Phase-field Models of Microstructure Evolution in a System with Elastic Inhomogeneity and Defects

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by

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Abstract

Solid state phase transformations are often utilized to control materials microstructures and thus properties. Quantitative understanding of the thermodynamics and kinetics of phase transformations and the accompanying microstructure evolution can provide a scientific basis for designing advanced materials. In this thesis, the phase-field approach is employed to study the effect of elastic inhomogeneity and structural defects on phase separation kinetics and morphological evolution in bulk and film systems, the precipitation of $\theta^\prime$ phase ($\text{Al}_2\text{Cu}$) in Al-Cu alloys, and solute strengthening of alloys.

An accurate and efficient iteration method is proposed to solve the mechanical equilibrium equations in a solid with elastic inhomogeneity. By combining the iteration method for calculating the elastic energy and a semi-implicit spectral method for solving the Cahn–Hilliard equation an extremely efficient phase-field model is developed for studying morphological evolution in coherent systems with large elastic inhomogeneity. The morphological dependence of isolated particles as well as a phase separated multi-particle system on the degree of elastic inhomogeneity is systematically studied.

The iteration method is further extended to a thin film system with the simultaneous presence of dislocations, compositional strains and a substrate constraint. Spinodal decomposition in a thin film with periodically distributed arrays of interfacial dislocations is simulated. The results show that the periodic stress field associated with the array of interfacial dislocations leads to a directional phase separation and the
formation of ordered microstructures. It is demonstrated that when the period of the dislocation array becomes small, the wave length of the ordered microstructure tends to be the same as that of the dislocation array. The results have important implications that an ordered nanostructure could be designed by controlling the interfacial dislocation distribution.

The metastable $\theta'$ ($\text{Al}_2\text{Cu}$) precipitates are one of the primary strengthening precipitates in Al-Cu alloys. They are of a plate-like shape with strong interfacial energy and mobility anisotropies. A phase-field model which can automatically incorporate the thermodynamic and kinetic information from databases is developed. The relationships between phase-field model parameters and material thermodynamic and kinetic properties are established. Systematic simulations of $\theta'$ growth in 1D, 2D and 3D are carried out. The growth of a single $\theta'$ precipitate in 1D exactly reproduces the results from analytical solutions. The equilibrium shape simulated in two dimensions is in good agreement with that predicted by the Wulff construction based on the interfacial energy anisotropy. 2D and 3D simulations produce typical precipitate morphologies and precipitate configurations that are observed in prior experiments. The simulation results on the growth of an isolated precipitate in 2D show that the lengthening is diffusion-controlled, and follows the $t^{1/2}$ growth law whereas the thickening follows the $t^{2/3}$ growth law. The elastic energy associated with the lattice mismatch between the precipitate and the matrix was shown to speed up the lengthening while decrease the thickening and coarsening process. The phase-field model can serve as a basis for
quantitative understanding of the influence of elastic energy, interface energy anisotropy and interface mobility anisotropy on the precipitation of \( \theta' \) in Al-Cu alloys.

Precipitates and solutes are commonly used to strengthen alloys. A phase field model of dislocation dynamics, which employs 12 order parameter fields to describe the dislocation distribution in a single fcc crystal, and one composition field to describe the solute distribution, is developed for a binary alloy. This model is able to simulate phase transformation, solute diffusion, dislocation motion as well as their interaction under applied stresses. A new functional form for describing the eigenstrains of dislocations is constructed, which eliminates the dependence of the magnitude of the dislocation Burgers vector on applied stresses and provides a correct dislocation stress field. A relationship between dislocation velocity and applied stresses is obtained by theoretical analysis, which can be used to determine phase-field model parameters with kinetic data of dislocation mobility. The effect of dislocation velocities on Cottrell atmosphere, and the dynamic dragging force of Cottrell atmosphere on the dislocation motion are simulated. The results demonstrate that the phase-field model correctly describes the long-range elastic interactions and short-range interaction that determines dislocation reactions.
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Chapter 1

Introduction

Many important properties of a material can be engineered by controlling its solid state phase transformations and the accompanying microstructure evolution. Examples include the improvement of mechanical properties through solid state precipitation reactions in alloys such as Ni-based superalloys and age-hardened Al-alloys, the useful dielectric properties and electro-mechanical coupling effects by manipulating phase transitions in ferroelectric crystals, the memory effect of shape-memory alloys by utilizing martensitic transformations. Essentially all solid state phase transformations produce coherent microstructures at their early stages. In a coherent microstructure, the lattice directions and planes are continuous across the interfaces separating the parent and product phases or separating different orientation domains of the product phase. In order to maintain this lattice continuity, the lattice mismatch between the product and parent phases and among the orientation domains of the product phase must be accommodated by elastic displacements of atoms from their equilibrium lattice positions. Therefore, formation of coherent microstructures generates coherency elastic strain energy whose magnitude depends on the degree of lattice mismatch, the elastic properties of both the parent and product phases, and the shape and spatial distributions of coherent particles or domains [1,2]. The coherency elastic strain energy not only affects the thermodynamic equilibrium properties such as transformation temperature, equilibrium composition and equilibrium precipitate shape but also kinetic properties such as interface mobility and
coarsening behavior [3-9]. There have been intensive theoretical studies and various computational simulations on the effect of coherency elastic strain energy on the morphology of a coherent microstructure and its coarsening behavior, and they have been recently reviewed [3,4]. Structural defects such as dislocations, grain boundaries, interfaces and free surfaces inevitably exist in a crystalline solid. The structural distortions around defects generate a stress field which may compensate the coherency stress field associated with the coherent microstructure. They may also dramatically changes the atom mobility. For example, the diffusivity along free surface, grain boundary and dislocation is often several orders larger than that in the corresponding bulk. As a consequence, the presence of defects may affect the nucleation, growth and coarsening [10–19]. Recrystallization is an excellent example of using a heterogeneous nucleation on dislocations to refine the grain size [20-27]. Therefore, quantitative understanding of the effect of coherency stresses and defects on thermodynamics and kinetics in solid state phase transformations would provide a scientific basis for controlling solid state phase transformation and obtaining desired properties of materials.

Phase-field method is based on a diffuse-interface description [28-30], which is used for modeling and predicting complex microstructure evolutions on a mesoscopic length scale in many important materials processes. In this method, an arbitrary microstructure is described by a set of field variables that are spatially continuous and time-dependent. There are two types of field variables, conserved and non-conserved. Conserved variables have to satisfy the local conservation condition. The most familiar example of conserved field variables is the concentration field characterizing composition
variation. The field variables that do not satisfy the local conservation condition are non-conserved variables, for example, the well-defined physical order parameters in order-disorder transformations which characterizes structural heterogeneity. Phase-field theory assumes that the microstructure evolution takes place to reduce the total free energy, including the bulk chemical free energy, interfacial energy, elastic energy and electrostatic energy. Following non-equilibrium thermodynamics, the conserved field variables satisfy the Cahn-Hilliard equation [31], and the non-conserved phase-field variables satisfy the Allen-Cahn equation (also called the Time Dependent Ginzburg-Landau equation) [32]. Therefore, modeling the microstructure evolution in the framework of phase-field theory is reduced to finding the solutions of Cahn-Hilliard and/or Ginzburg-Landau equations. When the Langevin noise terms associated with thermal fluctuations in composition and lro (long-range order) parameters [33,34] are introduced, nucleation phenomena could be simulated as well.

Throughout the past decade, the phase-field method has been extensively employed to simulate microstructure evolutions during solid state phase transformations, including spinodal decomposition [35-42], precipitation of an ordered phase from a disordered matrix [43-46], cubic to tetragonal transformation [47-52], hexagonal to orthorhombic transformations[53-56], grain growth[57-64], ferroelectric domain formation [65-68], and martensitic transformation [69-70]. However, most existing models are limited to bulk systems that are often assumed to be elastically homogeneous and free of structural defects. Moreover, most existing models are qualitative and usually employ model free energy functions and model parameters. In this thesis, phase-field
models are developed to simulate microstructure evolutions in an elastically inhomogeneous system with structural defects such as dislocations and stress free surfaces in film systems, dislocation dynamics in a single crystal with diffusive solutes and precipitates, and $\theta'$ precipitation in Al-Cu alloys which involves strongly interface energy anisotropy and interface mobility anisotropy.

1.1 Research Objectives

Elastic properties in different phases are often different. The elastic inhomogeneity could be very strong in many practical materials such as multi-void and film materials. Like the elastic anisotropy, the elastic inhomogeneity modifies the coherency stress field, and hence, affects the kinetics of microstructure evolution. The main challenge is to efficiently and accurately calculate the coherency stresses and elastic energy in an elastically inhomogeneous system. There have been a number of efforts to incorporate elastic inhomogeneity in diffuse-interface models. Onuki et al. [35-37] derived a first-order elastic solution assuming weak elastic inhomogeneity. The effect of elastic inhomogeneity on the particle morphology [35-39] and coarsening process [38,39] was studied with phase-field models in binary alloys. Schmidt et al. [71,72] studied the equilibrium shape of a coherent precipitate using a boundary integral method with a sharp-interface description. However, the temporal evolution of precipitate morphologies through the diffusion transport of atoms was not considered. Jou et al. [73] examined the temporal evolution of precipitate shapes in elastically inhomogeneous solids by simultaneously solving a diffusion equation and elasticity equations using the boundary
integral method. Since the interfaces are considered to be sharp in the boundary integral
method, it is difficult to handle certain topological changes that take place, for example,
the formation and disappearance of interfaces during the initial stage of spinodal phase
separation and during precipitate coalescence and splitting. Leo et al. [74] developed a
diffuse-interface model for modeling the microstructure evolution in elastically
inhomogeneous systems by coupling the Cahn–Hilliard diffusion equation with elasticity
equations. In his method, the elasticity equations are numerically solved by a conjugate
gradient method (CGM) at any given moment during microstructure evolution. A similar
diffuse-interface model using CGM was proposed by Zhu et al. [75]. However, the
numerical results show that CGM has a slow convergence, consequently is not a very
efficient method for an application in a system with an evolving microstructure.
Khachaturyan et al. [76] developed an analytical solution with a perturbation method
(PM) and sharp-interface description. The strain energy is expressed as a sum of
multiparticle interactions between finite elements of the constituent phases, pair-wise,
triplet, quadruplet and so on, the \( n \)-particle interaction energy being related to the \( (n-2) \)th
order term in the Taylor expansion of the Green function with respect to the elastic
modulus misfit. The order of approximation required for a given system depends on the
desired accuracy and the degree of elastic inhomogeneity. However, a direct application
of the analytical elastic energy expression to numerical simulations of coherent
microstructure evolutions in elastically inhomogeneous systems is difficult since the
elastic strain energy involves multidimensional integrals in both real and Fourier spaces.
More recently, Wang et al [77-78] proposed a new method by coupling the Eshelby’s
equivalent inclusion concept and Time Dependent Ginzburg-Landau equation. This
The method has an unknown tensor, i.e., the mobility coefficients in Time Dependent Ginzburg-Landau equations. The efficiency of the method depends on the choice of the unknown tensor as well as the microstructure.

In this thesis, an efficient iteration method is proposed to solve the mechanical equilibrium equations in a solid with strongly elastic inhomogeneity. It can be easily incorporated into phase field models, and can take into account elastic anisotropy, strongly elastic inhomogeneity and any kind of structural transformations such as cubic to tetragonal and hexagonal to orthorhombic. If a gas phase, where the elastic constants are zero, is introduced into a film system, the elastic solution in the film with a rough surface can be obtained with the iteration method. This enables phase-field model to simulate the effect of elastic energy on microstructure evolutions in films.

It has long been recognized that structural defects such as dislocations play an important role in diffusion processes and phase transformations in solids. For example, the interaction between solute atoms and a dislocation results in solute segregation and depletion, leading to the formation of so-called “Cottrell atmosphere” [79]. The nucleation of new phases around dislocations is often observed in experiments. Cahn [80] first studied the nucleation of a second-phase precipitate around a dislocation with a theoretical model that a cylindrical nucleus was assumed to replace the dislocation core, thus providing additional driving force for nucleation compared to that in the bulk. Dollins [81] and Barnett [82] considered the nucleation of a coherent precipitate on an edge dislocation under some assumptions such as elastic isotropy and dilatational lattice
mismatches between precipitates and the matrix. Xiao and Hassen [83] re-examined the coherent nucleation problem near an edge dislocation by considering the effect of Cottrell atmosphere on coherent nucleation. However, they again had to assume isotropic elastic modulus for the solid solution and a spherical shape for the nucleus. To relax many of the assumptions in the analytical theories and to study the kinetic diffusion process, there have been a number of computer simulation models proposed. For example, Wang et al. studied the segregation profile around an edge dislocation, and the effect of the segregation on dislocation dynamics using a discrete Monte-Carlo model [84]. The interactions between dislocations and coherent precipitates were studied by using the discrete atom method (DAM) [85]. The effect of dislocations on the morphological evolution during spinodal decomposition was investigated by Leónard and Desai [86]. They directly introduced the analytical elastic solution of a dislocation into the Cahn–Hilliard equation. In summary, the analytical and computational models reviewed above employ the analytical elastic solution of a dislocation. Although convenient in the study of the effect of static dislocations on phase transformations in two dimensions, it is difficult to do so in three dimensions with these models. Furthermore, dislocations might even move due to the elastic interaction between dislocations and the evolving microstructure during phase transformations. Therefore, a more realistic three-dimensional defect model needs to be developed.

In micromechanics [2], ‘eigenstrain’ has been used to describe the distortion associated with crystal defects for a long time. In this thesis, defects will be introduced into phase field models with the ‘eigenstrain’ concept, which demonstrates two main
advantages. One advantage is that it allows people to easily represent an arbitrary spatial distribution of defects into the systems and efficiently obtain the elastic solution by combining Khachaturyan’s microelasticity theory [1] and the iteration method developed in this thesis. The other advantage is that defect dynamics, such as dislocation motion and crack propagation, can be simulated in phase-field framework if the distribution of defects is described by order parameter field variables, as shown by Wang et al [87, 88].

The well-known advantage of phase-field models is that it avoids explicitly tracking a boundary in conventional sharp boundary models by using a diffuse-interface. However, the drawback is that it is hard to use phase-field models quantitatively. The limit for a quantitative simulation comes from two main challenges. One is that it is often computationally too stringent to choose a small enough gradient energy or grid size to resolve the desired sharp-interface limit of the phase-field model, even on computers of today. This severely restricts the size of simulation cell. The other one is how to incorporate thermodynamic data, kinetic data and material properties into a phase field model. Progress has recently been made to overcome these difficulties in solidification simulation. Karma and Rappel [89-90] developed a quantitative phase field model of alloy solidification with equal thermal conductivities in the solid and liquid by using a ‘thin-interface’ analysis. Their results show that the model parameters from ‘thin-interface’ analysis can map onto the standard set of sharp-interface limit, yield a much less stringent restriction on the interface thickness, and eliminate interface kinetic effects. Kim [91] developed a phase field model of alloy solidification that is free from the limit in the interface thickness and correctly generates the solute trapping phenomena at high
interface velocity. However, solid state phase transformations often evolve strongly elastic interaction, strong interface energy anisotropy and interface mobility anisotropy, which causes difficulties in the development of a quantitative phase field model.

In Al-Cu alloys, metastable $\theta'(Al_2Cu)$ precipitates are one of the primary strengthening precipitates [92-104]. The study of $\theta'(Al_2Cu)$ precipitation is interesting because the anisotropy of interfacial energy and interface mobility, and lattice mismatches affect the precipitation process, hence the microstructure and mechanical properties. With a conventional phase-field model, Li and Chen [105] simulated stress-oriented nucleation and growth of $\theta'$ precipitates. Vaithyanathan, et al [106] fitted a chemical free energy function based on first principle calculations. The effect of elastic energy, interface energy anisotropy and interface mobility anisotropy on the morphology and growth of $\theta'$ precipitates are simulated. However, to correctly describe $\theta'$ precipitation, the following factors should be further taken into consideration. $\theta'(Al_2Cu)$ is a compound phase. Its chemical free energy is only defined at $c = 1/3$ (the mole fraction of Cu composition). The question is how to construct the total chemical free energy of a system with compound phases. The experimental observations show that $\theta'$ precipitates are plate-like with a flat and broad interface. This implies that the expression of interface energy should have cusps according to the Wulff construction of an equilibrium precipitate shape. In addition, in order to develop a quantitative phase-field model, the relationship between phase-field model parameters and thermodynamic
and kinetic data should be established. In this thesis, Al-Cu alloy is considered as a model alloy for describing and verifying a quantitative phase field model.

Good understandings of dynamic interactions among dislocations, solutes, precipitates and other defects are important in developing high strength alloys. Within the continuum mechanics framework, there has been tremendous amount of effort devoted to dislocation dynamics. A number of analytical models based on the concept of low energy dislocation structures [107], reaction-diffusion approach [108-112], the concept of dislocation sweeping mechanism [113,114], and stochastic dislocation dynamic description [115,116]) have been proposed. A common feature of these models is that the behavior of a dislocation system is described in analogy to other physical problems such as spinodal decomposition, oscillating chemical reactions at a continuum level. The properties of individual dislocations are taken into account indirectly. Computer simulations of discrete dislocation dynamics in 2D and 3D have also been performed [117-123]. Due to the long-range nature of elastic interactions between dislocations, the direct numerical integration of dislocation dynamic equations is a very time-consuming process, and thus, the size of the simulation cell and the number of dislocations is limited. Recently, a significant advance in the application of phase-field models in dislocation dynamics was made by Wang et al [87,88]. In their phase-field model, the dislocation loops are labeled by a set of order parameter field variables. The temporal evolution of the order parameter fields, i.e., dislocation motion, is described by the phenomenological Time Dependent Ginzburg-Landau (TDGL) equation. The results show that both long-range elastic interactions among dislocations and short-range
interactions, such as multiplication and annihilation of dislocations, are taken into account in the model.

In this thesis, a phase field model of alloy strengthening is developed by coupling the phase-field model of dislocation dynamics with diffusive solutes, elastically inhomogeneity and defects. A new eigenstrain function of dislocations is constructed which can eliminate the dependence of Burgers vector on applied stresses in the original phase field model of dislocation dynamics [87]. Using phase plane analysis in two dimensions, a relationship between dislocation mobility, velocity and applied stresses is established, which can be used to determine the mobility coefficient in the evolution equations with dislocation mobility data calculated by molecular dynamic simulation, first-principle calculation and experiments.

1.2 Thesis Outline

This thesis has been organized into 7 chapters.

Chapter 1 consists of an introduction to the significance of coherency stresses and defects in solid state phase transformations, the application of phase-field models in solid state phase transformations, followed by the research objectives and the thesis outline.

Chapter 2 presents a phenomenological description of the phase-field approach in solid state phase transformations.
In Chapter 3, an iteration method is proposed to obtain the elastic solution in a solid with strongly elastic inhomogeneity and an arbitrary spatial distribution of defects. The accuracy and efficiency of the iteration method are verified by comparing to existing analytical solutions.

In Chapter 4, phase-field models are developed to simulate spinodal decomposition in a bulk system with strongly elastic inhomogeneity and in a thin film with a periodic array of interfacial dislocations. The iteration method described in Chapter 3 is employed to obtain the elastic solution. Morphological dependence of an isolated precipitate and multi-precipitates on elastic inhomogeneity is simulated in two-dimensions. Directional spinodal decomposition induced by the stresses of periodically distributed interfacial dislocations is studied.

In Chapter 5, a phase-field model of dislocation dynamics in a fcc single crystal with diffusive solutes and immobile defects is developed. One composition field variable that describes the solute concentration, and 12 order parameter field variables describing the dislocation spatial distribution of 12 dislocation slip systems are employed. As an example of the potential application of the developed phase-field model in alloy strengthening, it is used to study the interaction between moving dislocations and diffusive solutes.

In Chapter 6, a phase-field model is described for studying the $\theta'$ precipitation in Al-Cu alloys. This model takes into account interface energy anisotropy, interface
mobility anisotropy and elastic energy. The relationships between phase-field model parameters and material constants are established by analyzing the static and dynamic solutions of the kinetic equations in one dimension, which is the basis for a quantitative simulation. A systematical testing in 1D, 2D and 3D of the model is made.

Chapter 7 summarizes the contributions of this thesis to phase-field theory and discusses future work directions.
Chapter 2

Phase-field Model

2.1 Phenomenological description of solid state phase transformations

In order to better understand the phase-field model of microstructure evolution during solid state phase transformations, let us briefly review the phenomenological description of solid state phase transformations (see [124,125] for details). In principle, any solid-state phase transformation can be characterized by physically well-defined order parameters that distinguish the parent and product phases. For example, the magnitude of a long-range order parameter in order-disorder transformation is proportional to the intensity of a superlattice reflection corresponding to the ordered superstructure, and the order parameter for a ferroelectric phase transition is the local polarization vector which is proportional to the relative displacement of opposite-charged ions. Since solid state phase transformations always involve structural changes, the transformation strain, which is a measure of the strain state of a crystal during a phase transformation with respect to the parent phase, could be seen as an order parameter. For phase transformations in a homogeneous system, the transformation strain is determined by the constraint conditions. In stress free phase transformations the transformation strain (also called eigenstrain or stress-free strain) is a secondary order parameter in a sense that there is another primary physical order parameter which characterizes the phase transformation. In other word, it is a function of the primary physical order parameters.
In a phenomenological description, the local free energy function is typically expressed as a polynomial of order parameters using a conventional Landau-type of expansion. All the terms in the expansion are required to be invariant with respect to the symmetry operations of the high-temperature phase. The dependence of a phase transformation on strain is primarily determined by the coupling between the primary order parameters and strains, which has been discussed in great detail in an excellent textbook by Salje [126].

To illustrate the role of elastic strain in phase transformations in a homogeneous system, let us consider a simple model system with two degenerate states for the product phase [127]. With a clamped boundary condition, the transformation strains $\varepsilon_{ij}$ are given constants. The Helmholtz free energy density, $f$, of the homogeneous system is a function of order parameter $\eta$ and total strains, and expressed as

\[ f = f(\eta, \varepsilon_{ij}) \quad (2.1) \]

If Helmholtz free energy density $f$ is expanded with respect to the order parameter to the fourth order and to the strain to the second order. Including only terms in strain to second order is equivalent to assuming linear elasticity. Assuming that the coupling between the strain ($\varepsilon_{ij}$) and the order parameter ($\eta$) is linear-quadratic, the thermodynamics of the system can be described by
\[ f = \frac{1}{2} \alpha_o (T - T_c) \eta^2 + \frac{1}{4} \beta \eta^4 - \gamma \eta^2 \delta_{ij} \epsilon_{ij} + \frac{1}{2} \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl} \]  

(2.2)

where \( \alpha_o, \beta, \) and \( \gamma \) are phenomenological coefficients which can be obtained by fitting experimentally measured or computed properties with a clamped boundary condition. \( \delta_{ij} \) is the Kronecker-delta functions. \( \lambda_{ijkl} \) is the elastic modulus tensor.

The critical temperature, i.e., the temperature below which the high temperature phase becomes unstable, is obtained from

\[ \left( \frac{\partial^2 f}{\partial \eta^2} \right)_{\eta=0} = \alpha_o (T - T_c) - 2 \gamma \delta_{ij} \epsilon_{ij} = 0 \]  

(2.3)

where, \( T_c \) is the critical temperature at clamped boundary condition \( \delta_{ij} \epsilon_{ij} = 0 \). The equilibrium value for the order parameter at \( \delta_{ij} \epsilon_{ij} = 0 \) can be obtained from

\[ \frac{\partial f}{\partial \eta} = 0 \]  

(2.4)

It is given as a function of temperature by
Minimizing the Helmholtz free energy with respect to strain $\varepsilon_{ij}$

$$\frac{\partial f}{\partial \varepsilon_{ij}} = 0$$

(2.6)

we have

$$\varepsilon_{ij} = s_{ijkl} \delta_{kl} \eta^2$$

(2.7)

where $s_{ijkl}$ is the inverse elastic compliance tensor. With a linear elastic approximation, the stress and elastic strain, $\varepsilon^e_{ij}$, satisfy the following relationship

$$\sigma_{ij} = \frac{\partial f}{\partial \varepsilon_{ij}^e}$$

(2.8)

The elastic strain is equal to the difference between total strain (transformation strain in this case) and eigenstrain,

$$\varepsilon^e_{ij} = \varepsilon_{ij} - \varepsilon^0_{ij}$$

(2.9)
Equations (2.6-2.9) illustrate that Helmholtz free energy reaches the minimum when the transformation strain $\epsilon_{ij}$ is exactly equal to the stress free strain $\epsilon_{ij}^0$. This means that the phase transformation occurs under stress free boundary conditions. Therefore, the stress-free strain reads

$$\epsilon_{ij}^0 = \epsilon_{ij} = s_{ijkl} \delta_{kl} \gamma \eta^2$$

(2.10)

where $s_{ijkl}$ is the compliance tensor.

Substituting the strain, $\epsilon_{ij}$, into expression (2.2), the free energy as a function of order parameter at stress free can be expressed as

$$f = \frac{1}{2} \alpha_0 (T - T_c) \eta^2 + \frac{1}{4} \beta' \eta^4$$

(2.11)

where $\beta' = \beta - 2 \gamma^2 \delta_{ij} s_{ijkl} \delta_{kl}$. In equation (2.11), $\alpha_0$ and $\beta'$ should be measured at stress-free boundary conditions. $T_c$ should be measured at the clamped boundary condition ($\epsilon_{ij} = 0$).

With equation (2.11), the free energy at the clamped boundary condition, i.e., a given strain state, can be rewritten as
\[ f = \frac{1}{2} \alpha_o \left( T - T_c \right) \eta^2 + \frac{1}{4} \beta' \eta^4 + \frac{1}{2} \lambda_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^o) (\varepsilon_{kl} - \varepsilon_{kl}^o) \] (2.12)

Equation (2.2) and (2.12) are equivalent. From equations (2.3 and 2.12), it can be found that the clamped boundary condition affects the transformation temperature

\[ T = T_c + 2 \delta_{ij} \varepsilon_{ij} / \alpha_o \] (2.13)

One can also formulate the local free energy as a function of order parameter at a given stress state since

\[ f = \frac{1}{2} \alpha_o \left( T - T_c \right) \eta^2 + \frac{1}{4} \beta' \eta^4 + \frac{1}{2} \lambda_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^o) (\varepsilon_{kl} - \varepsilon_{kl}^o) - \sigma_{ij} \varepsilon_{ij} \] (2.14)

where \( \sigma_{ij} \) is the stress. Eliminating \( \varepsilon_{ij} \) from the equation (2.14), we have the free energy at a given stress state \( \sigma_{ij} \),

\[ f = \frac{1}{2} \alpha_o \left( T - T_c \right) \eta^2 + \frac{1}{4} \beta' \eta^4 - \frac{1}{2} \lambda_{ijkl} \sigma_{ij} \sigma_{kl} - \sigma_{ij} \varepsilon_{ij}^o \]

\[ = \frac{1}{2} \alpha_o \left( T - T_c \right) \eta^2 + \frac{1}{4} \beta' \eta^4 - \frac{1}{2} \lambda_{ijkl} \sigma_{ij} \sigma_{kl} - \sigma_{ij} s_{ijkl} \delta_{kl} \eta^2 \] (2.15)
It is evident that an applied stress will affect the critical temperature because \( \varepsilon^0_\eta \) is a quadratic function of \( \eta \). Therefore, the transformation temperature depends on both the clamped boundary conditions and applied stresses.

The shift from a chemical spinodal to a coherent spinodal is another example on the effect of elastic strain on phase transformations [3,31,128]. In a solid solution, the lattice parameter is a function of composition. For a cubic crystal, the stress-free strain can be written in terms of composition \( c \) as,

\[
\varepsilon^0_\eta = \varepsilon_0 \delta_\eta (c - c_0)
\] (2.16)

where \( c_0 \) is the composition of the reference state, \( \varepsilon_0 = \frac{1}{a_0} \frac{da}{dc} \), \( a \) and \( a_0 \) are lattice constant corresponding to composition \( c \) and \( c_0 \), respectively. Under clamped boundary conditions, elastic energy density due to the change in composition from the \( c_0 \) can be calculated by [3]

\[
E = 2\mu \frac{1 + \nu}{1 - \nu} \varepsilon^2_0 (c - c_0)^2
\] (2.17)

where \( \mu \) is the shear modulus, \( \nu \) the Poisson’s ratio. The total free energy density includes chemical free energy of the solute solution \( f_0(c) \) and the elastic energy
\[ f(c, T) = f_0(c, T) + 2\mu \frac{1+\nu}{1-\nu} \varepsilon_0^2 (c-c_0)^2 \] (2.18)

The phase boundary between stable (including metastable) and unstable states is determined by the condition,

\[ \frac{\partial^2 f(c, T)}{\partial c^2} = \frac{\partial^2 f_0(c, T)}{\partial c^2} + 4\mu \frac{1+\nu}{1-\nu} \varepsilon_0^2 = 0 \] (2.19)

The spinodal given by (2.19) is called the coherent spinodal. While the spinodal (without any strain effect) which is given by

\[ \frac{\partial^2 f_0(c, T)}{\partial c^2} = 0 \] (2.20)

is sometimes called the chemical spinodal [3]. It can be seen that the coherent spinodal differs from the chemical spinodal. When the system is inside the spinodal region,

\[ \frac{\partial^2 f_0(c, T)}{\partial c^2} < 0 \quad \text{and} \quad 4\mu \frac{1+\nu}{1-\nu} \varepsilon_0^2 > 0 \] (2.21)
The former promotes phase decomposition while the latter depresses it. Therefore, spinodal decomposition accompanied by elastic strain does not always take place throughout the chemical spinodal region. The chemical spinodal is shifted to a lower temperature due to elastic energy.

In actual metallic materials, the effect of elastic energy on phase transformation could be more complicated. The reason is that actual metallic materials are, in general, anisotropic and inhomogeneous arising from crystal structural anisotropy and inhomogeneity, composition inhomogeneity and the presence of structural defects. It is commonly accepted that the elastic energy might affect transformation temperature, critical nucleus size, precipitate morphology, precipitate arrangement, equilibrium composition, and kinetics of phase transformations. One of the main objectives of the present thesis is to study the effect of elastic energy on phase separation in bulk and thin solid films.

2.2 Phase-field model of solid state phase transformations

Microstructures are compositional and structural inhomogeneities that arise from processing of materials [129]. To model microstructure evolution during solid state phase transformations, one can simply extend the above phenomenological description of solid state phase transformations in homogeneous systems to inhomogeneous systems. In a heterogeneous microstructure, both the order parameters (and/or composition) and the strain (or stress) are space-dependent. A phase-field model describes a microstructure by
using a set of field variables that might be composition, order parameter, polarization vector and orientation. There are two types of field variables, conserved and non-conserved. Conserved variables have to satisfy the local conservation condition like composition. The field variables are continuous across the interfacial regions. In a phase-field model, the total free energy of an inhomogeneous microstructure system described by a set of conserved field variables \((c_1, c_2, \cdots, c_N)\) or/and non-conserved \((\eta_1, \eta_2, \cdots, \eta_p)\) field variables is given by

\[
E = \int \left[ f(c_1, c_2, \cdots, c_N, \eta_1, \eta_2, \cdots, \eta_p) + \sum_{n=1}^{N} \alpha_n (\nabla c_n)^2 + \sum_{\rho=1}^{P} \beta_{\rho} \frac{\partial \eta_{\rho}}{\partial x_i} \frac{\partial \eta_{\rho}}{\partial x_j} \right] d^3x
\]

\[
+ \int G(x-x')d^3xd^3x',
\]

where \(f\) is the local free energy density which defines the fundamental thermodynamics of the system. The gradient energy terms in the first volume integral, which are local contributions to the free energy, describe the interaction between long-wave fluctuations in adjacent finite volumes and are responsible for the field continuity. The gradient energy coefficients \(\alpha_n\) and \(\beta_{\rho}\) are related to interfacial energy and interface thickness. Therefore, the first volume integral represents the contribution from local and short-range chemical interactions. The second integral represents the contributions from long-range interactions, such as elastic interactions, electric dipole-dipole interactions and electrostatic interactions. The temporal and spatial evolution of the field variables is
governed by the reduction of the total free energy, and described by the Cahn-Hilliard nonlinear diffusion equation [130] for conserved field variables

\[ \frac{\partial c_i(x,t)}{\partial t} = \nabla M_{ij} \frac{\partial E}{\partial c_j(x,t)} + \xi_i(x,t) \]  

(2.23)

and the Ginzburg-Landau equation [32] for non-conserved field variables

\[ \frac{\partial \eta_p(x,t)}{\partial t} = -L_{pq} \frac{\partial E}{\partial \eta_q(x,t)} + \zeta_p(x,t) \]  

(2.24)

where \( M_{ij} \) and \( L_{pq} \) are related to atom or interface mobility, and \( \xi_i \) and \( \zeta_p \) are the noise terms. The origin of the noise terms comes from the microscopic degrees of freedom, i.e., from the thermal vibrations (phonons) and/or high-order correlations with short relaxation time. The noise terms, which aid in the nucleation of precipitates [131,132], are random numbers with Gaussian distributions, and their correlations satisfy requirements of the fluctuation-dissipation theorem [133].

For a given system under consideration, once the total free energy is formulated, modeling the microstructure evolution in the framework of phase-field theory is essentially reduced to find the solutions of Cahn-Hilliard and/or Ginzburg-Landau equations under initial and boundary conditions. In principle, the local free energy function can be obtained from thermodynamic calculations and data from atomic scale
simulations such as first principle calculations and molecular dynamic simulations, and experiments. All phenomenological model parameters ($\alpha_n$, $\beta_i$, $M_{ij}$ and $L_{pq}$) can be calculated with the relationships between model parameters and material properties, which can be derived by theoretical analysis of equilibrium solutions and dynamic solutions (see section 6.2 for details). Most existing phase-field models employ model free energy functions; see recent review papers [8] for details of free energy constructions and the calculations of long-range interaction energies in most important applications of phase-field models.
Chapter 3

Elastic Solution in a Solid with Strongly Elastic Inhomogeneity and Arbitrary Spatial Distribution of Defects

Microstructure evolution takes place to reduce the total free energy that may include the bulk chemical free energy, interface energy, elastic energy, and/or under applied external fields such as applied stresses [129]. In a coherent microstructure, the elastic energy arises from lattice mismatches is often comparable to the change in the interface energy or chemical free energy. Therefore, an efficient and accurate method to calculate the elastic energy is desirable for predicting microstructure evolutions. A number of calculation methods of elastic energy in a solid with an evolving microstructure were developed, which have been reviewed in the introduction. In this chapter, an accurate and efficient iteration method is proposed to calculate the elastic energy in a solid with strongly elastic inhomogeneity and arbitrary spatial distribution of defects during solid state phase transformations. It is quite convenient to incorporate this method into phase-field models. Furthermore, the elastic energy in a film subject to substrate constraint can also be obtained with the iteration method if a gas phase, where the elastic constant is zero, is introduced [134-136]. Thus, the application of phase-field models can be extended to an entirely new research field: the effect of elastic energy on microstructure evolutions in thin films.
3.1 Mechanical equilibrium equations

To present the method of solving the elastic problem in a solid with elastic inhomogeneity and arbitrary spatial distribution of defects, we take a binary solid solution with a compositional inhomogeneity $c(x)$ as an example, where $c(x)$ is the mole or atom fraction at position $x$. The local elastic modulus tensor is assumed to be a linear function of the compositional inhomogeneity through [137]

$$\lambda_{ijkl}(x) = \lambda_{ijkl}^m \frac{c_p^e - c(x)}{c_{eq}^p - c_{eq}^m} + \lambda_{ijkl}^p \frac{c(x) - c_{eq}^m}{c_{eq}^p - c_{eq}^m}$$  \hspace{1cm} (3.1)

where $\lambda_{ijkl}^m$ and $\lambda_{ijkl}^p$ are the elastic modulus tensors for the matrix with equilibrium composition $c_{ep}^m$ and for the precipitate with equilibrium composition $c_{ep}^p$, respectively. It is easy to show that the local elastic modulus tensor (3.1) can be rewritten as

$$\lambda_{ijkl}(x) = \lambda_{ijkl}^0 + \lambda_{ijkl}^i \delta c(x)$$  \hspace{1cm} (3.2)

where $\delta c(x) = c(x) - c_0$, $\lambda_{ijkl}^0$ is a constant representing the elastic modulus tensor for a homogeneous solid solution with composition $c_0$, and $\lambda_{ijkl}^i$ is given by $\frac{\lambda_{ijkl}^p - \lambda_{ijkl}^m}{c_{eq}^p - c_{eq}^m}$. We assume that the local stress-free strain tensor can be described in terms of the compositional inhomogeneity $\varepsilon_{ik}^e(x, c(x))$. If the variation of stress-free lattice
parameter, $a$, with composition obeys the Vegard’s law, the local stress-free strain associated with the compositional inhomogeneity is given by,

$$
\epsilon^c_{ij}(x,c(x)) = \epsilon_0 \delta c(x) \delta_{ij}
$$

(3.3)

where $\epsilon_0 = \frac{1}{a} \frac{da}{dc}$ is the composition expansion coefficient of the lattice parameter and $\delta_{ij}$ is the Kronecker–Delta function

Most structural defects such as dislocations, grain boundaries, cracks and slip bands can be introduced into a phase-field model using their corresponding spatially dependent stress free strain [2,87,88,138-142]. For the case of dislocations, the stress field of a dislocation loop on slip plane $p$ with a Burgers vector $\mathbf{b}$, is described by the stress free strain,

$$
\epsilon^{\text{dis}}_{ij}(x) = \frac{1}{2d_0} (b(i)n(j) + b(j)n(i)) \delta(x - x_0)
$$

(3.4)

where $\mathbf{n}$ is the unit vector normal to the slip plane, $d_0$ is the interplanar spacing of the slip planes, $\delta(x - x_0)$ is the Dirac delta function and $x_0$ is a point inside the dislocation loop on the slip plane. For a spatial distribution of many dislocation loops, the total stress free strain can be obtained by adding the stress free strain of individual dislocation loops.
We use $\varepsilon^{\text{dis}}_{ij}(x)$ to denote the total stress free strain due to the spatial distribution of dislocations or other defects. Therefore, the total stress free strain associated with the composition inhomogeneity and defects can be written as

$$\varepsilon^0_{ij}(x) = \varepsilon^{c}_{ij}(x) + \varepsilon^{\text{dis}}_{ij}(x)$$ (3.5)

Let’s use $\varepsilon^c_{ij}(x)$ to denote the total strain measured with respect to a reference lattice and assume linear elasticity, the Hooke’s law gives the local elastic stress,

$$\sigma^{\text{el}}_{ij} = [\lambda^0_{ijkl} + \lambda^c_{ijkl} \delta(x)] [\varepsilon_{kl}(x) - \varepsilon^0_{kl}(x)]$$ (3.6)

During the evolution of composition and defects, since the mechanical equilibrium with respect to elastic displacements is usually established much faster than any material processes, for any given distribution of composition, the system is always at mechanical equilibrium,

$$\frac{\partial \sigma^{\text{el}}_{ij}}{\partial x_j} = 0$$ (3.7)

where $x_j$ is the $j$th component of the position vector, $x$. Following Khachaturyan [143,144], the total strain $\varepsilon^c_{ij}(x)$ may be represented as the sum of homogeneous and heterogeneous strains:
where the homogeneous strain, $\bar{\varepsilon}_{ij}$, is defined so that

$$\int \delta \varepsilon_{ij}(x) d^3x = 0$$  \hspace{1cm} (3.9)$$

The homogeneous strain is the uniform macroscopic strain characterizing the macroscopic shape and volume change associated with the total strain, $\varepsilon_{ij}(x)$. Let us use $u_i(x)$ to denote the $i$th component of displacement of heterogeneous deformation. According to the relationship of strain and displacement, the heterogeneous strain can be expressed as,

$$\delta \varepsilon_{kl}(x) = \frac{1}{2} \left[ \frac{\partial u_k(x)}{\partial x_l} + \frac{\partial u_l(x)}{\partial x_k} \right]$$  \hspace{1cm} (3.10)$$

Substituting equations (3.4-6) and (3.10) to the mechanical equilibrium equation (3.7), one has

$$\varepsilon_{ij}(x) = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij}(x)$$  \hspace{1cm} (3.8)$$
The determination of the equilibrium elastic field for an elastically inhomogeneous solid with spatial arbitrary distribution of defects is reduced to solving the mechanical equilibrium equation (3.11) subject to appropriate boundary conditions.

### 3.2 Elastic solution in bulk systems with periodic boundary conditions

With periodic boundary conditions, Fourier transforms method can be employed to solving the mechanical equilibrium equation (3.11).

#### 3.2.1 Zeroth-order approximation

Because of the non-linearity of the mechanical equilibrium equation (3.11), in general, it cannot be solved analytically. However, if one ignores the elastic modulus inhomogeneity, \( \lambda_{ijkl} = 0 \), the mechanical equilibrium equation becomes linear and is given by

\[
\left[ \lambda'_{ijkl} \frac{\partial^2}{\partial x_j \partial x_l} + \lambda'_{ijkl} \frac{\partial}{\partial x_j} \left( \delta(x) \frac{\partial}{\partial x_l} \right) \right] u_k(x) = \frac{\partial}{\partial x_j} \left[ \lambda'_{ijkl} \delta(x) \left[ \epsilon_{kl}^0(x) - \bar{\epsilon}_{kl} \right] \right]
\]

(3.11)

The determination of the equilibrium elastic field for an elastically inhomogeneous solid with spatial arbitrary distribution of defects is reduced to solving the mechanical equilibrium equation (3.11) subject to appropriate boundary conditions.
where \( u_k^0(x) \) denotes the \( k \)th component of the displacement in the zeroth order approximation and Equation (3.12) can be readily solved in the Fourier space [144],

\[
v_k^0(g) = -i G_{ik}(g) g_j \lambda^0_{ijmn} \pi^0_{mn}(g)
\]

(3.13)

where \( v_k^0(g) \) and \( \pi^0_{mn}(g) \) are Fourier transforms of \( u_k^0(x) \) and \( \varepsilon^0_{mn}(x) \), respectively, \( g \) is a reciprocal lattice vector, \( g_j \) is the \( j \)th component of \( g \), and \( G_{ik}(g) \) is the inverse tensor to \( \lambda^0_{ijkl} n_j n_l \) with \( n = \frac{g}{|g|} \). The back Fourier transform of \( v_k^0(g) \) gives the real-space solution for the displacement field in the zeroth order approximation,

\[
u_k^0(x) = \frac{1}{(2\pi)^3} \int v_k^0(g) e^{ix \cdot g} d^3g
\]

(3.14)

3.2.2 First-order approximation

With the zeroth-order solution, one can analytically obtain the solution or the displacement field with a first-order approximation. To do this, we replace the displacement in the nonlinear term in equation (3.11) using the zeroth order solution and move it to the right-hand side,
\[ \lambda_{ijkl} \frac{\partial^2 u_k^1(x)}{\partial x_j \partial x_l} = \frac{\partial}{\partial x_j} [\lambda_{ijkl} + \lambda'_{ijkl} \delta_t(x)][\varepsilon_{kl}^0(x) - \bar{\varepsilon}_{kl}] - \lambda'_{ijkl} \frac{\partial}{\partial x_j} \left[ \delta_t(x) \frac{\partial u_k^0(x)}{\partial x_j} \right] \] (3.15)

where \( u_k^1(x) \) represents the \( k \)th component of displacement in the first-order approximation. Equation (3.15) has essentially the same structure as equation (3.12) except for a slightly more complicated right-hand side in equation (3.15). Therefore, the solution \( u_k^1(x) \) can also be analytically obtained using Fourier transforms, i.e.

\[ v_k^1(g) = -i G_{jk}(g) g_j \left[ [\lambda_{jmn} + \lambda'_{jmn} \delta_t(x)][\varepsilon_{mn}^0(x) - \bar{\varepsilon}_{mn}] - \lambda'_{jmn} \delta_t(x) \frac{\partial u_m^0(x)}{\partial x_n} \right] \] (3.16)

A significant difference between equation (3.12) and equation (3.15) is the fact that the homogeneous strain, \( \varepsilon_{kl} \), enters equation (3.15). As a result, with a first-order approximation, an applied strain or stress will affect the heterogeneous elastic displacements.

### 3.2.3 High-order approximations

Higher order solutions for \( u_k^\nu(x) \) can be obtained using an iteration process. For example, the \( n \)th order solution for displacement, \( u_k^\nu(x) \), can be obtained from the following equation,
\[
\lambda_{ijkl}^0 \frac{\partial^2 u^{n-1}_k(x)}{\partial x_j \partial x_l} = \frac{\partial}{\partial x_j} \left[ \lambda_{ijkl}^0 + \lambda_{ijkl}^1 \delta \varepsilon(x) \right] \left[ \varepsilon^{n-1}_{kl}(x) - \bar{\varepsilon}_{kl} \right] - \lambda_{ijkl}^1 \frac{\partial}{\partial x_j} \left[ \delta \varepsilon(x) \frac{\partial u^{n-1}_k(x)}{\partial x_l} \right]
\]

where \( u^{n-1}_k(x) \) is the solution from a lower-order approximation. Again the elastic displacement in the \( n \)th order approximation can be obtained from equation (3.17) using Fourier transforms.

### 3.2.4 Elastic energy

The elastic strain energy density for a given compositional distribution in an elastically inhomogeneous is given by

\[
\varepsilon_{el} = \frac{1}{2} \lambda_{ijkl}^{\epsilon} \varepsilon_{ijkl}^{\epsilon} = \frac{1}{2} \left[ \lambda_{ijkl}^0 + \lambda_{ijkl}^1 \delta \varepsilon(x) \right] \left[ \varepsilon_{ijkl} - \bar{\varepsilon}_{ijkl} \right] \left[ \varepsilon_{ijkl}^{\epsilon} - \bar{\varepsilon}_{ijkl}^{\epsilon} \right]
\]

The total strain energy is given by

\[
E_{el} = \int_v \varepsilon_{el} d^3 x
\]

In equation (3.18), \( \delta \varepsilon_{kl}(x) \) is given by

\[
\delta \varepsilon_{ij}(x) = \frac{1}{(2\pi)^3} \int \frac{i}{2} \left[ v_i(g) g_j + v_j(g) g_i \right] e^{igx} d^3 g
\]
where \( v_i(\mathbf{g}) \) is the \( i \)th component of the displacement. The corresponding elastic stress is given by equation (3.6). The homogeneous strain in equation (3.15) and equation (3.8) is determined by the boundary constraint. If the boundary is clamped so that the system is not allowed to have any homogeneous deformation, the homogeneous strain, \( \varepsilon_{ij} \), is equal to zero. Similarly, if the system is subject to an initial applied strain, \( \varepsilon_{ij}^{\text{a}} \), then the boundary is held fixed, \( \varepsilon_{ij} = \varepsilon_{ij}^{\text{a}} \). On the other hand, if the system is stress-free, i.e., the system is allowed to deform so that the average stress in the system is zero, the homogeneous strain is obtained by minimizing the total elastic energy with respect to the homogeneous strain [145].

### 3.2.5 Verification of the iteration method in bulk systems

Here, the convergence and accuracy of iteration method are examined systematically. In principle, the efficiency and accuracy of the proposed iteration method for a given order of approximation can be tested with analytical solutions which are available for certain special precipitate shapes [2]. However, the analytical solutions are available only for systems with a sharp-interface description whereas the interfaces in our numerical calculation are diffuse. Therefore, to examine accuracy, we compare the results from the proposed method with those obtained from an independent calculation using a conjugate gradient method (CGM) with the same diffuse-interface description [75]. In CGM, the elastic equation is numerically solved until the results converge.
For the sake of simplicity, we consider a two dimensional model binary alloy with its chemical thermodynamics described by the following local incoherent free energy density,

\[ f(c) = -(c - 0.5)^2 + 2.5(c - 0.5)^4, \]  

(3.21)

where \( c \) is the composition. The equilibrium compositions determined from equation (3.21) are 0.053 and 0.947, respectively. We introduce a circular precipitate with composition 0.947 and a radius of \( R = 10\Delta x \) in a square domain of matrix \((256\Delta x \times 256\Delta x)\) with composition 0.053. \( \Delta x \) is the dimensionless grid spacing. Periodic boundary conditions are applied along both Cartesian axes. The initially sharp composition profile describing the precipitate is allowed to relax for a certain number of time steps by solving the Cahn–Hilliard diffusion equation (4.5) with a gradient energy coefficient \( \kappa_0 = 1.5 \), but without including the stress effect. The resulting two-dimensional diffuse compositional profile is then used to calculate the stress distributions using the proposed iteration method with different orders of approximation and the CGM [75]. For comparing the results, the number of time steps to relax the profile is not particularly important since we use the same profile for the two independent calculations. Both calculations employed the spectral method for the spatial discretization of the elasticity equation. The composition expansion coefficient, \( \varepsilon_0 \), is chosen to be 0.05. The elastic constants used are \( C_{11}^0 = 300, C_{12}^0 = 100, C_{44}^0 = 100 \) for the matrix; \( C_{11}' = 150 \),
$C'_{12} = 50, \ C'_{44} = 50$ for hard precipitates and $C'_{11} = -150, \ C'_{12} = -50, \ C'_{44} = -50$ for soft precipitates, all in units of $N_i k_B T$. $C'_{ij}$ and $C'_{ij}$ is the elastic stiffness in Voigt's notation.

This set of elastic constants produce more than 50% difference in the elastic constants between the precipitate and matrix, which is artificially large compared to the typical elastic inhomogeneity in most of the practical two phase alloys.

Examples of equilibrium stress distributions, $\sigma_{xx} = \sigma_{11}$ and $\sigma_{yy} = \sigma_{22}$, as a function of position along a line cut through the center of the precipitate in the $x_1$ direction are shown in Fig. 3.1 for a hard precipitate, and Fig. 3.2 for a soft precipitate. The shear component, $\sigma_{xy} = \sigma_{12}$, is zero along the line, so it is not shown. In both Fig. 3.1 and 3.2, the squares and circles represent the results from the proposed perturbation method and the crosses and pluses represent those from the CGM. It can be seen that for both hard and soft precipitates, the results from two calculations agree very well for both stress components. Both calculations converge to essentially the same results although the two calculations were performed using two entirely independent computer codes. It is shown that although the stresses in the matrix are similar for both the hard and soft precipitates, the absolute magnitude within the hard precipitate is significantly higher than that within the soft precipitate. It is easily understandable since we used exactly the same two-dimensional compositional profile for the hard and soft precipitates and the larger elastic constants for the hard precipitates would produce larger stresses. To examine the convergence of the elastic solution as a function of iteration number, or the order of approximation, the stress components, $\sigma_{xx}$ and $\sigma_{yy}$, as a function of position for
a given composition profile are plotted for different iteration numbers in Fig. 3.3–3.6 for both hard and soft precipitates. We used the same materials parameters as in Fig. 3.1 and 3.2. In calculating the stress distributions, the elastic displacements and thus the elastic strains were obtained using various orders of approximations, with the stress calculated using equation (3.6). For example, in the legends of the figures, the number “0” represents the case that the elastic solution was obtained by using the zeroth-order approximation (3.13), but the elastic constants used in calculating the stress distributions in equation (3.6) are not homogeneous. Therefore, even with the zeroth order of approximation, some degree of elastic inhomogeneity has been taken into account in the elastic energy calculation. As a matter of fact, the level of approximation used in Koyama’s simulation for elastically inhomogeneous systems [146] corresponds to our zeroth order approximation. As one can see from Fig. 3.3–3.6, even with such a large elastic inhomogeneity, 50%, considered in the calculations, the elastic stress essentially converges after three to four iterations, indicating a third or fourth order approximation will be sufficient for the elastic energy calculations with a similar degree of elastic inhomogeneity assumed in this calculation. The zeroth order approximation overestimates the stress within the hard precipitate and underestimates the stress within the soft precipitate by about 25–30%. The error is reduced to 10% with a first order approximation. Table 3.1 shows the required iteration numbers or order of approximation to get converged elastic solution for a given ratio of elastic constants between precipitate and matrix. As expected, the number of iterations increases with the degree of elastic inhomogeneity. For a 10% elastic inhomogeneity, it is sufficient to use the first order approximation.
approximation. Even with inhomogeneities as large as 100%, it requires only about five iterations.
Table 3.1 Convergence of the iteration method

\[
\frac{C_{\bar{y}}^p}{C_{\bar{y}}^M} = 0.19 \quad 0.37 \quad 0.55 \quad 0.73 \quad 0.91 \quad 1.00 \quad 1.09 \quad 1.27 \quad 1.45 \quad 1.63 \quad 1.99
\]

<table>
<thead>
<tr>
<th>Iterations</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
</table>

Fig. 3.1  Stress distributions along the $x$-direction across the center of a hard precipitate. The open squares and circles represent the $\sigma_{xx}$ and $\sigma_{yy}$ components obtained from the proposed iteration method. The crosses and pluses represent the corresponding results from a conjugate gradient method (CGM).
Fig. 3.2  The $\sigma_{xx}$ component of the elastic stress along the $x$ direction across the center of the hard precipitate as a function of iteration numbers (or the order of approximations) from the perturbation iterative method.
Fig. 3.3 Stress distributions along the $x$-direction across the center of a soft precipitate.

The open squares and circles represent the $\sigma_{xx}$ and $\sigma_{yy}$ components obtained by the proposed iteration method. The crosses and pluses represent the corresponding results from a conjugate gradient method (CGM).
Fig. 3.4 The $\sigma_{yy}$ component of the stress along the $x$-direction across the center of the hard precipitate as a function of iteration numbers (or the order of approximations) from the iterative method.
Fig. 3.5  The $\sigma_{xx}$ component of the stress along the $x$-direction across the center of the soft precipitate as a function of iteration numbers (or the order of approximations) from the iterative method.
Fig. 3.6  The $\sigma_{yy}$ component of the stress along the $x$-direction across the center of the soft precipitate as a function of iteration numbers (or the order of approximations) from the iterative method.
3.3 Elastic solution in films with stress free surfaces and substrate constrain

Unlike periodic boundary conditions in bulk systems, the boundary conditions of stress free at surfaces increase the difficulty for solving the elastic equations in films. Very few analytical or efficient numerical methods are available. For example, in a monolayer subject to substrate constrain, Lu and Suo [147] derived the elastic solution by using the Green function method where the stresses in the thin film are assumed to be independent of the thickness. For a thick film with a spatial distribution of eigenstrains, Li and Hu et al. [65] developed an efficient method to calculate the elastic field with an assumption of elastic homogeneity. Although this method can be extended to the case that film and substrate have different elastic constant, it cannot handle the elastic problem with the elastic inhomogeneity associated with composition and structural inhomogeneity in films. Generally speaking, finite element method always can be employed to solve the elastic solution for any given microstructure and boundary conditions. However, The finite element method is not an efficient method for evolving microstructures. In fact, the iteration method described above can be extended to obtain the elastic solution in a film with elastically inhomogeneity and a defect distribution. In order to explain the application of the iteration method in film system, let us artificially add a gas phase above the film as shown in Fig. 3.7. Apply periodic boundary conditions to the film system in x-, y- and z- directions, then, we construct a three-dimensional bulk system. The iteration method can directly be employed to find the elastic solution in the film if we assign zero elastic constants in the gas phase. The eigenstrain and elastic modulus tensors are defined as
where $\varepsilon_{ij}^\text{dis}(x)$ is the eigenstrain associated with the distribution of real dislocations in the solid and image dislocations in the gas phase, $\varepsilon_{ij}^c(x)$ is the eigenstrain associated the composition inhomogeneity, $\varepsilon_{ij}^0(x)$ in the total eigenstrain. $\lambda_{ijkl}^0(x)$ is the elastic constant of one of the phases in the system, $\lambda_{ijkl}^\prime(x)$ is the change in elastic constants with respect to $\lambda_{ijkl}^0(x)$. Notice that the elastic constant is zero in the gas phase, so all stress components are zero in the gas phase. From the continuity of stresses at the interface between gas phase and solid phase, the elastic solution obtained satisfies the stress-free boundary conditions at the surface of the film ($x_3 = z = h_f$), and the bottom of the substrate ($x_3 = z = h_s$). In this thesis, we assume the film and substrate are elastic homogeneous, i.e., $\lambda_{ijkl}^\prime(x) = 0$, and the surface is flat. The iteration method has been employed to simulate the formation of quantum dots where the surface is rough [4].
Fig. 3.7 Schematic drawing of an elastically inhomogeneous system.
3.3.1 Verification of the iteration method in film system

To verify the iteration method in the film system, we consider a single edge dislocation below the surface as shown in Fig. 3.8, which has analytical solutions [138]. The simulation cell is $512 \times 1 \times 256$, where $h = 40$ and $l = 1$. The dislocation below the surface and its image dislocation in the gas phase form a dislocation loop. The nonzero eigenstrain associated with such a dislocation loop is

$$\epsilon_{11}^{\text{dis}}(x) = b / d_0 \delta(x - x_0)$$

(3.24)

where $b$ is the magnitude of the Burgers vector of the dislocation, $d_0$ is the grid spacing. $x_0$ is the point within the dislocation loop on the slip plane. Distributions of stress components $\sigma_{11}(z)$ and $\sigma_{22}(z)$ along A-A line shown in Fig. 3.8 are plotted in Fig. 3.9 and Fig. 3.10 for different iteration numbers. The analytical solutions are also included for a comparison. It is found that the numerical solution with 8 iterations agrees very well with the analytical solution. In the numerical simulation of spinodal decomposition, the elastic solution at time $t$ is used as the zeroth order solution for $t + \Delta t$, and hence, 3 iterations is sufficient for obtaining the elastic solution.
Fig. 3.8  The image dislocation in the gas phase and the real dislocation below the surface forms a dislocation loop.
Fig. 3.9 $\sigma_{xx}(z)/G$ along $A-A$ line shown in Fig. 3.8.
Fig. 3.10 $\sigma_z(z)/G$ along $A - A$ line shown in Fig.3.8.
3.4 Conclusion

For an elastically inhomogeneous bulk or film system with spatial arbitrary defects, an iteration method is proposed to calculate the elastic energy. The accuracy and the efficiency of the iteration method are numerically verified by comparing the analytical solution of testing problems. The numerical results demonstrate that once the $\lambda_{ijkl}^0$ are set to be the elastic constant of the hardest phase in the elastically inhomogeneous system the iteration method is always convergence, and 5~8 iterations even for strongly elastic inhomogeneity can give a good elastic solution. For the application of the iteration method for solving the elastic solution in evolving microstructures, 2~3 iterations are sufficient to obtain the elastic solution for a updated microstructures. Therefore, the iteration method is a very efficient approach for the simulation of microstructure evolutions. The defects are introduced by using the concept of “eigenstrains” in micromechanics which allow that the elastic fields from structural defects and coherent compositional/structural inhomogeneity are obtained within exactly the same formulation in the framework of Khachaturyan’s microelasticity theory.
Chapter 4

Spinodal Decomposition in Bulk and Film Systems

In spinodal decomposition, phase separation occurs by the spontaneous amplification of compositional fluctuations when a homogeneous solute solution is quenched to the unstable part of a miscibility gap. Because the two phases form by a continuous process they start out coherent with one another [147]. If the elastic constant is a function of composition, one phase becomes gradually harder and harder while the other phase becomes softer and softer during the spinodal decomposition. It is evident that the coherency stress field depends on the degree of such an elastic inhomogeneity. Therefore, the elastic inhomogeneity will affect the kinetics of spinodal decomposition and resulting patterns of separated phases. Furthermore, structural defects such as dislocations exist inevitably in crystalline solids. For example, in a film deposited on different substrates, a coherent interface becomes semi-coherent or incoherent by the generation of interfacial dislocations as the lattice mismatch between the film and the substrate increases. As a result, the uniform constraint stress field corresponding to the coherent interface becomes a localized constraint stress field corresponding the incoherent interface. If the film is unstable with respect to spinodal decomposition, different patterns of separated phases may form due to the density and distribution of interfacial dislocations.
Since Cahn first introduced the elastic energy term in the expression of the total free energy of the system [148], there have been numerous studies on the thermodynamics of coherent systems including the interaction of composition and stress in crystalline solids [1, 149-153]. The effect of dislocations on the morphological evolution during spinodal decomposition was investigated by Le´onard and Desai [154] who directly introduced the analytical elastic solution of a dislocation into the Cahn–Hilliard equation. Formulations for spinodal decomposition have recently been developed especially for confined geometry such as thin films or plates in accordance with recent interests in thin film applications of materials [155-157].

In this chapter, phase-field models are developed to simulate the spinodal decomposition in a bulk system with strongly elastic inhomogeneity and in a thin film with a periodic array of interfacial dislocations. The iteration method described in Chapter 3 is employed to obtain the elastic solutions. Morphological dependence of an isolated precipitate and multi-precipitates on elastic inhomogeneity is simulated in two-dimensions. Directional spinodal decomposition induced by the stresses of periodic distributed interfacial dislocations is studied.

4.1 Phase-field model of spinodal decomposition

We consider a binary solid solution which is unstable to spinodal decomposition. One phase-field variable, \( c(x,t) \), representing the mole or atom fraction at position \( x \) and time \( t \), is needed to describe the composition evolution or morphological evolution of
separated phases. For the elastic problem, the same notations and assumptions described in section 3.2 and section 3.3 are applied. Then, the Helmholtz free energy of the system includes three contributions: bulk chemical free energy, interfacial energy and elastic energy,

\[
E = \int \left[ f(c(x,t), T) + \frac{\kappa^2}{2} (\nabla c(x,t))^2 + \frac{1}{2} \lambda_{ijkl}(x,t) \varepsilon_{ij}(x,t) \varepsilon_{kl}(x,t) \right] d^3x. \tag{4.1}
\]

where \( f(c, T) \) is the chemical free energy density of the solid solution, \( \kappa \) is the gradient energy coefficient which is determined by the interfacial energy and thickness. The third term in (4.1) is the elastic energy density.

Since the composition is a conserved field variable, the kinetic equation of the composition field is described by the Cahn-Hilliard-type diffusion equation given by

\[
\frac{\partial c(x,t)}{\partial t} = \nabla M \frac{\delta E}{\delta c(x,t)} + \xi(x,t)
= \nabla \cdot \left[ \frac{df(c(x,t), T)}{dc(x,t)} - \kappa^2 \nabla^2 c(x,t) + \mu_{el} \right] + \xi(x,t) \tag{4.2}
\]

where \( \xi(x,t) \) is the noise term representing composition fluctuation. \( M \) is chemical mobility. If we assume that the atomic mobilities of species 1 and 2 are equal, the mobility, \( M \), is given by
\[ M = \frac{Dc(x,t)(1-c(x,t))}{k_BT} \]  

(4.3)

where \( D \) is the chemical diffusion coefficient, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. The mobility is further simplified by assuming that the factor \( c(x,t)(1-c(x,t)) \) is a constant given by \( c_0(1-c_0) \) where \( c_0 \) is the overall composition.

\( \mu_{el} \) is the elastic potential due to the coherency strain and is given by [158]

\[
N_v \mu_{el} = -\lambda^0_{ijkl}(\bar{\varepsilon}_{ij} + \varepsilon_{ij}^{\text{dis}}(x) + \delta \varepsilon_{ij}(x)) \varepsilon_{kl}^{00} + \lambda_{ijkl}^0 \varepsilon_{ij}^{00} \varepsilon_{kl}^{00} \delta \varepsilon(x) + \frac{1}{2} \lambda_{ijkl}^0 (\bar{\varepsilon}_{ij} + \varepsilon_{ij}^{\text{dis}}(x) + \delta \varepsilon_{ij}(x))(\bar{\varepsilon}_{kl} + \delta \varepsilon_{kl}(x)) - 2\lambda_{ijkl}^0 (\bar{\varepsilon}_{ij} + \varepsilon_{ij}^{\text{dis}}(x) + \delta \varepsilon_{ij}(x)) \varepsilon_{kl}^{00} \delta \varepsilon(x) + \frac{3}{2} \lambda_{ijkl}^0 \varepsilon_{ij}^{00} \varepsilon_{kl}^{00} (\frac{\delta \varepsilon(x) \delta \varepsilon(x)}{2})^2
\]

(4.4)

where \( N_v \) is the number of atoms per unit volume, and \( \varepsilon_{ij}^{00} = \varepsilon_0 \delta_{ij} \).

The simulations are performed in two or three dimensions. In simulations, periodic boundary conditions are employed. The elastic stress field is calculated by the iteration method proposed in section 3.3. The chemical free energy density of the solid solution is expressed by

\[
f(c(x,t),T) = -(c(x,t) - 0.5)^2 + 2.5(c(x,t) - 0.5)^4
\]

(4.5)

The equilibrium compositions determined from equation (4.5) are 0.053 and 0.947, respectively. The evolution equation (4.2) is solved by semi-implicit schemes [159].
4.2 Spinodal decomposition in a bulk system

4.2.1 Morphological dependence of isolated precipitates on elastic inhomogeneity

The shapes of a single coherent precipitate in elastically inhomogeneous systems have been studied with boundary integral equation method [71,72] and discrete atom method (DAM) [160]. With the phase-field model and the proposed iteration method, the shape evolution of an isolated precipitate and its dependence on elastic inhomogeneity are re-examined in this section. The shape evolution of an isolated particle towards equilibrium is obtained by solving the Cahn–Hilliard diffusion equation (4.2). A simulation cell of $256 \times 256$ grids is used. A circular precipitate ($R = 40$) is placed in the center of the simulation cell. The initial composition within the precipitate is assigned the incoherent equilibrium value determined from the local free energy density function $f(c,T)$, $c = 0.947$, whereas $c = 0.06$ in the matrix which is higher than the incoherent equilibrium composition, 0.053. The coherent equilibrium compositions are not known in advance and will be automatically achieved during the temporal evolution towards equilibrium. The dimensionless time step for integrating the Cahn–Hilliard equation is

$$\Delta t^* = \frac{k_B T M \Delta t}{(\Delta x)^2} = 0.5,$$

and the gradient energy coefficient is

$$\kappa^* = \frac{k^2}{k_B T (\Delta x)^2} = 1.5$$

where $\Delta x$ is the grid spacing. The composition expansion coefficient is $\varepsilon_0 = 0.05$. The elastic constants used are $C_{11}^0 = 232$, $C_{12}^0 = 153$ and $C_{44}^0 = 117$ in units of $N, k_B T$ [161], which has cubic anisotropy. To examine the effect of shear modulus inhomogeneity, keep the bulk modulus ($B = C_{11} + C_{12}$ for the plane problem) and the ratio of anisotropy...
\( \delta = 2C_{44}/(C_{11} - C_{12}) \) the same in the matrix and the precipitate, while changing the ratio of shear modulus \( \beta = C_{44}^p / C_{44}^m \) in which \( p \) and \( m \) denote the precipitate and matrix, respectively. As an example, the temporal evolution of a soft precipitate with \( \beta = 0.3 \) from the initially circular precipitate \( R = 40 \) is shown in Fig. 4.1. It can be seen that the particle shapes evolves from a isotropic circle to an anisotropic “star”. It is well known that the shape of the particle is controlled by the competition between interfacial energy and elastic strain energy. In this particular example, the interfacial energy is assumed to be isotropic, so the development of anisotropic particle shape shown is entirely due to an anisotropic elastic stress field caused by the cubically elastic anisotropy and elastic inhomogeneity. Simulation and experimental results [148] show that the precipitate has a cubic shape in elastically homogenous and cubically anisotropic solid. Therefore, it can be concluded that the elongation of the particle along the \( \langle 11 \rangle \) and \( \langle 1\overline{1} \rangle \) diagonal directions is due to the fact that the particle is softer than the matrix. A very similar shape change was observed by Lee using the discrete atom method [160]. The composition distributions along the \( \langle 10 \rangle \) direction and the \( \langle 11 \rangle \) diagonal direction passing through the center of the precipitate are plotted as a function of time in Fig. 4.2. The coherent composition within the precipitate decreases from the initially assigned value (the incoherent equilibrium composition of the precipitate) whereas in the matrix the composition increases the initial incoherent equilibrium composition. The composition distribution inside the precipitate is highly inhomogeneous due to the presence of coherent stress. The simulation results show that there is no significant change in the shape of the precipitate and the composition distribution inside the precipitate after about
$t = 16,500$. However, due to the application of the periodic boundary conditions and the slow solute redistribution towards equilibrium, the last morphology shown in Fig. 4.3 is close to, but not exactly the equilibrium shape of an isolated precipitate. Precipitate shape as a function of elastic inhomogeneity ($\beta = 1.70, 1.35, 1.00, 0.60, 0.45$ and $0.30$) is shown in Fig. 4.4. They all started with an initially circular precipitate with radius 40. For an elastically homogeneous precipitate, the equilibrium shape is cubic with rounded corners. With the decrease in $\beta$, i.e., when the precipitate becomes softer than the matrix, the boundaries of the cuboid along the $\langle 10 \rangle$ or $\langle 01 \rangle$ directions become concave, whose curvature strongly depends on the ratio of shear modulus $\beta$. The hard precipitate has convex boundaries, but the dependence of equilibrium shape on $\beta$ is rather weak compared to the elastically soft precipitate. Existing studies using other computational approaches predicted similar results [71,160].

### 4.2.2 Morphological dependence of multi precipitates on elastic inhomogeneity

In order to characterize the elastic inhomogeneity of a two-phase cubic system, three quantities, i.e., the bulk modulus ($B = C_{11} + C_{12}$), the shear modulus ($G = C_{44}$), and the anisotropy ($\delta = 2C_{44}/(C_{11} - C_{12})$) are used. The inhomogeneity effect of each of these three quantities by holding the other two constant on the morphologies of multi-precipitates are simulated. In the first case, the bulk and shear modulus are homogeneous
Fig. 4.1 The precipitate shape as a function of time for a soft precipitate 
($\beta = 0.3$, $R = 40$).
Fig. 4.2  Evolution of compositional profiles as a function of time for a soft precipitate $(\beta = 0.3, R = 40)$, (a) along the x-direction, (b) along the diagonal direction.
Fig. 4.3  The shape of an isolated precipitate as a function of elastic inhomogeneity, (a) $eta = 1.70$, (b) $eta = 1.35$, (c) $eta = 1.00$, (d) $eta = 0.60$, (e) $eta = 0.45$, (f) $eta = 0.3$. 
while the bulk modulus is a function of composition. As an example, the moduli are set to be $C_{11}^0 = 300$, $C_{12}^0 = 160$ and $C_{44}^0 = 70 [161]$. Keep the same bulk modulus ($B = 460$) and the shear modulus ($G = 140$) in the two phases, and change their anisotropy ratio ($\delta^p = 1.00, 1.14, 1.34, 1.63, 2.05, 2.80$, $\delta^M = 1.00, 0.89, 0.79, 0.72, 0.66, 0.61$). The angular dependent Young’s moduli as a function of direction for the precipitate, the matrix and a uniform solid solution are plotted in Fig. 4.4a for the case of $\delta^p = 2.80$ and $\delta^m = 0.61$. For cubic systems, Young’s modulus $E(\theta)$ is given by

$$E(\theta) = \frac{1}{4} (3C_{11} + C_{12} + 2C_{44}) + (C_{11} - C_{12} - 2C_{44} \cos(4\theta))$$  \hspace{1cm} (4.6)$$

where $\theta$ is the angle with respect to the elastic main axis. It is easy to see from Fig. 4.4a that the Young’s moduli along $\langle 11 \rangle$ and $\langle 1\bar{1} \rangle$ directions are the same for both phases while the precipitate has larger modulus than the matrix along the $\langle 01 \rangle$ and $\langle 10 \rangle$ directions. The morphological dependence of a phase-separated two-phase system on the anisotropy ratio is shown in Fig. 4.5. In the simulations, the gradient energy coefficient, composition expansion coefficient, and the time increment for integration are the same as in the last example for a single precipitate evolution. The simulations were started with an average concentration of 0.5 with a small random concentration fluctuation. The white regions in Fig. 4.5 stand for the phase with larger Young’s moduli along the $\langle 01 \rangle$ and $\langle 10 \rangle$ directions than the black regions. It is shown that with an increase in difference in the moduli between the two phases, the phase with larger moduli becomes disconnected.
and forms isolated cuboidal composition domains. It is worth pointing out that although
the elastically soft direction for the precipitate phase in Fig. 4.5f is along \(\langle 11 \rangle\) and \(\langle 1 \overline{1} \rangle\) directions, the overall spatial distribution of the isolated domains displays alignment
along the \(\langle 01 \rangle\) and \(\langle 10 \rangle\) directions. As expected, when the anisotropy for both the
precipitate and matrix is rotated by 45°, the hard phase still appears as isolated precipitates but the alignment is now along the \(\langle 11 \rangle\) and \(\langle 1 \overline{1} \rangle\) directions. In the second
case, the bulk modulus and the anisotropy are the same for the precipitate and matrix
phases while the shear modulus is a function of composition. In the numerical example,
\(C_{11}^0 = 300, C_{12}^0 = 200, C_{44}^0 = 100, B = 500\) and \(\delta = 2\) are used. The ratios of shear
modulus between the two phases are \(\beta = 1.0, 1.2, 1.5, 1.9, 2.6, 3.6\). The Young’s moduli
as a function of direction for the precipitate, the matrix and a uniform solid solution are
plotted in Fig. 4.4b for the case of \(\beta = 3.6\). In this case, one phase is harder than the
other in all directions. Fig. 4.6 presents the morphological dependence on elastic
inhomogeneity for this case. The result is quite similar to the first case. At large
inhomogeneity, the harder phase consists of isolated particles and the softer phase is a
connected matrix wrapping the hard phase. The particles are aligned along the elastically
soft directions, \(\langle 01 \rangle\) and \(\langle 10 \rangle\). The temporal morphological evolution during phase
separation of a homogeneous solid solution to a two-phase mixture is shown in Fig. 4.7.
The morphology during the initial stage of phase separation is very similar to spinodal
phase separation without elastic interactions since the elastic interaction is very weak. As
the phase separation process progresses, morphological alignment along the elastically
Fig. 4.4   Young’s modulus as a function of direction: dot-dashed line — matrix; dashed line — precipitate; and solid line — a homogeneous solution. (a) Homogeneous bulk and shear moduli but inhomogeneous elastic anisotropy; (b) homogeneous bulk modulus and anisotropy but inhomogeneous shear modulus; (c) homogeneous shear modulus and anisotropy but inhomogeneous bulk
Fig. 4.5 Two-phase morphology as a function of elastic inhomogeneity caused by different degrees of elastic anisotropy in the matrix and precipitate ($\delta^P$, $\delta^M$): (a) (1.00, 1.00), (b) (1.14, 0.89), (c) (1.34, 0.79), (d) (1.63, 0.72), (e) (2.05, 0.66), (f) (2.80, 0.61). Both the bulk and shear moduli are homogeneous.
Fig. 4.6 Two-phase morphology as a function of elastic inhomogeneity caused by different shear moduli in the two phases (a) $\beta = 1.0$, (b) $\beta = 1.2$, (c) $\beta = 1.5$, (d) $\beta = 1.9$, (e) $\beta = 2.6$, (f) $\beta = 3.6$. The precipitate and matrix have the same bulk moduli and the same degree of elastic anisotropy.
Fig. 4.7 Temporal evolution during phase separation of a homogeneous solid solution into a two phase mixture for the case of elastic inhomogeneity caused by different shear moduli in the two phases, $\beta = 2.6$.

The precipitate and matrix have the same bulk moduli and the same degree of elastic anisotropy.
Fig. 4.8 Two-phase morphology as a function of elastic inhomogeneity caused by different bulk moduli in the two phases (a) $B_p / B_M = 1.0$, (b) $B_p / B_M = 1.5$. The precipitate and matrix have the same shear moduli and the same degree of elastic anisotropy.
soft directions developed. With further coarsening, the initially interconnected hard phase breaks into isolated particles. In the third case, the shear modulus and anisotropy are independent of composition while the bulk modulus varies with composition. Fig. 4.4c shows the Young’s moduli as a function of direction for the hard and soft phases. The morphologies of a phase-separated two-phase system with different bulk modulus inhomogeneity is shown in Fig. 4.8. It is found that the bulk modulus inhomogeneity has essentially no important effect on the morphology. It should be emphasized although the first-order approximations [37-39] predict the qualitatively correct two-phase morphology, the local stress distributions described by a first-order approximation for a system with strongly elastic inhomogeneity can be in serious error as shown in section 3.2.5. Therefore, the elastic energy contribution to the driving force for microstructure evolution such as coarsening for two phase systems is not accurately determined in a first order approximation, As a result, kinetics of microstructure evolutions and resulting microstructures would be affected.

4.3 Spinodal decomposition in a film with periodically distributed interfacial dislocations

The translational symmetry in bulk materials is broken due to the presence of a surface and an interface in a thin film on a substrate [162]. As a result, the kinetics of phase transition in a film may differ dramatically from that in bulk materials. For example, quasi-two dimensional diffusion may occur in a very thin film, and results in the formation of cylindrical particles perpendicular to the surface during spinodal decomposition. For a thick film, the stress relaxation at surface or stress gradient along
the film thickness causes an inhomogeneous decomposition rate and the development of alternating layers of the phases lying parallel to the surface [42, 162-164]. Experiments demonstrated that a regular network of pure edge-type dislocations with a spacing of several nanometers could be formed directly at the heterointerface, which has extremely large lattice mismatches between the film and substrate [165,167]. Like a surface, a strained or patterned substrate breaks the translational symmetry in the film plane, which can be used to control the wavelength of spinodal decomposition and develop nanostructures [162,168-172]. Romanov, et al [170] investigate the possibility of using such dislocation arrays as to control the nucleation of self-assembled quantum dots. Johnson, et. al [162,168,169] performed two-dimensional simulations of phase decomposition in a film on a patterned substrate. Greaney, et al [172] studied the effect of a rigid, periodically strained substrate on spinodal decomposition in a film. A linear stability analysis [172] showed that a film will undergo spinodal decomposition with the dominant wavelength determined by the periodicity of the substrate strain. The propose of this section is to develop a three-dimensional (3D) phase field model for simulating the spinodal decomposition in a film with periodically distributed interfacial dislocations or lattice mismatches and subject to an elastically substrate constraint. The iteration method described in section 3.3 is employed to solve the mechanical equilibrium equations in thin films in the simultaneous presence of dislocations, compositional strains, and a substrate constraint. In the thesis, only the results of spinodal decomposition in films with a flat surface are presented. For the general case with a curve film surface, the formation of self-assembled quantum dots due to surface instabilities is reported in our paper [136].
4.3.1 Phase-field model

Consider a cubic thin film grown heteroepitaxially on a cubic substrate at high temperature and assume that a periodically dislocation array is formed at the interface shown in Fig. 4.9. The Burgers vectors of dislocations are assumed to be along $\frac{1}{2}[110]$ and $\frac{1}{2}[\overline{1}10]$, respectively. For simplicity, we assume the film is a binary solid solution, which is unstable with respect to spinodal decomposition at the temperature of interest. In the phase-field framework, the composition $c(x,t)$, which represents the mole or atom fraction at position $x$ and time $t$, is chosen as the phase variable. If we ignore the microstructural evolution of the substrate and the dislocation core energy, then the total energy of the system includes chemical free energy, gradient energy due to composition inhomogeneity, and elastic energy,

$$E = \int \left[ f(c(x,t)) + \frac{\kappa^2}{2} (\nabla c(x,t))^2 + \frac{1}{2} \lambda_{ijkl}(x,t) \varepsilon_{ij}(x,t) \varepsilon_{kl}(x,t) \right] d^3x \quad (4.7)$$

where $f(c(x,t))$ is the chemical free energy density, $\kappa$ is the gradient energy coefficient. The third term in (4.7) is the elastic energy density. The chemical free energy density (4.5) is employed. The elastic problem is described in the section 3.3, and is solved by the iteration method [158].
4.3.2 Evolution equation

The kinetic equation of the composition is the same as the equation (4.2). In the present work, we ignore the morphological instabilities in the film surface, and assume the composition flux at the surface of the film and interface between the film and the substrate are zero. Therefore, the temporal evolution of the composition field is obtained by solving the equation (4.2) together with the initial conditions and the following boundary conditions

\[ \frac{\partial c(x,t)}{\partial z} \bigg|_{z=-h_j} = 0 \quad \text{and} \quad \frac{\partial c(x,t)}{\partial z} \bigg|_{z=0} = 0 \]  

(4.8)

To numerically solve this evolution equation, a Fourier-spectral method is used in \( x \) and \( y \) directions. Since the zero-flux boundary conditions at film surface and film/substrate interface cannot be satisfied by a Fourier expansion, a second-order finite difference method with FFT (Fast Fourier Transform) is used in the \( z \)-direction. In time discretization, a semi-implicit method is employed [159].
Fig. 4.9 Simulation cell of a thin film system.
4.3.3 Results and discussions

In the simulation, $128 \times 128 \times 32$ discrete grid points are used. The thickness of the substrate is $h_s = 18$. In order to study the effect of the film thickness on the microstructure pattern, three different film thickness $h_f = 3, 5$ and $9$ are considered, respectively. The dimensionless time $\Delta t^*$ is chosen to be $0.05$. The interfacial energy is assumed to be isotropic, and the dimensionless gradient energy coefficient, $\kappa^{*2}$, is taken to be $0.5$. The overall reduced composition used in this study is $0.5$. The isotropic elastic constants are assumed for both film and substrate, $C_{11} = 300$, $C_{12} = 100$, $C_{44} = 100$, in the unit of $N_v k_B T$ where $N_v$ is the number of atoms per unit volume. Considering that the linear elasticity theory is only valid outside the dislocation core region, the characteristic length $d_o$ is taken to be $10b$ about dislocation core size, where $b$ is the magnitude of the Burgers’ vector of the dislocation. In the present work, our main concern is the effect of nonuniform lattice mismatches at the film/substrate interface on morphological evolution during spinodal decomposition. Particularly, the nonuniform interface lattice mismatches are related to a distribution of interfacial dislocations. Assume $n_x$ edge dislocations and $n_y$ edge dislocations are uniformly distributed in $x$- and $y$- directions, respectively. The nonzero components of the eigenstrain tensor related to such a dislocation distribution can be described as

\[
\varepsilon_{11}^{\text{dis}}(r) = \sum_{n_x=1}^{n_x} \frac{b}{d_\theta} \delta(x - \left(\frac{128}{n_x} - 0.5\right)), \quad \varepsilon_{22}^{\text{dis}}(r) = \sum_{n_y=1}^{n_y} \frac{b}{d_\theta} \delta(y - \left(\frac{128}{n_y} - 0.5\right)), \quad \text{if } z < 0
\]
First let us compare the composition evolution in two cases. In case I, the lattice mismatch is uniform, \( \varepsilon_{11}^{\text{dis}} = \varepsilon_{22}^{\text{dis}} = 0.00165 \). And in case II, the total lattice mismatch is the same as that in case I, but the uniform lattice mismatch is replaced by two dislocations in both \( x \)- and \( y \)-directions. The thickness of the film is \( 3d_0 \). We start the simulation with a very small composition fluctuation. Fig. 4.10 shows the snapshots of composition evolution in the course of spinodal decomposition. The red color denotes solute rich region while white color solvent rich region. It is clearly seen that two interconnected phases gradually formed in case I. Since the film is very thin, and the diffusion fluxes normal to the surface and the interface are assumed to zero, the diffusion occurs on the plane parallel to the interface. As a result, each phase has a columnar morphology perpendicular to the interface. Our previous results [42] show that as the film thickness increases, the morphology of each phase becomes a 3D network similar to that of bulk materials. For case II, the interaction between stress fields from interfacial dislocations and compositional strains dominates the spinodal decomposition process and causes a directional spinodal decomposition. Fig. 4.11 presents the morphological evolution during spinodal decomposition in the film. To see more clearly the composition wave evolution, Fig. 4.12 plots the temporal composition evolution along A-A line shown in Fig. 4.11. It can be seen that at the initial stage the local stress results in the formation of composition waves near the dislocation along the direction perpendicular to the dislocation line on the film plane as well as along the thickness direction. The composition wave along thickness is transient. As the time increases, such a composition wave disappears. The composition wave along the direction perpendicular to the
dislocation line on the film plane propagates directionally as time increases. Finally, an
mesoscopically ordered microstructure is formed.

To illustrate the effect of the wavelength of dislocation distributions on the microstructure pattern, four different dislocation distributions ($nx = ny = 2, 4, 8$ and $16$) are simulated. Fig. 4.13 presents the microstructure patterns at simulation step $t = 1000$. It can be seen that with the increase of the dislocation density or the decrease of the wavelength, the morphology of two decomposed phases changes dramatically from interconnected to isolated particles. The results demonstrate that a nanostructure can be obtained by decreasing the wavelength of dislocation distributions. Fig. 4.14 illustrates how the thickness of the film affects the microstructure patterns. The microstructures at simulation step $t = 1000$ are shown for three different simulations corresponding to three different film thickness $h_f = 3, 5$ and $9$ for the case with $8$ dislocations ($nx = ny = 8$). The left figure presents the morphology of the solute rich phase. It is clearly seen that as the thickness increases, the composition wave along the thickness direction starts to form. With sufficient thickness, a microstructure with two alternating layers of the phases is developed. In addition, the morphology of the phases in each layer is different from that in the thin films ($h_f = 3$).
Fig. 4.10 Temporal morphological evolution during spinodal decomposition in a thin film under a uniform substrate constraint.
Fig. 4.11 Temporal morphological evolution during spinodal decomposition in a thin film with two interfacial dislocations in both x- and y- directions.
Fig. 4.12 Composition profile along A-A line shown in Fig. 4.11 during spinodal decomposition.
Fig. 4.13 Microstructural patterns formed during spinodal decomposition with different interfacial dislocation arrays.
Fig. 4.14 Effect of film thickness on microstructural patterns with eight interfacial dislocations in both x- and y- directions.
4.4 Conclusion

A phase-field model is developed to simulate the spinodal decomposition in a solid with strongly elastic inhomogeneity and with a spatial distribution of dislocations. The iteration method is used to calculate the elastic energy. As examples, the morphological dependence of the separated phases on elastic inhomogeneity in 2D and spinodal decomposition in a film with periodically distributed interfacial dislocations in 3D are studied. For a solid with cubic elastic anisotropy the equilibrium shape of an isolated precipitate is studied as a function of the ratio of shear modulus in the precipitate and the matrix. The results show that the hard connected phase becomes gradually unconnected particles and the particles align along the softer directions (10) and (01) as the inhomogeneity in shear modulus or elastic anisotropy increases. The inhomogeneity of bulk modulus does not affect the morphology of separated phases. Simulation results in films demonstrate that dislocation stresses induce a directional spinodal decomposition. Periodically distributed interfacial dislocations can be used to create self-assembled nanostructures. The nanostructure can be changed by varying the film thickness and the wavelength of the interfacial dislocation distribution.
Chapter 5

A Phase-field Model of Dislocation Dynamics

To describe the phase-field model of dislocation dynamics, a binary alloy with mobile dislocations and diffusive solutes is taken as a model system. Two sets of phase field variables, i.e., compositional field $c(x,t)$ and order parameter fields $\eta(x,t)$, are employed to describe the mole fraction of solutes and dislocation distribution at position $x$ and time $t$, respectively. If the single crystal of interest has $N$ slip systems, $N$ order parameter fields $\eta_{\alpha\beta}(x,t)$ ($N = \sum_{\alpha=1}^{p} m_{\alpha}$, $\alpha = 1, 2, \ldots, p$; $\beta = 1, 2, \ldots, m_{\alpha}$) are needed to completely describe the dislocation distribution, where $p$ denotes the number of elementary slip planes and $m_{\alpha}$ denotes the number of elementary Burgers vectors on the slip plane $\alpha$. For instance, in a FCC single crystal, there are four slip planes: $(111)$, $(\bar{1}11)$, $(1\bar{1}1)$, $(11\bar{1})$, and three slip directions on each slip plane, and hence it requires 12 order parameter fields $\eta_{\alpha\beta}(x,t)$ ($p=4$, and $m_{\alpha} = 3$ ($\alpha = 1, 2, 3, 4$))

5.1 Total free energy of the system

The total free energy $E$ in a binary system with dislocations includes (1) the chemical free energy $E^{\text{chem}}$ which consists of both the local bulk free energy of a binary solution and the composition gradient energy, (2) elastic energy $E^{\text{elast}}$ associated with solutes, defects and applied stresses, and (3) ‘crystalline energy’ $E^{\text{cryst}}$ which includes the local structural energy and the structural gradient energy. For a perfect dislocation, the
crystalline energy is exactly associated with the dislocation core energy. Therefore, the total free energy of the system is described by

$$E = E^{\text{chem}} + E^{\text{elast}} + E^{\text{cryt}}$$  \hspace{1cm} (5.1)$$

### 5.1.1 Chemical free energy

In a binary system with a spatial composition distribution $c(x,t)$, the chemical free energy can be described as the sum of two contributions, i.e., the local bulk free energy and the gradient energy. It reads

$$E^{\text{chem}} = \int_V \left[ f_0(c) + \frac{\kappa^2}{2} (\nabla c)^2 \right] dV$$  \hspace{1cm} (5.2)$$

where the first term $f_0(c)$ is the bulk free energy density of a binary solution; the second term is the gradient energy density, and $\kappa$ is the gradient energy coefficient. For a regular solution, $f_0(c)$ has the form,

$$f_0(c) = RT[\varphi c(1-c) + c \ln(c) + (1-c) \ln(1-c)]$$  \hspace{1cm} (5.3)$$

where $R$ is the ideal gas constant, $T$ is the absolute temperature, and $\varphi$ is a material constant. For an ideal solution, $\varphi$ is equal to zero.
5.1.2 Elastic energy

The elastic energy can be calculated by (see [1,139] for detail)

\[ E_{\text{elast}}^{\text{el}} = \frac{1}{2} \int \lambda_{ijkl} \varepsilon_{ij}^{\text{el}} \varepsilon_{kl}^{\text{el}} dV \]  

(5.4)

where

\[ \varepsilon_{ij}^{\text{el}} = \varepsilon_{ij} + \delta \varepsilon_{ij}^{\text{c}} (x) - \varepsilon_{ij}^{\text{c}} (c(x,t)) - \varepsilon_{ij}^{\text{def}} (x) - \varepsilon_{ij}^{\text{dis}} (x, t) \]  

(5.5)

\[ \lambda_{ijkl} \] is the elastic stiffness tensor, \( \varepsilon_{ij} \) the homogeneous macroscopic strain characterizing the macroscopic shape and volume change, \( \delta \varepsilon_{ij}^{\text{c}} (x) \) heterogeneous strains, \( \varepsilon_{ij}^{\text{c}} (c(x,t)) \) the eigenstrain due to the composition inhomogeneity and \( \varepsilon_{ij}^{\text{def}} (x) \) the eigenstrain associated with immobile defects such as inclusions. The eigenstrain \( \varepsilon_{ij}^{\text{dis}} (x, t) \) is associated with the dislocation distribution,

\[ \varepsilon_{ij}^{\text{account}(x, t)} = \sum_{\alpha, \beta} b_{ij}^{\alpha\beta} \eta_{\alpha\beta} (x, t) = \sum_{\alpha, \beta} \varepsilon_{ij}^{\text{dis}} (\alpha, \beta) f (\eta_{\alpha\beta} (x, t)) \]  

(5.6)
where \( f(\eta(x,t)) \) is the shape function which describes the change of Burgers vector across the dislocation core. In the original phase-field model of dislocation dynamics [87,88], \( f(\eta(x,t)) \) has assigned a linear function of \( \eta(x,t) \),

\[
f(\eta(x,t)) = \eta(x,t) \quad (5.7)
\]

It is found that such a shape function leads to a dependence of Burgers vector on applied stress, hence, a wrong stress field of dislocations. In this thesis, a new shape function is constructed which can eliminate the dependence of the magnitude of the dislocation Burgers vector on the applied stress and provide a correct stress field of dislocations. The new shape function has the following form [173]

\[
f(\eta(x,t)) = \eta(x,t) - \frac{1}{2\pi} \sin(2\pi\eta(x,t)) \quad (5.8)
\]

The function \( f(\eta(x,t)) \) has two properties: (i) it is exactly equal to \( \eta(x,t) \) when \( \eta(x,t) \) is an integer; and (ii) its derivatives at integer values of \( \eta(x,t) \) are zero.

### 5.1.3 ‘Crystalline energy’ associated with dislocations

As a microscopic interpretation, the order parameter \( \eta_{\alpha\beta}(x,t) \) represents the relative displacement between two atomic planes on the slip plane. Imitating the ‘Peierls
potential’ in a crystal and the gradient energy in phase field theory, Khachaturyan et al [87, 88] constructed a ‘Crystalline energy’ of dislocations

\[
E^{\text{cryst}} = \int \left[ \sum_{a=1}^{p} \sum_{\beta=1}^{q} A(\alpha, \beta) \sin^2 \left[ \pi \eta_{\alpha \beta}(x, t) \right] + \frac{\gamma}{2} \sum_{a=1}^{p} \sum_{\alpha_1=1}^{\alpha_2=1} B_{\alpha \beta}(\alpha_1, \alpha_2) \frac{\partial b_1(\alpha_1, x, t)}{\partial x_j} \frac{\partial b_1(\alpha_2, x, t)}{\partial x_i} \right] d^3 x
\]

(5.9)

where \( \gamma \) is a positive constant, \( A(\alpha, \beta) \) and \( B_{\alpha \beta}(\alpha, \beta) \) are material constants that can be obtained by fitting the core energy and core size of dislocations, and \( b(\alpha, x, t) \) is the total Burgers vector of dislocations at \( x \) on slip plane \( \alpha \).

\[
b(\alpha, x, t) = \sum_{\beta=1}^{m} b_{\alpha \beta} \eta_{\alpha \beta}(x, t)
\]

(5.10)

In equation (5.9) the first term is the ‘Peierls potential’ (local structural energy), and the second term is the structural gradient energy.

5.2 Phase-field kinetic equations

The temporal evolution of solute composition \( c \) is described by the Cahn-Hilliard equation

\[
\frac{\partial c(x, t)}{\partial t} = \nabla M \frac{\delta E}{\delta c(x, t)} + \xi(x, t)
\]

(5.11)
where $E$ is the total free energy of the system, $M$ is a kinetic coefficient related to the solute diffusion mobility, and $\xi(x,t)$ is the noise term reflecting the thermal fluctuation.

Substituting the total energy into the Cahn-Hilliard equation (5.11) and taking the first variational derivatives with respect to the composition function $c(x,t)$. The composition field kinetic equation is given by

\[
\frac{\partial c(x,t)}{\partial t} = M\nabla^2 \{ -\lambda_{ijkl}\delta_{ij} [\bar{E}_{kl} + \delta E_{kl}(x,t)] + \lambda_{ijkl}\bar{E}^0 \delta_{ij} \delta_{kl} c(x,t) \\
+ \lambda_{ijkl}\bar{E}^0 \delta_{ij} \sum_{\alpha,\beta} E_{\alpha\beta} \bar{E}_{\alpha\beta}(x,t) + \delta E_{kl}(x,t) \}
\]

\[
+ \frac{\partial f_0(c(x,t))}{\partial c} - \kappa\nabla^2 c(x,t) \} + \xi(x,t)
\]

The order parameter fields describing the dislocation distribution are non-conserved, and their temporal evolutions are described by the time-dependent Ginzburg-Landau equations:

\[
\frac{\partial \eta_{\alpha\beta}(x,t)}{\partial t} = -L_{\alpha\beta} \frac{\partial E}{\partial \eta_{\alpha\beta}(x,t)} + \zeta(\alpha,\beta,x,t)
\]

(5.13)

where $L_{\alpha\beta}$ is the kinetic coefficient characterizing the dislocation mobility, and $\zeta(\alpha,\beta,x,t)$ is the Langevin Gaussian noise term simulating the thermal fluctuations.

Equation (5.13) can be rewritten as
\[
\frac{\partial \eta_{ab}(x,t)}{\partial t} = L_{ab} \{ \lambda_{ijkl}^* e_{ij}^{\text{def}}(\alpha, \beta) \frac{\partial f(\eta_{ab}(x,t))}{\partial \eta_{ab}} [\varepsilon_{kl} + \delta e_{kl}(x,t)] \\
- \varepsilon^0 \delta_{kl} c(x,t) - \sum_{\alpha, \beta} e_{ij}^{\text{dist}}(\alpha, \beta) f(\eta_{ab}(x,t)) - \varepsilon_{ij}^{\text{def}}(x) \\
- A \pi \sin(2\pi \eta_{ab}(x,t)) \frac{\gamma}{2} \frac{\partial \phi(x,t)}{\partial \eta_{ab}} + \zeta(\alpha, \beta, x, t)
\]

(5.14)

where \( A = A(\alpha, \beta) \) is assumed to be constant in the simulation for simplicity, and

\[
\phi(x,t) = \sum_{\alpha_1}^p \sum_{\alpha_2}^p \left[ B_{ijkl}(\alpha_1, \alpha_2) \frac{\partial b_j(\alpha_1, x,t)}{\partial x_j} \frac{\partial b_k(\alpha_2, x,t)}{\partial x_k} \right]
\]

(5.15)

To facilitate the computation, the following dimensionless parameters are introduced,

\[
\begin{align*}
x^* & = \frac{x}{d_0}, d^* = \frac{\Delta x}{d_0}, \varepsilon^* = \frac{\varepsilon_0}{d_0} \\
\lambda_{ijkl}^* & = \frac{\lambda_{ijkl}}{G}, e_{ij}^* = \frac{e_{ij}}{e_0}, \sigma_{ij}^* = \frac{\sigma_{ij}}{Gd_0^2} \\
A^* & = \frac{A}{Ge_0^2}, \gamma^* = \frac{\gamma}{2Ge_0^2d_0^2}, t^* = LGd_0^2 \\
M^* & = \frac{M}{Ld_0^2}, \kappa^* = \frac{\kappa}{Gd_0^2e_0^2} \\
f^*_0(c) & = \frac{f_0(c)}{Ge_0^2}, E^{\text{elas}} = \frac{E_{\text{elas}}}{Ge_0^2}, \chi^* = \frac{RT}{Ge_0^2}
\end{align*}
\]

(5.16)

where \( G \) is the shear modulus, and \( \Delta x \) is the grid spacing of the computational mesh.
The elastic equilibrium equation and the kinetic equations are solved numerically. The semi-implicit spectral method [159] is employed, which implies the use of periodic boundary conditions along x-, y- and z-directions \((x_1 = x, \ x_2 = y, \ x_3 = z)\). In all the simulations, the following parameters are fixed: \(C_{11} = 3.0, \ C_{12} = 1.0, \ C_{44} = 1.0, \ A^* = 0.05, \ \gamma^* = 0.25, \ \kappa^* = 0.05, \ \epsilon^0 = 0.075, \ \chi^* = 0.09, \ \epsilon_0 = 0.25, \ dt^* = 0.02; \ d^* = 1.0, \ d_0 = 4a_0\) where \(a_0\) is the length of Burgers vector. The dimensionless parameters \(M^*, \ \varphi, \ c_0\) and \(\bar{\epsilon}_{ij}^*\) are systematically changed to study their effect on dislocation-solute interactions under applied stresses. In the simulations, elastic inhomogeneity and immobile defects are not considered. But it is straightforward to incorporate these effects into the phase-field model of dislocation dynamics with the iteration method developed above.

5.3 Results and discussions

5.3.1 Stress fields of dislocations

Eigenstrain of dislocations is described by equation (5.6). Different shape functions \(f(\eta(x,t))\) might affect the dislocation stress field. To examine the dislocation stress field, a two-dimensional simulation cell with a dislocation loop shown in Fig. 5.1 is considered because an analytical elastic solution exists in this case. We assume that the composition of solutes is zero. The dislocation loop with \(R = 120\Delta x\) is introduced into the center of the simulation cell \(512 \times 512\) by assigning the initial value \(\eta = 1\) on the grid.
Fig. 5.1 Schematic illustration of a dislocation loop located at the center of a 2D computational cell.
points inside the dislocation loop on the slip plane and $\eta = 0$ outside the loop. The Burgers vector of the dislocation loop is $b = (100)$ along the $x$-direction, and its slip plane is the $n = (001)$ plane. The equilibrium profile $\eta_0(x)$ of kinetic equation (5.14) in the absence of applied stresses is used to calculate the stress field of the dislocation. Fig. 5.2 plots the normal and shear stress distributions of the edge dislocation in the right side of simulation cell along A-A line just below the slip plane shown in Fig. 5.1. The corresponding analytical solution is also plotted for comparison. The results show that the stress fields obtained with the new expression of dislocation eigenstrains (5.8) are in good agreement with the analytical elastic solution except for two or three points where the stresses of analytical solutions are singular. In addition, it is found that numerical stresses are continuous at the dislocation line. This means that the singularity of the stress field at the dislocation line is removed. It is a natural result since the discontinuous displacement at a dislocation line in classical elastic theory is replaced by a continuous displacement in the phase field model. Therefore, phase-field models of dislocations provide similar elastic stress fields as the non-local elastic theory [108,109]. The elimination of singularity not only brings the dislocation stress field much closer to the real situation but also benefits the stability of numerical calculations.

For a static dislocation, the linear expression (5.7) is able to provide a correct stress field. However, it results in the dependence of the magnitude of the dislocation Burgers vector on applied stresses, hence, an incorrect stress field for a moving dislocation. To examine the effect of two dislocation eigenstrain expressions on the stress
field of moving dislocations, the kinetic equation (5.14) is solved under different applied shear stresses $\bar{\sigma}_{31}^*$. Fig. 5.3 shows the temporal order parameter profiles at $t^* = 400dt^*$, $800dt^*$, $1200dt^*$, and $1600dt^*$ with a loading history $\bar{\sigma}_{31}^* = 0.0, 0.015, 0.02$ and $0.025$ for every 400 time steps. The related shear stress distributions on the slip plane are plotted in Fig. 5.4. It is observed in Fig. 5.3b that the order parameter values inside and outside the dislocation loop increase with the magnitude of the applied stress for the case that the dislocation eigenstrain expression is a linear function of the order parameter in equation (5.7). This implies that dislocation Burgers vector depends on the applied stress. From Fig. 5.4b, it can be seen that an extra stress field due to the change of Burgers vector greatly reduces the effect of the applied stress. As a result, the extra stress slows down the dislocation velocity. However, the new eigenstrain expression (5.8) proposed in the present thesis eliminates this dependence. The order parameter profiles in Fig. 5.3a show that the order parameter values far away from the dislocation core do not change under applied stresses with the new eigenstrain expression. The applied stresses and internal stresses affect only the order parameter profile in the dislocation core. Therefore, the dislocation stress field far away from the dislocation core remains the same during dislocation motion under different applied stresses, which can be seen from Fig. 5.4a. These results demonstrate that the new dislocation eigenstrain expression can provide a correct stress field for both static and moving dislocations. It should be pointed out that the internal stress fields produced by other crystal defects such as other dislocations and cracks will also lead to a change in the Burgers vector if the linear eigenstrain expression is employed. Such a dependency is eliminated using the new eigenstrain expression.
Fig. 5.2  Comparison of dislocation stress distributions calculated from numerical and analytical solutions along A-A line shown in Fig. 5.1, the solid lines for analytical solution and the symbol lines for numerical solutions.
Fig. 5.3a Order parameter profiles under different applied stresses $\bar{\sigma}_{31}^*$ with a nonlinear dependence of the dislocation eigenstrain on order parameter.
Fig. 5.3b Order parameter profiles under different applied stresses $\sigma_{31}^*$ with the linear expression of the dislocation eigenstrain on order parameter.
Fig. 5.4a Shear stress distributions along the slip plane for a moving dislocation with the non-linear eigenstrain expression.
Fig. 5.4b Shear stress distributions along the slip plane for a moving dislocation with the new dislocation eigenstrain expression.
5.3.2 Phase-plane analysis of dislocation velocity

The coefficient $L_{\alpha\beta}$ in the evolution equation (5.14) is unknown, which is the kinetic coefficient characterizing the dislocation mobility. A relationship among the coefficient $L_{\alpha\beta}$, the dislocation velocity and applied stresses can be established through the phase-plane analysis [174]. With such a relationship, experimental data about the dislocation velocity versus applied stress can be used to determine the coefficient $L_{\alpha\beta}$.

To do the phase plane analysis, consider a single dislocation located in the center of the simulation cell shown in Fig. 5.1. The evolution equation of dislocation (5.14) becomes

$$
\eta_t = L[\gamma \eta_{xx} - A\pi \sin(2\pi\eta) + 2\sigma_{31} \varepsilon_{31}^{\text{dis}} \frac{\partial f(\eta)}{\partial \eta}]
$$

with boundary conditions:

$$
\eta(-\infty, t) = \alpha, \ \eta(\infty, t) = \beta
$$

where $\sigma_{31}$ is the total stress component included the dislocation self-stress and the applied stress. The subscript of $\eta$ means its partial derivative, for instance, $\eta_t = \frac{\partial \eta}{\partial t}$.  

\[ \eta_{xx} = \frac{\partial^2 \eta}{\partial x^2} . \] 
\[ \alpha \text{ and } \beta, \text{ which depend on the form of function } f(\eta), \text{ are the roots of the following equation when } x \rightarrow \pm \infty, \text{ respectively,} \]

\[ -A \pi \sin(2\pi \eta) + 2\sigma_{31} \varepsilon_{31}^{\text{dis}} \frac{\partial f(\eta)}{\partial \eta} = 0 \] (5.19)

Because the dislocation self-stress field is zero as \( x \rightarrow \pm \infty \), \( 2\sigma_{31} \varepsilon_{31}^{\text{dis}} = \sigma_{31}^{0} \varepsilon_{31}^{\text{dis}} = \text{const.} \)

\( \sigma_{31}^{0} \) is the applied stress. If \( f(\eta) = \eta \), the equation becomes

\[ -A \pi \sin(2\pi \eta) + 2\sigma_{31}^{0} \varepsilon_{31}^{\text{dis}} = 0 \] (5.20)

It is found that the equilibrium values, \( \alpha \) and \( \beta \), depend on applied stress. However, for the new shape function (5.8), the equation reads

\[ -A \pi \sin(2\pi \eta) = 0 \] (5.21)

The equilibrium values, \( \alpha = 1 \) and \( \beta = 0 \), are independent of the applied stress. Therefore, the same conclusion, the new shape function can eliminate the dependence of Burgers vector on the applied stress, can be obtained from the analysis of equilibrium properties of the solution for the order parameter variable.
In the derivation of dislocation velocity under applied shear stress \( \sigma^0_{31} \) with phase-plane analysis, the new shape function \( f(\eta) = \eta - \frac{\sin(2\pi \eta)}{2\pi} \) is employed. The equation (5.17) in a dimensionless form is written as

\[
\eta_t = 2\gamma^* \eta_{\zeta\zeta} - A^* \pi \sin(2\pi \eta) + 2(\sigma_{31}^{0*} + \sigma_{31}^{dis*}) \epsilon_{31}^{dis*} (1 - \cos(2\pi \eta))
\]  
(5.22)

with boundary conditions

\[
\eta(-\infty, t^*) = 1, \quad \eta(\infty, t^*) = 0
\]  
(5.23)

where \( \sigma_{31}^{dis*} \) is the self-stress of the dislocation.

Assume equation (5.23) has a traveling wave \( \eta(x^*) \) solution and the velocity is \( v \). In the moving coordinate \( \zeta = x^* - vt^* \), equation (5.22) is rewritten as

\[
-v \eta_\zeta = 2\gamma^* \eta_{\zeta\zeta} - A^* \pi \sin(2\pi \eta) + 2(\sigma_{31}^{0*} + \sigma_{31}^{dis*}) \epsilon_{31}^{dis*} (1 - \cos(2\pi \eta))
\]  
(5.24)

with the boundary conditions

\[
\eta(-\infty) = 1, \quad \eta(\infty) = 0
\]  
(5.25)
Introduce a function \( \phi \) and let \( \phi = \eta \zeta \), equation (5.24) becomes

\[
2\gamma \phi = -v\phi + A^* \pi \sin(2\pi \eta) - 2(\sigma_{31}^{0*} + \sigma_{31}^{dis*})\epsilon_{31}^{dis*} (1 - \cos(2\pi \eta))
\]  
(5.26)

with the boundary conditions

\[
\phi(-\infty) = 0, \quad \phi(\infty) = 0
\]  
(5.27)

Multiply both sides of equation (5.26) with \( \phi \) and integrate from \((-\infty, \infty)\)

\[
\int_{-\infty}^{\infty} 2\gamma \phi \phi_{\zeta} \, d\zeta = \int_{-\infty}^{\infty} [ -v\phi^2 - A^* \pi \phi \sin(2\pi \phi) - 2\phi(\sigma_{31}^{0*} + \sigma_{31}^{dis*})\epsilon_{31}^{dis*} (1 - \cos(2\pi \eta))] \, d\zeta
\]  
(5.28)

the velocity is given by

\[
\nu = \frac{\int_{0}^{1} 2(\sigma_{31}^{0*} + \sigma_{31}^{dis*})\epsilon_{31}^{dis*} (1 - \cos(2\pi \eta)) \, d\eta}{\int_{0}^{1} \phi \, d\eta}
\]  
(5.29)

Since the stress component \( \sigma_{31}^{dis*} \) is asymmetric, it becomes
where $\phi$ is the solution of equation (5.26) under applied stresses. As a first order approximation, assume that $\phi$ is independent of applied stress when applied stress is small. Therefore, it can be seen that there exists a linear relationship between dislocation velocity $v$ and applied stress $\sigma_{31}^0$.

5.3.3 Dislocation velocity and discretization effect

To examine numerically the relationship between the velocity of a dislocation and the applied stress, the motion of dislocations in two dimensions shown in Fig. 5.1 is simulated under different applied stresses. The velocities (the displacement of the dislocation within a fixed number of time steps) are calculated. Fig. 5.5a shows the velocity of the dislocation as a function of applied stresses and grid sizes for eigenstrain expressions (5.8). There are three observations. First, the dislocation velocity strongly depends on the grid size (i.e., discretization effect). It increases as the grid size decreases for a given applied stress. However, the velocity is convergent when the grid size $d^*$ is less than 1.0. Second, a linear relationship between the dislocation velocity and the applied stress exists for the convergent cases. From the phase-plane analysis discussed in the last section, the dislocation velocity can be calculated with
Fig. 5.5a Average velocity of a dislocation vs applied shear stress shows the effect of discretization.
Fig. 5.5b Average velocity of a dislocation vs applied shear stress shows the effect of different eigenstrain expressions.
The value \( S^* = 5.3(d_0 / t^*) \) calculated is in good agreement with the numerical result \( S^* = 5.1(d_0 / t^*) \) for the convergent cases. Finally, the fact, that the velocity tends to zero as the applied stress tends to zero, implies that no critical stress exists for moving an isolated dislocation. In other words, Peierls stress is not taken into account in this phase field model although the total energy includes the term ‘Peierls potential’. Any critical stress appearing in the cases with larger grid sizes comes from discretization effect. For a comparison, the same simulations are performed by using eigenstrain expressions (5.7). Similar discretization effect is observed. From Fig. 5.5b, it can be found that the velocity obtained by using eigenstrain expressions (5.7) is much smaller than that obtained by using eigenstrain expressions (5.8) under the same applied stress. This is consistent with the discussion in section 5.3 that part of the work done by the applied stress is spent on increasing the Burgers vector of the dislocation for the case of eigenstrain expression (5.7), and hence the corresponding dislocation velocity is reduced.

### 5.3.4 Average velocity of dislocations

The dynamic interaction between moving dislocation and diffusive solutes will affect the response of dislocations to applied stress, hence, the average velocity of dislocations. Fig. 5.6 presents the average velocity of a dislocation during 1200 simulation steps as a function of the ratio \( M^* \) of solute mobility to dislocation mobility,
overall composition \( c_0 \) and applied stress. It is quite apparent from the results shown in Fig. 5.6a that average velocity decreases with the increase in overall composition \( c_0 \) for a given \( M^* \) and applied stress \( \sigma_{31}^{0\sigma} \). The reason is the fact that higher overall solute composition causes more solute segregation near a moving dislocation, hence larger dragging stress. Three characteristic velocities of dislocations can be observed from Fig. 5.6a-b for any given overall solute composition and applied stress. One extreme case is that \( M^* \) tends to zero. This implies that solute diffusion becomes very slow compared to dislocation motion. As a result, solute segregation mainly occurs in the dislocation core region where a high driving force exists due to the large stress gradient. The dislocation velocity reaches maximum which is almost independent of the overall compositions, but depends on the magnitude of the applied stress.

Another extreme case is the instantaneous establishment of equilibrium solute segregation profile around a dislocation, i.e. solutes diffuse much faster than the dislocation motion when \( M^* \) becomes very large. The average dragging stress exerted on the dislocations by the solutes decreases, and tends to a constant. Such a constant dragging stress depends on the equilibrium solute segregation affected by the overall solute composition and the dislocation velocity or applied stresses. As a result, dislocation velocity increases and becomes a constant. Finally, it is shown that there exists a certain ratio \( M^* \) of solute diffusion mobility to dislocation mobility that leads to the minimum in dislocation velocity. From the results it can be found that such a \( M^* \) is independent of solute overall
Fig. 5.6a Average velocity of a dislocation as a function of $M^* = M / L d_0$ for different overall compositions under an applied stress $\sigma_{31}^* = 0.04$. 
Fig. 5.6b Average velocity of a dislocation as a function of $M^* = M / Ld_0$ for overall composition $c_0 = 0.15$ under different applied stresses.
composition but increases with the increase in applied stresses. The solute atmosphere and dragging stress at such a critical situation will be analyzed in the following sections.

### 5.3.5 Solute atmosphere

For a given overall solute composition \( c_0 = 0.15 \) and applied stress \( \sigma_{31} = 0.04 \), three characteristic profiles of solute atmospheres around a moving dislocation are shown in Fig. 5.7a-c. As expected, \( \mathcal{M} \) dramatically affects the size, shape and composition profile of solute atmospheres. It is important to notice the position of the dislocation with respect to the solute atmosphere. Comparing the solute atmospheres and average velocities for the two cases in Fig. 5.7b-c, we find that it is not necessarily true that higher segregation causes larger dragging stress. \( \mathcal{M} \) affects not only the solute atmosphere profile but also the relative position of the profile with respect to the dislocation, and thus the dragging stress. For the case of \( \mathcal{M} = 0.5 \) under different applied stresses \( \sigma_{31} = 0.06, 0.1 \) and 0.14, steady-state solute atmospheres form around moving dislocations. Fig. 5.7d-f show the steady-state atmospheres. We can see that the size of atmosphere region decreases with the increase in applied stress.

### 5.3.6 Portevin-Le Chatelier effect and dynamic dragging stresses

Portevin-Le Chartelier (PLC) effect in solid solutions is related to the dynamic interaction between diffusing solute atoms and mobile dislocations, i.e., an alternating
Fig. 5.7  Solute atmosphere around a moving dislocation in a solid solution with overall composition $c_0 = 0.15$. (a), (b) and (c) were obtained under applied stress $\bar{\sigma}_{31} = 0.04$ and with $M^* = 0.005, 0.2$ and 3.0 respectively; (d), (e) and (f) were obtained with $M^* = 0.5$ under different applied stresses 0.06, 0.1 and 0.14, respectively.
Fig. 5.8a Dislocation velocity under applied stress $\bar{\sigma}_{31}^* = 0.1$. 
Fig. 5.8b Dynamic dragging stress of solute atmosphere under applied stress $\sigma_{31} = 0.1$. 
process of the formation of solute atmosphere at dislocations and the unlocking of dislocations from their solute atmospheres. The Portevin-Le Chatelier effect [175-179] is characterized by a number of experimental observations such as the upper yield point, serration in the tensile stress vs strain curves, and abnormal yield stress which increases and then decreases as temperature increases. The average dislocation velocity as a function of time presented in section 5.6 exhibits similar phenomenon to the macroscopic Portevin-Le Chatelier effect. $M^*$ is the ratio of solute mobility to dislocation mobility. Dislocation mobility depends on the atomistic structure of the dislocation core. If we assume that the dislocation mobility is constant, Fig. 5.6 shows a relation between average dislocation velocity and solute mobility. For substitutional solutes, its mobility strongly depends on temperature. Solute mobility increases as temperature increases. Therefore, the $x$-axes in Fig. 5.6 can be viewed as temperature axes. All results in Fig. 5.6 demonstrate a common tendency, i.e., the average dislocation velocity decreases and then increases as temperature increases. Such a dependence of dislocation velocity implies that the macroscopic yield stress increases and then decreases with an increase in temperature, i.e. the Portevin-Le Chatelier effect.

The origin of Portevin-Le Chatelier effect in solute solution is the dynamic interaction between diffusing solute atoms and mobile dislocations. In order to examine the dynamic interaction, temporal dislocation velocities and dynamic dragging stress of solute atmospheres are calculated for the cases shown in Fig. 5.7a-c in which the dislocation has the characteristic velocities. Temporal dislocation velocity versus the distance of dislocation motion is plotted in Fig. 5.8a. A number of observations can be
made from the results. First, the formation of solute atmosphere slows down the
dislocation velocity to the characteristic average velocity. For example, the velocity
decreases from 0.45 to 0.29\(\left(\frac{d_0}{t^*}\right)\) after dislocation moves about 5~10\(d_0\) distance for
the case of \(M^* = 0.2\). Since in our simulation we assume there is no solute segregation
around the dislocation at \(t^* = 0\), the initial velocity should be the same at 0.45 for
different \(M^*\). Secondly, the dynamic interaction between the moving dislocation and its
solute atmosphere, which results in a temporal composition change at the dislocation
core, causes a periodic variation of dislocation velocity. It is found that the strength of
dynamic dragging corresponding to the amplitude of velocity oscillation is almost
independent of \(M^*\). However, the frequency of dislocation velocity oscillation depends
on \(M^*\). Finally, it is interesting to find that the average dislocation velocity decreases as
the frequency of dislocation velocity oscillation increases.

In continuum mechanics, the dragging stress of the solute atmosphere is defined
as the stress at the dislocation line. Fig. 5.8b presents the dragging stress of solute
atmosphere at dislocation line \((\eta = 0.5)\) during the dislocation motion for the three cases
in Fig. 5.7a-c. As expected, the dragging stress changes periodically during the
dislocation motion, and the change frequency of the dragging stress is consistent with that
of the dislocation velocity. In our phase field model, the dislocation core is spread out
within the glide plane. Therefore, the stress at the dislocation line \((\eta = 0.5)\) is not exactly
the total dragging stress of the solute atmosphere. However, it is found that the average
value of the dragging stress during a periodic variety of the dislocation velocity might reflect a total dragging stress.

5.4 Conclusion

A phase field model is developed for modeling the dynamic interaction between moving dislocations and diffusive solutes. Both the chemical potential of solid solution and elastic interaction among solutes and dislocations are taken into consideration. A new shape function is constructed which can eliminate the dependence of Burgers vector on applied stress in the previous phase field model of dislocation dynamics. A relationship among dislocation mobility coefficient, applied stress and dislocation velocity is established which can be used to determine the dislocation mobility coefficient for quantitative simulation. The simulation results using a single dislocation in a two-dimensional model system demonstrate that the model is able to describe correctly the dynamic interaction between diffusive solutes and moving dislocation. The dynamic dragging stress, average velocity of dislocation and solute flow around a moving dislocation can be obtained. It is shown that the dynamic interaction between solutes and dislocation results in the Portevin-Le Chatelier phenomena under certain ratios of solute mobility to dislocation velocity. It is straightforward to extend this model to alloy system with elastic inhomogeneity and arbitrary spatial defects.
Chapter 6

Quantitative Simulations of $\theta'$ Precipitation in Al-Cu Alloys

The low density combined with high strength has made aluminum alloys one of the primary materials used for automobile and aircraft applications, where higher strength-to-weight ratio is a major design consideration. The significant contribution to the high strength of heat-treatable aluminum alloys is due to fine spatial distributed precipitates formed from a supersaturated solid solution that will act as obstacles to moving dislocations. Composition, heat treatment and manufacturing technology all affect the precipitation reactions, hence, the microstructures and the strengthening response. Understanding well, especially in a quantitative manner, how these controlling factors exert their influences on microstructures is central for developing advanced aluminum alloys that could achieve the progressively desired level of performance.

Al-Cu alloys with copper contents of around 3 ~ 4.5 wt% Cu form the basis of an important class of heat treatable aluminium alloys. It is a system with multi-stage precipitation reactions involving transitional metastable phases which include Al solid solution phase (\(\alpha\) phase with a disordered fcc structure), metastable phases GPI, GPII (also known as \(\theta''\) phase) and $\theta'$-Al$_2$Cu, and thermodynamic stable $\theta$-Al$_2$Cu phase. Fig. 6.1 presents the Al-Cu phase diagram in terms of temperature (F) and Cu composition (wt%) at the Al-rich portion that is constructed from thermodynamic calculations [180].
Fig. 6.1 Al rich portion of the Al-Cu phase diagram.
The full precipitation sequence in a binary Al-Cu alloy is [181-182]: Solid solution $\rightarrow$ GPI $\rightarrow$ GPII $\rightarrow$ $\theta'$ $\rightarrow$ $\theta$. However, for a given alloy system, a number of experimental conditions such as the quenching rate, aging temperature and applied stresses affect the real precipitation sequence. For example, around 150 ~ 190°C the precipitation sequence starts with the appearance of GP zones, while the sequence begins directly with $\theta'$ precipitates if the aging temperature is higher than 190°C. The metastable $\theta'$ (Al$_2$Cu) precipitates are one of the primary strengthening precipitates in Al-Cu alloys. There are extensive experimental investigations about the atomistic structures and morphologies of different phases in Al-Cu alloys [183-189]. However, little is known about the effect of interfacial energy anisotropy, interfacial mobility anisotropy, coherent or semi-coherent stress field and applied stressed on the morphology of $\theta'$ precipitates [190].

In this chapter, a quantitative phase-field model is developed for simulating $\theta'$ (Al$_2$Cu) precipitation process in Al-Cu alloys using thermodynamic and kinetic data and the material properties as input. The effect of interfacial energy anisotropy, interfacial mobility anisotropy, coherent/or semi-coherent stress field and applied stressed on growth behavior and morphology of theta prime precipitates are systematically studied.
6.1 Review of experimental facts

6.1.1 Crystal structures

The structures of GP zones, \( \theta \) and \( \theta' \) phases have been identified [181, 183-189]. Fig. 6.2 presents the crystal structures of stable and metastable phases observed during precipitation in Al-Cu alloys. Generally, GPI is considered to be a monolayer of copper along \{1 0 0\} planes, while GPII (also called as \( \theta'' \)) consists of two or more \{100\} layers of copper atoms separated by three layers of Al [189-191]. Both GPI and GPII are coherent with the matrix. Although GPI structure is commonly accepted, there are different opinions on the GPII structure. For example, other possible GPII structure proposed by Guinier is a periodic arrangement of one layer of Al and 3 Cu-rich layers. Some people consider GPII just to be a coarsened form of GPI [192]. But some people consider GPII a separate ordered phase based on the discontinuity observed in the hardness curves. First-principle calculation shows that the GPII structure is energetically favorable [193], however, kinetic Monte Carlo method fails to prove the prediction of First-principle calculation.

The \( \theta' \)-Al\(_2\)Cu phase is a metastable precipitate. It has a tetragonal structure with an orientation relationship \( (100)_{\theta'} \parallel (100)_{\text{matrix}} \). Experimental results demonstrate that \( \theta' \) precipitate is partially coherent [93,94], and its shape is plate-like [94,97,194]. The broad face of a plate-like \( \theta' \) precipitate is coherent while the interface is semicoherent around the rim of the plates. The orientation relationship \( (100)_{\theta'} \parallel (100)_{\text{matrix}} \) and the tetragonal crystal structure imply that there are three orientational variants of \( \theta' \)
precipitates with their c-axes parallel to the three cubic axes of the fcc matrix. Fig. 6.3 is a transmission electron micrograph obtained from an Al-1.7at% Cu alloy aged to peak hardness at 190°C for 30 hours. The morphologies of two \( \theta' \) precipitate variants, which are edge-on, are clearly observed in Fig. 6.3 because the thin foil is viewed along a \( \langle 001 \rangle_{\text{matrix}} \) direction. Experimental results also show that the maximum hardness is always associated with the presence of \( \theta' \) precipitates in the microstructure [195,196]. Therefore, \( \theta' \) precipitates are considered as one of the most favorable strengthening precipitates in Al-Cu alloys. In the present work, we focus on simulating the precipitation of \( \theta' \) precipitates.

\( \theta \)-Al\(_2\)Cu phase has a tetragonal structure (see Fig. 6.2). It is thermodynamically stable phase, but kinetically unfavorable for direct precipitation from the solid solution, especially at temperatures below 250°C. The large difference of lattice constants between \( \theta \)-Al\(_2\)Cu phase and the matrix (see Fig. 6.2) results in a large interfacial energy and elastic energy, leading to a large nucleation barrier. Therefore, to overcome this kinetic barrier, the precipitation reaction of the equilibrium \( \theta \)-Al\(_2\)Cu phase often proceeds through metastable transition phases that gradually change in structure from fcc to tetragonal. As a result, the precipitates gradually lose coherency in the precipitation reaction. Therefore, \( \theta \)-Al\(_2\)Cu precipitates are incoherent and have irregular-shape. To maximize the strength of Al-Cu alloys, its formation is undesirable because incoherent precipitates often reduce the strength of alloys.
Fig. 6.2  Crystal structure of the stable and metastable phases observed during precipitation in Al-Cu alloys (reconstructed from Hornbogen [93]).
Fig. 6.3 Transmission electron micrograph associated with the maximum peak of hardness in an Al-1.7at\%Cu alloy aged at 190°C for 30 hours. The foils were oriented along $\langle 001 \rangle_{\text{matrix}}$. (from Ringer et al [197]).
6.1.2 Stress-free strain of $\theta'$ phase

Fig. 6.4 shows a schematic graph of a plate-like $\theta'$ precipitate in the matrix. According to the orientation relationship between $\theta'$ and the matrix and lattice constants of $\theta'$ and the matrix, the stress-free strains can be calculated by

\[
\begin{align*}
\varepsilon_x^* &= \varepsilon_y^* = \frac{a_{\theta'} - a_\alpha}{a_\alpha} \\
\varepsilon_z^* &= \frac{m c_{\theta'} - na_\alpha}{na_\alpha}
\end{align*}
\]  

(6.1)

where $a_{\theta'}$, $c_{\theta'}$ and $a_\alpha$ are lattice constants of $\theta'$ and the matrix, respectively. $m$ and $n$ are the numbers of unit cells in $\theta'$ and the matrix sides, i.e., $m$ $\theta'$ unit cells align with $n$ unit cells of fcc matrix across the interface around the rim of the plate-like precipitate. Based on first-principle calculations at 0K [95], the stress free lattice constants of fcc solid solution and $\theta'$ are

\[a_\alpha = 0.3989 \text{ nm}, \quad a_{\theta'} = 0.4019 \text{ nm}, \quad c_{\theta'} = 0.5684 \text{ nm}\]  

(6.2)

The stress-free strains are $\varepsilon_x^* = \varepsilon_y^* = 0.00746$ which are independent of $m$ and $n$. Substituting the above lattice constants with different interface configuration $m:n$ into equation (6.2), Table 6.1 lists the stress-free strain $\varepsilon_z^*$ vs $m:n$. It can be clearly seen that
an interface configuration of m:n=2:3 generates a minimum lattice mismatch along the
thickness direction of the plate-like $\theta'$ precipitates, leading to a compressive stress field
outside of the precipitate around the rim of the plate. A m:n=3:4 interface configuration
has a similar magnitude of lattice mismatch, but produces a tensile stress field. Other
interface configurations all result in a huge lattice mismatch that causes a large elastic
energy and interfacial energy, hence, is energetically unfavorable. Based on experimental
observations of the strain fields around $\theta'$ precipitates with different thickness using
electron microscope, Stobbs and Purdy [198] found that the minimum thickness of $\theta'$
precipitates is two unit cells. The estimated stress-free strain is about –4.3% similar to
m:n=2:3 interface configuration. Another commonly observed interface configuration in
their experiments is m:n=3:4 with a stress-free strain 7.0%. Therefore, we can conclude
that m:n=2:3 or m:n=3:4 should be the most possible interface configuration of $\theta'$
precipitates. In the present work, we assume the interface configuration is m:n=2:3, the
stress-free strain tensor is given by

$$
\varepsilon_{ij}^* = \begin{pmatrix}
0.00746 & 0 & 0 \\
0 & 0.00746 & 0 \\
0 & 0 & -0.051
\end{pmatrix}
$$

(6.3)
Table 6.1 Stress-free strain $\varepsilon_z$ in terms of interface configuration m:n

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
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<tr>
<td>1</td>
<td>41.4%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>41.4%</td>
<td>-5.1%</td>
<td>-29.3%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>41.4%</td>
<td>6.9%</td>
<td>-14.5%</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>41.4%</td>
<td>41.4%</td>
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<td>5</td>
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<td>41.4%</td>
</tr>
</tbody>
</table>
Fig. 6.4 (a) orientation relationship of a plate-like $\theta'$ precipitate, (b) two different interface configurations around the rim of the plate where the interface is incoherent.

(a)

(b)

$\theta'$ Phase

$m:n = 2:3$

$\varepsilon_z = -5.1\%$

$\theta'$ Phase

$m:n = 3:4$

$\varepsilon_z = 6.9\%$
6.1.3 Nucleation of θ’ precipitates

There are varying views concerning the nucleation or formation of θ’. Hardy and Heal [199] found that the formation of θ’ stems from a rearrangement of atoms within a high Cu concentration zone in the solid solution. This occurs by a gradual evolution of the crystal structure rather than by nucleating a new phase by forming an embryo. Another view considers that θ’ precipitates nucleate heterogeneously at the θ''/Al matrix interface or at defects such as dislocations. There are some experimental evidences that θ’ precipitate nucleates around dislocations [200,201]. It is also observed that small amount of cold work prior to artificial aging enhances age hardening in a number of Al-Cu-Mg alloys because of the introduction of dislocations that act as preferential nucleation sites [202-208]. These results suggest that nucleation is independent of GP zones or θ'', and the initial distribution of θ’ is highly heterogeneous which reflects the initial dislocation density in a particular grain. In addition, an analysis of the lattice mismatch between θ’ and the matrix shows that θ’ preferentially nucleates on a/2<110> dislocations, which can relieve the lattice mismatch in the <100> matrix directions. From an estimate of the elastic interaction between coherent stresses associated with the lattice mismatch and dislocation stress, two possible locations of θ’ nucleation are schematically drawn in Fig. 6.5.

Like defect stresses, an applied stress also affects the nucleation of precipitates. Li [209] first explained the phenomenon using the classical nucleation theory in which external work by the applied stress compensates the strain energy associated with the lattice misfit
of the coherent precipitate nuclei. Tanaka et al. [210] employed a chemical reaction rate approach [211,212] in which the applied stress effect was incorporated as a change in the binding energy due to elastic interactions among solute atoms. They found that a very small perturbation imposed on the binding energy corresponding to the stress effect might change the nucleation rate drastically, which was in agreement with their experimental observation in Fe–N single crystals. A directional applied stress might lead to preferred directional nucleation and the precipitate alignment. Hosford and Agrawal’s results for Al–3.98Cu aged at 210°C [213] show that the stress-orienting effect occurred during both nucleation and growth stages of the θ’-precipitates but was more effective during the nucleation stage which agrees with a recent phase-field simulation [105]. Using a two-step (low-temperature+ high-temperature) aging procedure Eto et al’s observation [214] demonstrated that the stress-orienting effect was initiated and determined during the nucleation stage. The particular variant(s) of Guinier Preston (GP) zones was/were preferentially formed under the directional stress and the aligned GP zones grew to θ’ plates through GP[II]. Sankaran’s explanation [215] took into account the preferred nucleation on the stress-oriented dislocation structures.

In the present work, we ignore the nucleation process that involves atomistic scale events. Therefore, in our simulations, embryos of the θ’ precipitates, which are larger than the critical nucleus size, are arbitrarily put into the simulation cell.
Fig. 6.5 Two possible locations for \( \theta' \) nucleation near a dislocation.
6.1.4 Growth behavior of θ’ precipitate

Although there exist some experimental measurements about the lengthening and thickening of θ’ precipitates, the growth behavior still lacks complete understanding. A diffusion-controlled lengthening, i.e., it follows a $t^{1/2}$ law, can be reasonably explained based on the bulk diffusivity estimated from the measured lengthening rate. However, Boyd and Nicholson’s experiments [96,97] showed that at the beginning of aging the lengthening of θ’ precipitates followed a $t^{1/3}$ law. For the thickening, experimental measurements [216,217] showed that the thickening was much slower than the lengthening. Aaronson and Laid [216,217], based on their kinetic measurements and interface structure observations, concluded that thickening was interface-controlled with the ledge growth mechanism. However, Chen and Doherty [218,219] analyzed the thickening kinetics of plate-like precipitates. They found a diffusion-controlled thickening behavior, and showed that the thickening with the ledge mechanism does not imply an interface-controlled growth. A slower thickening kinetics was due to the lack of growth ledges. The ledge nucleation on a coherent interface needs to overcome a high-energy barrier because of the large lattice mismatch along the ledge’s edge. Hence, at the early stage of aging, there is not plenty of growth ledges. During this time, lengthening dominates and the aspect ratio increases monotonously. In the later stage of aging, sufficient growth ledges become available, and the thickening speeds up. It is expected that the aspect ratio decreases, and the precipitate return to its equilibrium shape. The kinetic measurements of Merle et al. [98,99], Sankaran et al. [100,101] and Lui et al [220] demonstrated that the aspect ratio of precipitates was changing during the aging
process. The measured aspect ratio increases monotonously to a maximum value and then decreases monotonously. These are consistent with Doherty’s analysis. In the present work, the growth of a single precipitate and the effect of the elastic energy, the interface mobility anisotropy and the interface energy anisotropy will be simulated systematically.

6.1.5 Equilibrium shape and interfacial energy

The equilibrium shape of a precipitate is determined by the minimization of interface energy if the effects of other energies such as elastic energies are ignored. For the case that the interfacial energy does not depend on orientation, the shape which gives the minimum surface to volume ratio is a sphere. In crystalline materials the interface energy is always dependent on orientation. The orientation dependence of interfacial energy can be represented by a radial vector whose magnitude is proportional to the energy. This is the so–called gamma-plot. The equilibrium shape can then be found by the Wulff construction [221]. The observed shape of \( \theta' \) precipitates is plat-like, which has a broad and flat interface and a large aspect ratio. This illustrates that the \( \theta' \) precipitate has a strong interfacial energy anisotropy. In addition, a plat-like precipitate implies that the gamma-plot should at least have two cusps shown as in Fig. 6.6. A direct experimental measurement of interfacial energies is difficult although there are some attempts to estimate the interfacial energies of \( \theta' \) precipitates. For example, the interface energies obtained by Boyd and Nicholson [96,97] were 1530 and 21520 mJ/m² for coherent and semicoherent interfaces, respectively. Aaronson et al [217] estimated
Fig. 6.6  Equilibrium shape of a precipitate from the Gamma plot and the Wulff Construction.
theoretically the interfacial energy that includes two energetic contributions. One arises from the difference in chemical bonding across the interface, and the other arises from the presence of misfit strain and/or misfit dislocations at the interface. Aaroson et al ignored the misfit strain at the coherent interface and replaced the lattice misfit at semi-coherent interface with equivalent dislocations. The estimated interface energies were about 30mJ/m² and 350mJ/m². At T=0K, first-principle calculation has been employed to determine the interfacial energies of θ' precipitates [95,106]. Assuming the interfacial configuration m:n=2:3, the interfacial energies from first-principles calculation are 235mJ/m² and 615mJ/m² for coherent and semi-coherent interfaces, respectively. It is interesting to find that the first-principle calculation and the simple theoretical estimates of Aaronson and Laird [217] produce a similar value for the semi-coherent interfacial energy. However, the coherent interface energy obtained from the first-principle calculation is one order of magnitude larger than that from Aaronson’s estimate. The interfacial energy anisotropy based on first-principle calculations is 3, which is four times smaller than Aaronson’s estimate. Such a difference gives a completely different estimate of the equilibrium shape of θ' precipitates.

6.1.6 Morphology of precipitates and interface mobility

The morphological evolution of θ' precipitates is determined by the kinetics of interface migration or, more specifically, the interface mobility and the driving force. The interface mobility is known to be a sensitive function of alloy composition, interface atomistic structure, and direction of interface migration and temperature. The driving
force could be from the chemical free energy for the θ' precipitation (growth), the interfacial energy (coarsening), or the interface curvature, internal stresses associated with composition and/or structural inhomogeneity and applied stresses. If the driving force is small, the interface velocity (V) can be approximated by a linear relation,

\[ V = MP \]  

(6.4)

where \( M \) is the interface mobility, and \( P \) is the driving force. The mobility is usually assumed to be a unique property of the interface and, therefore, should be independent of the nature of driving force. Generally speaking, a coherent interface has smaller mobility compared to semi-coherent and incoherent interfaces. Experimental [222] and simulation [223] data suggest that \( M \) is an Arrhenius function of temperature \( T \)

\[ M = M_0 e^{-\Delta H / kT} \]  

(6.5)

where \( \Delta H \) is the activation energy for interface migration.

Recent experiments [224-226] show that stresses may affect the interface mobility. The change in the mobility with stresses in certain cases can be linearly proportional to the stress. For a moving planar interface under uniform a uniaxial stress, the mobility increases with increasingly tensile stress. The stress dependence of the
interfacial mobility has been measured during the amorphous to crystalline transformation in Si [225]. The mobility, $M$, was found to depend upon stress $\sigma$ as

$$M(\sigma) = M_0 \exp(V_{ij} \sigma / kT)$$

where $\varepsilon_{ij}$ is the activation strain, $M_0$ is the mobility of the interface in the absence of stress, $k$ is Boltzmann's constant and $T$ is temperature.

Like the measurement of interface energy, it is difficult to directly measure the interface mobility. However, indirect experimental method and atomistic simulations such as the Monte Carlo method [227] and Molecular dynamics simulations [228] can be employed to examine the interface mobility. Unfortunately, as far as I know, there is no available data about the interface mobility of $\theta'$ precipitates in the literatures. Based on the observation of $\theta'$ precipitate thickening and lengthening behavior, it is clear that the interface mobility anisotropy may play an important role in $\theta'$ growth. Therefore, the present phase-model takes the interface mobility anisotropy into account, which are defined as a function of interface normal directions.

### 6.1.7 Effect of stresses on the morphology of precipitates

Stress is often present in solid-solid phase transformations, since the lattice constants of the phases are usually different, or due to an applied stress. Stresses give rise to elastic energy that can affect the equilibrium properties of a system and the driving
force of a phase transformation. It can also alter the diffusion coefficients in the solids [229,230]. For a system with coherent interfaces, i.e., the interfacial energy is small, and the total elastic energy is usually comparable to the total interfacial energy. Therefore, the stress can significantly modify the kinetics of precipitation, hence, the morphology of precipitates. This subject has been reviewed extensively in [4,127,231,233].

An applied stress not only affects the nucleation stage, but also the growth and coarsening stages of precipitation. The effect of a directional applied stress on the orientation distribution of precipitate structures has been investigated extensively in many age-hardenable alloy systems [105,217,233-252]. Particularly, for the Al–Cu system, Hosford and Agrawal [213] found that an alignment of θ’ precipitates takes place during aging of an Al–3.98wt%Cu alloy at 210°C under either a compressive or tensile stress of 48 MPa, whereas there was no noticeable orienting effect under a stress of 34.5 MPa. However, Eto et al. [214] could not reproduce these results under the same aging conditions using an alloy with lower copper content—Al–3.71wt%Cu. Their results demonstrated that the alignment of θ’ precipitates is due to the alignment of GP zone where θ’ precipitates form. Li and Chen [105] treated the stress effect with a phase-field model and conducted a computer simulation of nucleation and growth of θ’-precipitates in an Al–Cu system in two-dimensions. Focusing only on the θ’phase without possible precursor GP zones, they demonstrated that the stress-orienting effect occurred during both nucleation and growth stages of the θ’-phase but was more effective during the nucleation stage. This result is somewhat contradictory with Eto et al’s observation [214] in Al–3.71Cu but agrees with Hosford and Agrawal’s results for Al–3.98Cu aged at
210°C [213]. Skrotzki et al. [248] found that there were threshold values of the stress that must be exceeded for the formation of preferentially oriented plate-shaped precipitates in the tensile-stress-aged samples of Al–5Cu and of Al–Cu–Mg–Ag alloys. Hosford and Agrawal [253] proposed a different orienting mechanism based on stress-biased diffusion of solute atoms which was once suggested by Stobbs et al. [254].

6.1.8 Mechanical properties

In Al–Cu alloys, solute strengthening and precipitate strengthening coexist, but precipitate strengthening provides the main contribution. Experimental measurements show that the hardness or yield stresses depend on aging time, aging temperature and Cu composition as shown in Fig. 6.7 [255]. It can be easily seen that with the increase of aging time, the hardness increases, and then decreases for any given Cu composition and aging temperature. A lower aging temperature and a higher Cu composition usually result in a higher yield stress. Note the various phases that lead to the peaks in hardness. We can find that for a temperature of less than 150°C, the peak of hardness is found to occur with the formation of $\theta''$, while for a temperature larger than 190°C, the maximum hardness is associated with the presence of $\theta'$ in the microstructure. Although $\theta''$ precipitates result in higher strength compared to $\theta'$, enhancement of kinetics (shorter aging time to reach peak hardness) without compromising a lot on strength (by aging at higher temperatures) presents $\theta'$ as the most favorable strengthening precipitate.
Fig. 6.7  Hardness curves vs aging time (from Silcock [255])


6.2 Phase-field model

Fig. 6.8a shows one of three $\theta'$ orientation variants which has a broad interface with normal direction along $\langle 001 \rangle$. In order to describe the $\theta'$ (Al$_2$Cu) precipitation process in Al-Cu alloy, four field variables, i.e. composition field $c(x,t)$ associated with Cu composition and three order parameter fields $\eta_i(x,t)$ ($i = 1,2,3$) associated with three $\theta'$ orientation variants are employed. We define the order parameter $\eta_i(x,t) = 1$ in $\theta'$ precipitates and $\eta_i(x,t) = 0$ in $\alpha$ phase. In order to simplify the description in the deviation, in the following sections, we only consider one orientational variant $\eta_3(x,t)$ in the system. So two field variables are needed to describe the system, i.e., composition field $c(x,t)$ and order parameter field $\eta$. It is straightforward to rewrite the formula for a general case with three orientational variants.

Following the chemical free energy construction in Kim’s solidification model [91], the chemical free energy of the system is written as

$$G(c,\eta,T) = (1 - h(\eta))f^\alpha(c_\alpha,T) + h(\eta)f^{\theta'}(c_{\theta'},T) + wg(\eta)$$  \hspace{1cm} (6.6)

where $g(\eta)$ is a double-well potential, the function $h(\eta)$ is a monotonously changing function from $h(0) = 0$ to $h(1) = 1$. $w$ is the height of the double well potential. In solid-solid phase transformation, the total free energy $F(c,\eta,T)$ includes chemical free energy and interfacial energy as well as elastic energy $E^{\text{elast}}$. 
\[ F(c, \eta, T) = \int \left[ \frac{1}{\Omega_0} G(c, \eta, T) + \frac{k^2(\varphi)}{2} \left| \nabla \eta \right|^2 + E_{\text{elast}} \right] d^3x \]  

(6.7)

where \( \Omega_0 \) is the mole volume, \( k(\varphi) \) is gradient coefficient which is associated with anisotropically interfacial energy. \( \varphi \) is the angle between two normal directions of interface at \( x \) and broad interface of the \( \theta' \) precipitate as shown in Fig. 7.9.

Like Kim’s solidification model [91], we considered the interfacial region to be a mixture of \( \alpha \) phase and \( \theta' \) phase with compositions \( c_\alpha \) and \( c_{\theta'} \) and with the same chemical potential, i.e. \( c_\alpha \) and \( c_{\theta'} \) satisfy the following set of equations for a binary system,

\[
c = [1 - h(\eta)]c_\alpha + h(\eta)c_{\theta'}
\]

(6.8)

\[
\frac{\partial f^\alpha (c_\alpha)}{\partial c_\alpha} = \frac{\partial f^{\theta'} (c_{\theta'})}{\partial c_{\theta'}}
\]

(6.9)

There are two main advantages of Kim’s approach compared to the WBM model [256]. One is the fact that for an interface at equilibrium, there is no contribution of the actual chemical free energy, \( f^\alpha \) and \( f^{\theta'} \), to the total interfacial energy. The interfacial energy and interfacial width are entirely determined by the double-well potential and the gradient energy coefficient in the artificial phase field. As a result, a larger interfacial width may be employed to fit the same interfacial energy, thus increasing the length scale of a phase-field simulation even with the usual numerical methods using uniform grids. From the
mathematic point of view, Kim’s model is interface thickness free as they stressed [91] by choosing the depth of the double-well potential \((w)\). However, our numerical results show that the depth of the double-well potential \((w)\) cannot be chosen too small compared to the actual chemical driving force described by \(f^\alpha\) and \(f^{\theta'}\) for phase transformations during a phase-field simulation, and thus the interfacial width that one can use is also limited. Otherwise numerically stability may develop in a phase-field simulation, leading to incorrect path for the microstructure evolution. Furthermore, the additional constraint conditions (6.8) and (6.9) requires the numerically solve \(c_\alpha\) and \(c_{\theta'}\) for each set of \(c\) and \(\eta\) at each time step, and this process can be computationally very expensive. The other advantage of Kim’s model is that we found that it is able to directly use a potential of compound, i.e., which is only defined at a specific composition. This is one of our motivations to extend Kim’s model to simulate \(\theta'\)-Al\(_2\)Cu precipitation process in Al-Cu alloys.
Fig. 6.8  (a) Coordinate system associated with $\theta'$, (b) Definition of $\varphi$ which is used to describe the interfacial energy and mobility anisotropies.
6.2.1 Chemical free energy

The chemical free energy of $\alpha$ (FCC solid solution) and $\theta'$ phases are from Murray based on thermodynamic assessment [180]. They have the following forms,

$$f^\alpha(c_\alpha, T) = RT[c_\alpha \ln(c_\alpha) + (1 - c_\alpha) \ln(1 - c_\alpha)]$$
$$+ c_\alpha(1 - c_\alpha)[(-24085 - 18.18944T) + (40399.8 - 3.91235T)(1 - 2c_\alpha)]$$
$$+ (-19683 + 16.06993T)(-1 + 3(1 - 2c_\alpha)^2)/2] \quad [J / mol]$$
(6.10)

$$f^\theta(c_{\theta'}, T) = -9245.8 + 0.579T \quad [J / mol]$$
(6.11)

where $c_\alpha$ and $c_{\theta'}$ are the mole fraction of Cu atom in $\alpha$ and $\theta'$ phases, respectively, T is the absolute temperature, and R is the ideal gas constant. The chemical free energies versus the composition of Cu atoms are plotted in Fig. 6.9 at given temperatures. Since $\theta'$ phase is modeled as a line compound, its chemical free energy is defined at one point $c_{\theta'} = 1/3$. With the constraint conditions (6.8 and 6.9), for given composition $c$ and phase field $\eta$ if we assume the composition of $\theta'$ precipitates changes in a very small region around the equilibrium composition $c_{\theta'} = 1/3$, and the derivative $\frac{\partial f^\theta(c_{\theta'})}{\partial c_{\theta'}}$ at $c_{\theta'} = 1/3$ is undefined, then the constraint conditions are satisfied automatically for $c_{\theta'} = 1/3$ and $c_\alpha$ with
\[ c_\alpha = \frac{c - h(\eta)c^c_{\theta'}}{1 - h(\eta)} \quad (6.12) \]

Therefore, for free energies of solid solution and a compound, we can analytically obtain \( c_\alpha \) and \( c_{\theta'} \) from the constraint conditions for each set of \( c \) and \( \eta \) at each time step. It should be pointed out that when \( \eta \rightarrow 1 \) there are multiple solutions of the constraint conditions, but we can choose \( c_{\theta'} = c^c_{\theta'} = 1/3 \) and \( c_\alpha = c^c_\alpha \) based on the equilibrium conditions of the real system. In our simulations, two sets of free energy functions are tested. One is the actual free energy function described by equations (6.10 and 6.11). The other consists of parabolic approximations of the actual free energies for both of \( \alpha \) (FCC solid solution) and \( \theta' \) phases, i.e.

\[
\begin{align*}
 f^\alpha(c_\alpha, T) &= A_0 + A_1 c_\alpha + A_2 c^2_\alpha \\
 f^{\theta'}(c_{\theta'}, T) &= B_0 + B_1 c_{\theta'} + B_2 c^2_{\theta'}
\end{align*} \quad (6.13)
\]

where constants \( A_i \) and \( B_i \) are determined by fitting the values of the actual free energies, first and second derivatives at equilibrium compositions for a given temperature. With the parabolic approximation, the constraint conditions becomes,

\[
\begin{align*}
 c &= (1 - h(\eta))c_\alpha + h(\eta)c_{\theta'} \\
 A_1 + 2A_2 c_\alpha &= B_1 + 2B_2 c_{\theta'}
\end{align*} \quad (6.14)\]
Therefore, for given $c$ and $\eta$ at each time step, we also can analytically calculate $c_{c}$ and $c_{\theta'}$ from (6.14).

![Chemical free energies of $\alpha$ (FCC solid solution) and $\theta'$ phases calculated from equations (6.10) and (6.11) at different temperatures.](image)

Fig. 6.9  Chemical free energies of $\alpha$ (FCC solid solution) and $\theta'$ phases calculated from equations (6.10) and (6.11) at different temperatures.
6.2.2 Elastic energy

The third term in equation (6.7) represents the elastic energy associated with the compositional and structural inhomogeneity. Since the mechanical equilibrium is often established much faster than any other material processes, for any given microstructure, the system is always at mechanical equilibrium

\[
\frac{\partial \sigma_{ij}}{\partial r_j} = 0 \quad (6.15)
\]

\[
\sigma_{ij} = \lambda_{ijkl}(\epsilon_{kl}(r) - \epsilon_{kl}^0(r, c, \eta)) \quad (6.16)
\]

where \(\sigma_{ij}\) is the local elastic stress, \(r_j\) is the \(j\)th component of the position vector, \(\sigma\), \(\lambda_{ijkl}\) is the elastic stiffness tensor which may vary with space, \(\epsilon_{jk}(r)\) is the total strain state at a given position in a microstructure, and \(\epsilon_{kl}^0(r)\) is the local stress-free strain or transformation strain or eigenstrain which is also a function of position through its dependence on field variables. The method described in Chapter 3 will be used to obtain the elastic solution of the mechanical equilibrium equation (6.15). Then, the elastic energy density can be calculated

\[
E_{elas}^{cl} (r, c, \eta) = \frac{1}{2} \sigma_{ij}(\epsilon_{ij} - \epsilon_{ij}^0) \quad (6.17)
\]

Since the stress-free strain \(\epsilon_{kl}^0(r)\) is a function of phase-field variables, the elastic energy density depends on phase-field variables and thus the microstructure.
We employed two sets of phase-field variables, i.e., composition field $c$ and order parameter field $\eta$ to describe the microstructure during the precipitation process in Al-Cu alloys. For a given orientational $\theta'$ variant, the stress-free strain $\varepsilon_{ij}^0(r)$ could be described in three different ways

$$
\begin{align*}
\varepsilon_{ij}^0(r) &= \varepsilon_{ij}^0(c(r)) \\
\varepsilon_{ij}^0(r) &= \varepsilon_{ij}^0(\eta(r)) \\
\varepsilon_{ij}^0(r) &= \varepsilon_{ij}^0(c(r), \eta(r))
\end{align*}
$$

(6.18)

Since the stress-free strains reflect the lattice mismatch, these different forms of stress-free strains should be same in terms of the position vector, $r$, for a given microstructure. However, we have notice that the driving force of microstructure evolutions is the variation of total free energy with respect to the field variables, it is clear that the forms of stress-free strains will affect the driving force, hence the microstructural evolution. For simplicity, we assume the stress-free strains are a function of the order parameter field variable $\eta$. It is written as

$$
\varepsilon_{ij}^0(r) = \begin{pmatrix}
0.00746 & 0 & 0 \\
0 & 0.00746 & 0 \\
0 & 0 & -0.051
\end{pmatrix} \eta^2
$$

(6.19)

Therefore, the elastic energy density only depends on the order parameter field $\eta$. 

6.2.3 Kinetic equations

In all phase-field models, the temporal and spatial evolution of the field variables follows the same set of kinetic equations. A conserved field, composition field $c$, evolves with time according to the Cahn-Hilliard equation [31] (Cahn 1961), or simply the diffusion equation in the case that no gradient energy is introduced for the conserved variable, whereas the non-conserved fields, order parameter field $η$, are governed by the Allen-Cahn equation [257] (Allen and Cahn 1977), i.e.

$$\frac{\partial η}{\partial t} = -L(ϕ)\frac{\partial F}{\partial η} = \frac{L(ϕ)}{Ω_0}\left[-Ω_0\frac{\partial G}{\partial η} - Ω_0\frac{\partial}{\partial η}\left(\frac{κ(ϕ)}{2} |∇ η|^2\right) - Ω_0\frac{\partial E^{ ela}}{\partial η}\right]$$ (6.20)

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(\frac{D(η, T)}{G_{cc}} \nabla (\frac{\partial G}{\partial c})\right)$$ (6.21)

With the total free energy (6.6), they can be rewritten as

$$\frac{\partial η}{\partial t} = \frac{L(ϕ)}{Ω_0}\left[-Ω_0\frac{\partial}{\partial η}\left(\frac{κ(ϕ)}{2} |∇ η|^2\right) + h'(η)[f^a(c_α) - f^α(c_α)] \right.$$

$$\left.-(c_α - c_α')\frac{\partial f^a}{\partial c_α'}\right] - w'g(η) - Ω_0\frac{\partial E^{ els}}{\partial η}$$ (6.22)

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(\frac{D(η, T)}{G_{cc}} (G_{cη}∇ η + G_{cc}∇ c)\right)$$

$$= \nabla \cdot (D(η, T)∇ c) + \nabla \cdot (D(η, T)h'(η)(c_α - c_α')∇ η)$$ (6.23)

together with the constraint conditions,

$$c = (1 - h(η))c_α + h(η)c_α$$, (6.24)
\[
\frac{\partial f^{\alpha}(c_\alpha)}{\partial c_\alpha} = \frac{\partial f^{\theta'}(c_\theta')}{\partial c_\theta'},
\]

where \(D(\eta, T)\) is diffusion coefficient, and \(L(\phi)\) is interface mobility coefficient. In this model there are two sets of variables \((c, \eta)\) and \((c_\alpha, c_\theta')\). Their relationship is described by equations (6.24 and 6.25).

### 6.3 Determination of model parameters

There are three unknown model parameters in the evolution equation (6.20 and 6.21), i.e., \(L(\phi)\), \(\kappa(\phi)\) and \(w\) which relate to materials constants such as interface mobility \(M(\phi)\), interface thickness \(2\lambda(\phi)\) and interface energy \(\sigma(\phi)\). For a quantitative simulation, we first need to establish the relationships between these model parameters and material constants. To do so, we consider a system with a flat interface between two coexisting isotropic phases \(\theta'\) and \(\alpha\). The system can be viewed as one-dimensional problem. In the following sections, the relationships between model parameters and materials constants will be derived by analyzing equilibrium and kinetic properties of evolution equation (6.20 and 6.21) using \(g(\eta) = \eta^2 (1 - \eta)^2\) and \(h(\eta) = 3\eta^2 - 2\eta^3\).

#### 6.3.1 Equilibrium solution

At equilibrium, both the order parameter field and composition field become independent of time. Let \(c_\alpha(x)\) and \(\eta_\alpha(x)\) denote the equilibrium profiles of composition and order parameter field in one dimension. If the effect of elastic energies on
equilibrium properties is ignored, and the gradient coefficient $\kappa(\varphi)$ is assumed to be constant $\kappa$, from kinetic equations (6.20 and 6.21), we have

\[
\frac{-\partial G}{\partial \eta_0} + \Omega_0 \kappa^2 \frac{d^2 \eta_0}{d^2 x} = 0
\]  
\[
\frac{d}{dx} \left( \frac{D(\eta_0, T)}{G_{\alpha c_0}} \frac{d}{dx} \left( \frac{\partial G}{\partial c_0} \right) \right) = 0
\]

(6.26)  
(6.27)

At equilibrium the chemical potential should be constant throughout the system, hence, equation (6.27) is equivalent to

\[
\frac{\partial G}{\partial c_0} = G^e_c
\]

(6.28)

where $G^e_c$ is constant.

From equations (6.6), (6.8) and (6.9), we have

\[
\frac{\partial G}{\partial c_0} = \frac{\partial f^\alpha (c_\alpha)}{\partial c_\alpha} = \frac{\partial f^\varphi (c_\varphi)}{\partial c_\varphi}
\]

(6.29)

Therefore, $c_\alpha(x)$ and $c_\varphi(x)$ are constant, and equal to the equilibrium compositions,

\[
c_\alpha(x) = c^e_\alpha \quad \text{and} \quad c_\varphi(x) = c^e_\varphi
\]

(6.30)
Substituting $c_\alpha(x) = c_\alpha^e$ and $c_\beta(x) = c_\beta^e$ into equation (6.24), we have the equilibrium composition

$$c_0(x) = (1 - h(\eta_0(x)))c_\alpha^e + h(\eta_0(x))c_\beta^e$$  \hspace{1cm} (6.31)

Now let us find the equilibrium solution $\eta_0(x)$ of Equation (6.26). Substitute free energy $G$ (6.6) and solution (6.30) into equation (6.26), it becomes

$$\Omega_\eta \kappa^2 \frac{d^2 \eta_0}{dx^2} + h'(\eta_0)[f^\alpha(c_\alpha^e) - f^\beta(c_\beta^e) - (c_\alpha^e - c_\beta^e) \frac{\partial f^\alpha(c_a) = c_a^e}{\partial c_a}] - wg'(\eta_0) = 0$$  \hspace{1cm} (6.32)

After multiplying $d\eta_0/dx$ on both sides of equation (6.32) and integrating it from $x = -\infty$ to $x = \infty$, we get

$$f^\alpha(c_\alpha^e) - f^\beta(c_\beta^e) - (c_\alpha^e - c_\beta^e) \frac{\partial f^\alpha(c_a) = c_a^e}{\partial c_a} = 0$$  \hspace{1cm} (6.33)

Equations (6.29) and (6.33) show the well-known equilibrium condition

$$G_e = f^\alpha(c_\alpha^e) = f^\beta(c_\beta^e) = \frac{f^\alpha(c_\alpha^e) - f^\beta(c_\beta^e)}{c_\alpha^e - c_\beta^e}$$  \hspace{1cm} (6.34)
Therefore, equation (6.33) can be rewritten

\[
\Omega_0 \kappa^2 \frac{d^2 \eta_0}{dx^2} = wg'(\eta_0)
\] (6.35)

Multiply \( d\eta_0 / dx \) on both sides of the equation above,

\[
\Omega_0 \kappa^2 \frac{1}{2} \frac{d}{dx} \left( \frac{d\eta_0}{dx} \right)^2 = \frac{d}{dx} \left\{ wg(\eta_0) \right\}
\] (6.36)

we have

\[
\frac{1}{2} \Omega_0 \kappa^2 \left( \frac{d\eta_0}{dx} \right)^2 = wg(\eta_0)
\] (6.37)

Integrating equation (6.37) from \( x = -\infty \) to \( x = \infty \) with \( g(\eta) = \eta^2(1 - \eta)^2 \) and the following boundary conditions,

\[
x = -\infty, \eta = 1, \ g(\eta = 1) = 0, \ h(\eta = 1) = 0
\]

\[
x = \infty, \eta = 0, \ g(\eta = 0) = 0, \ h(\eta = 0) = 0
\] (6.38)

\[
\frac{d\eta(x = -\infty)}{dx} = 0
\]

\[
\frac{d\eta(x = \infty)}{dx} = 0
\]
we can get the equilibrium phase field $\eta_0(x)$

$$
\eta_0(x) = \frac{1}{2} \left[ 1 - \tanh \left( \sqrt{\frac{w}{\Omega_0}} x \right) \right]
$$

(6.39)

### 6.3.2 Interfacial energy

For an equilibrium interface $c_0(x)$ and $\eta_0(x)$, the interfacial energy (interfacial energy per unit area) can be calculated [130]

$$
\sigma = \frac{\Delta F}{S} = \frac{\int \left[ \frac{1}{\Omega_0} (G(c_0, \eta_0, T) - G_0(c_0, \eta_0, T)) + \frac{\kappa_0^2}{2} (\nabla \eta_0)^2 \right] dV}{S}
$$

(6.40)

$$
= \int \left[ \frac{\omega \eta}{\Omega_0} + \frac{\kappa^2}{2} \left( \frac{d\eta_0(x)}{dx} \right)^2 \right] dx
$$

$$
G_0(c_0, \eta_0, T) = (1 - h(\eta_0)) f^\alpha (c_\alpha^e, T) + h(\eta_0) f^\beta (c_\beta^e, T)
$$

where $S$ is the interfacial area and $G_0(c_0, \eta_0, T)$ is the bulk equilibrium free energy density as a function of composition represented by the common tangent line for a binary system.

With equation (6.37), the interface energy is given by

$$
\sigma = \kappa^2 \int_{-\infty}^{\infty} \left( \frac{d\eta_0(x)}{dx} \right)^2 dx
$$

(6.41)
For an interface at equilibrium, the total gradient energy is half of the total interfacial energy. Analytical expressions for the interfacial energy in terms of free energy parameters and the gradient energy coefficients are only available for very simple cases that an analytical solution for the equilibrium profile of field variable across the interface can be derived. For example, in our case we have an analytical solution (6.39) with the double well potential \( g(\eta) = \eta^2(1-\eta)^2 \). Substitute the solution into equation (6.41), a relationship between the interface energy and model parameters is obtained

\[
\sigma = \frac{\kappa \sqrt{w/\Omega_0}}{3\sqrt{2}}
\]  

(6.42)

From equation (6.39), we have

\[
d\eta_0 = \sqrt{\frac{2wg(\eta_0)}{\Omega_0 \kappa^2}} dx
\]

(6.43)

If we define that \( \xi \leq \eta_0 \leq 1-\xi \) is the interface, the interface thickness \( 2\lambda \) can be calculated by

\[
2\lambda = \int_{\xi}^{1-\xi} \frac{\sqrt{\Omega_0 \kappa^2}}{2 \sqrt{wg(\eta_0)}} d\eta_0 = \alpha \sqrt{2} \frac{\kappa}{\sqrt{w/\Omega_0}}
\]

(6.44)
where $\alpha$ is a constant which depends on $\xi$ (the definition of the interface). When $\xi = 0.1$, $\alpha = 2.2$. When $\xi = 0.05$, $\alpha = 2.94$. Equations (6.42) and (6.44) show the relationship between model parameters (the height of double well potential $w$ and gradient coefficient $\kappa$) and material constants (interface energy $\sigma$ and interface thickness $2\lambda$).

For the specific Al-Cu alloy system, $\theta'$ precipitates have strong interface energy anisotropy. A number of approaches have been proposed to describe the interfacial energy anisotropy in phase-field models. One straightforward and most often employed approach is to make the square root of the gradient coefficient have the same directional dependence as the interfacial energy (according to relation (13)). Another approach is to add higher order gradient energy terms [258-261]. In the present work, the interfacial energy anisotropy is described in terms of the normal of the interface as

$$
\sigma(\varphi) = \frac{\sigma_0}{1 + \gamma} \begin{cases} 
1 + \gamma_1 + \gamma_2 \sin(\varphi), & -\pi / 2 \leq \varphi \leq -\pi / 2 + \varphi_0 \\
1 + \gamma \cos(\varphi), & -\pi / 2 + \varphi_0 \leq \varphi \leq \pi / 2 - \varphi_0 \\
1 + \gamma_1 - \gamma_2 \sin(\varphi), & \pi / 2 - \varphi_0 \leq \varphi \leq \pi / 2 
\end{cases}
$$

(6.45)

where $\sigma_0$ is the interfacial energy at $\varphi = 0$, $\gamma_1 = \gamma \cos(\varphi_0) / \sin(\varphi_0)$, $\gamma_2 = \gamma / \sin(\varphi_0)$, $\gamma$ is determined by the interfacial anisotropy, and $\varphi_0 = \pi / 200$ is chosen as a very small angle to describe the cusps [262]. Equation (6.45) reflects a cylindrical symmetry of the interfacial energy for plate-like $\theta'$ precipitates. The gama plot of the interface energy has
two cusps at \( \varphi = \pm \pi / 2 \) for describing the flat interface of \( \theta' \) precipitates. As a result, the interfacial energy along the edge is assuming isotropic.

### 6.3.3 Thin-interface limit

In this section we focus on deriving the relationship between the phase field mobility coefficient and the interface kinetics coefficient, which is a proportionality constant between the driving force for an interface motion and the interface moving velocity. Let us consider a system with a flat interface which moves with a constant velocity \( V \). In a moving coordinate system with the same velocity \( V \), we can rewrite kinetic equations (6.20) and (6.21) by using the following transformations

\[
x' = x - V t, \quad t' = t
\]

\[
c(x,t) = c(x'), \quad \eta(x,t) = \eta(x') \tag{6.46}
\]

\[
\frac{\partial \eta(x,t)}{\partial t} = \frac{\partial \eta(x')}{\partial t} = \frac{\partial \eta}{\partial x'} \frac{\partial x'}{\partial t} = -V \frac{\partial \eta}{\partial x'}
\]

\[
\frac{\partial \eta(x,t)}{\partial x} = \frac{\partial \eta(x')}{\partial x} = \frac{\partial \eta}{\partial x'} \frac{\partial x'}{\partial x} = \frac{\partial \eta}{\partial x'}
\]

where \( x' \) is the coordination in the moving coordinate system. In the new coordinate system, the equations (6.20) and (6.21) are rewritten as
\[-V \frac{\partial \eta}{\partial x'} = \frac{L}{\Omega_0} \left[ \Omega_0 \kappa^2 \frac{d^2 \eta}{d x'^2} + h'(\eta)[f^a(c_a) - f^\theta(c_{\theta'}) - (c_a - c_{\theta'}) \frac{\partial f^a(c_a)}{\partial c_a}] - wg'(\eta) \right] \tag{6.47} \]

\[-V \frac{\partial c}{\partial x'} = \frac{d}{d x'} \left( \frac{D(\eta, T)}{G_{cc}} \frac{d}{d x'} f^a_{c_a}(c_a) \right) \tag{6.48} \]

Integrating equation (6.48) from \(x' = -\lambda\) to \(x'\)

\[-V[c(x') - c_{\theta'}^\text{int}] = \frac{D(\eta)}{G_{cc}} \frac{d}{d x'} f^a_{c_a}(c_a) \bigg|_{x'=-\lambda} - \frac{D(\eta)}{G_{cc}} \frac{d}{d x'} f^a_{c_a}(c_a) \bigg|_{x'=-\lambda} \]

\[= \frac{D(\eta)}{G_{cc}} \frac{d}{d x'} f^a_{c_a}(c_a) - \frac{D(\eta)}{G_{cc}} G_{cc} \frac{dc(x')}{dx'} \bigg|_{x'=-\lambda} \tag{6.49} \]

where \(c_{\theta'}^\text{int}\) is the composition of \(\theta'\) phase at the interface \(x' = -\lambda\). Assume

\[D(\eta) \bigg|_{x'=-\lambda} = 0.0 \quad \text{or} \quad \frac{dc(x')}{dx'} \bigg|_{x'=-\lambda} = 0.0, \quad \text{then} \]

\[\frac{d}{d x'} f^a_{c_a}(c_a) = -\frac{G_{cc}}{D(\eta)} V[c(x') - c_{\theta'}^\text{int}] \tag{6.50} \]

Since \(f^a_{c_a}(c_a) = f^\theta_{c_{\theta'}}(c_{\theta'})\), we have

\[\frac{d}{d x'} f^\theta_{c_{\theta'}}(c_{\theta'}) = -\frac{G_{cc}}{D(\eta)} V[c(x') - c_{\theta'}^\text{int}] \tag{6.51} \]
Integrating equation (6.50) and (6.51) from \( x' = -\lambda \) to \( x' \),

\[
f_{\alpha}^{\alpha}(c_{\alpha}) = f_{\alpha}^{\alpha}(c_{\alpha}^{\text{int}}) - \int_{-\lambda}^{x} \frac{G_{cc}}{D(\eta)} V[c(x) - c^{\text{int}}_{\theta}] \, dx
\]  

\[
f_{\alpha}^{\alpha}(c_{\alpha}) = f_{\alpha}^{\theta'}(c_{\alpha}^{\text{int}}) - \int_{-\lambda}^{x} \frac{G_{cc}}{D(\eta)} V[c(x) - c^{\text{int}}_{\theta'}] \, dx
\]  

Assume there is a very small fluctuation in composition profile of traveling wave, to first order,

\[
c_{\alpha} = c_{\alpha}^{e} + \delta c_{\alpha}
\]

\[
c_{\theta'} = c_{\theta'}^{e} + \delta c_{\theta'}
\]

\[
f^{\alpha}(c_{\alpha}) = f^{\alpha}(c_{\alpha}^{e}) + f^{\alpha}(c_{\alpha}^{e}) \delta c_{\alpha}
\]

\[
f^{'\theta'}(c_{\theta'}) = f^{'\theta'}(c_{\theta'}^{e}) + f^{'\theta'}(c_{\theta'}^{e}) \delta c_{\theta'}
\]

\[
f_{\alpha}^{\alpha}(c_{\alpha}) = f_{\alpha}^{\alpha}(c_{\alpha}^{e}) + f_{\alpha}^{\alpha}(c_{\alpha}^{e}) \delta c_{\alpha}
\]

we have

\[
f^{\alpha}(c_{\alpha}) - f^{'\theta'}(c_{\theta'}) - (c_{\alpha} - c_{\theta'}) f_{\alpha}^{\alpha}(c_{\alpha}) = -(c_{\alpha}^{e} - c_{\theta'}^{e}) (f_{\alpha}^{\alpha}(c_{\alpha}) - f_{\alpha}^{\alpha}(c_{\alpha}^{e}))
\]

\[
= f^{\alpha}(c_{\alpha}^{e}) - f^{'\theta'}(c_{\theta'}^{e}) - (c_{\alpha}^{e} - c_{\theta'}^{e}) f_{\alpha}^{\alpha}(c_{\alpha})
\]  

(6.55)
Multiply eq.(6.47) with $\frac{d\eta}{dx}$, and integrate from $[-\lambda, \lambda]$,

$$
-\frac{V\Omega_0}{L} \int_{-\lambda}^{\lambda} (\frac{d\eta}{dx})^2 dx' = \int_{-\lambda}^{\lambda} \left[ f^\alpha (c_a) - f^\theta (c_\theta) - (c_a - c_\theta) \frac{\partial f^\alpha (c_a)}{\partial c_a} \right] h'(\eta) d\eta
$$

(6.56)

Using equation (6.51), (6.55) and $f^\alpha (c_a^e) - f^\theta (c_\theta^e) = (c_a^e - c_\theta^e) f^\alpha c_a (c_a^e)$,

$$
V = \frac{(c_a^e - c_\theta^e)(f^\alpha c_a (c_a^e) - f^\theta c_\theta (c_\theta^e))}{\frac{\Omega_0}{L} \int_{-\lambda}^{\lambda} (\frac{d\eta}{dx})^2 dx' \left[ f^\alpha c_a (c_a^e) - f^\theta c_\theta (c_\theta^e) \right]}
$$

(6.57)

To the first order in the Peclet number, $p = 2\lambda V / \tilde{D}$ ($\tilde{D}$ is average interface diffusivity), and assume $\eta(x') = \eta_0(x')$ and $c(x') = c_0(x')$, we can calculate interface velocity $V$ for given interfacial mobility coefficient $L$ by

$$
V = M \left\{ \frac{1}{\Omega_0} (c_a^e - c_\theta^e) [G^e c_a - f^\theta c_\theta (c_\theta^e)] \right\}
$$

(6.58)

Where $M$ is the interface kinetic coefficient,
\[
\frac{1}{M} = \frac{\sigma}{L \kappa^2} - \frac{\kappa \zeta(c_{\alpha}^e, c_{\theta}^e)}{D_i \sqrt{2w/\Omega_0}}
\]  

(6.59)

and

\[
\zeta(c_{\alpha}^e, c_{\theta}^e) = \frac{1}{\Omega_0} \int_0^1 \frac{h(\eta)[1-h(\eta)]}{(1-h(\eta)) f_{c_{\alpha}^e c_{\alpha}}(c_{\alpha}^e, T) + h(\eta) f_{c_{\theta}^e c_{\theta}}(c_{\theta}^e, T) \eta(1-\eta)} \, d\eta
\]  

(6.60)

Equation (6.59) shows the relationship between \(M\) and \(L\).

### 6.4 Model parameters used in the simulation

In the sections above, the relationships between model parameters and material constants are established. For given material constants, interface energy \(\sigma(\phi)\), interface thickness \(2\lambda(\phi)\) and interface kinetic coefficient \(M(\phi)\), the model parameters \(w\), \(\kappa(\phi)\) and \(L(\phi)\) can be determined by

\[
\sigma(\phi) = \frac{\kappa(\phi) \sqrt{w/\Omega_0}}{3\sqrt{2}}
\]  

(6.61)

\[
2\lambda(\phi) = \alpha \sqrt{2} \frac{\kappa(\phi)}{\sqrt{w/\Omega_0}}
\]  

(6.62)
\[
L(\varphi) = \frac{\sigma(\varphi)}{\kappa^2(\varphi)} \frac{1}{M(\varphi)} \left( \frac{1}{D_i \sqrt{2w/\Omega_0}} + \kappa(\varphi) \zeta(c_o^e, c_o^e) \right)
\]

Input parameters in simulations include the grid spacing \( \Delta x \), the interface thickness \( 2\lambda \), the constant \( \alpha \) in equation (6.62), the interfacial energies of semi-coherent interface, mole volume \( \Omega_0 \), and \( \varphi_0 \) in equation (6.45). With these parameters, the model parameters \( w , \kappa(\varphi) \) can be determined. For example, consider the \( \theta' \) precipitate shown in Fig. 6.8, with \( \Delta x = 1nm \), the semi-coherent interface thickness of \( \theta' \) precipitates \( 2\lambda = 6\Delta x \) at \( \varphi = 0 \), the interfacial energy \( \sigma_1 = 600mJ/m^2 \), mole volume \( \Omega_0 = 10^{-5} m^3/mol \), and \( \alpha = 2.2 \), the height of the double potential can be calculated from equation (6.61) and (6.62).

\[
w = \frac{6\sigma_1 \alpha}{2\lambda}
\]

The coherent interface energy at \( \varphi = \pi/2 \) is taken to be \( \sigma_2 = 200mJ/m^2 \). From equation (6.61) and (6.45) with the values of \( \sigma_1, \sigma_2 \) and \( \varphi_0 = \pi/200 \), \( \kappa(\varphi) \) can be fitted. Since there is no available experimental data of interface kinetic coefficient \( M(\varphi) \), the interface mobility coefficient \( L(\varphi) \) are artificially defined as
\[
L(\varphi) = \frac{L_0}{1 + \beta} \begin{cases} 
1 + \beta_2 + \beta_1 \sin(\varphi), & -\pi/2 \leq \varphi \leq -\pi/2 + \varphi_0 \\
1 + \beta \cos(\varphi), & -\pi/2 + \varphi_0 \leq \varphi \leq -\pi/2 - \varphi_0 \\
1 + \beta_2 - \beta_1 \sin(\varphi), & \pi/2 - \varphi_0 \leq \varphi \leq \pi/2
\end{cases}
\] 

(6.65)

where \( L_0 \) is the interface mobility coefficient at \( \varphi = 0 \), \( \beta_1 = \beta \cos(\varphi_0)/\sin(\varphi_0) \), \( \beta_2 = \beta/\sin(\varphi_0) \), and \( \beta \) is determined by the interface mobility anisotropy. \( \varphi_0 = \pi/200 \) is chosen as a very small angle, which implies that only the broad interface has a very small mobility. In simulations, the system is assumed to be elastically homogeneous. The elastic constants of Al-Cu alloys [243] are

\[
C_{11} = 108 \text{GPa}; \quad C_{12} = 61 \text{GPa}; \quad C_{44} = 29 \text{GPa}
\]

For simplicity, assume that the diffusion coefficient \( D(\eta,T) \) only depends on temperature \( T \) [180],

\[
D(T) = D_0 \exp \left[ -\frac{Q}{RT} \right] 
\]

(6.66)

where \( D_0 = 0.45 \text{cm}^2/\text{s}, \ Q = 31.8 \text{kcal/mol} \), and \( R \) is the universal gas constant. The precipitate temperature \( T = 500 \text{K} \) is used in simulations.
Using dimensionless variables $t^* = D_0 t / l^2$ and $x^* = x / l$ where $l$ represents the grid spacing ($\Delta x$) or the characteristic length, the kinetic equations (6.22) and (6.23) are simplified to

$$
\frac{\partial \eta}{\partial t} = L^*(\varphi)[\nabla^* \cdot \kappa^*(\varphi)^2 \nabla^* \eta + h'(\eta)[f^{a*}(c_{a}) - f^{\theta*}(c_{\theta})]$$
$$- (c_a - c_{\theta}) \frac{\partial f^{a*}(c_{a})}{\partial c_a} - w^* g'(\eta) - \frac{\partial E^{els*}}{\partial \eta} (6.67)
$$

$$
\frac{\partial c}{\partial t} = \nabla^* \cdot (D^*(T)\nabla^* c) + \nabla^* \cdot (D^*(T)h'(\eta)(c_a - c_{\theta})\nabla^* \eta) (6.68)
$$

where

$$L^*(\varphi) = \frac{L(\varphi)C_{44} l^2}{D_0}; \quad \kappa^*(\varphi)^2 = \frac{\kappa(\varphi)}{C_{44} l^2}; \quad f^{a*}(c_a) = \frac{f^a(c_a)}{C_{44} \Omega_0}; \quad f^{\theta*}(c_{\theta}) = \frac{f^\theta(c_{\theta})}{C_{44} \Omega_0};
$$

$$w^* = \frac{w}{C_{44} \Omega_0}; \quad E^{els*} = \frac{E^{els}}{C_{44}}; \quad D^*(T) = \frac{D(T)}{D_0}
$$

In simulations, periodic boundary conditions in x-, y- and z-directions are employed. The kinetic equations are solved numerically using Fourier-Spectral method [159].

**6.5 Results and discussions**

Extensive testing on the dimensionless time $t^*$ and the grid spacing or the characteristic length $l = \Delta x$ were first conducted to ensure the stability of numerical
solutions. For a given precipitation temperature $T$, all material properties such as the chemical free energies $f^a(c_a)$ and $f^{\theta'}(c_{\theta'})$, interfacial energy, diffusion coefficient are known. With a few grid points to resolve the thickness of coherent interface, the numerical stability mainly depends on the value of grid spacing $l = \Delta x$, or $w$, the height of double-well potential with given dimensionless time $t^*$ and dimensionless interface mobility coefficient $L^*$. The maximum thickness which can be used is limited by the chemical free energies of phases in the system. For example, for a given interfacial energy, the smaller the height of potential shown in Fig. 6.10 is, the thicker interface can be used. To verify this, consider a one dimensional model system with a flat interface. The chemical free energies of two phases are described by two parabolic functions. The height of potential $\Delta f^r$ is similar to that in Al-Cu alloys at $T = 500K$. The interfacial energy $\sigma = 200 mJ.m^2$ is used. The interfacial thickness is assumed to be $6 \Delta x$. Scale $\Delta f^r$ by a scale factor, the dependence of maximum grid spacing on the height of potential $\Delta f^r$ is listed in Table 6.2. It is clearly seen that the maximum grid spacing increases with the decrease of $\Delta f^r$. If interfacial thickness is $4 \Delta x$, the maximum grid spacing increases.

Testing simulations in a one-dimensional model show that the dimensionless time $t^* = 0.05$ and the grid spacing or the characteristic length $l = \Delta x \leq 2 nm$ can give a stable numerical solution for the simulation of $\theta'$ precipitation. For two and three-dimensional simulation a smaller grid spacing $l = \Delta x \leq 1 nm$ should be used because of the effect of the interface curvature of precipitates and elastic energy on equilibrium properties, hence,
numerical stability. Therefore, the grid spacing $l = \Delta x = 1\,\text{nm}$ and $t^* = 0.05$ are used in all simulations except for very special cases.

Table 6.2 The dependence of maximum grid spacing on the height of potential $\Delta f$

<table>
<thead>
<tr>
<th>Scale factor</th>
<th>$\Delta x \times 10^{-9},\text{m}$</th>
<th>$w\ (J/mol)$</th>
<th>$\Delta f\ (J/mol)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>22000</td>
<td>7500</td>
</tr>
<tr>
<td>0.2</td>
<td>1.8</td>
<td>3666</td>
<td>1500</td>
</tr>
<tr>
<td>0.1</td>
<td>3.5</td>
<td>1650</td>
<td>750</td>
</tr>
<tr>
<td>0.02</td>
<td>18</td>
<td>366</td>
<td>150</td>
</tr>
<tr>
<td>0.002</td>
<td>200</td>
<td>26</td>
<td>15</td>
</tr>
</tbody>
</table>
Fig. 6.10 The height of chemical potentials in two phase equilibrium system.
6.5.1 Velocity of a flat interface

Based on the discussions presented in the last several sections, the interface mobility coefficient $L^*$ is the only remaining parameter to be determined. To evaluate the role of this parameter, a one-dimensional model of $\theta^o$ precipitate growth is considered. The velocity of a flat interface and composition evolutions are simulated for different values of $L^*$. Fig. 6.11 shows a $\theta^o$ precipitate placed in the center of a simulation cell. The size of the precipitate and the simulation cell are $40\Delta x$ and $2048\Delta x$, respectively. $\Delta x$ is 0.5nm. The initial composition is set to be the equilibrium composition $c=0.33$ in the precipitate and $c=0.08$ in the $\alpha$ phase (the solid solution). The moving distance of the interface as a function of time and square root of time is presented in Fig. 6.12a and Fig. 6.12b, respectively. It can be clearly seen that the relationship between the moving distance and time becomes increasingly linear as $L^*$ decreases, and more parabolic as $L^*$ increases. These reveal a fact that the model parameter $L^*$ can be used to describe the growth of $\theta^o$ precipitates either interface-controlled or diffusion-controlled. For the set of model parameters of Al-Cu alloys at $T = 500K$, the simulation results illustrate that when $L^* < 0.05$, the growth is interface-controlled, and diffusion-controlled when $L^* > 50$.

In one dimension, the growth of a $\theta^o$ precipitate can also be modeled using the commercial program (DICTRA) [263] assuming a sharp interface and purely diffusion-controlled growth. In the case of constant diffusion coefficient, one can easily find an analytic solution for the growth kinetics. Fig. 6.13 presents a comparison of the evolved
composition profiles obtained by the phase-field simulation and calculated with an analytical solution. Dashed lines and solid lines represent the analytical solution and the numerical solution, respectively. It can be seen that the evolved composition profiles obtained by two methods are in good agreement except at the interface region where the analytical solution has a sharp interface while the phase-field solution has a diffusion interface.

Fig. 6.11 One-dimensional model of a \( \theta' \) precipitate growth.
Fig. 6.12 Moving distance of the interface as a function of time, (a) vs t (b) vs $\sqrt{t}$
Fig. 6.13 Comparison of composition profiles obtained by the phase-field simulations and analytical solutions at different times.
6.5.2 Equilibrium shape of an isolated $\theta'$ precipitate

In this section, the equilibrium shape of an isolated $\theta'$ precipitate in two dimensions is simulated. The equilibrium shape is determined by the minimization of the total free energy of the system which includes interface energy and elastic energy. The kinetic process, i.e., how the precipitate reaches its equilibrium shape, should not affect the equilibrium shape. Therefore, the simulations take the interface energy anisotropy and elastic energy into account while the interface mobility anisotropy is ignored. In the simulations, an elliptic $\theta'$ precipitate with a long axis $a = 45\Delta x$ and a short axis $b = 20\Delta z$ is initially placed in the center of the simulation cell $256\Delta x \times 128\Delta z$. The precipitate and the matrix are assigned their equilibrium compositions, $c = 0.33$ and $c = 0.0072$, respectively. The thickness of the coherent interface is assumed to be $6\Delta x$.

In order to eliminate the effect of grid numerical pinning, a smaller grid size $\Delta z = 0.333\Delta x = 0.333\, nm$ in $z$-direction is used. As a result, the dimensionless time $t^*$ should be reduced. Fig. 6.14 shows the evolution of an initially non-equilibrium precipitate without the contribution of elastic energy. The blue region denotes the matrix and the red for the precipitate. The transition region of the color implies the interfacial region. Since the interfacial energy of the coherent interface ($\sigma_i = 200mJ/m^2$) is lower than that of the semi-coherent interface ($\sigma_i = 600mJ/m^2$), it can be seen that the thickness of the coherent interface is smaller than that of the semi-coherent interface. The composition evolution along the long and short axes of the elliptic precipitate is showed
Fig. 6.14 Morphological evolution of a precipitate from an initially non-equilibrium shape to equilibrium in the absence of elastic energy.
Fig. 6.15 Composition evolution, (a) along the long axis, and (b) along the short axis of the elliptic precipitate in the absence of elastic energy.
in Fig. 6.15a-b, respectively. It is found that the initially elliptic precipitate becomes a plate-like precipitate at equilibrium. The aspect ratio of the equilibrium precipitate is close to 3 as it can be expected from the Wulff construction. A closer observation shows that the equilibrium compositions in both precipitate and matrix are slightly higher than that calculated from the chemical free energies. It can be explained with the Gibbs Thomson effect that the solubility increases with the decrease of precipitate size or the curvature increase of precipitate interfaces.

Fig. 6.16 shows the morphological evolution of the precipitate with the contribution of elastic energy. It can be seen that the effect of stresses around the \( \theta' \) precipitate on the equilibrium shape is obvious. From the stress-free strain tensor (6.19) associated with the \( \theta' \) precipitate, it is found that the maximum component of the stress-free strain is \( \varepsilon_{33} = -0.051 \), which generates a large tensile stress \( \sigma_{33} \) in both precipitate and matrix. A thinner precipitate results in a lower elastic energy. Unlike the case without elastic energy, the thickness of the precipitate is smaller in the presence of the elastic energy, i.e., the elastic energy increases the aspect ratio of the precipitate. In this case the aspect ratio is about 8.5. The composition evolution along the long and short axes of the elliptic precipitate is showed in Fig. 6.17a-b. It can be seen that the presence of elastic energy shifts the equilibrium composition in both the precipitate and the matrix.
Fig. 6.16  Morphological evolution of a precipitate from an initially non-equilibrium shape to equilibrium in the presence of elastic energy.
Fig. 6.17 Composition evolution, (a) along the long axis, and (b) along the short axis of the elliptic precipitate in the presence of elastic energy.
6.5.3 Growth of an isolated $\theta'$ precipitate

In this section, the phase-field model is employed to study the growth behavior of a single $\theta'$ precipitate. In the simulations, the interfacial energy and mobility are described by functions (6.45) and (6.65), respectively. The model parameters are $\sigma_0 = 600 mJ/m^2$, $\gamma = 2$, $\beta = 1000$ and $L^* = 100$. The nucleation process of the precipitate is ignored, so an elliptic $\theta'$ precipitate with a long axis $a = 40 \Delta x$ and a short axis $b = 20 \Delta z$ is initially placed in the center of the simulation cell $256 \Delta x \times 512 \Delta z$. The initial composition in the precipitate and the matrix are $c = 0.33$ and $c = 0.05$, respectively. The thickness of the coherent interface is assumed to be $6 \Delta x$. In order to eliminate the effect of grid numerical pinning, a smaller grid size $\Delta z = 0.333 \Delta x = 0.333 nm$ in $z$-direction is used. Fig. 6.18 and Fig. 6.19 show the morphological evolution of the single precipitate without and with the elastic energy, respectively. The figures are contours of composition field. The white lines in the figure show the contour lines with $c = 0.03$. From Figs. 6.18 and 6.19, it is found that the stresses associated the lattice mismatch between the precipitate and the matrix speed up lengthening and slow down thickening. The composition evolution along the length and thickness directions is plotted in Fig. 6.20 and Fig. 6.21. It can be clearly seen that the velocity of the interface decreases as time increases. Fig. 6.22 plots the moving distance of the interface as a function of time. These curves are fitted with non-linear functions. For example, the thickness is described by $H = H_0 + H_1 t''$. For comparison, the fitted curves are also plotted in the Fig. 6.22 with solid or dashed lines. A large fitting error demonstrates that one function cannot completely describe the whole growth process.
The precipitate growth might be separated into three stages, i.e., at initial stage, growth stage and later growth stage. At the initial stage, because a small precipitate with a sharp interface is put into the simulation cell, such an initial condition might be different from that in a real situation. The precipitate undergoes an initial relaxation in both composition and shape. At the latter growth stage, the interaction among precipitates due to periodic boundary conditions becomes strong. Therefore, for the growth behavior of an isolated precipitate, the data at initial and later growth stage should be removed. The fitted curves and functions are redrawn in Fig. 6.23. These results show that the thickening follows $t^{2/3}$ law. Elastic energy affects the lengthening law, which leads to a faster lengthening and a slower thickening compared with the case without elastic energies. The growth behavior of an isolated precipitate is also simulated for an extreme case, i.e., the coherent interface is almost immobile. In this case, a smaller interface mobility coefficient $\beta = 2000$ in the coherent interface, and a larger grid spacing $\Delta z = \Delta x = 1nm$ in $z$-direction are used. The other model parameters are the same as that in the previous case. Fig. 6.24 shows lengthening and thickening without elastic energies for different initial thickness ($H_0 = 24, 30 and 36nm$). It is evident that the length increases linearly while the thickness remains the same for different initial thickness. The thinner the precipitate is, the faster it grows. In the presence of elastic energy, the lengthening and thickening kinetics are plotted in the Fig. 6.25. One can reach the same conclusion, i.e., elastic energy speeds up the lengthening of the precipitates.
Fig. 6.18  Morphological evolution of a single precipitate represented by the composition field in the absence of elastic energy. The white line is a contour of composition $c = 0.03$. 
Fig. 6.19  Morphological evolution of a single precipitate represented by the composition field in the presence of elastic energy. The white line is a contour of composition $c = 0.03$. 
Fig. 6.20  Composition evolution, (a) along the length direction, and (b) along the thickness direction in the absence of elastic energy.
Fig. 6.21  Composition evolution, (a) along the length direction, and (b) along the thickness direction in the presence of elastic energy.
Fig. 6.22  Lengthening and thickening of an isolated precipitate.
Fig. 6.23 Lengthening and thickening of an isolated precipitate at the growth stage.
Fig. 6.24  Lengthening and thickening of a precipitate without elastic energy and the coherent interface is immobile.
Fig. 6.25 Lengthening and thickening of a precipitate with elastic energy and the coherent interface is immobile.
6.5.4 Coarsening of two precipitates in two dimensions

Coarsening is driven by the reduction in the interface energy. During coarsening, the oversize size of precipitates increases. As a result, elastic energy increases. If the change in the elastic energy during coarsening is comparable to the change in the interface energy, the coarsening process depends on the competition between the interface energy decrease and elastic energy increase. In the simulations, two precipitates, a small one and a large one, are placed in the simulation cell. It is checked that the size of the small one is larger than the critical size. The simulation cell and model parameters are the same as that used in section 6.5.3, but the precipitate and the matrix have their own equilibrium compositions $c = 0.33$ and $c = 0.0072$, respectively. Fig. 6.26 and 6.27 show the morphological evolution for the cases without and with elastic energies, respectively. It can be found that the small precipitate gradually disappears in both cases. After that, the single precipitate will reach its equilibrium shape as presented in section 6.5.2. Notice the time shown in the figure, it can be seen that the elastic energy slows down the coarsening process. These results demonstrate that the developed phase-field model can properly describe the coarsening process.
Fig. 6.26 Coarsening of two precipitates in the absence of elastic energy.
Fig. 6.27 Coarsening of two precipitates in the presence of elastic energy.
6.5.5 Growth of multi-precipitates in two and three dimensions

All derivations in section 6.2 are carried out for one \( \theta' \) orientational variant \( \eta_i \) which has a coherent interface with a normal direction \( \langle 001 \rangle \). In three dimensions, there are three orientational variants. The function \( h(\eta) \) and \( g(\eta) \) are replaced by

\[
\begin{align*}
\eta_1^2 + \eta_2^2 + \eta_3^2 - 2(\eta_1^3 + \eta_2^3 + \eta_3^3) \\
(\eta_1^2 \eta_2^2 + \eta_3^2 \eta_1^2 + \eta_2^2 \eta_3^2) \\
+ \eta_1^2 (\eta_2^4 + \eta_3^4) + \eta_2^2 (\eta_1^4 + \eta_3^4) + \eta_3^2 (\eta_2^4 + \eta_1^4) + \eta_1^2 \eta_2^2 \eta_3^2
\end{align*}
\]

(6.69)

The stress-free strain tensor is defined as

\[
\varepsilon_0^0(r) = \begin{pmatrix}
-0.051 & 0 & 0 \\
0 & 0.00746 & 0 \\
0 & 0 & 0.00746
\end{pmatrix} \eta_i^2 \\
+ \begin{pmatrix}
0.00746 & 0 & 0 \\
0 & -0.051 & 0 \\
0 & 0 & 0.00746
\end{pmatrix} \eta_2^2 \\
+ \begin{pmatrix}
0.00746 & 0 & 0 \\
0 & 0.00746 & 0 \\
0 & 0 & -0.051
\end{pmatrix} \eta_3^2
\]

(6.70)

The chemical free energy and total free energy of the system are given by

\[
G(c, \eta_1, \eta_2, \eta_3, T) = \left(1 - h(\eta_1, \eta_2, \eta_3)\right) f^{\alpha}(c_\alpha, T) \\
+ h(\eta_1, \eta_2, \eta_3) f^{\beta}(c_\beta, T) + f(\eta_1, \eta_2, \eta_3),
\]

(6.71)
\[ F(c, \eta_1, \eta_2, \eta_3, T) = \int \left[ \frac{1}{\Omega_0} G(c, \eta_1, \eta_2, \eta_3, T) + \sum_{i=1}^{3} \frac{k(\varphi_i)^2}{2} \left| \nabla \eta_i \right|^2 + E_{\text{elast}} \right] \text{d}x \quad (6.72) \]

where \( \varphi_i \) is the angle between two normal directions of interface at \( x \) and broad interface of the \( i \)th \( \theta' \) precipitate variant.

Kinetic equations of the order parameter fields and concentration field can be described as,

\[
\frac{\partial \eta_i}{\partial t} = -L(\varphi_i) \frac{\delta F}{\delta \eta_i} = \frac{L(\varphi_i)}{\Omega_0} \left[ -\frac{\partial G}{\partial \eta_i} - \frac{\kappa(\varphi_i)^2}{2} \left| \nabla \eta_i \right|^2 \right] - \frac{\partial E_{\text{elast}}}{\partial \eta_i} \quad (6.73)
\]

\[
\frac{\partial c}{\partial t} = \nabla \cdot \left( \frac{D(\eta_1, \eta_2, \eta_3, T)}{G_{cc}} \nabla (\frac{\partial G}{\partial c}) \right) \quad (6.74)
\]

with the constraint conditions

\[
c = \left[ 1 - h(\eta_1, \eta_2, \eta_3) \right] c_{\alpha} + h(\eta_1, \eta_2, \eta_3) c_{\varphi}
\]

\[
\frac{\partial f^\alpha}{\partial c_{\alpha}} = \frac{\partial f^\varphi}{\partial c_{\varphi}} \quad (6.75)
\]

It is clear that three variables \( \eta_1, \eta_2, \) and \( \eta_3 \) are equivalent in the phase-field model described above. If any two of the three variables are equal to zero, the kinetic equations are degenerated to equations (6.20) and (6.21). Therefore, all results deduced in section (6.2) are applicable to any one of \( \eta_1, \eta_2, \) and \( \eta_3 \).
In the simulations of the growth of multi-precipitates in two and three dimensions, an uniform grid spacing \((\Delta x = \Delta y = \Delta z = 1nm)\) are employed to enlarge the simulation cell and time step \(t^*\). The same expressions (6.45) and (6.65) and parameters: \(\sigma_0 = 600mJ/m^2\), \(\gamma = 2\), \(\beta = 1000\) and \(L_0^* = 100\) are used just by replacing \(\varphi\) with \(\varphi_i\). Simulation results show that the coherent interfaces are mobile with such an uniform grid and interface mobility anisotropy. Some extent of numerical grid pinning is observed at the coherent interface because the grid spacing is a little large for coherent interfaces, to completely eliminate the grid pinning the grid spacing should be \(\Delta x = \Delta y = \Delta z = 0.33nm\).

6.5.5.1 Growth of multi-precipitates in two dimensions

60 small precipitates with different sizes are randomly placed into a 2D simulation cell \(1024\Delta x \times 1024\Delta x\). In the precipitates, the composition is \(c = 0.33\), and the order parameter fields \(\eta_1\) or \(\eta_3\) are assigned to be 1 which depends on the orientation of the precipitates. In the matrix, the composition is \(c = 0.05\), and the order parameter fields \(\eta_1\) and \(\eta_3\) are assigned to be 0. The morphological evolutions of the precipitates are shown in Fig. 6.28. It can be clearly seen that the lengthening of precipitates is much faster than thickening, which consists with experimental observations. Some typical configurations of precipitates are the same as that observed in the experiments shown in Fig. 6.29. For example, when one precipitate hits another precipitate which has a different orientation, it stops growing. As a result, a “T” like precipitate configuration is formed as marked by “T” in the Fig. 6.28 and 6.29. When two precipitates with same orientations grow in opposite directions and hit each other, they connect or coarsen only
if the spacing between the precipitates is very small as marked by “C” in the Figures.

The simulation results reveal that the coarsening behavior of plat-like precipitate should be totally different from that of spherical precipitates, which could be explained by the difference in composition fields and precipitate shapes. For plate-like precipitates the composition field with large gradient is localized around the ram of the precipitate, which is a very small fraction of the interface area while localized around the whole interface for a spherical precipitate. Two particles connect or coarsen depends on the overlap of their composition and/or parameter fields. As a result, the connection and coarsening of plate-like precipitates are mostly controlled by the interaction among the fields around the rams of precipitates. Therefore, the probability of connection or coarsening of two plate-like precipitates is small compared to spherical precipitates. More simulations are needed to reveal the coarsening behavior of $\theta'$ precipitates. This will be left for future work.
Fig. 6.28  Growth of multi-precipitates in two dimensions.
Fig. 6.29 SEM graph of $\theta'$ precipitates from Weiland [180].
6.5.5.2 Growth of multi-precipitates in three dimensions

Because of the limitation of computer resources, it is hard to perform a large-scale 3D simulation even with a parallel code. However, to demonstrate the performance of the developed phase-field model in 3D, the growth of two precipitates is simulated in a small simulation cell $128\Delta x \times 64\Delta x \times 128\Delta x$. The simulation includes interface energy anisotropy, interface mobility anisotropy and elastic energy. In the precipitates, the initial composition is $c = 0.33$, and the order parameter fields $\eta_2$ or $\eta_3$ are assigned to be 1 which depends on the orientation of the precipitates. The composition is $c = 0.05$, and the order parameter fields $\eta_1$ and $\eta_3$ are assigned to be 0 in the matrix. Fig. 6.30 shows the morphological evolution of the precipitates. Comparing Fig. 6.2 and Fig. 6.30, it can be found that the simulation reproduces a similar precipitate morphology observed in the experiments [180]. Although the model can be used to study and reveal the fundamental features and mechanisms about plate-like precipitate growth in 1D, 2D and 3D, challenges remain. These include increasing the length and time scales, and extending the model to multi-component systems.
Fig. 6.30 Growth of two precipitates in three dimensions.
6.6 Conclusion

A phase-field model which can automatically incorporate the thermodynamic and kinetic information from databases is developed for studying the precipitation of $\theta$ phase in Al-Cu alloys. In addition, the relationships between model parameters and material thermodynamic and kinetic properties are established, which enable people to quantitatively simulate the microstructure evolution in material processes. Systematical test in 1D, 2D and 3D has been carried out. The growth of a single $\theta$ precipitate in 1D exactly reproduces the results from analytical solutions. The equilibrium shape simulated in two dimensions is in good agreement with that predicted by the Wulff construction based on the interface energy anisotropy. 2D and 3D simulations produce typical precipitate morphologies and precipitate configurations which are observed in the experiments. The simulation results show that the lengthening and thickening laws of an isolated precipitate in 2D depends on the mobility of coherent interface and the elastic energy. If the coherent interface is immobile, the lengthening follows $t$ law while the thickness remains no change during growth. The elastic energy associated with the lattice mismatch between the precipitate and the matrix speeds up the lengthening, but slows down the thickening and coarsening process. All simulation results demonstrate that the developed phase-field model is able to simulate the precipitation of $\theta$ in Al-Cu alloys, which involves plate-like precipitates, strong interface energy anisotropy, interface mobility anisotropy and elastic energy.
7.1 Conclusions

In this thesis, the phase-field approach is applied to a number of microstructure problems involving elastic inhomogeneity, structural defects such as dislocations, and precipitates with strong interfacial energy and mobility anisotropy. The main contributions to the phase-field theory includes:

1) An efficient iteration method is proposed to solve the mechanical equilibrium equations in a solid with elastic inhomogeneity, even with voids or a vapor phase where the elastic constants are zero. Therefore, the phase-field model can be extended to study the effect of strongly elastic inhomogeneity on microstructure evolutions, and simulate microstructure evolutions in films with curved surface and subject to substrate constraint.

2) The structural defects such as dislocations are introduced into the phase-field model with the concept “eigenstrain” in mesomechanics. Two unique features are realized. The first one is that the lattice distortion due to structural defects and compositional and/or structural inhomogeneity is expressed with one eigenstrain tensor. The calculation of elastic energy is computationally efficient, particularly for three-dimensional cases. The second is that it becomes particularly convenient
to simulate defect dynamics. As a matter of fact, phase-field models of dislocation dynamics [87,88] is based on the same idea proposed in this thesis.

3) A general phase-field model of dislocation dynamics in an alloy with mobile dislocations, diffusive solutes and immobile defects such as inclusions is developed. A new eigenstrain function of a dislocation loop is constructed, which eliminate the dependence of dislocation Burgers vector on applied stresses in the original phase-field model of dislocation dynamics. As a result, it provides a correct dislocation stress field for both static and moving dislocations. This model can be applied to study the strengthening of alloys.

4) A phase-field model is extended to simulate the precipitation of \( \theta' \) phase in Al-Cu alloys. The effect of elastic energy associated with the lattice mismatch between \( \theta' \) precipitates and matrix, the interface energy anisotropy and the interface mobility anisotropy on the growth of \( \theta' \) precipitates are taken into account. The relationships between phase-field model parameters and thermodynamic and kinetic data of alloys are established, which is the basis for quantitative simulations. A systematic testing of the growth of \( \theta' \) precipitates is performed in 1D, 2D and 3D with the developed model. The results demonstrate the potential applications to simulating the growth of precipitates with abnormal shape such as plate-like and needle-like precipitates.
7.2 Future directions

The phase-field models developed in this thesis could further be improved or applied to other interesting microstructure problems. For example:

(1) The formation of three-dimensional islands or self-assembly microstructure patterns on a substrate is of both scientific interest and technological importance. The developed phase-field model in a solid with elastic inhomogeneity is applicable to studying such a material process.

(2) The phase-field model of dislocation dynamics is able to correctly describe the elastic interaction among coherency microstructures, dislocations and other defects, the dislocation multiplication by Frank-Read mechanism, and dislocation annihilation. However, it cannot take the crystal friction resistance, dislocation climb and dislocation reactions such as dissociation into account. To incorporate these features into the model will broaden its practical applications.

(3) For the phase-field model of the precipitation of $\theta'$ precipitates in Al-Cu alloys, it is desired to increase the simulation time step and simulation cell size for a practical application. To do so, the following three aspects could be explored: the efficient numerical method for solving the kinetic equations, a similar adaptive or multi-scale treatment in coherent interfaces and multi-time scale methods. A practical alloy is usually a multi-component system. Therefore, it will be important to extend the model to a multi-component system. In addition, experimental
observation shows that defects such as dislocations are preferential nucleation locations for $\theta'$. Therefore, it will be interesting to study the nucleation near dislocations.
References


[180] H. Weiland. Private Communication


Vita

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