Dirichlet boundary conditions on \( \theta \), \( \theta(\pm \infty) = \theta_{\pm} \), and Neumann boundary conditions on \( \eta \), \( \nabla \eta(\pm \infty) = 0 \) and \( \epsilon = 0 \). A schematic is presented in Fig. 1-4. The equilibrium form of \( \theta \) is a step function, Eq. 1.19. The equilibrium form of \( \eta \) is exponential with \( \eta_0 = \frac{1}{1 + e^\Theta} \) and \( \Theta \equiv \frac{\epsilon \Delta \theta}{\nu} \), Eq. 1.20.
Figure 1-4: Schematic of equilibrium profile of a grain boundary in the KWC model for $s = 0.1$, $\nu = 0.01$, and $f(\eta) = \frac{1}{2}(1 - \eta)^2$.

\[
\theta(x) = \begin{cases} 
\theta_-, & -\infty < x < 0, \\
\theta_+, & 0 < x < \infty 
\end{cases} \tag{1.19}
\]

\[
\eta(x) = 1 - (1 - \nu_0) \exp \left\{ -\frac{|x|}{\nu} \right\} \tag{1.20}
\]

The authors show that, for $s \gg \nu$ and $\Theta \gg 1$, the interfacial energy scales like $\nu$ and the interfacial thickness is $O(\nu)$.

In order to examine the dynamics of grain growth, the Allen-Cahn evolution equations are derived, Eqs. 1.21 and 1.22, for the two non-conserved fields. A semi-implicit finite difference technique is used to solve numerically for the fields at each time step.

\[
\frac{\partial \eta}{\partial t} = -M_\eta \left( \frac{df}{d\eta} + 2s|\nabla \theta| - \nu_0^2 \nabla^2 \eta \right) \tag{1.21}
\]

\[
\frac{\partial \theta}{\partial t} = -\frac{M_\theta}{\eta^2} \left( -\nabla \cdot \left[ s\eta^2 \frac{\nabla \theta}{|\nabla \theta|} \right] - \epsilon^2 \nabla^2 \theta \right) \tag{1.22}
\]

A singularity is introduced into the dynamics by $\nabla \cdot \frac{1}{|\nabla \theta|}$. The concept of extended gradient systems is employed so that Eq. 1.23 is substituted with $\chi_{\gamma}(p)$ defined in Eq. 1.24 [41]. $\gamma$ is a large positive parameter equal to the value of the function at
Figure 1-5: Comparison of $\chi_\gamma(p)$ (red) and $g(p) = \frac{1}{|p|}$ (blue). $\chi_\gamma(0) = \gamma$ removes the singularity at $g(0)$.

$x = 0$, Fig. 1-5.

$$\nabla \cdot \frac{1}{|\nabla \theta|} = \nabla \cdot (\chi_\gamma(\nabla \theta))$$  \hspace{1cm} (1.23)

$$\chi_\gamma(p) = \frac{\tanh \gamma p}{p}$$  \hspace{1cm} (1.24)

The dynamics illustrate that the model captures grain boundary motion by curvature and grain rotation.

1.8.2 Chemical Adsorption

Incompressible three-component polymeric systems have been studied using a Flory-Huggins mean field free energy per site and diffuse interface theory by Huang et al. [42, 43]. The Flory-Huggins free energy per unit site is

$$\frac{\Delta f_0}{k_B T} = \frac{\phi_a \log \phi_a}{N_a} + \frac{\phi_b \log \phi_b}{N_b} + \frac{\phi_c \log \phi_c}{N_c} + \chi_{ab}\phi_a\phi_b + \chi_{bc}\phi_b\phi_c + \chi_{ac}\phi_a\phi_c$$  \hspace{1cm} (1.25)

Where $\phi_i$ is the mole fraction of component $i$, $N_i$ is the degree of polymerization of component $i$, and $\chi_{ij}$ is the Flory interaction parameter for components $i$ and $j$. The Flory-Huggins free energy reduces to the regular solution free energy when $N_i = 1$ and $\chi_{ij} = \omega_{ij}/kT$, where $\omega_{ij}\phi_i\phi_j$ is the enthalpy of mixing of components $i$ and $j$. 

40
Figure 1-6: Equilibrium interphase interface exhibiting minority component adsorption in a metallic system with $\chi_{ij} = 3$ from Huang’s model.

The interfacial free energy for an interface between bulk equilibrium phases extending to infinity is given in Eq. 1.26.

$$\sigma = N_V \int_{-\infty}^{\infty} \left( \Delta f_0^m + \sum_i \kappa_{ii} \left( \frac{d\phi_i}{dx} \right)^2 \right) dx$$

(1.26)

$N_V$ is the number of monomers per unit volume, $\Delta f_0^m$ is the difference in the homogeneous free energy and the equilibrium homogeneous free energy given in Eq. 1.27, and $\kappa_{ii}$ is the gradient energy coefficient for component $i$.

$$\Delta f_0^m = \Delta f_0(\phi_i) - \sum_i \frac{\phi_i}{N_i} \mu_{0,i}^{\alpha(\beta)}$$

(1.27)

The chemical potential of component $i$ in the equilibrium phases is $\mu_{0,i}^{\alpha(\beta)}$. Huang shows that for symmetric homogeneous free energies, i.e., $\chi_{ij} = 3$, in monomer systems, $N_i = 1$, and, for example, initial bulk composition $(0.45275, 0.45275, 0.0945)$, the lowest energy of the interface requires adsorption of the minority component, $\phi_c$, Fig. 1-6.

Many authors in the polymer community have investigated these kinds of models for adsorption effects. Halperin and Pincus, for example, have analyzed the profile of
a large homopolymer in segregating monomeric liquids [44]. These methods apply in various limits that are not accessible to molecular liquids and solids.

However, the solution of this model predicts the interfacial adsorption which is observed in many simple systems. Similar work by Eyre in ternary systems of monatomic species indicates that there is no nucleation barrier for formation of the third phase at the interphase boundary after significant metastable adsorption of a minority component [45].

1.9 Incorporating Information from Other Length Scales

The phase-field models presented above contain parameters, such as $s$, $\epsilon$, and $\nu_0$ in Eq. 1.18, and approximations to bulk thermodynamic potentials, such as $\Delta f_0$, in Eq. 1.25. Phase-field models are inherently mesoscopic in that they cannot capture atomic or subatomic information precisely, but at the same time, are used to explore microstructural effects. In order to incorporate as much experimental information as possible into a phase-field model, macroscopic, microscopic, and atomistic information must be related to the parameters and approximations used.

1.9.1 Incorporating Information from Higher Length Scales

Often, it is only possible to assess bulk-equilibrium energy densities experimentally. In ionic systems, these energies correspond to charge-neutral compositions. The thermodynamic potentials used in phase-field models must be able to capture the energetic contribution of non-bulk equilibrium states including non-neutral compositions.

For an idealized homogeneous free energy, the relative energy values of the equilibrium phases and the curvature at the consolute point may be related to observables. Relative energy densities can be related to the critical nucleus size given a geometric approximation to the shape of the nucleus. Using spinodal theory, the wavenumber of
the fastest growing perturbation in a spinodally decomposing material can be related to the gradient energy coefficient and the curvature of the homogeneous free energy at the consolute point. Other macroscopic quantities, such as the latent heat of fusion, can be related to model parameters by examining sharp interface limits for particular functional forms, see, for example, Wheeler et al. [29].

1.9.2 Incorporating Information from Lower Length Scales

Some information is not obtainable from macroscopic observables. For example, the structural gradient energy coefficients in a complicated coupled model, such as the one developed in Chapter 4, are not accessible. As the parameters govern the different measures of interfacial thickness and energy along with the homogeneous free energy, it is possible to alter the parameters to reproduce general forms of interfacial profiles observed by experimental techniques and atomistic simulations.

In a phase-field model, the width of an interface (both structural and chemical) can be determined by examining the full-width half maximum or equivalent for the appropriate field \( \eta(\bar{x}) \) or \( X_i(\bar{x}) \).

Experimentally, EELS techniques are used to calculate the chemical width of a sample grain boundary by identifying the region where the composition deviates from that in the grains. The structural width is identified from lattice-fringe imaging. A set of lattice planes in each grain is imaged and the width of the discontinuity at the grain boundary gives the film width [46]. These methods of determining boundary film width give different numbers. This may be because the deviation from bulk structure occurs over a different length-scale from the length-scale over which the chemistry deviates or because the intrinsic averaging of the two measuring techniques may be over different length-scales.

Calculating boundary film widths from a set of discrete atomic positions from MD or MC is equally challenging and may have similar ambiguities. For chemical and structural determinations, some averaging or coarse-graining of the atomic in-
formation is necessary. But, in addition, for the structural width an appropriate measure of local structure must first be devised and calculated for each atom in the set. Chapter 2 details several techniques for generating continuum measures from discrete data that can be compared to fields in phase-field models.

1.10 Overview of Thesis

This thesis is organized into several chapters and appendices. The chapters are organized to allow a logical progression of ideas that build up to the design of a coupled phase-field model for examining grain boundary films in CaO-doped Si₃N₄.

Chapter 2 describes methods of generating continuum representations of discrete atomic data. Two methods of calculating local atomic structure are presented. The first method is based on Voronoi tessellations and the second on bond angle distribution functions (BADFs). A coarse-graining method based on volume averaging data over Voronoi tessellations is applied to the two measures of structure and to multi-component data sets. These methods are the bridge between atomistic computations and continuum models such as that derived in Chapter 4.

Chapter 3 explores the stability of locally charged regions in simple ionic systems. A kinetic stability analysis for simple ionic systems which are unstable with respect to cation disordering is presented. The resulting analysis illustrates an important coupling between chemical instability and electrostatics with analytic results and computer simulations. The thermodynamic functional derived in this analysis is the basis of the functional used for the model in Chapter 4.

Chapter 4 details the construction of the free energy functional for modeling intergranular films in CaO-doped Si₃N₄. A discussion of appropriate measures of charge and composition is presented. A modified associate model is introduced to model the homogeneous free energy of the solid phases. This model is relatively simple yet allows the incorporation of experimentally-determined bulk-equilibrium thermodynamic in-
formation. The equilibrium equations are derived for this system. Appropriate kinetic equations and a numerical scheme for simulating them are presented.

Chapter 5 presents simulations of intergranular films in Si$_3$N$_4$ using the model derived in Chapter 4. The results are discussed and compared to coarse-grained atomistic simulation results in similar systems.

Chapter 6 speculates on the credibility of the phase-fields model and associated coarse-graining techniques. A discussion of extensions of the model to problems not explicitly treated here, such as wetting and phase separation in intergranular pockets, concludes the chapter.
Chapter 2

Comparing Atomic Data Sets to Continuum Descriptions of Systems: Coarse-Graining\(^1\)

This chapter presents methods for mining data from discrete sets of atom positions and species and coarse-graining the data to create continuum descriptions of chemistry and structure. These continuum descriptions can be compared to macroscopic fields in the phase-field model. The phase-field free energy functional can then be tuned, for example, by altering the parameters in the gradient energy coefficients to adjust the equilibrium phase-fields to display key characteristics of the continuized atomistic data such as chemical and structural interfacial widths.

While the chemistry or species is known for each atom, the structure is not known \textit{a priori} and must be calculated. Once the data to be continuized is obtained, an averaging or coarse-graining method is employed. This method samples “nearly”-local data and includes it in the final continuum description. However, this is precisely what occurs in experimental measuring techniques with finite beam sizes.

The field for quantifying local structure, \(\eta(\vec{x})\), described in the KWC phase-field

\(^1\)Parts of this Chapter were published in [47].
model of grain boundaries, Section 1.8.1, will be related to atomistic data and coarse-grained using two methods [37]. The first method employs Voronoi tessellations to measure structure, while the second method uses bond angle distribution functions (BADF) [47, 48]. Both methods use the geometry of Voronoi tessellations for the coarse-graining. The two measures of local structure are reference frame invariant. Each generates a comparison of the local environment of an atom to the local environment in a perfect crystal. Finally, Voronoi tessellations will be discussed as a method for coarse-grain discrete composition information.

2.1 Introduction to Measures of Structure

There are a class of phase-field models of grain growth that are not reference-frame invariant, such as those proposed by Venkitachalam et al. and Kazaryan et al., which have a finite set of long-range order parameters (LRO), $\eta_k(\vec{x})$, representing the distinct orientations for each grain [49, 50]. Khachaturyan has suggested a method for extracting structural information, a LRO parameter, from atomistic coordinates [51]. However, this method is not reference-frame invariant and the multiple fields from such a method are neither necessary nor physically correct in resulting formulations of phase-field models for grain growth. Khachaturyan’s method defines a reference-frame dependent LRO parameter for each grain orientation in a simulation. Consequently, a system of grains with $p$ distinct orientations, this results in a phase-field representation with $p$ fields and evolution equations. This method also prohibits the grain rotation that has been observed experimentally, for example, in gold thin films and 2-D nanocrystalline MD grain growth simulations, and that is naturally included in the KWC method [52, 53, 37].

The radial distribution function (RDF) is used to look for non-crystalline structures by examining the second-nearest neighbor peak. This method is reference-frame invariant but loses the angular information that is required in the KWC model in ad-
dition to generating a spatially averaged distribution rather than a position dependent order-parameter field.

Other reference-frame invariant methods of characterizing structure such as bond-center distributions, angle-cosine distributions, and invariants of spherical harmonics are reviewed by McGreevy [54]. The bond center distribution method assigns points to the center of the vectors connecting neighboring atoms and the structure factor or radial distribution function of these is then used to characterize the structural order. The angle-cosines of the vectors between neighboring atoms are calculated to generate bond angle distributions that relate directly to the dominant local symmetry. Steinhardt et al. introduced spherical harmonics in the description of short-range order (SRO) in liquid and glass structures [55]. Comparison of the Steinhardt’s distribution in a sample to known distributions for reference samples gives an indication of local ordering. Van Duijneveldt and Frenkel use a rotationally invariant combination of spherical harmonics averaged over all atoms, $Q_6$, as an orientational order parameter for a sample [56]. This single number is chosen as it is relatively insensitive to crystal structure, but at the same time is sensitive to local order and disorder.

Steinhardt’s method has been generalized with the use of Legendre polynomials by Rodriguez de la Fuente and Soler [57]. The authors calculate the total number of atoms in a simulated quenched bulk metallic glass with structures similar to different references, for example, icosahedral and fcc environments, by comparing the rotationally invariant moments, Eq. 2.1, to those for reference atoms.

$$Q_l = \frac{1}{N_n} \sum_{ij}^N \frac{P_l(\cos \theta_{ij})^l}{2}$$

(2.1)

The rotationally invariant moments are $Q_l$, the total number of bonds for an atom is $N_n$ calculated by including all neighboring atoms closer than the first minimum in the RDF. The sum is over all of the bonds where the angle between bonds $i$ and $j$ is $\theta_{ij}$, and $P_l$ are Legendre polynomials. The invariants are calculated for $0 \leq l \leq 10$ and form a vector for each atom $k$, $Q_k$. The vector of invariants is calculated for reference
environments, \(\tilde{Q}_{\text{ref}}\). An atom is characterized as having a local environment similar to the reference if the Euclidean distance between \(\tilde{Q}_k\) and \(\tilde{Q}_{\text{ref}}\) is less than a cut-off. This method is very similar to that for determining structure using BADFs outlined in Section 2.3.

The methods described above generate either a distribution or a single order parameter to characterize the whole sample. The next two sections describe methods of turning discrete atomic data into a continuum field, \(\eta(\vec{x})\), that smoothly varies in space across a grain boundary and provides a measure of the local structural environment of an atom.

### 2.2 Voronoi Tessellations as a Measure of Structure

#### 2.2.1 Background

An alternate way of characterizing the structure of a material in a reference-frame independent scheme is to utilize a geometric method. Several authors have dismissed the use of Voronoi tessellations in the characterization of order in materials but have only considered the usefulness of the Voronoi histogram which is very sensitive to small perturbations of the atomic positions [56, 58]. However, Voronoi tessellations have been used extensively for material characterization at the microstructural length-scale and to examine single and multiple component atomic structures [59, 2, 60]. An anisotropy factor, typically a non-sphericity, is calculated as a ratio of tessellation properties and used in a statistical analysis.

One such analysis of single-component ordered and disordered structures was completed by Montoro and Abascal [2]. The authors performed 3-D simulations using a Lennard-Jones potential to produce data structures that they characterize as solid, liquid, quenched liquid, and gas. The Voronoi tessellation is calculated for each atom.
Figure 2-1: Schematic of Fig. 6 from Montoro and Abascal showing non-sphericity for some generated structures [2]. Data from solid (S), liquid (L), glass (G), and quenched liquid (Q) structures is presented. The average $\alpha$ for each structure (except solid) is significantly larger than $\alpha_{ws} = 1.117$, the non-sphericity of the Wigner-Seitz cell.

in a structure and the non-sphericity, $\alpha$, given in Eq. 2.2, is calculated where $V$ is the volume, $S$ is the surface area, and $R$ is the average radius of curvature of the convex body. The average radius of curvature for a polyhedron is given in Eq. 2.3 where the sum is over the edges, $l_i$ is the length of the $i$th edge, and $\phi_i$ is the angle between the faces intersecting at the $i$th edge. The authors distinguish the different structures by examining the histogram of the anisotropy factors for each sample.

$$\alpha = \frac{RS}{3V} \tag{2.2}$$

$$R = \frac{1}{8\pi} \sum_{\text{edges}} l_i \phi_i \tag{2.3}$$

For each crystal structure there is a characteristic value of the anisotropy factor for the Wigner-Seitz cell (Voronoi tessellation for the undistorted crystal). For example, for a simple cubic crystal structure, the Wigner-Seitz cell is a cube with $\alpha_{ws} = \frac{3}{2}$. For non-crystalline structures the anisotropy factor has a dispersion that characterizes a disordered system as shown in Fig. 2-1. Note that the average values of $\alpha$ for the quenched liquid, liquid, and gas structures are greater than $\alpha_{ws}$. 

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2.2.2 Local Environment of Each Atom from Voronoi Tessellations

The general method of calculating a measure of local structure based on geometric properties of Voronoi tessellations is first defined for a single-component solid structure. It is then applied to the specific case of a relaxed $\Sigma 5$ grain boundary from a simulation at 0K in diamond cubic silicon [47].

In this section, a general method for calculating atomic structure information to a continuum SRO parameter is described. The results of MD or MC simulation are a set of atomic positions, usually in three dimensions. To illustrate the method it is useful to describe its application to a two-dimensional MD grain boundary equilibration for a Lennard-Jones solid, although it is applied below to a three-dimensional data set obtained from atomistic simulation.\(^2\)

From the list of positions, the Voronoi tessellation for each atom is constructed using Qhull [61], a convex-hull calculation code, and stored, as shown in Fig. 2-2. Qhull calculates the surface area and volume of each tessellation. Using output from Qhull, required geometric quantities, such as the mean curvature and anisotropy factor, were calculated for each tessellation. The anisotropy factor for each tessellation, $\alpha_i$, is calculated.

The anisotropy factor for each atom, $\alpha_i$, can be compared to that for the Wigner-Seitz cell, $\alpha_{ws}$, to generate a measure of the crystalline SRO denoted $\eta_i$ for each atom. Disordered solid structures may have $\alpha_i > \alpha_{ws}$ or $\alpha_i < \alpha_{ws}$. The proposed scaling in Eq. 2.4, which has an upper bound of $\eta = 1$ but no lower bound, naturally handles either case, Fig. 2-3\(^3\). The case for which $\alpha_i = \alpha_{ws}$ and $\eta_i \equiv 1$ corresponds to the

\(^{2}\)The description of the algorithm is in three-dimensions, but the illustration in Fig. 2-2 is in two. The reduction is straightforward.

\(^{3}\)The linear scaling is chosen as the simplest function meeting the requirements. Another function, such as $\eta_i = 1 - (1 - \alpha_i/\alpha_{ws})^2$, could be used.
definition of the crystalline solid as described in the KWC model [37].

\[ \eta = 1 - \frac{|\alpha_{ws} - \alpha_i|}{\alpha_{ws}} \]  

(2.4)

A cubic mesh of a given size is superimposed on the data so that at least 100 mesh points fall within each tessellation. Each mesh point is assigned a measure of structure, \( \eta_{ijk} \) where \( ijk \) reference the mesh point, based on the tessellation in which it falls. Next, the center of a measurement volume or aperture is placed at some position in space, \( \vec{x} \), where the averaging is to be assigned. The value of \( \eta \) at this point, \( \eta(\vec{x}) \), is the average over all the \( \eta_{ijk} \) that fall within the measurement aperture.

### 2.2.3 Grain Boundary Example

This method for structure determination and coarse-graining is applied to the specific example of a \( \Sigma 5 \) grain boundary in diamond cubic silicon. I computed the equilibrium configuration of a \( \Sigma 5 \) boundary in silicon using the EDIP potential developed by Bazant et al. [62, 63]. The relaxation was performed at \( T = 0\text{K} \) and for several different system sizes. A regression was used to fit the energy vs. volume data. The volume corresponding to the minimum in the fitted curve was calculated, \( V_{\text{min}} \). A final relaxation was performed at \( T = 0\text{K} \) and \( V = V_{\text{min}} \) to generate the data set used to illustrate the structure determination algorithms. The results are qualitatively similar to previous numerical experiments, for example [64, 65]. The orthorhombic cell containing two grain boundaries (at \( z = 0 \) and \( z - Z/2 \)) has cell dimensions \( X = 8.577\text{Å}, Y = 8.577\text{Å}, \) and \( Z = 33.517\text{Å}, \) or a 2.875% elongation in the \( z \)-direction after relaxation. The purpose of obtaining this structure was to procure a data set to illustrate the procedure of relating atomic positions to a continuous field variable. The details of the simulation are less important to this thesis than the relation of the results to a continuous measure of SRO.
Figure 2-2: Illustration of the Voronoi tessellation method of determining structure and the Voronoi tessellation method of coarse-graining on averaged results of an MD tilt boundary equilibration of Lennard-Jones solid. The anisotropy factor here is defined as \( \beta = \frac{L^2}{A} \) where \( L \) is boundary length and \( A \) is area of the tessellation. The normalization from \( \beta_i \) to \( \eta_i \) is chosen as \( \eta_i = 1 - \frac{|\beta_{ws} - \beta_i|}{\beta_{ws}} \). (a) Schematic of equilibrium-averaged atomic positions for complete data set. (b) Voronoi tessellations are constructed from a central subset of atoms. The anisotropy, \( \beta_i \), and structure, \( \eta_i \) are calculated for each atom. (c) A square mesh is superimposed over the tessellations. The value of \( \eta_{ij} \) for each mesh point is determined from the tessellation in which it lies. (d) The measurement aperture of size \( r \) is centered at \( (x, y) \) and the local value of \( \eta(x, y) \) is the average of all mesh points that fall within the aperture. (e) Example of \( \eta(x) \) profile perpendicular to grain boundary. Note local deviation of \( \eta(x) \) in vicinity of grain boundary at \( x = 0 \).

Figure 2-3: Proposed scaling of \( \alpha \) to \( \eta \). Note that \( \alpha > 0 \) (\( \eta < 1 \)) but there is no upper bound on \( \alpha \), or equivalently, no lower bound on \( \eta \) for this scaling.
The equilibrium atomic positions were input to Qhull to calculate the Voronoi tessellation of each atom. The anisotropy factor for each tessellation, \( \alpha_i \), was then calculated and scaled to \( \eta_i \) using Eq. 2.4. Next, cubic meshes with spacings 0.5\AA and 0.25\AA were created with \( O(10^2) \) and \( O(10^3) \) mesh points per tessellation, respectively. The \( \eta_{ijk} \) at each mesh point was assigned. The meshes and the corresponding \( \eta_{ijk} \) values were stored in a file for use in further calculations.

Both cubic and spherical apertures with characteristic sizes \( r = 1\AA \) and \( r = 2\AA \) were used for averaging. The local value of \( \eta(\vec{x}) \) was calculated from the average of the mesh values within the aperture volume. Profiles were calculated at constant height, \((x, y, z_0)\), and also for variable height, \((x_0, y_0, z)\), for both meshes with measurements spaced by 0.25\AA in every case.

Grain boundary profiles of \( \eta(x_0, y_0, z) \) are presented in Figs. 2-4 and 2-5. The profile \( \eta(0, 0, z) \) traverses the boundary through a grain boundary coincidence lattice site in the unrelaxed structure. The other profiles at \((2, 2, z)\) and \((3.5, 3.5, z)\) pass through arbitrary points in the grain boundary. It should be noted that no computational calculation generates a truly continuous field, but only a field that can be sampled anywhere in a domain such as this \( \eta(\vec{x}) \).

It is apparent that the 0.25\AA mesh approximates the intersection of the aperture with each tessellation better than the 0.5\AA mesh. The 2\AA aperture generates a smoother profile than the 1\AA aperture. Also, the spherical aperture produces a smoother profile than the cubic aperture. Thus, the smoothest profiles are generated for the 0.25\AA mesh with a spherical aperture of radius 2\AA. The larger aperture and smaller mesh size imply that more points are averaged for each measurement. The spherical aperture has higher symmetry than the cubic aperture, thus reducing geometric noise in the averaging.

These profiles show that there is a deviation from the perfect crystalline environment between the center of each simulated grain and the center of the grain boundary. Just to either side of the center of each grain there is a small deviation from unity.

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Figure 2-4: Comparison of $\eta(\vec{x})$ profiles across the grain boundaries based on 0.5Å tessellation mesh with different aperture shapes and sizes at (a) (0,0,z), (b) (2,2,z), and (c) (3.5,3.5,z).
Figure 2-5: Comparison of $\eta(x)$ profiles across the grain boundaries based on 0.25 Å tessellation mesh with different aperture shapes and sizes at (a) $(0,0,z)$, (b) $(2,2,z)$, and (c) $(3.5,3.5,z)$. 
This may indicate local strain in the structure and will be discussed further in Section 2.5. The large deviation from unity at \( z = 0 \) and \( z = Z/2 \) is the hallmark of the grain boundary itself.

These profiles resemble those diffuse interfaces found in the phase-field model representing grain boundaries. The smaller the mesh size and sampling distance, the smoother the grain boundary profiles tend to become. However, convergence is somewhat subjective for this coarse-graining technique. For the "smoothest" profile (i.e., 0.25Å mesh and 2Å spherical aperture) the deviation from perfect SRO is 4.8% at \((2, 2, z)\). In contrast, the maximum variation within the \((x, y, z)\) plane section (i.e., in the crystalline region) is 0.09%.

## 2.3 BADF Overlap as a Measure of Order

### 2.3.1 Background

This section presents another method of calculating \( \eta \) from a bond angle distribution function overlap calculated for each atom. The overlap is a comparison of the BADF of an atom to the BADF of a reference atom in a perfect crystalline environment [48]. The method is applicable to single component systems as described here. A discussion of ways that it can be applied to multicomponent systems is presented in the Discussion section of this chapter.

### 2.3.2 Local Environment of Each Atom from BADFs

For each atom, the neighbors to be used in the distribution function are calculated using a hard cutoff at a distance corresponding to the second minimum in the RDF for the sample. The vectors from the central atom to the "neighbors" are called bonds. These do not have to be physical bonds but are instead a mathematical construction. The angle between bonds \( a \) and \( b \) is \( \omega_{ab} \). The BADF, \( f(\cos \omega) \), is the distribution
function of the cosines of the bond angles, Eq. 2.5.

\[
f(\cos \omega) = \frac{1}{N_b^2} \sum_{a,b=1}^{N_b} \delta(\cos \omega - \cos \omega_{ab})
\]  \hspace{1cm} (2.5)

The number of mathematical bonds is \(N_b\), \(\delta(x-x_0)\) is the Kronecker delta function, and the sum is a double sum over all combinations including \(a = b\).

Because \(f(\cos \omega)\) is defined on the interval \(-1 \leq \cos \omega \leq 1\), it is convenient to expand the BADF in Legendre polynomials, Eq. 2.6.

\[
f(\cos \omega) = \sum_{l=0}^{I_{max}=\infty} A_l P_l(\cos \omega)
\]  \hspace{1cm} (2.6)

The Legendre polynomials, given by the recursion relation in Eq. 2.7 are an orthogonal basis in the \(L^2\) norm [66]. Therefore, the Legendre coefficients, \(A_l\) are defined in Eq. 2.8.

\[
P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} \left[(x^2 - 1)^l\right]
\]  \hspace{1cm} (2.7)

\[
A_l = \frac{2l + 1}{2N_b^2} \sum_{a,b=1}^{N_b} P_l(\cos \omega_{ij})
\]  \hspace{1cm} (2.8)

Just as each crystal has a characteristic anisotropy factor, \(\alpha_{ws}\), each has a characteristic BADF for a given neighbor cutoff, \(f_p(\cos \omega)\). The overlap, \(S_{pi}\), of the BADFs of atom \(i\) and the reference perfect structure, \(p\), is given by Eq. 2.9 where the correlation, \(< f_p | f_i >\), is defined in Eq. 2.10.

\[
S_{pi} = \frac{< f_p | f_i >}{[< f_p | f_p > < f_i | f_i >]^{1/2}}
\]  \hspace{1cm} (2.9)

\[
<f_p | f_i> = \int_{-1}^{1} f_p(\cos \omega) f_i(\cos \omega) d(\cos \omega) = \sum_{l=0}^{I_{max}=\infty} \frac{2}{2l+1} A_{p,l} A_{i,l}
\]  \hspace{1cm} (2.10)
This overlap ranges from $0 \leq S_{pi} \leq 1$. Where $S_{pi} = 1$ corresponds to $f_p(\cos \omega) = f_i(\cos \omega)$ or the atom $i$ having the same BADF as the perfect crystal reference. $S_{pi}$ decreases toward 0 when the BADFs contain a finite number of bonds with no angles in common. The limits of $S_{pi}$ allow it to be used with no further rescaling as a measure of the local structural environment of an atom, Eq. 2.11.

$$\eta_i \equiv S_{pi}$$ \hspace{1cm} (2.11)

The coarse-graining is performed using Voronoi tessellations in the same manner described in Section 2.2.2. The discrete structural information, $\eta_i$, is spread over space using the mesh to abstract the geometry of the Voronoi tessellations with each mesh point having a $\eta_{ijk}$. An averaging aperture is used to calculate the coarse-grained $\eta(\bar{x})$.

### 2.3.3 Grain Boundary Example

The set of atomic positions from the equilibrated $\Sigma 5$ grain boundary described in Section 2.2.3 was used to test the BADF method. The mathematical bonds were defined between each atom and its neighbors within a 3Å cutoff radius. The BADFs were calculated and expanded in Legendre polynomials to order $l_{max} = 30$. The BADF overlaps, $S_{pi}$, were calculated for each atom. The volume averaging of $\eta_i \equiv S_{pi}$ was performed over the volume of the corresponding tessellations abstracted by a mesh with spacing 0.25Å. A spherical aperture with radius $r = 2\text{Å}$ was used for the coarse-graining. The mesh size, aperture geometry, and aperture size were chosen because this combination gave the best results for coarse-graining the anisotropy factor derived $\eta_{ijk}$ in Section 2.2.3.

$\eta(x_o, y_0, z)$ profiles perpendicular to the boundary were calculated through a coincidence lattice site on the boundary, $(0, 0, z)$, and through two general sites, $(2, 2, z)$ and $(3.5, 3.5, z)$. The results are presented in Fig. 2-6. The profiles have the charac-
Figure 2-6: \( \eta \) profiles perpendicular to the boundaries calculated using the \( S_{pl} \) method for \((0, 0, z)\), \((2, 2, z)\), and \((3.5, 3.5, z)\).

The characteristic shape for grain boundaries. Within each grain \( \eta = 1 \) while there is a local decrease in \( \eta \) in the vicinity of each grain boundary. The maximum deviation from \( \eta = 1 \) is 0.0006\% for the \((3.5, 3.5, z)\) profile.

2.4 Calculating Composition Fields from Discrete Data

In contrast to the previous sections, where the appropriate structural measure must be determined before coarse-graining, here the atomic species are known \textit{a priori}. This section describes a method of generating continuum composition fields from discrete atomic data sets. The method is performed on a set of positions resulting from an MD simulation of an intergranular film.

2.4.1 Coarse-Graining Method

The method is outlined for a general system of N components. The Voronoi tessellations corresponding to atomic coordinates are calculated. Again, a mesh is used
to abstract the geometry of the tessellations. The composition vector at each mesh point \( \vec{n}_{ijk} \) is a vector of dimension \( N \) where all elements are zero except that one corresponding to the atom type of the atom at the tessellation center, \( n_i \). An averaging volume is used to calculate the average composition vector for the sampled point, \( \vec{n}_i \). The average composition vector is normalized to calculate the equivalent mole fraction vector, \( \vec{X}(\vec{x}) \). The norm in Eq. 2.12 is given by the Manhattan metric or \( |\vec{n}| = n_1 + n_2 + n_3 + \ldots n_N \).

\[
\vec{X}(\vec{x}) = \frac{\vec{n}(\vec{x})}{|\vec{n}(\vec{x})|}
\]  

(2.12)

### 2.4.2 CaO-Doped Si\(_3\)N\(_4\) IGF Example

Steve Garofalini supplied the data set on which this method is demonstrated. The initial condition is a 19.16Å slab of 0.12 mole fraction CaO-0.88 mole fraction SiO\(_2\) sandwiched between Si\(_3\)N\(_4\) grains. The Si\(_3\)N\(_4\) grains have a misorientation \( \Delta \theta = 0 \). The molecular dynamics simulation entailed high temperature annealing at constant NVE followed by cooling and equilibration at 300K at constant NPT where \( P = 0.1 \text{MPa} \) using three-dimensional periodic boundary conditions. The resulting data set is a list of atomic species and positions.

The Voronoi tessellations corresponding to each atomic position were calculated using Qhull. A 0.15Å mesh was used to approximate the geometry where the composition vector at each mesh point was \( \vec{n}_{ijk} = (n_{Si}, n_{Ca}, n_{N}, n_{O}) \). Flat cylindrical volumes with radius \( r \) and half-height \( h \) were used for averaging where the axis of the cylinder was oriented parallel to the line traversed by the aperture to generate the profile. This was done to ensure enough mesh points in the averaging to approximate a one-dimensional plane average at each point \((x_0, y_0, z)\) in the profile. Cylinders with geometries specified by \( r = 5 \text{Å} \) and \( h = 2 \text{Å} \), \( r = 7.5 \text{Å} \) and \( h = 2 \text{Å} \), and \( r = 7.5 \text{Å} \) and \( h = 3 \text{Å} \) were used. The results are shown in Fig. 2-7.

Figure 2-7 illustrates the sets (Si, Ca, O, and N curves) resulting from three different coarse-grainings. Each set of composition curves has the same basic shape.
Figure 2-7: Comparison of atomistic and coarse-grained continuum fields for 19.16Å 0.12 mole fraction CaO-88 mole fraction SiO$_2$ film sandwiched between Si$_3$N$_4$ grains. (a) Schematic of atomistic data where the spheres represent atomic positions for Si (yellow), N (blue), O (red), and Ca (grey). (b) Coarse-grained composition profiles perpendicular to the IGF calculated using cylinders with $r = 5\text{Å}$ and $h = 2\text{Å}$, $r = 7.5\text{Å}$ and $h = 2\text{Å}$, and $r = 7.5\text{Å}$ and $h = 3\text{Å}$.

All of the composition sets display essentially constant composition values within the Si$_3$N$_4$ grains, for example. The smoothest grain profiles belong to the solid lines, or to the $t = 3\text{Å}$ and $r = 7.5\text{Å}$ set. This geometry corresponds to the largest averaging aperture and is predicted to produce the smoothest profiles. This will be taken to be the representative set for the rest of the discussion.

There are three general morphological features of the composition profiles: small wavelength fluctuations, localized transitions from grain to film values, and film profiles that vary on a length scale greater than that of the small wavelength fluctuations. The short wavelength fluctuations have a wavelength of approximately 3Å. The localized (relatively sharp) transitions occur over the space of approximately 7Å.

The N profile is constant in the grains and after a sharp transition is constant in the film. The O profile is constant in the grains and after a sharp transition fluctuates about a constant average in the film. The Si profile is constant in the grains then changes continuously across the film with small wavelength fluctuations. The Ca profile is constant in the grains and changes continuously across the film but displays
no short wavelength fluctuations. The short wavelength fluctuations in the O and Si profiles are anti-correlated.

The initial atomic film thickness is 19.16Å. The chemical thickness measured from the full-width half maximum of the oxygen profile is 17Å and from the nitrogen profile is 17.5Å. The Ca profile is smooth and has a local maximum at the center of the film. The Ca concentration is non-zero over approximately 13Å.

The ratio of Si to N in Si₃N₄ is $X_{Si}/X_N = 0.75$. This coarse-graining method gives a ratio closer to $X_{Si}/X_N = 0.5$. This discrepancy is an artifact of the tessellation based volume averaging because this volume averaging method treats the atoms as points, whereas the atoms have finite and different radii. The ratio of the atomic radii of Si and N is $r_{Si}/r_N = 1.69$.

### 2.5 Discussion

Both the Voronoi tessellation and BADF based measures of structure generate a short-range structural order parameter. The local measure of SRO in the system, not LRO, should control the localized structural contribution to the total energy. In fact, this is the basic assumption in the phase-field model: that the energy density is a local quantity or field. The local energy density is represented as the Taylor expansion of the homogeneous energy about small gradients in the fields. Therefore, the structural energy that is calculated for an infinitesimal volume element should depend only on SRO. For example, consider a covalently bonded material such as a silicate where the basic structural unit is a SiO₄⁻⁴ tetrahedron. In the amorphous solid, the O-Si-O bond angles and distances are approximately the same for each unit. Consider two tetrahedra surrounded by different local environments, one more crystalline and the other more liquid-like. It is the relation of each unit to the neighboring units that is captured in the gradient terms and properly contributes to the difference in energy.

In this coarse-graining method, the mesh is used as a way of approximating the
geometry of each tessellation. The best method is to find the exact intersection of the measuring aperture and each tessellation. This is straightforward for the polyhedral aperture using Qhull. However, in order to find the intersection with a spherical aperture, the sphere must be approximated as a convex polyhedron with very many faces. Finding the intersection of the volumes is equivalent to finding the convex hull of the tessellation and the approximated sphere. Qhull is capable of this but is much slower than the proposed stored-mesh method and must be performed for every sampling.

Another possible averaging technique is to spread the properties of each atom out in space according to a Gaussian relation. In other words, treat η or \( \bar{n} \) like a position dependent quantity with a probability density given by a Gaussian distribution. For example, the averaged η at a point \( \bar{x} \) is given by:

\[
\eta(\bar{x}) = \sum_i \frac{\eta_i}{\sigma\sqrt{2\pi}} \exp \left[ -\frac{(\bar{x} - \bar{x}_i)^2}{2\sigma^2} \right] \tag{2.13}
\]

In the above, the sum is over all the atoms \( i \), \( \eta_i \) is the structural measure of the tessellation corresponding to the atom located at \( \bar{x}_i \), and \( \sigma \) is the standard deviation of the distribution or a measure of the spread. I attempted to use this method but \( \eta(\bar{x}) \) does not exhibit the required uniform value in a perfect crystal, even for large \( \sigma \).

Two methods were shown for generating measures of structure to be compared to the \( \eta(\bar{x}) \) field of phase-field calculations. Figure 2-8 shows a comparison of the (3.5, 3.5, z) profiles generated using the anisotropy factor of Voronoi tessellations and the BADF overlap. Both methods used the same coarse-graining parameters.

The size of the maximum deviation from \( \eta = 1 \) for the two methods is separated by four orders of magnitude. However, the full-width half minimum interfacial widths are approximately the same although the BADF width is slightly narrower. Consequently, as a measure of interfacial widths the two methods appear comparable for this \( \Sigma 5 \)
Figure 2-8: Comparison of $\eta$ profiles from a Si $\Sigma 5$ grain boundary simulation set at (3.5, 3.5, $z$) based on Voronoi tessellations and the BADF overlap. Both use the same coarse-graining scheme.

grain boundary. The scaling rules for $\eta_t(\alpha_t)$, Eq. 2.4, and $\eta_t(S)$, Eq. 2.11, are linear. However, these are somewhat arbitrary and could be chosen to reduce the disparity (i.e., four orders of magnitude.) Therefore, the numerical deviation at the grain boundary is not important unless comparing different grain boundaries in the same system using the same structure determination method.

Both structural methods contain neighbor distance and angular information. Small changes in mathematical bond angle or bond length can eliminate a Voronoi nearest neighbor. For the BADF method, the choice of cutoff dictates which neighbors’ and bonds’ angular information is included. All atoms falling within the cutoff have the same weight in the BADF. For atoms located near the edge of the cut-off, a small change in bond length can radically change the BADF. It may be advantageous to apply a distance weighting to the BADF so that the sharp neighbor cutoff is smoothed over a small distance. For example, an exponential decrease in the weighting is illustrated in Eq. 2.14. The neighbors are all atoms within the outer cutoff of $R_o$. The BADF is weighted depending on the location of the atoms that contribute the bonds from which the angle is calculated. Full neighbors are within the inner cutoff of $R_i$ and the rest are weighted by $W(R)$ where $C$ is the weighting for $R = R_o$ and is chosen
to be a small number.

$$f_w(\cos \omega) = \frac{1}{N_b^2} \sum_{a,b=1}^{N_b} W(R_a)W(R_b)\delta(\cos \omega - \cos \omega_{ab}) \quad (2.14)$$

where

$$W(R) = \begin{cases} 1 & R \leq R_i \\ \exp \left[ \frac{C(R-R_i)}{(R_o-R_i)} \right] & R_i < R \leq R_o \end{cases} \quad (2.15)$$

The structural coarse-graining methods demonstrated in this paper have been illustrated for a single component solid simulation. Both methods are equally applicable to multicomponent substitutional solid solutions as long as the atomic radii of the species are similar. The geometry of the Voronoi tessellation or BADF of every atom in the perfect crystal at any composition is identical. The composition is measured with another phase-field and so should not be taken into account in the structural measure.

If the multicomponent system is more complex, then the neighbors for each method could be calculated from a subset of all of the atoms. For example, the BADF for measuring structure in Si$_3$N$_4$ ought to be the BADF corresponding to Si atoms using the subset of all N atoms for bonds. The coarse-graining can then be performed using only the Si positions to calculate the Voronoi tessellations. A similar construction could be used for the anisotropy method described in Section 2.2.2.

The scalings from the local measures of structure to $\eta$ are arbitrary. Consistency of method is the only important feature. In order to compare grain boundaries in Si, the scaling from $\alpha$ to $\eta$, Eq. 2.4, is sufficient for solid systems with some structural disorder. However, in materials near the melting point where grain boundary melting is important, a different scaling may be appropriate. It is possible that liquids and gases will have $\alpha_i > 2\alpha_{ws}$ and, therefore, $\eta_i < 0$, Fig. 2-1. For liquids and gases, a normalizing value different from $\alpha_{ws}$ may be needed, such as the average $\alpha_i$ for the
liquid or gas. In these cases, it may be preferable to use the BADF method.

The coarse-graining method for calculating continuum composition fields yields realistic results for a flat cylindrical averaging aperture. While the relative magnitudes of the mole fractions of Si and N in Si₃N₄ are incorrect, the interfacial widths measured by full-width half maximum are reasonable. The short-wavelength variation in the Si and O profiles within the film appears to be a real effect suggesting an alignment of Si and O rich regions within the film and parallel to the grain edges. The Ca is concentrated within the center of the film.

The structural methods were illustrated using a simulated grain boundary relaxed at zero temperature. For non-zero temperature simulations, there is a further complication due to thermal noise.

In MC simulations, phase space is sampled using, for example, the Metropolis algorithm. After a large number of steps, the equilibrium state is that which has the most occurrences in phase space. This equilibrium configuration, set of positions, can be input directly into the coarse-graining method.

However, for MD, the atoms are moved around according to the force on each atom. When the total energy converges to a roughly constant (minimum) value or the force on each atom drops below some limit, the system is taken to be equilibrated for constant temperature simulations. However, thermal vibrations (Debye-Waller effect) imply that the atoms are moving about their equilibrium positions. Commonly, the trajectories of the atoms are then followed and averaged to give the equilibrium positions which may be input to the coarse-graining method.

One possible problem with the phase-field model is the assumed spreading of interfaces which may, in fact, be sharp. Using these coarse-graining methods, the structural width of the interface is also increased. This method, therefore, allows a direct comparison between atomistic grain boundary simulations and phase-field simulations. Boundary widths can be computed from a phase-field model and matched to those generated from coarse-graining simple atomistic simulations. This will allow
the incorporation of small-scale physics into larger-scale phase-field calculations of complicated microstructures.

The three-dimensional atom probe (3DAP) provides data on the spatial distribution of chemical species evaporated from the tip of a probe [67, 68]. The spatial resolution of the technique is 2Å laterally and 0.6Å in the perpendicular direction for a pure metal [67]. The effectiveness of this method applied to ceramic systems exhibiting intergranular glassy films should be limited by thermal effects and the difference in ionization potentials for the constituents. However, using MD or MC experiments in concert with 3DAP could provide data sets for coarse-graining. These results could be used to develop phase-field models.

In the KWC phase-field model, Section 1.8.1, there are two fields, \( \eta \) and \( \theta \). I have addressed methods of extracting the local measure of structure, \( \eta \), from atomic data sets. It is more difficult to extract a local measure of orientation, \( \theta \). The orientation is an angular measure relating the rotation of a unit to a reference unit located in the laboratory reference frame and is therefore reference-frame dependent. The unit could be a BADF or a Voronoi tessellation.

For example, consider an atom in a grain away from the grain boundary. The Voronoi tessellation of the atom has the same anisotropy factor as the reference Wigner-Seitz cell, however it is rotated with respect to the reference. Some characteristic features must be defined for the cell so that a relative rotation of these will bring the Voronoi tessellation of the atom into coincidence with that for the reference. In three dimensions, the rotation is measured by three angles so \( \vec{\theta} \) is a three dimensional vector.

In order to use this method, the atom's Voronoi tessellation must be a Wigner-Seitz cell. At the grain boundary, that is not the case. Therefore, a consistent method of shearing and rescaling a distorted tessellation must be devised before the relative rotation is calculated. The information on the transformation from an arbitrary Voronoi tessellation to the Wigner-Seitz cell would be a useful way of measuring local
strain.

In parallel, similar concepts can be applied to the BADF. In order to define some characteristic features for the BADF of an atom in a grain away from a grain boundary, a subset of atoms within the neighbor cut-off could be used, for example the four nearest neighbors in Si. A reference atom in a crystal oriented in the laboratory reference frame is chosen. Three directional bonds are added to the neighbor bonds for the reference and the BADF is calculated. The bonds ought to be generated from the vectors $(1,0,0)$, $(0,1,0)$, and $(0,0,1)$. The BADF of an arbitrary atom in the data set is calculated including the three additional reference bonds. The smallest angular rotation necessary to get coincidence of the BADFs of the reference and atom give $\tilde{\theta}$.

For an atom near the grain boundary, a consistent way of mapping the BADF of an atom onto the BADF of the reference is necessary. This information can be used to calculate local strain. Once the BADF of the atom and reference are the same, the directional bonds are added and $\tilde{\theta}$ is calculated.

Both of these suggested procedures must include symmetry information for the perfect crystal. The rotation angles must be reduced to the smallest subset allowed by the point group of the crystal.

### 2.6 Summary and Conclusions

A set of methods for calculating continuum representations of structure and chemistry from discrete atomic data sets have been developed. Two methods for calculating a coarse-grained measure of local structure or SRO from atomic data sets based on Voronoi tessellations and on BADFs, respectively, are illustrated. These methods are reference-frame invariant. The structure determination is based on the geometric properties of the Voronoi tessellations or the BADF of discrete atomic positions. A continuous parameter suitable for comparison to the $\eta(\vec{x})$ phase-field is produced.
The structural methods were applied to simulation results for a Σ5 grain boundary in silicon. The coarse-grained profiles of the structural order parameter, $\eta(x_0, y_0, z)$, reveal a smooth transition across the interface similar to the results of phase-field simulations [37]. Both methods give approximately the same interfacial thickness. A comparison of the two methods for the same profile indicates strain but no bond distortion near the grain boundaries.

In addition, a coarse-graining method for calculating continuous composition profiles across interfaces with non-bulk equilibrium chemistries is examined. The method was illustrated on a simulated CaO-SiO$_2$ IGF between Si$_3$N$_4$ grains. The resultant profiles exhibit a reasonable film thickness, calcium adsorption to the center of the film, and apparent ordering of Si and O within the film.

The methods as described above can be applied readily to MD or MC simulation results. Further development is needed to calculate appropriate measures of SRO in multi-component systems. Also, a suitable method for calculating the local orientation is necessary to connect atomistic simulations to continuum grain boundary descriptions. Some approaches to this problem and possible measures of local strain were discussed.
Chapter 3

Stability of Locally Charged Domains in Phase-Separating Ionic Systems

3.1 Introduction

The classical approach to spinodal decomposition formulates the chemical instability of an alloy [24]. The theory predicts the conditions for and the characteristic length-scale of instability with respect to composition fluctuations. It is possible in ionic systems that a composition fluctuation would also induce a charge-density fluctuation that is not considered in the classical analysis. While deviations from electro-neutrality will always increase the electrostatic energy in systems with other energetic effects, it is conceivable that in some systems for which like neighbor bonds are favored (such as with partially covalent bonding or van der Waals interactions) that small regions with nonzero charge density could be stable. The long-range effect of a periodic charge-density fluctuation would be similar to a Madelung energy and therefore systems with large dielectric constant would be candidates for such

\[1\] Parts of this Chapter were published in [69].
charged instabilities. Furthermore, because the energy will increase with the size of the charged domains, it should be expected that an upper bound for the size of the charged domain will exist. There are unpublished experimental observations in partially-ionic systems that suggest that such charged composition fluctuations may exist [70].

This chapter presents theory, stability analysis, and phase-field simulations of the early stages of spinodal decomposition in an ionic solid with a comparison to simple chemical and elastic systems. The minimum stable size, the fastest growing wavelength, and the coarsening limit are predicted from theory [69].

The object of this work is to present a thermodynamic approach to unstable ionic systems that incorporates Maxwell's equations naturally. An ionic material with constituents $A^{+a}$, $B^{+b}$, and $C^{-c}$ that is chemically unstable with respect to fluctuations in cation concentration is considered. The neutral composition is $A_{y_0}B_{1-y_0}C_{z_0}$ where $y_0$ is the fraction of $A^{+a}$ ions on the cation sites and $z_0$, the ratio of the number of anion to cation sites, is fixed. This Chapter examines the stability of systems that are unstable with respect to fluctuations in $y$, the fraction of $A^{+a}$ ions on the cation sites, about $y_0$, the neutral fraction.\footnote{The current work is consistent with a general approach described in a recent paper on the application of a general thermodynamics-based approach to materials problems in electrically and magnetically active systems [71].}

After completion of this work, it was pointed out by L-Q. Chen and B. Stephenson that the same result had been derived in a different manner in a Ph.D. Thesis by K.M. Gupta [72]. The work presented here was completed without knowledge of the earlier work. Gupta's thesis examines the effect of charge in spinodally decomposing ionic systems of three components.\footnote{Gupta's work was not published elsewhere. The present Chapter differs from Gupta's work in the form of the free energy and treatment of Maxwell's Equations and also extends the results with numerical simulations.}

Experimentally observed and simulated non-uniform composition profiles in ionic systems were discussed in Sections 1.3 and 1.4. In these systems, in addition to
the normal bulk interactions, there is a competition between surface adsorption of a particular ionic species and electrostatic interactions, Fig. 3-1. Therefore, the method illustrated below should be directly applicable to finite or constrained systems.

Other authors have considered the effects of charged boundaries and defects in ionic systems. A brief description of some of those treatments of the electrostatic contributions to the energy is given to provide background and for comparison with the method presented in this chapter. The present treatment includes energetic contributions from externally applied as well as internally generated electric fields.

Yan et al. examine the relative strengths of elastic, electrostatic (\(\frac{1}{2} \phi \rho\)), and bipolar (\(-\frac{1}{2} \vec{F} \cdot \vec{E}\)) contributions to the free energy of a boundary region of a ceramic grain boundary [73]. The authors split up the electric contributions for the case that there are no externally applied fields.

Chen and Khachaturyan examine the effect of long-range Coulombic interactions during simultaneous microscopic ordering and phase separation [74]. The authors explicitly include a screened Coulomb potential with exponential form. Simulations suggest that the Coulombic term halts the coarsening in Fourier spectral space simulations at a finite wavelength. A typical scale for the decomposition is derived by minimizing the energy represented in spectral space with respect to wavenumber. In the present derivation, neither the form of the electrostatic energy nor a cutoff is
imposed.

Clarke et al. examine the effects of a double-layer on the stability of intergranular glassy films [35]. This work, described in Section 1.7, does not include an energetic description of the system, but instead considers only forces on a planar boundary.

This chapter presents a stability analysis and confirming phase-field simulations for a ternary ionic material that is unstable to fluctuations in cation site fraction implying local deviations from neutrality at the temperature of interest. The general theory and stability analysis for systems of this type are presented in Section 3.2. The results of the stability analysis are discussed along with the simulations later in Section 3.4.

### 3.2 Theory

The differential of the internal energy of a system with charged species is given by Eq. 3.1 where the natural variables, $S, V, n_i, q$, and $\vec{D}$, are entropy, volume, number of atoms of the $i$th species, the total charge, and the electric displacement vector, respectively. The conjugate intensive variables, $T, P, \mu_i, \phi$, and $\vec{E}$, are temperature, pressure, chemical potential of the $i$th species, electric potential, and applied electric field, respectively.

$$dU(S, V, n_i, q, \vec{D}) = TdS - PdV + \mu_i dn_i + \phi dq + V_0 \vec{E} \cdot d\vec{D}$$  \hspace{1cm} (3.1)

The internal energy is a first-order homogeneous function of its natural variables. In Eq. 3.1, the electric work is split into two contributions: that from the charge in the system, $\phi dq$, and that from the total applied fields, $V_0 \vec{E} \cdot d\vec{D}$, where $V_0$ is a stress-free reference volume. This splitting allows the model to account for electric potential resulting from the charge distribution within the system as well as any superposed externally imposed potential gradient.

For the analysis of materials at fixed $T, V, n_i, q$, and $\vec{E}$, the appropriate thermody-
namic state function that is minimized at equilibrium is a partial Legendre transform of the internal energy \( F = U - TS - V_0 \tilde{E} \cdot \tilde{D} \), the Helmholtz free energy, given in differential form below [75].

\[
dF(T, V, n_i, q, \tilde{E}) = -SdT - PdV + \mu_i dn_i + \phi dq - V_0 \tilde{D} \cdot d\tilde{E}
\] (3.2)

This function is homogeneous degree one in \( V, n_i \), and \( q \). The Helmholtz free energy that serves as a state function of the variables \( (T, V, n_i, q, \tilde{E}) \) results from integrating this function from an initial state to an arbitrary state, Eq. 3.3. The conjugate variables are, in general, functions of all of the natural variables for \( F \), e.g., \( \mu_i = \mu_i(T, V, n_i, q, \tilde{E}) \). But as \( F \) is a state function, each integration is performed in succession to incrementally generate the total free energy by holding all other natural variables constant. The stress-free reference state is taken to have the temperature and volume of interest, so these become parameters in this problem.

\[
F(n_i, q, \tilde{E}; T_0, V_0) = F_0(n_{i,0}, q_0, \tilde{E}_0, T_0, V_0) + \int_{n_{i,0}}^{n_i} \mu_i dn_i' + \int_{q_0}^{q} \phi dq' - V_0 \int_{\tilde{E}_0}^{\tilde{E}} \tilde{D} \cdot d\tilde{E}' (3.3)
\]

A linear constitutive relation between \( \tilde{D} \) and \( \tilde{E} \), \( \tilde{D} = \varepsilon \tilde{E} \), where \( \varepsilon \) is the dielectric permittivity tensor, gives Eq. 3.4 and dividing by the reference volume gives the Helmholtz free energy density, Eq. 3.5.

\[
F(n_i, q, \tilde{E}; T_0, V_0) = F_0 + \mu_i n_i + \phi q - \frac{1}{2} V_0 \varepsilon \cdot \varepsilon \tilde{E} \] (3.4)

\[
\tilde{F}(c_i, \rho, \tilde{E}; T_0) = \tilde{F}_0 + \mu_i c_i + \phi \rho - \frac{1}{2} \tilde{E} \cdot \varepsilon \tilde{E} \] (3.5)

Above, \( \tilde{F}_0 \) is the free energy density of the reference state in J/m\(^3\), \( c_i \) is the concentration of the \( i \)th species in moles/m\(^3\), and \( \rho \) is the charge density in C/m\(^3\).

Using the assumption of local equilibrium, the Helmholtz free energy density for a heterogeneous system is represented as a Taylor expansion of the homogeneous free energy density in gradient terms, Eq. 3.6 [24, 76, 77]. The thermodynamic variables
vary with position and the local values are representative of macroscopically small but microscopically large volumes such that these are appropriate to calculate the local contribution to the free energy. The gradient energy terms, where $\kappa_i^{\dagger}$ is the gradient energy coefficient tensor for the $i$th species, intrinsically account for the interfacial free energy of internal diffuse interfaces. Assuming negligible magnetic effects, $\nabla \times \vec{E} = 0$ and $\vec{E} = -\nabla \phi$. The total free energy of the system is the integral of the free energy density over the volume, $\Omega$.

$$F[c_i, \rho, \phi; T_0, \Omega] = \int_{\Omega} \left[ \left\{ \vec{F}_0 + \mu_i c_i + \phi \rho \right\} + \left\{ \frac{1}{2} \nabla c_i \cdot (\kappa_i^{\dagger} \nabla \phi) \right\} \right] dV$$  

(3.6)

The electrostatic free energy term has a similar form to the first order gradient energy terms with a negative gradient energy coefficient, $-\kappa_i^{\dagger}$. However, its origin is the integration of the differential electrostatic enthalpy ($-V_0 \vec{D} \cdot d\vec{E}$), while the gradient terms derive from a Taylor expansion about a homogeneous system in gradients of the composition fields. A discussion of why this term doesn’t lead to infinitely large gradients in $\phi$ is given below.

By considering an infinite three-component ionic solid composed of $A^{+a}$, $B^{+b}$, and $C^{-c}$ possessing at least cubic symmetry, the tensors reduce to scalars. Let the average composition of the solid be $A_{y_0} B_{1-y_0} C_{z_0}$ so that in one formula unit the neutral solution gives the following relation: $a y_0 + b (1-y_0) - c z_0 = 0$. While requiring global charge neutrality, relaxing the restriction of local charge neutrality permits the possibility of the formation of charged domains. The local number density of electrons is $\sigma(\vec{x})$ given by $\sigma(\vec{x}) = y(\vec{x}) (b-a) + (c z_0 - b)$. This is a rescaling that allows the local charge density to be written as a linear function of the local occupation of cation sites by $A^{+a}$ that is convenient for the following mathematics.

For example, consider bulk MgTiO$_3$ or Mg$_{y_0}$Ti$_{1-y_0}$O$_{1.5}$. The local excess electron density is zero when $y(\vec{x}) = y_0 = 0.5$. When the local cation site fraction is $y(\vec{x}) = 0$, the composition is TiO$_{1.5}^{+1}$ and the number density of electrons is $\sigma(\vec{x}) = -1$. When
Figure 3-2: Schematic of the chemical contribution to the homogeneous free energy, $f(\sigma)$, as a function of number density of electrons, $\sigma$, for a ternary system with fixed anion concentration and variable site fraction of cations, $y$. The maximum corresponds to the neutral composition and the minima correspond to charged structural units. Because the charge is linearly related to the site fraction of cations, $y$, $f(y)$ has a similar but rescaled double well form.

the local cation site fraction is $y(\bar{x}) = 1$, the composition is MgO$_{1.5}$ and $\sigma(\bar{x}) = 1$.

The charge density is $\rho(\bar{x}) = -\frac{e}{V_m} \sigma(\bar{x})$ where $F$ is Faraday's constant or the magnitude of the charge of a mole of electrons and $V_m$ is the molar volume. The model system has fixed $z(\bar{x}) = z_0$ and is unstable with respect to fluctuations in $y(\bar{x})$. The chemical contribution to the homogeneous free energy density at fixed volume, temperature, and anion concentration is a function of only the charge (or cation site occupation density, $y(\bar{x})$) and has the following form, Fig. 3-2.

The constraint of global mass conservation, $0 = \int_{\Omega} \sigma(\bar{x}) dV$, is included with a constant Lagrange multiplier, $\lambda$, so that the constrained Helmholtz free energy takes the following form, Eq. 3.7, where $f(\sigma) = F_0 + \mu_A c_A + \mu_B c_B + \mu_C c_C$.

$$F[\sigma, \phi] = \int_{\Omega} \left[ \left\{ f(\sigma) - \frac{F}{V_m} \sigma \phi - \frac{1}{2} \epsilon \nabla \phi \cdot \nabla \phi + \lambda \sigma \right\} + \frac{1}{2} \kappa |\nabla \sigma|^2 \right] dV \quad (3.7)$$

An equilibrium state of the system is described by the condition $\delta F = 0$ where $\delta F$ represents a variation in the free energy [32]. In this case, there are two independent field parameters, $\sigma$ and $\phi$. A necessary condition for a weak extremum in the free
energy is given by the Euler-Lagrange equations in Eq. 3.8 and Eq. 3.9 [32].

\[
\frac{\delta F}{\delta \sigma} = 0 = \frac{df}{d\sigma} - \frac{\mathcal{F}}{V_m} - \phi - \kappa \nabla^2 \sigma + \lambda \tag{3.8}
\]

\[
\frac{\delta F}{\delta \phi} = 0 = -\frac{\mathcal{F}}{V_m} \sigma + \epsilon \nabla^2 \phi \tag{3.9}
\]

The electric potential is assumed to be in steady state (instantaneous equilibrium with the composition field.) Therefore, Eq. 3.9 is always satisfied. This is Coulomb’s Law that states that the charge density is the source of electric field.

The stability of an extremal solution can be determined by analyzing the stability of the appropriate kinetic equation for \( \sigma \). As mass is conserved, \( \sigma \) is a conserved order parameter and the appropriate kinetic equation is the Cahn-Hilliard equation, Eq. 3.10, where \( M \) is a mobility [33].

The Lagrange multiplier is the electro-chemical potential of the system at equilibrium and does not appear in the kinetic equation.

\[
\frac{\partial \sigma}{\partial t} = M \left[ \nabla^2 \frac{df}{d\sigma} - \frac{\mathcal{F}}{V_m} \nabla^2 \phi - \kappa \nabla^4 \sigma \right] \tag{3.10}
\]

Substitution of Coulomb’s Law, Eq. 3.9, yields

\[
\frac{\partial \sigma}{\partial t} = M \left[ \nabla^2 \frac{df}{d\sigma} - \frac{\mathcal{F}^2}{V_m^2} \sigma - \kappa \nabla^4 \sigma \right] \tag{3.11}
\]

Introducing non-dimensional parameters, \( \xi, \tau, \) and \( \gamma \), with \( \bar{\omega} = \frac{\omega}{\tau M f_0^2} \), \( t = \tau \left( \frac{\kappa}{M f_0} \right) \) and \( \gamma = \frac{\mathcal{F}^2}{f_0^2 V_m^2} \). Here, \( f_0 \) is the magnitude of the curvature of \( f(\sigma) \) at the consulate composition, \( f_0 = \frac{df}{d\sigma} \bigg|_{\sigma = \sigma_0} \). The working form of the kinetic equation is Eq. 3.12.

\[
\frac{\partial \sigma}{\partial \tau} = \frac{1}{f_0} \nabla^2 \frac{df}{d\sigma} - \gamma \sigma - \nabla^4 \sigma \tag{3.12}
\]

The kinetic equation for the initial stages of decomposition is obtained by expanding the free energy density, \( f(\sigma) \), to second order about the consulate point and
introducing a one-dimensional perturbation in composition about \( \sigma_0 = 0 \) along the \( \xi_1 \)-direction with small time-dependent amplitude, \( A(\tau, \beta) \), and dimensionless wavenumber \( \beta \).

\[
\sigma(\tau, \xi_1) = \sigma_0 + A(\tau, \beta) \sin \beta \xi_1
\]  
(3.13)

Substitution of the Taylor expansion and Eq. 3.13 into Eq. 3.12 gives Eq. 3.14 for the time dependence of the amplitude of the Fourier mode with wavenumber \( \beta \).

\[
\frac{dA}{d\tau} = A \left[ \beta^2 - \gamma - \beta^4 \right]
\]  
(3.14)

The form of \( A(\tau, \beta) \) that satisfies Eq. 3.14 is given in Eq. 3.15 where \( R(\beta) \) is the growth factor.

\[
A(\tau, \beta) = A(0, \beta) \exp [R(\beta) \tau]
\]  
(3.15)

\[
R(\beta) = \beta^2 - \gamma - \beta^4
\]  
(3.16)

If the growth factor is positive, the amplitude of a fluctuation will grow in time (the perturbation is stable). However, if the growth factor is negative, the amplitude will decay in time (the perturbation is unstable). In the electro-chemical case there are maximum and minimum wavenumber cutoffs, \( \beta_{chem} \) and \( \beta_{elec} \), respectively, beyond which the system is stable with respect to perturbations. The critical values of the wavenumbers, \( \beta_{elec} \) and \( \beta_{chem} \) satisfy \( R(\beta) = 0 \), the static case. Figure 3-3 is a graphical representation of the results of the linear stability analysis for short times. The stability limits are given by the roots of Eq. 3.16 where \( \beta_{max}^2 = \frac{1}{2} \) is the wavenumber corresponding to the maximum \( R(\beta) \).

\[
\left( \frac{\beta}{\beta_{max}} \right)^2 = 1 \pm \sqrt{1 - 4\gamma}
\]  
(3.17)

These stability limits may be compared to those from analyses by Cahn and Hilliard of the chemical case and Cahn of the elasto-chemical case [24, 26]. In the second
Figure 3.3: Depictions of the stability limits for an unstable ionic system. a) For a given value of $\gamma$, the amplitude of Fourier modes with normalized wavenumbers corresponding to the interior area grow in time. b) Wavenumbers with $R(\beta) > 0$ grow in time. The present case (electro-chemical) is compared to two other previously analyzed cases (chemical and elasto-chemical).

of these, Cahn assumes that the molar volume is a linear function of composition so that a composition fluctuation introduces a corresponding strain energy density fluctuation. A stability analysis shows that the effect of the elastic terms is to alter the shape of $R(\beta)$ so as to reduce the $\beta_{\text{max}}$ and the maximum value of $R(\beta)$. It is straightforward to include strain effects in the present scheme to consider the stability of an ionic material with a size mismatch between the ions to small perturbations in composition.

3.3 Simulations

The kinetic equation, Eq. 3.12, was simulated on a periodic two-dimensional ionic system like $\text{Mg}_{0.5}\text{Ti}_{0.5}\text{O}_{1.5}$ that is unstable to small fluctuations in cation site occupation in the absence of Coulombic effects. Therefore, the free energy is written as a quartic function given by $f(\sigma) = \frac{K}{4}(\sigma^2 - 1)^2$. The dimensionless kinetic equation for the composition field, Eq. 3.12, transformed to Fourier space is given in Eq. 3.18
where \( \hat{\sigma} \) indicates the Fourier transform, \( \hat{\sigma} \) is the amplitude of each Fourier mode, 
\( g(\sigma) = \frac{1}{p_{0}} \frac{df}{d\sigma} = \sigma^{3} - \sigma \), and \( k = |\vec{k}| = |k_{x}i + k_{y}j| \) is the magnitude of the wave vector.

\[
\frac{d\hat{\sigma}}{d\tau} = -k^{2}g(\sigma) - \gamma \hat{\sigma} - k^{4}\hat{\sigma}
\]  
(3.18)

A semi-implicit, Fourier-spectral scheme where the derivatives are accurate in space and accurate to first-order in time is employed [78].

\[
\hat{\sigma}^{t+1}(1 + \Delta\tau(\gamma + k^{4})) = \hat{\sigma}^{t} - \Delta\tau k^{2}g(\sigma)^{t}
\]  
(3.19)

The simulation parameters are \( n_{x} = n_{y} = 200 \), \( \Delta\tau = 10^{-2} \), and the grid spacing (half the shortest wavelength) is \( \Delta \xi = \frac{\lambda_{\min}}{2} = 0.1 \). The initial condition is assigned in real space according to \( \sigma(\vec{x}) = 0.05(2r - 1) \) where \( r \) is a random number from a uniform distribution, \( 0 \leq r \leq 1 \), then transformed into spectral space. However, the magnitudes of the initial Fourier amplitudes are not part of a uniform random distribution but exhibit a maximum around \( k = 100 \). This effect damps out after a very short time. Simulations with different values of \( \gamma \) were performed, \( 0 \leq \gamma \leq 0.25 \). The simulation results are presented as the amplitude of each Fourier mode versus the magnitude of the wavevector for different times during simulations for the pure chemical case with \( \gamma = 0 \) and for the electro-chemical case with small dielectric constant or large gradient energy, \( \gamma = 0.23 \), in Fig. 3-4.

### 3.4 Discussion

In this section, the stability of this electro-chemical system is compared to chemical and elasto-chemical systems. For the electro-chemical case, there is a range of growing wavenumbers within the bounds determined by the undercooling, effective permittivity of the material, molar volume, and the gradient energy coefficient. Figure 3-3 shows the normalized range of values of \( \beta \) corresponding to growing amplitudes.
Figure 3-4: Graphs of the amplitude of each Fourier mode against the magnitude of each wavenumber for different number of iterations for experiments with $n_x = n_y = 200$ and $\Delta \tau = 10^{-2}$ with (a) $\gamma = 0$ and (b) $\gamma = 0.23$. The maximum magnitude of the wavenumber in this work is $k_{max} = 100\sqrt{2}$, but these plots focus on the low wavenumbers because the large wavenumbers damp out very fast. Both plots show approximately the same magnitude of the fastest growing wavenumber at the longest time, but the electro-chemical system takes longer to reach this state.

cause $\gamma \propto 1/\epsilon$, small values of $\gamma$ are representative of large values of $\epsilon$. This case approaches the chemical limit where $\left(\frac{\beta_{\text{chem}}}{\beta_{\text{max}}}\right)^2 = 2$ and $\left(\frac{\beta_{\text{chem}}}{\beta_{\text{max}}}\right)^2 = 0$, consistent with Fig. 3-3. If $f_0$ is small, then $\gamma$ approaches 0.25 and there is a small range of wavenumbers for stable perturbations.

The maximum or fastest initial growing wavenumber in the electro-chemical case $\beta_{\text{max}} = \frac{1}{2}$ is the same as the maximum growing wavenumber in the pure chemical case. The amplification factor for the electro-chemical case is shifted by a constant equal to $-\gamma$ with respect to the chemical case. For $\gamma \geq 0.25$, there are no wavenumbers corresponding to growing amplitudes. This means that for short times the system is stable with respect to fluctuations of all wavenumbers within this linear analysis. For $0 \leq \gamma < 0.25$ (large dielectric constant) there is a short wavenumber cutoff in the electro-chemical case. This cutoff comes about from the electrostatic energy of charged regions separated by large distances. In the energy functional, Eq. 3.6, this is the third term contributing like a gradient energy penalty even though its origin is the homogeneous free energy term. A gradient energy term with a negative
coefficient might be expected to induce infinitely large gradients in the corresponding independent field in order to minimize the free energy functional at equilibrium. However, that is not the case here because the values of the corresponding independent parameter, $\phi$, are coupled to the composition field through $\epsilon$.

The plots of the Fourier amplitudes, Fig. 3-4, as a function of wavenumber for the chemical case ($\gamma = 0$) and an electro-chemical case ($\gamma = 0.23$) support the above conclusions. The large wavenumber modes decay most rapidly for both cases. For the chemical case, all wavenumbers below some critical value initially grow. In contrast, for the electro-chemical case, small wavenumber modes decay as well as large wavenumber modes so that the system doesn't coarsen beyond a cutoff wavenumber. This suggests that coarsening will be limited in the electro-chemical case; this is in contrast to the elasto-chemical case where domains of arbitrarily large size will develop. Also, the amplitude of the fastest growing mode is larger for the chemical case than for the electro-chemical case at any given time, compare Fig. 3-4 a) $t=100$ to Fig. 3-4 b) $t=500$. This effect is also illustrated in Fig. 3-3 where $R(\beta_{\text{chem}}) > R(\beta_{\text{electro-chem}})$. In addition, the initial curves for the data exhibit sharp peaks which smooth out in time as the distribution of stable wavenumbers narrows.

3.5 Summary and Conclusions

The Helmholtz free energy functional for a system with separate terms for the electrostatic work due to introducing charges into the system and for polarizing the medium can be used to model the instability in an ionic system. This functional is defined for a system at constant $T, V, n_i, q$, and $\vec{E}$, but the extension to other conditions is straightforward. A linear stability analysis for a model ternary system of ions decomposing into $A^{+a}$-rich and $B^{+b}$-rich domains due to small fluctuations in cation site occupation shows that, unlike the pure chemical case, there is a small wavenumber cut-off below which the system is stable with respect to fluctuations in cation
site occupation. This conclusion was confirmed with numerical calculations. The results suggest that for given undercoolings, dielectric permittivities, molar volumes, and gradient energy coefficients, decomposing systems will cease to coarsen beyond a cutoff scale given by $\beta_{\text{electro-chem}}$.

This analysis implies that charged domains may be observed in some ionic systems and quantifies the material properties that are required for their existence. It also presents microstructural scales that can be used to compare with experimental observations. The behavior of charged domains in an alternating electric field may significantly influence the behavior of ferroelectric materials. The behavior of model systems as a function of the frequency of an applied field remains an interesting problem.

The Helmholtz free energy density derived in this chapter is the correct thermodynamic potential to use for the basis of the analysis of intergranular films in silicon nitride. This potential naturally incorporates Coulomb's Law and introduces a coupling between chemical and electrostatic effects. The analysis here predicts that this coupling is enough to stabilize locally charged domains. In the model to be presented in Chapter 4, additional effects that are not included in macroscopic thermodynamic analysis are introduced.
Chapter 4

Phase-Field Model for CaO-doped Si$_3$N$_4$

In this chapter, a phase-field model for examining intergranular glassy films in CaO-doped Si$_3$N$_4$ is developed. The model incorporates bulk-equilibrium thermodynamic information as well as general energetic trends in the couplings. The parameters in the model are a small set that can be adjusted so that the macroscopic fields predicted herein fit coarse-grained atomistic and experimental data.

4.1 General Form of the Functional

For a non-uniform system with constant molar volume $V_m$, the free energy functional that produces the total Helmholtz free energy of a heterogeneous system containing a grain boundary is given by Eq. 4.1. The mole fraction of each chemical species is $X_i$, $\rho$ is the charge density, $\phi$ is the electrostatic potential, $\eta$ is a measure of local structure defined so that $\eta(x) = 1$ represents a perfect crystalline environment and $\eta(x) < 1$ represents decreasing crystallinity, $\theta$ is a local measure of orientation, and $T$ and $\Omega$ are parameters in this model, where $T$ is the temperature and $\Omega$ is the total volume of the system. The integrand is non-dimensionalized to facilitate the analysis.
\[
F[X_i, \rho, \phi, \eta, \theta; T, \Omega] = \frac{1000RT}{V_m} \int_\Omega \left\{ f(X_i; \eta; T) + \frac{V_m}{1000RT} \rho \phi - \frac{1}{2} \frac{V_m}{1000RT} \epsilon (\nabla \phi)^2 \\
+ \frac{1}{2} \sum_i (\kappa_i^2 (\nabla X_i)^2) \\
+ \frac{1}{2} \nu^2 |\nabla \eta|^2 \right\} dV
\] (4.1)

The homogeneous free energy contributions are outlined in the first line of the integrand. The chemical and structural contributions to the homogeneous molar free energy are given by \( f(X_i; \eta; T) \). An appropriate form for this homogeneous free energy is discussed in Section 4.2. The electrostatic contributions to the homogeneous free energy are formulated as in Chapter 3 and allow externally applied fields to be included in the energetics. The temperature is a parameter that is fixed for this calculation.\(^1\)

The second line of the integrand contains the gradient energy penalties that intrinsically include chemical contributions to the interfacial energy, where \( \kappa_i \) is the gradient energy coefficient for component \( i \). These gradient energy coefficients are chosen to be constants for this work. In general, these are tensors and depend on the temperature and other independent fields, \( \text{e.g.}, \kappa_{Si}^+ = \kappa_{Si}^- (X_i; T) \).

The final line of the integrand contains gradient energy penalties that intrinsically include structural contributions to the interfacial energy. These terms are based on the KWC model outlined in Section 1.8.1 [37]. The \( s, \beta, \) and \( \nu \) are adjustable parameters. These parameters determine the structural width and energy of interfaces in concert with the homogeneous free energy. However, due to the multiple couplings introduced here, an analytic solution to the coupled Euler-Lagrange equations for equilibrium has yet to be found. So these parameters should be adjusted in order to give equilibrium interfacial profiles that agree with coarse-grained atomistic and

\(^1\)If the temperature were an independent field, then the appropriate thermodynamic potential for the analysis would be based on the entropy not the free energy [79].
Figure 4-1: Illustrations of the effect of network modifiers on the structure and viscosity of SiO$_2$-based glasses. (a) Schematic representation of the structure of a sodium silicate glass with oxygen (green), silicon (blue) and sodium (red). Each Na$_2$O addition results in the formation of two non-bridging oxygen-terminated silica tetrahedra. Reproduced from Fig. 5.5 in Kingery [3]. (b) Effect of modifier oxides on the viscosity of fused silica. □, Li$_2$O-SiO$_2$, 1400°C; ○, K$_2$O-SiO$_2$, 1600°C; Δ, BaO-SiO$_2$, 1700°C. Reproduced from Fig. 14.50 in Kingery [3].

experimental data.

The change in orientation in an IGF in the CaO-doped Si$_3$N$_4$ system occurs in the silicate based glass. The energetic penalties for orientational gradients should be reduced by network modifiers in the glass. Network modifiers decrease the number of bridging oxygen bonds, Fig 4-1(a). Calcium is a network modifier in silicate based glasses [80]. In dynamic experiments, small additions of Ca decrease the viscosity of silicate based glasses by orders of magnitude, Fig. 4-1(b). Therefore, as Ca reduces the stiffness of the network it ought to decrease the energetic penalty for bending bonds. The function $g(X_{Ca})$ ought to be a monotonically decreasing function of $X_{Ca}$ in the domain $0 \leq X_{Ca} \leq 1$. 

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4.2 The Homogeneous Free Energy for Non-Bulk Equilibrium Compositions and Structures

The chemical and structural contributions to the homogeneous free energy, \( f(X_i, \eta; T) \), must be defined not only for bulk equilibrium compositions and structures but also for non-bulk equilibrium states as they exist at the diffuse interfaces implied by this model. All bulk-solid equilibrium compositions are charge-neutral and most are crystalline. Using the assumption of fixed formal charge allows the bulk-equilibrium phase relations to be illustrated on an equivalence salt diagram [80].

More information must be included in \( f(X_i, \eta; T) \) so that the chemical contribution to the total energy density of net-charged compositions can be calculated. The analysis in Chapter 3 illustrates that non-neutral compositions can be stabilized under certain conditions. As the intergranular material has non-bulk equilibrium compositions and structures, which, in addition, are expected to vary in space, it is necessary to calculate an energetic contribution for these.

4.2.1 Expansion of the General Homogeneous Free Energy

The following approximation is employed in order to self-consistently use as much bulk-equilibrium information as possible. The chemical and structural contribution to the homogeneous free energy is approximated by an expansion of the dimensionless energy about a corresponding net-neutral composition, Eq. 4.2.

\[
 f(X_i, \eta; T) = f^n(X^n_i, \eta; T) + c_1(T)d + \frac{1}{2}c_2(T)d^2 \quad (4.2)
\]

The corresponding neutral composition is given by the \( X^n_i \) and the free energy of a net-neutral composition with structure measured by \( \eta \) is given by the function \( f^n(X^n_i, \eta; T) \). The measure of the difference between the composition and the net-neutral composition is given by the scalar \( d \) which will be discussed in Section 4.2.2.
Figure 4-2: The neutral molar line (blue) is the intersection of the neutral plane (green), $P_0$, and the molar plane (purple), $P_n$.

In general, the expansion coefficients, $c_1$ and $c_2$, are functions of temperature.

### 4.2.2 Corresponding Neutral Composition

In ternary alloy composition space, the equations that place restrictions on the number of moles of each ionic species are Eqs. 4.3 and 4.4. The number of moles of each species is $n_i$ with corresponding valence or formal charge $z_i$.

\[
\begin{align*}
  n_1 + n_2 + n_3 &= 1 & (4.3) \\
  z_1 n_1 + z_2 n_2 + z_3 n_3 &= 0 & (4.4)
\end{align*}
\]

These can be represented graphically, Fig. 4-2. Equation 4.3 defines the molar plane, $P_n$, and Eq. 4.4 defines the neutral plane, $P_0$. The allowed neutral compositions fall on the neutral-molar line at the intersection of $P_n$ and $P_0$.

In an atomic system of $N$ components at constant pressure and temperature, there are $(N - 1)$ independent composition variables. In a net-neutral ionic system of $N$ components at constant pressure and temperature, there are $(N - 2)$ independent
composition variables. This allows the phase relations in a ternary, ionic system to be plotted against the mole fraction of one neutral end member. The mole fraction is equivalent to the distance along the neutral-molar line, Fig. 4-3.

In general ternary composition space, where a point is given by a vector from the origin \( \vec{n} = (n_1, n_2, n_3) \) and the vector of valences is given by \( \vec{z} = (z_1, z_2, z_3) \), the equation for the molar plane is given in Eq. 4.5, where \( \vec{I} = (1, 1, 1) \) is the vector of ones. The equations of a plane with constant number of moles of electrons, \( q \), is given by Eq. 4.6. The equation of the neutral plane is a special case of Eq. 4.6 with \( q = 0 \), \( \vec{n} \cdot \vec{z} = 0 \).

\[
\vec{n} \cdot \vec{I} = 1 \tag{4.5}
\]
\[
\vec{n} \cdot \vec{z} = q \tag{4.6}
\]
Figure 4-4: The molar plane, $P_n$, given by Eq. 4.5 is purple, the neutral plane, $P_0$, given by Eq. 4.6 with $q = 0$ is green, and a plane of constant charge, $P_q$, given by Eq. 4.6 is red.

All compositions in this phase-field model are restricted to the molar plane, while they may have a net-charged composition. In this case, the composition lies on the line of intersection of the charged and molar planes, Fig. 4-4. For this work, a corresponding neutral composition that lies on the neutral-molar line is calculated.

There are several choices of methods for calculating a corresponding neutral composition; the following is used in this work. For a general composition, $\tilde{n}_q$, lying at the intersection of the $P_n$ and $P_q$ planes, the corresponding neutral composition, $\tilde{n}_0$, is calculated by translating the general point along the molar plane in a direction perpendicular to the lines of intersection of the planes of constant charge, as illustrated in Fig. 4-5. The relation between the points is given in Eq. 4.7, with $\hat{\nu}$ given by the solution of Eqs. 4.8-4.11, and $l$ given by 4.12.

$$\tilde{n}_0 = \tilde{n}_q + l \hat{\nu}$$  \hspace{1cm} (4.7)
Figure 4-5: In three dimensions, it is possible to rotate the system of planes to look along the edges of a section. The planes of constant charge, \( P_q \) and \( P_0 \), are parallel and intersect \( P_n \) at an angle \( \phi \). The translation vector has a direction \( \hat{v} \) and a length \( l \). The Euclidean distance between the charged planes is \( q/|z| \).

\[
\hat{v} \cdot \hat{t} = 0 \tag{4.8}
\]
\[
\hat{z} \cdot \hat{v} = \sin \phi \tag{4.9}
\]
\[
\hat{v} \cdot \hat{v} = 1 \tag{4.10}
\]
\[
\hat{v} \cdot \vec{v}_{qm} = 0 \tag{4.11}
\]

\[ l = \frac{q}{|z| \sin \phi} \tag{4.12} \]

The unit normal to the planes of constant charge is \( \hat{z} \), the angle of intersection of the molar and charged planes is \( \phi \), an arbitrary vector along the charged-molar line is \( \vec{v}_{qm} \), and the magnitude of \( z \) is \( |z| = (\hat{z} \cdot \hat{z})^{\frac{1}{2}} \). Any measure of the distance between the general and corresponding neutral composition is proportional to \( q \). For example, the Euclidean distance between the planes of constant charge is \( q/|z| \).

Once the corresponding neutral composition is calculated, an equivalent representation of this composition is sought in terms of neutral end-members.\(^2\) It is possible to

\(^2\)The neutral end members are an arbitrary choice of neutral units that may have an effect on the entropic contributions to the free energy of mixing. Consider for example, \( \text{Si}_3\text{N}_4 \) vs. \( \text{Si}_{3/4}\text{N} \).
represent a neutral composition, $\bar{n}_0$, with $(N - 2)$ independent components in atomic space by $(N - 2)$ mole fractions of neutral associates, $n_a$, if the matrix $\bar{A}$ in Eq. 4.13 has a non-zero determinant.

$$\bar{n}_0 = \bar{A} \bar{n}_a$$

(4.13)

### 4.2.3 The Associate Model

In order to stabilize certain bulk equilibrium phases and include miscibility gaps, a free energy model must be selected. The model should allow the inclusion of bulk-equilibrium thermodynamic data. It will be used to calculate the zeroth order term in Eq. 4.2.

The associate model is used by the CALPHAD community for calculating the chemical free energy using end-members that are associates (compounds or molecules) rather than atomic species [81]. The model is used to model liquids where the fundamental assumption is that the associates act and are distributed in solution as independent entities.

A regular solution form of the normalized molar free energy, $f^a(X^a_i, \eta; T)$, with $M$ neutral associates, $X^a_i$, is used, Eq. 4.14. There are three parts to the model: the first sum’s terms are the reference chemical potentials, the second’s are the ideal entropies of mixing, and the third’s are the enthalpies of mixing with interaction constants, $\Omega_{ij}$.

$$f^a(X^a_i, \eta; T) = \sum_{i=1}^{M} X^a_i f_i(\eta; T) + \sum_{i=1}^{M} X^a_i \ln X^a_i + \sum_{i=1}^{M} \sum_{j=i+1}^{M} \Omega_{ij} X^a_i X^a_j$$

(4.14)

The normalized reference chemical potentials, $f_i(\eta; T)$, have a dependence on the local structure of the material, $\eta$, after Wheeler et al. [29]. The form of the reference chemical potential is given in Eq. 4.15, where the free energy of the equilibrium solid
phase, $f_{i,s}(T)$, is a piecewise continuous function of temperature representing the equilibrium phases. $L_i$ is a measure of the energy difference between the equilibrium states and $T_{i,m}$ is the temperature at which the equilibrium states have equal energies.

$$
\begin{align*}
    f_{i,0}(\eta; T) &= \frac{1}{RT} f_{i,s}(T) \\
    &\quad + \frac{1}{RT} L_i \left\{ \left( 1 - \frac{T}{T_{i,m}} \right) + 12 \int_0^\eta \left( p(p - 1) \left( p - \frac{1}{2} \left( 1 - \frac{T}{T_{i,m}} \right) \right) \right) dp \right\}
\end{align*}
\tag{4.15}
$$

A schematic of the $\eta$ dependence of the reference chemical potential is presented in Fig. 4-6. This reference energy is constructed so that $f_{i,0}(1; T)$ is the bulk equilibrium free energy of the $i$th associate at the temperature $T$. At any temperature the difference in free energy between the $\eta = 1$ and $\eta = 0$ states is $f_{i,0}(0; T) - f_{i,0}(1; T) = L_i \left( 1 - \frac{T}{T_{i,m}} \right)$. This is a standard approximation in studies on solidification for $T \approx T_{i,m}$ where $L_i$ is the enthalpy of fusion and $T_{i,m}$ is the melting point [82]. Here, the relation is assumed at all temperatures, which implies that the heat capacity of the crystal and the $\eta = 0$ state are identical at all temperatures. If the $\eta = 0$ state is identified with the glass, then $L_i$ is the enthalpy of vitrification and $T_{i,m}$ is the temperature at which the free energy of the crystal and glass are the same. However, these values are not available for compounds that cannot be observed in a vitreous state. As the enthalpy of fusion is a measure of the energy released upon the breakdown of long range structural order in these molecular liquids, the enthalpy of fusion and melting point are used in the model.

### 4.3 Functional Form for Calcia-doped Silicon Nitride

In this section, the specific homogeneous free energy function is introduced for CaO-doped Si$_3$N$_4$. The relations between the dependent and independent composition
variables are described as well as the expressions for the fractions of the selected associates in the corresponding neutral composition.

### 4.3.1 Measuring Composition

The system of interest is a quaternary with components Si, Ca, N, and O and charge measured by the number of excess moles of electrons per mole of ions, \( q \). Therefore, the composition and valence vectors are

\[
\vec{n} = \begin{pmatrix} n_{Si} \\ n_{Ca} \\ n_{N} \\ n_{O} \end{pmatrix} \quad \text{and} \quad \vec{z} = \begin{pmatrix} +4 \\ +2 \\ -3 \\ -2 \end{pmatrix}.
\]  

(4.16)

The two constraints on the general composition are given by Eqs. 4.5 and 4.6. For convenience, the three independent measures of charge and composition are taken to be \( X_{Si}, X_{Ca}, \) and \( q \). The dependent measures of composition are functions of the
independent variables, Eqs. 4.17 and 4.18.

\[
\begin{align*}
X_N &= -2 + 4X_{Ca} + 6X_{Si} - q \\
X_O &= 3 - 5X_{Ca} + 7X_{Si} + q
\end{align*}
\]  
(4.17)  
(4.18)

The relations between the general composition and the corresponding neutral
atomic composition are given as Eqs. 4.19 and 4.20.

\[
\begin{align*}
X^n_{Si} &= X_{Si} - \frac{15}{131}q \\
X^n_{Ca} &= X_{Ca} - \frac{7}{131}q
\end{align*}
\]  
(4.19)  
(4.20)

The associate end-members are chosen to be \( \text{SiO}_2 \), \( \text{CaO} \), and \( \text{Si}_3\text{N}_4 \).\(^3\) The two chosen independent measures of associate composition are \( X_{\text{SiO}_2} \) and \( X_{\text{Si}_3\text{N}_4} \). The relations between the the independent measures of actual composition and charge
and the mole fractions of the neutral associates are given below in Eqs. 4.21- 4.23.

\[
\begin{align*}
X_{\text{Si}_3\text{N}_4} &= \frac{131(1 - 2X_{Ca} - 3X_{Si}) + 59q}{-131(2 - 2X_{Ca} - 4X_{Si}) - 74q} \\
X_{\text{SiO}_2} &= \frac{131(3 - 6X_{Ca} - 7X_{Si}) + 147q}{131(2 - 2X_{Ca} - 4X_{Si}) + 74q} \\
X_{\text{CaO}} &= 1 - X_{\text{SiO}_2} - X_{\text{Si}_3\text{N}_4}
\end{align*}
\]  
(4.21)  
(4.22)  
(4.23)

4.3.2 Homogeneous Free Energy

The approximation of the chemical and structural contributions to the homogeneous
free energy is expressed in Eq. 4.24. The independent variable \( q \) is chosen as a
measure of the distance between the general and corresponding neutral compositions.

The expansion coefficient and scaling terms are expressed as \( \alpha^2 \). The first term in

\(^3\text{SiO}_2, \text{Si}_3\text{N}_4, \text{and} \ \text{Ca}_3\text{N}_2 \) is another choice. This choice is reflected in the fact that equivalence
salt diagrams for this system have an end-member at each of the four corners, \( \text{SiO}_2 \), \( \text{Si}_3\text{N}_4 \), \( \text{CaO} \),
and \( \text{Ca}_3\text{N}_2 \).
the expansion is abandoned because the energy should be a minimum for the neutral compositions and increase with the magnitude of charge.\(^4\)

\[
f(X_{\text{Si}}, X_{\text{Ca}}, q, \eta; T) = f^a(X_{\text{SiO}_2}(X_{\text{Si}}, X_{\text{Ca}}, q), X_{\text{Si}_3\text{N}_4}(X_{\text{Si}}, X_{\text{Ca}}, q), \eta; T) + \frac{1}{2} \alpha^2 q^2 \tag{4.24}
\]

The normalized free energy of the corresponding neutral composition, \(f^a(X_{\text{SiO}_2}, X_{\text{Si}_3\text{N}_4}, \eta; T)\) is given by Eq. 4.25. The reference chemical potentials are given by Eq. 4.15. The bulk thermodynamic data, free energies, melting points, and enthalpies of fusion, are taken from the literature \([83, 4]\). These values are given in Appendix A.

\[
f^a(X_i^a, \eta; T) = X_{\text{SiO}_2} \left( f_{\text{SiO}_2,0}^a(\eta; T) - f_{\text{CaO,0}}^a(\eta; T) \right) + X_{\text{Si}_3\text{N}_4} \left( f_{\text{Si}_3\text{N}_4,0}^a(\eta; T) - f_{\text{CaO,0}}^a(\eta; T) \right) + f_{\text{CaO,0}}^a(\eta; T)
\]

\[
+ X_{\text{SiO}_2} \ln \frac{X_{\text{SiO}_2}}{(1 - X_{\text{SiO}_2} - X_{\text{Si}_3\text{N}_4})} + X_{\text{Si}_3\text{N}_4} \ln \frac{X_{\text{Si}_3\text{N}_4}}{(1 - X_{\text{SiO}_2} - X_{\text{Si}_3\text{N}_4})}
\]

\[
+ \ln(1 - X_{\text{SiO}_2} - X_{\text{Si}_3\text{N}_4}) + \Omega_{\text{SiO}_2}\Sigma_{\text{Si}_3\text{N}_4} X_{\text{SiO}_2} X_{\text{Si}_3\text{N}_4} + (\Omega_{\text{SiO}_2}\Sigma_{\text{CaO}} X_{\text{SiO}_2})
\]

\[
+ \Omega_{\text{Si}_3\text{N}_4}\Sigma_{\text{CaO}} X_{\text{Si}_3\text{N}_4}(1 - X_{\text{SiO}_2} - X_{\text{Si}_3\text{N}_4})
\]

### 4.3.3 Total Free Energy

The final form of the free energy functional is given in Eq. 4.26 where the independent fields \(X_{\text{Si}}(\vec{x}), X_{\text{Ca}}(\vec{x}), q(\vec{x}), \overline{\phi}(\vec{x}), \eta(\vec{x})\), and \(\theta(\vec{x})\), are the mole fraction of Si, mole fraction of Ca, number of moles of excess electrons per mole of atoms, a rescaled electrostatic potential given by \(\overline{\phi}(\vec{x}) = \frac{V_m}{1000RT} \phi(\vec{x})\), a local measure of the crystallinity, and a local measure of the orientation, respectively.

---

\(^4\)A leading order term of the form \(|q|\) would fulfill these requirements, but would generate a cusp in the energetics.
\[ F[X_{\text{Si}}, X_{\text{Ca}}, \rho, \bar{\phi}, \eta, \theta; T, \Omega] = \frac{1000RT}{V_m} \int_\Omega \left\{ f^a(X_{\text{Si}}, X_{\text{Ca}}, q, \eta; T) + \frac{1}{2} \alpha^2 q^2 \right\} \]

\[ + \frac{\mathcal{F}}{V_m} q \bar{\phi} - \frac{1}{2} \tilde{\varepsilon}(\nabla \bar{\phi})^2 \]

\[ + \frac{1}{2} (\tilde{\kappa}_{\text{Si}}^2 (\nabla X_{\text{Si}})^2 + \frac{1}{2} (\tilde{\kappa}_{\text{Ca}}^2 (\nabla X_{\text{Ca}})^2 + \frac{1}{2} (\tilde{\kappa}_q^2 (\nabla q)^2) \]

\[ + \tilde{\kappa}_{\text{SiCa}}^2 \nabla X_{\text{Si}} \cdot \nabla X_{\text{Ca}} + \tilde{\kappa}_{\text{Siq}}^2 \nabla X_{\text{Si}} \cdot \nabla q \]

\[ + \tilde{\kappa}_{\text{Caq}}^2 \nabla X_{\text{Ca}} \cdot \nabla q + \frac{1}{2} s \eta^2 (1 - \lambda X_{\text{Ca}})^2 |\nabla \theta| \]

\[ + \frac{1}{2} \beta^2 |\nabla \theta|^2 + \frac{1}{2} \nu^2 |\nabla \eta|^2 \} \, d\bar{x} \]

The charge density is represented by the number of moles of excess electrons \( \rho = \frac{\mathcal{F}}{V_m} q \), where \( \mathcal{F} \) is Faraday's constant. The dielectric constant is rescaled according to \( \tilde{\varepsilon} = \varepsilon_r \varepsilon_0 \frac{1000RT}{V_m} \), where \( \varepsilon_r \) is the relative dielectric constant and \( \varepsilon_0 \) is the permittivity of free space. The chemical gradient energy terms are grouped using the new gradient energy coefficients defined in Eqs. 4.27 to 4.32. The coefficients \( \tilde{\kappa}_{\text{Siq}}^2 \) and \( \tilde{\kappa}_{\text{Caq}}^2 \) are negative because of the negative signs in Eqs. 4.17 and 4.18.

\[ \tilde{\kappa}_{\text{Si}}^2 = \kappa_{\text{Si}}^2 + 36 \kappa_N^2 + 49 \kappa_O^2 \quad \text{(4.27)} \]

\[ \tilde{\kappa}_{\text{Ca}}^2 = \kappa_{\text{Ca}}^2 + 16 \kappa_N^2 + 25 \kappa_O^2 \quad \text{(4.28)} \]

\[ \tilde{\kappa}_q^2 = \kappa_N^2 + \kappa_O^2 \quad \text{(4.29)} \]

\[ \tilde{\kappa}_{\text{SiCa}}^2 = 24 \kappa_N^2 + 35 \kappa_O^2 \quad \text{(4.30)} \]

\[ \tilde{\kappa}_{\text{Siq}}^2 = -(6 \kappa_N^2 + 7 \kappa_O^2) \quad \text{(4.31)} \]

\[ \tilde{\kappa}_{\text{Caq}}^2 = -(4 \kappa_N^2 + 5 \kappa_O^2) \quad \text{(4.32)} \]

The gradient energy coefficient for \(|\nabla \theta|\) has the form \( \frac{1}{2} s \eta^2 g(X_{\text{Ca}}) \). For this work, \( g(X_{\text{Ca}}) = (1 - \lambda X_{\text{Ca}})^2 \), which is monotonically decreasing on \( 0 \leq X_{\text{Ca}} \leq 1 \). The parameter \( \lambda \) is positive and less than one.
4.4 Equilibrium Condition

The equilibrium states of a system correspond to extrema in the free energy. I propose that Eq. 4.26 is the appropriate free energy for examining the stability of an intergranular film in CaO-doped Si₃N₄. A necessary condition for an extremum is that the Euler-Lagrange equations are satisfied, Eqs. 4.33 to 4.38. The stable equilibrium state (one with lowest free energy) will satisfy Eqs. 4.33 to 4.38 and also have positive second variational derivatives.

\[
\frac{\partial f^a}{\partial X_{Si}} - \kappa_{Si}^2 \nabla^2 X_{Si} - \kappa_{SiCa}^2 \nabla^2 X_{Ca} - \kappa_{Siq}^2 \nabla^2 q = 0 \quad (4.33)
\]

\[
\frac{\partial f^a}{\partial X_{Ca}} - \lambda s \eta^2 (1 - \lambda X_{Ca}) |\nabla \theta| - \kappa_{Ca}^2 \nabla^2 X_{Ca} - \kappa_{SiCa}^2 \nabla^2 X_{Si} - \kappa_{Caq}^2 \nabla^2 q = 0 \quad (4.34)
\]

\[
\frac{\partial f^a}{\partial q} + \alpha^2 q + \frac{F}{V_m} \phi - \kappa_q^2 \nabla^2 q - \kappa_{Siq}^2 \nabla^2 X_{Si} - \kappa_{Caq}^2 \nabla^2 X_{Ca} = 0 \quad (4.35)
\]

\[
\frac{\mathcal{F}}{V_m} q + \epsilon \nabla^2 \phi = 0 \quad (4.36)
\]

\[
\frac{\partial f^a}{\partial \eta} + s \eta (1 - \lambda X_{Ca})^2 |\nabla \theta| - \nu^2 \nabla^2 \eta = 0 \quad (4.37)
\]

\[-\beta^2 \nabla^2 \theta - \nabla \cdot \left( \frac{1}{2} s \eta^2 (1 - \lambda X_{Ca})^2 \frac{\nabla \theta}{|\nabla \theta|} \right) = 0 \quad (4.38)
\]

As in Chapter 3, I assume that the electrostatic potential adjusts instantaneously to satisfy Eq. 4.36 so that the potential is always in equilibrium with the charge density. This equation is Coulomb’s Law, one of Maxwell’s Equations.

This set of highly non-linear coupled differential equations has not been solved analytically, therefore a numeric method is employed. For a given initial condition and set of boundary conditions, the appropriate kinetic equations can be iterated until the energy reaches a minimum.
4.5 Appropriate Kinetic Equations

The appropriate kinetic equations for the conserved fields, $X_{Si}$, $X_{Ca}$, $q$, are of the Cahn-Hilliard type, Eqs. 4.39 to 4.41. The appropriate kinetic equations for the non-conserved fields, $\eta$ and $\theta$, are of the Allen-Cahn type, Eqs. 4.42 and 4.43. The $M_i$ are constant mobility coefficients for each field. The mobility for the $\theta$ field is weighted by $1/\eta^2$ as the rate at which atoms can rearrange to change the local orientation is expected to increase with decreasing crystallinity.

$$\frac{\partial X_{Si}}{\partial t} = -\nabla \cdot \left( -M_{Si} \nabla \left\{ \frac{\delta F}{\delta X_{Si}} \right\} \right)$$  \hspace{1cm} (4.39)

$$\frac{\partial X_{Ca}}{\partial t} = -\nabla \cdot \left( -M_{Ca} \nabla \left\{ \frac{\delta F}{\delta X_{Ca}} \right\} \right)$$  \hspace{1cm} (4.40)

$$\frac{\partial q}{\partial t} = -\nabla \cdot \left( -M_{q} \nabla \left\{ \frac{\partial q}{\partial t} \right\} \right)$$  \hspace{1cm} (4.41)

$$\frac{\partial \eta}{\partial t} = -M_{\eta} \left\{ \frac{\delta F}{\delta \eta} \right\}$$  \hspace{1cm} (4.42)

$$\frac{\partial \theta}{\partial t} = -\frac{M_{\theta}}{\eta^2} \left\{ \frac{\partial F}{\partial \theta} \right\}$$  \hspace{1cm} (4.43)

A dimensionless time and length, $\hat{t}$ and $\hat{x}$, are introduced where $L$ is a characteristic dimension of the system and $M$ is a mobility.

$$\hat{t} = \frac{M}{L^2} t$$  \hspace{1cm} (4.44)

$$\hat{x} = \frac{1}{L} \bar{x}$$  \hspace{1cm} (4.45)

The rescaled kinetic equations are given in Eqs. 4.46- 4.50. The rescaled mobility coefficients and gradient parameters are given by the following relations: $M_{Si} = \frac{M_{Si}}{M}$, $M_{Ca} = \frac{M_{Ca}}{M}$, $M_{q} = \frac{M_{q}}{M}$, $M_{\eta} = \frac{M_{\eta} L^2}{M}$, $M_{\theta} = \frac{M_{\theta} L^2}{M}$, $\hat{s} = \frac{s}{L}$, $\hat{\kappa}_{Si}^2 = \frac{\kappa_{Si}^2}{L^2}$, $\hat{\kappa}_{Ca}^2 = \frac{\kappa_{Ca}^2}{L^2}$, $\hat{\kappa}_{q}^2 = \frac{\kappa_{q}^2}{L^2}$, $\hat{\kappa}_{Siq}^2 = \frac{\kappa_{Siq}^2}{L^2}$, $\hat{\kappa}_{Caq}^2 = \frac{\kappa_{Caq}^2}{L^2}$, $\hat{\kappa}_{SiCa}^2 = \frac{\kappa_{SiCa}^2}{L^2}$, $\hat{\epsilon} = \frac{\epsilon}{\kappa_{Si}^2}$, $\hat{\nu}^2 = \frac{\nu^2}{\kappa_{Ca}^2}$, and $\hat{\beta}^2 = \frac{\beta^2}{\kappa_{q}^2}$.

Coulomb's Law is substituted into Eq. 4.41 so that no explicit $\bar{\phi}$ dependence remains.
in Eq. 4.48.

\[
\frac{\partial X_{Si}}{\partial \hat{t}} = \hat{M}_{Si} \left\{ \hat{\nabla}^2 \frac{\partial f^a}{\partial X_{Si}} - \hat{\kappa}^2_{Si} \hat{\nabla}^4 X_{Si} - \hat{\kappa}^2_{SiCa} \hat{\nabla}^4 X_{Ca} - \hat{\kappa}^2_{Siq} \hat{\nabla}^4 q \right\} \tag{4.46}
\]

\[
\frac{\partial X_{Ca}}{\partial \hat{t}} = \hat{M}_{Ca} \left\{ \hat{\nabla}^2 \frac{\partial f^a}{\partial X_{Ca}} - \hat{\nabla}^2 [\lambda \hat{s} \eta^2 (1 - \lambda X_{Ca}) |\hat{\nabla} \theta|] - \hat{\kappa}^2_{Ca} \hat{\nabla}^4 X_{Ca} \right\} \tag{4.47}
\]

\[
\frac{\partial q}{\partial \hat{t}} = \hat{M}_q \left\{ \hat{\nabla}^2 \frac{\partial f^a}{\partial q} + \alpha^2 \hat{\nabla}^2 q - \frac{1}{\epsilon} q - \hat{\kappa}^2_{q} \hat{\nabla}^4 q - \hat{\kappa}^2_{Siq} \hat{\nabla}^4 X_{Si} \right\} \tag{4.48}
\]

\[
\frac{\partial \eta}{\partial \hat{t}} = -\hat{M}_\eta \left\{ \frac{\partial f^a}{\partial \eta} + \hat{s} \eta (1 - \lambda X_{Ca})^2 |\hat{\nabla} \theta| - \hat{\nu}^2 \hat{\nabla}^2 \eta \right\} \tag{4.49}
\]

\[
\frac{\partial \theta}{\partial \hat{t}} = \frac{\hat{M}_\theta}{\eta^2} \left\{ \beta^2 \hat{\nabla}^2 \theta + \hat{\nabla} \cdot \left[ \frac{1}{2} \hat{s} \eta^2 (1 - \lambda X_{Ca})^2 \frac{\hat{\nabla} \theta}{|\hat{\nabla} \theta|} \right] \right\} \tag{4.50}
\]

### 4.6 The Numerical Method

The iteration equations are discretized in one dimension using finite differences on a regular grid of \( n \) points with spacing \( \Delta \hat{x} \). The temporal scheme is semi-implicit with a time step \( \Delta \hat{t} \). The semi-implicit method allows an increased stable time step. The iteration equations are given in Appendix B.

The iteration equations can be written as matrix equations for each of the fields, \( y_i \), as in Eq. 4.51. The vectors \( \vec{y}_i^t \) and \( \vec{y}_i^{t+1} \) have \( n \) entries and \( \hat{A}_i \) is an \( n \times n \) matrix. The values of the field at each node in space are given at the next time-step in the vector \( \vec{y}_i^{t+1} \). The matrix \( \hat{A}_i \) is sparse, tri- or penta-diagonal, with two or three diagonals neighboring the central diagonal. The non-zero matrix elements depend only on the current values of all the fields. The vector \( \vec{b}_i^t \) depends only on the fields evaluated at the current time-step.

\[
\hat{A}_i \vec{y}_i^{t+1} = \vec{b}_i^t \tag{4.51}
\]
This equation is solved at each time step using a sparse matrix solver included in the gmres package [84]. The package uses an implicit method to approximately solve sparse systems of linear equations. The allowed error tolerance is specified as $10^{-5}$. Therefore, it is necessary to re-normalize some fields to maintain the conservation condition for a large number of iterations of the evolution equations. In the case of the field $q$, this normalization is accomplished by subtracting the mean value of the field from every point in order to maintain the charge neutrality of the system, 
\[ \sum_{k=0}^{k=n-1} q_k = 0. \]

## 4.7 Summary and Conclusions

A phase-field model that couples chemistry, structure, and electrostatics was developed. The model captures contributions to the total free energy for interface-stabilized chemistries and structures. The parameters in the model should be related to coarse-grained atomistic simulation and experimental results.

The free energy functional has contributions from homogeneous terms and gradient energy terms. The homogeneous free energy depends on the electrostatic, chemical, and structural measures of the system. The gradient energy terms ensure that interfacial energies are included in the description of heterogeneous systems.

The chemical and structural contributions to the homogeneous free energy are expressed in the zeroth order term in an expansion about net-neutral compositions. The zeroth order term is an associate model approximation. The local charge is used as the measure of the deviation of a general composition from the corresponding neutral composition. In general, this term could be a function of composition, temperature or structure.

The structural contribution to the homogeneous free energy is contained in the reference chemical potentials. An approximation to the structural energy of the intergranular phase is used. The material in the intergranular film is characterized as
a partially ordered glass. However, as temperature and enthalpy information are unavailable for the vitreous state of the compounds used here, the melting points and enthalpies of fusion are used.

Gradient energy terms are necessary to stabilize diffuse interfaces containing nonequilibrium chemistries and structures. The forms of the gradient energy coefficients are assumed based on the success of models that capture aspects of adsorption in multi-component systems and simple grain boundary structure.

The parameters in the model are given reasonable values then adjusted based on the equilibrated structures. In general, increasing a gradient energy coefficient for a variable increases the width of the transition associated with the variable in the equilibrated structure. However, due to the coupled nature of the fields in this model, the response of changing one gradient energy coefficient is more complicated. Trial and error can be used to tune the phase-field model based on comparison with experimental and coarse-grained atomistic simulation results.

The results of simulations on intergranular films in Si$_3$N$_4$ are presented and discussed in Chapter 5. A discussion of the applicability of this model to related problems in multicomponent systems, such as wetting and surficial films, is contained in Chapter 6.
Chapter 5

Phase-Field Simulation Results and Discussion

In this Chapter, the results of select simulations using the phase-field model developed in Chapter 4 are presented. The results are compared to coarse-grained composition profiles from MD simulations performed in similar systems. The Chapter concludes with a discussion of these results and implications for future modeling in the CaO-doped Si$_3$N$_4$ system.

5.1 Phase-Field Simulations

5.1.1 Simulation Conditions

The phase-field simulations are performed in a one-dimensional finite domain, $0 \leq x \leq L$, with symmetry at $x = 0$. The center of the IGF is located at $x = 0$ and $L$ is large enough so that an infinite system is approximated. Due to the geometry, illustrated in Fig. 5-1, the boundary conditions on the $\eta$, $X_{Si}$, $X_{Ca}$, and $q$ fields are periodic in $-L \leq x \leq L$ with an implied mirror plane at $x = 0$. While Dirichlet boundary conditions are applied to the $\theta$ field at $x = 0$ and $x = L$. 

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Figure 5-1: Initial condition for 10Å film in undoped silicon nitride. The full space (a) is reduced to the half space (b) for numerical efficiency. The boundary conditions on the fields are implied by this geometry.

The boundary conditions and kinetic equations fix the total charge and total number of moles of each species. The initial condition determines the composition of the simulated sample. However, the chemical and structural widths measured using full-width half maximum (or minimum) are determined from equilibrium solution profiles. Finite gradients are specified, as illustrated in Fig. 5-1, for the composition profiles at the interphase interface in the initial condition in order to use a uniform time step.

Simulation parameters are summarized in Table 5.1. The experimental values of the Gibbs free energy are used for the reference chemical potentials, as described in Section 4.3.2. While the dielectric constant of any anisotropic material is a tensor, a scalar value was assumed in the derivation of the model. A relative dielectric constant $\varepsilon_r = 4.4$ is chosen. The dielectric constants for SiO$_2$ and Si$_3$N$_4$ are of this size [85]. The molar volume is a constant for the calculations, $V_m = 2.6 \cdot 10^{-5}$m$^3$/molc. The molar volumes of different solid SiO$_2$ phases are all approximately equal to $V_m$ [85]. The selected temperature is below the melting points of SiO$_2$, Si$_3$N$_4$, and CaO.

Two different chemistries were analyzed for 10Å initial film widths, 0 mole fraction CaO and 0.01 mole fraction CaO in the film.$^1$ The initial compositions of the

---

$^1$The film widths are measured from full-width half maximum (or minimum) of any of the initial
Figure 5-2: Schematic of the low $X_{\text{CaO}}$ region of the $T = 1500$K isotherm of the crystalline $X_{\text{SiO}_2}$-$X_{\text{Si}_3\text{N}_4}$-$X_{\text{CaO}}$ phase diagram calculated from the associate model. The solubility limits for the SiO$_2$ and Si$_3$N$_4$-rich phases are shown.

Table 5.1: Phase-field model simulation parameters defined in Section 4.5.

<table>
<thead>
<tr>
<th>$\Omega_{ij}$</th>
<th>$\epsilon_r$</th>
<th>$\epsilon$</th>
<th>$T$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ 50Å</td>
<td>$\gamma$ 1000</td>
<td>$\hat{s}$ 0.1</td>
<td>1500K</td>
<td></td>
</tr>
<tr>
<td>$\nu$ 0.01</td>
<td>$\lambda$ 0.5</td>
<td>$\hat{\beta}$ 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ 10</td>
<td>$\hat{\kappa}_{\text{Si}}^2$ 0.0086</td>
<td>$\hat{\kappa}_{\text{Ca}}^2$ 0.0042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\hat{\kappa}_q^2$ 0.0002</td>
<td>$\hat{\kappa}_{\text{SiCa}}^2$ 0.0059</td>
<td>$\hat{\kappa}_{\text{Si}}^2$ -0.0013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\hat{\kappa}_{\text{Ca}}^2$ -0.0009</td>
<td>$M_{\text{Si}}$ 0.004</td>
<td>$M_{\text{Ca}}$ 0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_q$ 0.004</td>
<td>$M_\theta$ 10$^5$</td>
<td>$M_\eta$ 10$^5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_m$ 2.6 $\cdot$ 10$^{-5}$ m$^3$/mole</td>
<td>$n$ 200</td>
<td>$\Delta \hat{x}$ 0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \hat{t}$ 10$^{-11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

film and grain for the 0 mole fraction CaO simulation correspond to the solubility limits of the single phase fields from the isotherm of the phase diagram, Fig. 5-2, $(X_{\text{SiO}_2}, X_{\text{Si}_3\text{N}_4}, X_{\text{CaO}}) = (0.9788, 0.0212, 0)$ and $(0.02125, 0.97875, 0)$, respectively. In the 0.01 mole fraction CaO simulation, the film contains no nitrogen and the grain composition corresponds to the solubility limit of SiO$_2$ in Si$_3$N$_4$, $(X_{\text{SiO}_2}, X_{\text{Si}_3\text{N}_4}, X_{\text{CaO}}) = (0.99, 0, 0.01)$ and $(0.2125, 97875, 0)$, respectively.

The effect of changing a single gradient energy parameter was investigated for the 0.01 mole fraction CaO simulation by setting $\nu = 0.005$ while fixing the other parameters to the values specified in Table 5.1.
5.2 Phase-Field Simulation Results

For a general fourth order partial differential equation, $\frac{\partial y}{\partial t} = D \frac{\partial^4 y}{\partial x^4}$, the Courant Condition places a restriction on the size of the numerically stable time-step, $\Delta t \leq \frac{\Delta x^4}{D}$ [86]. Due to this restriction and the nonlinear form of the equations, Eq. 4.46-4.50, the stable time-step is very small. The simulations in this thesis are not equilibrated as the total time of the simulations is still a small percent, 0.25%, of the characteristic time in the system. As the total energy of the simulated system decreases towards the equilibrium value, the incremental rate of change in each field is expected to decrease as well. Figure 5-3 shows plots of the energy and summed change in the fields, $\Delta^2$, Eq. 5.1, for the undoped IGF simulation as a function of the number of iteration steps.

$$\Delta^2 \theta = \sum_{k=0}^{n-1} \left( \frac{\partial \theta}{\partial t} \right)_{k}^2$$ (5.1)

The terms in the integrand of Eq. 4.26 are grouped into four contributions to the total free energy: chemical homogeneous, chemical gradient, structural gradient, and electrostatic.

\begin{align*}
\text{chemical homogeneous} & = \int_{\Omega} \left\{ f^a(X_{Si}, X_{Ca}, q, \eta; T) + \frac{1}{2} \alpha^2 q^2 \right\} dx \quad (5.2) \\
\text{chemical gradient} & = \int_{\Omega} \left\{ \frac{1}{2} (\kappa_{Si}^2 (\nabla X_{Si})^2) + \frac{1}{2} (\kappa_{Ca}^2 (\nabla X_{Ca})^2) \\
& \quad + \frac{1}{2} (\kappa_{q}^2 (\nabla q)^2) + \kappa_{SiCa}^2 \nabla X_{Si} \cdot \nabla X_{Ca} \\
& \quad + \kappa_{Siq}^{2} \nabla X_{Si} \cdot \nabla q + \kappa_{Caq}^{2} \nabla X_{Ca} \cdot \nabla q \right\} dx \quad (5.3) \\
\text{structural gradient} & = \int_{\Omega} \left\{ \frac{1}{2} s\eta^2 (1 - \lambda X_{Ca})^2 |\nabla \theta| + \frac{1}{2} \beta^2 |\nabla \theta|^2 \\
& \quad + \frac{1}{2} \nu^2 |\nabla \eta|^2 \right\} dx \\
\text{electrostatic} & = \int_{\Omega} \left\{ -\frac{F}{V_m} q \phi - \frac{1}{2} \epsilon (\nabla \phi)^2 \right\} dx \quad (5.5)
\end{align*}
Initially, the structural gradient contributions to the energy dominate. However, at longer times the gradient energies from the chemical and structural terms are of the same order of magnitude. The values of the contributions from the homogeneous free energy and electrostatic energy increase monotonically with the number of iterations. In addition, the size of the summed changes for the \( \theta \) field, \( \Delta^2 \theta \), decreases by six orders of magnitude during the simulation time.

As the summed changes in the fields are approaching negligible values and the total energy has decreased by two orders of magnitude, the intermediate solutions are indicative of trends and are sufficiently equilibrated to justify the conclusions in this thesis. Further numerical analysis of the solutions is pending, but the conclusions are unlikely to differ.

The intermediate results are presented in Figs. 5-4 and 5-5. There are some common features of the three sets. All display diffuse interfaces with non-bulk equilibrium field values. For example, the equilibrium phase diagram, Fig. 5-2, predicts a two phase equilibrium with a sharp interface for a bulk sample with the average composition employed in the undoped film simulation, \( X_{\text{Si}_3\text{N}_4} \approx 0.88 \) mole fraction. However, the interfacial energy is not neglected in the equilibrium calculation (as is done in the common tangent construction). There is an energetic trade off between minimizing gradient contributions and minimizing homogeneous contributions to the total energy. The results of this competition are diffuse interfaces.

The resulting orientation fields vary within the film material only. Variations in the structural field, \( \eta \), are not restricted to the film region. The two 0.01 mole fraction CaO-doped simulations display approximately the same behavior, but the structural width of the film is larger in the \( \tilde{\nu} = 0.01 \) simulation than in the \( \tilde{\nu} = 0.005 \) simulation, compare Fig. 5-5 (a) and (b). The structural widths of the \( \tilde{\nu} = 0.01 \) simulations (undoped and 0.1 mole fraction CaO-doped) are larger than the chemical widths. However, the structural width in the \( \tilde{\nu} = 0.005 \) simulation is approximately the same as the chemical width. For this non-equilibrium result, it is not possible
Figure 5-3: Plots illustrating the undoped system's approach to equilibrium with the number of iterations of the evolution equations. (a) The total excess energy and breakdown of contributions, (b) the percentage contributions to the total excess energy, and (c) the summed change for the $\theta$ and $X_{\text{Si}}$ fields. The excess energy is the energy of the system normalized by the energy of the corresponding bulk equilibrium energy of the system. The axes are linear-log to show all of the data.

Figure 5-4: Intermediate phase-field simulation results for undoped $\text{Si}_3\text{N}_4$ with 10Å film. (a) The structural and composition fields (b) The charge, normalized electrostatic potential and normalized electric field, $\overline{E} = \frac{d\overline{\phi}}{dx}$. 

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Figure 5-5: Comparison of intermediate simulation results for 10Å 0.01 mole fraction CaO films with \( \nu = 0.01 \) and \( \nu = 0.005 \). (a) and (b) The structural and composition fields, (c) and (d) the charge, normalized electrostatic potential and normalized electric field, \( \overline{E} = \frac{d\overline{\phi}}{dx} \), and (e) and (f) the calcium profile.
to say what effect the smaller $\hat{v}$ coefficient will have on the equilibrated boundary profiles. The trend is that smaller $\hat{v}$ values decrease the structural width.

There are locally charged regions and non-zero electric fields in the intermediate results. The magnitude of the excess charge is not negligible. The excess charge, $q$, is several orders of magnitude greater in the CaO-doped simulations than in the undoped simulation. These values represent a significant excess charge corresponding, for comparison, to Si vacancies in $\frac{1}{10000}$ Si sites in Si$_3$N$_4$.

Both of the doped sample simulations exhibit non-uniform Ca profiles. The shapes of the profiles are similar, with the maximum in the Ca profile located near the film-grain interface. It is predicted from the form of the free energy functional derived in Chapter 4 that it is energetically favorable for Ca to accumulate near the film-grain interface. The coupling of the homogeneous free energy with the chemical gradient energy terms promotes minority component adsorption to interphase interfaces. In addition, the energy penalty for gradients in $\theta$ is decreased by Ca.

5.3 Comparison of Phase-Field and Molecular Dynamics Simulations

5.3.1 Coarse-Grained CaO-doped Si$_3$N$_4$

The coarse-graining technique described in Section 2.4 was applied to MD data resulting from a simulation of a 9.01Å thick 0.12 mole fraction CaO-0.88 mole fraction SiO$_2$ film sandwiched by Si$_3$N$_4$ grains supplied by Stefano Carofalini [23]. The results for the 9.01Å and 19.16Å thick films are compared in Fig 5-6. The $\tau = 7.5\,\text{Å}$ and $h = 3\,\text{Å}$ cylindrical aperture was used for both coarse-grainings.

There are similarities between the two coarse-grained composition profile sets in Fig 5-6. Both sets display diffuse variations from the Si$_3$N$_4$ crystalline values to the film. In both graphs, the Ca profile is smooth while the Si, N, and O profiles exhibit
Figure 5-6: Comparison of coarse-grained composition sets for (a) 9.01Å thick and (b) 19.16Å thick 0.12 mole fraction CaO-0.88 mole fraction SiO₂ films sandwiched by Si₃N₄ grains. Both sets are coarse-grained using \( r = 7.5\text{Å} \) and \( h = 3\text{Å} \) cylinders.

The thinner film has an equilibrated thickness of 8.5Å measured from the full-width half maximum of the O profile (or full-width half minimum of the N profile). The O profile in the thinner (10Å) film does not fluctuate about an average in the film but instead attains a maximum in the center of the film. While the maximum O fraction in the film is greater in the thinner film, the transition regions for the two films are approximately the same at 7.5Å.

In contrast to the 19.16Å results, the Ca profile has non-zero values over a width of 10Å that exceeds the chemical width defined above. In addition, the maximum Ca value in the thinner film is 0.060 mole fraction as compared to 0.074 mole fraction in the thicker film. The size of the averaging aperture will introduce a spread in the discrete data. Constant Ca atom distributions when convolved with the averaging aperture would produce profiles with a maximum in the center as shown in Fig. 5-6. Further, if the Ca distributions were constant and the film width were increased, then at a critical film width the continuized profiles would exhibit a plateau in the center of the films and gradients near the edges. For the continuized curves in Fig. 5-6, a plateau is observed in the thinner film's Ca profile rather than the thicker film's. This suggests that this observation corresponds to a real difference in the Ca atom
distributions between the two films, and not to an artifact of the method.

5.3.2 Comparison of Phase-Field and MD Simulations

The high doping level, 0.12 mole fraction CaO, in the MD simulations allows a small simulation cell size (approximately 18,000 atoms). While specific measures of the fields can not be compared because the phase-field calculations are not equilibrated and there is an order of magnitude difference in the doping levels, general trends can be discussed. The rest of this Chapter refers to the 9.01Å 0.12 mole fraction CaO-SiO₂ set presented in Fig. 5-6(a).

Preliminary phase-field simulations indicate that the Ca atoms are located near the film-grain interface. This observation contrasts the MD results that exhibit a maximum in the Ca distribution at the center of the film. (As discussed above, this may indeed correspond to a uniform Ca atom distribution.) None of the short wavelength fluctuations observed in the O, N, and Si profiles in Fig. 5-6(a) are apparent in the profiles in Fig. 5-5 (a) or (b). These phase-field calculations have a sampling grid capable of resolving fluctuations of that wavelength. However, it is unknown whether the kinetic equations would support such regular composition field fluctuations.

5.4 Discussion

The intermediate simulation results exhibit local non-charge-neutral domains in the vicinity of the intergranular film. It was demonstrated in Chapter 3 that in a simple, unconstrained system such domains are kinetically stabilized through the coupling of chemistry and electrostatics. In these simulations, there is an additional coupling between the structure and chemistry. Therefore, in this work, locally charged domains are kinetically stabilized through a coupling of chemistry, structure, and electrostatics.

If the locally charged domains persist into the equilibrium state of the system, defects in the crystalline Si₃N₄ must be considered, see for example Yan et al. [73].
Because the intergranular phase is amorphous, only defects in the crystal must be considered. The free energy functional presented in Chapter 4 does not include the physics and chemistry of crystalline defects.

To compare these phase-field simulations to atomistic calculations, a method of calculating measures of structure and orientation, $\eta$ and $\theta$, must be devised for multi-component systems. This is a problem that remains to be solved and a discussion of possible approaches was presented in Chapter 2.

The simulation method presented in this thesis is one of fixed composition. The film in the simulation is not free to select the composition and thickness that minimize the energy of the system. In order to simulate a grain boundary without restricting the allowed widths, a chemical reservoir must be included in the simulated system. A simple simulation that would present this flexibility would be a two-dimensional simulation where intergranular pockets serve as reservoirs, Fig. 5-7. In such a simulation, the orientation and structure fields, $\theta$ and $\eta$, would stabilize intergranular films. If these fields were not included (consider a structureless treatment of the same initial condition), the thermodynamics would drive the minority phase into a single, circular domain at equilibrium. Instead, because of the couplings between chemistry, orientation, and structure, the grain boundaries will persist.

The simulations presented above were run on a variety of machines, but on average, $10^5$ iterations of the evolution equations took 10 minutes. Decreasing the number of spatial nodes will decrease the size of the matrix equations and increase the speed of the calculation. I tried variable grid methods for the simulations with little success. In order to increase the speed of the calculations, more sophisticated numerical methods must be explored. It may also be possible to simulate the film with fixed boundary conditions to duplicate the film-grain interface. An alternative approach is to solve the Euler-Lagrange equations using conjugate gradient methods. This is a subject for future numerical research.
Figure 5-7: Illustration of a two-dimensional simulation domain that would allow the chemistry and width of the film to adjust to minimize the energy. The grains are blue and the intergranular pockets and film are red. The structural and orientational fields stabilize the grain boundary. The pockets serve as a chemical reservoir.

5.5 Summary and Conclusions

Phase-field simulations were performed to solve the Euler-Lagrange equations, Eqs. 4.33 to 4.38, for different chemistries in the CaO-doped Si₃N₄ system. An undoped grain boundary and two doped grain boundaries were examined. The effect of altering a single gradient energy parameter was explored in the doped samples. Due to the complex nature of the free energy functional, the phase-field calculations did not reach equilibrium in the simulation time, but the results appear to have reached an asymptote. General trends for the equilibrated fields are identified from the intermediate results. Additional methods for calculating the solutions to the Euler-Lagrange equations must be developed.

The intermediate results indicate that non-neutral charge densities, non-uniform Ca distributions in the films, and distinct structural and chemical widths are viable. The charge density in the doped simulations is two orders of magnitude greater than that in the undoped simulation. In neither case is the charge density negligible.

A coarse-grained MD simulation result of a 9.01Å 0.12 mole fraction CaO-0.88 mole fraction SiO₂ film between Si₃N₄ grains was calculated. The coarse-grained
composition profiles exhibit diffuse interfaces similar to typical phase-field results. For this thin film, there is no characteristic average oxygen fraction within the film, Fig. 5-6(a). The O, Si, N, and Ca profiles all vary over the width of the film in contrast to the wider film, Fig 5-6(b). However, the widths of the diffuse interfaces for both the thick and thin films are approximately the same. It is premature to make specific comparisons between the intermediate phase-field composition profiles and these coarse-grained MD sets. In part, this is due to the uncertainty in the temperature of the MD sets. Also, due to the MD simulation procedure and initial condition, there is no N in the film. Physical observations suggest that the anion ratio \( \frac{N}{N+O} \approx 0.30 \). This suggests that the MD procedure does not allow sufficient time for N dissolution from the grain faces into the film.

The procedure for altering the phase-field parameters in order to tune the phase-field model to coarse-grained information in comparable systems is illustrated in the doped film simulations, Fig. 5-5. Adjusting the structural gradient energy coefficient, \( \tilde{\nu} \), illustrates the effect on the structural width of the film while affecting no measurable change on the composition profiles at this intermediate time.

In order to completely tune this phase-field model to the CaO-doped Si₃N₄ system, additional atomistic and experimental data sets must be generated. MC techniques, where the simulations are carried out in phase space not real space and the speed is dictated by numerical efficiency rather than by physical mobilities, may be more efficient for calculating equilibrated IGF structures than MD. The coarse-graining techniques outlined in Chapter 2 can be applied to atomistic data sets to calculate corresponding continuum descriptions.

While it is not possible to tune the phase-field model to small-scale data sets at this time, major advances have been made in the development of continuum models of interface-stabilized chemistries and structures. The model developed in Chapter 4 is the first diffuse interface based model of intergranular films to incorporate the coupling between chemistry and structure necessary to stabilize these films. In addition, the
treatment of the electrostatics is intrinsically included in the model and generates Coulomb's Law as one of the Euler-Lagrange equations. The discussion of this phase-field model is continued in Chapter 6 and includes a critique of the assumptions used in deriving the model.
Chapter 6

Critique of Assumptions Contained in the Model and Proposals for Subsequent Research

This chapter presents a discussion of applications and extensions of the phase-field model of Chapter 4 that were implied but not explicitly discussed hitherto.\(^1\) Extensions of the phase-field model require adaptations of the coarse-graining methods of Chapter 2. Consequently, suggestions for adaptations of the coarse-graining techniques and novel ways of generating atomistic data sets are discussed. This chapter illustrates that the methods described in this thesis form a general approach to treating materials using continuum thermodynamic methods.

6.1 Unknowns in the Phase-Field Model

The phase-field model has several kinds of parameters such as the simulation temperature, an approximation to the physical homogeneous free energy, and measures

\(^{1}\text{Many of the ideas that are developed and described in this Chapter were initiated by useful conversations with Rowland Cannon.}\)
of the interfacial energy. These topics will be discussed in this section with respect to comparing phase-field results to experimental and atomistic simulation data.

6.1.1 Temperature and Atomistic Simulations

While it is straightforward to set the temperature in the phase-field model, it is not obvious what temperature to use in order to simulate a particular experiment. If the model is to be tuned to MD results on an intergranular film, the appropriate temperature is not well defined because of experimental uncertainty. To generate an initial condition with some randomness, MD simulations can be “annealed” at very high temperatures, e.g. 10000K, before cooling in stages to the intended simulation temperature. The silicate-based intergranular phase is expected to have high viscosity so that in the simulation time allowed for cooling, the system may not evolve to the global energy minimum. Therefore, the correspondence between \( T \) and \( T_{MD} \) is unknown. In addition, during the high temperature annealing, the grain structures are frozen to prevent total melting. Upon subsequent cooling, the times allowed may not be sufficient to allow \( N \) from the grains to dissolve into the films.

A similar problem with defining temperature exists with physical samples. Most samples are cooled slowly from high temperature. It cannot be determined without additional experiment whether the resultant microstructures give insight into the high temperature equilibrium structures, the final low temperature, or an intermediate temperature. The question of temperature and its specification is revisited in Section 6.2.4.

6.1.2 Homogeneous Free Energy

In the phase-field model developed in Chapter 4, an approximation to the chemical contribution to the homogeneous free energy is employed. A corresponding neutral composition is calculated and used in an associate model to calculated the zeroth order approximation to the energy. This is employed in order to use as much exper-
imental information as possible. However, the associate model may not be optimal for describing the thermodynamics of ionic solids. Ionic liquids are often modeled with the associate model while ionic solids have been modeled with the compound energy model [87]. Furthermore, no intermediate stoichiometric compounds such as Si$_2$N$_2$O have been included in this model, but the method described in this thesis could be extended to more complex phase diagrams. It is possible that the choice of thermodynamic model is less important than the couplings between structure, chemistry, and electrostatics. This can be tested by comparing equilibrated boundaries using different models for the homogeneous free energy while keeping all other model parameters fixed.

The first-order correction in the homogeneous energy approximation depends on a corresponding electrically-neutral composition. Therefore, the energy surface measuring the difference in energy between compositions corresponding to the same neutral composition is parabolic with respect to charge with slope given by $\alpha^2 q$. In the most general case, the expansion coefficient is a function of temperature, structure and chemistry. The magnitude of $\alpha \geq 0$ and its functional dependence on other fields are to be tuned to experimental and simulation results using coarse-graining methods. Physical values for $\alpha$ could be estimated by creating, for example, an Si vacancy in Si$_3$N$_4$ and removing four electrons from the surface. The energy of this non-stoichiometric (non-bulk equilibrium composition), charge-neutral solid is calculated by subtracting the Coulombic interaction energy (between the vacancy and the holes) from the total energy. Different deviations from stoichiometry and different compositions can be sampled to calculate $\alpha$ in composition space. These experiments could be performed using atomistic simulation.

### 6.1.3 Gradient Energy Parameters

There are several parameters that determine the size of the gradient energy coefficients in this model. An initial set of parameters is chosen based on the values that
stabilize simple reductions of the full problem. For example, as $s = 0.1$ and $\nu = 0.01$ produce stable grain boundaries for a system with fixed composition, these values are used in the initial set. The relative magnitudes should be adjusted to best fit experimental and coarse-grained atomistic simulation data. To this end, it is important to understand the temperature corresponding to the experimental and simulation data.

The width of the intergranular films is on the same order as the spread of the electron beam used in TEM measurements. The spread of the electron beam results in an experimental coarse-graining which is too large to discern composition profiles across an IGF. On account of this, it is necessary to get spatially resolved profiles of composition and structure in intergranular films from 3D-atom probe experiments or atomistic simulations. At the same time, the average composition of the films can be determined by experimental measurements. Consequently, if the representative temperatures of the sample and MD simulation are different, the data used for tuning will result in a phase-field model that is not consistent with atomistic simulation and experiments.

6.2 Extensions of the Phase-Field Model

6.2.1 Other Material Systems

To study other alloy systems, the phase-field model would be adjusted to incorporate the reference free energies of the appropriate neutral associates. In an $N$-component system, there are $N - 1$ independent measures of composition. If the species have non-zero, finite formal charges, there are $N - 2$ independent neutral associates. For metallic systems (species have zero formal charge), there are $N - 1$ independent associates. For example, if the system is a quaternary ionic system, $N = 4$, then there are $N - 1 = 3$ independent measures of composition and $N - 2 = 2$ independent neutral associates. In the model developed in Chapter 4, $X_{\text{Si}}, X_{\text{Ca}}$ and $q$ were chosen as independent composition fields for convenience. If the competing effects of two network
modifiers, e.g. \( X_{Ca} \) and \( X_Y \) in the CaO-Y\(_2\)O\(_3\)-doped Si\(_3\)N\(_4\) system, on intergranular film structure were to be studied, then \( X_{Si}, X_{Ca}, X_Y \), and \( q \) are appropriate choices for the independent composition fields.

In addition, corresponding physical experiments and atomistic simulations must be performed. There are data in the literature on intergranular films in CaO-doped Si\(_3\)N\(_4\)(see Section 1.3 for an overview and references). There are related studies of Y\(_2\)O\(_3\)-doped Si\(_3\)N\(_4\), because atomistic potentials for \( Y \) are available. The resultant data sets could be used with the techniques described in this thesis for tuning a phase-field model of intergranular films in Y\(_2\)O\(_3\)-doped Si\(_3\)N\(_4\).

### 6.2.2 Intergranular Pockets

The grain boundary phase is in equilibrium with the material in the intergranular pockets. These pockets serve as a reservoir. The size of these pockets makes them more amenable to experimental characterization of composition and crystalline state than the intergranular films. Non-uniform composition profiles, liquid phase separation, and secondary phase crystallization in the pockets for different materials systems have been observed experimentally. Some of these observations are discussed in Section 1.3.

Extending the simulations to two-dimensions is straightforward.\(^2\) However, in order to distinguish between the glassy material at the grain boundaries and the liquids phase-separating at the intergranular pockets, an additional phase-field, \( \zeta \), must be introduced. This field will allow the free energy of the liquids to be characterized separately from the free energy of the glassy grain boundary film material. The values of \( \zeta \) can be chosen arbitrarily. The free energy, however, must be consistent with these. For example, let \( \zeta = 1 \) be solid and \( \zeta = 0 \) be liquid. Then \((\eta, \zeta) = (1, 1)\) is a crystalline, ordered solid, \((\eta, \zeta) = (0, 1)\) is an amorphous solid, \((\eta, \zeta) = (0.8, 0)\) is an

---

\(^2\)The local orientation is a vector in three-dimensions, but is a scalar in one and two. In order to treat three-dimensional problems a full orientation vector must be formulated.
example of a partially ordered liquid, and \((\eta, \zeta) = (0, 0)\) is a completely disordered liquid.

The homogeneous free energy is a continuous function of its fields. The energy is extended in a continuous manner between points in composition and structure space for which the energy is known. An example of this is Fig. 4-6 where energies are assigned to all values of \(0 \leq \eta \leq 1\) although thermodynamic data is only known for \(\eta = 1\), the crystal, and \(\eta = 0\), the amorphous solid. Physically reasonable schemes are employed to interpolate the energy for non-bulk equilibrium states, while the bulk-equilibrium states correspond to minima in the homogeneous energy function. In order to include the energetics of liquids and amorphous solids, the enthalpy of fusion and the enthalpy of vitrification should be specified for each of the associates. If the state of the system is defined by a structure, phase, temperature triplet, \((\eta, \zeta, T)\), then these heats can be related to differences in the reference chemical potential for an associate \(i\).

\[
\begin{align*}
    f_{i,0}(0, 1, T) - f_{i,0}(1, 1, T) & \propto \text{enthalpy of vitrification at } T \quad (6.1) \\
    f_{i,0}(0, 0, T) - f_{i,0}(1, 1, T) & \propto \text{enthalpy of fusion at } T \quad (6.2)
\end{align*}
\]

For single component systems, Kobayashi et al. have constructed a homogeneous free energy that depends on a liquid-solid field, \(\phi\), and also an order-disorder field, \(\eta\) [30]. Their model was applied to solidification from a melt, coarsening, and subsequent grain growth. During grain growth the \(\phi\) and \(\eta\) fields didn’t contain appreciably different information so the \(\phi\) field was abandoned in subsequent models of grain boundaries in solid systems [37]. In intergranular pockets, the \(\eta\) and \(\zeta\) fields are expected to contain different information and so both are necessary.
6.2.3 Surficial Films

Experimental observations of surficial films in a variety of systems indicate that there is a rich set of behaviors to explore. Surficial films have been observed in Bi$_2$O$_3$-ZnO, Bi$_2$O$_3$-Fe$_2$O$_3$, WO$_3$-TiO$_2$ and MoO$_3$-Al$_2$O$_3$ by Luo [88]. The surficial films are equilibrium features of these materials. The films have thicknesses on the order of a nanometer. Luo formulated an energetic model for the change in Gibbs free energy per unit area of surficial film created, $\Delta G$, Eq. 6.3. The free energies of the various interfaces, liquid–crystal, liquid–vapor, and crystal–vapor, are given by $\gamma_{cl}$, $\gamma_l$, and $\gamma_c$, respectively. The van der Waals and short-range interaction energies are $E_{vdW}$ and $E_{short-range}$ and both depend on film thickness, $h$. The volumetric energy change, $\Delta G_{vol}$, is the difference in energy density between film material with an average composition and the bulk equilibrium phases corresponding to that average composition.

$$\Delta G = (\gamma_{cl} + \gamma_l - \gamma_c) + E_{vdW}(h) + E_{short-range}(h) + (\Delta G_{vol}h) \tag{6.3}$$

The equilibrium thickness of the film corresponds to $\frac{\partial\Delta G}{\partial h} = 0$. Luo concludes that near the solidus the van der Waals interactions are important for film stability, while at much lower temperatures the volumetric energy term is most important.

While the phase-field model developed in Chapter 4 does not explicitly treat surficial films, it can be adapted to examine this class of problems. Again, an additional phase-field, $\vartheta$, in this case measuring the phase, solid, liquid, or vapor, would be introduced. The homogeneous free energy must depend on the measures of composition, $X_i$, structure, $\eta$, and phase, $\vartheta$. Approximations to the chemical contributions to the free energy of the vapor require formulation. Furthermore, formulation of phase-field methods that involve large volume changes during transformation are not yet satisfactory. If the corresponding simulations and experimental data are unavailable for the surficial films, it may be possible to use phase-field parameters tuned to intergranular
film simulations and experimental data, in a manner similar to that developed in this thesis, in the same material system.

6.2.4 Wetting

In his 1977 paper, “Critical Point Wetting”, Cahn shows that it is possible for a surface layer of a wetting phase to exist at a fluid inter-phase boundary when it is no longer stable in the bulk [89]. His predictions are based on diffuse interface theory in structureless liquids. This thesis is concerned with modeling interfaces wetted by phases that are not stable in the bulk. The principal difference is that the solid systems treated here have a structure measured by \( \eta \) that takes non-bulk equilibrium values near the interface.

There are many approaches to adsorption and wetting including Brunauer–Emmett–Teller theory developed from Langmuir’s classic adsorption theory and mean field lattice gas approaches [90, 91, 92, 93, 94, 95]. Some of these theories predict liquid structures at grain boundaries below the melting point, wetting and pre-wetting transitions, and solute adsorption in simple systems.

Kleebe and Pezzotti examine boundary character in nitride-based ceramics [96]. SiAlON samples were HIPed and slowly cooled. One small sample was heated to 1380°C with a laser then quenched to retain the high temperature microstructure. The low temperature sample displayed no intergranular film on the imaged boundaries while films were observed in the quenched samples. The intergranular pockets in the low temperature sample contained mullite precipitates while the high temperature pockets contained a fewer smaller precipitates. The authors suggest that mullite precipitation in the intergranular pockets buffers the chemistry and renders intergranular films unstable at low temperature. Therefore, a transition from wet (with continuous film) to dry (without film) exists between 1380°C and room temperature.

The phase-field model described in this thesis can be used without alteration to study wetting of solid phases. The parameters in the model are generally functions of
temperature. If appropriate functional forms are chosen and phase-field simulations are tuned to several temperatures, then the coefficients in the general functional forms can be fit. For example, consider the parameter $\nu$ that determines the energetic penalty for gradients in structure. If $\nu = \nu(T)$ values are determined from equilibrated boundaries at several temperatures, $T_1, T_2, \ldots$, and the general functional form is chosen to be $\nu(T) = A + BT + CT^2$, the constants $A, B$ and $C$ can be fit to the $\nu(T_1), \nu(T_2), \ldots$ data using a least squares regression. Then the model can be equilibrated at different temperatures to study wetting transitions. If a boundary equilibrated at $T = T_a$ displays a film and a boundary equilibrated at $T = T_b$ does not, then a wetting transition occurs at a temperature $T_b < T < T_a$.

In order to study phase-transitions, including wetting, in the intergranular pocket, the formulation including the solid-liquid phase-field, $\zeta$, would be used with the methods developed herein. The temperature dependence of the model parameters is to be determined for particular functional forms. Two-dimensional simulations must be performed at different temperatures to locate phase transformations in the pockets.

### 6.2.5 Anisotropic Interfacial Energies

Wetting and faceting transitions at grain boundaries as a function of misorientation are predicted from energy minimization techniques. These techniques suggest that for anisotropic surface energies, both rough and faceted boundaries should be observed. A Wulff construction that compares the solid–liquid interfacial energy with the energy of a grain boundary with a given misorientation was devised. Combinations of wet and dry and rough and faceted portions of a grain boundary with an average inclination and fixed misorientation are found [97].

The three grain boundaries in Fig. 6-1 exhibit three distinct morphologies of strontium barium aluminum silicate phase at grain boundaries in $\text{Al}_2\text{O}_3$. The lower right boundary is fully wet with rough film-grain interfaces, the upper right boundary is partially wet with lens-shaped second phase, and the left boundary is fully wet with
rough upper and faceted lower film-grain interfaces. Different misorientations are expected to correspond to different chemistries and structures. Therefore, the coupled approach of the phase-field model is a plausible framework within which to examine the stability of these films.

Kobayashi et al. formulate an anisotropic grain boundary energy by including an inclination dependence in the gradient energy coefficient for gradients in the structural field, $\eta$ [30]. The inclination can be calculated at every point in the system. In their two-dimensional, one-component, solid model, the inclination is measured by the difference between the angle that the $\nabla \eta$ vector forms with a reference $x$-axis and the local orientation measured with respect to the reference $x$-axis. The inclination, $\psi$, is illustrated in Fig. 6-2.

$$\psi + \theta = \tan^{-1} \left[ \frac{\partial \eta}{\partial y} \div \frac{\partial \eta}{\partial x} \right]$$  \hspace{1cm} (6.4)$$

In order to include an inclination dependence in the interfacial energies, the gradient energy coefficients for the appropriate fields must depend on the inclination. For a solid model, the grain boundary inclination is defined with respect to $\nabla \eta$. And the $\eta$ gradient energy coefficient must depend on this inclination. However, in a solid-liquid model the location of solid-liquid interfaces is given by non-zero values of $\nabla \zeta$. 

Figure 6-1: Strontium barium aluminum silicate phase at grain boundaries in $\text{Al}_2\text{O}_3$. There are three grain boundary morphologies. Reproduced from Clarke and Gee [5].
Figure 6-2: Schematic of the inclination calculated at two points in the vicinity of a solid grain boundary. The light blue curves are level sets of $\eta$. The inclination is $\psi$ with magnitude shown by the red arc.

Therefore, the inclination of the solid–liquid boundaries is related to $\nabla \zeta$ and the $\zeta$ gradient energy coefficient should depend on the inclination for anisotropic surfaces.

6.3 Enhancing Data used for Tuning the Phase-Field Model

In order to explore atomistic configurations in the intergranular films and pockets, additional experiments and simulations are necessary. In this section, I propose a hybrid Monte Carlo method for incorporating experimental information into simulations of intergranular pockets.

6.3.1 Monte Carlo Simulations

The MC method has a numerical efficiency advantage over the MD technique in that it does not have time constraints imposed by physical mobilities. Whereas, MD simulations of highly viscous materials will take longer to equilibrate than simulations of less viscous material, there is no similar computational time difference for MC simulations. Therefore, it is numerically expeditious to perform MC simulations on intergranular films. It is also possible to perform simulations at constant temperature, pressure and chemical potential whereby the composition of the film will adjust to
minimize the energy of the system.

The output from such simulations can be used to tune the phase-field model after continuizing using techniques such as those outlined in Chapter 2.

6.3.2 Diffraction from Nano-Volumes and Reverse Monte Carlo Simulations

Local information about structure in non-crystalline materials can be accessed in the electron microscope. The electron probe is focused on a small area less than 1 nm wide and diffraction data is collected. The structure factor and radial distribution function for the sampled nano-volume are calculated.

Reverse Monte Carlo (RMC) is a technique for generating non-crystalline atomic structures that are consistent with structure factors or radial distribution functions from a set of experiments [98]. The technique is based on standard MC methods but uses a modified acceptance criterion to account for observed structure factors in allowing changes to the system. An initial condition is chosen for $N$ atoms and the structure factor, $S(q_i)$, is calculated where $q_i$ is the wavenumber. A random virtual change is made and the new structure factor is calculated, $\tilde{S}(q_i)$. A $\chi^2$ test is used to compare the simulated structure factors to the experimentally generated one, $S_{exp}(q_i)$, where the experimental error is $\sigma_{exp}(q_i)$ and the wavenumber cut-off is $q_{nr}$.

$$\chi^2 = \sum_{i=1}^{n_r} \frac{(S(q_i) - S_{exp}(q_i))^2}{\sigma_{exp}(q_i)} \quad (6.5)$$

$$\tilde{\chi}^2 = \sum_{i=1}^{n_r} \frac{(\tilde{S}(q_i) - S_{exp}(q_i))^2}{\sigma_{exp}(q_i)} \quad (6.6)$$

The virtual change is accepted if $(\tilde{\chi}^2 - \chi^2) < 0$ and accepted with probability $\exp[-(\tilde{\chi}^2 - \chi^2)/2]$ if not. The particle positions are evolved until $\chi^2$ oscillates about an equilibrium value, and then states are sampled and averaged to compute a final
equilibrium state.

This technique has been supplemented with additional constraints in order to model glassy carbon by, among others Opletal et al. [99]. In order to remove unphysical 3 and 4 carbon rings, the acceptance criterion was weighted with a measure of the energy change of the system as calculated by an EDIP potential for carbon. The RMC technique is also formulated using RDFs, \( g(r) \), instead of structure factors.

### 6.3.3 Proposed Hybrid Monte Carlo Technique

RMC has been applied to bulk amorphous samples. I propose that it could be used in conjunction with other techniques to incorporate position dependent RDF information from the intergranular pockets in Si₃N₄. For example, if RDF information is obtained from a set of \( P \) positions in the intergranular pocket, Fig. 6-3, a modified \( \chi^2 \) of the form in Eq. 6.7 can be formulated.

\[
\chi^2 = \sum_{j}^{P} \chi_j^2
\]

where

\[
\chi_j^2 = \sum_{i=1}^{n_{r}} \frac{(g_j(r_i) - g_{exp,j}(r_i))^2}{\sigma_{exp}^2(r_i)}
\]

The experimental error, \( \sigma_{exp}^2(r_i) \), would be formulated over all of the experimentally obtained RDFs. The points in physical sample space \( \vec{x}_j \) with RDFs \( g_{exp,j}(r_i) \) would be mapped onto corresponding points \( \vec{x}_j \) in simulation space with RDFs \( g_j(r_i) \).

An MC simulation could be devised to equilibrate an intergranular pocket with the average composition indicated by corresponding TEM experiments. The arrangement of atoms in the film could then be further adapted by an RMC algorithm based on that described above. For example, instead of random changes in the system, a randomly selected atom from the set within the intergranular pocket could be moved in a random manner within some small cutoff distance. This virtual change is accepted
Figure 6-3: Schematic of intergranular films and pocket. Radial distribution functions are calculated for the $P$ points in the pocket. A method is proposed for refining MC simulations of the intergranular pockets using the $P$ experimentally determined radial distribution functions in a hybrid RMC technique.

if the modified acceptance criterion, Eq. 6.9, is negative or accepted with probability, $\exp[-\Delta F]$, if it is positive.

$$\Delta F = \frac{(\chi^2 - \chi^2)}{2} + \frac{\tilde{E} - E}{kT}$$  \hspace{1cm} (6.9)

The virtual state is represented by $\chi$ and $E$ is the energy calculated using the same set of interatomic potentials used in the MC simulation. In this case, a virtual temperature is associated with the denominator in the first term.

This method is likely to change the data sets produced from the MC simulations. The MC simulations yield the equilibrium state for given atomic potentials and subsidiary conditions. I posit that as interatomic potentials are typically based on crystalline information (structures and defect energies, e.g.), the set results will be empirically improved by the changes made using the hybrid RMC algorithm. It may be necessary to adjust the weight of the two terms in the acceptance criterion.
6.4 Coarse-Graining Information for Further Phase-Field Models

Zallen describes fused silica as "the archetypal example of a three-dimensional continuous random network formed by a binary compound [100]." While the structure of the amorphous material in the IGFs in Si$_3$N$_4$ is expected to differ from bulk unconstrained fused silica, the structure of the intergranular pocket material is less constrained. In SiO$_2$, each silicon is bonded to four oxygens, and each oxygen is bonded to two silicons. The Si-O-Si bond angles are less rigid than the O-Si-O bond angles. This suggests that the BADF constructed from the subset of Si-O-Si bond angles will provide insight into the state of the system and potentially a method of empirically refining atomic potentials. An additional insight into the structure of the intergranular pockets may be available from the BADF constructed from the subset of Si-Si (mathematical) bond angles. This subset has the advantage that it can be applied to silicates containing multiple anions, such as the Si-N-O material in undoped Si$_3$N$_4$.

Development of an algorithm that distinguishes between liquid and amorphous solid states in materials is challenging. The radial distribution functions for liquid and amorphous structures display the same basic characteristics, sharp first and second nearest neighbor peaks and marginally discernible peaks beyond the third nearest neighbors. The BADFs are also expected to be similar for the two structures. In general, the free volume in a glass is greater than the free volume in an undercooled liquid at the same temperature [3]. It is possible to calculate a local measure of free volume from the volume of the Voronoi tessellations generated from the atomic positions resulting from an MC simulation. The Voronoi tessellations calculated from the subset of the Si atomic positions may be useful. In order to determine the best method of distinguishing liquid and amorphous structures, comparisons should be made on bulk liquid and amorphous simulated structures.
It should be noted that liquid and glass structures may not be distinguishable in the IGF due to the small number of atoms. The material at the intergranular film is highly constrained by the proximity of the neighboring grains. It is this proximity of the grains that is expected to induce an ordering in the amorphous material adjacent to the grain faces. The identification of partially ordered amorphous material must be made based on the comparison to bulk unconstrained structures. And then, those empirical measures may only be compared to others in the same material system.

6.5 Dispersion Forces and Intergranular Films

The London dispersion forces result from induced dipole-induced dipole interactions between materials [101]. For two slabs of material 1 separated by a slab of material 2 with a thickness $h$, the interaction energy per unit area can be written in terms of a full spectral Hamaker constant, $A_{121}$, Eq. 6.10. The Hamaker constant can be derived from the associated dielectric spectra of materials 1 and 2. The symmetric Hamaker constant, $A_{121}$, is always negative implying attractive forces. However, in general the Hamaker constant for three different materials or, in the case of intergranular films, three materials with different spectra, $A_{123}$, can have either sign. Because the dielectric constant is a tensor, it may be possible for an intergranular film to have a positive Hamaker constant or repulsive force.

$$E = \frac{A_{121}}{12\pi h^2}$$ (6.10)

French et al. have calculated the Hamaker constants for IGFs in Si$_3$N$_4$ from interband transition energies measured using spatially-resolved valence electron energy loss spectrum imaging (VEELs) [102]. This technique can also be used as a measure of IGF thickness based on the deviation of the index of refraction from that in the Si$_3$N$_4$ grains.

French has developed a method of calculating Hamaker constants for arbitrary
multilayer stacks of materials [103, 104]. Within each layer the optical properties can vary with a linear or parabolic relation to distance. For a film thickness $h$, the energy of the dispersion interactions can be calculated based on an approximation to the composition profile. However, this method requires a priori the spectra for each of the structures and compositions. It may eventually be possible to calculate the Hamaker constant for an empirical fit of the composition across an IGF.

Incorporating the dispersion interaction into a phase-field formulation is not straightforward. Ackler does this for the formulation described in Section 1.7 and reproduced here, Eq. 6.11 [36]. He models the interfacial energy as an integral over the film thickness of an energy density plus a Hamaker term.

$$\sigma(h) = \int_{h_1}^{h_2} \left[ \nu^2 \phi(x)^2 + \epsilon^2 |\nabla \phi(x)|^2 \right] dx + \frac{A_{121}}{12\pi h^2}$$

He analyzes the energy of the system for different thicknesses, misorientations, and Hamaker constants. However, the field profile is calculated by minimizing the functional analytically and then minimizing with respect to $h$. Field values at the boundaries are fixed.

If the Hamaker constant corresponding to the structures and chemistries of an IGF could be calculated, then an approximation to the dispersion interactions could be included in an energetic description described by Ackler. A minimization of the total energy with respect to film thickness would allow the equilibrium film thickness to be determined parametrically.

6.6 Summary and Conclusions

The phase-field model and supporting techniques described in this thesis comprise a comprehensive approach to modeling complex interfaces using continuum thermodynamics. The model developed in Chapter 4 is the first to incorporate the coupled energetic effects of structure, chemistry, and electrostatics. A parameter set is intro-
duced in the model. These parameters dictate the relative magnitudes of the different energetic contributions. I propose that these parameters are adjusted to produce equilibrated microstructures that correspond to continuized information from atomistic simulations and experimental observations.

The phase-field model was tuned to the CaO-doped Si$_3$N$_4$ system in order to investigate intergranular films. However, the methods described here can be applied to other material systems. While the effect of altering a gradient energy parameter was illustrated through comparison of the results in Fig. 5-5 fro $\tilde{\nu} = 0.01$ and $\tilde{\nu} = 0.005$, the phase-field model was not tuned here because the atomistic and experimental data sets do not as yet exist.

MC simulations (that are not restricted by physical time constants) should be performed to generate equilibrated grain boundary and intergranular pocket structures. In addition, I have proposed a hybrid RMC algorithm for refining intergranular pocket structures using experimental RDFs from nano-volume diffraction. These kinds of equilibrated data sets should be used to tune the phase-field model.

The coarse-graining methods discussed in Chapter 2 should be applied to atomistic data sets in order to calculate continuized measures of structure and chemistry. Continuized composition profiles from MD simulations of IGFs in Si$_3$N$_4$ are calculated using Voronoi tessellations as averaging tools. Two methods of calculating measures of structure, one using a geometric measure of Voronoi tessellations and the other using a comparison of BADFs, are developed for single component systems. The extension of these methods to multicomponent systems and the derivation of a scheme for calculating local orientation are problems that remain to be solved.

The framework of this phase-field model can be extended to treat intergranular pockets, surficial films, and wetting phenomena. While the phase-field simulations presented here are a prohibitively slow way of solving for equilibrium in a system, additional computational methods must be investigated. This is especially relevant for the two-dimensional calculations that allow a film to select its chemistry freely.
Appendix A

Physical Data

The reference free energies of the solid phases used in Eq. 4.15 are taken as the Gibbs free energies of the solid phases. As solids generally have low compressibilities, the Gibbs free energy and Helmholtz free energies are very similar. Gibbs free energies which are available in the literature are used here. The functions are piece-wise continuous.

The Gibbs free energy data for SiO₂ and CaO are taken from Hillert et al. [83]. The transformation temperatures and the enthalpies of fusion for SiO₂ and CaO are calculated from this data.

The Gibbs free energy function for solid Si₃N₄, the melting point and entropy of

<table>
<thead>
<tr>
<th>SiO₂ [83]</th>
<th>T_{\text{trans}}</th>
<th>\Delta H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz to Tridymite</td>
<td>1143K</td>
<td></td>
</tr>
<tr>
<td>Tridymite to Cristobalite</td>
<td>1744K</td>
<td></td>
</tr>
<tr>
<td>Cristobalite to Liquid</td>
<td>1996K</td>
<td>8918.32J/moleK</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CaO [83]</th>
<th>T_{\text{trans}}</th>
<th>\Delta H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid to Liquid</td>
<td>3172K</td>
<td>79495.9J/moleK</td>
</tr>
</tbody>
</table>

Table A.1: Thermodynamic data for SiO₂ and CaO.
fusion are taken from Hillert et al. [83]. The melting point and entropy of fusion for 
$\text{Si}_3\text{N}_4$ are $T_{m, \text{Si}_3\text{N}_4} = 2600\text{K}$ and $\Delta \overline{S}_f = 80.5\text{J/moleK}$. 

\footnote{Hillert et al. used data from a thesis by Weiss for $T_m$ and $\Delta \overline{S}_f$.}
Appendix B

Iteration Equations

This Appendix presents the finite difference schemes used to simulate the evolution equations for the fields Eqs. 4.46- 4.50. These equations use a semi-implicit scheme. Forward differences are used for the time derivative. The spatial derivatives are semi-implicit and use information from both the current and next time-step. These equations apply for the \( k \)th grid point. The boundary conditions effect the form of the equations for points \( k = 0, 1, n - 2, n - 1 \).

\[
X_{Si,k}^{t+1} = \left[ 1 + 6 \frac{\dot{M}_{Si} \Delta \tilde{k}^2_{Si}}{\Delta x^4} \right] X_{Si,k}^t + \frac{\dot{M}_{Si} \Delta \tilde{k}^2_{Si}}{\Delta x^4} (X_{Si,k-2}^{t+1} - 4X_{Si,k-1}^{t+1} - 4X_{Si,k+1}^{t+1} + X_{Si,k+2}^{t+1}) = X_{Si,k}^t + \frac{\dot{M}_{Si} \Delta \tilde{k}^2_{Ca}}{\Delta x^4} \left[ \left( \frac{\partial f^a}{\partial X_{Si}} \right)_k^{t+1} - 2 \left( \frac{\partial f^a}{\partial X_{Si}} \right)_k^t + \left( \frac{\partial f^a}{\partial X_{Si}} \right)_{k-1}^t \right] \]

\[
- \frac{\dot{M}_{Si} \Delta \tilde{k}^2_{Si}}{\Delta x^4} (X_{Ca,k-2}^t - 4X_{Ca,k-1}^t + 6X_{Ca,k}^t - 4X_{Ca,k+1}^t + X_{Ca,k+2}^t)
- \frac{\dot{M}_{Si} \Delta \tilde{k}^2_{Si}}{\Delta x^4} (q_{k-2}^t - 4q_{k-1}^t + 6q_k^t - 4q_{k+1}^t + q_{k+2}^t)
\]
\[
\begin{align*}
&\left[ 1 + 6 \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{Ca}^2}{\Delta \dot{x}^4} + \frac{\dot{M}_{Ca} \Delta \dot{i} \lambda^2 \dot{s}}{\Delta \dot{x}^3} (\eta_k^t)^2 |\theta_{k+1}^t - \theta_{k-1}^t| \right] X_{Ca,k}^{t+1} \\
&- \left( 4 \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{Ca}^2}{\Delta \dot{x}^4} + \frac{\dot{M}_{Ca} \Delta \dot{i} \lambda^2 \dot{s}}{2 \Delta \dot{x}^3} (\eta_{k+1}^t)^2 |\theta_{k+2}^t - \theta_{k}^t| \right) X_{Ca,k+1}^{t+1} \\
&- \left( 4 \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{Ca}^2}{\Delta \dot{x}^4} + \frac{\dot{M}_{Ca} \Delta \dot{i} \lambda^2 \dot{s}}{2 \Delta \dot{x}^3} (\eta_{k-1}^t)^2 |\theta_{k}^t - \theta_{k-2}^t| \right) X_{Ca,k-1}^{t+1} \\
&+ \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{Ca}^2}{\Delta \dot{x}^4} (X_{Ca,k+2}^{t+1} + X_{Ca,k-2}^{t+1}) = \\
X_{Ca,k}^{t} + \frac{\dot{M}_{Ca} \Delta \dot{i}}{\Delta \dot{x}^2} \left[ \left( \frac{\partial f^a}{\partial X_{Ca}} \right)_{k+1}^t - 2 \left( \frac{\partial f^a}{\partial X_{Ca}} \right)_{k}^t + \left( \frac{\partial f^a}{\partial X_{Ca}} \right)_{k-1}^t \right] \\
- \frac{\dot{M}_{Ca} \Delta \dot{i} \lambda \dot{s}}{2 \Delta \dot{x}^3} \left[ (\eta_{k+1}^t)^2 |\theta_{k+2}^t - \theta_{k}^t| - 2(\eta_k^t)^2 |\theta_{k+1}^t - \theta_{k-1}^t| + (\eta_{k-1}^t)^2 |\theta_{k}^t - \theta_{k-2}^t| \right] \\
- \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{SiCa}^2}{\Delta \dot{x}^4} (X_{Si,k-2}^t - 4X_{Si,k-1}^t + 6X_{Si,k}^t - 4X_{Si,k+1}^t + X_{Si,k+2}^t) \\
- \frac{\dot{M}_{Ca} \Delta \dot{i} \dot{\kappa}_{Caq}^2}{\Delta \dot{x}^4} (q_{k-2}^t - 4q_{k-1}^t + 6q_k^t - 4q_{k+1}^t + q_{k+2}^t) \\
\end{align*}
\]

\[
\begin{align*}
&\left[ 1 + 2 \frac{\dot{M}_q \Delta \dot{i} \alpha^2}{\Delta \dot{x}^2} + \frac{\dot{M}_q \Delta \dot{i} \dot{\kappa}_{aq}^2}{\Delta \dot{x}^4} \right] q_{k}^{t+1} \\
&\left[ \frac{\dot{M}_q \Delta \dot{i} \alpha^2}{\Delta \dot{x}^2} + \frac{\dot{M}_q \Delta \dot{i} \dot{\kappa}_{aq}^2}{\Delta \dot{x}^4} \right] (q_{k+1}^{t+1} + q_{k-1}^{t+1}) \\
&+ \frac{\dot{M}_q \Delta \dot{i} \dot{\kappa}_{aq}^2}{\Delta \dot{x}^4} (q_{k+2}^{t+1} + q_{k-2}^{t+1}) = \\
q_{k}^t + \frac{\dot{M}_q \Delta \dot{i}}{\Delta \dot{x}^2} \left[ \left( \frac{\partial f^a}{\partial q} \right)_{k+1}^t - 2 \left( \frac{\partial f^a}{\partial q} \right)_{k}^t + \left( \frac{\partial f^a}{\partial q} \right)_{k-1}^t \right] \\
- \frac{\dot{M}_q \Delta \dot{i} \dot{\kappa}_{Siq}}{\Delta \dot{x}^4} (X_{Si,k-2}^t - 4X_{Si,k-1}^t + 6X_{Si,k}^t - 4X_{Si,k+1}^t + X_{Si,k+2}^t) \\
- \frac{\dot{M}_q \Delta \dot{i} \dot{\kappa}_{Caq}^2}{\Delta \dot{x}^4} (X_{Ca,k-2}^t - 4X_{Ca,k-1}^t + 6X_{Ca,k}^t - 4X_{Ca,k+1}^t + X_{Ca,k+2}^t) \\
\end{align*}
\]
\[
1 + \frac{\dot{M}_\eta \Delta \hat{t}}{2 \Delta \hat{x}} (1 - \lambda X_{\text{Ca},k}^t)^2 (\theta_{k+1}^t - \theta_{k-1}^t) + 2 \frac{\dot{M}_\eta \Delta \hat{t} \Delta \hat{v}^2}{\Delta \hat{x}^2} \eta_{k+1}^t \eta_{k-1}^t
\]
\[
- \frac{\dot{M}_\eta \Delta \hat{t} \Delta \hat{v}^2}{\Delta \hat{x}^2} (\eta_{k+1}^t + \eta_{k-1}^t) = \eta_k^t - \dot{M}_\eta \Delta \hat{t} \left( \frac{\partial f^a}{\partial \eta} \right)_k^t
\] (B.4)

\[
1 + \frac{\dot{M}_\theta \Delta \hat{t}}{\Delta \hat{x} (\eta_k^t)^2} \left( \frac{1}{2} \ddot{s} (\eta_{k+\frac{1}{2}})^2 (1 - \lambda X_{\text{Ca},k+\frac{1}{2}}^t)^2 \chi_\gamma \left( \frac{\theta_{k+1}^t - \theta_k^t}{\Delta \hat{x}} \right)^2 + \beta^2 \right) \theta_{k+1}^t
\]
\[
+ \frac{1}{2} \ddot{s} (\eta_{k-\frac{1}{2}})^2 (1 - \lambda X_{\text{Ca},k-\frac{1}{2}}^t)^2 \chi_\gamma \left( \frac{\theta_k^t - \theta_{k-1}^t}{\Delta \hat{x}} \right)^2 + \beta^2 \right) \theta_{k-1}^t
\] (B.5)

\[
- \frac{\dot{M}_\theta \Delta \hat{t}}{\Delta \hat{x} (\eta_k^t)^2} \left[ \frac{1}{2} \ddot{s} (\eta_{k+\frac{1}{2}})^2 (1 - \lambda X_{\text{Ca},k+\frac{1}{2}}^t)^2 \chi_\gamma \left( \frac{\theta_{k+1}^t - \theta_k^t}{\Delta \hat{x}} \right)^2 + \beta^2 \right] \theta_{k+1}^t
\]
\[
- \frac{\dot{M}_\theta \Delta \hat{t}}{\Delta \hat{x} (\eta_k^t)^2} \left[ \frac{1}{2} \ddot{s} (\eta_{k-\frac{1}{2}})^2 (1 - \lambda X_{\text{Ca},k-\frac{1}{2}}^t)^2 \chi_\gamma \left( \frac{\theta_k^t - \theta_{k-1}^t}{\Delta \hat{x}} \right)^2 + \beta^2 \right] \theta_{k-1}^t
\]
Bibliography


