FINITE ELEMENT METHOD FOR CONSERVED PHASE FIELD MODELS:
SOLID STATE PHASE TRANSFORMATIONS

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FINITE ELEMENT METHOD FOR CONSERVED PHASE FIELD MODELS:
SOLID STATE PHASE TRANSFORMATIONS

Abstract

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Cahn-Hilliard type of phase field model coupled with elasticity equations is used to derive governing equations for the stress-mediated diffusion and solid state phase transformations. The partial differential equations governing diffusion and mechanical equilibrium are of different orders. A mixed-order finite element formulation is developed, with \( C^0 \) interpolation functions for displacements, and \( C^1 \) interpolation functions for the phase field variable – the concentration. Uniform quadratic convergence, expected for conforming elements, is achieved for both one and two dimensional systems.

The developed finite element model (FEM) is used to simulate the nucleation and growth of the intermediate phase in a thin film diffusion couple as one-dimensional (1D) problem and the results are compared with Johnson’s finite difference model (FDM). Two-dimensional (2D) simulations are divided into two categories. In the first category, 2D model is applied to study phase transformations of single precipitates in solid state binary systems, and the effects of using complete and incomplete Hermite cubic elements
on the transformation rate of systems with isotropic and anisotropic gradient energy coefficients are investigated. In the second category, 2D model is used to study the stability of multilayer thin film diffusion couples in solid state. Maps of transformations in multilayer systems are carried out considering the effects of thickness of layers, volume fraction of films, and compositional strain on the instability of the multilayer thin films. It is shown that at some cases phase transformations and intermediate phase nucleation and growth lead to the coarsening of the layers which can result in different mechanical and materials behaviors of the original designed multilayer.
Dedication

This dissertation is dedicated to

My father: Naser Asle Zaeem
My mother: Tooba Kashan Deghan,
My wife: Sanaz Yazdan Parast

who provided all supports during my study.
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CHAPTER ONE: Introduction

1.1 Microstructural Evolution and Phase Field Model

Evolution of microstructures takes place in many fields including biology, hydrodynamics, chemical reactions, and phase transformations. During the processing of materials, the microstructural evolution occurs to reduce the free energy of the system and force the system to a low energy equilibrium condition. The size, shape, and spatial arrangement of the local structural features in a microstructure play a critical role in determining different properties of a material. These structural features usually have an intermediate mesoscopic length scale in the range of nanometers to microns. Because of the complexity and nonlinearity nature of microstructural evolution, numerical models are often employed to investigate the behaviors of the microstructures under different conditions. In the sharp-interface model (Caginalp and Xie 1993) which is the traditional method for capturing the microstructural evolution, the regions separating the compositional or structural fields are considered as mathematically sharp interfaces so one or more variables (or their derivatives) are typically discontinuous across an interface. The local velocity of interfacial regions is then determined as part of the boundary conditions or calculated from the driving force for interface motion and the interfacial mobility. This involves the explicit tracking of the interface positions. This interface-tracking approach can be very successful in one-dimensional systems, but it
becomes impractical for complicated two and three-dimensional microstructures those include intermediate phase growth, triple junctions, and etc.

Recently, the phase-field method has been found as a powerful computational tool for modeling mesoscale microstructural evolution in materials. Phase-field model is based on a diffuse-interface description developed more than a century ago by van der Walls (Rowlinson 1979) and almost 50 years ago independently by (Cahn and Hilliard 1958). Phase-field models describe microstructure phenomena at the mesoscale and include field variables corresponding to physical order parameters such as long-range order parameters for order-disorder transformations and the composition fields for phase separation. Phase-field models have been extensively applied to simulate solidification and solid-state phase transformations (Ode et al. 2001; Chen and Wang 1996) and also have been employed for modeling a number of other important materials processes including grain growth and coarsening (Chen and Wang 1994; Steinbach et al. 1996; Lusk 1999; Kobayashi et al. 2000), phase transformations in thin films (Li et al. 2001; Seol et al. 2003; Atemev et al. 2008), crack propagation (Aranson et al. 2000; Karma et al. 2001; Karma and Lobkovsky 2003; Spatschek et al. 2006; Song et al. 2007), dislocation dynamics (Wang et al. 2001; Wang et al. 2003; Koslowski and Ortiz 2004), and etc.

Phase-field models are characterized by the dependence of the free energy of a non-uniform system on the phase field variable. Mathematically, the phase-field formulation gives rise to two types of problems. The non-conserved phase-field variables, such as solidification and melting problems (Fan et al. 2006; Provatas et al. 1998; Sabouri
et al. 2001), are often assumed to evolve according to the “first-order relaxation”, whereby the rate of change of the phase variable is proportional to the variational derivative of the free energy, mediated by the kinetic mobility. Such formulation leads to a 2nd order, diffusion-type, evolution PDE for the phase field variable (Wang and Khachaturyan 1997; Wen et al. 1999). However, if the phase-field variable is subject to a conservation law, then the rate of the phase field variable is proportional to the divergence of the flux, which, in turn, is proportional to the gradient of a potential. This potential is equal to the variational derivative of the free energy. Examples include diffusion-controlled solid state phase transformations (Cahn and Hilliard 1958; Cahn and Kobayashi 1995; Johnson 2000; Leo and Johnson 2001), and interfaces between immiscible fluids (Jacqmin 1999; Anderson et al. 1998). Typically, the 4th order evolution PDE is coupled to a 2nd order PDEs (stress, heat, etc.). For example, in solid state phase transformations, the lattice continuity across the interfaces between mismatched phases produces elastic strains (Khachaturyan 1983; Cahn and Larche 1982; Larche and Cahn 1992; Khachaturyan et al. 1996), so that the 2nd order elasticity PDEs are coupled to the phase field equation (Cahn and Hilliard 1958; Cahn and Kobayashi 1995; Johnson 2000; Leo and Johnson 2001; Leo et al. 1998; Chen et al. 1991).

The problems in this class have been addressed in the past, with the numerical tools tailored for specific problems. However, a general numerical method for solving the coupled equations, applicable to variety of geometries and boundary conditions, has remained a challenging problem. The finite difference method (FDM) was used by (Cahn and Kobayashi 1995) for one-dimensional modeling of the rapid coarsening and
buckling in coherently self-stressed thin plates. (Johnson 2000) used FDM to study the growth of the immediate phase in a thin film diffusion couple. Leo et al [35] used a pseudo-spectral method for the phase-field model for the coarsening of a two dimensional, elastically stressed binary alloys. Fourier transform techniques (Chen et al. 1991; Chen et al. 1992; Wang et al. 1993; Wang and Khachaturyan 1995; Li and Chen 1998], and related Fourier-spectral methods (Chen and Shen 1998; Hu and Chen 2001; Zhu et. al. 2001; Vaithyanathan and Chen 2002; Vaithyanathan et al. 2004; Boisse et al. 2007), have been used to investigate the microstructure evolution (mostly coarsening) during the solid state phase transformation. The drawbacks of such methods are seen in the difficulties in modeling irregular domains, nonlinear, and history-dependent problems. A versatile method, such as the finite element method, or the mesh-free method, applicable to irregular domains, variety of boundary conditions, and various forms of geometric and material nonlinearities is needed. Recently, (Kay and Welford 2006) considered a single, uncoupled, 4th order Cahn-Hilliard equation, and developed a mixed finite element formulation with independent linear interpolation for the phase variable and its potential. Previously different Hermite cubic finite elements have been used for the plate bending problems (Hrabok and Hrudey 1984) which include 4th order elliptic equations (Taylor and Govindgee 2002; Li et al. 2008; Chien and Shih 2009; Petera and Pittman 1994). Some of the Hermite cubic interpolation functions don’t have the completeness conditions as they don’t include higher order mixed derivate terms and these types of elements are found to be too stiff for plate bending problems. In this
research, these two types of Hermite cubic elements (complete and incomplete) are used and compared for 4th order parabolic equations.

1.2 Thesis Layout

This thesis is organized as follows. In Chapter 2, one-dimensional finite element model is developed for the coupled 4th order conserved phase-field equations and 2nd order continuum mechanics PDEs. For the finite element implementation the weak form of governing Cahn-Hilliard and elasticity equations is developed which is equally applicable to finite element and mesh-free methods. As the mechanical and diffusion/phase field equations are of different orders, uniform convergence of the results requires different order of continuity for interpolation functions (Hughes 2000). The developed one-dimensional finite element model is used to study phase transition and growth of intermediate phase in Al-Zn thin film diffusion couples.

In Chapter 3, the mixed order finite elements is formulated and implemented, with $C^0$ interpolation functions for displacement, and $C^1$ interpolation functions for concentration for both 1D and 2D interpolation functions. First the developed model is applied to simulate a one-dimensional problem of the growth of intermediate phase in a thin-film diffusion couple and the results are compared to those from Johnson’s finite difference solutions (Johnson 2000). Convergence study of 2D FE model is conducted by modeling the shape evolution of single precipitates during the growth of intermediate phase. Two types of Hermite cubic interpolation functions are used, one has the completeness condition which previously confirmed for the plate bending studies and
another one doesn’t have the completeness condition which we want to examine if it works for parabolic equations like Cahn-Hilliard equation and under what conditions.

In chapter 4, the 2D model is applied to study the stability of multilayer thin film diffusion couples in solid state. Maps of transformations in multilayer systems are carried out considering the effects of interface thickness between phases, thickness of layers, and elastic strain on the stability of the multilayer systems.
CHAPTER TWO: Investigation of Phase Transformation in Thin Film Using Finite Element Method

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Abstract

Cahn-Hilliard type of phase field model coupled with elasticity is used to derive governing equations for the stress-mediated diffusion and phase transformation in thin films. To solve the resulting equations, a finite element (FE) model is presented. The partial differential equations governing diffusion and mechanical equilibrium are of different orders; Mixed-order finite elements, with $C^0$ interpolation functions for displacement, and $C^1$ interpolation functions for concentration are implemented. To validate this new numerical solver for such coupled problems, we test our implementation on a 1D problem and demonstrate the validity of the approach.

Keywords: Phase transformation, solid state, thin film, phase field model, finite element (FE).
2.1 Introduction

A sequential formation of the intermediate phase occurs in binary diffusion couples and the intermediate phase nucleates and grows until one of the end phases is consumed. Several researches have been done to find proper diffuse interface models for capturing the evolution of microstructure formed during the diffusion between two major phases in binary alloys (Cahn and Kobayashi 1995; Leo et al. 1998; Johnson 1997; Johnson 2000; Hu and Chen 2001; Hinderliter and Johnson 2002; Ahmed 2007; Wang et al. 2007). Cahn and Kobayashi (Cahn and Kobayashi 1995) showed that the coupling between stress and diffusion can have a strong effect on the microstructural evolution. (Johnson 2000) studied the growth of the intermediate phase in binary alloys. He showed that the compositional strains can lead to bending of the mechanically unconstrained thin plates. In this class of coupled problems, the question of a general, versatile numerical method for solving the coupled equations, applicable to a variety of geometries and boundary conditions, is the main issue. The finite difference method used by (Johnson 2000), and the more common Fourier-spectral methods (Hu and Chen 2001), have own limitations. The finite element method seems to be the most versatile tool for modeling this class of problems, especially when coupled with visco-plasticity and large deformation, most commonly modeled in a Lagrangean framework with the resulting nonlinearities.

In this paper we use a weak form of the Cahn-Hilliard type of phase-field model (Cahn and Hilliard 1958) coupled with elasticity, to derive the governing FE equations. The equations are derived for a binary system that can exist in three phases and the lattice parameter assumed to be both linear and quadratic function of the composition. As the
mechanical and diffusion/phase field equations are of different orders, uniform convergence of the results requires different order of continuity for interpolation functions (Hughes 2000). We formulate and implement such mixed-order finite elements, with \( C^0 \) interpolation functions for displacement, and \( C^1 \) interpolation functions for concentration. To test our formulation and implementation we consider different cases for the Al-Zn binary system. The results are in good agreement with Johnson’s finite difference method results (Johnson 2000).

2.2 Formulation

2.2.1 Phase field model

A binary alloy with two components A and B is considered. The alloy forms three different phases that are assumed to be isostructural. The \( \alpha \) phase is rich in component A and has initial composition \( C_{\alpha}^0 \), and the \( \gamma \) phase is rich in component B and has initial composition \( C_{\gamma}^0 \). The intermediate phase is denoted \( \beta \) and has about 50% of each component. Average composition \( C_0 \) is taken as the reference composition for the analyses. The lattice parameter \( a(C) \) is assumed to be a linear or quadratic function of composition:

\[
a(C) = a(C_0) \left[ 1 + \eta_1 (C - C_0) + \eta_2 (C - C_0)^2 \right],
\]

(2.1)
The material parameters $\eta_1$ and $\eta_2$ are the measures of the compositional strain; $\eta_2$ is a measure of the derivation of Vegard’s law (Denton and Ashcroft 1991) ($\eta_2$ is 0 when the system obeys Vegard’s law). The compositional strain has the form:

$$e = \frac{a(C) - a(C_0)}{a(C_0)} = \eta_1 (C - C_0) + \eta_2 (C - C_0)^2.$$  \hspace{1cm} (2.2)

The total free energy of a non-uniform system with volume $V$, bounded by surface $S$, is given as:

$$F = \int_V [f(C) + U(\mathbf{\epsilon}, C) + \frac{k}{2} (\nabla C)^2] dV + \int_S \gamma(C) dS - \int_S \mathbf{t} \cdot \mathbf{u} dS,$$  \hspace{1cm} (2.3)

where the last term represents the loading potential, with surface tractions $\mathbf{t}$ and displacement vector $\mathbf{u}$. $C$ is the mole fraction of component B, $U(\mathbf{\epsilon}, C)$ is the strain energy density, $\mathbf{\epsilon}$ is the total strain tensor, $k$ is the composition-independent gradient energy coefficient (scalar for a cubic system (Cahn and Hilliard 1958)), $\gamma(C)$ is the surface free energy density. The Helmholtz free energy density of a uniform unstressed system at concentration $C$, $f(C)$, is assumed to be a three well potential (Johnson 2000) as illustrated in Figure 2.1:

$$\frac{f(C)}{\rho_0 KT} = W_1 (C - C_\alpha)^2 (C - C_\beta)^2 (C - C_\gamma)^2 + W_2 (C - C_\alpha)^2 (C - C_\gamma)^2,$$  \hspace{1cm} (2.4)

where $W_1$ and $W_2$ are the energy coefficients, $\rho_0$ is density of the lattice sites, $K$ is Boltzmann’s constant, and $T$ is the temperature. $C_\alpha$, $C_\beta$ and $C_\gamma$ are the mole fractions of component B at which the Helmholtz free energy of the uniform unstressed system has minima. The parameters in (2.4) are chosen so that $C_\beta = (C_\alpha + C_\gamma)/2$. Depending on
parameters $W_1$ and $W_2$, the intermediate phase can be a stable, or a meta-stable
equilibrium phase, as illustrated in Figure 2.1. The strain energy density, $U(\varepsilon, C)$, is
defined as:

$$U(\varepsilon, C) = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - e(C)\delta_{ij}) (\varepsilon_{kl} - e(C)\delta_{kl}).$$

(2.5)

Index notation with summation over repeated indices is used; $\delta_{ij}$ is the Kronecker delta,
and $C_{ijkl}$ are the components of the elastic stiffness tensor. The stress is defined as:

$$\sigma_{ij} = \partial U / \partial \varepsilon_{ij} = C_{ijkl} (\varepsilon_{kl} - e(C)\delta_{kl}).$$

(2.6)

Figure 2.1. Free energy density as a function of composition. The minima are at 5, 50 and 95%.
2.2.2 Equilibrium Conditions

Considering zero flux on the boundaries, the conservation of mass requires:

$$\int_V (C - C_0) dV.$$  \hfill (2.7)

The equilibrium problem is one of constrained minimization of free energy (2.3), under constraint (2.7). Upon introducing the Lagrange multiplier, $M_0$, we seek to minimize the functional:

$$\bar{F} = F - M_0 \int_V (C - C_0) dV.$$  \hfill (2.8)

For isothermal chemical and mechanical equilibria, we require that variational derivatives of (2.8) with respect to $C$ and $u$, vanish: $\delta_c \bar{F} = 0$, and $\delta_u \bar{F} = 0$. The chemical equilibrium requires

$$\delta_c \bar{F} = \int_V \left[ f' + U' - kV^2 C - M_0 \right] \delta C dV + \int_V \left[ \gamma' + U' - kn \cdot \nabla C \right] \delta C dS = 0 ,$$  \hfill (2.9)

for arbitrary variation $\delta C$. The primes denote partial derivatives with respect to concentration, e.g., $f' = \partial f / \partial C$. This implies:

$$f' + U' - kV^2 C = M_0 = \text{constant, \quad in } V ,$$  \hfill (2.10)

$$\gamma' + kn \cdot \nabla C = 0 , \quad \text{on } S .$$  \hfill (2.11)

The mechanical equilibrium requires:

$$\delta_u \bar{F} = \int_V C_{ij,k} u_{j,k} \delta u_{j,i} dV - \int_V e C_{ij,k} \delta u_{j,i} dV - \int_S t_j \delta u_j dS = 0 .$$  \hfill (2.12)
2.2.3 Diffusion

Local conservation of concentration, $C$, implies that its local value changes according to the divergence of its flux $\mathbf{J}$:

$$\rho_0 \dot{C} = -\nabla \cdot \mathbf{J}.$$  \hspace{1cm} (2.13)

In a multi-component solid under stress, the chemical potential, which is constant at equilibrium (2.10) is determined from the variational derivative of free energy respect to composition (Larche and Cahn 1978):

$$M = \delta F/\delta C = (f' + U' - k \nabla^2 C).$$ \hspace{1cm} (2.14)

The flux of $C$ is proportional to gradient of the chemical potential, $M$:

$$\mathbf{J} = -\rho_0 B \nabla M,$$ \hspace{1cm} (2.15)

where $B$ is the mobility, assumed to be a function of temperature only. The equation for the time evolution of composition becomes:

$$\dot{C} = B \nabla^2 (f' + U' - k \nabla^2 C).$$ \hspace{1cm} (2.16)

Since the chemical potential (2.14) depends on second order derivatives of composition, (2.16) is fourth order PDE in composition. For finite element implementation, we start from (2.13) and follow the usual procedure to derive the week form:

$$\int_V \rho_0 \dot{C} \delta C \, dV - \int_V \mathbf{J} \cdot \delta \nabla C \, dV + \int_S \mathbf{n} \cdot \mathbf{J} \delta C \, dS = 0.$$ \hspace{1cm} (2.17)

Since there is no flux on the boundaries, the third integral in (2.17) vanishes. Then, using (2.15) and (2.16):

$$\int_V \dot{C} \delta C \, dV + \int_V B \left[ (f'' + U'') C_{,i} + \frac{\partial U'}{\partial \varepsilon_{pq}} \varepsilon_{pq,i} - k C,_{,ii} \right] \delta C_{,i} \, dV = 0.$$ \hspace{1cm} (2.18)
2.2.4 Finite element method

The coupled mechanical equation (2.12) and phase field/diffusion equation (2.18) are solved numerically for a thin film diffusion couple, schematically shown in Figure 2.2, using the finite element method. The partial differential equations governing diffusion and mechanical equilibrium are of different orders so mixed-order finite element implementation is needed. Two-node linear elements with regular $C^0$ interpolation functions are used to generate the mesh along the plate-thickness for the mechanical equation (2.12). As the diffusion/phase field equation is 4th order in concentration, the standard convergence theorems require $C^1$ continuity (like beam elements) (Hughes 2000), so two-node nonlinear elements with Hermite cubic polynomials are used to discretize the domain for concentration, (2.18). Different mesh sizes are examined along the plate thickness of the thin-film diffusion couple to find the proper mesh size.

The resulting FE equations consist of two sets of equations: a set of algebraic equilibrium equations for displacement, and a set of 1st ODE for concentration degrees of freedom. The FE equations resulting from equation (2.12) can be written in matrix form as:

$$[K]\{u\} = \{F\}, \quad (2.19)$$

$\{u\}$ is the vector of nodal displacements, $[K]$ is the stiffness matrix, and $\{F\}$ is the force vector that depends on compositional strain. The FE equations resulting from equation (2.18) can be written in matrix form as:

$$[M]\{\ddot{\Gamma}\} + [d]\{\dot{\Gamma}\} = \{h\}, \quad (2.20)$$
\{\Gamma\} is the vector of nodal concentrations and its gradients. The order of the governing equations dictates that the interpolation includes both nodal concentration, and its gradients. Note that both matrix \([d]\) and vector \([h]\) depend on mechanical equations (stress).

A special time integration scheme was developed consisting of implicit time-stepping and equilibrium iterations in each time step. At time \(t\), the matrix \([d]\) and vector \([h]\) are known. We first estimate \(\{\Gamma\}\) at \(t + \Delta t\) by applying the Euler time integration scheme to (2.20). Then, we iterate to satisfy equilibrium (2.19) at \(t + \Delta t\), with corrections to (2.20), to obtain the values of both \(\{\Gamma\}\) and \(\{u\}\) at \(t + \Delta t\).

\[\text{Figure 2.2. (a) Schematic representation of initial } \beta \text{ phase grows as the intermediate phase and the plate is free to bend. (b) condition of the thin plate diffusion couple.}\]
2.3 Results and discussions

Components A and B in the thin-film diffusion couple are assumed to be Aluminum and Zinc, respectively, and the initial compositions (mole fraction of Zn) for the $\alpha$ and $\gamma$ phases are assumed to be $C_0^\alpha = 0.05$ and $C_0^\gamma = 0.95$, respectively. Initial composition profile for the interface is assumed to be 50% of $\alpha$ and 50% of $\gamma$. The gradient energy coefficient, $k$, at 300°C, is assumed to be $1.2 \times 10^{-11}$ (J/m) according to the pair-wise interaction between the atoms (Wang et al. 2007; Cahn and Hilliard 1958). All the other parameters used for Al-Zn system are at the temperature of 300°C (Lass et al. 2006; Dinsdale 1991, Cui et al. 2006) [14-16]. The results are divided in two groups, first the results for the systems that the intermediate phase, $\beta$, is an equilibrium phase ($W_2 = -0.04$). The second case includes systems in which the intermediate phase is a meta-stable phase ($W_2 = 0.01$). We have determined that the optimal time step is 0.02 seconds and have used it in all computations.

2.3.1 An equilibrium intermediate phase ($W_2 = -0.04$)

The characteristic length of the problem is the thickness of the interface (Cahn and Hilliard 1958):

$$ l = (\frac{C^\alpha - C^\gamma}{dC/dx}) = 2\Delta C \left( \frac{k}{2|f_{\text{max}}|} \right)^{1/2}, \quad (2.21) $$
where $\Delta f_{\text{max}}$ is the maximum free energy difference in Figure 2.1,

$$\Delta C = C^\gamma - C^c = C^c - C^\alpha \sim 0.45$$

and two phases attain same critical composition, $C^c$, at the critical temperature. For $W_2 = -0.04$, the interface thickness is $l \sim 0.47 \mu m$. We first study the convergence of the FE method for $W_2 = -0.04$, $\eta_1 = 0.001$ and $10 \mu m$ plate thickness. The results are shown in Figures 2.3 and 2.4. The computational time increases drastically with the mesh density, so that finding the optimal mesh size is of practical importance. For element size $h$, we define the non-dimensional mesh parameter:

$$\lambda = l/h. \quad (2.22)$$

From the results in Figure 2.3, the optimal mesh size seems to be about 1/10 of the interface width (interface of $\alpha - \beta$ and $\beta - \gamma$, or 1/5 of the $\alpha - \beta$ interface), i.e., $\lambda = 10$. Since the exact solution is unknown, we define the relative error in quantity $S(\lambda)$, the thickness of the interface as a function of non-dimensional mesh parameter $\lambda$, with respect to the most accurate results which is from $\lambda = 20$:

$$R_s(\lambda) = \left| \frac{S(\lambda) - S(20)}{S(20)} \right|. \quad (2.23)$$

From Figure 2.4 it is evident that the relative error is approximately quadratic in mesh size. Thus, the application of mixed-order interpolation (linear and Hermite cubic) results in uniform convergence. Using the optimal mesh $\lambda = 10$, we study the evolution of the intermediate phase.
Figure 2.3. The evolution of thickness of an equilibrium intermediate phase, as function of mesh size.

Figure 2.4. Dependence of the relative error in thickness of an equilibrium intermediate phase, after 50,000 time steps, as function of mesh size.
In Figure 2.5, there is an example for the evolution of the composition profile for a case that obeys Vegard’s law \((\eta_2 = 0)\). Dependence of kinetics on the compositional strain coefficient \(\eta_1\) for the cases that the system obeys Vegard’s law \((\eta_2 = 0)\), is shown in Figure 2.6. The thickness of the intermediate phase is roughly proportional to the square root of time.

![Figure 2.5](image)

**Figure 2.5.** Time sequence of composition profiles. Dotted lines represent increments of 2,500 time steps, while solid lines represent increments of 10,000 time steps.
The time-dependence of the growth of the intermediate phase is shown in the Figure 2.7 for the cases that the compositional strain includes the derivations of Vegard’s law ($\eta_2 \neq 0$). When the effects of compositional strain are not included in (2.15) ($\eta_2 = 0$), the $\beta$ phase thickens proportional to the square root of time but with increasing $\eta_2$, the rate of thickening of the $\beta$ phase changes and it thickens faster and the thickness of the intermediate phase is a function of higher order of time (thickness of the $\beta$ phase $\propto t^b, b \geq 0.5$).

Figure 2.6. The growth of the intermediate phase, as function of the concentration strain parameter $\eta_1$. The thickness is proportional to the square root of time.
In Figure 2.8, the contributions of strain energy density ($F^s$) and chemical energy density ($F^c$) to the total free energy density ($F = F^s + F^c$) are shown for a system that $\beta$ phase is an equilibrium phase ($W_2 = -0.04$), and lattice parameter is a linear function of composition ($\eta_1 = 0.001, \eta_2 = 0.0$).

The strain energy density and chemical energy density (J/mol) are obtained from

$$F^s = \frac{m}{I} \int_0^l [U(\varepsilon_{xx}, C)]dx$$

and

$$F^c = \frac{m}{I} \int_0^l [f(C) + \frac{k}{2}(\nabla C)^2]dx$$

respectively, that the $m$ is the average molar density of Al and Zn. As it is shown in Figure 2.8, the highest strain energy density occurs in the beginning of the diffusion process because of the deferent lattice parameters of two major phases and it results in the bending of the thin plate.

**Figure 2.7.** The growth of the intermediate phase, as function of the concentration strain parameter $\eta_2$.
While the intermediate phase grows and thickens, the strain and chemical energies decrease. The contribution of the elastic strain energy to the free energy is non-negative and it is according to the analytical work previously done by (Larche and Cahn 1992).

There is a jump in Figure 2.8 after about 63000 time units because the phase transformation stops as the $\beta$ phase reaches to the end of the both sides of the thin plate.

![Figure 2.8](image.png)

Figure 2.8. The chemical, elastic and free energies of the thin-plate diffusion couple when the intermediate phase is in equilibrium.
2.3.2 Meta-stable intermediate phase \((W_2 = 0.01)\)

For the cases with meta-stable intermediate phase, the characteristic interface thickness is \(l \sim 0.71 \mu m\) according to (2.21). Different mesh sizes are examined and the results for \(W_2 = 0.01, \eta_1 = 0.002\) and \(15 \mu m\) plate thickness, are shown in Figure 2.9. The convergence is again quadratic that is shown in Figure 2.10. The time-dependent growth of the intermediate phase, as function of the concentration strain parameter \(\eta_1\) is shown in the Figure 2.11. As \(\eta_1\) decreases, the \(\beta\) phase thickens very slowly, and, for sufficiently low \(\eta_1\), the growth of the intermediate phase stops. In the Figure 2.12, we show an example of such arrested growth that the growth of the intermediate phase stops after approximately 60,000 time steps.

The contributions of strain energy density \((F^s)\) and chemical energy density \((F^c)\) to the total free energy density \((F = F^s + F^c)\) are shown in the Figure 2.13 for a system that obeys Vegard’s law \((\eta_1 = 0.002, \eta_2 = 0.0)\). Once again the highest strain energy density occurs in the beginning of the diffusion process that is because of the deferent lattice parameters of two major phases and it results in the bending of the plates but, unlike the case that the intermediate phase is in equilibrium, while the \(\beta\) grows and thickens only the strain energy decreases and the chemical energy density increases.
Figure 2.9. The evolution of thickness of a meta-stable intermediate phase, as function of mesh size.

Figure 2.10. Dependence of the relative error in thickness of a meta-stable intermediate phase after 30,000 time steps, as function of mesh size.
Figure 2.11. The growth of the meta-stable intermediate phase, as function of the concentration strain parameter $\eta_i$.

Figure 2.12. Time sequence of composition profiles for the case of arrested growth. Dotted lines represent increments of 3,000 time steps, solid line represent increments of 12,000 time units. The growth of the intermediate phase stops after approximately 60,000 time steps.
2.4 Conclusion

The effects of compositional stress on the growth of the intermediate phase in a thin-film diffusion couple are investigated by using Cahn-Hilliard type of phase-field model. To solve the coupled diffusion and stress equations numerically, finite element method has been used. To ensure uniform convergence of the FE method, mixed interpolation, linear in displacements and cubic in concentration, is used. Uniform quadratic convergence, expected for conforming elements, is achieved.

The model has been applied to the both equilibrium and non-equilibrium intermediate phase. When the system obeys Vegard’s law and the intermediate phase is

![Figure 2.13. The chemical, elastic and free energies of the thin-plate diffusion couple when the intermediate phase is meta-stable.](image)
an equilibrium phase, for different values of $\eta_1$, the intermediate phase thickens approximately proportional to the square root of time; and when the intermediate phase is a meta-stable phase, with decreasing $\eta_1$, the growth of intermediate phase reduces, even in very small $\eta_1$ the growth stops after a very short time steps. When the system includes the derivation of Vegard’s law and the intermediate phase is an equilibrium phase, as $\eta_1$ increases, the thickness of the $\beta$ phase gets proportional to the higher order of the time ($\beta$ thickness $\propto t^b, b \geq 0.5$). For the case that the intermediate phase is meta-stable, as $\eta_1$ decreases, the $\beta$ phase thickens very slowly and for very low $\eta_1$, the growth of the intermediate phase stops after few steps.
CHAPTER THREE: Finite element method for conserved phase fields:

Stress-mediated diffusional phase transformation

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Abstract

The phase-field models with conserved phase-field variables result in a 4\textsuperscript{th} order evolution partial differential equations (PDE). When coupled with the usual 2\textsuperscript{nd} order thermo-mechanics equations, such problems require special treatment. In the past, the finite element method (FEM) has been successfully applied to non-conserved phase fields, governed by 2\textsuperscript{nd} order PDE. For higher order equations, the uniform convergence of the standard Galerkin FEM requires that the interpolation functions belong to a higher continuity class.

We consider the Cahn-Hilliard phase-field model for diffusion-controlled solid state phase transformation in binary alloys, coupled with elasticity of the solid phases. A Galerkin finite element formulation is developed, with mixed-order interpolation: $C^0$ interpolation functions for displacements, and $C^1$ interpolation functions for the phase-field variable.
To demonstrate uniform convergence of the mixed interpolation scheme, we first study a one-dimensional problem – nucleation and growth of the intermediate phase in a thin-film diffusion couple with elasticity effects. Then, we study the effects of completeness of $C^1$ interpolation on parabolic problems in two space dimensions by considering the growth of the intermediate phase in solid state binary systems.

Uniform quadratic convergence, expected for conforming elements, is achieved for both one- and two-dimensional systems.

**Keywords:** phase-field model, Galerkin finite element method, binary alloys, convergence

### 3.1 Introduction

A broad spectrum of moving boundary problems can be successfully handled with the diffuse-interface or phase-field models. Such models are constructed by assuming that the free energy of a non-uniform system $F$, depends on – among other variables – the phase-field variable $\phi$, and its gradient $\nabla \phi$. In the volume $V$:

$$F = \int_V g(\phi,\nabla \phi)dV. \quad (3.1)$$

Mathematically, the phase-field formulation gives rise to two types of problems.

The non-conserved phase-field variables, such of those in solidification and melting problems (Fan et al. 2006; Provatas et al. 1998; Sabouri et al. 2001), are often
assumed to evolve according to the “first-order relaxation”, whereby the rate of change of the phase variable, $\dot{\phi}$, is proportional to the variational derivative of the free energy, mediated by the kinetic mobility $B$:

$$\dot{\phi} = -B \frac{\delta F}{\delta \phi}.$$  

Such formulation leads to a 2nd order, diffusion-type partial differential equation (PDE) for $\phi$ (Wang et al. 1997; Wen et al. 1999). However, if the phase-field variable is subject to a conservation law, e.g.,

$$\frac{d}{dt} \int_V \phi dV = 0,$$  

then the rate $\dot{\phi}$ is proportional to the divergence of the flux, which in turn, is proportional to the gradient of a potential. This potential is equal to the variational derivative of the free energy:

$$\dot{\phi} = -\nabla \cdot [-B \nabla (\delta F / \delta \phi)].$$

Examples include diffusion-controlled solid-state phase transformations (Cahn and Hilliard 1958, Cahn and Kobayashi 1995; Johnson 2000; Leo and Johnson 2001), and interfaces between immiscible fluids (Jacqmin 1999; Anderson et al. 1998). Typically, the 4th order evolution PDE (3.3) is coupled to a 2nd order PDEs (stress, heat, etc.). For example, in solid state phase transformations, the lattice continuity across the interfaces between mismatched phases produces elastic strains (Khachaturyan 1983; Cahn and Larche 1982; Larche and Cahn 1992; Khachaturyan et al. 1996), so that the 2nd order elasticity PDEs are coupled to the phase field equation (3.3) (Cahn and Kobayashi 1995; Johnson 2000; Leo and Johnson 2001; Leo et al. 1998; Chen et al. 1991; Chen et al. 1992; Wang et al. 1993; Wang and Khachaturyan 1995, Li and Chen 1998).
The problems in this class have been addressed in the past, with the numerical tools tailored for specific problems. However, a general numerical method for solving the coupled equations, applicable to variety of geometries and boundary conditions, has remained a challenging problem. The finite difference method (FDM) was used by (Cahn and Kobayashi 1995) for one-dimensional modeling of the rapid coarsening and buckling in coherently self-stressed thin plates. (Johnson 2000) used FDM to study the growth of the intermediate phase in a thin film diffusion couple. (Leo et al. 1998) used a pseudo-spectral method for the phase-field model for the coarsening of a two dimensional, elastically stressed binary alloys. Fourier transform techniques (Chen et al. 1991; Chen et al. 1992; Wang et al. 1993; Wang et al. 1995; Li and Chen 1998), and related Fourier-spectral methods (Chen and Shen 1998; Hu and Chen 2001; Zhu et al. 2001; Vaithyanathan and Chen 2002; Vaithyanathan et al. 2004; Boisse et al. 2007), have been used to investigate the microstructure evolution (mostly coarsening) resulting from solid-state phase transformations. The drawbacks of such methods are seen in the difficulties in modeling irregular domains, nonlinear and history-dependent problems. A versatile method is needed, such as the finite element method (FEM), or the mesh-free method, which is applicable to irregular domains, variety of boundary conditions, and various forms of geometric and material nonlinearities.

The key issue in formulating the finite element method for 4th order problem is the order of interpolation. To ensure convergence in the classical continuous Galerkin method, $C^1$ continuity is required (Hughes 2000). In dimensions higher than one, standard Hermit cubics are incomplete. The elements used to solve the 4th order elliptic
plate bending problems are too stiff (Hrabok and Hrudey 1984; Taylor and Govindjee 2002; Li et al. 2008; Chien et al. 2009; Petera and Pittman 1994). Alternatives include: (i) augmentation of the interpolation functions to insure completeness (Hrabok and Hrudey 1984; Li et al. 2008; Chien et al. 2009), (ii) mixed, discontinuous formulation (Engel 2002), and, (iii) the continuous-discontinuous formulation (Engel 2002). The advantages and disadvantages are well understood for elliptic problems (Engel 2002). Parabolic phase-field problems have received little attention. Only the mixed, discontinuous Galerkin formulation has been applied to a single, uncoupled, 4th order Cahn-Hilliard equation (Kay and Welford 2006).

In this paper we present the finite element formulation for coupled conserved phase-field 4th order equations, and 2nd order continuum mechanics PDEs. We opt for the classic continuous Galerkin formulation.

The weak form of governing Cahn-Hilliard and elasticity equations, developed in Section 3.2, is equally applicable to finite element and mesh-free methods. As the mechanical and diffusion/phase field equations are of different orders, uniform convergence of the results requires different order of continuity for interpolation functions. In Section 3.3, we formulate and implement such mixed-order finite elements, with $C^0$ interpolation functions for displacement, and $C^1$ interpolation functions for concentration. The computational results are presented in Section 3.4. We first benchmark our code by comparing the results to Johnson’s (Johnson 2000) finite difference solutions of one-dimensional problem of the growth of intermediate phase in
binary alloys (Asle Zaeem and Mesarovic 2009). Then, we consider two-dimensional nucleation and growth of intermediate phase in binary alloys.

### 3.2 Phase field formulation, the weak form

A binary alloy, with components A and B, forms three phases, characterized by the molar concentration $c$ of the component A. The phases correspond to the minima of the stress-free Helmholtz free energy density of a uniform system $f(c)$. The total free energy, $F$, of a non-homogeneous system with volume $V$, bounded by surface $S$, is constructed as:

$$F(c, u) = \int_V \left[ f(c) + U(\varepsilon, c) + \frac{1}{2} (\nabla c) \cdot \mathbf{K} \cdot (\nabla c) \right] dV + \int_S \gamma(c) dS - \int_S \mathbf{t} \cdot \mathbf{u} dS, \quad (3.4)$$

The concentration $c(x)$ is now a scalar field over the domain. $\gamma$ is the surface energy of the outer surface $S$ of the domain, and $\varepsilon$ is the total strain tensor:

$$\varepsilon = \frac{1}{2} (u \nabla + \nabla u). \quad (3.5)$$

$U(\varepsilon, c)$ is the strain energy density:

$$U = \frac{1}{2} (\varepsilon - eI) : C : (\varepsilon - eI), \quad (3.6)$$

with the purely volumetric compositional strain $e$ and $C$ as the elastic coefficient tensor. The simplest model follows the linear Vegard’s law (Denton and Ashcroft 1991):

$$e = \eta(c - c_0). \quad (3.7)$$
The reference composition $c_0$ is taken to be the average of composition over the domain.

In (3.4), the surface energy of the outer boundary $S$ is neglected, and the last term is the mechanical loading potential, with the surface traction $t$, and the displacement vector $u$. The last term under the volume integral in (3.4) represents the interface energy density between the phases. To ensure positive interface energy, the gradient energy coefficient tensor, $K$, is assumed symmetric and positive definite. For an isotropic system it simplifies to a scalar: $K = K \mathbf{1}$, where $\mathbf{1}$ is the unit tensor.

With the strain energy (6), the stress is defined as:

$$\sigma = \partial U/\partial \epsilon = C : (\epsilon - e\mathbf{1}).$$

(3.8)

### 3.2.1 Equilibrium

When the total flux on the boundaries vanishes, the conservation of mass requires:

$$\int_V (c - c_0) dV = 0.$$  

(3.9)

The equilibrium problem is one of constrained minimization of free energy (3.4), under constraint (3.9). Upon introducing the Lagrange multiplier, $M_0$, we seek to minimize the functional:

$$\bar{F} = F - M_0 \int_V (c - c_0) dV.$$  

(3.10)
For isothermal chemical and mechanical equilibria, the variational derivatives of (3.10) with respect to \( c \) and \( u \) must vanish: \( \delta_c F = 0 \), and, \( \delta_u F = 0 \). Imposing this condition for arbitrary variation \( \delta c \), we obtain the chemical equilibrium:

\[
\int_V \{ f' + U' - K : (\nabla \nabla c) - M_0 \} \delta c \, dV + \int_S \{ \gamma' + n \cdot K \cdot (\nabla c) \} \delta c \, dS = 0 ,
\]

(3.11)

where primes indicate partial derivatives with respect to \( c \), e.g., \( U' = \partial U / \partial c \), and \( n \) is the unit outer normal to \( S \). From (3.11), we extract the governing partial differential equation and natural boundary conditions for chemical equilibrium:

\[
f' + U' - K : (\nabla \nabla c) = M_0 \quad \text{in } V ,
\]

(3.12)

\[
\gamma' + n \cdot K \cdot (\nabla c) = 0 \quad \text{on } S .
\]

(3.13)

The governing 2\textsuperscript{nd} order PDE for the equilibrium concentration (3.12) is elliptic, owing to the positive definiteness of \( K \). The Lagrange multiplier \( M_0 \) is the chemical potential, uniform at equilibrium. For isotropic case, (3.13) specifies the vanishing normal gradient at the boundary. For the sake of simplicity, we consider only the case \( \gamma' = 0 \).

Owing to the indeterminacy of \( M_0 \), the boundary condition (3.13) is insufficient for uniqueness, so that the conservation of mass (3.9) must be enforced explicitly. On the physical side, the argument is obvious; all three phases are equilibrium phases, but at different concentration.

For arbitrary variation \( \delta u \), (3.10) is minimized if:

\[
\int_V \sigma : \delta(u \nabla) \, dV - \int_S t \cdot \delta u \, dS = 0 .
\]

(3.14)

The differential equations governing mechanical equilibrium have the form:
\[ \nabla \cdot C : (\nabla u) = \tilde{C} \cdot \nabla e, \quad \tilde{C} = C : I \quad \text{in } V. \tag{3.15} \]

The mathematical structure of boundary conditions is standard; at each point of the boundary three of the six scalar components of traction \( \mathbf{n} \cdot \sigma = t \) and displacement \( \mathbf{u} \) are prescribed, but not the same components at one point.

For the purpose of finite element formulation, we write the weak form of mechanical equations as:

\[
\int_{V} (\nabla u) : \delta(u \nabla) dV = \int_{V} e\tilde{C} : \delta(u \nabla) dV + \int_{S} t \cdot \delta u dS. \tag{3.16}
\]

Diffusion-controlled phase transformations take place at the time scales much longer than those required for wave propagation and attenuation in solids. Therefore, the mechanical equilibrium will be assumed throughout the process, so that the weak form (3.16) will be coupled to the weak form of the Cahn-Hilliard evolution equations (3.25).

The first term on the right hand side, effectively acting as a body force, introduces the effects of concentration on the strains.

### 3.2.2 Diffusion

In the non-equilibrium case, local conservation of concentration implies that its local value changes according to the divergence of its flux \( q \):

\[
\rho_{0} \dot{c} = -\nabla \cdot q. \tag{3.17}
\]

where \( \rho_{0} \) is the density of lattice sites. The flux is proportional to the gradient of chemical potential, \( M(\mathbf{x}) \):
\[ q = -\rho_0 B \cdot \nabla M, \quad (3.18) \]

where \( B \) is the symmetric, positive definite mobility tensor. It reduces to \( B = BI \) for isotropic systems.

To simplify derivation, we will assume that mobility is uniform throughout the domain. The weak form of (3.18) can be written as:

\[
\int_V [\dot{c} \delta c - q \cdot \delta \nabla c] dV - \int_S Q \delta c dS = 0, \quad (3.19)
\]

where \( \rho_0 Q = -n \cdot q \) is the normal inward flux to the boundary. After some manipulation:

\[
\int_V [\ddot{c} - \nabla \cdot (B \cdot \nabla M)] \delta c dV + \int_S (-Q + n \cdot B \cdot \nabla M) \delta c dS = 0. \quad (3.20)
\]

From (3.20), we extract the governing differential equation:

\[
\ddot{c} - \nabla \cdot (B \cdot \nabla M) = 0, \quad \text{in } V. \quad (3.21)
\]

The chemical potential is the variational derivative of the free energy (3.11, 3.12) and is a function of strain, concentration, and its second gradients: \( M(\varepsilon, c, \nabla \nabla c) \) (Larche and Cahn 1978). \( M = f' - U' - K : (\nabla \nabla c), \quad (3.22) \)

so that (3.21) is 4th order PDE in composition.

The natural boundary condition, arising from (3.20), provides the normal flux at the boundary:

\[
Q = n \cdot B \cdot \nabla M, \quad \text{on } S. \quad (3.23)
\]
The equation (3.21) is parabolic, so that, prescription of the initial field \( c(x,t = 0) \) enables integration. Normal boundary flux may be prescribed if warranted by physical conditions.

To obtain the weak form appropriate for FE implementation, we write the gradient of the chemical potential (3.22) as

\[
\nabla \mathcal{M} = (f'' + U' + \tau e') \nabla c - \nabla (e' \tau + \mathbf{K} : (\nabla \nabla c)), \quad \tau = \tilde{\mathbf{C}} : \varepsilon, \tag{3.24}
\]

where \( \tilde{\mathbf{C}} \) has been defined in (3.15).

Upon substitution of (3.24) into (3.20) and some manipulation, we obtain the weak form appropriate for FE implementation. The required interpolation, the coupling between mechanical and Cahn-Hilliard equations, and the boundary conditions are most transparently shown in this form:

\[
\int_V \dot{c} \delta c \, dV + \int_V \left[ f'' \nabla c \cdot \mathbf{B} \cdot \delta \nabla c + (\nabla \nabla c) : \mathbf{K} \mathbf{B} : \delta \nabla \nabla c \right] dV
- \int_S (\nabla \nabla c) : \mathbf{K} \mathbf{B} : \mathbf{n} \cdot \delta \nabla c \, dS + \int_S \left( U'' + \tau e' \right) \nabla c \cdot \mathbf{B} \cdot \delta \nabla c \, dV \tag{3.25}
= \int_V \tau \varepsilon \mathbf{B} : \delta \nabla \nabla c dV + \int_S \tau e \mathbf{n} \cdot \mathbf{B} \cdot \delta \nabla c \, dS + \int_S Q \delta c \, dS.
\]

The effects of elasticity appear as body forces (the last integral on the left and the first integral on the right) and surface forces (the second integral on the right).

Consider the boundary condition such that the boundary flux \( Q \) is given at each point of the boundary. Then, the last term in (3.25) contributes to the surface forces.

Alternatively, the total flux may be prescribed:

\[
\int_S Q \delta c \, dS = \tilde{Q}. \tag{3.26}
\]
Then, by means of (3.23, 3.24) and the finite element interpolation, this condition reduces to the set of additional algebraic equations for nodal variables representing concentration and its gradients. The implementation of similar integral conditions has been discussed in (Mesarovic and Padbidri 2005; Mesarovic and Padbidri 2006) for both quasistatic and dynamic problems.

In the case of periodic boundary conditions, all the surface integrals in (3.25) vanish. The vanishing total flux (3.26), i.e., the conservation of mass, is imposed implicitly.

### 3.3 Finite element discretization

In the weak form (3.25), the presence of second gradients of \(c\), requires \(C^1\) continuity of interpolation functions. This is accomplished by defining the set of nodal variables to include concentration and components of the concentration gradient, i.e., four variables at each node in 3D. With interpolation functions defined as products of 1D Hermit cubics, the resulting elements are incomplete – incapable of representing constant values of mixed second gradients, \(\partial^2 c/\partial x_i \partial x_j (i \neq j)\) (Hrabok and Hrudey 1984). For plate bending problems, this is unacceptable. However, a closer look into our governing equations (3.25) reveals that such mixed derivatives do not appear if the tensors \(K\) and \(B\) are isotropic\(^1\). In such case, the incomplete Hermit elements with four degrees of freedom per node may suffice. Commonly used complete elements (e.g., (Chien and Shih 2009))

---

\(^1\) In fact, owing to the difficulties in defining parameters for an anisotropic model experimentally, most of the computational results reported in literature are for the isotropic case. Note that all this refers to anisotropy of \(K\) and \(B\), not to elastic anisotropy.
require additional three degrees of freedom per node in 3D – the three mixed second
derivatives. Let the vector of all \((M)\) nodal variables be
\[
\{\Gamma\} = \{\Gamma_1, \Gamma_2, \ldots, \Gamma_M\}^T.
\] (3.27)

With a \(C^1\) interpolation, the interpolated function \(c\) is written as
\[
c(x) = \sum_{i=1}^{M} \Gamma_i \psi_i(x).
\] (3.28)

The interpolation functions for both, complete and incomplete elements are given in the
Appendix A.

When (3.28) is substituted into (3.25), and the integration of performed, the
resulting FE system of ordinary differential equations has the form:

\[
[M][\dot{\Gamma}] + ([D_0] + [D_\varepsilon])\{\Gamma\} = \{h_x\} + \{h_\varepsilon\}.
\] (3.29)

The matrix \([M]\), arising from the 1\(^{st}\) integral in (3.25), is constant. The matrix \([D_0]\),
arising from the 2\(^{nd}\) and 3\(^{rd}\) integrals in (3.25), depends on the concentration only, while
\([D_\varepsilon]\) (from the 4\(^{th}\) integral) defines the direct coupling, since it depends on the
mechanical part of the problem (3.16). Similarly, the right hand side consists of the
external forcing \(\{h_x\}\) [the last integral in (3.25)], and, the effective coupling forces \(\{h_\varepsilon\}\)
[the first two integrals on the right hand side in (3.25)].

In case of periodic boundary conditions, all surface integrals vanish. Therefore,
\(\{h_x\}\) vanishes, while \([D_0]\) and \(\{h_\varepsilon\}\) have a somewhat simpler form. Moreover,
additional algebraic equations, involving boundary degrees of freedom and enforcing
periodicity, are added to the system.
The mechanical equations (3.16) require only a $C^0$ interpolation. They are quasistatic, so that the resulting finite element equations are algebraic:

$$[\mathbf{A}]\{\mathbf{u}\} = \{\mathbf{f}_x\} + \{\mathbf{f}_c\},$$

(3.30)

where $\{\mathbf{u}\}$ is the vector of nodal displacements, $[\mathbf{A}]$ is the stiffness matrix, and $\{\mathbf{f}_x\}$ and $\{\mathbf{f}_c\}$ represent external surface forces and coupling to (3.29), respectively.

A special time integration scheme was developed consisting of implicit time-stepping and equilibrium/consistency iterations in each time step. At time $t$, $[\mathbf{D}_0] + [\mathbf{D}_\epsilon]$ and $\{\mathbf{h}_x\} + \{\mathbf{h}_\epsilon\}$, are known. We first estimate $\{\mathbf{\Gamma}\}$ at $t + \Delta t$ by applying the Euler time integration scheme to (3.29). Then, we iterate to satisfy equilibrium (3.30) at $t + \Delta t$, while simultaneously correcting $\{\mathbf{\Gamma}\}$ and $\dot{\{\mathbf{\Gamma}\}}$ to satisfy (3.29).

### 3.4 Results and discussions

The growth of the intermediate phase in solid state binary systems is investigated in one and two spatial dimensions. The Helmholtz free energy density of a uniform unstressed system, $f(c)$ in (3.4), is assumed to be a triple well potential (Johnson 2000):

$$f(c) = W_1(c - c^\alpha)^2(c - c^\beta)^2(c - c^\gamma)^2 + W_2(c - c^\alpha)^2(c - c^\gamma)^2,$$

(3.31)

where $W_1$ and $W_2$ are the energy coefficients, $c^\alpha$, $c^\beta$ and $c^\gamma$ are the mole fractions of component B at which $f(c)$ is minimized. Depending on parameters $W_1$ and $W_2$ in (3.31), the intermediate phase, $\beta$, can be a stable, or a meta-stable equilibrium phase, as illustrated in Figure 3.1. The thickness of the interface between phases $\alpha$ and $\beta$ in
general depends on the compositional strain (3.7). For vanishing compositional strain, \( \eta = 0 \), the nominal interface thickness is (Cahn and Hilliard 1958):

\[
I_0 = (c^\beta - c^\alpha) \left( \frac{K}{2\Delta f_{\text{max}}} \right)^{1/2},
\]

(3.32)

where \( \Delta f_{\text{max}} \) is the difference between the neighboring maximum and minimum of the free energy (3.31), as illustrated in Figure 1.

In what follows, we use non-dimensional variables only. The particular dimensional reduction described in Appendix B has been used by (Johnson 2000). It is rendered unique by two requirements. First is that the non-dimensional composition varies between \(-1\) and 1. Second is that the non-dimensional gradient coefficient is 1 in the isotropic case. The non-dimensional variables are identified by overbars, e.g., \( \bar{K} = 1 \), for details, see Appendix B.

To compare our results to (Johnson 2000), instead of the concentration strain parameter \( \eta \) (3.7), we use the non-dimensional compositional strain energy parameter:\(^2\)

\[
\bar{\theta} = 2\eta^2 \frac{E}{\rho_0 kT(1-\nu)} \left( \frac{2}{c^\gamma - c^\alpha} \right)^4,
\]

(3.33)

where \( \rho_0 \) is the density of lattice sites, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( E \) is the Young’s modulus, and \( \nu \) is the Poisson ratio. In all cases, we consider isotropic elasticity and mobility; only the anisotropy of gradient coefficients tensor \( K \), is studied.

\(^2\) In 1D problems, the non-dimensional compositional strain energy is simply given as \( \bar{\theta} \bar{\sigma}^2 \).
To study the convergence of the mixed interpolation scheme, we first consider a one-dimensional (1D) problem, where the question of completeness does not arise. In this case, we are able to test the convergence of scheme under different regimes modes of elasticity-chemistry interactions. Then, to understand the effects of using incomplete elements for parabolic systems, we consider a two-dimensional (2D) problem.

Figure 3.1. The non-dimensional triple-well free energy density, as function of scaled concentration (scaling is given in Appendix B). Depending on the value of $\bar{W}_2$, the intermediate phase is stable or metastable.
3.4.1 Growth of intermediate phase in 1D

Growth of the intermediate phase in a thin-film diffusion couple is schematically shown in Figure 3.2. Depending on the compositional strain energy parameter $\bar{\Theta}$ (3.33), the intermediate phase may grow to a finite thickness and stop, or, it may consume the whole film. This is the results of interplay of elastic and chemical parts of the chemical potential. The mechanism has been explained by (Johnson 2000). The complete analysis of this problem using continuous Galerkin FE has been given in (Asle Zaeem and Mesarovic 2009). Here, we only summarize the main results.

The boundary conditions include the rigid body motion prevention (Mesarovic and Padbidri 2005), and the vanishing mass flux, so that mass conservation (3.9) is guaranteed. No traction boundary conditions are applied.

The non-dimensional gradient energy coefficient is $\bar{K} = 1$, and the non-dimensional interface thickness (3.32) for the stable intermediate phase is $\bar{l}_0 \approx 3.2$. The total thickness of the thin-film diffusion couple (Figure 3.2) is 100 non-dimensional length units (see Appendix B).

---

Figure 3.2. (a) Schematic representation of initial condition of the thin plate diffusion couple. (b) $\beta$ phase grows as the intermediate phase and the plate is free to bend.
The computational time increases rapidly with the mesh density, so that finding the optimal mesh density is of practical importance. For element size $h$, we define a non-dimensional mesh parameter:

$$\lambda = l_0/h.$$  \hfill (3.34)

In Figure 3.3, the thickness of the stable ($\bar{\Theta} = 0.1$) intermediate phase is plotted as function of time for different mesh densities. By comparing our results to (Johnson 2000) finite difference results, the optimal mesh size seems to be about $1/5$ of the interface width, i.e., $\lambda = 5$. The optimal mesh provides sufficient accuracy with reasonable computational cost.

The exact solution is unknown. To study the convergence rate, we define the relative error with respect to the most accurate results ($\lambda = 10$). Let $S(\lambda)$, be the thickness of the intermediate phase. Then the relative error is a function of the non-dimensional mesh parameter $\lambda$:

$$R_S(\lambda) = \left| \frac{S(\lambda) - S(10)}{S(10)} \right|. \hfill (3.35)$$

In Figure 3.4, the relative error is plotted as a function of mesh parameter. The quadratic convergence is evident.
Figure 3.3. The non-dimensional thickness of the intermediate phase $\bar{S}$, as function of the non-dimensional time, $\bar{t}$ (Appendix B). Different mesh sizes are used and the Johnson’s finite difference results (FDM) (Johnson 2000) are shown for comparison.
Next, using the optimal mesh, $\lambda = 5$, we test the accuracy of our computations for different values of the compositional strain energy parameter, $\theta$.

In Figure 5, the thickness of the meta-stable intermediate phase is plotted as a function of time for the different values of $\theta$. The growth rate of the intermediate phase decreases with decreasing $\theta$. For sufficiently low $\theta$, the growth of the intermediate phase stops. For high values of $\theta$, the process is driven by the elastic mismatch between phases and continues until the whole film is consumed by the $\beta$ phase. Evidently, the scheme retains its accuracy in both, elasticity-dominated, and chemistry-dominated regimes. As an aside, we have identified the threshold value of $\theta \approx 0.06$.

![Figure 3.4. Relative error (3.35) in the thickness of intermediate phase as function of mesh parameter $\lambda$, at $\bar{t} = 16 \times 10^3$.](image)
3.4.2 Growth of the intermediate phase in 2D – isotropic case

We consider a representative volume element with periodic boundary conditions. In such case, the boundary integrals in (3.25) vanish.

In all 2D cases, $200 \times 200$ non-dimensional square domains are used. The nucleation and growth of the stable intermediate phase, $\beta$, from an initially circular $\gamma$ precipitate in $\alpha$ matrix, is illustrated in Figure 3.6. In this case, the growth of intermediate phase continues until the initial precipitate phase is consumed. As the 1D

\begin{figure}
\centering
\includegraphics[width=0.7\textwidth]{figure3_5.png}
\caption{The thickness of meta-stable intermediate phase as function of time for the different values of the compositional strain energy parameter $\bar{\theta}$. Johnson’s finite difference results (FDM) (Johnson 2000) are shown for comparison.}
\end{figure}
case, we investigate the convergence of the model. The isotopic gradient energy coefficients, $\overline{K} = 1$, and the nominal interface thickness (3.32) is $\overline{l_0} \approx 3.2$. Initially, precipitate has circular shape with radius 20 and the final relaxed configuration is a circle with radius $\sim 27.5$.

The effects of mesh density and type of element – complete and incomplete – are shown in Figure 3.7. For the systems with isotropic gradient energy coefficients, the complete and incomplete elements yield very similar results. The incomplete elements only slow down the process slightly, but the final configurations are identical. We note that, in contrast with plate-bending problems, the current isotropic problem does not include the mixed derivatives of the variable $c$ in its formulation. They only appear in numerical calculations owing to the different orientation of the element. Thus, the incompleteness does not obliterate important terms in governing equations (such as torsional stiffness in plate bending). Hence, its effect is minor. We expect – and indeed confirm in the next subsection – that the effect is much stronger in the anisotropic case where mixed derivatives enter the formulation directly.
Figure 3.6. (a) The growth of the stable-intermediate phase $\bar{\theta} = 0.05$. Color bar shows the composition. (b) Mesh corresponding to the rectangle in (a) $\bar{T} = 0$. Complete elements are used, with $\lambda = 5$ in the interface region.
As for 1D systems, the optimal mesh size is about 1/5 of the interface width, i.e., \( \lambda = 5 \). The relative error is defined as before (3.35), and plotted as function of mesh parameter (3.34) in Figure 3.8. The results show that the expected quadratic convergence for 2D systems.

2D problems offer much richer behavior than 1D problems. Consider the example shown in Figure 3.9. When the intermediate phase is a stable phase (the case \( W_2 = -0.04 \) in Figure 1), global minimum of chemical energy is achieved at the

\[ S = \ldots \]

\[ t = \ldots \times 10^3 \]

Figure 3.7. For the geometry shown in Figure 3.6: thickness of the intermediate phase as function of time for different mesh sizes and different types of elements.
intermediate phase. However, the elastic mismatch between the phases results in strain energy, and both, strain energy and surface energy, are minimized for a uniform system. If the initial precipitate is small compared to the computational cell, the average concentration is close to the matrix concentration, so that the chemical energy, although not minimized, is close to its minimum. Thus, for sufficiently high $\bar{\theta}$ and sufficiently small precipitate, the final equilibrium is determined by elasticity. The example is shown in Figure 3.9. First, the chemical energy drives the growth of the intermediate phase. The temporary intermediate phase precipitate is circular to minimize the surface energy. Then, driven by elasticity, the intermediate phase vanishes and the final equilibrium consists of uniform concentration close to the matrix phase. For the geometry shown in Figure 3.9 with $\bar{W}_2 = -0.04$, the final equilibrium has uniform concentration if $\bar{\theta} > 0.15$.

![Figure 3.8](image.png)

**Figure 3.8.** Relative error in intermediate phase thickness as function of the mesh parameter. The points correspond to the time 15,000 in Figure 3.7.
For meta-stable phase intermediate phase (case \( \bar{W}_2 = 0.01 \) in Figure 3.1), the behavior is more complicated, as illustrated in Figure 3.10. Consider the geometry with a circular precipitate shown in Figure 3.6. For \( \bar{\theta} < 0.02 \), the growth of intermediate phase stops before the original precipitate phase is consumed, so that three phases exist in the final equilibrium of the system. For \( 0.02 < \bar{\theta} < 0.05 \), intermediate phase completely consumes the precipitate phase, so that the final equilibrium has only two phases. For \( \bar{\theta} > 0.05 \), the temporary intermediate phase continues to transform until the final uniform state is reached.
Figure 3.9. Phase transition is presented for the stable-intermediate phase, $\tilde{W}_2 = -0.04$, with a relatively high compositional strain energy parameter, $\tilde{\theta} = 0.2$ ($\lambda = 5$, color bar shows the composition).
3.4.3 Growth of the intermediate phase in 2D – anisotropic case

To study systems with anisotropic gradient energy coefficients, we define the anisotropy coefficient, \( \mu = \frac{K_{11}}{K_{22}} \), where components of \( \mathbf{K} \) on the principal axes are:

\[
\mathbf{K} = \begin{bmatrix}
K_{11} & 0 \\
0 & K_{22}
\end{bmatrix}.
\]
For arbitrary coordinate system, the off-diagonal components of $K$ will have non-zero values, so that the mixed derivatives of concentration enter the formulation (3.25) directly. To ensure sufficiently dense mesh, i.e., at least ten elements ($\lambda = 5$) across the interface, the smaller of $K_{11}$ and $K_{22}$ is used to calculate the nominal interface thickness (3.32). The shape evolution of an initially circular precipitate is shown in Figure 3.11, for a system having stable intermediate phase and anisotropic $K$ matrix, $\mu = 0.25$. Complete elements are used for this simulation. The initial phase of precipitate vanishes quickly, but the resulting intermediate phase precipitate then slowly evolves until reaching its equilibrium elliptical shape.

As expected, in the anisotropic case, the incomplete elements not only slow down the kinetics but also result in different equilibrium size of the resulting intermediate phase precipitate. This is illustrated in Figure 3.12, where the longer diameter of the ellipse is taken to be the measure of the size, $\bar{S}$. During the short first phase of the process, while the initial precipitate phase is consumed by the intermediate phase ($\bar{t} = 15 \times 10^3$ to $20 \times 10^3$ depending on $\mu$), the differences in results obtained with complete and incomplete elements are minor. However, the effect on shape evolution is strong, so that the error in final configuration, resulting from use of incomplete elements, increases with increasing anisotropy coefficient.
Figure 3.11. Shape evolution of an initially circular precipitate for a system with stable intermediate phase ($\bar{\theta} = 0.05$), and anisotropy coefficient $\mu = 0.25$. Color bar shows composition.
3.5 Conclusions

The problem of coupled Cahn-Hilliard phase-field model and elasticity is considered. Mixed-order finite element model is developed, with $C^0$ interpolation functions for displacement and $C^1$ interpolation functions for concentration, and applied to study the solid state phase transformations in binary alloys in 1 and 2 spatial dimensions. An implicit time-stepping algorithm with mechanical equilibrium iterations is developed. The results for the 1D problem – a thin film diffusion couple were compared Johnson’s
finite difference results (Johnson 2000). The expected quadratic convergence to the correct value is confirmed.

In 2D, we also studied the effect of element completeness of interpolation functions. We used: (a) simple incomplete elements developed as product of Hermit cubics, and (b) augmented complete elements. Both were developed earlier in the context of elliptic problems (plate bending), where the inability of incomplete elements to represent plate torsion proved fatal. In our parabolic problem, the effects of incompleteness are different.

When the gradient coefficients tensor is isotropic, the incompleteness (i.e., the lack of ability to describe mixed derivatives) proved to have only a minor effect on kinetics. This is not surprising since the governing equations do not contain mixed spatial derivatives of concentration. The equilibrium was reached with very small delay compared to the results with complete elements. When gradient coefficients tensor is anisotropic, the governing equations contain mixed derivatives of concentration, so that the effect of incompleteness is significant. In addition, to the delayed kinetics, the final equilibrium configurations are also measurably different. The deviations increase with increasing anisotropy coefficient.

The 2D formulation with complete elements exhibits the expected quadratic convergence.

In both, 1D and 2D problems, we have studied different regimes, notably the distinction between chemically energy dominated and elasticity dominated case, as well
as different stability of intermediate phases. The developed FE scheme shows consistent quadratic convergence.

Acknowledgements

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Appendix A

One-dimensional finite element

The coupled mechanical equation (3.16) and phase field /diffusion equation (3.25) are considered for a thin film diffusion couple. Two-node elements with regular C0 interpolation functions are used to generate the mesh along the plate thickness for mechanical equation (16). The diffusion/phase field equation is 4th order in concentration, so the standard convergence theorems require C1 continuity (like beam elements) (Hughes 2000).

Two-node nonlinear elements with Hermite cubic polynomials are used to discretize the domain for concentration (3.25). The Hermite cubics in natural coordinates are given as (Hughes 2000):

\[
H_1(\xi) = \frac{1}{4}(\xi - 1)^2 (2 + \xi) \]
\[
H_2(\xi) = \frac{1}{4}(\xi - 1)^2 (\xi + 1) \]
\[
H_3(\xi) = \frac{1}{4}(\xi + 1)^2 (2 - \xi) \]
\[
H_4(\xi) = \frac{1}{4}(\xi + 1)^2 (\xi - 1) \]  

(A1)

For given nodal values of the concentration and its gradient for a two-node element, the interpolation within the interval \([-1,1]\) is:

\[
c(\xi) = H_1(\xi)c_1 + H_2(\xi)\frac{\partial c_1}{\partial \xi} + H_3(\xi)c_2 + H_4(\xi)\frac{\partial c_2}{\partial \xi}, \]

(A2)
where \( c_1 \) and \( c_2 \) are the concentration at \(-1\) and \(1\), while \( \partial c_1 / \partial \xi \) and \( \partial c_2 / \partial \xi \) are the gradient of concentration at \(-1\) and \(1\).

**Two-dimensional finite element**

For the elasticity equation (3.16), four-node and three-node elements with regular \( C^0 \) interpolation functions are used to generate the mesh in two dimensions. The diffusion/phase field equation is \( 4^{th} \) order in concentration, so \( C^1 \) type elements are required for the convergence (Hughes 2000). We define four-node (rectangular) and three-node nonlinear elements by using the one dimensional Hermite cubic shape functions to discretize the two dimensional domain for concentration (3.25).

The interpolation functions for a 2D element must satisfy similar conditions to 1D interpolation functions. We express the value of the concentration within the 2D quad element (in natural coordinates) as:

\[
c(\xi, \eta) = \sum_{n=1}^{4} c_n \Psi_{4n-3}(\xi, \eta) + \frac{\partial c_n}{\partial \xi} \Psi_{4n-2}(\xi, \eta) + \frac{\partial c_n}{\partial \eta} \Psi_{4n-1}(\xi, \eta) + \frac{\partial^2 c_n}{\partial \xi \partial \eta} \Psi_{4n}(\xi, \eta).
\]

(A3)

To construct the interpolation functions, we note that for (A3) to be true, they must satisfy conditions similar to those satisfied by 1D interpolation functions (Hermite cubics), i.e., the value that corresponds to the particular degree of freedom (DOF) at particular node must be one, while all other values that correspond to other DOFs at the same or other node, must be zero. That can be achieved by making products of the type
$H_i(\xi)H_j(\eta)$. Such products will form 6th order polynomials in $(\xi, \eta)$. The interpolation functions for a rectangular element are (Chien and Shih 2009):

\[
\begin{align*}
\Psi_1(\xi, \eta) &= H_1(\xi)H_1(\eta) \\
\Psi_2(\xi, \eta) &= H_2(\xi)H_1(\eta) \\
\Psi_3(\xi, \eta) &= H_1(\xi)H_2(\eta) \\
\Psi_4(\xi, \eta) &= H_2(\xi)H_2(\eta)
\end{align*}
\]

node 2:

\[
\begin{align*}
\Psi_5(\xi, \eta) &= H_3(\xi)H_1(\eta) \\
\Psi_6(\xi, \eta) &= H_4(\xi)H_1(\eta) \\
\Psi_7(\xi, \eta) &= H_3(\xi)H_2(\eta) \\
\Psi_8(\xi, \eta) &= H_4(\xi)H_2(\eta)
\end{align*}
\]

node 3:

\[
\begin{align*}
\Psi_9(\xi, \eta) &= H_3(\xi)H_3(\eta) \\
\Psi_{10}(\xi, \eta) &= H_4(\xi)H_3(\eta) \\
\Psi_{13}(\xi, \eta) &= H_1(\xi)H_2(\eta) \\
\Psi_{12}(\xi, \eta) &= H_4(\xi)H_4(\eta)
\end{align*}
\]

node 4:

\[
\begin{align*}
\Psi_{13}(\xi, \eta) &= H_1(\xi)H_3(\eta) \\
\Psi_{14}(\xi, \eta) &= H_2(\xi)H_3(\eta) \\
\Psi_{15}(\xi, \eta) &= H_1(\xi)H_4(\eta) \\
\Psi_{16}(\xi, \eta) &= H_2(\xi)H_4(\eta)
\end{align*}
\]

(A4)

For the incomplete element, which does not include the mixed derivatives, the last terms in (A3) vanish, so that the interpolation functions $\Psi_4$, $\Psi_8$, $\Psi_{12}$, and $\Psi_{16}$ do not enter the formulation. The interpolation functions for a triangular element are derived from the quad interpolation functions by the standard node-coincidence method (Hughes 2000).
Appendix B

The particular dimensional reduction has been used by (Johnson 2000). It is rendered unique by two requirements. First – that the re-scaled composition \(\bar{c}\) varies between \(-1\) and 1, with intermediate phase at \(\bar{c}^\beta = 0\). Therefore:

\[
\bar{c} = \frac{2c - c_m - c_m^\alpha}{(c_m^\gamma - c_m^\alpha)}.
\]  

(B1)

Second – that the non-dimensional gradient coefficient is \(\bar{K} = 1\), in the isotropic case. The non-dimensional and scaled variables are identified by overbars.

With these requirements, the characteristic length \(L\), the characteristic time \(\Omega\), and the characteristic energy density \(W\), are:

\[
X = \sqrt{\frac{K}{\rho_0 k T}} \left(\frac{2}{c_m^\gamma - c_m^\alpha}\right)^2, \quad \Omega = \frac{K}{2B(\rho_0 k T)^2} \left(\frac{2}{c_m^\gamma - c_m^\alpha}\right)^6,
\]

\[
W = \rho_0 k T \left(\frac{c_m^\gamma - c_m^\alpha}{2}\right)^6. \quad \text{(B2)}
\]

In (B2) \(\rho_0\) is density of the lattice sites, \(k\) is Boltzmann’s constant, and \(T\) is the temperature. The non-dimensional gradient energy coefficient, \(\bar{K}\), becomes 1 for all isotropic systems. For 2D systems with anisotropic gradient energy coefficients, we keep \(\bar{K}_{22} = 1\), and vary \(\bar{K}_{11}\).

Considering isotropic mobility, the non-dimensional flux is:
\[
\bar{q} = \frac{q}{\rho_0 A_0 BW} \left( \frac{2}{c^\gamma - c^\alpha} \right)^s,
\]

so that non-dimensional mobility coefficient, \( \bar{B} = 1 \).
CHAPTER FOUR: Morphological Instabilities in Thin Films

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Abstract

Cahn-Hilliard type of phase-field model coupled with elasticity equations is used to study the instability of multilayer thin film diffusion couples in solid state. A mixed order finite element model which we previously developed for solving the coupled phase-field and mechanical governing equations is used for the computations. Maps of transformations in multilayer systems are carried out considering the effects of thickness of layers, volume fraction of films, and compositional strain on the instability of the multilayer thin films. It is shown that at some cases phase transformation, intermediate phase nucleation and growth, or deformation of layers due to high compositional strain can lead to the coarsening of the layers which can result in different mechanical and materials behaviors of the original designed multilayer.

Key words: Phase field modeling, elasticity, multilayer thin films, instability
4.1 Introduction

Multilayer thin films have been a very active research area in the past decade. When the thickness of individual layer is reduced to micro- or nano-scale, novel mechanical (Jankowski 1995; Movchan and Lemkey 1997; McKeown et al. 2002; Eizadjou et al. 2008; Mara 2004), optical (Atkinson and Dodd 1997), electronic (Stobiecki et al. 1998; Czapkiewicz et al. 1996), and magnetic (Atkinson and Dodd 1997; Stobiecki et al. 1998; Czapkiewicz et al. 1996) properties emerge, which make such materials attractive for a number of potential applications. In multilayer micro- and nano-films, the stability of phases is required to maintain the desirable properties. For example, significant drop of hardness occurs after annealing of Ni/Ru multilayers at 600°C (Wen et al. 2008). Different temperature or stress fields may result in instability of multilayers. For example breakdown of the Ni layers happens when multilayer Ni/Ag is annealed at 600°C (Lewis et al. 2003), and pinch-off (holes in grain boundary triple junctions) of Co layers in Co/Cu multilayers is observed after creep test at 830°C (Josell et al. 1999).

(Greer 1986 and 1993) classified the changes that can occur in thin film multilayers as their microstructures evolve. He divided these processes to the following categories: inter-diffusion (same phases coexist with changed compositions) (Ag/Au (Yang and Greer 1996), Ni/Al and Ag/Zn (Ghosh and Paul 2007), Al/Ni (Grag et al. 1999)), interfacial reaction (nucleation and growth of a new phase) (Si/Ni (Gosele and Tu 1982), Ni/Zr (Highmore et al. 1987), Al/Mn (Srivastava et al. 2007), Ni/Al (Noro et al. 2008)), transformation in one phase of the multilayer without any changes in other
phase(s) (Si/Al (Konno et al. 1992)), and, coarsening or spinodal decomposition of the layers (Ni/Ag (Wen et al. 2008), Ni/C (Chernov et al. 2000)).

In solid state, microstructural evolution can be affected by elasticity of the system; the lattice continuity across the interfaces between mismatched phases produces elastic strains and can have significant effects on the stability of the multilayered systems (Larche and Cahn 1978 and 1992; Cahn and Larche 1982; Grinfeld 1986; Srolovitz 1989; Chirranjeevi et al. 2009).

The theory of phase transition and spinodal decomposition in solid state was developed by (Cahn and Hilliard 1958). The numerical studies in the area of solid state phase transformation are mostly based on diffusive-interface or phase-field models (Kassner et al. 2001; Leo and Johnson 2001; Wang et al. 2004; Chen et al. 1991; Wang et al. 1993; Wang and Khachaturyan 1995; Chen and Shen 1998; Hu and Chen 2001; Vaithyanathan et al. 2004; Cahn and Kobayashi 1995; Johnson 2000; Seol et al. 2005; Yeon et al. 2006; Ratz et al. 2006). Among these studies, a few looked at thin films which either are one-dimensional models (Cahn and Kobayashi 1995; Johnson 2000) which can not predict all the possible phase transformations in multilayers, or are focused on the films and fluid interactions (Seol et al. 2005; Yeon et al. 2006; Ratz et al. 2006). Recently, (Chirranjeevi et al. 2009) used a phase field model to study the instability of a special two-phase multilayer with one phase much stiffer than the other.

Here, we present a comprehensive study of binary multilayer thin films, including the two-phase systems, and systems with an intermediate phase (meta-stable or stable). Following the dimensional analysis, we develop the maps of the evolution behavior of
multilayers, including the effects of initial geometry and elasticity of the system. We use the recently developed Galerkin finite element formulation (Asle Zaeem and Mesarovic 2009 and 2010) of the Cahn-Hilliard diffuse interface model (Cahn and Hilliard 1958), coupled with elasticity (Johnson 2000).

The paper is organized as follows. In Section 2, formulation, dimensional analysis and numerical solver for the coupled phase field-elasticity equations are presented; the maps of transformations for two-phase systems, systems with stable intermediate phase, and systems with meta-stable intermediate phase are presented in Sections 3, 4 and 5, respectively; a short conclusion is presented in Section 6.

4.2 Formulation and Numerical Method

In solid state phase transformations, the lattice continuity across the interfaces between mismatched phases produces elastic strains (Cahn and Larche 1982; Larche and Cahn 1992), so that the 2nd order elasticity PDEs need to be coupled to the phase field equation (Leo and Johnson 2001; Cahn and Kobayashi 1995; Johnson 2000). Phase field models are characterized by the dependence of the free energy of a non-uniform system on the phase field variable (e.g., composition, c). In this work, a binary system is considered, with components A and B, which forms three phases (α, β, and γ), and characterized by the molar fraction of the component A, c. The total free energy, \( F \), of a non-homogeneous system with volume \( V \), bounded by surface \( S \), is constructed as:
\[
F(c, u_i) = \int_V \left[ f(c) + U(e_{ij}, c) + \frac{\kappa}{2} (\nabla c)^2 \right] dV - \int_S t_i u_i dS .
\] (4.1)

\(f(c)\) is the stress-free Helmholtz free energy density of a uniform system. \(\kappa\) is the isotropic gradient energy coefficient. \(t_i\) is the surface traction component, and \(u_i\) is the displacement component. In (4.1), the surface energy of the outer boundary \(S\) is neglected. \(U(e_{ij}, c)\) is the strain energy density and \(e_{ij}\) is the total strain tensor:

\[
e_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) = e_{ij}^e + e \delta_{ij} ,
\] (4.2)

where \(u_i\) is the displacement component, \(e_{ij}^e\) is the elastic strain and \(e\) is the purely volumetric compositional strain. The simplest model follows the linear Vegard’s law (Denton and Ashcroft 1991):

\[
e = \eta (c - c_0) .
\] (4.3)

The reference composition \(c_0\) is taken to be the average of composition over the domain. \(\eta\) is the compositional strain parameter.

For solid state phase transformation, the phase-field variable is subject to a conservation law. This kind of conserved phase field formulations results in a 4th order evolution PDE (Asle Zaeem and Mesarovic 2010):

\[
\dot{c} = B \nabla^2 M ,
\] (4.4)

where \(B\) is the isotropic mobility coefficient, and the chemical potential, \(M\), is equal to the variational derivative of the free energy respect to composition (Larche and Cahn 1978):
\[ M = f' - U' - \kappa \gamma^2 c. \quad (4.5) \]

The Helmholtz free energy density of a uniform unstressed system, \( f(c) \) in (4.1), is assumed to be a triple well potential that can produce binary systems with no-intermediate phase, stable intermediate phase, and meta-stable intermediate phase:

\[ f(c) = W_1 (c - c^\alpha)^2 (c - c^\beta)^2 (c - c^\gamma)^2 + W_2 (c - c^\alpha)^2 (c - c^\gamma)^2, \quad (4.6) \]

where \( W_1 \) and \( W_2 \) are the energy coefficients, \( c^\alpha, c^\beta \) and \( c^\gamma \) are the mole fractions of component B at which \( f(c) \) is minimized.

By using a particular dimensional reduction (Johnson 2000; Asle Zaeem and Mesarovic 2010) we can find the non-dimensional independent parameters of the system. The scaled composition, \( \bar{c} \), varies between \( \bar{c}^\alpha = -1 \) and \( \bar{c}^\gamma = -1 \), with intermediate phase at \( \bar{c}^\beta = 0 \):

\[ \bar{c} = \frac{2c - c^\gamma - c^\alpha}{(c^\gamma - c^\alpha)}. \quad (4.7) \]

The characteristic length \( X \), the characteristic time \( \Omega \), and the characteristic energy density \( W \), are:

\[ X = \sqrt{\frac{\kappa}{\rho_0 kT} \left( \frac{2}{c^\gamma - c^\alpha} \right)^2 }, \quad (4.8a) \]

\[ \Omega = \frac{\kappa}{2B(\rho_0 kT)^2} \left( \frac{2}{c^\gamma - c^\alpha} \right)^8, \quad (4.8b) \]
\[ W = \rho_0 kT \left( \frac{c' - c^a}{2} \right)^6, \quad (4.8c) \]

where \( \rho_0 \) is density of the lattice sites, \( k \) is Boltzmann’s constant, and \( T \) is the temperature. \( \kappa \) affects only the length and time scale, and \( B \) affects only the time scale (non-dimensional gradient energy coefficient and mobility are \( \kappa = B = 1 \) for isotropic cases). Therefore, their variations in numerical runs are superfluous. One only needs to rescale length and time in the solution to get the results. The scaled compositional strain parameter is:

\[ \bar{\eta} = \eta \frac{E}{\sqrt{\rho_0 kT (1 - \nu) \left( \frac{2}{c' - c^a} \right)^2}}, \quad (4.9) \]

where \( E \) is the Young’s modulus, and \( \nu \) is the Poisson ratio (in this paper \( \nu = 0.3 \)). The non-dimensional elastic modulus are:

\[ \bar{C}_{11} = \frac{(1 - \nu)^2}{(1 + \nu)(1 - 2\nu)}, \quad \bar{C}_{12} = \frac{\nu(1 - \nu)}{(1 + \nu)(1 - 2\nu)}, \quad \text{and} \]

\[ \bar{C}_{44} = \frac{(1 - \nu)}{(1 + \nu)}. \]

By applying this particular dimensional reduction all the parameters of the system will be reduced to three independent non-dimensional parameters, \( \bar{\eta}, \bar{W}_1 = \frac{W_1}{W} \)

and \( \bar{W}_2 = \frac{W_2}{W} \). By varying \( \bar{W}_1 \) and \( \bar{W}_2 \) in (4.6), we can produce different binary alloy systems with no-intermediate phase (\( \bar{W}_1 = 0 \) and \( \bar{W}_2 = 0.02 \)), stable intermediate phase (\( \bar{W}_1 = 0.4 \) and \( \bar{W}_2 = -0.04 \)), and meta-stable intermediate phase (\( \bar{W}_1 = 0.4 \) and \( \bar{W}_2 = 0.02 \)), which are shown in Figure 1, and \( \beta \) is the intermediate phase.
The details of deriving the coupled governing equations of phase field and elasticity can be found in (Asle Zaeem and Mesarovic 2010). The numerical solvers which have been used in one-dimensional phase field problems are based on finite difference method (Cahn and Kobayashi 1995; Johnson 2000) and in two-dimensional problems mostly Fourier transform techniques (Chen et al. 1991; Wang et al. 1993; Wang and Khachaturyan 1995) and related Fourier-spectral methods (Chen and Shen 1998; Hu and Chen 2001; Vaithyanathan et al. 2004) have been employed, which have some difficulties in modeling irregular domains, nonlinear and history-dependent problems. In a recent work, we have developed a finite element method for these kinds of coupled problems (Asle Zaeem and Mesarovic 2010). For the purpose of using finite element as the numerical method, the weak forms of the governing equations were derived. As the mechanical and diffusion/phase field equations are of different orders, uniform
convergence of the results requires different order of continuity for interpolation functions (Hughes 2000). We formulated and implemented such mixed-order finite elements, with $C^0$ interpolation functions for displacement, and $C^1$ interpolation functions for composition. A special time integration scheme was developed consisting of implicit time-stepping and equilibrium/consistency iterations in each time step. Special boundary settings are considered to simulate the multilayer thin films, and for all of our 2D cases, left and right boundaries have periodic boundary condition and top and bottom boundaries have no-traction and no-flux boundary conditions (shown in Figure 4.2).

For the finite element mesh, the optimal mesh size was determined to be about $1/5$ of the interface width which it guarantees the uniform quadratic convergence, expected for conforming elements (Asle Zaeem and Mesarovic 2010). The nominal interface thickness (for coexisting isotropic phases $\alpha$ and $\gamma$) is derived by (Cahn and Hilliard 1958):

$$l_0 = (c^\gamma - c^\alpha \left(\frac{K}{2\Delta f_{\text{max}}}\right))^{1/2},$$

where $\Delta f_{\text{max}}$ is the difference between the neighboring maximum and minimum of the free energy (4.6), as illustrated in Figure 4.1.
4.3 Two Phase Multilayer

In this section we look at the phase transformations in binary multilayer systems with two phases in Figure 4.1. We use variables, $d_\alpha$ and $d_\gamma$ as the initial thicknesses of $\alpha$ and $\gamma$ layers (Figure 4.2), which are non-dimensionalized by (4.8a).

There is an example in Figure 4.2 that shows the effects of compositional strain parameter, $\eta$, on the stability of layers. In this case, threshold value of compositional strain parameter to make the break-up of the films into particles is $\eta = 0.07$, and $\eta = 0.15$ makes the $\alpha$-phase vanishes (homogenization- the final matrix will have average composition of the system).

![Figure 4.2](image-url)

**Figure 4.2.** Microstructural development in a single $\gamma$-layer embedded between two $\alpha$-layers. Initially $d_\gamma = 15$ and $d_\alpha = 30$; $\eta = 0.07$, color bar shows the composition, the finite element mesh consists of 14182 triangular elements.
In Figure 4.3, there is an example of coarsening of $\gamma$-layers in $\alpha$-matrix. In this case, first fragmentation of $\alpha$-layer between $\gamma$-layers happens and then $\alpha$-phase disappears between $\gamma$-layers; final configuration of the system has one thicker $\gamma$-layer.

The map of transformations for the multilayer systems initially having 5 layers (2 $\gamma$-layers and 3 $\alpha$-layers), and with the possibility of two phases (no-intermediate phase) are shown in Figures 4.4 and 4.5, for $\overline{\eta} = 0$ and $\overline{\eta} = 0.1$, respectively. To plot each map of transformations more than 150 computer runs were performed. There are five different regions. As it can be seen in the maps, for initially very thin $\gamma$-layers, homogenization happens which means $\gamma$-layers disappear and the final matrix will have average composition of the system. For thicker $\gamma$-layers and when there is enough $\gamma$-phase in the system, $\gamma$-phase doesn’t disappear and at least $\gamma$-phase particles will be produced. For much thicker $\gamma$-layers, depending on $d_\alpha$ (the thickness of the $\alpha$-layer between two $\gamma$-layers), two different types of coarsening are defined. In first type, both $\gamma$-layers remain layers during the transformations and fragmentation happens to the $\alpha$-layer between the two $\gamma$-layers then $\alpha$-phase between the two $\gamma$-layers disappear and a thicker $\gamma$-layer remains in the final configuration of the system; there is an example of these kinds in Figure 4.3. In second type, fragmentation occurs to one of $\gamma$-layers and $\gamma$-particles will be produced in the system, then these $\gamma$-particles join the other $\gamma$-layer and make a thicker $\gamma$-layer. The last region where no changes appear is for those systems with initially thick $\gamma$-layers and a very thick $\alpha$-layer between them.
Figure 4.3. Coarsening of $\gamma$-layers. Initially $d_\gamma = 25$ and $d_\alpha = 15$; $\eta = 0.1$, and color bar shows the composition. The finite element mesh consists of 22248 triangular elements.

Figure 4.4. Map of transformations for the systems with possibility of two phases (no-intermediate phase) and $\bar{\eta} = 0$. The non-dimensional interface thickness calculated form (4.10) is $\bar{t}_0 \approx 7$. All the results are from $\bar{t} = 10^7$. 
4.4 Three Phase Multilayer with Stable Intermediate Phase

In this section we study the phase transformations in binary multilayer systems with possibility of stable-intermediate phase growth in Figure 4.1. There is an example of these kinds in Figure 4.6. First the growth of the intermediate phase takes place and all the γ-phase and part of the α-phase will be consumed by β-phase and the original γ-layers will be replaced by thicker β-layers. Fragmentation happens in the α-layer between two β-layers and then all the α-phase between two β-layers disappear. A thick β-layer remains in the final configuration of the system.
The maps of transformations for binary multilayer systems with possibility of stable-intermediate phase growth are shown in Figure 4.7 and 4.8 for $\bar{\eta} = 0$ and $\bar{\eta} = 0.2$, respectively. Because $\beta$-phase is a stable intermediate phase and has lower energy level than $\alpha$-phase and $\gamma$-phase, and because there is not external forces on the system, phase

Figure 4.6. Phase transition is presented for a system with stable-intermediate phase. Initially $d_{y} = 15$ and $d_{x} = 20$; $\bar{\eta} = 0.2$ and color bar shows the composition. The finite element mesh consists of 45108 triangular elements.
transformation happens to lower the energy of the system and in all regions for both values of \( \overline{\eta} \), growth of intermediate phase occurs until all the \( \gamma \)-phase is consumed.

For \( \overline{\eta} = 0 \), there is not any region in the map of transformation for homogenization (Figure 7), because even initially very thin \( \gamma \)-layers will transform into thicker \( \beta \)-layers so at least \( \beta \)-particles will be produces from the \( \beta \)-layers without homogenization. For bigger values of \( \overline{\eta} \) (like \( \overline{\eta} = 0.2 \)), there is an small region where initially very thin \( \gamma \)-layers vanish and homogenization occurs. By comparing Figures 4.7 and 4.8, it can be seen by increasing \( \overline{\eta} \), the \( \beta \)-particle region becomes larger because higher values of \( \overline{\eta} \) make the break-up of thicker films into particles easier.

\[ \text{Figure 4.7. Map of transformations for the systems with possibility of three phases (stable-intermediate phase) and } \overline{\eta} = 0 . \text{ The non-dimensional interface thickness between } \beta \text{ and } \gamma \text{ phases calculated form (4.10) is } \overline{l}_0 \cong 3.2 . \text{ All the results are from } \overline{t} = 10^7 . \]
4.5 Three Phase Multilayer with Meta-Stable Intermediate Phase

In this section we study phase transformations in binary multilayer systems with possibility of meta-stable intermediate phase growth in Figure 4.1. An example of these kinds is presented in Figure 4.9. In this example, initially, $\beta$-phase will grow to produce a very thin film on $\gamma$-layers but because $\beta$-phase is an unstable phase, growth will stop. Then because of the high value of $\eta = 0.2$, two layers will deform and become closer and necking happens in a small region. $\beta$-phase will grow again to help the coarsening process and growth continues until all the $\alpha$-phase between $\gamma$-layers is consumed by $\beta$-
phase, then as $\beta$-phase is an unstable phase it will disappear, and final configuration of the system will have a thicker $\gamma$-layer and very thin $\beta$-film on it.

The maps of transformations for the binary multilayer systems with possibility of unstable-intermediate phase growth are shown in Figure 4.10 and 4.11 for $\eta = 0$ and $\eta = 0.2$, respectively. In these systems, because $\beta$-phase is a meta-stable intermediate
phase and has higher energy level than $\alpha$-phase and $\gamma$-phase, and also because there is not any external forces on the system, for low values of $\eta$, intermediate phase doesn’t continue to grow and growth stops after producing very thin film of $\beta$-phase on $\gamma$-layers. But when $\gamma$-layers are very thin initially, this small growth of $\beta$-phase is enough to consume all $\gamma$-phase in the system and depending of initial size of $\gamma$-layers and value of $\eta$, final configuration of the system can include $\beta$-particles or $\beta$-layers. For initially thicker $\gamma$-layers with a thin $\alpha$-layer between them, $\beta$-phase will grow to help the coarsening processes of $\gamma$-layers then $\beta$-phase vanishes, similar to the case in Figure 4.9. For higher values of $\eta$, to lower the total elastic energy of the system, more $\beta$-phase will partially grow and remain in the final and relaxed configuration of the multilayer system, so final configuration of the system has three phase layers.
Figure 4.10. Map of transformations for the systems with possibility of meta-stable intermediate phase growth and $\bar{\eta} = 0$. The non-dimensional interface thickness between $\beta$ and $\gamma$ phases calculated from (4.10) is $\bar{t}_0 \approx 2.8$. All the results are from $\bar{t} = 10^8$.

Figure 4.11. Map of transformations for the systems with possibility of meta-stable intermediate phase growth and $\bar{\eta} = 0.2$. The non-dimensional interface thickness between $\beta$ and $\gamma$ phases calculated form (4.10) is $\bar{t}_0 \approx 2.8$. All the results are from $\bar{t} = 10^8$. 
4.6 Conclusion

Maps of transformations for multilayer thin films are carried out considering the effects of thickness of layers, volume fraction of films, and compositional strain on the instability of the multilayer system. Three different binary systems are considered representing multilayer thin films with no-intermediate phase, stable intermediate phase, and meta-stable intermediate phase. It is shown that at some cases phase transformation, intermediate phase nucleation and growth, or fragmentation of layers due to high compositional strain can result in instability of multilayer thin films.

Although, without considering the effects of compositional strain on the multilayer systems we can determine the map of transformations, but from our results it is clear that the elastic force coming from compositional strain is an effective factor to make the multilayer unstable and can change the map of transformations significantly.
CHAPTER FIVE: Summary and Future Works

The problem of coupled Cahn-Hilliard phase-field model and elasticity is considered. Mixed-order finite element model is developed, with C0 interpolation functions for displacement and C1 interpolation functions for concentration. An implicit time-stepping algorithm with mechanical equilibrium iterations is developed. The developed FE scheme shows consistent quadratic convergence for both 1D and 2D.

In Chapter 2, the developed FE model is applied to study growth of intermediate phase in Al-Zn thin film diffusion couple.

In 2D FE model, the effect of element completeness of interpolation functions is studied in Sections 3.4.2 and 3.4.3. We used: (a) simple incomplete elements developed as product of Hermit cubics, and (b) augmented complete elements. For isotropic gradient coefficients tensor (Sections 3.4.2), the incompleteness (i.e., the lack of ability to describe mixed derivatives) proved to have only a minor effect on kinetics. This is not surprising since the governing equations do not contain mixed spatial derivatives of concentration. The equilibrium was reached with very small delay compared to the results with complete elements. For anisotropic gradient coefficients tensor (Sections 3.4.3), the governing equations contain mixed derivatives of concentration, so that the effect of incompleteness is significant. In addition, to the delayed kinetics, the final equilibrium configurations are also measurably different. The deviations increase with increasing anisotropy coefficient. In both, 1D and 2D problems, we have studied different regimes,
notably the distinction between chemically energy dominated and elasticity dominated case, as well as different stability of intermediate phases.

In Chapter 4, maps of transformations for multilayer thin films are carried out. The effects of thickness of layers, volume fraction of films, and compositional strain on the instability of the multilayer system are considered. Three different binary systems are considered representing multilayer thin films with no-intermediate phase, stable intermediate phase, and meta-stable intermediate phase.

Suggestions for future work in this area include: 1. investigating the effects of anisotropic elastic modulus in both microstructure evolution of particles and multilayer thin films; 2. apply developed finite element model for wetting problem in which governing equations can be derived by coupling Navier-Stokes and Phase Field equations which results in coupled 2\textsuperscript{nd} and 4\textsuperscript{th} order PDEs; 3. Develop 3D mixed order finite element model which can be applied for coupled 2\textsuperscript{nd} and 4\textsuperscript{th} order PDEs.
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