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**Coupled Nonlinear Ginzburg-Landau and
Mechanics Model for Martensitic
Transformations in Polycrystals**

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Everybody has a capacity for a happy life. All these talks about how difficult times we live in, that's just a clever way to justify fear and laziness.

-Lev Landau

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Abstract

Martensitic transformation (MT), in a narrow sense, is defined as the change of the crystal structure to form a coherent phase, or multi-variant domain structures out from a parent phase with the same composition, by small shuffles or co-operative movements of atoms. Over the past century, MTs have been discovered in different materials from steels to shape memory alloys, ceramics, and smart materials. They lead to remarkable properties such as high strength, shape memory/superelasticity effects or ferroic functionalities including piezoelectricity, electro- and magneto-striction, etc.

Various theories/models have been developed, in synergy with development of solid state physics, to understand why MT can generate these rich microstructures and give rise to intriguing properties. Among the well-established theories, the Phenomenological Theory of Martensitic Crystallography (PTMC) is able to predict the habit plane and the orientation relationship between austenite and martensite. The re-interpretation of the PTMC theory within a continuum mechanics framework (CM-PTMC) explains the formation of the multi-variant domain structures, while the Landau theory with inertial dynamics unravels the physical origins of precursors and other dynamic behaviors. The crystal lattice dynamics unveils the acoustic softening of the lattice strain waves leading to the weak first-order displacive transformation, etc. Though differing in statics or dynamics due to their origins in different branches of physics (e.g. continuum mechanics or crystal lattice dynamics), these theories should be inherently connected with each other and show certain elements in common within a unified perspective of physics. However, the physical connections and distinctions among the theories/models have not been addressed yet, although they are critical to further improving the models of MTs and to develop integrated models for more complex displacive-diffusive coupled transformations.

Therefore, this thesis started with two objectives. The first one was to reveal the physical connections and distinctions among the models of MT by means of detailed theoretical analyses and numerical simulations. The second objective was to expand the Landau model to be able to study MTs in polycrystals, in the case of displacive-diffusive coupled transformations, and in the presence of the dislocations.

Starting with a comprehensive review, the physical kernels of the current models of MTs are presented. Their ability to predict MTs is clarified by means of theoretical analyses and simulations of the microstructure evolution of cubic-to-tetragonal and cubic-to-trigonal MTs in 3D. This analysis reveals that the Landau model with irreducible representation of the transformed strain is equivalent to the CM-PTMC theory and microelasticity model to predict the static features during MTs but provides better interpretation of the dynamic behaviors. However, the applications of the Landau model in structural materials are limited due its the

complexity.

Thus, the first result of this thesis is the development of a nonlinear Landau model with irreducible representation of strains and the inertial dynamics for polycrystals. The simulation demonstrates that the updated model is physically consistent with the CM-PTMC in statics, and also permits a prediction of a classical 'C shaped' phase diagram of martensitic nucleation modes activated by the combination of quenching temperature and applied stress conditions interplaying with Landau transformation energy.

Next, the Landau model of MT is further integrated with a quantitative diffusional transformation model to elucidate atomic relaxation and short range diffusion of elements during the MT in steel. The model for displacive-diffusive transformations includes the effects of grain boundary relaxation for heterogeneous nucleation and the spatio-temporal evolution of diffusion potentials and chemical mobility by means of coupling with a CALPHAD-type thermo-kinetic calculation engine and database. The model is applied to study for the microstructure evolution of polycrystalline carbon steels processed by the Quenching and Partitioning (Q&P) process in 2D. The simulated mixed microstructure and composition distribution are compared with available experimental data. The results show that the important role played by the differences in diffusion mobility between austenite and martensite to the partitioning in carbon steels.

Finally, a multi-field model is proposed by incorporating the coarse-grained dislocation model to the developed Landau model to account for the morphological difference between steels and shape memory alloys with same symmetry breaking. The dislocation nucleation, the formation of the 'butterfly' martensite, and the redistribution of carbon after tempering are well represented in the 2D simulations for the microstructure evolution of the representative steels. With the simulation, we demonstrate that the dislocations account for the experimental observation of rough twin boundaries, retained austenite within martensite, etc. in steels.

Thus, based on the integrated model and the in-house codes developed in thesis, a preliminary multi-field, multiscale modeling tool is built up. The new tool couples thermodynamics and continuum mechanics at the macroscale with diffusion kinetics and phase field/Landau model at the mesoscale, and also includes the essentials of crystallography and crystal lattice dynamics at microscale.

Resumen

Las transformaciones martensíticas (MT) se definen como un cambio en la estructura del cristal para formar una fase coherente o estructuras de dominio multivariante, a partir de la fase inicial con la misma composición, debido a pequeños intercambios o movimientos atómicos cooperativos. En el siglo pasado se han descubierto MT en diferentes materiales partiendo desde los aceros hasta las aleaciones con memoria de forma, materiales cerámicos y materiales inteligentes. Todos muestran propiedades destacables como alta resistencia mecánica, memoria de forma, efectos de superelasticidad o funcionalidades ferroicas como la piezoelectricidad, electro y magneto-estricción etc.

Varios modelos/teorías se han desarrollado en sinergia con el desarrollo de la física del estado sólido para entender por qué las MT generan microestructuras muy variadas y ricas que muestran propiedades muy interesantes. Entre las teorías mejor aceptadas se encuentra la Teoría Fenomenológica de la Cristalografía Martensítica (PTMC, por sus siglas en inglés) que predice el plano de hábito y las relaciones de orientación entre la austenita y la martensita. La reinterpretación de la teoría PTMC en un entorno de mecánica del continuo (CM-PTMC) explica la formación de los dominios de estructuras multivariantes, mientras que la teoría de Landau con dinámica de inercia desentraña los mecanismos físicos de los precursores y otros comportamientos dinámicos. La dinámica de red cristalina desvela la reducción de la dureza acústica de las ondas de tensión de red que da lugar a transformaciones débiles de primer orden en el desplazamiento. A pesar de las diferencias entre las teorías estáticas y dinámicas dado su origen en diversas ramas de la física (por ejemplo mecánica continua o dinámica de la red cristalina), estas teorías deben estar inherentemente conectadas entre sí y mostrar ciertos elementos en común en una perspectiva unificada de la física. No obstante las conexiones físicas y diferencias entre las teorías/modelos no se han tratado hasta la fecha, aun siendo de importancia crítica para la mejora de modelos de MT y para el desarrollo integrado de modelos de transformaciones acopladas de desplazamiento-difusión.

Por lo tanto, esta tesis comenzó con dos objetivos claros. El primero fue encontrar las conexiones físicas y las diferencias entre los modelos de MT mediante un análisis teórico detallado y simulaciones numéricas. El segundo objetivo fue expandir el modelo de Landau para ser capaz de estudiar MT en policristales, en el caso de transformaciones acopladas de desplazamiento-difusión, y en presencia de dislocaciones.

Comenzando con un resumen de los antecedentes, en este trabajo se presentan las bases físicas de los modelos actuales de MT. Su capacidad para predecir MT se clarifica mediante el análisis teórico y las simulaciones de la evolución microestructural de MT de cúbicoatetragonal y cúbicoatrigonal en 3D. Este análisis revela que el modelo de Landau con representación irreducible de la deformación transformada es equivalente a la teoría CM-PTMC y al modelo

de microelasticidad para predecir los rasgos estáticos durante la MT, pero proporciona una mejor interpretación de los comportamientos dinámicos. Sin embargo, las aplicaciones del modelo de Landau en materiales estructurales están limitadas por su complejidad.

Por tanto, el primer resultado de esta tesis es el desarrollo del modelo de Landau no-lineal con representación irreducible de deformaciones y de la dinámica de inercia para policristales. La simulación demuestra que el modelo propuesto es consistente fcamente con el CM-PTMC en la descripción estática, y también permite una predicción del diagrama de fases con la clásica forma 'en C' de los modos de nucleación martensítica activados por la combinación de temperaturas de enfriamiento y las condiciones de tensión aplicada correlacionadas con la transformación de energía de Landau.

Posteriormente, el modelo de Landau de MT es integrado con un modelo de transformación de difusión cuantitativa para elucidar la relajación atómica y la difusión de corto alcance de los elementos durante la MT en acero. El modelo de transformaciones de desplazamiento y difusión incluye los efectos de la relajación en borde de grano para la nucleación heterogénea y la evolución espacio-temporal de potenciales de difusión y movilidades químicas mediante el acoplamiento de herramientas de cálculo y bases de datos termo-cinéticos de tipo CALPHAD. El modelo se aplica para estudiar la evolución microestructural de aceros al carbono policristalinos procesados por enfriamiento y partición (Q&P) en 2D. La microestructura y la composición obtenida mediante la simulación se comparan con los datos experimentales disponibles. Los resultados muestran el importante papel jugado por las diferencias en movilidad de difusión entre la fase austenita y martensita en la distribución de carbono en los aceros.

Finalmente, un modelo multi-campo es propuesto mediante la incorporación del modelo de dislocación en grano-grueso al modelo desarrollado de Landau para incluir las diferencias morfológicas entre aceros y aleaciones con memoria de forma con la misma ruptura de simetría. La nucleación de dislocaciones, la formación de la martensita 'butterfly', y la redistribución del carbono después del revenido son bien representadas en las simulaciones 2D del estudio de la evolución de la microestructura en aceros representativos. Con dicha simulación demostramos que incluyendo las dislocaciones obtenemos para dichos aceros, una buena comparación frente a los datos experimentales de la morfología de los bordes de macla, la existencia de austenita retenida dentro de la martensita, etc.

Por tanto, basado en un modelo integral y en el desarrollo de códigos durante esta tesis, se ha creado una herramienta de modelización multiescala y multi-campo. Dicha herramienta acopla la termodinámica y la mecánica del continuo en la macroescala con la cinética de difusión y los modelos de campo de fase/Landau en la mesoescala, y también incluye los principios de la cristalografía y de la dinámica de red cristalina en la microescala.

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Acronyms

2D	Two-Dimensional
3D	Three-Dimensional
3DAP	Three-Dimensional Atomic Probe
CALPHAD	Calculation of Phase Diagram
CCE	Constrained Carbon Equilibrium
CEF	Compound Energy Formalism
CM	Continuum Mechanics
EBS	Electronic BackScatter Diffraction
EPMA	Electronic Probe of Microscopic Analysis
FFT	Fast Fourier Transformation
G-T	Greninger-Troiano
IRS	Irreducible Representation formed Strain
K-S	Kurdjumov-Sachs
LR	Lagrange Rayleigh
MT	Martensitic Transformation
N-W	Nishiyama-Wassermann
OP	Order Parameter
PF	Phase Field
PTMC	Phenomenological Theory of Martensite Crystallography
Q&P	Quenching and Partitioning
SMA	Shape Memory Alloy
TDGL	Time Dependent Ginzburg Landau

Chapter 1

Introduction

Phase transformations and physical metallurgy realized a fruitful synergy with solid state physics, as the rate of discovery of the key physical phenomena, theorizing and paradigm building hit a peak in the 1950s.

-J.W. Cahn, 1999

1.1 Where the Legend of Microstructure Starts. . .

Figure 1.1: (a) The ancient sword made of a high-carbon steel and (c) the microstructure of polished and etched meteoric iron. (b, d) The portraits of Carl von Schreibers and Henry Clifton Sorby.

The legend of microstructure and its evolution in solid state phase transformation dates from 2500BC when the sophisticated skills had been taken advantages of carbon gradients and/or cooling rates in the fabrication of swords with a hard, higher carbon concentration surface region supported by tougher, lower carbon content interiors. Despite the ill-suited understandings of phase transformation in pre-history, the solid state phase transformations, especially for the internal structures of alloys, would not be explicitly recognized until Alois

von Widmansten and Carl von Schreibers invented then-advanced metallography to reveal the distinctive microstructure of polished and etched meteoric iron to the naked eyes in 1808 and Henry Clifton Sorby lifted the veil on metallic microstructure of a carburized Swedish iron by using a reflected light microscopy in 1880 [PE12]. In the century to follow, the perception of solid state phase transformation has been taking major steps forward accompanying with the invention and application of advanced characterization techniques to explore the interior microstructural features of steels. The utilization of optical microscopy (OM) contributed to the identification of the pearlite, which opened the door to explore the world of microstructure. The drawing of iron-base phase diagrams and the identification of phase transformation temperature cannot be achieved without the thermal analysis. The application of X-ray diffraction (XRD) to steels more than revealed an indisputable fact that steels and other alloys are crystalline materials packed with atoms and defects, but ushered in the research upsurge for martensitic transformation(MT) and other displacive transformations. The advances in transmission electronic microscopy (TEM) allowed the twinned microstructure of martensite and the relevant interfaces to be examined in great detail. The advent of atom probe provided deeper insights into composition partitioning during the phase transformations involving diffusion, like austenite decomposition, bainite transformation, intermetallic precipitation, tempering, spinodal decomposition, etc. The employment of advanced characterization techniques and the renewal of experimental data also inspired new theories and approaches to explore the physical natures of microstructural development and properties in perspective of solid-state physics. These laws of physics nowadays are widely followed by a number of alloys more than applicable to steels. For example, the adoption of principle of least action to strain energy led to Phenomenological Theory of Martensite Crystallography (PTMC) which hits a great success to explain habit planes and orientation relationships in a wide variety of ferrous and non-ferrous alloy systems undergoing MT[BM54a, BM54b, MB54]. The power law of self-organized criticality helped to identify the nucleation and growth as the fundamental processes with characteristic rates to govern solid state phase transformation. Darken[Dar48] recast Fick's continuum diffusion flux equations in terms of the chemical potentials to account for the uphill diffusion rather than concentrations. Hillert et al.[Hil07] developed the computational thermodynamics and kinetics to tackle the problems of equilibrium phase diagram, phase instability, precipitate morphology, sizescaling, and pattern selection in diffusion controlled transformations. The developed thermodynamic models and the corresponding functions, which are competent to predicate energetic competition between phases [KRC62, ADP66a, ADP66b, MD69], have been generalized as the CALPHAD (Calculation of Phase Diagram) approach today. Cahn and Hilliard proposed the chemically diffuse interface model[CH58, Cah59, CH59] to ex-

plain the spinodal decomposition. The model prototyping the continuous transformations was then generalized into phase-field approaches[Ell89, WBM92]. Therefore, the encounter with solid state physics in the mid 20th century indeed boosted the advance of metallurgical solid state phase transformations in view of the precise physical notions which are brought to understand microstructural features. At the turn of the century, the PTMC has been reinterpreted in the language of continuum elasticity[Bha03]; the multicomponent diffusion has been viewed in Onsagers non-equilibrium thermodynamics; the weak first-order MT has been connected with Landau's phenomenological theory of phase transitions and crystal lattice dynamics[Kru92]. With the help of computers, these physical models, understandings and intuitions have been applied to materials system with more complexity during solid-state phase transformation. However, the theoretical studies nowadays are not going far away from the key words of thermodynamics, crystallography, defects, diffusion, nucleation, and growth, but are mainly focused on the adjustment of the microstructure and thus the tuning of the properties of materials.

1.2 Martensites and Martensitic Transformation

Figure 1.2: The portrait of Adolf Martens and the martensites in steel [Smi92] and shape memory alloy [Chu93]

The terminologies of 'martensite' and 'martensitic phase transformation' were first used in honor of Adolf Martens to identify the plate-like hard phase in a quenched carbon steel [Nis12]. It is now common to find the term applied to structures in titanium alloys [GP00], shape memory alloys(SMA) [OW99], ceramics [KR02] and other smart materials. The morphology, crystal structures, nucleation modes, growth kinetics, and properties of various martensites are divergent. The sole similarity that defines them as martensites is they are formed via a shear-like diffusionless MT. According to Zhang [ZK09], the MT is one of

two categories of phase transformations in crystalline solids. (The other class is diffusional transformation) MT has its distinctive characteristics as follows:

Among the most prominent is the simultaneous, cooperative movements of atoms over distances less than an atomic diameter to product martensites as well as coherent or at least approximating coherent interfaces paralleling with certain crystallographic planes. A coherent invariant plane is formed between a signal martensite plate and parent phase when the constraint of invariant plane strain condition is satisfied. The habit plane is an abstract crystallographic plane separating parent phase and aggregation of twin-related martensite variants. Moreover, the mid-rib is also a kind of habit plane. The crystallographic lattice correspondence exists between parent and martensite phases, which describes a relationship between two involved lattices. It also allows the mechanism of atomic movements to explain how each atom need move only a small fraction of an interatomic distance while as a whole produce large macroscopic strain. The most famous lattice correspondence is the Bain lattice correspondence [BD24] as the schematic drawing shown in Figure 1.3. A contraction along Z' axis and the expansions along X' and Y' axes transform an FCC lattice into a BCC one with a matrix representation of lattice correspondence as

$$\begin{bmatrix} m \\ k \\ l \end{bmatrix}_{BCC} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} m \\ k \\ l \end{bmatrix}_{FCC}$$

Figure 1.3: Bain and Bain lattice correspondence

where the $[mkl]$ is lattice direction index in Bravias lattice. The orientation relationships which reveal the real planes and directions relationship between martensite and austenite, like Kurdjumov-Sachs(K-S) [KS30] and Nishiyama-Wasserman (N-W) in experiments, show small deviations from Bain correspondence. In mathematics, the deviation can be rep-

resented by a rigid body rotation. MT doesn't involve long range diffusion, such that the parent and product phases have no distinct compositional difference, although recent atom probe tomographic analysis reveals that atomic relaxation and short range diffusion can take place during MTs [TMH⁺14, TMR15].

In dynamics, MT proceeds at fast speed approaching the velocity of sound in the matrix crystal, if nothing more than small 'shuffles' or co-operative atom movements occurs during MT. MT requires an undercooling to trigger the transformation, thus the onset temperature of MT, i.e. M_s , is measured lower than the T_0 temperature at which the parent phase and martensite have the same Gibbs energy. The M_s varies with composition and mechanical deformation but is scarcely influenced by the quenching processing. MT is usually athermal, which means no thermal activation is necessary for the transformation to proceed. The amount of generated martensite is not linearly related to temperature fall between the M_s and M_f (at which the MT halts). Actually, the athermal MT can occur in most of systems, even for those of particular steels and copper alloys which have ability to introduce an isothermal MT at a constant temperature.

The thermoelasticity is another generic feature of MT in SMAs and gives rise to the temperature hysteresis and shape memory effect. The different behaviors of hysteresis in SMAs are more than relevant to the eigen transformation strains but also affected by the dislocation creation and the friction of the interfaces. The irreversibility of MT in carbon and low alloy steels are related to other diffusional transformations in competition with MT. At A_s temperature (at which reversion to austenite occurs on heating) of carbon steel, the decomposition of martensite to carbides and ferrite occurs before the austenite can reform due to the fast diffusion of carbon.

Based on the reviewing, none of the above characteristics can be acted as the sufficient and necessary criterion to define a transformation as MT or not. For example, the surface relief was discovered in $\gamma - AlAg_2$ phase [LA69] after a phase transformation involving composition changes. The burgers orientation relationship was identified in $\beta - \alpha$ transformation in titanium alloys. The existence of aforementioned counterexamples leads to a long term controversy and challenge in the definition of MT. The precise definition of the MT becomes increasing difficult as the accumulation of evidences and theoretical reconsiderations. In a narrow sense [HSU80], the MT is a first-order phase transformation undergoing nucleation and growth through diffusionless atomic displacement, either uniform or non-uniform. It leads to particular microstructural features such as shape change, surface relief and satisfaction of invariant plane strain condition. In contrast, the general definition of MT in accordance with Khachaturyan [Kha13] is depicted as 'a phase transformation that can be treated in terms of displacement only is called a MT'. The significant difference between

two definitions is that the latter takes the improper MT into consideration, such that a MT not necessarily is a classical first-order transformation undergoing a nucleation and growth process. It is because the threshold for first-order and high-order displacive transformations and the dividing line of nucleation and growth in some weak MTs are no longer clear in perspective of the crystal lattice dynamics. In an extreme case, a transformation triggered by the shuffle that generates a zero deformation strain without any macroscopic shape change can also be recognized as a MT. However, most of the improper MTs exhibit transformation strains, which are always treated as the secondary order parameters(OPs) in modern Landau theory of phase transformation. Moreover, invariant plane condition is not necessary either to define a MT. The MT can be only with the dilatational deformation. In this thesis, we accept the general definition of the MT by Khachaturyan, which is in accordance with nonlinear nonlocal Landau theory of the phase transformation.

1.3 Motivations

From the definition of MT, we understand that the MT is a relative complex transformation sensitive to chemical, thermal and mechanical conditions and also competes with other diffusional transformations. Therefore, various theories and models have been developed to understand the physical natures of the MT in different perspectives. The most important theories include: the PTMC to account for the microstructural features based on *kinematic compatibility*, the microelasticity phase-field model to present the intriguing microstructure of martensites based on *Green's function in continuum mechanics of elasticity and Allen-Cahn equation in statistical mechanics*, Landau theory to focus on the dynamical behaviors with the wisdom of *crystal lattice dynamics and hydrodynamics*, etc., which are all introduced in the following chapters. Although differing in statics and/or dynamics due to their individual origins in branches of physics, these theories must share certain common ingredients with each other and exhibit distinctive advantages. However, the physical connections and distinctions among the theories/models have not been addressed yet. A deeper understanding of the theories with a unified perspective of physics benefits to building a panorama of phase transformations and enables us to select the most appropriate theory for a real problem, which is the first motivation of the thesis.

Moreover, the investigation of martensite and the relevant phase transformations are far from complete with the current theories and models: Martensitic nucleation is one of outstanding challenges. In experiments, an accurate measurement of absolute interfacial energies remains the biggest source of uncertainty [LEA89], not to mention the continuing inability to directly observe nucleation at the atomic scale. Another challenge is that the

complexity of real microstructures, as the consequence of the interplaying of different fields including strains, compositions, dislocations, grain boundaries in multiscales, still eludes the rigorous quantitative description and control of microstructure to satisfy the requirement of industry. Therefore, the second motivation of the thesis is to put forward a prototype model that couples various fields of transformation strain, diffusion potential, grain orientations, and dislocation density to simulate the nucleation and growth of martensites under more complex conditions.

1.4 Outline of the Thesis

The thesis is organized into three sections. The first section in chapter 2 details the current state-of-the-art models for exploring the microstructural features and the mechanical behaviors of martensites. They are the Phenomenological Theory of Martensite Crystallography (PTMC) as well as its reinterpretation within the framework of the continuum mechanics (CM-PTMC), Khachaturyans microelasticity phase field method, and the Landau theory based on the Irreducible Representation of the point groups and transformation Strains (IRS). The similarities and differences among these theories/models are detailed by means of theoretical analyses and/or simulations for two-dimensional square-to-rectangle as well as three-dimensional cubic-to-tetragonal and cubic-to-trigonal martensitic transformations.

The second section, which encompasses chapters 3 and 4, presents a novel nonlinear dynamic Landau model and its application to describe the first-order MTs in polycrystalline ferroelastic materials. The mathematical description is developed in chapter 3, where the construction of Landau energy and numerical solution scheme are presented in detail. Simulations of 2D polycrystalline square-to-rectangle and triangle-to-centered rectangle MTs are used to validate our model and demonstrate the physical consistence of the model with CM-PTMC. In chapter 4, the nonlinear dynamic Landau model is applied to study dynamical nucleation in MTs. It shows how the quenching temperature, the applied stress and the intrinsic transformation energy can be combined to activate particular mechanisms of martensitic nucleation and growth in polycrystals.

The third section of the thesis in chapters 5-6 is devoted to further developing the Landau model, which is integrated with models that take into account diffusional transformations and the effect of dislocations. The development of the model for diffusive-displacive coupled phase transformations is presented in chapter 5. In this approach, the Landau model is coupled with the information provided by thermo-kinetic calculation and databases to obtain the material parameters that control the diffusion potential and the quantitative mobility during diffusive transformations. As an example of application, this coupled model is used

to study the carbon redistribution in steels manufactured by the quenching and partitioning (Q&P) process. In chapter 6, a modified continuum dislocation model is proposed and seamlessly embedded into the coupled Landau model introduced in chapter 5. This model is used to analyze the interplay among dislocations, driving forces for martensitic transformations and diffusion on the microstructure evolution of steels.

Finally, the conclusions and the avenues for future work within the framework of integrated computational materials engineering are briefly summarized in Chapter 7.

Chapter 2

Models of Martensitic Transformation

A method is more important than a discovery, since the right method will lead to new.

-Lev Landau

This chapter reviews the various current models of MT from viewpoints of geometry, elasticity, wave mechanics and their integration. The intrinsic connections and distinctions in physics are comprehensively discussed via theoretical analysis and the comparison of simulation results. It serves as the fundamental task to develop novel integrated models for the coupled phase transformation.

2.1 Preliminaries of Continuum Mechanics

According to Khachaturyan's general definition [Kha13], MT is one category of phase transformations which could be only described in terms of displacements. Therefore, modeling of MT can be started with the definition of the austenite and martensite lattices in mean of vector algebra, followed by the description of lattices and symmetries changes during the MT [Bha03]. Mathematically, a perfect crystal can be abstracted as a point lattice, generated by periodically stacking of unit cell in 3D space. An arbitrary lattice position can be expressed as fractions or multiples of unit-cell dimensions, or in a viewpoint of continuum mechanics, as a vector of

$$\mathbf{v} = a_1 \mathbf{e}_1 + a_2 \mathbf{e}_2 + a_3 \mathbf{e}_3 \quad (2.1)$$

linking origin and lattice position in a reference coordinate system, where $\{a_i\}$ is the projected length of the vector $\{\mathbf{e}_i\}$ along each of the three independent unit axes. The description of lattice in atomic lattice scale is actually a particular case in continuum scale when the

edges of unit cell are chosen as the reference coordinate system. The lattice-continuum connection is revealed by Cauchy-Born hypothesis [Zan96], which will be detailed later. Based on this connection, the concepts of deformation and displacement in an elastic continuum are introduced into MT, such that a MT can be described as a deformation linking austenite and martensite. Provided that any material point at position $\mathbf{x}$ in non-deformed austenite moves to a new position $\mathbf{y}(\mathbf{x})$ in deformed martensite, the martensitic configuration, or the deformation itself, is expressed as

$$\mathbf{y}(\mathbf{x}) = \mathbf{x} + \mathbf{u}(\mathbf{x}) \quad (2.2)$$

where $\mathbf{u}(\mathbf{x})$ is displacement of any material point. The deformation gradient $\mathbf{F}$ is defined as the partial derivatives of the deformation $\mathbf{y}$ with respect to space coordinates $\mathbf{x}$; then the matrix of deformation gradient reads

$$\begin{aligned} \mathbf{F} &= \nabla \mathbf{y}, \\ F_{ij} &= \frac{\partial y_j}{\partial x_i}, (i, j = 1, 2, 3) \end{aligned} \quad (2.3)$$

With a deformation gradient, most of the variables in continuum elasticity can be readily expressed. Expanding the displacement term in the full differentiation form of Eq(2.2) $d\mathbf{y}(\mathbf{x}) = d\mathbf{x} + d\mathbf{u}(\mathbf{x})$ into the Taylor series, and dropping the second and higher terms leads to

$$d\mathbf{y}(\mathbf{x}) = d\mathbf{x} + \frac{\partial \mathbf{u}(\mathbf{x})}{\partial \mathbf{x}} d\mathbf{x} = (\mathbf{I} + \nabla \mathbf{u}) d\mathbf{x}. \quad (2.4)$$

where $\mathbf{I}$ is the identity matrix. Thus, deformation gradient is connected with displacement gradient by

$$\mathbf{F} = \mathbf{I} + \nabla \mathbf{u}(\mathbf{x}) \quad (2.5)$$

The full differentiation form

$$d\mathbf{y} = \mathbf{F}(\mathbf{x}_0) d\mathbf{x} \quad (2.6)$$

also describes that an infinitesimal line element $d\mathbf{x}$ at given point $\mathbf{x}_0$ goes to the element $d\mathbf{y}$ after deformation.

In addition, strain in any given direction $\mathbf{e}_i$ can be defined as the ratio of the local deformation to initial length

$$\varepsilon = \frac{|\mathbf{dy}| - |\mathbf{dx}|}{|\mathbf{dx}|} = \frac{\sqrt{\mathbf{dy} \cdot \mathbf{dy}}}{|\mathbf{dx}|} - 1 \quad (2.7)$$

Applying full differentiation Eq.(2.6) gives rise to

$$\begin{aligned} \varepsilon &= \frac{\sqrt{\mathbf{F} d\mathbf{x} \cdot \mathbf{F} d\mathbf{x}}}{|\mathbf{dx}|} - 1 = \sqrt{\mathbf{F} \frac{d\mathbf{x}}{|\mathbf{dx}|} \cdot \mathbf{F} \frac{d\mathbf{x}}{|\mathbf{dx}|}} - 1 \\ &= \sqrt{\mathbf{F} \mathbf{e} \cdot \mathbf{F} \mathbf{e}} - 1 = \sqrt{\mathbf{e} \cdot (\mathbf{F}^T \mathbf{F} \mathbf{e})} - 1 \end{aligned} \quad (2.8)$$

such that the finite strain tensor written in deformation gradient is

$$\boldsymbol{\varepsilon} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) = \frac{1}{2} (\mathbf{C} - \mathbf{I}) \quad (2.9)$$

where $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is Cauchy-Green deformation tensor, and $\mathbf{F}^T$ is the transpose of deformation gradient $\mathbf{F}$. Inserting Eq. (2.5) into Eq.(2.9), we obtain the finite strain tensor written in displacement gradient, with the strain component

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_k \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right) \quad (2.10)$$

Neglecting the non-linear term, the infinitesimal strain is

$$\boldsymbol{\varepsilon} = \frac{1}{2} [(\nabla \mathbf{u}) + (\nabla \mathbf{u})^T], \varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (2.11)$$

Recalling the theorem of polar decomposition, any nonsingular matrix $\mathbf{F}$ with determinant of deformation gradient $\det \mathbf{F} > 0$ can be certainly factored into the product of an orthogonal matrix $\mathbf{Q}$ to undergo a rigid body rotation and a symmetric matrix $\mathbf{U}$ with the column arraying eigenvectors of the symmetry part of $\mathbf{F}$,

$$\mathbf{F} = \mathbf{Q} \mathbf{U} \quad (2.12)$$

Figure 2.1: Schematic drawing of the polar decomposition of the deformation gradient [Bha03]

The theorem of polar decomposition ensures the existence of at least one set of mutually orthogonal principle axes, displaying in $\mathbf{U}$ matrix, which remain orthogonal after the deformation $\mathbf{F}$. The transformation stretch tensors $\mathbf{U}$ are independent with the reference coordinate system and adopted as inputs in CM-PTMC and microelasticity PF models. Moreover,

the eigenvalues corresponding to the eigenvectors are determined by solving $|\mathbf{C} - \lambda^2 \mathbf{I}| = 0$ or in a bilinear form

$$\mathbf{F}^T \mathbf{F} = \lambda_1^2 \mathbf{e}_1^{ig} \otimes \mathbf{e}_1^{ig} + \lambda_2^2 \mathbf{e}_2^{ig} \otimes \mathbf{e}_2^{ig} + \lambda_3^2 \mathbf{e}_3^{ig} \otimes \mathbf{e}_3^{ig} \quad (2.13)$$

Besides the deformation of a line element, Figure 2.2 illustrates the deformation of volume and area elements. Considering a parallelepiped material volume spanned by three independent vectors $\mathbf{a} = a_1 \mathbf{e}_1 + a_2 \mathbf{e}_2 + a_3 \mathbf{e}_3$, $\mathbf{b} = b_1 \mathbf{e}_1 + b_2 \mathbf{e}_2 + b_3 \mathbf{e}_3$, and $\mathbf{c} = c_1 \mathbf{e}_1 + c_2 \mathbf{e}_2 + c_3 \mathbf{e}_3$ in the reference, the volume is expressed as the absolute value of scalar triple product $(\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$, which can be reformulated as

$$V = \left| \det \begin{bmatrix} c_1 & c_2 & c_3 \\ a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \end{bmatrix} \right| \quad (2.14)$$

Using the definition of deformation gradient, a differential material volume dv with local volume change is connected to non-deformed configuration dV by the determinant of deformation gradient,

$$dv = (\det \mathbf{F}) dV \quad (2.15)$$

Analogically, if a material area $\mathbf{A}$ (expressed in vector $\mathbf{A}\mathbf{n} = \mathbf{x} \times \mathbf{z}$ with unit normal $\mathbf{n}$) is transformed into the area $\mathbf{a}$ ($\mathbf{a}\mathbf{m} = \mathbf{x}' \times \mathbf{z}'$ with unit normal $\mathbf{m}$) after deformation, and the edge vectors are deformed via the deformation gradients as $\mathbf{x}' = \mathbf{F}\mathbf{x}$ and $\mathbf{z}' = \mathbf{F}\mathbf{z}$, the deformed area can be connected with non-deformed area by

$$da = |(\text{cof} \mathbf{F}) \mathbf{n}| dA, \quad \mathbf{m} = \frac{\mathbf{F}^{-T} \mathbf{n}}{|\mathbf{F}^{-T} \mathbf{n}|} \quad (2.16)$$

where $\text{cof} \mathbf{F} = (\det \mathbf{F}) \mathbf{F}^{-T}$ is cofactor of $\mathbf{F}$.

It should be note that the deformation depicted by all of models in the thesis is such a deformation where neither a finite volume (a point) is compressed (expanded) to a point (a finite volume), nor the body penetrates itself. Thus, it ensures a satisfaction of the condition $\det \mathbf{F} > 0$. As the right-hand sets of coordinates are appointed in the thesis, the positive determinant condition is equivalent to that the triple product of unit vectors before and after transformation must have the same sign, viz. $\mathbf{e}_1 \cdot (\mathbf{e}_2 \times \mathbf{e}_3) > 0$.

2.2 Prototype Phenomenological Theory of Martensite Crystallography (PTMC)

The prototype PTMC theory were developed independently by Wechsler et al. (WLR) [WRL60, Lie58, Wec59, LRW57] and Bowles and Mackenzie (BM) [BM54a, BM54b, MB54]

Figure 2.2: The deformation takes the reference configuration on the left to the deformed configuration on the right.

in 1950s-1960s . Later on, Wayman and Christian proved that the Wechsler-Lieberman-Read and Bowles-Mackenzie presentations are equivalent[Way64, Chr02].

Based on the experimental observations and the premise that the martensite is plate-like, the prototype PTMC considers that the habit plane between single (fault) martensite and surrounding austenite must be an invariant plane, in which all lines are neither distorted nor rotated by the deformation, such that the strains in the vicinity of habit plane can be reduced. The generated invariant plane distortion $\mathbf{P}_1$ consists of an expansion or contraction normal to the habit plane (invariant plane) $\mathbf{m}_1$ and a shear in the habit plane $\mathbf{b}_1$, namely

$$\mathbf{P}_1 = \mathbf{I} + \mathbf{b}_1 \otimes \mathbf{m}_1 \quad (2.17)$$

Thus, the prototype PTMC seems a pure geometric approach aimed at predicting habit plane and shear direction as well as the orientation relationship. To realize it, the invariant plane distortion is decomposed into the Bain strain ($\mathbf{B}$) in accordance with Bain correspondence which converts austenite structure into the martensite product structure, a lattice invariant shear ($\mathbf{P}_2^{-1}$) that does not change the crystal structure of the phase, and a rigid body rotation ($\mathbf{R}$). Herein, the two distortions $\mathbf{B}$ and $\mathbf{P}_2$ are combined via matrix multiplication to make the habit plane undistorted, while the implementation of rotation $\mathbf{R}$ to the strained configuration is necessary to make the habit plane unrotated, which gives rise to the matrix representation as

$$\mathbf{P}_1 = \mathbf{R} \mathbf{B} \mathbf{P}_2^{-1} \quad (2.18)$$

Polar decomposing the matrix $\mathbf{B} \mathbf{P}_2^{-1}$ into the product of orthogonal matrix $\mathbf{Q}_3$ and a symmetry matrix $\mathbf{U}$, and then diagonalizing the symmetry matrix $\mathbf{U}$ with a orthogonal matrix

$\mathbf{Q}_4$, the invariant plane distortion $\mathbf{P}_1$ is reformulated as

$$\mathbf{P}_1 = \mathbf{R}\mathbf{Q}_3\mathbf{Q}_4\mathbf{U}_d\mathbf{Q}_4^T \quad (2.19)$$

where $\mathbf{U}_d = \begin{bmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \lambda_3 \end{bmatrix}$ is a diagonal matrix describing the transformation stretch in principal space. Thus, we obtain the identical relationship $\mathbf{P}_1^T\mathbf{P}_1 = \mathbf{Q}_4\mathbf{U}_d^2\mathbf{Q}_4^T$, which indicates that $\mathbf{P}_1^T\mathbf{P}_1$ and $\mathbf{U}_d^2$ have same eigenvalues and the eigenvectors of $\mathbf{P}_1^T\mathbf{P}_1$ can be linked to the orthogonal basis of $\mathbf{U}_d^2$ by a pure rotation. In geometry, it means that any vector $\mathbf{v}$ in habit plane remains unchanged in magnitude, and the property can be depicted in austenite coordinates $\mathbf{v}^T\mathbf{v} = \mathbf{v}^T\mathbf{P}_2^{-T}\mathbf{B}^T\mathbf{B}\mathbf{P}_2^{-1}\mathbf{v}$ or in principal space $\mathbf{v}_d^T\mathbf{U}_d^2\mathbf{v}_d = \mathbf{v}_d^T\mathbf{v}_d$. In this way, the task of solving $\mathbf{b}$ and $\mathbf{m}$ thoroughly comes down to an eigenvalue-eigenvector problem.

2.2.1 Wechsler-Lieberman-Read Method

Starting with a predefined lattice invariant shear $\mathbf{P}_2^{-1}$ written in principal bases expanded by eigenvectors of $\mathbf{U}_d^2$, the shear takes the form of simple shear

$$\langle C_d | \mathbf{P}_2^{-1} | C_d \rangle = \begin{bmatrix} 1 & g & \\ & 1 & \\ & & 1 \end{bmatrix} \quad (2.20)$$

here, the Dirac notation is used to specify the coordinates where the vector or tensor spans. $|C_d\rangle$, $|C_{fcc}\rangle$, and $|C_{bcc}\rangle$ are bases to describe the space coordinates of principal space, austenite and martensite, respectively. The principal bases can be transformed to the bases of austenite via a rotation $\mathbf{Q}_5$. The $\mathbf{Q}_5$ has the column vectors of unit shear direction of invariant plane $\mathbf{b}_2$, unit direction of shear plane normal $\mathbf{m}_2$, and a third vector given by the vector product $\mathbf{v}_2 = \mathbf{b}_2 \times \mathbf{m}_2$ expressed in austenite coordinates, viz. $\mathbf{Q}_5 = (\mathbf{b}_2, \mathbf{m}_2, \mathbf{v}_2)$. Therefore, we rewrite the Bain strain (distortion) in principal space by $\langle C_d | \mathbf{B} | C_d \rangle = \langle C_d | \mathbf{Q}_5^T | C_{fcc} \rangle \langle C_{fcc} | \mathbf{B} | C_{fcc} \rangle \langle C_{fcc} | \mathbf{Q}_5 | C_d \rangle$, and the total distortion in principal space is $\langle C_d | \mathbf{B} | C_d \rangle \langle C_d | \mathbf{P}_2^{-1} | C_d \rangle$. Solving the characteristic equation $|\mathbf{P}_2^{-T}\mathbf{B}^T\mathbf{B}\mathbf{P}_2^{-1} - \lambda^2\mathbf{I}| = 0$ and inserting $\lambda_2^2 = 1$, we can get two sets of eigenvalues of $(\lambda_1^2, \lambda_3^2)$ associated with two values of g in Eq.(2.20) as well as the eigenvectors. Representing these eigenvectors in austenite coordinates by means of rotation matrix $\mathbf{Q}_5$ and utilizing the bilinear form $\mathbf{P}_1^T\mathbf{P}_1 = \mathbf{Q}_4\mathbf{U}_d^T\mathbf{U}_d\mathbf{Q}_4^T = \mathbf{P}_2^{-T}\mathbf{B}^T\mathbf{B}\mathbf{P}_2^{-1}$, the orthogonal matrix $\mathbf{Q}_4$ and $\mathbf{B}\mathbf{P}_2^{-1}$ are determined. Now admitting an invariant line vector in the habit plane defined by $\mathbf{v}_d^T\mathbf{U}_d^2\mathbf{v}_d = \mathbf{v}_d^T\mathbf{v}_d$, the trial solutions of $\mathbf{v}_d$ are used to determine the possible habit plane normal $\mathbf{m}_1$ and invariant plane deformation $\mathbf{b}_1$. Using the Eqs.(2.17) and (2.19), the rotation $\mathbf{R}$ can be solved.

2.2.2 Bowles-Mackenzie Method

In practice, there is little difference in calculation procedures between Bowles-Mackenzie and Wechsler-Lieberman-Read methods. The implementation of Bowles-Mackenzie method firstly introduces the concept of invariant line defined as the vector of intersection of the two invariant planes $\mathbf{m}_1$ and $\mathbf{m}_2$, which is unaltered in both magnitude and direction during two distortions. Correspondingly, an invariant line distortion $\mathbf{S}$ is defined as the resultant of invariant plane distortion $\mathbf{P}_1$ and $\mathbf{P}_2$,

$$\mathbf{P}_1\mathbf{P}_2 = \mathbf{S} = \mathbf{R}\mathbf{B} \quad (2.21)$$

With a predefined lattice invariant shear $\mathbf{P}_2$ and an established invariant line distortion $\mathbf{S}$ written in the coordinates of austenite, an elaborate analysis in geometry results in the expression of shear direction

$$\mathbf{b}_1 = \frac{\mathbf{S}\mathbf{b}_2 - \mathbf{b}_2}{\mathbf{m}_1 \cdot \mathbf{b}_2} \quad (2.22)$$

and the habit plane normal $\mathbf{m}_1$ is related to the normal of invariant plane shear $\mathbf{m}_2$ as

$$\mathbf{m}_1 \parallel \mathbf{S}^{-T}\mathbf{m}_2 - \mathbf{m}_2 \quad (2.23)$$

Therefore, determination of invariant line distortion $\mathbf{S}$ is the key issue in BM method. Opposite to WLR method solving eigenvalues in principal space and then transforming to austenite coordinates, the BM method firstly obtains the invariant lines $\mathbf{x}$ and invariant normals by solving a set of ellipsoid equations describing the direction and plane normal on unextended cones along with the predefined lattice invariant shear $\mathbf{P}_2$ in austenite coordinates. Similar to WLR, the obtained invariant line $\mathbf{x}$, plane normal of lattice shear $\mathbf{m}_2$, and a third vector given by the vector product $\mathbf{v}_1 = \mathbf{x} \times \mathbf{m}_2$ are served as the column vectors of a rotation $\mathbf{R}_1 = (\mathbf{x}, \mathbf{m}_2, \mathbf{v}_1)$, which represent the orthogonal bases $\langle C_{inv} | \mathbf{I} \rangle$ in the coordinates of austenite. Analogously, another orthogonal bases will be defined as $\mathbf{R}_2 = (\underline{\mathbf{x}}, \underline{\mathbf{m}}_2, \mathbf{v}_2)$ by using the position of the invariant line after the Bain distortion $\underline{\mathbf{x}}$, unit vector parallel to the final position of the normal $\underline{\mathbf{m}}_2$, and $\mathbf{v}_2 = \underline{\mathbf{x}} \times \underline{\mathbf{m}}_2$. In a specific way, we have

$$\underline{\mathbf{x}} = \langle C_{fcc} | \mathbf{B} | C_{fcc} \rangle \langle C_{fcc} | \mathbf{x} \rangle \quad (2.24)$$

$$\underline{\mathbf{m}}_2 = \frac{\langle C_{fcc} | \mathbf{B} | C_{fcc} \rangle^{-1} \langle C_{fcc} | \mathbf{m}_2 \rangle}{(\langle \mathbf{m}_2 | C_{fcc} \rangle \langle C_{fcc} | \mathbf{B} | C_{fcc} \rangle^{-2} \langle C_{fcc} | \mathbf{m}_2 \rangle)^{1/2}} \quad (2.25)$$

It is easy to find that there is a distortion $\mathbf{S}_p = \mathbf{R}_1 \mathbf{R}_2^T \mathbf{B}$ that leaves the invariant line $\mathbf{x}$ and shear plane normal $\mathbf{m}_2$ unextended. Representing the pure shear distortion $\mathbf{S}_p$ in principle space by similarity transformation, we have

$$\begin{aligned} < C_d | \mathbf{S}_p | C_d > = \\ < C_d | \mathbf{R}_1^T | C_{fcc} > < C_{fcc} | \mathbf{R}_1 | C_d > < C_d | \mathbf{R}_2^T | C_{fcc} > < C_{fcc} | \mathbf{B} | C_{fcc} > < C_{fcc} | \mathbf{R}_1 | C_d > \\ = < C_d | \mathbf{R}_2^T | C_{fcc} > < C_{fcc} | \mathbf{B} | C_{fcc} > < C_{fcc} | \mathbf{R}_1 | C_d > \end{aligned} \quad (2.26)$$

The most general invariant line distortion in principal space only requires rotating the invariant line by $\mathbf{R}$ to make itself unextended and unrotated.

$$< C_d | \mathbf{S} | C_d > = < C_d | \mathbf{R} | C_d > < C_d | \mathbf{R}_2^T | C_{fcc} > < C_{fcc} | \mathbf{B} | C_{fcc} > < C_{fcc} | \mathbf{R}_1 | C_d > \quad (2.27)$$

where the rotation $< C_d | \mathbf{R} | C_d >$ in principal axes is expressed as

$$< C_d | \mathbf{R} | C_d > = \begin{bmatrix} 1 & & \\ & \cos \beta & -\sin \beta \\ & \sin \beta & \cos \beta \end{bmatrix} \quad (2.28)$$

By solving the equation of invariant normal $< C_d | \mathbf{S} | C_d > < C_d | \mathbf{n} > = < C_d | \mathbf{n} >$, the rotation matrices $< C_d | \mathbf{R} | C_d >$ and $< C_d | \mathbf{S} | C_d >$ are uniquely calculated, and the invariant line distortion $\mathbf{S}$ in austenite coordinates can be completely determined by mean of similarity transformation,

$$< C_{fcc} | \mathbf{S} | C_{fcc} > = < C_{fcc} | \mathbf{R}_1 | C_d > < C_d | \mathbf{S} | C_d > < C_d | \mathbf{R}_1^T | C_{fcc} > \quad (2.29)$$

Substituting Eq.(2.29) into Eqs.(2.22) and (2.23), the invariant plane normal and shear can be solved.

2.3 Continuum Mechanical Reinterpretation of PTMC (CM-PTMC)

The prototype PTMC theories in pure geometry have been further developed by Ericksen [Eri85, Eri05], Ball and James [BJ89, Bal02, Bal04], and Bhattacharya et al. [Bha03] They utilized the Cauchy-Born hypothesis to describe the invariance of properties, including the invariance of geometry and Hamiltonian under certain crystallographic symmetry operation. Rendering elasticity theory flexible enough by incorporating the perspectives of group theory

and implementing the variation, the linear/nonlinear elastic models of MT in crystals were developed. It also laid foundations for long outside its range of elasticity, leading to an increasing bulk of achievements, especially aimed at the understanding and prediction of microstructure formation during MTs. With the elastic model, the microstructural features of martensites and their orientation relationship with parent austenite can be solved by the minimization of energy with respect to the constraint of kinematic compatibility, all of which are consolidated in Bhattacharya's prestigious textbook [Bha03].

2.3.1 Cauchy-Born Rule

The original standpoint of elastic model is the Cauchy-Born rule, which is a natural hypothesis bridging the lattices in atomic scale and elastic deformation of crystalline configurations in macro scale with the help of continuum theories. The Cauchy-Born rule states that the lattice vectors behave as infinitesimal material line elements in continuum, i.e. the variation of crystal structure is 'embedded' in the macroscopic deformation. Assuming that the crystalline lattice in the reference is generated by a set of lattice vectors $\mathbf{e}_i^0$, we can constitute a set of determinative lattice vectors of the crystal in the deformed configuration as

$$\mathbf{e}_i = \mathbf{F} \mathbf{e}_i^0 \quad (2.30)$$

by exerting the same deformation gradient $\mathbf{F}$ as what defines a macro deformation process on the lattice. In this way, the elastically deformed states in the atomistic model are closely approximated by solutions of the continuum model with stored energy functional.

Figure 2.3: Illustration of Cauchy-Born rule for deformation in continuum. [Bha03]

The classical Cauchy-Born rule is adequate for systems without discontinuities. Such phenomena as severer plastic deformation, diffusion, lattice defect, slips, shuffling or other non-homogeneities are initially not taken into consideration. During the past decade, great

efforts have also been devoted to the development of integrated models incorporating dislocation and plasticity, which will be detailed in chapters 5 and 6. Anyway, the Cauchy-Born rule and the elastic model can be safely applied to MTs in SMAs and other materials whose crystalline structure is given by a simple Bravais lattice.

2.3.2 Frame Indifference and Materials Symmetry

Distinct from the pure geometric prototype PTMC, the CM-PTMC considers geometric and energetic invariance under symmetry operations of crystals. In CM-PTMC, we assume that the energy density stored in a crystalline lattice depends on the lattice vectors and temperature and satisfies frame-indifference and constraint of materials symmetry, which coincide with Landau theory for the second order phase transitions. The property of frame-indifference signifies that the energy density φ is observed in an inertial reference system, and a rigid body rotation of the lattice or a change of observer will not change the energy itself, i.e.

$$\varphi(\mathbf{e}_i, T) = \varphi(\mathbf{Q}\mathbf{e}_i, T) \quad (2.31)$$

If the same reference coordinates are chosen for both lattices configurations before and after transformation, and the Cauchy-Born rule is utilized, the lattice based energy density can be reformulated as a continuum energy density with independent variable of deformation gradient. The frame-indifference property expressed in continuum energy density follows

$$\varphi(\mathbf{F}, T) = \varphi(\mathbf{Q}\mathbf{F}, T) \quad (2.32)$$

It can be seen that, the CM-PTMC has advantage to describe the deformation gradient in an independently defined coordinates, avoiding the error-prone transformations between the principal space where eigenvalues and eigenvectors are explicitly revealed and the laboratory coordinates where the materials actually exist.

The materials symmetry indicates that the properties of a crystalline solid, including energy density and its derivatives, are identical in crystallographic equivalent directions. In other words, exerting same deformation on two identical materials from two crystallographic equivalent directions gives rise to the same energy density. In mathematics, the property of materials symmetry reads

$$\varphi(\mathbf{F}\mathbf{R}, T) = \varphi(\mathbf{F}, T) \quad \text{for all rotations} \quad \mathbf{R} \in P(\mathbf{e}_i^\circ) \quad (2.33)$$

or conventionally

$$\varphi(\mathbf{R}^T \mathbf{F} \mathbf{R}, T) = \varphi(\mathbf{F}, T) \quad \text{for all rotations} \quad \mathbf{R} \in P(\mathbf{e}_i^\circ) \quad (2.34)$$

where $P(\mathbf{e}_i^\circ)$ is the point group of a lattice.

It is obvious that the similarity transformation by an orthogonal matrix of pure rotation does not alter the eigenvalues of deformation gradient. For this reason, the development of the (meta) stable microstructure in MT is simplified as the representation of the piecewise deformation gradients lying in austenite and/or martensite variants. In the thesis, we confine the symmetry operations in point group $P(\mathbf{e}_i^\circ)$ instead of symmetry groups of lattice, because we limit the deformation associated with MT is small compared to the lattice.

Figure 2.4: The relationship between various point groups. A group at the bottom level is a subgroup of that on the top. The number of symmetry elements is also shown.

2.3.3 Martensite Variants

Antecedent to the Landau's theory of phase transformations, the group theory had been served as a powerful tool to study structural transformation. The core argument of the group based construction of structural transformation indicates that the deformation variants are subjected to constraints of transformation path degeneracy and the symmetry of Hamiltonian. With the wisdom of group theory blended in, the MT in CM-PTMC is modeled by the free energy with multiply energy wells for parent phase and martensite variants. The martensite variants are provided with characteristic transformation strains and identical energy density associated with iso-energetic wells on energy surface. If only the invariant rotations are considered, the martensite variants can be transformed into each other by implementing any symmetry operation belonging to the point group. And the number of deformation variants can be determined by calculating the symmetry operations lost in the martensitic lattice in comparison with those in parent phase. [Bha03].

$$nv = \frac{n [P_{Austenite}(\mathbf{e}_i^\circ)]}{n [P_{Martensite}(\mathbf{e}_i^\circ)]} \quad (2.35)$$

It is noteworthy that we confine the proper rotational operations in group and subgroups hereinafter. The other invariant operations, such as reflections, translations and their combination, constituting the lattice group are ignored. Thus, the slip martensite variants associated with the orientation relationship are not taken into consideration in this thesis. For the details of two different transformation paths of degeneracy can be referenced in [Gao13].

2.3.4 St.-Venant's Compatibility and Kinematic Compatibility

Recalling the prototype PTMC, it is understood that the deformation gradient not only describes the continuum elastic energy density at a specific temperature, but also determines the microstructure features. A MT to form a coherent interface requires a continuous, single-valued displacement or deformation field to indicate that the material is unbroken. The continuous field constraint, named St.-Venant's compatibility, refers as the curl of deformation gradient vanishes everywhere in mathematics.

$$\nabla \times \mathbf{F} = 0 \quad (2.36)$$

which is of significance in the following chapters relevant to long-range elastic compatibility kernel in IRS description of martensites (in chapters 3-4) and the MT coupled with dislocation (Chapter 6). Besides the continuous displacement field, the formation of coherent

interface also requires the satisfaction of the 'invariant plane condition'. Although the deformation gradients are not required continuous to describe an invariant plane, they can not be arbitrary matrices across the interface, and must satisfy kinematic compatibility condition in CM-PTMC, which is the generalized form of invariant plane condition [Bha91, BC99] .

$$\begin{aligned}\mathbf{F} &= \mathbf{I} + \mathbf{b} \otimes \mathbf{m} \\ \mathbf{F}_j - \mathbf{F}_i &= \mathbf{a} \otimes \mathbf{n}\end{aligned}\tag{2.37}$$

where $\mathbf{F}_i$ is the deformation gradient matrix, $\mathbf{m}$ and $\mathbf{n}$ are the plane normals; $\mathbf{a}$ and $\mathbf{b}$ are the shear vectors. $\otimes$ designates dyadic product and $\mathbf{I}$ is the identity matrix. If an arbitrary vector $\mathbf{v}$ is considered lying on the interface, we have

$$\mathbf{F}_i \mathbf{v} - \mathbf{F}_j \mathbf{v} = (\mathbf{a} \otimes \mathbf{n}) \cdot \mathbf{v} = \mathbf{a} (\mathbf{v} \cdot \mathbf{n}) = 0\tag{2.38}$$

The kinematic compatibility condition is proven equivalent to invariant plane condition in prototype PTMC. Hereafter in the thesis, we no longer distinguish the 'lattice invariant shear' ($\mathbf{P}_2$) condition and 'invariant plane distortion' ($\mathbf{P}_1$) condition to form habit plane, but utilize the kinematic compatibility equation in Eq.(2.37).

2.3.5 Solution of Invariant Plane (Austenite and Single Martensite Interface)

Figure 2.5: Schematic drawing of invariant plane between austenite and single martensite

For the interface of single martensite and austenite, the deformation gradients on both sides of the interface are

$$\nabla \mathbf{y}(\mathbf{x}) \begin{cases} \mathbf{I} & (\mathbf{x} \in A) \\ \mathbf{F} = \mathbf{Q}\mathbf{U}_i & (\mathbf{x} \in M) \end{cases} \quad (2.39)$$

Considering the kinematic compatibility condition in Eq.(2.37), we have Cauchy-Green deformation tensor

$$\begin{aligned} \mathbf{C} &= \mathbf{F}^T \mathbf{F} = (\mathbf{I} + \mathbf{b} \otimes \mathbf{m})^T (\mathbf{I} + \mathbf{b} \otimes \mathbf{m}) \\ &= (\mathbf{I} + \mathbf{m} \otimes \mathbf{b}) (\mathbf{I} + \mathbf{b} \otimes \mathbf{m}) \\ &= \mathbf{I} + \mathbf{b} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{b} + (\mathbf{m} \otimes \mathbf{b}) (\mathbf{m} \otimes \mathbf{b}) \\ &= \mathbf{I} + \mathbf{b} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{b} + m_i (b_k b_k) m_j \\ &= \mathbf{I} + \mathbf{b} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{b} + \frac{\mathbf{b} \cdot \mathbf{b}}{2} \mathbf{m} \otimes \mathbf{m} + \mathbf{m} \otimes \frac{\mathbf{b} \cdot \mathbf{b}}{2} \mathbf{m} \\ &= \mathbf{I} + \left(\mathbf{b} + \frac{\mathbf{b} \cdot \mathbf{b}}{2} \mathbf{m} \right) \otimes \mathbf{m} + \mathbf{m} \otimes \left(\mathbf{b} + \frac{\mathbf{b} \cdot \mathbf{b}}{2} \mathbf{m} \right) \end{aligned} \quad (2.40)$$

Recalling Eq.(2.13) and subtracting an identity matrix on the both sides of the equation, we have

$$\mathbf{F}^T \mathbf{F} - \mathbf{I} = (\lambda_1^2 - 1) \mathbf{e}_1^{eig} \otimes \mathbf{e}_1^{eig} + (\lambda_2^2 - 1) \mathbf{e}_2^{eig} \otimes \mathbf{e}_2^{eig} + (\lambda_3^2 - 1) \mathbf{e}_3^{eig} \otimes \mathbf{e}_3^{eig} \quad (2.41)$$

To make the form of Cauchy-Green tensor satisfying both Eqs.(2.40) and (2.41), one of the eigenvalues of Cauchy-Green tensor should be less than 1, the second one must be equal to 1 and the remaining one is larger than 1. Provided that

$$\lambda_1^2 < 1, \quad \lambda_2^2 = 1, \quad \lambda_3^2 > 1 \quad (2.42)$$

there are two sets of solutions for invariant plane normal and shear direction

$$\begin{cases} \mathbf{m}_1 = \sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} + \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \\ \bar{\mathbf{b}}_1 = \frac{1}{2} (\lambda_3^2 - \lambda_1^2) \left(\sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} - \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \right) \end{cases} \quad (2.43)$$

$$\begin{cases} \mathbf{m}_2 = \sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} - \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \\ \bar{\mathbf{b}}_2 = \frac{1}{2} (\lambda_3^2 - \lambda_1^2) \left(\sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} + \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \right) \end{cases} \quad (2.44)$$

Substituting the solution of $\bar{\mathbf{b}}$ and $\mathbf{m}$ into $\bar{\mathbf{b}} = \mathbf{b} + \frac{\mathbf{b} \cdot \mathbf{b}}{2} \mathbf{m}$ leads to the solutions of $\mathbf{b}$,

$$\mathbf{b}_1 = \frac{1}{2} (\lambda_3 - \lambda_1) \left(\lambda_1 \sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} - \lambda_3 \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \right) \quad (2.45)$$

$$\mathbf{b}_2 = \frac{1}{2}(\lambda_3 - \lambda_1) \left(\lambda_1 \sqrt{\frac{\lambda_3^2 - 1}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_3^{eig} + \lambda_3 \sqrt{\frac{1 - \lambda_1^2}{\lambda_3^2 - \lambda_1^2}} \mathbf{e}_1^{eig} \right) \quad (2.46)$$

Here, we utilize the Cauchy-Green tensor instead of deformation gradient $\mathbf{F}$ to solve the eigenvalues and eigenvectors. In other words, any contribution from rotation is eliminated due to $\mathbf{Q}^T \mathbf{Q} = \mathbf{I}$. The calculated invariant plane normal and shear are exclusively determined by the reference independent transformation stretch $\mathbf{U}$. Thus in practice, the inspection of kinematic compatibility condition for a specific material in laboratory should allow an additional degree of freedom of a rigid-body rotation.

2.3.6 Solution of Twin Boundary of Correspondence Variants

Figure 2.6: Illustration of a twinned region formed by two martensite variants and the twinning elements.

Recalling the polar decomposition of deformation gradient for two martensite variants, the deformation gradient reads

$$\nabla \mathbf{y}(\mathbf{x}) \begin{cases} \mathbf{F}_i = \mathbf{Q}_1 \mathbf{U}_i & (\mathbf{x} \in V_1) \\ \mathbf{F}_j = \mathbf{Q}_2 \mathbf{U}_j & (\mathbf{x} \in V_2) \end{cases} \quad (2.47)$$

Let $\mathbf{Q} = \mathbf{Q}_2^T \mathbf{Q}_1$ with a multiply factor $\mathbf{Q}_2^T$, we have kinematic compatibility equation for twin boundary

$$\mathbf{Q} \mathbf{U}_j - \mathbf{U}_i = \mathbf{a} \otimes \mathbf{n} \quad (2.48)$$

The characteristic equation

$$\left| (\mathbf{U}_j \mathbf{U}_i^{-1})^T (\mathbf{U}_j \mathbf{U}_i^{-1}) - \lambda^2 \mathbf{I} \right| = 0 \quad (2.49)$$

has solutions only if one of the eigenvalues λ is equal to 1 and the remaining two are greater and smaller than 1, respectively. If the conditions hold, the shear direction and twin plane

normal are derived

$$\mathbf{a} = \rho \left(\sqrt{\frac{\lambda_3(1-\lambda_1)}{\lambda_3-\lambda_1}} \mathbf{e}_1^{eig} + \kappa \sqrt{\frac{\lambda_1(\lambda_3-1)}{\lambda_3-\lambda_1}} \mathbf{e}_3^{eig} \right) \quad (2.50)$$

$$\mathbf{n} = \frac{\sqrt{\lambda_3} - \sqrt{\lambda_1}}{\rho \sqrt{\lambda_3 - \lambda_1}} \left(-\sqrt{1-\lambda_1} \mathbf{U}_j^T \mathbf{e}_1^{eig} + \kappa \sqrt{\lambda_3-1} \mathbf{U}_j^T \mathbf{e}_3^{eig} \right) \quad (2.51)$$

where $\kappa = \pm 1$ are chosen in accordance with two solutions, and ρ is used to minimize plane normal $\mathbf{n}$. The twinning elements in PTMC including twin plane $\kappa(\mathbf{n})$, direction of shear $\eta(\mathbf{a})$ and the magnitude of twin shear s , are given by

$$s = |\mathbf{a}| |\mathbf{U}_j \mathbf{n}|, \quad \eta = \frac{\mathbf{a}}{|\mathbf{a}|}, \quad \kappa = \frac{\mathbf{U}_j^{-1} \mathbf{n}}{|\mathbf{U}_j^{-1} \mathbf{n}|} \quad (2.52)$$

The solutions specify the twinning elements with a described deformation of one side relative to other side of the twin plane. In particular, if the martensite variants are related through a rotation of π , i.e. $\mathbf{F}_j = \mathbf{F}_i \mathbf{R}$, solving the kinematic equation of twin planes

$$\mathbf{QF}_j - \mathbf{F}_i = \mathbf{a} \otimes \mathbf{n} \quad (2.53)$$

leads to solutions which define the types of twinning

$$\begin{aligned} \mathbf{a}_1 &= 2 \left(\frac{\mathbf{F}_i^{-T} \bar{\mathbf{e}}}{|\mathbf{F}_i^{-T} \bar{\mathbf{e}}|^2} + \mathbf{F}_i \bar{\mathbf{e}} \right), & \mathbf{n}_1 &= \bar{\mathbf{e}} \\ \mathbf{a}_2 &= \rho \mathbf{F}_i \bar{\mathbf{e}}, & \mathbf{n}_2 &= \frac{2}{\rho} \left(\bar{\mathbf{e}} - \frac{\mathbf{F}_i^T \mathbf{F}_i \bar{\mathbf{e}}}{|\mathbf{F}_i \bar{\mathbf{e}}|^2} \right) \end{aligned} \quad (2.54)$$

where $\bar{\mathbf{e}}$ is the axis of rotation $\mathbf{R}$ with a representation $\mathbf{R} = -\mathbf{I} + 2\bar{\mathbf{e}} \otimes \bar{\mathbf{e}}$. Therefore, the type I twin with a rational twin plane is associated with solution 1, while the type II twin has a rational shear direction associated with solution 2. If the solutions coincide with each other, they are called compound twins.

In this thesis, a term of correspondence variant pair or a pair of twin martensites is used to distinguish microstructure containing two twin-related martensite from the microstructure of a single martensite variant equilibrium with austenite.

2.3.7 Solution of Habit Plane

Experimental observation proves the existence of a relatively unstretched habit plane between austenite and aggregation of martensite variants. In general, the habit plane is not an invariant plane because the incompatibility is non-vanishing between any type of the martensite variant and austenite. To approximate the condition of invariant plane, the martensites

have to form a set of internally micro twins, i.e. layers of twins of martensite variants are alternatively arranged on a scale of a few atomic distance, to vanish the lattice misfit stress with the maximum possibility. In this way, we can introduce a parameter ξ to indicate a ratio of two twin related martensite variants, then the kinematic compatibility condition is written in the average deformation as

$$\mathbf{Q}' (\xi \mathbf{Q} \mathbf{U}_j - (1-\xi) \mathbf{U}_i) = \mathbf{I} + \mathbf{b} \otimes \mathbf{m} \quad (2.55)$$

With the twinning equation $\mathbf{Q}_0 \mathbf{U}_j - \mathbf{U}_i = \mathbf{a} \otimes \mathbf{n}$ and inspecting the necessary and sufficient conditions for the existence of a solution, the volume ratio ξ is calculated

$$\xi = \frac{1}{2} \left(1 - \sqrt{1 + \frac{2}{\delta}} \right) \quad (2.56)$$

where $\delta = \mathbf{a} \cdot \mathbf{U}_i (\mathbf{U}_i^2 - \mathbf{I})^{-1} \mathbf{n} \leq -2$, and $\mathbf{a}$ and $\mathbf{n}$ are twinning shear and twin plane. Calculating the eigenvalues and eigenvectors of matrix $\mathbf{C} = \mathbf{U}_i (\xi \mathbf{n} \otimes \mathbf{a}) (\mathbf{U}_i + \xi \mathbf{a} \otimes \mathbf{n})$, the habit plane normal and effective shear direction are determined via

$$\mathbf{b} = \rho \left(\sqrt{\frac{\lambda_3 (1 - \lambda_1)}{\lambda_3 - \lambda_1}} \mathbf{e}_1^{eig} + \kappa \sqrt{\frac{\lambda_1 (\lambda_3 - 1)}{\lambda_3 - \lambda_1}} \mathbf{e}_3^{eig} \right) \quad (2.57)$$

$$\mathbf{m} = \frac{\sqrt{\lambda_3} - \sqrt{\lambda_1}}{\rho \sqrt{\lambda_3 - \lambda_1}} \left(-\sqrt{1 - \lambda_1} \mathbf{e}_1^{eig} + \kappa \sqrt{\lambda_3 - 1} \mathbf{e}_3^{eig} \right) \quad (2.58)$$

2.3.8 Example of CM-PTMC

In this section, the cubic-to-tetragonal transformation is used as example. The lattice vectors of austenite $\{ \mathbf{e}_1^a \ \mathbf{e}_2^a \ \mathbf{e}_3^a \}$ and martensite $\{ \mathbf{e}_1^m \ \mathbf{e}_2^m \ \mathbf{e}_3^m \}$ are selected based on the Bain correspondence and expressed in a same orthogonal reference XYZ, as is shown in Figure 2.8. The lattices vectors of austenite are

$$\mathbf{e}_1^a = \frac{1}{2} \begin{pmatrix} a_0 \\ a_0 \\ 0 \end{pmatrix}, \mathbf{e}_2^a = \frac{1}{2} \begin{pmatrix} a_0 \\ -a_0 \\ 0 \end{pmatrix}, \mathbf{e}_3^a = \frac{1}{2} \begin{pmatrix} a_0 \\ 0 \\ a_0 \end{pmatrix}; \quad (2.59)$$

while the lattice vectors of martensite in reference coordinates are

$$\mathbf{e}_1^m = \frac{1}{2} \begin{pmatrix} a \\ a \\ 0 \end{pmatrix}, \mathbf{e}_2^m = \frac{1}{2} \begin{pmatrix} a \\ -a \\ 0 \end{pmatrix}, \mathbf{e}_3^m = \frac{1}{2} \begin{pmatrix} a \\ 0 \\ c \end{pmatrix}; \quad (2.60)$$

Figure 2.7: Schematic drawing of the internal twin and habit plane

where a_0 is the lattice parameter of austenite and a and c are parameters relative to lattice of martensite. Since MT is described by using deformation, there must be a stretch $\mathbf{U}$ homogeneously deforming the austenite lattice to the martensite one, with a mathematical expression

$$\mathbf{e}^m = \mathbf{U}_3 \mathbf{e}^a, \quad \text{with} \quad \mathbf{U}_3 = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix} \quad (2.61)$$

where $\alpha = a/a_0$, $\beta = c/a_0$. The diagonal matrix $\mathbf{U}_3$ indicates that the principle axes coincide with the edges of the cubic unit cells, and the diagonal components of stretch matrix of are eigenvalues of deformation gradients. In cubic-to-tetragonal transformation, there are three different stretch matrices associated with three Bain correspondence relevant martensite variants. By inspecting the elements in the point group of $m\bar{3}m$, two other stretch matrices are

$$\mathbf{U}_1 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix}, \quad \mathbf{U}_2 = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix} \quad (2.62)$$

If the twinning of martensite variants 1 and 2 with stretch matrices $\mathbf{U}_1$ and $\mathbf{U}_2$ is considered, we can verify the existence of the 180° rotation $\mathbf{R}$ about $\mathbf{e} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$ to make

$\mathbf{R}^T \mathbf{U}_1 \mathbf{R} = \mathbf{U}_2$. By using Eq.(2.54) along with the lattice parameters, the solutions of twin plane normal and twinning shear are obtained

$$\begin{aligned} \mathbf{a}_1 &= \frac{\sqrt{2}(\beta^2 - \alpha^2)}{\beta^2 + \alpha^2} \begin{pmatrix} -\beta \\ \alpha \\ 0 \end{pmatrix}, \mathbf{n}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \\ \mathbf{a}_2 &= \frac{\sqrt{2}(\beta^2 - \alpha^2)}{\beta^2 + \alpha^2} \begin{pmatrix} -\beta \\ -\alpha \\ 0 \end{pmatrix}, \mathbf{n}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} \end{aligned} \quad (2.63)$$

We use Fe-30%Pd alloy as an example, where $a_0 = 3.756\text{\AA}$, $a = 3.795\text{\AA}$, $c = 3.725\text{\AA}$. [SNY88] Substituting the values of α and β into Eq.(2.62), the solutions of twinning shear and twin normal by using Eqs.(2.50) and (2.51) are

$$\begin{aligned} \mathbf{a}_1 &= \begin{pmatrix} 0.0321 \\ 0.0328 \\ 0 \end{pmatrix}, \mathbf{n}_1 = \begin{pmatrix} 0.7152 \\ -0.6989 \\ 0 \end{pmatrix} \\ \mathbf{a}_2 &= \begin{pmatrix} -0.0321 \\ 0.0328 \\ 0 \end{pmatrix}, \mathbf{n}_2 = \begin{pmatrix} -0.7152 \\ -0.6989 \\ 0 \end{pmatrix} \end{aligned} \quad (2.64)$$

The results show the $\{110\}$ twin planes in austenite coordinates.

Figure 2.8: The MT transforms a cubic austenite to tetragonal martensite.

2.3.9 Geometrically Linear Model with Infinitesimal Strain

The geometrically nonlinear elastic model of MT based on the deformation gradient provides mathematically accurate solutions for the microstructural features. However, the geometrical nonlinearity also brings in the complexity when the physical nonlinearity is taken into consideration in modeling. The physical nonlinearity includes the anharmonic energy density, which is no longer quadratic form in terms of strain, and nonlinear dynamics that microstructure follows to evolve. Because of that, the linear approximation is a long term using strategy to overcome the difficulties in geometrical nonlinearity in solid mechanics. The linearized geometry simplifies the modeling of microstructural features in MT, providing a not accurate but effective approximation due to the irrational indices of characteristic plane and normal in martensites and/or austensite.

As is mentioned in section 2.3, the Lagrangian finite strain tensor with geometrical nonlinearity is written as

$$\mathbf{e} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_k \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right) \quad (2.65)$$

wherein the displacement gradient $\nabla \mathbf{u}$ is defined as the matrix of the partial derivatives of the displacement with the component $(\nabla u)_{ij} = \frac{\partial u_i}{\partial x_j}$. If the nonlinear term of the cross product in Eq.(2.65) is neglected based on the fact that the displacement gradient in solid state phase transformation is small enough, the infinitesimal strain tensor can be expressed as

$$\mathbf{e} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) = \frac{1}{2} (\mathbf{F}^T + \mathbf{F} - 2\mathbf{I}) = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \quad (2.66)$$

Applying the approximation to a rotation, the skew matrix (anti-symmetric rotation tensor) in geometrically linear theory reads

$$\mathbf{w} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right) = \frac{1}{2} (\mathbf{F} - \mathbf{F}^T) \quad (2.67)$$

Since the stretch and rotation are approximated as follows

$$\mathbf{U} \approx \mathbf{I} + \mathbf{e}, \quad \mathbf{Q} \approx \mathbf{I} + \mathbf{w} \quad (2.68)$$

the polar decomposition of the multiplying rotation and stretch is accordingly simplified by adding anti-symmetric rotation to linear strain and identity, i.e.

$$\mathbf{F} = \mathbf{I} + \nabla \mathbf{u} = \mathbf{I} + \mathbf{e} + \mathbf{w} \quad (2.69)$$

And the materials symmetry of energy is expressed in strain as

$$\varphi(\mathbf{R}^T \mathbf{e} \mathbf{R}, \mathbf{T}) = \varphi(\mathbf{e}, \mathbf{T}), \quad \text{for any rotation } \mathbf{R} \in P(\mathbf{e}_i^\circ) \quad (2.70)$$

Substituting the Eq.(2.69) into the Eq.(2.37), the kinematic compatibility equation in geometrically linear elastic model is expressed in the independent variables of displacement gradient.

$$(\nabla \mathbf{u})_I - (\nabla \mathbf{u})_J = \mathbf{a} \otimes \mathbf{n} \quad (2.71)$$

Considering infinitesimal strain in Eq.(2.66), the strain compatibility equation widely utilized in the geometrically linear elastic model of MT is derived

$$\mathbf{e}_I - \mathbf{e}_J = \frac{1}{2} (\mathbf{a} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}) \quad (2.72)$$

And the skew matrices satisfy

$$\mathbf{w}_I - \mathbf{w}_J = \frac{1}{2} (\mathbf{a} \otimes \mathbf{n} - \mathbf{n} \otimes \mathbf{a}) \quad (2.73)$$

With the strain compatibility equation, the twin plane normal and the twinning shear can be determined by solving the eigenvalues and eigenvectors of $\mathbf{E} = \mathbf{e}_I - \mathbf{e}_J = \frac{1}{2} (\mathbf{a} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a})$. Sorting the eigenvalues of $\mathbf{E}$ by assuming $\varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3$, and when the eigenvalues satisfy $\varepsilon_1 \leq 0, \varepsilon_2 = 0, \varepsilon_3 \geq 0$, there are two solutions of twinning shear and twin plane normal

$$\begin{aligned} \mathbf{a} &= \sqrt{2(\varepsilon_3 - \varepsilon_1)} (\kappa \sqrt{-\varepsilon_1} \mathbf{e}_1^{ig} + \sqrt{\varepsilon_3} \mathbf{e}_3^{ig}) \\ \mathbf{n} &= \frac{1}{\sqrt{(\varepsilon_3 - \varepsilon_1)}} (-\kappa \sqrt{-\varepsilon_1} \mathbf{e}_1^{ig} + \sqrt{\varepsilon_3} \mathbf{e}_3^{ig}) \end{aligned} \quad (2.74)$$

Similar to the analysis of the twinned martensite variants related by the 180° rotation with the axis $\bar{\mathbf{e}}$, two sets of solutions corresponding to the type I and type II twins are available, which read

$$\begin{aligned} \mathbf{a}_1 &= 4 [(\bar{\mathbf{e}} \cdot \mathbf{e}_I \bar{\mathbf{e}}) \bar{\mathbf{e}} - \mathbf{e}_I \bar{\mathbf{e}}], & \mathbf{n}_1 &= \bar{\mathbf{e}} \\ \mathbf{a}_2 &= 4 |(\bar{\mathbf{e}} \cdot \mathbf{e}_I \bar{\mathbf{e}}) \bar{\mathbf{e}} - \mathbf{e}_I \bar{\mathbf{e}}| \bar{\mathbf{e}}, & \mathbf{n}_2 &= \frac{(\bar{\mathbf{e}} \cdot \mathbf{e}_I \bar{\mathbf{e}}) \bar{\mathbf{e}} - \mathbf{e}_I \bar{\mathbf{e}}}{|(\bar{\mathbf{e}} \cdot \mathbf{e}_I \bar{\mathbf{e}}) \bar{\mathbf{e}} - \mathbf{e}_I \bar{\mathbf{e}}|} \end{aligned} \quad (2.75)$$

The invariant plane between austenite and single martensite is solved by using the same procedures with the equation

$$\mathbf{E} = \mathbf{e}_I - 0 = \frac{1}{2} (\mathbf{a} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}) \quad (2.76)$$

Based on the solved twin plane normal and shear direction, the habit plane normal and the shear direction of the average deformation is calculated by using

$$\xi \mathbf{e}_j - (1 - \xi) \mathbf{e}_i = \frac{1}{2} (\mathbf{b} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{b}) \quad (2.77)$$

if the one eigenvalue of the average strain $\xi \mathbf{e}_j - (1 - \xi) \mathbf{e}_i$ is equal to zero with an appropriate chosen value of ξ . The more detailed procedures is referenced in [Bha03].

2.4 Landau Theory with IRS

Detailed in the previous sections, the prototype PTMC and CM-PTMC theories achieve great success in illuminating the static microstructure features of a material undergoing MT by unveiling the crucial effect of the kinematic compatibility. Integrated with the wisdom of group theory, crystallography, and matrix algebra, most of intriguing microstructural patterns, including wedge-like, herringbone, etc. [Bha03] more than habit planes and twin boundaries, are elaborately analyzed in mathematics. However, the static model is limited to understand the stable morphology of martensites. It fails to capture most of meta-stable microstructural features governed by dynamics. Moreover, the temperature relevant thermodynamic and thermomechanical behaviors, such as shape memory effects and temperature dependent hysteresis of stress-strain curve in SMAs, acoustic phonon softening, varying driving force with temperature, etc., are not taken into consideration in PTMC theories. Therefore, a dynamical modeling is required.

Among the phenomenological approaches, Landau theory not only provides an excellent interpretation for the formation of static patterns in phase transition, but has ability to integrate with various dynamic formulism to explain fascinating dynamic behaviors. The born of Landau type model for first-order displacive transformation with Irreducible Representation form of Strains (IRS) was traced back to 1970s, when the progress of the renormalization group technique enabled Landau theory to approximately handle the problem of fluctuations on critical phenomena. Cook [Coo76] interpreted the fluctuations as large amplitude, quasi-static wave packets to extend the Landau's theory of second-order phase transition to first-order structural transition. With a justified hypothesis that systems having the same symmetry were expected to have similar critical properties, Cowley [Cow76] applied these ideas to a static analysis of the first-order structural phase transition triggered by homogeneous deformation and included the effect of fluctuations. He creatively connected fluctuation in lattice dynamics with the stability of crystals against deformation in macroscopic elasticity by inspecting the velocities of acoustic waves and irreducibly representing them as the functional of the linear combination of elastic constants. In his static analysis, the homogeneous deformations were written in Landau polynomial expanded to forth order with homogeneous strain as a primary Order Parameter(OP). The fluctuation of elastic heterogeneity entered Hamiltonian via the strains with nonzero wave vectors in reciprocal space.

2.4.1 Landau Free Energy

Realizing the Landau model has advantages of yielding the whole temperature dependent physical nonlinearity, Falk [Fal80, Fal82] initiatively proposed Landau model accounting for thermodynamic and thermomechanical behaviors of MT in SMAs. With the temperature dependent Landau polynomial expanded in strain up to sixth order, the model of temperature induced MT in one-dimensional homogeneous medium qualitatively derived the temperature dependent thermodynamic properties and shape memory behaviors, such as the latent heat in transformation, the stress-strain curves at various temperatures (especially the hysteresis below critical temperature), the lattice softening, the stress effect on the temperature-induced phase transition, etc. Afterwards, the one-dimensional Landau potential was applied to different structural transitions, and the various solutions of domain walls characterized in soliton, kink or periodon, were also analyzed [Fal83, SS03, SSL01], which are directly associated with the morphology of twinned or single martensite in the subsequent chapters.

To extend the one-dimensional Landau free energy to 2D or 3D phase transformations, the free-energy function should be expanded to anharmonic terms with the OPs of a second-rank tensor of strain, and be kept invariant with respect to the operations in the high symmetry group of parent phase. However, the requirement of identifying the broken symmetry in crystallography and representing them in Landau free energy renders the determination of OPs difficult. To overcome the difficulty, the method of irreducible representation of the more symmetric, high temperature phase was naturally incorporated, in which appropriate combinations of the components of strain tensor (in IRS form) were adopted as OPs. The great success of identification of the IRS OPs and the determination of the analytic form of the Landau free energy for all the structural phase transitions were credited to Toledano and Toledano [TFA83, TT80], Likaos[LS82], Salje[Sal90], Stokes[SH84] and Hatch[HS84, HLSS03]. The details of the irreducible representation theory and the application to the construction of Landau energy can refer to the textbook [TD96]. Herein, only the general methodology is briefly introduced.

Since the Landau energy density for MT is in terms of strain components and keep invariant under any symmetry operation $\mathbf{R}$ in the point group of austenite, we have

$$\mathbf{e}' = \mathbf{R}^T \mathbf{e} \mathbf{R} \quad F'(\mathbf{e}', T) = F(\mathbf{e}, T) \quad (2.78)$$

Provided the strain tensor written in Cartesian coordinates with orthogonal bases $\hat{\mathbf{e}}_{0i}$ is

$$\begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33} \end{pmatrix} \quad (2.79)$$

the strain tensor can be represented as a vector in a six-dimensional space $\hat{S}$ spanned by $\hat{\varphi}_i$ using Voigt notation.

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} = \begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \varepsilon_{23} + \varepsilon_{32} \\ \varepsilon_{13} + \varepsilon_{31} \\ \varepsilon_{12} + \varepsilon_{21} \end{pmatrix}, \quad (2.80)$$

$$\begin{aligned} \hat{\varphi}_1 &= \hat{\mathbf{e}}_{01} \otimes \hat{\mathbf{e}}_{01} \\ \hat{\varphi}_2 &= \hat{\mathbf{e}}_{02} \otimes \hat{\mathbf{e}}_{02} \\ \hat{\varphi}_3 &= \hat{\mathbf{e}}_{03} \otimes \hat{\mathbf{e}}_{03} \\ 2\hat{\varphi}_4 &= \hat{\mathbf{e}}_{02} \otimes \hat{\mathbf{e}}_{03} + \hat{\mathbf{e}}_{03} \otimes \hat{\mathbf{e}}_{02} \\ 2\hat{\varphi}_5 &= \hat{\mathbf{e}}_{01} \otimes \hat{\mathbf{e}}_{03} + \hat{\mathbf{e}}_{03} \otimes \hat{\mathbf{e}}_{01} \\ 2\hat{\varphi}_6 &= \hat{\mathbf{e}}_{01} \otimes \hat{\mathbf{e}}_{02} + \hat{\mathbf{e}}_{02} \otimes \hat{\mathbf{e}}_{01} \end{aligned}$$

Thus, the symmetry operations R_{ij} of the point group are represented as r_{MN} to keep the identity

$$\varepsilon_M' = r_{MN} \varepsilon_N \quad (2.81)$$

Since the representation r_{MN} is reducible into the irreducible representation, the symmetry adapted strains are expressed as the linear combination of strain components, and strain space $\hat{S}$ is accordingly decomposed into the subspaces spanned by the direction vectors of symmetry adapted strains, namely

$$\begin{aligned} e_1 &= \frac{1}{\sqrt{3}}(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \\ e_2 &= \frac{1}{\sqrt{2}}(\varepsilon_{11} - \varepsilon_{22}) \\ e_3 &= \frac{1}{\sqrt{6}}(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{33}) \\ e_4 &= (\varepsilon_{23} + \varepsilon_{32}) \\ e_5 &= (\varepsilon_{13} + \varepsilon_{31}) \\ e_6 &= (\varepsilon_{12} + \varepsilon_{21}) \end{aligned} \quad (2.82)$$

$$\begin{array}{ll} S_1 & (dilatation) \quad \hat{\psi}_1 = \hat{\varphi}_1 + \hat{\varphi}_2 + \hat{\varphi}_3 \\ S_{12} & (deviatoric) \quad \hat{\psi}_2 = \hat{\varphi}_1 - \hat{\varphi}_2 \\ & \quad \hat{\psi}_3 = \hat{\varphi}_1 + \hat{\varphi}_2 - 2\hat{\varphi}_3 \\ S_{25} & (shear) \quad \hat{\psi}_4 = 2\hat{\varphi}_4 \\ & \quad \hat{\psi}_5 = 2\hat{\varphi}_5 \\ & \quad \hat{\psi}_6 = 2\hat{\varphi}_6 \end{array}$$

On the other hand, the Landau energy density is expanded in Taylor series with respect to strains

$$F(e, T) = F^0(T) + F^1(e, T) + F^2(e, T) + \dots \quad (2.83)$$

Since the n^{th} degree in Landau polynomial of MT is written as the scalar product of n^{th} elastic constants $\mathbf{C}$ and strains $\mathbf{e}$, elastic constants $\mathbf{C}$ can be decomposed into the sum of the product of symmetry adapted elastic constant F_j^n (linear combination of n^{th} order elastic constants) and invariant direction in a symmetrised product space according to the same irreducible representation. On each invariant direction, there is an invariant J_j^n expressed as polynomial of strain components. So that, the n^{th} degree in Landau energy expansion reads

$$F^n(e, T) = \sum_j F_j^n J_j^n \quad (2.84)$$

Falk has summarized parts of the strain invariants listed in Tables(1-2) of [FK90]. Based on these, the Landau energy for specific MT is constructed by selecting the invariants and truncating at an appropriate high order term. The Landau free energy for typical MTs are available in literature, for example the energy expression for cubic-to-tetragonal transition by Barsch and Krumhansl [BK84] and cubic-to-trigonal by [SLS10, Sal09], cubic-to-orthorhombic by [NK82, SLS10, SSF12] and cubic-monoclinic I by [FK90, SLS10, SSF12].

2.4.2 Dynamics

Fascinating dynamic behaviors during MTs can be revealed when the Landau energy is equipped with different dynamic formalisms. The Landau energy based on the IRS is suitable for most of dynamics, including static stress equilibrium, TDGL, Bales-Gooding and displacement based Lagrange-Rayleigh dynamics, etc. [LSR⁺03] The representative achievements on depicting dynamic phenomena, such as the near-sound velocity of propagation of domain walls and 'dynamical twinning', attribute to the inertia dynamics, either Bales-Gooding type or Lagrange-Rayleigh type. The inertia dynamics has a distinctive feature of including kinetic energy to account for inertial effects of material point in real space or elastic oscillators with different wave vectors in reciprocal space. Sometimes, a Rayleigh dissipation term is additionally incorporated representing the sound-wave viscosity. Two formulations of inertia dynamics, i.e. Bales-Gooding in strains or Lagrange-Rayleigh in displacement, differ in the deductions of dynamic equations. The Bales-Gooding dynamics works only with strain fields, in which the Lagrangian is written in primary OP strain(s) and explicitly appends the St. Venant's compatibility constraint via a Lagrange multiplier. The procedure yields an anisotropic long-range kernel indicating the preferential orientation of twinning. While in displacement based Lagrange-Rayleigh dynamics, a general equation

of motion is straightforwardly obtained from Lagrange mechanics by implementing variation of Lagrangian with respect to displacement or displacement gradient field, in which the displacement are served as independent variables.

2.4.3 Motions of Domain Walls

The first issue the inertia dynamics settled in MT is the movement of domain walls. Barsch and Krumhansl [BK84, BG91] included anharmonic strain energy and nonlocal contribution of strain gradient to formulate inhomogeneous strain fields associated with heterogeneity of martensites and domain boundaries. The results of motion equations either in Lagrange mechanics involving displacement or Bales-Gooding dynamics led to the same kinked solitary wave solution describing the moving twin boundaries that separate alternatively arranged martensite variants. These soliton solution was further evidenced by Jabcob and Curnoe in their 2D (3D) calculations of strain fields after square-rectangular (cubic-tetragonal) MT [Jac85, CJ00]. The 'dynamical twinning', different from the classical argument that dislocations stabilize twinned structure, revealed a different physical scenario that the long-range elastic interaction in austenite with a kinetic energy renders a dispersion giving rise to twinned structure [BHK87]. Attempting to minimize the kinetic energy, a perpetually propagation of twinning interfaces through the system is energetically and dynamically favored. The 'dynamical twinning' provides a new perspective to study the shape memory effect and autocatalytic twinning.

2.4.4 Precursors

The nucleation and the formation of precursors are two other topics of nonlinear Landau model. The combination of anharmonic Landau energy with strain gradient and inertia dynamics gives an ingenious physical scenario beyond the classical nucleation theory [SLSB99, LSD⁺00]. Looking back to the beginning of Section 2.4, Cook [Coo76] argued that a high density of the hetero-phase fluctuations in a system with anharmonic energy interplaying with interface energy would lead to the formation of precursor above the critical temperature, whereas it nucleates into low symmetric phase at the temperature below the coherent transformation point. The statement was further clarified by Krumhansl and Gooding [KG89] that the anomalous low values of elastic constants or in phonon dispersion were discovered in a few directions, rather than harmonic instability of soft-mode, which accounted for the intrinsic features of precursors and were associated with 'central peaks'. Kartha [KKS95] simulated the meso-scale tweed pattern and interpreted its formation by introducing the concept of the static long-range elastic kernel in a heterogeneous system.

The tweed, recognized as a distinct thermodynamically meta-stable phase, is mediated by the coupling between strain dependent anharmonic energy and spatial dependent nonlocal strain gradient [BK88]. In a modern statement considering inertia dynamics by Lookman [LSR⁺03], the elastic oscillators have different 'strain-mass' densities $\rho(k) \sim 1/k^2$ and damping $1/\rho(k) \sim k^2$, such that the lighter large- k oscillators equilibrate first, corresponding to earlier formation of smaller-scale oriented tweed. The following nucleation to form the twinned pattern or other microstructure can be achieved by autocatalysis mechanism with a varying localized stress, which will be detailed in Chapter 4.

2.4.5 Microstructure Simulation

With the development of the computer science, the dream of representing the temporal evolution of microstructure is turned into reality. Kartha [KKS95] carried out a Monte Carlo simulation with Landau free energy to represent the microstructure of tweed and twins during the square-to-rectangular MT. Jacob [Jac95] simulated the static morphology of the same transformation in a constrained system, while the TDGL simulation using OP strains and long-range compatibility kernel was found in [SLSB99]. The displacement based underdamped Lagrange-Rayleigh dynamics was also applied to 2D simulations analogs of tetragonal-to-orthorhombic and hexagonal-to-orthorhombic ferroelastic transformations [CJ01a, CJ01b]. Ahluwalia [AA01] included a coupling term between squares of the OP strains in Landau free energy and dropped the non-OP strains in Bales-Gooding formalism to represent the avalanches in MT. Most of 3D simulations of microstructural evolution were utilizing displacement based Lagrange dynamics, like the cubic-to-tetragonal ferroelastics in [LSR⁺03, ALS06], with the exceptions of Rasmussen and Shenoy who considered the St. Venant's compatibility constraint in three dimension in strain based overdamped equation. The most intriguing discovery in microstructure simulation is the richness of morphology which were formed due to the selective transformation paths in different dynamics, for example the hierarchical microstructure of tweed, twin and chessboard patterns [SLSB99, SSB⁺98] and 'maze' like pattern with 'zoom lens' moving boundaries in the intermediate state of transformation [LSR⁺03].

In the following subsections, the nonlinear Landau model with displacement based Lagrange - Rayleigh dynamics are detailed. Especially, the simulation procedures, numerical strategy and results of the 3D simulations are presented with the examples of the Fe-Pd alloy for cubic-to-tetragonal MT and Au-Cd alloy for cubic-to-trigonal MT. It is known that the constructions of Lagrangian and dynamic equations are two key issues in modeling. The

Lagrangian is defined as

$$\mathcal{L} = \int_V d\mathbf{r} \{T - f\} \quad (2.85)$$

where f is Landau free energy density with the expression $f = f_{local} + f_{non-OP} + f_{grad}$. The individual energy density contributions are expanded in terms of symmetry adapted strain following the strategy in subsection 2.4.1. With geometrically linear approximation, the symmetry adapted strain can be directly linked with the displacements by

$$e_i = \lambda_{kj}^{(i)} \varepsilon_{kj} = \lambda_{kj}^{(i)} \left(\frac{\partial u_k}{\partial x_j} + \frac{\partial u_j}{\partial x_k} \right) \quad (2.86)$$

where, λ_{kj} is the symmetry related coefficient to keep that the energy is invariant. For example, $1/\sqrt{2}$ and $-1/\sqrt{2}$ are adopted as the coefficients of ε_{11} and ε_{22} in the expression of e_2 , see Eq. (2.82).

The kinetic energy density T is also linked with displacement and written as

$$T = \frac{\rho}{2} \sum_i^{N-\dim} \dot{u}_i(\mathbf{r}, t)^2 \quad (2.87)$$

where ρ is mass density. The incorporation of kinetic energy is capable of describing the inertial effect of the finite velocity of interface motion. The near sound velocity indicates the rates of strain evolution in position space and associates with the propagation of the acoustic waves in Fourier space.

In a system consisting of kinetic and potential energies, the internal friction plays a crucial role in dissipating the excess energy and drives the system towards the energy minima of martensitic state. With the friction, the motion of elastic oscillators as a result of the kinetic energy gained from the lowered Landau energy in phase transformation is certainly damped. Consequently, a simple Rayleigh dissipation density can be included to describe the elastic viscosity, with the mathematical expression as square summation of strain velocity for all the OP strains with viscosity parameter γ

$$R = \sum_i^{n-OP} \frac{\gamma_i}{2} \dot{e}_i^2(\mathbf{r}, t) \quad (2.88)$$

It is noteworthy that the system is energetic conserved if the Rayleigh dissipation term is removed, such that the system oscillates indefinitely.

With a constructed Lagrangian, the time evolution of the microstructure is implemented by numerically solving the Lagrange-Rayleigh equation

$$\frac{d}{dt} \frac{\delta \mathcal{L}}{\delta \dot{U}_i} - \frac{\delta \mathcal{L}}{\delta U_i} = - \frac{\delta \mathcal{R}}{\delta \dot{U}_i} \quad (2.89)$$

2.4.6 Chain Rule for Functional Differentiation

Before deriving the general equation of motion from Lagrange-Rayleigh equation, we have to prove that the chain rule is also applied to the functional differentiation, i.e.

$$\frac{\delta F}{\delta Q_i} = \sum_k \frac{\delta F}{\delta q_k} \frac{\partial q_k}{\partial Q_i} \quad (2.90)$$

where $F = \int_r I [Q_i, \nabla Q_i, q (Q_i, \nabla Q_i)] dr$, and I denotes the full integrand of Landau energy density.

In the proof, we simplify the Lagrange-Rayleigh equation to the static limit, i.e. the inertia (on the left) and the real damping (second right) parts are removed. By doing so, the dynamic equation is degenerated into the static equation of stress equilibrium. Generally, the equilibrium solution can be found by implementing the variation of F (including a gradient regularization) with respect to variables Q_i , which reads

$$\frac{\delta F}{\delta Q_i} = \frac{\partial I}{\partial Q_i} - \nabla \frac{\partial I}{\partial \nabla Q_i} = 0 \quad (2.91)$$

If the variables Q_i are obtained via an unambiguous transformation $\mathbf{T} [\cdot]$ of the variables q_j , i.e. $\mathbf{Q} = \mathbf{T} [\mathbf{q}]$, the inverse transformation must be expressed as $\mathbf{q} = \mathbf{T}^{-1} [\mathbf{Q}]$. Thus, the derivatives in Eq.(2.91) can be expanded via the chain rule as

$$\begin{aligned} \frac{\partial I}{\partial Q_i} &= \sum_k \frac{\partial I}{\partial q_k} \frac{\partial q_k}{\partial Q_i} + \frac{\partial I}{\partial \nabla q_k} \frac{\partial \nabla q_k}{\partial Q_i} \\ \nabla \frac{\partial I}{\partial \nabla Q_i} &= \nabla \left[\sum_k \frac{\partial I}{\partial q_k} \frac{\partial q_k}{\partial \nabla Q_i} + \frac{\partial I}{\partial \nabla q_k} \frac{\partial \nabla q_k}{\partial \nabla Q_i} \right] \end{aligned} \quad (2.92)$$

It is then easy to reformulate the Eq.(2.91) with these two summations as follows,

$$\begin{aligned} \frac{\delta F}{\delta Q_i} &= \sum_k \frac{\partial I}{\partial q_k} \frac{\partial q_k}{\partial Q_i} + \sum_k \frac{\partial I}{\partial \nabla q_k} \frac{\partial \nabla q_k}{\partial Q_i} - \sum_k \nabla \left(\frac{\partial I}{\partial q_k} \frac{\partial q_k}{\partial \nabla Q_i} \right) \\ &\quad - \sum_k \left(\nabla \frac{\partial I}{\partial \nabla q_k} \right) \frac{\partial \nabla q_k}{\partial Q_i} - \sum_k \frac{\partial I}{\partial \nabla q_k} \left(\nabla \frac{\partial \nabla q_k}{\partial \nabla Q_i} \right) \end{aligned} \quad (2.93)$$

Because $\mathbf{Q}$ and $\mathbf{q}$ are related by a spatial independent transformation $\mathbf{T}$, it is clear that $\frac{\partial q_k}{\partial \nabla Q_i} = 0$. Therefore, the third sum in the above equation is equal to 0, and then

$$\frac{\delta F}{\delta Q_i} = \sum_k \left[\frac{\partial I}{\partial q_k} \frac{\partial q_k}{\partial Q_i} - \left(\nabla \frac{\partial I}{\partial \nabla q_k} \right) \frac{\partial \nabla q_k}{\partial \nabla Q_i} \right] + \sum_k \frac{\partial I}{\partial \nabla q_k} \left[\frac{\partial \nabla q_k}{\partial Q_i} - \nabla \frac{\partial \nabla q_k}{\partial \nabla Q_i} \right] \quad (2.94)$$

Using the chain rule again leads to the relationships of

$$\begin{aligned} \nabla q_k &= \sum_i \frac{\partial q_k}{\partial Q_i} \nabla Q_i \\ \frac{\partial \nabla q_k}{\partial \nabla Q_i} &= \partial \sum_j \frac{\partial q_k}{\partial Q_j} \nabla Q_j / \partial \nabla Q_i = \frac{\partial q_k}{\partial Q_i} \end{aligned} \quad (2.95)$$

Thus, the first sum in Eq(2.94) is compressed as $\sum_k \left(\frac{\partial I}{\partial q_k} - \nabla \frac{\partial I}{\partial \nabla q_k} \right) \frac{\partial q_k}{\partial Q_i}$

In addition, a set of similar relationships

$$\begin{aligned} \frac{\partial \nabla q_k}{\partial Q_i} &= \partial \sum_j \frac{\partial q_k}{\partial Q_j} \nabla Q_j / \partial Q_i = \sum_j \frac{\partial^2 q_k}{\partial Q_i \partial Q_j} \nabla Q_j \\ \nabla \frac{\partial q_k}{\partial Q_i} &= \frac{\partial \nabla q_k}{\partial Q_i} = \sum_j \frac{\partial^2 q_k}{\partial Q_i \partial Q_j} \nabla Q_j \end{aligned} \quad (2.96)$$

is obtained formally by utilizing chain rule of derivatives. It is apparent that second sum would vanish in Eq(2.94), which leads to the conclusion that the chain rule of derivatives also applies to the functional differentiation, viz.

$$\frac{\delta F}{\delta Q_i} = \sum_k \left(\frac{\partial I}{\partial q_k} - \nabla \frac{\partial I}{\partial \nabla q_k} \right) \frac{\partial q_k}{\partial Q_i} = \sum_k \frac{\delta F}{\delta q_k} \frac{\partial q_k}{\partial Q_i} \quad (2.97)$$

In our particular case for the displacement field, let $Q_i = u_{i,j}$ and $q_k = e_k$. The symmetry adapted strain e_k and the displacement gradient $u_{i,j}$ are linked via a matrix

$$\begin{aligned} e_k &= \mathbf{T}_k^{-1} u_{i,j} \\ \begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix} &= \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{-2}{\sqrt{6}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \text{sym}(u_{1,1}) \\ \text{sym}(u_{2,2}) \\ \text{sym}(u_{3,3}) \\ \text{sym}(u_{2,3}) \\ \text{sym}(u_{1,3}) \\ \text{sym}(u_{1,2}) \end{bmatrix} \end{aligned} \quad (2.98)$$

In 2D, the transformation matrix $\mathbf{T}$ is simplified as follow

$$\begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \\ & & 1 \end{bmatrix} \begin{bmatrix} \text{sym}(u_{1,1}) \\ \text{sym}(u_{2,2}) \\ \text{sym}(u_{1,2}) \end{bmatrix} \quad (2.99)$$

Therefore, $\frac{\delta F}{\delta u_{i,j}} = \sum_k \left(\frac{\partial f_{\text{landau}}}{\partial e_k} - \nabla \frac{\partial f_{\text{landau}}}{\partial \nabla e_k} \right) \frac{\partial e_k}{\partial u_{i,j}} = \sum_k \sigma_k \frac{\partial e_k}{\partial u_{i,j}}$.

By taking the functional differentiation along with the chain rule, the general equation of motion in displacements is obtained.

$$\rho \ddot{u}_i = \sum_k \sigma_k \frac{\partial e_k}{\partial u_{i,j}} + \sum_k \dot{\sigma}_k \frac{\partial \dot{e}_k}{\partial \dot{u}_{i,j}} \quad (2.100)$$

2.4.7 Numerical Strategy

The general equation of motion was numerically solved in a periodic 3D box by using a operator-splitting-based, quasi-spectral, semi-implicit time stepping scheme in the following subsections.

For simplicity,

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = \mathbf{f}(\mathbf{u}, \nabla \mathbf{u}) \quad (2.101)$$

The $\mathbf{f}(\mathbf{u}, \nabla \mathbf{u})$ was the nonlinear term relevant to energy density. The variation of gradient energy density, named Ginzburg term, was written as the functional of OP strains and treated fully explicitly in Fourier space.

$$\frac{\delta(\nabla e_k)^2}{\delta e_k} = -2\nabla^2 e_k = 2k^2 \hat{e}_k \quad (2.102)$$

During the time evolution, the nonlinear term was evaluated at each time step t , and the acceleration was approximated by using central-difference formula

$$\frac{\partial^2 u_i}{\partial t^2} \approx \frac{u_i^{t+\Delta t} - 2u_i^t + u_i^{t-\Delta t}}{\Delta t^2} \quad (2.103)$$

In this work, the anisotropic Rayleigh dissipation term was simplified into an isotropic viscous term with the viscosity γ i.e.

$$\frac{\delta \mathcal{R}}{\delta u_{i,j}} = \nabla \cdot \frac{\partial \boldsymbol{\sigma}}{\partial t} \approx \gamma \nabla^2 \frac{\partial \mathbf{u}}{\partial t} \quad (2.104)$$

Numerically, the viscous term was treated in semi-implicit form, and then transformed into Fourier space.

$$\gamma \nabla^2 \frac{\partial \mathbf{u}}{\partial t} \approx \gamma \nabla^2 \left(\frac{\mathbf{u}^{t+\Delta t} - \mathbf{u}^t}{\Delta t} \right) = -\frac{\gamma k^2}{\Delta t} (\hat{\mathbf{u}}^{t+\Delta t} - \hat{\mathbf{u}}^t) \quad (2.105)$$

where, the implicit displacements at $t + \Delta t$ step can be served as the linear term $\hat{s} [\hat{u}^{t+\Delta t}]$ in numerical calculation. Otherwise, we can elaborately choose a linear term $\hat{s} [\hat{u}^{t+\Delta t}] = \hat{s} \left(\sum_1^i (-1)^i \gamma_i k^{2i} \hat{u}^{t+\Delta t} \right)$ adding to both sides of dynamic equation to tackle the numerical instability, which had been used to solve the Cahn-Hilliard equation with composition dependent mobility [ZCST99]. Reformulating the dynamic equation resulted in the following explicit time-stepping scheme in the spectrum

$$\hat{u}_i^{t+\Delta t} = \left(1 + \frac{1}{1 + \gamma k^2 \Delta t} \right) \hat{u}_i^t - \frac{1}{1 + \gamma k^2 \Delta t} \hat{u}_i^{t-\Delta t} + \frac{(\Delta t)^2}{1 + \gamma k^2 \Delta t} \hat{f}(\mathbf{u}^t, u_{i,j}^t, \nabla e_k^t) \quad (2.106)$$

Because there was neither a bound ensuring that the free energy converged to the equilibrium state nor was an artificial modification of the spatial solution of u_i after a time step, the results could lead to instabilities in spectral method. Thus, the explicit-implicit splitting viscosity parameter should be cautiously chosen.

Figure 2.9: Snapshots of simulated pattern presented by the primary order parameter of e_2 with time. (a). 0.78ns (b). 3.55ns. The faces of each display cube are cubic $\{100\}$ planes; the red, white, and blue regions correspond to the three tetragonal correspondence variants.

2.4.8 Cubic-to-Tetragonal Transformation

The cubic-to-tetragonal MT in Fe-Pd alloys is governed by acoustic softening of transverse mode polarized along $\begin{bmatrix} 1 & \bar{1} & 0 \end{bmatrix}$. The associated eigenvalue of the elastic constant matrix is $c_{11} - c_{12}$, thus the deviatoric strains $e_2 = \frac{1}{\sqrt{2}}(\varepsilon_{11} - \varepsilon_{22})$ and $e_3 = \frac{1}{\sqrt{6}}(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{33})$ are chosen as primary OPs, while the bulk strain $e_1 = \frac{1}{\sqrt{3}}(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})$ and three shear strains $e_4 = \varepsilon_{23}$, $e_5 = \varepsilon_{13}$ and $e_6 = \varepsilon_{12}$ are non-OP symmetry adapted strains. The nonlinear free energy density in elasticity is written as

$$\begin{aligned}
 f &= f_{local} + f_{non-OP} + f_{grad} \\
 &= \frac{c_{11} - c_{12}}{2} (e_2^2 + e_3^2) + \frac{1}{6\sqrt{6}} (c_{111} - 3c_{112} + 2c_{123}) e_3 (e_3^2 - 3e_2^2) \\
 &\quad + C(e_2^2 + e_3^2)^2 + \frac{c_{11} + 2c_{12}}{3} e_1^2 + c_{44} \sum_{i=4}^{4-6} e_i^2 + \frac{g}{2} (\nabla e_2)^2 + \frac{g}{2} (\nabla e_3)^2
 \end{aligned} \tag{2.107}$$

where c_{ij} and c_{ijk} are second order and third order elastic constants. The first three terms are 2-3-4 order polynomial of Landau free energy to construct three energetic equivalent wells of martensite variants. The term with e_1 is associated with the energy cost of bulk dilatation

in transformation; the summation term is the shear energy density and the remaining are nonlocal gradient terms.

For numerical simulation, it is proven that a system of 128^3 cube size is eligible for revealing the characteristic features in microstructure evolution. Since deviatoric strain e_2 is the primary OP which contributes greater than any other factor in cubic-to-tetragonal MT, it is adopted to represent different martensitic domains. We present both transient and full converged results of 3D structure in Figure 2.9. Three types of colored domains are easily seen, i.e. red, blue and white ones in the structure snapshot, which represent three martensite variants. The red one is of a positive magnitude of e_2 , while the blue one is negative and the white one has the similar value of e_2 as austenite. The austenite is not considered to be retained here. The pattern reveals the nature of cubic-to-tetragonal MT with the walls lying in cubic $\{110\}$ planes to minimize dilatational and shear energy, which is consistent with what CM-PTMC predicts in subsection 2.3.8. What to be highlighted is the length scale of twinned martensites in transient state is smaller than that of converged martensites, which is the result of energy minimization by eliminating the interface. Moreover, needle like twins and collisions of identical/different variants can be found even for a long time simulation. The morphology of tapering needle is favored by energy minimization. The slice of the converged martensites with three variants is shown in Figure 2.10. Clearly, three martensite variants have not equivalently grown. The microstructure consists of two primary bands, here blue and white; each primary extends in $[\bar{1} \ 0 \ 1]$ direction and is penetrated by the third variant, here red ones. At the top and bottom parts, only blue and white variants organize the two-variant microstructure similar to that in 2D. The central part shows chevron or herringbone patterns; some red domains are continuous across the blue-white boundaries, where they bend through 90° and are slightly shrunk as well.

2.4.9 Cubic-to-Trigonal Transformation

From the CM-PTMC, we understand that the system undergoing cubic-to-trigonal MT produces four martensite variants, with unique transformation stretch matrices as follows

$$\begin{aligned} \mathbf{U}_1 &= \begin{pmatrix} \alpha & \gamma & \gamma \\ \gamma & \alpha & \gamma \\ \gamma & \gamma & \alpha \end{pmatrix}, \mathbf{U}_2 = \begin{pmatrix} \alpha & -\gamma & -\gamma \\ -\gamma & \alpha & \gamma \\ -\gamma & \gamma & \alpha \end{pmatrix}; \\ \mathbf{U}_3 &= \begin{pmatrix} \alpha & -\gamma & \gamma \\ -\gamma & \alpha & -\gamma \\ \gamma & -\gamma & \alpha \end{pmatrix}, \mathbf{U}_4 = \begin{pmatrix} \alpha & \gamma & -\gamma \\ \gamma & \alpha & -\gamma \\ -\gamma & -\gamma & \alpha \end{pmatrix} \end{aligned} \quad (2.108)$$

Because individual variants differ in the shear components of the strain tensors, the shear strains e_4 , e_5 , and e_6 are selected as primary OPs. The Landau polynomial depicting local

Figure 2.10: The 2D snapshot of the cubic-to-tetragonal martensite sliced from Fig. 2.9

symmetry breaking is expanded to eighth order with the variables of shear strains, and the energy contributions due to the non-OP strains, i.e. dilatation and deviatoric strains, are kept in quadratic expressions.

$$\begin{aligned}
 f &= f_{local} + f_{non-OP} + f_{grad} \\
 &= c_{44} \sum_{i=4-6} e_i^2 + A_{tri} e_4 e_5 e_6 + A_8 (e_4^2 + e_5^2 + e_6^2)^4 + \frac{c_{11} - c_{12}}{2} (e_2^2 + e_3^2) \\
 &\quad + \frac{c_{11} + 2c_{12}}{3} e_1^2 + \frac{g}{2} (\nabla e_4)^2 + \frac{g}{2} (\nabla e_5)^2 + \frac{g}{2} (\nabla e_6)^2
 \end{aligned} \tag{2.109}$$

Different from the cubic-to-tetragonal case, the temperature dependence of the second order elastic coefficients is neglected in cubic-to-trigonal simulation. The elastic constants of c_{44} and A_{tri} are set negative constants. Figure 2.11 illustrates the isoenergetic surface of Landau potential of cubic-to-trigonal transformation in the space of shear strains. The exchangeable X, Y, and Z axes are e_4 , e_5 , and e_6 . All the points with the components of OP strains (e_4, e_5, e_6) on the green isoenergetic surfaces have the same normalized local strain energy density of $0.05 J/m^3$, while those on the yellow surface indicate a smaller value of $-0.34 \times 10^{-3} J/m^3$. From Figure 2.11, the non-convex surface is composed by two penetrating dumbbells. Decreasing with the energy density, the central part of dumbbell is shrinking, leaving four minima indicating the martensite variants. When the isoenergetic surface is

Figure 2.11: The multi-well Landau free energy of cubic-to-trigonal MT with the energy density of $5e^{-2} J/m^3$ (in green) and $-0.34e^{-3} J/m^3$ (in yellow)

shrunk to form four isolated ellipsoids, the interfaces of twin boundaries are no longer movable and the microstructure is frozen. By inspecting the coordinates of the minima in the space of shear strains, the values of coordinates coincide with the off-diagonal shear strain components in transformation strain tensors.

Figure 2.12 shows the microstructure evolution of the cubic-trigonal MT with Lagrange-Rayleigh dynamics as analog of Au-Cd SMA. The MT is triggered by the temperature, thus in simulation it is induced by the negative values of the elastic constants in front of second- and third- order shear invariants. Evolving with time, the OP shear strains are promptly dropping into four isoenergetic wells to generate domains characterized by different strain combinations, viz. the four types of martensite variants represented in red, coral, light-blue and blue, respectively, are forming. At the initial stage of simulation, the twin boundaries are not straight-lines due to the curvature driven motion of the boundaries. However in the later time, the twin boundaries are unbending to form twin-related variants with a sharp twin plane between them. In Figure 2.13(a), the typical 'herring-bone' structure self-accommodated by four variants is clearly shown. The twin boundaries are measured to be (010) for blue and red (light blue and coral) correspondence variant pair, (110) for coral and blue correspondence variant pair, and (-110) for light blue and red ones, which are consistent with the results of CM-PTMC and confirmed by TEM observation in experiments for R phase in Ni-Ti based SMAs [OR05]. The microstructure consisting of four martensite variants in Figure 2.13(a)

Figure 2.12: Microstructure evolution of cubic-to-trigonal MT to form the herring-bone structure

reaches an energetic more favored state by decreasing the number of interfaces, when the energy surface is separated into four isolated ellipsoids. Figure 2.13 also illustrates different morphology obtained from Lagrange-Rayleigh simulations together with the 'herring-bone' structure. The transient microstructures in Figure 2.13(b) and (c) are frozen when the inertial effect is considered in Lagrange-Rayleigh dynamics, such as the $(1/2, 3/4, 3/4)\pi$ nodes with 'zoom-in' moving boundaries are found in our simulation by choosing a set of appropriate parameters. The 'zoom-in' moving boundaries are also found in a Lagrange-Rayleigh or Bales-Gooding dynamic modeling for the cubic-to-tetragonal MT with a small bulk modulus [LSR⁺03]. Particularly, two $(1/2, 3/4, 3/4)\pi$ nodes in Figure 2.13(c) construct the twin boundaries similar to that of 'roof' structure in experiments highlighted in dashed black, although simulation fails to capture the fine-twinning structure in each macro-twin. Correct description of the hierarchy structures containing both macro- and fine- twins in cubic-to-trigonal and other complex MTs will be the one of the hot topics in Lagrange-Rayleigh dynamics of Landau phase transformation.

Figure 2.13: The intriguing microstructure of trigonal martensite generated by Lagrange dynamics characterized in various types of twin boundaries. (a) 'herring-bone' structure with $(1/4, 1/4, 3/4, 3/4)\pi$ node, (b) 'maze' pattern with $(1/2, 3/4, 3/4)\pi$ and $(3/2, 1/4, 1/4)\pi$ nodes (c) 'roof' pattern with two $(1/2, 3/4, 3/4)\pi$ nodes

2.4.10 Cubic-to-Orthorhombic and -Monoclinic I Transformations

Figure 2.14: The multi-well Landau free energy surfaces of (a) cubic-to-orthorhombic and (b) cubic-to-monoclinic I MTs in the space of shear strains

The Landau free energy for cubic-orthorhombic MT has been developed by Falk [FK90] and Oleg [SSF12] with different expressions. The former adopted deviatoric strains e_2 and e_3 as secondary OPs to construct the Landau free energy with six iso-energetic wells

with the primary OP of shuffle to represent the displacement within unit cell. However, by inspecting the transformation strains of orthorhombic martensite variants, both deviatoric and shear strains contribute to the anharmonic Landau energy, thus both should be expanded to higher order. The Landau energy density in [SSF12] is expanded to six order along with a coupling of deviatoric strain and square of shear strain. The iso-energy surface in the space of shear strains is shown in Figure 2.14(a). Similar to cubic-to-trigonal MT, the continuous energy surface will shrink to six isolate domains with the decreasing of energy. To this end, the microstructure is frozen, and the transformation strains of six martensite variants are associated with extrema of the convex hulls, i.e. $[\pm \frac{\alpha - \gamma}{2}, 0, 0]$, $[0, \pm \frac{\alpha - \gamma}{2}, 0], [0, 0, \pm \frac{\alpha - \gamma}{2}]$, which are consistent with the shear transformation strains in CM-PTMC. The free energy for cubic-to-monoclinic I MT is also developed by Oleg[SSF12]. The iso-energy surface spanned in the space of shear strains is shown in Figure 2.14(b). A pair of dumbbells in same color corresponds to four martensite variants which have the same diagonal strain components. Decreasing the energy, the connected iso-energy surface will change into 12 isolated domains.

Figure 2.15: The simulated microstructure of Monoclinic-I martensite[SSF12, SS11] by using Landau energetic description

With the potential, Oleg[SS11] simulated the microstructure of the monoclinic I martensites by using TDGL dynamics shown in Figure 2.15. Because of the existence of the non single-value points in phase space, the simulated morphology in Figure 2.15 shows some ir-

regular patterns incompatible with those in experiments and predicted by CM-PTMC. Thus, the development of Landau models for cubic-to-orthorhombic and cubic-to-monoclinic MTs is still far beyond closure.

2.4.11 Compatibility Kernel

The discovery of compatibility enforced long-range anisotropic kernel is no doubt a milestone in the development of the nonlinear Landau model to understand the mechanisms behind the formation of twin related microstructure in MTs. It provides a fundamental interpretation of the preferential orientations observed in austenite and/or martensites. Detailed in [LSR⁺03], the St. Venant's compatibility condition connects non-OP strains with OP strains, such that the non-OP harmonic energy yields an anisotropic long-range compatibility kernel with the OPs as independent variables. The minimum of this compatibility kernel, which is the energy cost associated with the non-OP strains that the system tries to expel, gives the domain boundary orientation. In the subsection, we revisit the compatibility kernels of cubic-to-tetragonal and cubic-to-trigonal MTs, particularly, calculate the values of compatibility kernel in directions and/or planes with the wave vector components $k_i = 0$

The compatibility kernel is derived from the St. Venant's compatibility. Since the true independent variables to describe the deformation gradient in MT are the displacements, the six symmetrized infinitesimal strain components are not independent. Thus, the St. Venant's compatibility can be expressed in strain tensor as

$$\begin{aligned} \nabla \times (\nabla \times \mathbf{e})^T &= 0 & (\text{in coordinate space}) \\ \mathbf{k} \times \mathbf{e}(\mathbf{k}) \times \mathbf{k} &= 0 & (\text{in Fourier space}) \end{aligned} \quad (2.110)$$

in which, the incompatibility, defined as the double-Curl operation on strain, is vanishing for a smooth compatible state. Eq. (2.110) can be expanded as two sets of three equations with the independent variables of diagonal strain components,

$$\begin{aligned} 2k_y k_z \varepsilon_{23} &= k_y^2 \varepsilon_{33} + k_z^2 \varepsilon_{22} \\ 2k_x k_z \varepsilon_{13} &= k_x^2 \varepsilon_{33} + k_z^2 \varepsilon_{11} \\ 2k_x k_y \varepsilon_{12} &= k_x^2 \varepsilon_{22} + k_y^2 \varepsilon_{11} \end{aligned} \quad (2.111)$$

or with the independent variables of off-diagonal strain components,

$$\begin{aligned} k_y k_z \varepsilon_{11} &= -k_x^2 \varepsilon_{23} + k_x k_y \varepsilon_{13} + k_x k_z \varepsilon_{12} \\ k_x k_z \varepsilon_{22} &= -k_y^2 \varepsilon_{13} + k_y k_z \varepsilon_{12} + k_x k_y \varepsilon_{23} \\ k_x k_y \varepsilon_{33} &= -k_z^2 \varepsilon_{12} + k_x k_z \varepsilon_{23} + k_y k_z \varepsilon_{13} \end{aligned} \quad (2.112)$$

These equations yield the St. Venant's constraints in terms of symmetry adapted strains in Fourier space as

$$\bar{O}_1^{(s)} \hat{e}_1 + \bar{O}_2^{(s)} \hat{e}_2 + \bar{O}_3^{(s)} \hat{e}_3 + \hat{e}_{s=4,5,6} = 0 \quad (2.113)$$

The coefficients in above equation are

$$\begin{aligned}\bar{O}_1^{(4)} &= \frac{-1}{\sqrt{3}} \left(\frac{k_y}{k_z} + \frac{k_z}{k_y} \right); \bar{O}_2^{(4)} = \frac{1}{\sqrt{2}} \left(\frac{k_z}{k_y} \right); \bar{O}_3^{(4)} = \frac{1}{\sqrt{6}} \left(2\frac{k_y}{k_z} - \frac{k_z}{k_y} \right) \\ \bar{O}_1^{(5)} &= \frac{-1}{\sqrt{3}} \left(\frac{k_x}{k_z} + \frac{k_z}{k_x} \right); \bar{O}_2^{(5)} = \frac{-1}{\sqrt{2}} \left(\frac{k_z}{k_x} \right); \bar{O}_3^{(5)} = \frac{1}{\sqrt{6}} \left(2\frac{k_x}{k_z} - \frac{k_z}{k_x} \right) \\ \bar{O}_1^{(6)} &= \frac{-1}{\sqrt{3}} \left(\frac{k_x}{k_y} + \frac{k_y}{k_x} \right); \bar{O}_2^{(6)} = \frac{1}{\sqrt{2}} \left(\frac{k_x}{k_y} - \frac{k_y}{k_x} \right); \bar{O}_3^{(6)} = \frac{-1}{\sqrt{6}} \left(\frac{k_x}{k_y} + \frac{k_y}{k_x} \right)\end{aligned}\quad (2.114)$$

Take the cubic-to-tetragonal MT for example, the quadratic energy of the non-OPs as a part of Landau free energy can be rewritten in Fourier space with the compatibility coefficients in Eq.(2.114)

$$\begin{aligned}\hat{f}_{non} &= A_1 \hat{e}_1(\vec{k}) \hat{e}_1^*(\vec{k}) + \sum_{i=4,5,6} A_i \hat{e}_i(\vec{k}) \hat{e}_i^*(\vec{k}) \\ &= A_1 \hat{e}_1 \hat{e}_1^* + \sum_{i=4,5,6} A_i \left(- \sum_{j=1,2,3} \bar{O}_j^{(i)} \hat{e}_j \right) \left(- \sum_{j'=1,2,3} \bar{O}_{j'}^{(i)} \hat{e}_{j'} \right)^* \\ &= A_1 \hat{e}_1 \hat{e}_1^* + \sum_{i=4,5,6} \sum_{j,j'=1,2,3} A_i \bar{O}_j^{(i)} \bar{O}_{j'}^{*(i)} \hat{e}_i \hat{e}_{j'}^*\end{aligned}\quad (2.115)$$

Denoting $G_{l,l'} = \sum_{i=4,5,6} \frac{A_i}{A_1} \bar{O}_l^{(i)} \bar{O}_{l'}^{*(i)}$, we have

$$\begin{aligned}\hat{f}_{non} &= A_1 \hat{e}_1(k) \hat{e}_1^*(k) + \sum_{i=4,5,6} A_i \hat{e}_i(k) \hat{e}_i^*(k) \\ &= A_1 \left[\hat{e}_1(k) \hat{e}_1^*(k) + \sum_{i,j=1,2,3} G_{i,j} \hat{e}_i(k) \hat{e}_j^*(k) \right] \\ &= A_1 \begin{bmatrix} \hat{e}_1 \hat{e}_1^* & +G_{1,1} \hat{e}_1 \hat{e}_1^* & +G_{1,2} \hat{e}_1 \hat{e}_2^* & +G_{1,3} \hat{e}_1 \hat{e}_3^* \\ & +G_{2,1} \hat{e}_2 \hat{e}_1^* & +G_{2,2} \hat{e}_2 \hat{e}_2^* & +G_{2,3} \hat{e}_2 \hat{e}_3^* \\ & +G_{3,1} \hat{e}_3 \hat{e}_1^* & +G_{3,2} \hat{e}_3 \hat{e}_2^* & +G_{3,3} \hat{e}_3 \hat{e}_3^* \end{bmatrix}\end{aligned}\quad (2.116)$$

Minimizing the dilatation strain via variation $\frac{\delta \hat{f}_{non}}{\delta \hat{e}_1^*} = \hat{e}_1 + G_{1,1} \hat{e}_1 + G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3 = 0$, the solution of e_1 is expressed in terms of OPs e_2 and e_3 , which reads $\hat{e}_1 = -\frac{G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3}{1 + G_{1,1}}$. Substituting the static solution of dilatation strain e_1 into the non-OP potential in Fourier space leads to

$$\hat{f}_{com} = A_1 \left[(1 + G_{1,1}) \left(\frac{G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3}{1 + G_{1,1}} \right) \left(\frac{G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3}{1 + G_{1,1}} \right)^* + (G_{1,2} \hat{e}_2^* + G_{1,3} \hat{e}_3^*) \left(-\frac{G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3}{1 + G_{1,1}} \right) + (G_{2,1} \hat{e}_2 + G_{3,1} \hat{e}_3) \left(-\frac{G_{2,1} \hat{e}_2^* + G_{3,1} \hat{e}_3^*}{1 + G_{1,1}} \right)^* + \sum_{i=2,3} G_{i,j} \hat{e}_i \hat{e}_j^* \right]\quad (2.117)$$

Thus,

$$\begin{aligned}
\hat{f}_{com} &= \frac{A_1}{(1 + G_{1,1})} \left[- (G_{1,2}\hat{e}_2^* + G_{1,3}\hat{e}_3^*) (G_{2,1}\hat{e}_2 + G_{3,1}\hat{e}_3) \right. \\
&\quad \left. + \sum_{i=2,3} G_{i,j}\hat{e}_i\hat{e}_j^* + G_{1,1} \sum_{i=2,3} G_{i,j}\hat{e}_i\hat{e}_j^* \right] \\
&= \frac{A_1}{(1 + G_{1,1})} \left[-G_{1,2}G_{2,1}\hat{e}_2\hat{e}_2^* - G_{1,2}G_{3,1}\hat{e}_3\hat{e}_2^* - G_{1,3}G_{2,1}\hat{e}_2\hat{e}_3^* - G_{1,3}G_{3,1}\hat{e}_3\hat{e}_3^* \right. \\
&\quad \left. + \sum_{i=2,3} G_{i,j}\hat{e}_i\hat{e}_j^* + G_{1,1} \sum_{i=2,3} G_{i,j}\hat{e}_i\hat{e}_j^* \right] \\
&= \frac{A_1}{(1 + G_{1,1})} \sum_{i=2,3} [G_{i,j} + (G_{i,j}G_{1,1} - G_{i,1}G_{j,1})]\hat{e}_i\hat{e}_j^*
\end{aligned} \tag{2.118}$$

Finally, the static compatibility kernel for cubic-tetragonal MT is derived.

$$\hat{U}_{ll'} = \left(1 - \delta_{(\vec{k},0)}\right) \frac{G_{i,j} + (G_{i,j}G_{1,1} - G_{i,1}G_{j,1})}{(1 + G_{1,1})} \tag{2.119}$$

However, the values of the compatibility kernel at the special points in Fourier space, where at least one of the wave vector components is equal to zero, should be carefully evaluated to ensure the smoothness of the compatibility kernel.

Now we take the case of $k_x \neq 0, k_y \rightarrow 0, k_z \rightarrow 0$ as example. Assuming $k_y = \mathcal{O}(k_z)$, we have

$$\begin{aligned}
\bar{O}_1^{(4)} &= \frac{-2}{\sqrt{3}}; \bar{O}_2^{(4)} = \frac{1}{\sqrt{2}}; \bar{O}_3^{(4)} = \frac{1}{\sqrt{6}} \\
\bar{O}_1^{(5)} &= \frac{-1}{\sqrt{3}} \frac{k_x}{k_z}; \bar{O}_2^{(5)} = 0; \bar{O}_3^{(5)} = \frac{2}{\sqrt{6}} \frac{k_x}{k_z} \\
\bar{O}_1^{(6)} &= \frac{-1}{\sqrt{3}} \frac{k_x}{k_y}; \bar{O}_2^{(6)} = \frac{1}{\sqrt{2}} \frac{k_x}{k_y}; \bar{O}_3^{(6)} = \frac{-1}{\sqrt{6}} \frac{k_x}{k_y}
\end{aligned} \tag{2.120}$$

$$\begin{aligned}
G_{1,1} &= \bar{O}_1^{(4)}\bar{O}_1^{(4)} + \bar{O}_1^{(5)}\bar{O}_1^{(5)} + \bar{O}_1^{(6)}\bar{O}_1^{(6)} = \frac{4}{3} + \frac{1}{3} \left(\frac{k_x^2}{k_z^2} \right) + \frac{1}{3} \left(\frac{k_x^2}{k_y^2} \right) \\
G_{2,2} &= \bar{O}_2^{(4)}\bar{O}_2^{(4)} + \bar{O}_2^{(5)}\bar{O}_2^{(5)} + \bar{O}_2^{(6)}\bar{O}_2^{(6)} = \frac{1}{2} + 0 + \frac{1}{2} \left(\frac{k_x^2}{k_y^2} \right) \\
G_{3,3} &= \bar{O}_3^{(4)}\bar{O}_3^{(4)} + \bar{O}_3^{(5)}\bar{O}_3^{(5)} + \bar{O}_3^{(6)}\bar{O}_3^{(6)} = \frac{1}{6} + \frac{4}{6} \left(\frac{k_x^2}{k_z^2} \right) + \frac{1}{6} \left(\frac{k_x^2}{k_y^2} \right) \\
G_{1,2} &= \bar{O}_1^{(4)}\bar{O}_2^{(4)} + \bar{O}_1^{(5)}\bar{O}_2^{(5)} + \bar{O}_1^{(6)}\bar{O}_2^{(6)} = -\frac{2}{\sqrt{6}} + 0 + \frac{1}{\sqrt{6}} \left(\frac{k_x^2}{k_y^2} \right) \\
G_{1,3} &= \bar{O}_1^{(4)}\bar{O}_3^{(4)} + \bar{O}_1^{(5)}\bar{O}_3^{(5)} + \bar{O}_1^{(6)}\bar{O}_3^{(6)} = -\frac{2}{\sqrt{18}} - \frac{2}{\sqrt{18}} \left(\frac{k_x^2}{k_z^2} \right) - \frac{1}{\sqrt{18}} \left(\frac{k_x^2}{k_y^2} \right) \\
G_{2,3} &= \bar{O}_2^{(4)}\bar{O}_3^{(4)} + \bar{O}_2^{(5)}\bar{O}_3^{(5)} + \bar{O}_2^{(6)}\bar{O}_3^{(6)} = \frac{1}{\sqrt{12}} - \frac{1}{\sqrt{12}} \left(\frac{k_x^2}{k_y^2} \right)
\end{aligned} \tag{2.121}$$

$$\begin{aligned}
U_{22} &= \frac{G_{2,2} + G_{2,2}G_{1,1} - G_{1,2}G_{1,2}}{1 + G_{1,1}} \\
&= \frac{\frac{1}{2} \left(1 + \frac{k_x^2}{k_y^2}\right) + \frac{1}{6} \left(1 + \frac{k_x^2}{k_y^2}\right) \left(4 + \frac{k_x^2}{k_z^2} + \frac{k_x^2}{k_y^2}\right) - \frac{1}{6} \left(2 - \frac{k_x^2}{k_y^2}\right)^2}{1 + \frac{4}{3} + \frac{1}{3} \left(\frac{k_x^2}{k_z^2}\right) + \frac{1}{3} \left(\frac{k_x^2}{k_y^2}\right)} \quad (2.122) \\
&= \frac{3 \left(1 + \frac{k_x^2}{k_y^2}\right) + \left(1 + \frac{k_x^2}{k_y^2}\right) \left(4 + \frac{k_x^2}{k_z^2} + \frac{k_x^2}{k_y^2}\right) - \left(2 - \frac{k_x^2}{k_y^2}\right)^2}{6 + 8 + 2 \left(\frac{k_x^2 k_y^2}{k_z^2}\right) + 2 \left(\frac{k_x^2}{k_y^2}\right)} \sim \frac{k_x^2}{2(k_y^2 + k_z^2)}
\end{aligned}$$

Provided $k_y(0) \approx \frac{1}{N_y}$, $k_z(0) \approx \frac{1}{N_z}$ are used in numerical calculations, the minimum approximate value of U_{22} along the direction is $N_y^2 N_z^2 k_x^2 / 2 (N_y^2 + N_z^2)$. Similarly, we have derived the expressions and values of compatibility kernel on other planes or along directions listed in Appendix A as well as those for cubic-to-trigonal MT in Appendix B. With the compatibility kernel, the preferential twinning orientation can be discerned, e.g. the $\pm\pi/4$ in each $k_i = 0$ plane. It indicates the correspondence variant pair of cubic-to-tetragonal martensites favors twinning orientation of $\pm\pi/4$ on these planes.

Figure 2.16: Compatibility kernel components U_{22} , U_{33} , and U_{23} for 3D cubic-to-tetragonal transition. The strength of the kernel is represented by number of the side legend and color coding.

Figure 2.17: Compatibility kernel components for 3D cubic-to-trigonal transition. There is a butterfly anisotropy in the plane $k_x = 0$. The clover-leaf pattern is shown in the plane $k_y = 0$ of U_{44} , similar to that of the square to rectangle kernel in 2D. The compatibility kernel proves the $\{100\}$ and $\{110\}$ planes have the smallest energy cost to form the twin boundaries.

2.5 Microelasticity Phase Field Model

The microelasticity phase field model is a powerful tool to simulate the microstructural domains in a non-uniform crystalline solid with defined crystal structure. Originating from the 'Eshelby's inclusion' [Esh59] problem, Khachaturyan [Kha13] built the microelasticity theory by splitting the inelastic energy contribution from total energy and introducing the field variables to describe microstructural domains in a non-uniform crystalline solid. The microstructural domains can differ in either arrangement of atoms or certain sub-atom functionalities. The domains of inclusions or second phases are assigned the value of 1, while the matrix is symbol in 0 in a phenomenological way instead of detailing the structure at atomic scale. The set of abstract and spatial dependent field variables, named shape functions, is utilized as the OP to describe a field of mixture containing matrix and arbitrary coherent inclusions. Consolidated by Khachaturyan [Kha13] himself and his colleagues Chen[Che02], Wang[WL10], Jin [JAK01] and Ni [NK09] et al., the microelasticity phase field model has been generalized from the elastic coherent problem into various media of functionalities covering elasticity, compositions, polarizations, grain orientations, etc. With the advantages of the abstract indicators of field variables, the modern phase field model as the generalization of microelasticity no longer restricts its applications in solid state phase transformations, and has been extended to other materials processes including grain growth and coarsening [KIC02], spinodal decomposition in thin films[LJ01], crack propagation [AKV00], dislocation-solute interactions [LD98], dislocation dynamics [WJCK01], electromigration [BKB00], and multicomponent inter-diffusion [WMW01].

Now we return to microelasticity theory for MT, which is more close to the origination of the microelasticity, i.e. 'Eshelby's inclusion' problem. The strategy of microelasticity phase field model to solve MT starts at splitting the total free energy into elastic and inelastic contributions as follow

$$F = \int d^3\mathbf{r} \left[f(\{\eta_p\}) + \sum_p \frac{\kappa_p}{2} (\nabla \eta_p)^2 \right] + \Delta E(\eta_p, \varepsilon_{ij}^T) \quad (2.123)$$

In Eq.(2.123), $f(\{\eta_p\})$ implies chemical or inelastic energy density written in Landau polynomial of shape functions η_p . Each type of martensite variants is viewed as a kind of elastic inclusion with a specific transformation strain (stress-free strain tensor) $\varepsilon_{ij}^{\circ T}(p)$ and is assigned an indicator η_p to represent it. The total elastic energy of a system during the MT, ΔE , is described in the viewpoint of the elastic response of hosting medium (mixture of austenite and martensites) to the intrinsic MT itself, which includes two contributions: 1) an shape restoration energy in elastic quadratic form to offset the intrinsic distortion due to MT and 2) an relaxation energy to 'weld on' all of martensite variants to the parent (austenite)

phase by adjusting the lattice arrangement in the vicinity of austenite/martensite interface. Figure 2.18 details the origination of two contributions of total elastic energy.

Figure 2.18: The procedures to derive the heterogeneous relax strain in microelasticity phase field model [MBW08]

In accordance with these two contributions, the total strain is decomposed into the real time transformation strain and the elastic strain for relaxation.

$$\varepsilon_{ij}(\mathbf{r}, t) = e_{ij}^{el}(\mathbf{r}, t) + \varepsilon_{ij}^T(\mathbf{r}, t) = e_{ij}^{el}(\mathbf{r}, t) + \sum_p \eta_p(\mathbf{r}, t) \varepsilon_{ij}^{\circ T}(p) \text{ (proper)}$$

$$\varepsilon_{ij}(\mathbf{r}, t) = e_{ij}^{el}(\mathbf{r}, t) + \varepsilon_{ij}^T(\mathbf{r}, t) = e_{ij}^{el}(\mathbf{r}, t) + \sum_p \eta_p^2(\mathbf{r}, t) \varepsilon_{ij}^{\circ T}(p) \text{ (improper)}, \quad (2.124)$$

where the real time transformation strain is a sum over each individual transformation strain tensor $\varepsilon_{ij}^{\circ T}(p)$ with a weight of shape function, e.g. $\varepsilon_{ij}^T(\mathbf{r}, t) = \sum_p \eta_p(\mathbf{r}, t) \varepsilon_{ij}^{\circ T}(p)$ for proper MT. In micro-elasticity, it is assumed that the linear constitutive relationship between eigenstresses and eigenstrains (or non-diagonalized transformation stresses and strains) is preserved. In a manner of speaking, the constitutive relation of $\sigma_{ij} = C_{ijkl} e_{kl}$ is valid for total (σ/ε), elastic (σ^{el}/e^{el}), and transformation (σ^T/ε^T) stresses/strains, if homogeneous modulus assumption $C_{ijkl} = C_{ijkl}^0$ is applied. Thus, the total elastic energy is expressed as

$$\begin{aligned} \Delta E = \Delta E^{restore} + \Delta E^{relax} = & \frac{1}{2} \sum_p V_p(\mathbf{r}, t) C_{ijkl} \varepsilon_{ij}^{\circ T}(p) \varepsilon_{kl}^{\circ T}(p) \\ & + \int_V \left(- \sum_p C_{ijkl} \varepsilon_{kl}^{\circ T}(p) \eta_p(\mathbf{r}, t) \varepsilon_{ij} + C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \right) dV \end{aligned} \quad (2.125)$$

where V_p and is the volume fraction of p^{th} martensite variant. With the specific energy, the microstructure and its evolution can be represented by monitoring the spatiotemporal

evolution of η_p under a quasi-equilibrium condition, assuming that the elastic equilibrium state is achieved instantly at each time step. Therefore, there are actually one kinetic equation and one static equation. The kinetic equation is the well-known Allen-Cahn equation to record the evolution of OPs η_p

$$\frac{\partial \eta_p(\mathbf{r}, t)}{\partial t} = -L_p \frac{\delta F}{\delta \eta_p(\mathbf{r}, t)} + \xi_p(\mathbf{r}, t) \quad (2.126)$$

where L_p is kinetic coefficient and ξ_p is Langevin random force term of thermal fluctuation. The static one is a variational minimization of the relaxation energy with respect to the displacement under certain boundary conditions to attain the elastic equilibrium state.

$$\frac{\delta \Delta E^{relax}}{\delta u} = 0 \quad (2.127)$$

Since all parts in total elastic energy are formally quadratic and the total strain is the symmetric part of the displacement derivatives to space by applying infinitesimal approximation

$$\varepsilon_{ij}(\mathbf{r}, t) = \frac{1}{2} \left(\frac{\partial u_i(\mathbf{r}, t)}{\partial x_j} + \frac{\partial u_j(\mathbf{r}, t)}{\partial x_i} \right) \quad (2.128)$$

the variation in Eq(2.127) can be equivalently transformed into the mechanical equilibrium equation,

$$\begin{aligned} \frac{\partial \sigma_{ij}}{\partial x_j} &= \frac{C_{ijkl} \partial \sigma_{kl}}{\partial x_j} = 0 \\ \frac{\partial}{\partial x_j} C_{ijkl} \frac{1}{2} \left(\frac{\partial u_k(\mathbf{r}, t)}{\partial x_l} + \frac{\partial u_l(\mathbf{r}, t)}{\partial x_k} \right) &= \frac{\partial}{\partial x_j} C_{ijkl} \varepsilon_{ij}^T(\mathbf{r}, t) \end{aligned} \quad (2.129)$$

However, an analytical solution of Eq.(2.129) in Fourier space requires a homogeneous boundary condition that displacement $\mathbf{u}$ and displacement gradient $\nabla \mathbf{u}$ do vanish at external surfaces. These conditions can be valid when displacement and total strain are divided into homogeneous ($\bar{u}$, $\bar{\varepsilon}_{ij}$) and heterogeneous ($\Delta \mathbf{u}$, $\delta \varepsilon_{ij}$) parts, viz.

$$\mathbf{u}(\mathbf{r}) = \bar{u} + \Delta \mathbf{u}(\mathbf{r}), \quad \varepsilon_{ij}(\mathbf{r}) = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij}(\mathbf{r}) \quad (2.130)$$

In this formalism, the homogeneous strain $\bar{\varepsilon}_{ij}$ describes the spatial independent, uniform shape deformation of a crystal. While, the spatial varying heterogeneous strain is written as the symmetric part of local displacement gradient in infinitesimal approximation

$$\delta \varepsilon_{ij}(\mathbf{r}, t) = \frac{1}{2} \left(\frac{\partial \Delta u_i(\mathbf{r}, t)}{\partial x_j} + \frac{\partial \Delta u_j(\mathbf{r}, t)}{\partial x_i} \right) \quad (2.131)$$

The homogeneous strain together with heterogeneous strain leads to the total strain satisfying

$$\int d\mathbf{r} \delta \varepsilon_{ij}(\mathbf{r}) \equiv 0 \quad (2.132)$$

Representing the equation $\delta \Delta E^{relax} / \delta \Delta u = 0$ in Fourier space, i.e.

$$-\mathbf{k}_j \mathbf{k}_l C_{ijkl} \Delta \hat{u}_k(\mathbf{k}, t) = i \mathbf{k}_j C_{ijkl} \hat{\varepsilon}_{ij}^T(\mathbf{k}, t) \quad (2.133)$$

leads to an explicit solution of local displacement

$$\Delta \hat{u}_k(\mathbf{k}, t) = -i \mathbf{k}^{-2} \Omega_{ik}^0(\mathbf{n}) \mathbf{k}_j \hat{\sigma}_{ij}^T(\mathbf{k}, t) \quad (2.134)$$

where $\hat{\sigma}_{ij}^T(\mathbf{k}, t) = C_{ijkl} \left[\sum_p \eta_p(\mathbf{r}, t) \varepsilon_{ij}^{\circ T}(p) \right]$, $[\Omega_{ik}^0]^{-1}(\mathbf{n}) = C_{ijkl} n_j n_l$ and $\mathbf{n} = \mathbf{k}/|\mathbf{k}|$.

Substituting the solution (2.134) into Eqs. (2.124, 2.130), the expressions of total strain and elastic strain are obtained.

$$\begin{aligned} \varepsilon_{ij}(\mathbf{r}) &= \bar{\varepsilon}_{ij} + \frac{1}{2} \mathcal{F}^{-1} \left\{ [n_j \Omega_{ki}^0(\mathbf{n}) + n_i \Omega_{kj}^0(\mathbf{n})] \mathbf{n}_j \hat{\sigma}_{kl}^T(\mathbf{k}, t) \right\} \\ e_{ij}^{el}(\mathbf{r}) &= \bar{\varepsilon}_{ij} + \frac{1}{2} \mathcal{F}^{-1} \left\{ [n_j \Omega_{ki}^0(\mathbf{n}) + n_i \Omega_{kj}^0(\mathbf{n})] \mathbf{n}_j \hat{\sigma}_{kl}^T(\mathbf{k}, t) \right\} - \varepsilon_{ij}^T(\mathbf{r}, t) \end{aligned} \quad (2.135)$$

as well as the updated total elastic energy

$$\begin{aligned} \Delta E &= \frac{1}{2} \int C_{ijkl} e_{ij}^{el} e_{kl}^{el} d\mathbf{r}^3 \\ &= \frac{1}{2} \int C_{ijkl} \varepsilon_{ij}^T(\mathbf{r}, t) \varepsilon_{kl}^T(\mathbf{r}, t) d\mathbf{r}^3 + \frac{V}{2} C_{ijkl} \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl} - \bar{\varepsilon}_{ij} \int C_{ijkl} \varepsilon_{kl}^T(\mathbf{r}, t) d\mathbf{r}^3 \\ &\quad - \frac{1}{2} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} [n_i \hat{\sigma}_{ij}^T(\mathbf{k}, t) \Omega_{jk}^0(\mathbf{n}) \hat{\sigma}_{kl}^T(\mathbf{k}, t) n_j] \\ &= \frac{1}{2} \sum_{p,q} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \mathbf{B}_{pq} \hat{\eta}_p(\mathbf{k}, t) \hat{\eta}_q^*(\mathbf{k}, t) \end{aligned} \quad (2.136)$$

where, $\mathcal{F}$ and $\mathcal{F}^{-1}$ denote the Fourier and inverse Fourier transformations; $\int^\circ$ is the integral

$$\text{without the point } k = 0. \mathbf{B}_{pq} = \begin{cases} C_{ijkl} \varepsilon_{ij}^{\circ T}(p) \varepsilon_{kl}^{\circ T}(q) & (\mathbf{n} = 0) \\ C_{ijkl} \varepsilon_{ij}^{\circ T}(p) \varepsilon_{kl}^{\circ T}(q) - n_i \sigma_{ij}^T(p) \Omega_{jk}^0 \sigma_{kl}^T(q) n_j & (\mathbf{n} \neq 0) \end{cases}.$$

The new shape function satisfies $\int \frac{d^3 \mathbf{k}}{(2\pi)^3} \hat{\eta}_p(\mathbf{k}, t) \hat{\eta}_q^*(\mathbf{k}, t) = \delta_{pq} V_p - \frac{V_p V_q}{V}$. V is the total volume fraction of all martensites. So far, the elastic energy density is the sum over the product of the materials dependent kernel $\mathbf{B}_{pq}$ and the spatiotemporal dependent shape functions

η . Substituting the static equilibrium solution of elastic strains into Allen-Cahn equation, the microstructure evolution and relevant behaviors of MT can be numerically solved in microelasticity phase field method. The microelasticity phase field model has been used to simulate the microstructure evolution in most of MTs, including cubic-to-tetragonal, cubic-to-trigonal, cubic-to-orthorhombic, and tetragonal-to-monoclinic in 2D and 3D. Figure 2.19(a) illustrates the $\{110\}$ polytwinned martensite plates induced by cubic-to-tetragonal MT in the Fe31%Ni alloy under the constraint boundary conditions with a dilatation strain of 0.065 [AJK01]. The orientated martensite variants are arranged in alternating lamellae accompanying with small fractions of austenite in black located at the interface between polytwinned plates. While in Figure 2.19(b), only two martensite variants in red and blue have been considered in Ref.[MZRZ11] by assuming $\eta_3(\mathbf{r}, t) = 0$

Figure 2.19: Simulated cubic-to-tetragonal martensites in 3D by using microelasticity phase field model(a) [AJK01], (b) [MZRZ11]

Figure 2.20 shows the simulated 3D microstructures of cubic-to-trigonal martensites in a single crystal with the surfaces of $\{100\}$ planes [JAK01, Sal09]. The typical 'herring-bone' structure of the $\zeta'/2$ martensites in Au-Cd alloys is well represented by the assembly of four domains in green, dark violet, red and blue. The four types of martensites accommodate themselves to produce zero crystal lattice misfit on the interfaces.

Gao[GZWW14] systematically investigated the connections between PTMC and microelasticity by inspecting the microstructure features from the PTMC calculation and the phase field modeling for the B2-B19/B19' MT in Ni based SMAs. The twin planes obtained from phase field modeling are the same as what PTMC predict if the kinematic compatibility condition rigidly holds for the inputs of transformation strain tensors. Figure 2.21 shows three types of twinning in NiTiPt system, and Figure 2.22 illustrates the crossing-twin structure

Figure 2.20: The simulated microstructure of the cubic-to-trigonal martensites[JAK01, Sal09] by using microelasticity phase field model

with the orientations of twin planes satisfying the sets of kinematic compatibility along with the rotation invariance and coplanar conditions.

$$\begin{aligned}
 \mathbf{Q}_1 \mathbf{U}_2 - \mathbf{U}_1 &= \mathbf{a}_1 \otimes \mathbf{n}_1 \\
 \mathbf{Q}_2 \mathbf{U}_3 - \mathbf{U}_2 &= \mathbf{a}_2 \otimes \mathbf{n}_2 \\
 \mathbf{Q}_3 \mathbf{U}_4 - \mathbf{U}_3 &= \mathbf{a}_3 \otimes \mathbf{n}_3 \\
 \mathbf{Q}_4 \mathbf{U}_1 - \mathbf{U}_4 &= \mathbf{a}_4 \otimes \mathbf{n}_4 \\
 \mathbf{Q}_1 \mathbf{Q}_2 \mathbf{Q}_3 \mathbf{Q}_4 &= \mathbf{I} \\
 (\mathbf{d}_i \times \mathbf{d}_j) \mathbf{d}_k &= 0
 \end{aligned} \tag{2.137}$$

Figure 2.21: Three kinds of twinning in NiTiPt system: (a) (110) compound twinning; (b) (01-1) Type I twinning; (c) (-0.2796, 0.6789, 0.6789) Type II twinning [GZWW14]

The same conclusion is also valid for the prediction of habit planes. If the transformation strain of single martensite satisfies the invariant plane condition, the simulated invariant plane normal [Fig.2.23(a)] coincides with the result of PTMC. However, if the internal-twins are

Figure 2.22: Crossing-twin structure: (a) Simulation result[GZWW14]; (b) Schematic of twin plane normals of $d_1 = d_3 = (-1, 0, 0)$, $d_2 = (0.2796, 0.6789, 0.6789)$, $d_4 = (0.2796, -0.6789, -0.6789)$

formed to coexist with austenite, the habit planes between austenite and internal-twinned microstructure determined by phase field modeling are slightly deviated from those obtained from PTMC [Fig.2.23(b)].

Figure 2.23: (a) Single martensite variant in NiTiCu with $(0.544, -0.638, -0.544)$ habit plane and (b) the internal-twinned martensites in NiTiPt system [GZWW14]

2.6 Thermomechanical Phase Field Model

In sections 2.3 and 2.4, the IRS-Landau and microelasticity phase field models have been advanced as powerful tools to represent and predict fine martensitic microstructure. However, these works are insufficient to represent some of mechanical properties of SMAs such as weakly temperature dependent stress hysteresis, and nonzero tangent elastic moduli at the phase transformation point. In microelasticity, the Landau free energy used in [WK97, MZEKC13], predicts the total transformation strain varying with direct and inverse transformations. The IRS based Landau potential[Fal83] predicts stress hysteresis changing with temperatures, in contrast with the typical stress-strain curves of SMA exhibit a constant transformation strain and stress hysteresis at different temperatures[LP02]. Therefore, Levitas and Lee [LPL03] developed thermomechanical phase field model incorporating elasticity and Landau energetics for the multivariant stress- and temperature- induced MTs, which can correctly describe the aforementioned mechanical features of SMAs. In thermomechanical model, the total strain tensor $\boldsymbol{\varepsilon}$ is also decomposed into the elastic $\boldsymbol{\varepsilon}^{el}$ and transformation $\boldsymbol{\varepsilon}^{tk} \varphi(a, \eta_k)$ parts, i.e.

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^{el} + \boldsymbol{\varepsilon}^{tk} \varphi(a, \eta_k) \quad (2.138)$$

where $\boldsymbol{\varepsilon}^{tk}$ is the transformation strain tensor of k^{th} martensite variant at thermodynamic equilibrium state, and $k = 0$ corresponds to austenite. Such that, the Gibbs energy density is expressed as

$$G = -\frac{1}{2} \boldsymbol{\sigma} : \mathbf{S} : \boldsymbol{\sigma} + \boldsymbol{\sigma} : \boldsymbol{\varepsilon}^t + \sum_{i=1}^{n-1} \sum_{j=i+1}^n H_{ij}(\eta_i, \eta_j) \quad (2.139)$$

$$\boldsymbol{\varepsilon}^t = \sum_{k=1}^n \boldsymbol{\varepsilon}^{tk} \left[\frac{a}{2} \eta_k^2 + (3-a) \eta_k^4 + \frac{1}{2} (a-4) \eta_k^6 \right] - \sum_{i=1}^{n-1} \sum_{j=i+1}^n \eta_i^2 \eta_j^2 (\eta_i^2 \mathbf{D}_{ij} + \eta_j^2 \mathbf{D}_{ji}) \quad (2.140)$$

$$\mathbf{D}_{ij} = \frac{1}{2} (a-3) \boldsymbol{\varepsilon}_j^t + \frac{3}{2} \boldsymbol{\varepsilon}_i^t \quad (2.141)$$

$$H_{ij}(\eta_i, \eta_j) = B \eta_i^2 \eta_j^2 + \left(\frac{\bar{A}}{2} - \frac{A}{2} - B \right) \eta_i^4 \eta_j^2 + C |\eta_i|^3 |\eta_j|^3 + \left(\frac{\bar{A}}{2} - \frac{A}{2} - B \right) \eta_i^2 \eta_j^4 \quad (2.142)$$

$$A = A_0 (T - T_c) \quad (2.143)$$

Here, η_k is the OP ($0 < \eta_k < 1$). $\boldsymbol{\sigma} : \boldsymbol{\varepsilon} = \sigma_{ij} \varepsilon_{ij}$ are the contraction of tensors over one and two indices, $\boldsymbol{\sigma}$ is stress tensor, $\mathbf{S}$ is forth-rank elastic compliance tensor. T_c , a , A_0 , B , and C

are critical temperature and material parameters. The evolution of the OP η_k is implemented by TDGL equation,

$$\sum_{k=1}^n \frac{\partial \eta_k}{\partial t} = - \sum_{k=1}^n L_k \frac{\delta G_{GL}}{\delta \eta_k} = \sum_{k=1}^n L_k \left(2g \nabla^2 \eta_k - \frac{\partial G}{\partial \eta_k} \right) \quad (2.144)$$

where L_k is a positive kinetic coefficient, and g is a gradient coefficient. Based on the review of the microstructure simulations for various MTs in SMAs, we are aware of few simulation for the cubic-to-monoclinic II MT. It primarily arises from two difficulties, (1) it's hard to capture unique features of SMA; (2) the computational resources are expensive for 3D simulation while a 2D approximation may lead to losing some key issues of the transformations [MZEKC13, MZEK14]. The only works relevant to cubic-to-monoclinic II are recently reported by Mamivand et al. [MZEKC13, MZEK14] with phase field modeling of the tetragonal-to-monoclinic II MT of ZrO_2 . However, they only considered two martensite variants or average of variants that produce compound twins and V-shaped morphology of twinning. Though the scientific and technological importance of the discovery of the large reversible cubic-to-monoclinic II SMAs, we develop a 2D phase field model in the thesis to represent and investigate the formation of cubic-to-monoclinic II martensites under the plane strain condition by a combination of the square-to-rectangular and square-to-oblique transformations, such that the cubic-to-monoclinic II MT can be fully represented under the plane strain condition without losing any essential physics and issues of microstructures.

The cubic-to-monoclinic II MT differs from cubic-to-monoclinic I with its twofold symmetry axis along an edge of the original cubic unit rather than along a face-diagonal axis of cubic unit. As the transformation stretch matrices $\mathbf{U}$ displayed in [Bha03], the cubic-to-monoclinic II transformation produces 12 martensite variants. When considering the plane strain condition in 2D, the strain components ε_{31} , ε_{32} and ε_{33} are ignored. As such, the 12 martensite variants are divided into 3 groups, namely, $\{M_{1+}, M_{1-}, M_{2+}, M_{2-}\}$, $\{M_3(M_{3+}, M_{3-}), M_6(M_{6+}, M_{6-})\}$, and $\{M_4(M_{4+}, M_{4-}), M_5(M_{5+}, M_{5-})\}$. The first group is regarded as the square-to-oblique transformation in 2D, whereas the second and third groups are regarded as square-to-rectangular transformation that corresponds to 2D analog of cubic-to-tetragonal transformation. It is noticed that, cubic-to-monoclinic II MT, e.g. in CuZnAl [LLP10] and ZnAuCu [LP02], has the invariant plane strain variants that differ only in sign in the transformation strains manifested by a product of the sign function, $sign(\eta_k) = \eta_k/|\eta_k|$ and $\varphi(a, \eta_k)$. If the homogeneous part of the transformation strain $\bar{\varepsilon}^{tk}$ is the same and the heterogeneous $\bar{\varepsilon}^{tk}$ part is of opposite sign for the M_{k+} and M_{k-} variants, both M_{k+} and M_{k-} can be described by a single OP $-1 = M_{k-} < \eta_k < M_{k+} = 1$ upon substituting $\bar{\varepsilon}^{tk} + \bar{\varepsilon}^{tk} sign(\eta_k)$ for ε^{tk} in Eqs.(2.138-141)

Figure 2.24: Spatiotemporal evolution of initially randomly distributed fields η_1 and η_2 in the square-to-rectangle martensites at time (a) 3.5 ps and (b) 34.7 ps, and the square-to-oblique martensites with two variants at time (c) 4.6 ps and (d) 11.6 ps.

In this section, the cubic-to-monoclinic II MT in the CuZnAl alloys is considered, however, the simulations are expected to be applicable to other materials undergoing the cubic-to-monoclinic II transformation. From the lattice parameters and stretch tensors of CuZnAl, the transformation strain tensors are obtained by $\alpha = 0.0866$, $\beta = 0.0101$, $\gamma = -0.0907$ and $\delta = 0.0249$ [Bha03]. Other material parameters include $a = 2.980$, $A_0 = 4.4 \text{ MPa/K}$, $\bar{A} = 5320 \text{ MPa}$, $T_c = 200 \text{ K}$, $L_k = 8653.5 \text{ m}^2/\text{ns}$, $g = 2.33 * 10^{-11} \text{ N}$, $B = 0$, $C = -5 \text{ GPa}$, the Young's modulus $E = 104 \text{ GPa}$ and the Poisson ratio $\nu = 0.3$. In simulations, the square specimens are constructed with the dimensions of $10 * 10 \text{ nm}$ in Figure 2.24, of $50 * 50 \text{ nm}$ in Figure 2.25(a)-(b), and of $70 * 70 \text{ nm}$ in Figure 2.25(c)-(d). The initial conditions for the coupled systems are set as follows: (1) two OPs η are randomly distributed varying from 0 to 1 for representing $\{M_4, M_5\}$ in Figure 2.24(a)-(b) or $\{M_{1+}, M_{2-}\}$ in Fig. 2.24(c)-(d); (2) two other OPs ranging from -1 to 1 for representing $\{M_{1+}, M_{1-}, M_{2+}, M_{2-}\}$ in Figure 2.25

are randomly seeded in the whole specimens.

Figure 2.24(a)-(b) show the characteristic (a) needle and (b) lamellar twins of the square-to-rectangular martensites as analog of the cubic-to-monoclinic II ones, wherein the observed interface directions of $\pm 45^\circ$ are formed at transient state resulted from kinematic compatibility condition, while the martensite variant coalescence is promoted by the surface energy in the later stage. It should be stressed that the compound twins, such as $\{M_4, M_5\}$ or $\{M_3, M_6\}$ obtained from the square-to-rectangular transformation and $\{M_{1+}, M_{2+}\}$ or $\{M_{1-}, M_{2-}\}$ from the square-to-oblique transformation, have the $\pm 45^\circ$ direction angles of twin planes, which are originating from the difference between the diagonal components in the transformation strain. As one may expect, the twinning directions of the correspondence variant pairs of $\{M_{1+}, M_{2-}\}$ and $\{M_{1-}, M_{2+}\}$ deviate from $\pm 45^\circ$ and 0° or 90° . Figure 2.24(c)-(d) show the laths/needles aligning along the $\pm 61.5^\circ$ or $\mp 28.5^\circ$ due to the difference between the diagonal and shear components in the transformation strains. Figure 2.25(a)-(b) show the richness of the intricate microstructures of the square-to-oblique transformation as analog of the different cubic-to-monoclinic II alloys, including polygons like triangle, trapezoid and hexagon, which may occur under different experimental conditions. The twins of $\{M_{1+}, M_{2-}\}$ and $\{M_{1-}, M_{2+}\}$ have the $\pm 61.5^\circ$ or $\mp 28.5^\circ$ directions of twin planes, thus lead to the polygon morphology. Increasing the specimen dimension, Fig. 2.25(c)-(d) predict the V-tapered accommodated microstructures observed in the CuZnAl alloys by Zhang et al. [ZZZ99] (see the inset of Figure 2.25(d)). Similar to the classic wedge microstructures, the V-shaped twins play a major role in the initiation and growth of MT, which might in turn governing direct and reverse MTs. Note that, another possible compound twins, e.g. $\{M_{1+}, M_{1-}\}$ and $\{M_{2+}, M_{2-}\}$ embracing 0° or 90° interface directions with lamellar microstructure are not observed in our simulations, but they are allowed according to the kinematic compatibility.

The simulated martensite microstructure also can be verified with the CM-PTMC by using the Eqs.(2.45-58) in Section 2.3 and Ref.[Bha03]. When $\kappa_{12} = \pm 1$ and $\rho \neq 0$ are chosen to make $|\mathbf{n}| = 1$, from Eq. (2.51), we obtain the twin plane normal $[\pm 1, 0, 0]$ or $[0, \pm 1, 0]$ perpendicular to the interface between M_{1+} and M_{1-} (or M_{2+} and M_{2-}), $[\pm 1/\sqrt{2}, \mp 1/\sqrt{2}, 0]$ or $[\pm 1/\sqrt{2}, \pm 1/\sqrt{2}, 0]$ to the one between M_{1+} and M_{2+} (M_{1-} and M_{2-} , M_3 and M_6 , or M_4 and M_5), and $[\mp 0.476673, \pm 0.879081, 0]$ or $[\pm 0.879081, \pm 0.476673, 0]$ to one between M_{1+} and M_{2-} (M_{1-} and M_{2+}). All the simulated twin plane normals in Figures 2.24 and 2.25 exactly coincide with these calculated results based on Eq. (2.53).

From the thermodynamic equilibrium conditions, see Eqs. (14) and (16) in Ref.[LLP10], the parametric representation of the unstable branch of equilibrium stress-strain curves can be obtained. They characterize the mechanical behaviors of cubic-to-monoclinic II SMAs at

Figure 2.25: Spatiotemporal evolution of initially randomly distributed fields $\eta_1 + 2\eta_2$ in the square-to-oblique martensites at time (a) 40.4 ps and (b) 347 ps with the size of 50*50 nm, and (c) 80.9 ps and (d) 347 ps with the size of 70*70 nm. The V-shaped pattern is compared with experiment [ZZZ99]

various temperatures (Figure 2.26). The $A \rightarrow M$ ($M \rightarrow A$) transformation takes place at higher (lower) stress in each hysteresis. The stress-strain curve at equilibrium temperature, = 300K, is termed 'pseudoplasticity', while at higher temperatures is 'pseudoelasticity'; both curves resemble that of a SMA.

2.7 Connections and Distinctions among Models

In the previous Sections 2.2-2.5, we highlighted the widely used models of MT which have ability to present/predict the intriguing microstructural features. These models have

Figure 2.26: Equilibrium stress-strain curves of the cubic-to-monoclinic II SMA at various temperatures with $A_0 = 300 \text{ MPaK}^{-1}$, $T = 330 \text{ K}$; $\varepsilon^{et} = 0.087$, $T_c = 290 \text{ K}$; $T_e = 300 \text{ K}$. Unstable regions are dashed.

their origins in different branches of physics, and thus differ in statics or dynamics. In fact, solid state physics itself is never an isolated branch of physics, but a recognizable field coalescing out of previously research lines into a unified perspective. Therefore, the aforementioned models of MT must have certain ingredients in common which are shared with each other, and exhibit distinctive advantages. In this section, a deeper insight into the physical natures of the models is provided focusing on elucidating the connections and distinctions among the models.

In the thermodynamic point of view, the common denominator in these approaches, explicitly or implicitly, is the minimization of free energy under the constraint of lattice coherency.

- The prototype PTMC is always viewed as a pure geometrical method with a constraint of invariant plane condition. It is worth noting that the invariant plane condition or the existence of invariant plane strain implies the energy minimization. The atomic movement in MT gives rise to lattice misfit across the interface between parent phase and martensites and leads to a stress field of high energy. One way of reducing the

stress is to create up an incoherent interface. It has never been adopted by most of SMAs to solve the problem since the phase transition proceeds by rapid interface motion that only allows coherent interfaces. Thus, the formation of coherent interface with invariant plane strain is the exclusive way for SMAs to vanish lattice misfit stress. Moreover, the lattice correspondence served as a priori discipline in fact corresponds to the minimum transformation energy, which is determined by an ergodic comparison of energy costs of displacing the lattice directions of parent phase to martensites.

The feature of energy minimization is apparent in the remaining models.

- The CM-PTMC approach minimizes a nonconvex harmonic elastic energy in terms of the deformation gradient subject to the kinematic compatibility (Hadamard jump) condition across the interface. The invariant plane strain condition in prototype PTMC is one of special cases of kinematic compatibility condition.
- In microelasticity phase field model [Kha13], the total strain is written as the summation of transformation strains and elastic strain. The elastic free energy is harmonic with respect to the elastic strain, which is effectively eliminated by using the static equilibrium equation of elastic stress. Thus, the microelasticity phase field model minimizes a transformation strain energy in terms of OPs η instead of total strains. Nevertheless, the OP η in phase field modeling for MT is actually coupled to the transformation strain. It should be noted that while the growth of the martensite is mostly driven by the chemical free energy, the refining and coalescence of the microstructure are driven by the strain energy and the interfacial energy reduction in microelasticity.
- The IRS based Landau model is equipped with the multi-well Landau free energy in terms of symmetry adapted strains, which are linked with components of transformation strain tensors and displacements. To this sense, IRS-Landau model minimizes an anharmonic strain energy, which drives structural transformations from higher symmetry to lower one. However, IRS based Landau energetics with different dynamics exhibit different ways to achieve the minima of the transformation strain energy.

In dynamics,

- two PTMC methods depict the static microstructure features either obtained from stress equilibrium or as variational result of elastic energy with respect to the deformation gradient/strain components. Since the PTMC methods only involve the elastic energy density, neither coordinate variables nor time dependent dynamics is taken into models, they are incompetent to represent the morphology under TEM observation and hence incapable of monitoring the evolution of microstructure with time. By the end, the calculated habit planes and twin domain walls in statics only have geometric ex-

pressions in crystallography.

- The microelasticity and thermomechanical phase field models consider a split dynamics. The elastic strain reaches equilibrium state instantly, however, the transformation strains represented by OPs η_i are evolving with overdamped TDGL dynamics. Thus, the rate of evolution (by tracking the local value of the OP η in a given region of phase space) is proportional to the thermodynamic driving force, such that the elastic system simply follows the gradient of the energy surface until it ends up in a local minimum. The TDGL dynamics applied to the constructed free energy enables heterogeneous microstructure of martensite, but some of the dynamic behaviors such as dynamical twinning, precursors will be missing. It is particularly suitable for steels and other systems in which MTs undergo classical transformation paths with remarkable dissipation originating from evolution of dislocation and friction of interface motion.
- The IRS based Landau approach is flexible to various dynamics, including static equilibrium of stress, full dissipative overdamped, TDGL, and inertia ones. The inertia dynamics can be performed using either displacements or strains as basic variables in simulation. The displacement-based inertia dynamics (Lagrange dynamics in the thesis) utilizes the general equation of motion, which is adopted in most of the simulations in following chapters. The strain-based inertia dynamics [denominated Bales-Gooding (BG) dynamics] requires the St. Venant's compatibility constraint to serve as the Lagrangian multiplier and the elimination of the dependent strain components by rewriting the non-OP strains in terms of the OP strains, which results in an anisotropic, long-range integral kernel of OP strains. (detailed in 2.4.11) The compatibility enforces the continuity across the interface and guarantees strain matching [LSR⁺03]. If the dissipation (real damping) term is removed, the conservation equation of inertia dynamics describes a physical picture that the reduction in local free energy triggers the formation of the habit planes and/or twin boundaries during the martensitic nucleation and drives the interface propagation during martensite growth. In fact, the existence of dissipation term will minimize the finite kinetic energy density. Finally, damping term dissipates the energy to the state of stress equilibrium, which corresponds to an energy minimum.

The inertia dynamics has ability to present a full physical picture of MT, including conversion of Landau potential energy and kinetic energy, finite velocity of interface propagation (inertial effect), dissipation of the excess energy due to friction, etc., such that the equations of inertia dynamics in fact contain all of the essential elements of other dynamics. If both inertia and viscous terms are dropped, the dynamic equation degenerates into the static equilibrium of stress utilized in CM-PTMC, by doing so the static martensitic microstructure will

be presented. If only the inertia term is dropped, i.e. double time-derivatives of the OP strain in Bales-Gooding dynamics, or double time-derivatives of the displacement in the displacement Lagrange dynamics, the equation is of a generalized TDGL (overdamped) form. The only difference lies in that the generalized TDGL equation includes nonlocal, anisotropic Onsager coefficients in comparison with a local, constant and scalar coefficient in conventional TDGL (see the curved transformation paths on energy surface in Figure 2.27). With generalized TDGL, the system will rapidly evolve to a single variant state or coverage to two-variant microstructure with a twin boundary separating them. In a full inertia dynamics in conjunction with IRS based Landau energy, the short-wavelength oscillators tend to equilibrate at the early stage of MT leaving the long-wavelength oscillators with larger inertia frozen, from which the under-damped nature of MT is discerned; whereas the late-time envelop dynamics guides all the oscillations exhibiting an over-damped form.

Figure 2.27: The curved the transformation paths due to the different values of deviatoric elastic coefficient $C_{11} - C_{12}$ and shear elastic constant C_{44} served as anisotropic Onsager coefficients. The inertia dynamics is recorded every 1000 steps and represented in white, while the over-damped dynamics is in black with recording frequency of 200 steps.

Since the long-wavelength elastic oscillators have larger inertia, the microstructure evo-

lution by inertia dynamics is slower than that of TDGL, therefore gives rise to the twinned martensites to be preserved after a long-time simulation, see the comparison of square-to-rectangular MT between overdamped and inertia dynamics in Figure 2.28. In inertia dynamics, the multi-dimensional energy surface alone can not determine whether the evolution is towards the stable product phase or not, while the dissipation and inertia do effects too. In this way, more intriguing microstructure, both metastable and stable ones, can be captured by running a full dynamic simulation. Particularly, the 'elastic photocopying' of tweed like precursors is the result of interplaying between anharmonic strain energy and nonlocal strain gradient, reflecting the physical essential that the short-wavelength oscillators promptly reach equilibrium state at the early stage of MT. In summary, the inertia dynamics surpasses the overdamped ones for studying the inherent richness of static and dynamics behaviors in MT, including the dynamical twinning, diverse (meta) stable microstructure, domain wall propagation at the near-sound speed, and the precursors. The IRS based Landau model is appropriate for less dissipative system undergoing weak first-order MT.

As far as the genesis of models in physics is concerned, the CM-PTMC and microelasticity phase field are rooted in the continuum mechanics of rigid body. It is apparent for CM-PTMC that the solving of habit plane and twin boundaries finally turns out to be the problem of eigenvalue-eigenvector and all of the core variables like deformation gradient, stretch, rigid body rotation, etc. can be found in any textbook of elasticity. The microelasticity phase field model, dating back to the work of Eshelby [Esh57, Esh59], considers martensites as 'inclusions' in a parent matrix with different shapes and properties [Mur12]. The key issue of microelasticity is to obtain the equilibrium state of stress induced by the heterogeneous strain energy in reciprocal space with a static Green's function. It is the dominant strategy in micromechanics of defects in solid [Mur12]. The IRS based Landau has a strong physical background of wave mechanics and crystal lattice dynamics. The early works such as the Lagrange-Rayleigh one-dimensional strain dynamics exhibited the solitary solutions of propagating interfaces. The acoustic softening of elastic wave oscillators accounting for the weak first-order MT is directly derived from the crystal lattice dynamics.

Meanwhile, the above methods also differ in whether they hold for finite deformation/strain or only in the infinitesimal strain limit. The microelasticity phase field model assumes geometric linearity and thus has so far been limited to infinitesimal strains approximation. In contrast, the PTMC is natively geometrically nonlinear when deformation gradients are adopted as the variables in calculation. The thermomechanical phase field and IRS based Landau models have been extended to the application of finite deformations [PL13, FLBGS10, LLZF09].

The models also present distinct applicability owing to their different origins in physics,

Figure 2.28: The square-to-rectangular MT is simulated by overdamped (upper panel) and inertia (bottom panel) dynamics with the same material and simulation parameters. The numbers indicate the simulation time steps.

especially comparing microelasticity phase field model with IRS based Landau model. Based on the previous discussion, we understand IRS based Landau model has advantages in representing precursor, predicting transformation paths with anisotropic Onsager coefficients, working with finite strains, monitoring displacement and deformation gradient and revealing the underdamped nature. All these events are missing in microelasticity phase field model. From Sections 2.3-2.5, we also found that the phase field models and IRS Landau model are nearly equivalent in predicting the accurate twin plane and invariant plane consistent with what PTMC predicts. However, phase field models possess an apparent advantage in representing the habit planes. Few works for predicating habit plane between austenite and internal twins have been reported by using IRS based Landau model, except for the theoretical work of Barsch et al. [BHK87]. In contrast, it is a matured technique in all phase field models, e.g. the Figure 2.23(b). It is because, the transformation strains are inputs of sim-

Figure 2.29: The simulated tweed structure in square-to-rectangular and triangle-to-centered-rectangular [CKO⁺07] MTs.

ulation in phase field models, such that the so-called prediction is more like a morphology recapturing with a set of scalar indicators of OPs η . However, in IRS based Landau, only temperature dependent elastic coefficients are served as inputs.¹ Since the morphology is represented by the OP strains shared by both austenite and martensites, the control of average transformation strain with a ratio of two martensite variants becomes a challenge. Moreover, neither of phase field and Landau models is capable of predicting the orientation relationship deviated from the lattice correspondence because the extra freedom of rigid body rotation without free energy change is not determined. The comparison of the applicability is listed in Table 2.1.

Besides the aforementioned common ingredient and distinctions, one more point is worthy being addressed between microelasticity phase field and IRS based Landau models. In both methods, the homogeneous deformation with $\vec{k} = 0$ mode evolves at a constant rate, so that the energy is not minimized with respect to the homogeneous part of the strain fields, evidenced by the removal of the point $\vec{k} = 0$ in both Green's functions in microelasticity phase field and long-range integral kernel of OP strains. In fact, long-range integral kernel of OP strains is formally a Green's function. The only difference lies in the fact that the anharmonic contribution of OP strains is not included in Green's function of long-range integral kernel, while harmonic heterogeneous relax energy contributed by all strain components is included

¹If the high order elastic constants were available, the manipulating of Landau potential is avoided, such that can lead to a true prediction.

in Green's function in microelasticity phase field.

In summary, while the models of MT stated in the thesis are endowed with the common ingredient of energy minimization, they differ in the ways how to achieve the energy minima and interface coherency. Different models have individual advantages and disadvantages in predicting different properties.

2.8 Objectives

As is summarized in Section 2.7, the most complete model for MTs from the viewpoint of the underlying physics is the Landau theory based on the IRS and inertia dynamics. However, this approach has disadvantages from the application perspective. This doctoral thesis is aimed at improving the IRS based Landau model towards advanced applications in structural materials.

The specific objectives of the thesis are:

1. To develop a Landau model based on the irreducible representation of the point group and transformation strains for MTs in polycrystals that describes accurately the microstructural features of polycrystalline ferroelastic materials.
2. Investigate the variant selection of martensites in polycrystals subjected to external loading, and the dynamical nucleation of martensites in polycrystals under the combined effect of external loading and temperature changes.
3. Develop a coupled model for displacive-diffusive transformations by integrating the Landau model with information provided by thermo-kinetic calculation and database.
4. Extend the previous model to incorporate the effect of dislocations by incorporating the continuum theory of dislocations.

Table 2.1: Summary of models for MT and their applicability

	PTMC	Microelasticity PF	IRS-LR	Simulation Results of IRS-LR
Precursor(Tweed) or Postcursor			✓
Twin Plane	✓	✓	✓
Habit Plane	✓	✓	Numerical
Orientation Relationship	✓	Only with Infinitesimal Strains		
Displacement or Deformation Gradient	✓		✓
Applicability for Finite Strains	✓		✓
Anisotropic Transformation Pathway			✓
Damping			✓

Chapter 3

Nonlinear Ginzburg-Landau Model of Martensitic Transformation in Polycrystals

This work contains many things which are new and interesting. Unfortunately, everything that is new is not interesting, and everything which is interesting, is not new.

-Lev Landau

3.1 Introduction

We understand that crystalline materials of technological interest are always polycrystalline and include a very large number of grains with different grain orientations. Since MTs occurring in polycrystals show some interesting features different from those in single crystal, important progress has also been made on the modeling of MT in polycrystals with the approaches revisited in chapter 2. Correspondingly, Bhattacharya [BS05] introduced the fix-point iterative algorithm to evaluate the recoverable strains in polycrystalline SMAs undergoing MTs in the language of continuum mechanics. Great success of modern phase-field methods was achieved on this topic [AJK02, JAK01, HC14, MABÅ13a]. Recently, Heo et al. [HC14] updated the micro-elasticity phase field model with a misfit strain relaxation that permits elucidating the effects of elastic anisotropy and grain boundary curvature on polycrystalline MTs. Malik et al. [MABÅ13a] used an elasto-plastic phase field model to simulate the microstructure features of MTs in Fe-C alloy subjected to external loadings. In the scheme of IRS, Ahluwalia et al. [ALS03, ALSA04] coupled grain orientations to elastic strains in the over-damped TDGL dynamics to model the polycrystalline square-to-rectangular MT and its response under the uniaxial tension, which was further extended by

Cui et al. [CKO⁺07] to triangle-to-centered-rectangular case analogues to more complex hexagonal-to-orthorhombic MT.

The IRS energetic scheme has proven useful to describe MT, and manifests itself by capturing the nature of the damped system and propagated interfaces in proper MT once it was applied with the Lagrange-Rayleigh dynamics [BG91, RG94, SLSB99]. Note that most of the modeling for polycrystalline MTs adopted the TDGL dynamics in the past decades. Very recently, utilizing Lagrange-Rayleigh dynamics with IRS based Landau energy (IRS-LR), Ahluwalia et al. [AQW15] developed the 2-4-6 Landau polynomial with local symmetry-adapted strains as OPs and then reformulated them in terms of global strains. They solved the general equation of motion to investigate the grain size effects on the MT in nano-polycrystalline Fe-Pd alloy and the stress-strain response in strain induced MT. Nevertheless, we believe their model is solely applicable to some nano-scale materials wherein the martensitic nucleation and growth at grain boundaries were inhibited, or the effects of grain orientations on martensite alignments¹ were smeared out by the dense grain boundary network. However, the microscopic images of martensites generally show that the alignments of martensite variants favor rotating certain angles with respect to the grain orientations in polycrystals, which is yet evidently recognized in the simulated microstructure of Ref.[AQW15].

In this chapter, we will modify the existing IRS-LR model to investigate the formation of spatially varying martensite variants in polycrystals to include the following features: (1) the transformation strains and characteristic microstructure signatures inside individual grains, (2) the variation of the habit plane/twinning elements (i.e. twin/habit plane normal and shear vector) of martensite, with different grain orientations, and (3) the microstructural change due to external loading. By analyzing the simulated microstructure, we will gain insight into how the IRS-LR model is connected with the CM-PTMC and, as a result, will demonstrate physical inherency between these models and the theory.

3.2 Model

The physical nature of polycrystalline MTs, which shows the competition and constraints between the martensite variants that are developed in each grain and the surrounding grains, permits the grain orientation-transformation strain coupled field that need to be expressed in a fixed global coordinate system. In single crystal model, Landau free energy is developed based on the linearized strain tensor with the component $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, where u_i denotes the local displacement, and $u_{i,j} = \partial u_i / \partial x_j$ is the displacement gradient in the

¹in order to avoid any confusion, we use the alignment to describe the variants and twinning and reserve the orientation exclusively for grain orientation in square-to-rectangular case.

intragranular coordinates. The symmetry-adapted linear strains ε_k , written in the linear combination of the strain components, are selected as the OPs. Now we consider a MT in polycrystals: The real freedoms in a system undergoing MT are the global displacements, U_i , and they should be connected with the OP strains by introducing an additional variable $\theta(\mathbf{r}, t)$ describing grain orientation field. As such, the local strains and symmetry-adapted OP strains are the functional of the global displacement gradients, viz. $\varepsilon_{ij}(U_{I,J})$ and $\varepsilon_k(U_{I,J})$. In order to distinguish the variables described in different references or coordinates, the variables in global coordinates are denoted by capital letters while those in local coordinates by lowercase. The specific expressions of free energy and dynamic equations for the simulations of 2D square-to-rectangular and triangle-to-centered-rectangular martensitic nucleation are detailed as follows. As usual, the Landau free energy in the expansion of coupled OPs and deterministic dynamic equations are still two key issues in Landau modeling.

3.2.1 Lagrange Description of Polycrystals

The starting point to work out a corrected IRS-LR model for polycrystals, as in Ref [AQW15] and the phase field model [CY94], is to describe the grain orientation field of polycrystals by defining the spatially distributed grain orientation $\theta(\vec{\eta}, \mathbf{r})$ with respect to a set of arbitrarily selected intragranular coordinates which should serve as the reference global system. Similar to Refs. [AQW15, CY94], θ is written as the functional of vectorial indicator $\vec{\eta}(\eta_1, \eta_2 \dots \eta_Q)$,

$$\theta(\vec{\eta}, \mathbf{r}) = \frac{\theta_m}{Q-1} \left[\sum_{i=1}^Q i\eta_i / \sum_{i=1}^Q \eta_i - 1 \right] \quad (3.1)$$

where the grain orientation i corresponds to $\eta_i > 0$ while the remaining components are equal to zero. To obtain a coupled field, the grain orientation at the position $\mathbf{r}$ subsequently enters the co-rotated local strain field expressed in global coordinates via a similarity transformation with an orthogonal rotation matrix, i.e. $\mathbf{E} = \mathbf{R}[\theta(\vec{\eta}, t)] \boldsymbol{\varepsilon} \mathbf{R}^T[\theta(\vec{\eta}, t)]$, where $\mathbf{E}$ and $\boldsymbol{\varepsilon}$ are the strains in global and local coordinates, respectively, and $\mathbf{R}$ is rigid body rotation matrix $\begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix}$.

Unlike a TDGL dynamics with the IRS based Landau free energy functional, we explicitly express the Lagrangian incorporating the kinetic energy density $T = \rho \dot{\mathbf{U}}^2/2$ and the Landau free energy density f as $\mathcal{L} = \int_V d\mathbf{r} \{T - f\}$, where ρ is the mass density, and $\mathbf{U}$ and $\dot{\mathbf{U}}$ stand for the displacement and the velocity in the global reference, thereby ensuring the total energy density to be given in global coordinates. The free energy density f is intuitively

defined as the summation of elastic energy density, $f_{elastic}$, the free energy density due to the grain orientation

$$f_{grain} = \sum_{i=1}^Q \left[\frac{g_{a1}}{2} \eta_i^2 + \frac{g_{a2}}{2} \eta_i^3 + \frac{g_{a3}}{2} \eta_i^4 \right] + \frac{g_{a4}}{2} \sum_{i=1}^Q \sum_{j>i}^Q \eta_i^2 \eta_j^2 + \sum_{i=1}^Q \frac{\kappa_g}{2} (\nabla \eta_i)^2 \quad (3.2)$$

and the free energy contribution due to the applied load f_{load} , according to $f := f_{elastic} + f_{grain} + f_{load}$, [CKO⁺07]. The elastic energy density $f_{elastic}$ can be further divided into three parts, i.e. local free energy density f_{local} , the energetic contribution originating from non-OP strains $f_{non-OPs}$, and the gradient of OP strains f_{grad} . The first term f_{local} describes the symmetry breaking during the phase transformation by adopting the symmetry-adapted strains $\varepsilon_i(\mathbf{r})$ as the independent OPs, i.e. linear combinations of the components of strain tensor in intragranular coordinates. In case of the square-to-rectangular transformation, the deviatoric strain $\varepsilon_2 = c_2 (\varepsilon_{xx} - \varepsilon_{yy}) / 2$ is selected as the primary OP, so the local free energy density is written as

$$f_{local} = \frac{A_{20}}{2} \left(\frac{T - T_c}{M_s - T_c} \right) \varepsilon_2^2 + \frac{A_4}{4} \varepsilon_2^4 + \frac{A_6}{6} \varepsilon_2^6 \quad (3.3)$$

where $A_2 = A_{20} \left(\frac{T - T_c}{M_s - T_c} \right)$ is temperature dependent deviatoric modulus, A_4 and A_6 are related to higher order nonlinear elastic constants, and T_c and M_s are the critical point and the MT starting temperature. While in the triangle-to-centered-rectangular case, both deviatoric strain ε_2 and shear strain $\varepsilon_3 = c_3 (\varepsilon_{xy} + \varepsilon_{yx}) / 2$ are adopted as OPs, and the local free energy density is formulated as

$$f_{local} = \frac{A_{20}}{2} (T - T_c) (\varepsilon_2^2 + \varepsilon_3^2) + \frac{B_3}{3} (\varepsilon_2^3 - 3\varepsilon_2\varepsilon_3^2) + \frac{A_4}{4} (\varepsilon_2^2 + \varepsilon_3^2)^2 \quad (3.4)$$

where B_3 is the linear combination of third order elastic constants, and c_i are symmetry-related constants corresponding to individual MTs with $c_2 = \sqrt{2}$, $c_3 = 1$ for square-to-rectangular and $c_2 = c_3 = 1$ for triangle-to-centered-rectangular in this work [PL13]. It is noteworthy to point out that, Ahluwalia et al. [ALS03, ALSA04] and Cui et al. [CKO⁺07] constructed the anharmonic Landau polynomials directly in global reference with TDGL dynamics and employed the St.-Venant's compatibility condition in local reference. In contrast, Ahluwalia et al. [AQW15] recently preserved the link between the local symmetry-adapted OPs $\varepsilon_i(\mathbf{r})$ and local strains ε_{ij} in the intragranular coordinates [SSF12], and then rewrite the local OP strains, the non-OP strains (e.g. local dilatation strain $\varepsilon_1 = c_1 (\varepsilon_{xx} + \varepsilon_{yy}) / 2$) and nonlocal gradient terms (e.g. $(\nabla \varepsilon_2)^2$ for square-to-rectangular) as the components of the global displacement fields $\mathbf{U}$, therefore express them in the reference coordinates for the

Lagrangian. For example, the symmetry adapted deviatoric strain is expressed in global displacements as,

$$\begin{aligned}\varepsilon_2 &= [u_{x,x}(U, \theta) - u_{y,y}(U, \theta)]/\sqrt{2} \\ &= [\cos 2\theta (U_{X,X} - U_{Y,Y}) + \sin 2\theta (U_{X,Y} + U_{Y,X})]/\sqrt{2}\end{aligned}\quad (3.5)$$

where, U and u are displacements in different coordinates, and θ is the angle of grain orientation in Eq.(3.1). The dilatation strain and shear strain are

$$\begin{aligned}\varepsilon_1 &= (\varepsilon_{xx} + \varepsilon_{yy})/\sqrt{2} = (U_{X,X} + U_{Y,Y})/\sqrt{2} \\ \varepsilon_3 &= (\varepsilon_{xy} + \varepsilon_{yx})/2 = -\frac{\sin(2\theta)}{2}(U_{X,X} - U_{Y,Y}) + \frac{\cos(2\theta)}{2}(U_{X,Y} + U_{Y,X})\end{aligned}\quad (3.6)$$

This approach is followed in this chapter. The construction of Landau polynomials in global and local reference would be equivalent only if the $C_{11} - C_{12} = 2C_{44}$ (i.e. $A_2 = A_3/2$) is rigidly satisfied in isotropic case and the contribution of the anharmonic terms is negligible so that local free energy density degenerates in the full quadratic form.

3.2.2 Dynamical Equations

The evolution of grain orientation and displacement fields are treated differently in this chapter. The TDGL equation

$$\frac{\partial \vec{\eta}(\mathbf{r}, t)}{\partial t} = -L_\eta \frac{\delta f_{\text{grain}}}{\delta \vec{\eta}(\mathbf{r}, t)} \quad (3.7)$$

is used to describe the evolution of the OP field $\vec{\eta}(\mathbf{r}, t)$ of the grain orientations with L_η as kinetic coefficient for interface mobility.

When the spatiotemporal evolution of displacements and strain fields is considered, a variation method of Lagrange mechanics is utilized. By taking the variation of the Lagrangian with respect to the displacement $\mathbf{U}$ and $\dot{\mathbf{U}}$ in the global reference and explicitly substituting the Lagrangian into the Lagrange-Rayleigh equations $\frac{d}{dt} \frac{\delta \mathcal{L}}{\delta \dot{U}_i} - \frac{\delta \mathcal{L}}{\delta U_i} = -\frac{\delta \mathcal{R}}{\delta \dot{U}_i}$, the Lagrange-Rayleigh equations yield the general equations of motion in polycrystals

$$\rho \ddot{U}_i = \frac{\partial}{\partial X_j} \left\{ \frac{\partial f}{\partial \varepsilon_k} \frac{\partial \varepsilon_k}{\partial \varepsilon_{pq}} \frac{\partial \varepsilon_{pq}}{\partial U_{i,j}} - \nabla \cdot \frac{\partial f}{\partial \nabla \varepsilon_k} \frac{\partial \nabla \varepsilon_k}{\partial \varepsilon_{pq}} \frac{\partial \varepsilon_{pq}}{\partial U_{i,j}} + \frac{\partial R}{\partial \dot{\varepsilon}_k} \frac{\partial \dot{\varepsilon}_k}{\partial \dot{\varepsilon}_{pq}} \frac{\partial \dot{\varepsilon}_{pq}}{\partial \dot{U}_{i,j}} \right\} \quad (3.8)$$

where, ρ is density, $\mathcal{R}$ and R are Rayleigh dissipation and dissipation density, written as the functional of velocity of elastic waves to describe the friction in system. Generally, the dissipative stress tensor should anisotropically depend on the space derivatives of the velocity

field. For the sake of simplicity, an isotropic approximation of dissipation with viscosity is utilized in this work. If the local stress expressed in global coordinates is defined as

$$\sigma_{ij} = \frac{\delta F}{\delta U_{i,j}} = \frac{\partial f}{\partial \varepsilon_k} \frac{\partial \varepsilon_k}{\partial \varepsilon_{pq}} \frac{\partial \varepsilon_{pq}}{\partial U_{i,j}} - \nabla \cdot \frac{\partial f}{\partial \nabla \varepsilon_k} \frac{\partial \nabla \varepsilon_k}{\partial \varepsilon_{pq}} \frac{\partial \varepsilon_{pq}}{\partial U_{i,j}} \quad (3.9)$$

the dynamics of displacement fields is given by dissipative force balance equations

$$\rho \ddot{U}_i = \frac{\partial \sigma_{ij}}{\partial X_j} + \gamma \nabla^2 \dot{U}_i \quad (3.10)$$

Different from Ref. [ALS03], the local stresses in our model enter dissipative force balanced equations via the chain rule of functional differentiation of free energy with respect to global displacement gradients. By numerical solving Eqs. (3.7) (3.9) and (3.10), the spatiotemporal evolution of displacements, strains and grain orientations is obtained. Finally, the viscous term drives the system to the mechanical equilibrium state. Moreover, in Al-huwalia's latest work with IRS-LR [AQW15], they took the global stress in the dissipative force equation, leading to the global stress equilibrium in the laboratory reference. As such, the morphology of martensite variants failed to exhibit the rotation of alignments across the grain boundary. According to Mura [Mur12], the precondition of describing MT by the displacement field is to assume that the elastic stress reaches its equilibrium instantly, as a consequence the transformation strain components are derivatives of the total displacements. In the case of polycrystals, the MT in individual grains should be equivalent when external field is free. Thus, the stress in dissipative force equation should be the local transformation stress, i.e. the functional of the Landau free energy with respect to local transformation strains expressed, however, in global reference.

Lookman et al. [LSR⁺03] derived the OP strain-based Bales-Gooding under-damped dynamics by reformulating both non-OP strain(s) and strain compatibility in terms of OPs. While the description with long-range OP strains has intrinsic advantages, e.g. the ability to explicitly display the symmetry-specific compatibility kernels in both Fourier and real spaces and to reveal the information of the energetically favored orientations and habit planes, the same under-damped dynamics could be equivalently obtained via either the strain-based Bales-Gooding or displacement-based Lagrange-Rayleigh descriptions. With the emphasis to unveil the competency of displacement-based IRS-LR dynamics on describing orientations and habit planes and its connection with CM-PTMC, the displacement and displacement gradients in this chapter are required to serve as inputs to kinematic compatibility equation of CM-PTMC for numerically solving the unit shear and habit/twin plane normal. To this end, we choose the displacements $\mathbf{U}$ as the basic independent variables. By doing this, the constraint of strain compatibility does not have to be solved explicitly [SLS10, RLS⁺01],

and this is particularly useful when this model is extended to 3D.

3.2.3 Connection to CM-PTMC

In the IRS-LR model, the displacements are served as the basic independent variables. They enter the OPs and Landau free energy via Eq.(2.66) in case of the infinitesimal strain approximation. The information of the symmetry breaking has been included in the anharmonic terms in Landau free energy. Due to the transformation strains are small in most of SMAs, the equi-energetic minima constructed by anharmonic Landau free energy to present the martensite variants are located in the vicinity of original point of phase space. In the regions far beyond the original point or when the anharmonic terms are fully ignored, the Landau free energy shows a quadratic form, same as the one expressed in the linear elasticity, i.e. $f = \boldsymbol{\sigma} : \boldsymbol{\varepsilon}$. In our polycrystalline model, the corotational or similarity transformation of the strain tensor, $\mathbf{E} = \mathbf{R}\boldsymbol{\varepsilon}\mathbf{R}^T$, will not change the eigenvalues of right Cauchy-Green deformation tensor $\mathbf{C} = \mathbf{F}^T\mathbf{F}$, nor those of deformation gradient $\mathbf{F}$. However, the common eigenvectors of $\mathbf{C}$ and $\mathbf{F}$ in individual grains will be rotated with respect to the grain orientations. Based on the established Landau free energy and dynamic equations, the martensite morphology is achievable through eliminating the elastic stress inside the martensite domains while the dissipative stress drives the system to a mechanical equilibrium state corresponding to the minima of the potential energy. The dynamic processes are associated with the formation, growth and propagation of the interface between phases/domains by solving Eq.(3.8) or (3.10). Reviewing Eq. (3.10), this equation is actually a general form of the momentum balance $\rho\ddot{\mathbf{U}} = \nabla \cdot \boldsymbol{\Sigma}$ in continuum mechanics, if no Rayleigh dissipation is considered, where $\boldsymbol{\Sigma}$ is the corotational stress tensor given by $\boldsymbol{\Sigma} = \mathbf{R}\boldsymbol{\sigma}\mathbf{R}^T$, which essentially reflects a direct coupling of primary OP to grain orientation in Eq.(3.9)

With this dynamic equation, when the mechanical equilibrium state coincides with the phase equilibrium between martensite and austenite, the evolution of the system means also its seeking the lattice correspondence, e.g. the Bain correspondence in cubic-to-tetragonal MT. In essence, most of the key elements, including the displacement related transformation strains, the lost symmetry elements when undergoing MT to form twin planes, and the lattice correspondence obtained from energy minimization, are common to CM-PTMC and IRS-LR theories. As a consequence, the final state of martensitic morphology and microstructure features, like twin/habit plane, twinning shear, invariant plane shear, etc. conveyed by expressions in CM-PTMC, can be equivalently captured by IRS-LR modeling. However, some intrinsic distinctions, both in statics and dynamics, between the two theories can be addressed. In general, the CM-PTMC and IRS-LR are analogous to rigid-body and

wave mechanics for describing the same MT. The distinctness resulting from the dynamics, as Lookman et al. elaborated in Ref. [LSR⁺03], is related to the under-damped nature of IRS-LR. As for the statics, it lies in the higher gradient regularization along with the anharmonic contribution included in the IRS based free energy. In addition, since the IRS based Landau potential does not explicitly use the lattice parameters as inputs, the deviation of the real habit plane from the ideal lattice correspondence plane can only be numerically handled by the coupling between OP and non-OP strains. The analytic solution of the dependence of habit plane on lattice parameters between austenite and internal twins for IRS-LR or stain-only Bale-Gooding dynamics is still on working. In the following sections, we implement the numerical simulation to reveal and verify our IRS-LR model of MT in polycrystals, as exemplified in 2D square-to-rectangular and triangle-to-centered-rectangular cases, and to understand the simulated microstructure by itemizing and referring to the common ingredients of the analytical CM-PTMC.

3.3 Numerical Implementation

Upon the proposed model, we started our simulation with generating a polycrystalline microstructure of austenite. Our simulations were carried out using a Fast Fourier Transformation (FFT) based spectral method under periodic boundary conditions in 256×256 grids with 5 grain orientations of 0° , 7.5° , 15° , 22.5° and 30° ($= \theta_{max}$), respectively (Fig 3.1a). For the formation of the polycrystalline structure, we used the parameters, $g_{a1} = -1$, $g_{a2} = -1$, $g_{a3} = 1$, and $g_{a4} = 2$. k_g was adjustable to produce appropriate configuration. While the model is developed for generic materials undergoing square-to-rectangular and triangle-to-centered-rectangular transformations, we chose the Fe-Pd alloy in these simulations as the representative of square-to-rectangular in 2D as the analog of 3D cubic-to-tetragonal MT and the Mg-Cd alloy for triangle-to-centered-rectangular as the analog of hexagonal-to-orthorhombic, respectively. For Fe-Pd ferroelastic alloy, the following materials parameters were chosen based on the experimental results of elastic constants: $A_1 = 333.91 GPa$, $A_{20} = 11.5 GPa$, $A_3 = 282 GPa$, $A_4 = -1.7 * 10^3 GPa$, $T_m = 295 K$ and $T_c = 270 K$ [GLS08, MOF90, ALS03]. It is noted that the temperature dependence of the elastic constant A_2 in experiments and linear fitting was well represented by the parameter $A_2 = A_{20} \frac{T - T_c}{M_s - T_c}$ in simulations, while the other elastic constants were unchanged with temperature for simplicity. A_6 was determined from A_{20} , A_4 , and quenching temperature T , satisfying the constraints of Landau polynomial for first-order transformation in Ref. [Fal80]. The value of gradient coefficient was set to $g = 3.0 * 10^{-8}$ [AQW15, ALSA04] based on

microstructure observation, while the dissipation coefficient was estimated as $0.015Ns/m^2$ according to Ref. [ALSA04]. Upon these parameters, the interface energy density of full twinned martensites can be estimated around $0.5J/m^2$ from multi-well degenerated Landau free energy near the critical point². The retrieved value of interface energy density in our simulation has the correct order of magnitude, consistent with theoretical estimations and first principles calculations [OC76, WCLM10]. While the corresponding MgCd parameters were $A_1 = 45.8GPa$, $A_{20} = 10.9GPa$, $B_3 = -1.35 * 10^3GPa$, $A_4 = 2.0A_3^2 / (9.0 |A_2|)$, and $T_c = 526K$ [GSZ⁺09, VC12]. To tackle the numerical instability, the materials and simulation parameters were subjected to a normalization by following [Sal09], wherein the spatial and energetic variables were rescaled by introducing normalization factors $d_0 = 7 * 10^{-9}m$ and $f_0 \sim 10^{10}J$, respectively; such that $\tilde{x} = x/d_0$, and $\tilde{A}_i = A_i/f_0$. The time scale was rescaled as $\tilde{t} = t/t_0 = t / \sqrt{\rho d_0^2 / f_0}$, and the rescaled viscosity is $\tilde{\gamma} = \gamma / (d_0 \sqrt{f_0 \rho})$. At the beginning of simulation, the random fluctuations of displacements ζ_{u_i} obtained from a Gaussian noise were introduced. The mean and correlation of fluctuations satisfy

$$\langle \zeta_{u_i}(\mathbf{r}, t) \rangle = 0, \langle \zeta_{u_i}(\mathbf{r}, t) \zeta_{u_j}(\mathbf{r}', t') \rangle = 2\gamma k_B T \rho \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (3.11)$$

More details of the model and of the numerical implementation can be found in Refs. [CKO⁺07, Sal09].

3.4 Microstructure Analysis

3.4.1 Polycrystalline Microstructure of Square -to- Rectangular Martensites

A 2D polycrystalline structure of the parent austenite with randomly distributed grains is shown in Figure 3.1a. The grains with different orientations are displayed in different colors, along with the values of the grain mis-orientation angles with respect to the reference blue grain. Figure 3.1b illustrates the snapshot of the morphology of the square-to-rectangular polycrystals without external loading encoded by a combination of the deviatoric strain ε_2 and the grain orientation angle. In the grains with orientation $\theta = 0$, the domain morphology is characterized by two different types of martensite variants, i.e. red and blue ones, with opposite stretch tensors alternatively arranged. The twin boundaries are stretching in the directions of $\pm\pi/4$. Further inspection of the microstructure in each grain of the polycrystal

²If the viscous term is removed, the conservation equation of motion utilized in our simulation describes a physical picture that the dropping local free energy in Landau potential triggers the formation of the habit planes and/or twin boundaries during the martensitic nucleation and drives the interface propagation during martensite growth. In fact, the existence of viscous term will minimize the finite kinetic energy density.

reveals that they present the very same features of the single crystal but simply rotate to align with their respective grain orientations, e.g. the perpendicular lath variants in the grains with orientation $\theta = \pi/12$ (green grains in Figure 3.1a) turn to align along the $\pi/3$ and $5\pi/6$ orientations with respect to the horizontal X axis of the global reference. Some needle-like martensites with tapering tips occur in the $\theta = \pi/6$ grain, resulting from reducing the interface energy when the variants with the orientation alignments of $(\pm\pi/4 + \pi/6)$ are anticipated to intersect each other. If finite strain is considered, bending will occur at the tips of variants [FLBGS10]. Note that the alignments of martensite variants in individual grain rotate certain angle in accordance with the grain orientation in global reference as evidenced in Ahluwalia's work when using the Landau energetics with TDGL dynamics [ALS03, ALSA04]. Unfortunately, it was unclearly shown in his latest work by using LR dynamics [AQW15]. This has been significantly improved in our IRS-LR model.

3.4.2 Polycrystalline Microstructure of Triangle -to- Centered-Rectangular Martensites

The intricate microstructures in the triangle-to-centered-rectangular polycrystals, visualized by shear strain ε_3 , are shown in Figure 3.1c, wherein three distinguishable centered-rectangular martensite variants (i.e. red, blue and green) build various polygonal patterns including rectangular, rhombus, trapezoidal, etc. More interestingly, the self-accommodation of variants leads to the intriguing nested-stars pattern in triangle-to-centered-rectangular transformation, while the collision of domain walls gives rise to the formation of various types of junctions or nodes. As expected, the nested and un-nested stars (highlighted by circles in Figure 3.1c), as well as the characteristic nodes, such as (1,3,5,3) (2,5,5), (1,4,7), (1,1,10) and (1,3,5,3) (following the notation of Curnoe et al. [CJ01a]), are found in the simulated triangle-to-centered-rectangular patterns. Moreover, a small number of imperfect (1,1,1,1,7) nodes and many spiral branched patterns containing (1,3,5,3) nodes are observed since a relatively large bulk modulus associated with Mg-Cd alloys is used in our simulation. All the patterns and/or nodes well represent the morphology in Mg-Cd alloy undergoing the analogous hexagonal-to-orthorhombic MT characterized by Kitano [KKK88, KK91] et al. and Sinclair et al. [SD77]. The high resolution TEM images with the node notations are compared with our simulated pattern in Figure 3.2. Inside individual grains, the optimal arrangement of CR variants with respect to their grain orientations can be recognized by tracking the directions of domain walls that connect red and blue variants in the spiral branched pattern. The twin boundary stretches along the global X axis in the grain $\theta = 0$, and perfectly changes to 7.5° , 15° and 30° in the grains with orientations

Figure 3.1: (a) Spatial distribution of the grain orientation angle as indicated in each grain; morphology of stabilized martensites in polycrystals undergoing (b) square-to-rectangular MT represented by the spatial distribution of the deviatoric strain ε_2 and (c) triangle-to-centered-rectangular MT by shear strain ε_3 .

$\theta = \pi/24, \pi/12$ and $\pi/6$, respectively, following the angles indicated in Figure 3.1c. However, not all of the domain walls show the perfect rotations, i.e. the twin boundaries between the same correspondence variant pair of martensites at different nodes exhibit some deviations from the ideal angles. For example, the directional angles of the domain walls connecting red and green variants in the (1,1,1,1,7) nodes are 30.3° and 120.9° (with the difference between being close to $\pi/2$) in the bottom-right $\theta = 0$ grain in comparison with 33.8° and 137.9° in the neighboring (2,5,5) nodes (see Figure. 3b and 3c). This reveals a deviation of less than $+1.0^\circ$ from the ideal rigid body rotations of $(\pi/6 + n\pi/2)$ in (1,1,1,1,7) nodes and of positive $+3.8^\circ$ or negative -2.1° in (2,5,5) nodes. Meanwhile, the domain walls between red and green variants in the $\theta = \pi/12$ grain have directional angles of 45.0° in (1,3,5,3) node and 42.8° in (2,5,5) node (Figure 3.3c) with respect to global X axis. Therefore, they extend towards 30.0° and 27.8° for these two nodes in intragranular coordinates, and present a vanishing deviation in (1,3,5,3) node but a negative deviation of -2.2° in (2,5,5) node. Thus, we conclude that the triangle-to-centered-rectangular variants (also the domain walls) rotate by an approximate angle from their respective grain orientations, while the deviation from ideal angles is related to "disclination". The ideal domain walls in the spiral branched pattern are ascribed to the assembly of the four disclination-free (1,3,5,3) nodes. The formation of (1,1,1,1,7) node, as analyzed by Curnoe [CJ01a] and Kitano [KKK88, KK91], accompanies with disclination angle of 0.24° . In the case of the (2,5,5) node, it shows two disclination angles of -2.92° and 2.72° depending on the mirror (m) or rotation (r) type of the twin boundaries. The simulated results reveal the same trend of the variation of disclination angles for different nodes. In a simulation conditioned with the infinitesimal strain approximation, it is difficult to accurately measure a disclination angle because the angles of disclination at a particular node will be smeared out and/or shared by the deviated domain walls. And the larger disclination angle at a node, the larger deviation would display at the simulated domain walls.

For the triangle-to-centered-rectangular, some transitive and irregular martensite variants and domain walls persist even at the late growth stage in Figure 3.1c. This departure from full relaxation configurations reflects the propagation and collision of elastic waves in polycrystals. During the MT, the effective long-range interactions between the strains are generated, so the creation or vanishing of a domain requires a global change in the displacement field across different grains. The adjustment of the displacement or the deformation gradient field is the consequence of competitive effects of the twinning orientations that originate from transformation strains of MT and misorientations among grains, respectively. As already discussed, the geometry compatibility is always obeyed in our model, and not all characteristic twin boundaries can be perfectly satisfied to form the pairs (groups) of fascinating

Figure 3.2: The simulated characteristic domain configurations are in comparison with observed (HR)TEM images with the notations of various boundary nodes during the 3D hexagonal-to-orthorhombic MT in Mg-Cd system [SD77, KKK88, KK91].

patterns assembled by martensite variants, thus leading to a few isolated martensite variants. It is more clearly evidenced by the fact that the morphology of the triangle-to-centered-rectangular martensite in the vicinity of grain boundaries exhibits complicate patterns, unlike the sole "kink" in the square-to-rectangular case.

3.5 Discussion

3.5.1 Understand the Microstructural Features in the Perspective of CM-PTMC

The symmetry permissible orientations of domain walls in square-to-rectangular and triangle-to-centered-rectangular single crystal (or 3D cubic-to-tetragonal and hexagonal-to-orthorhombic) martensites have been theoretically investigated by Aizu [Aiz69], Sapriel [Sap75], Boulesteix et al. [BYS⁺86], Manolikas et al. [MA80a, MA80b], and Bendersky [BB93], following equivalent methodologies as the prototypical PTMC contributed by Bowles et al. [BM54a, MB54, BM54b] and Wechsler et al. [Wec59, WRL60], and later interpreted by Wayman [Way64]. Hatch et al. [HLSS03] thoroughly elucidated the domain wall orientations for all of the 2D ferroelastic martensites and calculated the directions of ideal habit planes based on the long-range compatibility kernel in Fourier space and homogenous quadratic equation in spatial space. In square-to-rectangular martensitic single crystal, the orientations of domain walls are the reflection planes with the directions of multiples of $\pi/4$,

which are symmetry elements of parent phase but no longer persist in martensite variants. This can be verified by the fact that reflection planes with the plane normal $\mathbf{n} = [1, 1]$ or $[1, -1]$ satisfy Eq.(2.72) and as twin boundaries under the predefined transformation strains $\alpha \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ and $\alpha \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$ corresponding to the strains of red and blue martensite variants in the $\theta = 0$ grain (the dark blue grain in Figure 3.1a) at the final state of our simulation. The simulated twin boundaries with the directions of $\pm\pi/4$ in Figure 3.1b are consistent with the analysis based on the group theory and CM-PTMC. It thus concludes that the elastic strain is expelled from martensite domains in the numerical implementation of the IRS-LR model, leaving transformation strains as the indicators for individual martensite variants at the final state. Nevertheless, the kinematic compatibility in Eqs.(2.72) and (2.76) in the polycrystals should be rewritten into Eq.(3.12) following the orthogonal transformation of the transformation strain $\mathbf{E} = \mathbf{R}\boldsymbol{\varepsilon}\mathbf{R}^T$. It gives rises to the kinks/rotations of both twin plane normal $\mathbf{n}$ and shear vector $\mathbf{a}$ by a specific angle with respect to their grain orientations when the twin reaches a grain boundary. It explains why the martensite turn to align along the $(7\pi/24, 19\pi/24)$, $(\pi/3, 5\pi/6)$, $(3\pi/8, 7\pi/8)$ and $(5\pi/12, 11\pi/12)$, respectively, in the grains $\theta = \pi/24, \pi/12, \pi/8$ and $\pi/6$ as shown in Figure 3.1b. Another peculiarity of polycrystalline patterns in our square-to-rectangular simulation is that certain variant seeks to retain its variant type when passing a grain boundary. This is because the displacements, as the basic independent variables, impose the geometry compatibility as a prior condition. Following the argument of Bhattacharya [Bha03], the variant with same sub-matrix of the strain tensor, i.e. the same variant in our 2D case, is automatically selected when the front of the elastic wave propagates across the grain boundary. If there is a spatial inhomogeneous distribution of the residual localized stress accumulated at grain boundaries, the grain boundaries may arrest the growth of individual martensite variant, yet induce the other martensite variant at the other side of the grain boundary.

$$\begin{aligned}
 \mathbf{E}^I - \mathbf{E}^J &= \mathbf{R} (\boldsymbol{\varepsilon}^I - \boldsymbol{\varepsilon}^J) \mathbf{R}^T = \frac{1}{2} (\mathbf{R}\mathbf{a} \otimes \mathbf{R}\mathbf{n} + \mathbf{R}\mathbf{n} \otimes \mathbf{R}\mathbf{a}); \\
 \nabla \mathbf{U} &= \mathbf{R}\mathbf{b} \otimes \mathbf{R}\mathbf{m}
 \end{aligned} \tag{3.12}$$

Similarly, Eq.(3.12) in PTMC can also be visualized in our numerical benchmark of the IRS-LR for polycrystalline triangle-to-centered-rectangular MT. In the single crystal triangle-to-centered-rectangular MT, the orthogonal transformation with a rotation of $2\pi/3$ for $\mathbf{e}^I = \zeta \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ in the coordinates of orthogonal axis of CR phase generates two other martensite variants with the transformation strains $\mathbf{e}^{II} = \zeta \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$ and $\mathbf{e}^{III} = \zeta \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$. Defining the variants II and III with Eq.(2.72), two orthogonal planes

($\mathbf{n} = [0, 1]$) and ($\mathbf{n} = [1, 0]$) play as twin boundaries between variants II and III. The austenite can transform into itself by reflection at these two planes, but the martensite fails. These two elements of symmetry are lost during triangle-to-centered-rectangular MT. Similarly, the I-II pair of martensite variants embrace the twin planes $y = \sqrt{3}x/3$ ($\mathbf{n} = [-1/2, \sqrt{3}/2]$) and $y = -\sqrt{3}x$ ($\mathbf{n} = [\sqrt{3}/2, 1/2]$), while the I-III pair have $y = \sqrt{3}x$ ($\mathbf{n} = [-\sqrt{3}/2, 1/2]$) and $y = -\sqrt{3}x/3$ ($\mathbf{n} = [1/2, \sqrt{3}/2]$). In our simulation, the principal axes of transformation strains of the CR martensites coincide with the global coordinates of simulation box, and the final strain matrices within the red and blue martensites in the grain with orientation $\theta = 0$ are approximately given by $\beta \begin{bmatrix} -1.024 & 1.770 \\ 1.770 & 1.032 \end{bmatrix}$ and $\beta \begin{bmatrix} -0.948 & -1.744 \\ -1.744 & 1.005 \end{bmatrix}$, respectively. The twin boundaries, parallel and perpendicular to the global X axis (Figure 3.1c) represent adequately the group-theory based analysis above, and are consistent with two twin planes $\mathbf{n} = [0, 1]$ and $[0, 1]$ calculated by mean of the PARAFAC algorithm [Bro97] solving Eq.(2.72) with the Tensor Toolbox in MATLAB. Moreover, the rotation of the twin plane with respect to the grain orientation, depicted in subsection 3.4.2 as the consequence of the generalized kinematic compatibility Eq.(3.12), is evidenced by the kink of red-blue (III-II) twin boundary stretching over the red ($\pi/6$) and green ($\pi/12$) grains (indicated by the black arrow in Figure 3.1c). It is also observed from Figure 3.1c that the twin plane rotates anticlockwise by an angle of $\pi/12$, identical to the grain misorientation between the red and green grains as predicted by Eq.(3.12).

The determination of the habit planes is another key issue to discover the connection of CM-PTMC and IRS-LR. In IRS, the direction of the habit plane can be derived explicitly from the long-range elastic compatibility kernel as detailed in most of the classical literature of Landau theory [SLS10, LSR⁺03]. The anisotropic kernel undoubtedly grasps the physical nature of the MT and is strictly applicable for different dynamics and boundary conditions [LSR⁺03]. However, if only the static morphology of proper MT is concerned without including the coupling between strain and other functionality, the derivation of the habit planes via the numerically solved displacement fields and Eq.(2.76) is simpler and practical because the displacements and their gradients can be explicitly obtained in the IRS-LR method. It is noteworthy that each single variant of martensite is allowed to be in equilibrium with austenite in 2D benchmark due to a fact that one of the eigenstrains in the principal space has to be $\lambda_3 > 0$ and the other one $\lambda_1 < 0$, so the third one λ_2 in the degenerated dimension automatically vanishes to satisfy the invariant plane condition. Thus, the habit plane in 2D simulation is naturally an invariant plane. When the coupling between non-OP dilatation strain ε_1 and OP strains (deviatoric strain ε_2 and/or shear strain ε_3), viz. the volume change accompanying with MT, is neglected in this 2D benchmark, the simulated habit (invariant) planes must reconcile with what lattice correspondence predicts.

Figure 3.3: (a) The calculated invariant plane normals in square-to-rectangular polycrystalline martensite are represented by white arrows. The two perpendicular invariant plane normals in grains with $\theta > 0$ anticlockwise rotated the corresponding angles approximating the grain misorientation angles with respect to the alignment of $\pm\pi/4$ in the grain with $\theta = 0$. (b)-(c) The magnifying morphology of characteristic domains exhibit the minor discrepancies of the directional angles of the particular boundaries in various nodes, implying the information of disclination. (b) and (d) illustrate the calculated invariant plane normals in various domains of individual grains.

Therefore, the most possible invariant plane normals and lattice correspondence shears could be estimated by decomposing numerically the displacement gradient tensor $U_{i,j}$ into the dyadic product of two vectors by the PARAFAC algorithm, although they are not unique solutions. The arrows illustrated in Figure 3.3 are the calculated invariant plane normals in the vicinity of the characteristic patterns. In Figure 3.3a, the invariant plane normals of the square-to-rectangular case aligns with the same directions as the twin plane normal. Although the vectors point in different directions in individual grains, they all imply the $[1, 1]$ or $[1, -1]$ crystallographic indexes of austenite, consistent with the invariant plane normal predicted by PTMC with the Bain correspondence. Figure 3.3b displays the calculated invariant normals of triangle-to-centered-rectangular martensites at the $(1, 1, 1, 1, 1, 7)$ and $(2, 5, 5)$ nodes next to the spiral branched pattern in the grain with the orientation $\theta = 0$. The invariant normals of the green martensite point to $\pm\pi/4$ in the global coordinates, which are associated with $[1, 1]$ and $[1, -1]$ directions of tetragonal axes. These findings are in good agreement with those predicted by Sapriel [Sap75] and Boulesteix [BYS⁺86] for single crystal hexagonal-to-orthorhombic martensite with the PTMC [Way64]. Moreover, the red and blue domains at the very $(2, 5, 5)$ node exhibit the directions of invariant plane normals of $7\pi/12$ and $5\pi/12$. It is apparent that the invariant plane normal of the blue domain is directly related to that of green domain ($-\pi/4$) via a symmetry operation of 3-folded rotation, whereas red domain adopts the perpendicular solution for the invariant plane normal in Eq.(2.76). As a consequence, not all of the invariant planes at a node are 3-folded rotational related. Figure 3.3d illustrates the calculated invariant plane normals in the nested star. The red, blue and green martensite variants of clover leaves with the same area are related by 3-folded rotation, but they have no common twin boundaries each other. Among them, the outer green martensite shows the invariant plane normal at the direction of $-\pi/6$ referencing to the global X axis. Because the nested star is located in the grain with the orientation angle of $\pi/12$, the direction angle is a sum of direction angles of invariant plane normal in single crystal and the grain orientation ($-\pi/4 + \pi/12 = -\pi/6$), meaning that invariant plane normal would rotate by the angles of the grain orientation as what Eq.(3.12b) requires. From the comparison between the results of IRS-LR simulation and CM-PTMC analysis detailed above, it concludes that most of the simulated microstructural features by IRS-LR are in good agreement with what kinematic compatibility equation predicts in CM-PTMC. It is due to the common ingredients, including lattice correspondence, kinematic compatibility, crystal symmetry etc., that the results of IRS-LR model in equilibrium state is proven to rest consistency with CM-PTMC.

3.5.2 Under-Damped Dynamics

As pointed out by Lookman [LSR⁺03], the incorporation of internal term $\rho\ddot{U}_i$ depicts a sequential evolution of martensite nucleation and growth, where the long-wavelength strains will decay later than the small ones, like tweeds, will be oriented preceding the larger scale texture. In contrast, the over-damped TDGL limit corresponds to an infinite propagation speed for excitation of all the elastic oscillators, indicating that the system simply evolves along the gradient of energy surface until it ends up in a local minimum. Thus, the evolution rate of LR dynamics with inertia effect is much slower than those with conventional TDGL dynamics and static formulation. In this work, we track the symmetry-adapted strains $(\varepsilon_2, \varepsilon_3)$ in both square-to-rectangular and triangle-to-centered-rectangular MTs to unveil the phase transformation pathways during the formation of individual martensite variants, which could also demonstrate the under-damped features of MT by LR dynamics. Monitoring the variation of strains $(\varepsilon_2, \varepsilon_3)$ in square-to-rectangular MT, Figure 3.4a clearly exhibits that the deviatoric strain ε_2 approaches one of the energetic wells along with the increase of non-OP shear strain ε_3 , as a whole leaving a twisty pathway. Subsequently, the elimination of the non-OP strain ε_3 associated with the long-range elastic interaction takes place, following a modulated pathway. The fact that the asynchronized convergence of OP and non-OP strains, accompanied with the modulated the transformation pathways, are governed by the competing effects of the non-OP inertia and friction, in good agreement with the moment analysis in Ref. [LSR⁺03]. Such phenomenon is missing from conventional TDGL dynamics that simply exhibits the steepest phase transformation pathway. However, the absence of the asynchronized convergence in our simulated triangle-to-centered-rectangular MT is due to that ε_2 and ε_3 are both served as the local OP strains, see Figure 3.4b, rather than a cause of the dynamics

3.5.3 Kinematic Compatibility and Mechanical Equilibrium Manipulate/Mediate the Variant Selection

Because of the technological relevance, great efforts have been made to predict the microstructural and mechanical response under external load. Falk [Fal89] put forward to an averaging procedure over an assembly of statistically oriented single crystals to obtain the tensile stress-strain curve of a polycrystalline SMA that enabled the prediction of the pseudo-elasticity effect. Expanding the thermomechanical phase field model proposed by Levitas et al. [Lev13] for presenting the stress-strain hysteresis in SMA [LXC14], Cho et al. [CILP12], by a finite element scheme, were able to simulate the stress induced square-to-rectangular and cubic-to-tetragonal MTs in polycrystals. Meanwhile, Ahluwalia et al., applying IRS-

Figure 3.4: (a) The transformation pathway by tracking the variation of (e_2, e_3) for individual square-to-rectangular martensite variant with the normalized dissipation coefficient $\gamma = 0.01$. The sequential convergence of short range OP strain e_2 followed by the non-OP strain e_3 as well as the modulated convergence path of e_3 in the energy valley indicated the underdamped dynamics described by the Lagrange equation. (b) The curved transformation pathway in triangle-to-centered-rectangular MT depicts the synchronous convergence of the OP strains e_2 and e_3 .

TDGL [ALS03, ALSA04] and IRS-LR [AQW15] models respectively, simulated the polycrystalline square-to-rectangular MT under uniaxial tensile loading and predicted the stress-strain response as a function of strain rate.

In this chapter, we utilize the modified IRS-LR approach to explore the morphological change of the martensite variants in polycrystals under uniaxial external loading. Choosing the global X axis as the uniaxial loading direction, its contribution to the energy density is expressed as $f_{load} = -\sigma_{app}\varepsilon_{xx}(\mathbf{r})$. When applying uniaxial tensile stress in the global [1 0] direction to the polycrystalline square-to-rectangular martensites, the morphological evolution involves movement of twin boundaries, coalescence of both red and blue variants and change of variant fraction, as shown in Figures 3.5a and 3.5b. Contrary to the rapid growth of the energy-favored red variant at the expense of the unfavorable blue variants in all the grains by the strain-based TDGL modeling [ALS03], the tensile stress fails to alter profoundly the twin structure of martensite plates. However, the twin boundaries are slightly curved towards the blue variants. Both red and blue martensite variants are preserved even at a long-time relaxation with a moderate applied stress, consistent with neutron diffraction study of Fe-Pd alloys. The volume fraction of the favored variant is estimated to be 0.55, lower than the value of 0.67 measured by neutron diffraction [OMDW03]. Under uniaxial compression (Figure 3.5c), the system gives an opposite response, and more blue variants are grown at the expense of the red, but sustain the alignment of twin boundaries. The long-time preservation of the twinned pattern originates from the under-damped dynamics. The elimination of external stress drives the rearrangement and movement of twinning boundaries, and the residual energy is accumulated at twin and grain boundaries at the end and the twinning boundaries are unlikely eliminated to evolve into the single-variant microstructure. This casts the most significant distinction between the under-damped Lagrange dynamics and the over-damped TDGL one. If no Rayleigh dissipation (viscous term) is introduced, the conserved Lagrange dynamics and the fully dissipative TDGL dynamics will respectively act as the lower and upper limits to provide the volume fraction of the favored variants in the SMA subjected to applied stress.

The morphology changes as response to applied stresses are rich in our triangle-to-centered-rectangular simulations, including rearrangement of the twinned domains, variants selection, and detwinning. In Figure 3.6a, the triangle-to-centered-rectangular MT in a relatively 'soft' system (with smaller A_1 in the order of magnitude of 10^{10}) gives rise to a self-accommodation microstructure of three martensite variants, as a whole produces approximate zero net macroscopic shape change. When a uniaxial tension is loaded to a self-accommodated triangle-to-centered-rectangular polycrystals, the deformation in martensitic state results in twinning in Figure 3.6b, followed by the formation of certain regions of single

Figure 3.5: (a) Full martensitic morphology in square-to-rectangular MT; strain morphology of square-to-rectangular polycrystals under the (b) uniaxial tension of 1GPa in the direction of global X and (c) uniaxial compression of -1GPa at time step of 6×10^5 .

Figure 3.6: (a) Full martensitic morphology in triangle-to-centered-rectangular MT; morphological evolution of polycrystalline triangle-to-centered-rectangular MT under (b)-(c) uniaxial tension stress of 1 GPa in the direction of global X axis in a soft system with normalized $A_1=9.18$; and (d-e) uniaxial compression of -1 GPa.

martensite variant (i.e. detwinning, Figure 3.6c). In IRS-LR dynamics, the rebalance of the transformation stress in system driven by the viscous term firstly develops the microstructure into a well-formed lamellar twinning in all grains. The behaviors of variant selection diversify in individual grains as the transformation strains in global coordinates differ, for specific, in the grains with $\theta = \pi/6$, the system accommodates itself by ruling out the blue variant to form the green/red lamellar twin structure with the alignment of twin boundaries of $\pi/3$ and $5\pi/6$, while the kinematic compatibility retains. The formation of lamellar twins is energetically favored by the Level rule of thermodynamics. The direction of lamellar twin plane in the $\theta = 0$ grain is measured to be same as those in the $\theta = \pi/6$ grain, but the dominated twin is composed of different green and blue variants, with the red ones appear only in the vicinity of grain boundaries. In the $\theta = \pi/12$ grain, both green-blue and green-red lamellar twins are observed with the twin boundaries along $5\pi/12$ and $3\pi/4$. All such alignments of lamellar twin boundaries apparently remain to satisfy the kinematic compatibility Eq.(3.12). The twin boundaries of the red-green variants in $\theta = \pi/6$ grain rotate by $\pi/6$ with respect to the grain orientation while those of blue-green variants in the $\theta = 0$ grain exhibit the same alignments as what have in single crystal. The late morphology in Figure 3.6c demonstrates that the well-formed lamellar twins progressively give their way to the green variant at the expense of the unfavorable red or blue twins. In one word, a long time tensile test enables approaching a single-variant state rapidly in grains $\theta = 0$ and $\pi/6$ while the other grains sustain the lamellar twin structure. Thus, the green single variant martensite dominates the microstructure with debris of isolated red or blue variants and a few lamellar twins, indicating the occurrences of detwinning. Similar to the square-to-rectangular MT, a complete single-variant microstructure is hardly obtained even after long time simulation due to the inertia effect of LR dynamics. By monitoring the invariant plane normals for both regions of lamellar twins and single variant martensite in Figure 3.7, the kinematic compatibility of the austenite and martensite remains preserved in the region of lamellar twins with the directions of $\pi/3$ in the $\theta = \pi/12$ grain. However, it no longer rigidly obeys in some regions of the detwinned single martensite.

When applying a compression up to 1 GPa to the triangle-to-centered-rectangular martensites, the lamellar twins of red and blue variants fairly well present in grains with $\theta = \pi/6$, whereas the green-red twins are discovered with $\theta = \pi/24$ and $\theta = 0$, (see Figures 3.6d and 3.6e). As it evolves, the green variant tends to be suppressed, thus developing the red and blue martensitic domains that intersect grain boundaries and exhibit coarse 'macro' blocks or lamella. It should be stressed that it is extremely hard to establish the grid-to-grid mapping for the variants before and after loading since the morphology changes due to applied stress involves complicated physical metallurgical scenarios such as the extinction and nucleation,

coarsening or shrinking of martensites, interface movements etc. As a consequence, we only present the martensite morphology upon the loading observed in laboratory reference as an analog of orientation screening in EBSD.

Figure 3.7: The calculated invariant plane normal in the lamellar twinned and detwinned regions in $\theta = \pi/12$ grain with uniaxial tension stress of 1GPa.

To sum up, all the above findings provided by our simulation coincide with the CM-PTMC based analysis: the variant selections staged in lamellar twinning and single variant martensite are, respectively, consistent with the criteria of Buchheit et al.[BW96] and Bhattacharya et al [Bha03] in single crystal. The theoretical analyses and our LR simulations conclude that the martensite variants that lead to the largest elongation strain (in laboratory reference) along the tensile axis will be selected to grow (i.e. for variant selection), and smallest one for the compression. Thus, of two most favored variants that have larger(smaller) projections along tensile(compression) direction will preferentially constitute the lamellar twin, whereas of maximum $\hat{n} \cdot \epsilon_I \hat{n}$ in tension or minimum in compression will be the favorite selective single martensite variant.

3.6 Conclusion

A modified model is proposed to describe the martensitic phase transformation in polycrystals based on the Lagrange-Rayleigh dynamics with the Landau energetics. The stress term in the dissipative force equation is reformulated in terms of the functional of local Landau energy with respect to global displacement gradients. Through a coupling of primary OPs to grain orientation, the model enables the description of the microstructures of MT and elucidates its response to the external loads, with particular emphasis in the twin/habit planes related to the crystallographic orientations and their changes. For polycrystalline square-to-rectangular and triangle-to-centered-rectangular ferroelastic materials, the simulations reveal the key microstructural features found in real 3D cubic-to-tetragonal and hexagonal-to-orthorhombic martensites, including the self-similarity of variant across grain boundaries and the variant selection upon external loading, in agreement with what the CM-PTMC has predicted.

Chapter 4

Dynamical Nucleation of Martensite in Polycrystals

The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.

-William Lawrence Bragg

4.1 Martensitic Nucleation

A preference for heterogeneous nucleation in MT has been evidenced by a wide body of experimental explorations on steels [MXX⁺03, VBS09, SDC14], shape-memory alloys [FCY⁺04, KADE02], ceramics [CC83, HR85], etc. The heterogeneous processes of nucleation and subsequent growth at various defects present distinct microstructure [MSO⁺05, BBG98], diversiform transformation pathways [Wai05, CSC⁺98], and hence different properties of materials [Kaj86, SJNS09]. To understand the mechanisms underlying the observed phenomena, different theoretical studies for the nucleation of MTs have been developed for different defects like dislocations [KC58, Chr51, OC81, RO01] and grain boundaries [AJK02, JAK01, HC14, MABÅ13a] in perspectives of thermodynamics, kinetics and crystal lattice dynamics. These models are at least classified into two categories considering the classical and non-classical nucleation paths [OC82, Ols99]. The models describing classical nucleation paths believe that the embryos of martensites are formed via the dislocation dissociation mechanism and thereafter increase in size by motion of interface. During these processes, the nuclei have a structure and/or a composition same as those of full-formed martensite variants, such that the driving force and kinetics of martensitic nucleation can be discerned by evaluating the time evolution of individual energy contributions from misfit

elastic energy, chemical energy in bulk (composition-dependent lattice stability) and surface energy. Pioneered by Kaufman [KC58], Christian [Chr51], etc. and consolidated by Olson [OC81, OC82, Ols99], the classical model has been developed into a self-consistent and unified interpretation to heterogeneous martensitic nucleation on a basis of dislocation theories, thermodynamics and crystallography of MT, and it has been widely applied to the martensitic nucleation in steels and a few SMAs, where the dislocation are evidenced to play the primary role.

In contrast, the non-classical nucleation models describe MT paths involving a continuous change in structure and/or composition in a finite temperature region. Among the most prominent is the dynamical nucleation model [RG93], where the Landau-type free energy, incorporating physical nonlinearity describing the symmetry breaking in MT and nonlocal terms accounting for the long-range interactions of elastic oscillators, is formulated in a frame of Lagrangian-Rayleigh (LR) or Bales-Gooding (BG) [BG91, LSR⁺03] dynamics to present a physics scenario of 'elastic solitary wave' for martensitic nucleation. Different from the classical models characterized in the quantitative thermodynamic analysis of martensitic nucleation via the explicit decomposition of the total free energy, the dynamical nucleation method is competent to investigate the complete process of martensitic interface motion and interpret the phenomena at early stage of MT such as the formation of tweed or precursors, dynamical twinning, autocatalysis, etc. Thus, it is intrinsically helpful and has persistently been used in studying the homogeneous coherent nucleation of improper and weak proper MTs in SMAs, which arise from lattice softening and/or weak distortion near the critical point. However, further uses of the models towards studying heterogeneous nucleation in weak proper MT also have been performed. The fundamental physical picture of heterogeneous dynamical nucleation model is depicted as follows: The interaction of the defects with the material allows a spatiotemporally varying potential of phase transformation and gives rise to local stress and coupled strain fields in the correct tensor expression and magnitude to exert influence on MT [Kru98]. Clapp et al. [Cla73] incorporated for the first time the Ginzburg-Landau phenomenological theory to determine the 'spinodal' strains during martensitic nucleation by introducing the interaction of a single 'misfit' planar defect with the host. They denominated this fashion of the nucleation as 'localized soft mode'. Later, the initial concept of heterogeneous dynamical nucleation was further consolidated with the efforts of Cao [CKG90, CK90], Reid [RG93, RG94, RO99, RG92], Chu [CMOR00], van Zyl [VZG96a, VZG96b] and Gröger [GLS08] et al. Based on the dynamical twinning [BG91], Reid et al. [RG94] extensively analyzed the dynamical nucleation with a predefined localized strain field (as an analog of heterogeneous nucleus) along with generalized boundary conditions. Their results demonstrated that the variation of morphol-

ogy in MT, e.g. the presence of twinned or single-domain martensitic state, depends on the quenching temperature and dissipation, while it is independent of the boundary condition. Afterwards, van Zyl [VZG96a, VZG96b] et al. inferred that the surface nucleation, a mode by which the intrinsic inhomogeneous strain field coupled with the boundaries leads to a lower saddle point on the transformation energy surface, would always be preferred over homogeneous bulk nucleation. As another representative work in the topic, Cao's numerical analysis [CKG90, CK90], by exemplifying in square-to-rectangular MT in single crystal ferroelastic materials, introduced a planar defect with a predefined stress field (instead of aforementioned predefined strain field) and ascertained the critical stress and the effective temperature for the onset of MT. A similar formalism of heterogeneous nucleation was also presented by Gooding et al. [GB91], yet the latter focused on the concentration of the local strain at the defect arising from undercooling. It was further applied by Reid et al. [RG92] to the Eshelby's inclusion problem in that the functional form of localized stress field as a presence of inclusion become available.

Owing to the efforts of aforementioned theoretical works [GLS08, Kru98, RG92, GB91, CK90], dynamical nucleation model is eligible to study heterogeneous nucleation of MT induced by various defects. However, most of such works by now focus on the MT induced by the single planar defect with a predefined stress or strain. There are few works that impose the complete dynamic model to the defects with more complicated geometry like grain boundary, in comparison with the great achievements of modern phase-field methods on this topic [AJK02, WK06, LIP04, HC14, MABÅ13b]. The phase-field models have advantages to represent the perfect martensitic microstructure by taking a mutually advantageous conjunction of interface motion and clarified energy contributions in classical model and continuously varying OPs in non-classical model that as a whole describes a hybrid transformation path. However, the over-damped dynamics in phase field method has the intrinsic insufficiency on describing dynamic behaviors, which has been detailed in chapter 2. Therefore, the development of complete dynamical nucleation model in polycrystals remains open. Our modified model of MT developed in chapter 3 is not only consistent with kinematic compatibility in PTMC, but also has ability to explicitly explore the spatiotemporal distribution of local stress during the MT. It encourages us to generalize the conceptual dynamical nucleation theory within our updated model to simulate the heterogeneous martensitic nucleation in polycrystals in this chapter. The present simulations aim at extending the application of dynamical nucleation model and gaining an in-depth understanding of the collective (competitive and/or cooperative) effects of the martensitic nucleation and subsequent growth assisted by grain boundaries and external loadings following the non-classical transformation paths. In turn, it allows evaluating the ability of different defects/positions as martensitic

nucleation sites originating from the interaction of intrinsic polycrystalline defects with the applied loading in a weak proper MT.

4.2 Dynamical Nucleation Model in Polycrystals

The dynamical nucleation of MT induced by grain boundary in a polycrystal can be achieved once the predefined planar defects in Refs. [CKG90, CK90, GB91] are specified as the grain boundaries and triple junctions. Rather than considering an inhomogeneous stress field explicitly induced by the defects [CKG90, CK90], we make an effort to study what effects may produce during MT when the uniaxial tensile loading interacts with grain boundary. The grain boundaries can perceive the applied stress and feel back to couple with Landau transformation potential, thereafter, lead to a localized stress field and modify the transformation temperature. Similar to Cao's work on single crystal [CKG90], we assume that 1) the inhomogeneous distribution of stress is produced by defects, specifically in this work, the localized stress fields around the grain boundaries and triple junctions, rather than the defects themselves; 2) the interface between austenite and martensite is coherent which is imposed by the compatibility condition; 3) the displacement at grain boundary is continuous as required by the displacement-based Lagrange-Rayleigh dynamics [LSR⁺03]. It infers that free surfaces and incoherent grain boundaries are not taken into consideration. It is also noted that we are not intending to obtain various morphology by mediating the damping parameters as what conventional dynamical nucleation modeling did, rather, we focus on how intrinsic MT potential involving with grain boundaries and applied stresses leads to different nucleation modes or sites.

In this chapter, the Fe-Pd alloy is still adopted to exemplify our dynamical nucleation model. The Landau free energy and dynamic equations in this chapter are same as those in chapter 3. The only difference is that the simple uniaxial stress is exerted at the initial stage of simulation and does effects on martensitic nucleation. The free energy contribution due to the applied stress σ_{app} can be yielded as

$$f_{app} = -\sigma_{app}e_{xx} \quad (4.1)$$

Thus, the free energy is finally expressed in global coordinates as

$$F = \int d\mathbf{r} \left[\frac{A_1}{2}e_1^2(\mathbf{r}, \theta) + \frac{A_{20}}{2} \left(\frac{T - T_c}{M_s - T_c} \right) e_2^2(\mathbf{r}, \theta) + \frac{A_4}{4}e_2^4(\mathbf{r}, \theta) + \frac{A_6}{6}e_2^6(\mathbf{r}, \theta) + \frac{A_3}{2}e_3^2(\mathbf{r}, \theta) \right. \\ \left. + g(\nabla e_2(\mathbf{r}, \theta))^2 + f_{grains}(\theta) - \sigma_{app}e_{xx}(\mathbf{r}, \theta) \right] \quad (4.2)$$

The materials parameters were exactly same as those in chapter 3. During the simulations, the different external stresses were applied to the simulation box. The simulation results are discussed in the following paragraphs.

4.3 Microstructure Evolution

The martensitic nucleation and the relevant microstructure evolution are studied by the simulations under the conditions of (1) different applied stresses at a fixed temperature, (2) different temperatures with a constant applied stress, and (3) the combination of varying stresses and temperatures. These external processing conditions interacting with intrinsic MT energy lead to different scenarios of martensitic nucleation.

4.3.1 Heterogeneous Nucleation under the Applied Stress of 50 MPa

To examine the martensitic nucleation in the vicinity of grain boundaries, the system was first quenched to $T = 275\text{K}$ ($T_c < T < M_s$), followed by an isothermal simulation under a constant applied stress of $\sigma_{app} = 50\text{MPa}$. The setting temperature, slightly higher than T_c , ensures the existence of an energy barrier to describe the nature of first-order MT yet allows a small thermal activation to jump over. The sequential process of the nucleation and growth of the martensite is shown in Figure 4.1, where the martensite is depicted by distribution of the deviatoric strain e_2 at different times during the isothermal simulation. The thermal fluctuations give rise to local inhomogeneity of the deviatoric strain at the initial stage of the isothermal simulation that trigger the onset of a fine-scale assembly of cross-hatched tweeds (Figure 4.1-b). Differing from single crystals [KKS95], the tweeds exhibit different stretch directions in individual grains. Note that tweeds similar to those in Figure 4.1b can also develop above M_s in the absence of the applied stress. There is local distortion of deviatoric strain caused by the localized stress field accumulating at the grain boundaries with larger misorientation, as those between blue and red grains in Figure 4.1b. It indicates that the free energy minima have been momentarily shifted toward the grain boundaries due to the synergistic contribution of the grain boundary energy and the strain gradients. For $\sigma_{app} = 50\text{MPa}$, no concentration of deviatoric strain is found in the vicinity of triple junctions because the superposition of strain gradients stemming from individual grain boundaries leads to a relatively more homogeneous strain field at the triple junction. The fine tweeds inside the grains and deviatoric strain distortion at grain boundaries are fading away with time, and the system subjected to $\sigma_{app} = 50\text{MPa}$ responds to the localized

stress field with a metastable microstructure exhibiting a long-range straining pattern (Figure 4.1c), denominated 'postcursor' [BK88]. The postcursors, modulated partially transformed martensites, show the same texturing pattern as what the subsequent twins would have. They arise from a balance between the nonlinearity of transformation energy represented by the anharmonic terms and nonlocality stemming from the contribution of strain gradients in Eq.(4.2). This modulated metastable equilibrium will be broken when the reduction of local energy cannot be compensated by the increase of energy originating from the steeper strain gradient with respect to the spatial coordinates, and the total strain energy is progressively reduced to the stable energetic wells of martensite [BK88]. Therefore, the postcursor can play the role of potential embryo of martensite inside the grains, as shown by the martensite plate marked (1) in Figure 4.1e, which grows from intragranular postcursor. Simultaneously, the strain distortion at the grain boundary can assist nucleation. If the grain boundary is parallel to one of the postcursors, the first stable martensite plate would form preferentially along the grain boundary, as shown in Figure 4.1d. As soon as the first stable martensite plate forms (see the blue variant and the local deviatoric stress $\sigma_2(\mathbf{r}) = (\sigma_{xx}(\mathbf{r}) - \sigma_{yy}(\mathbf{r}))/\sqrt{2}$ in inset of Figure 4.1d), it grows rapidly in length following the tracks of postcursors due to the large local stress and the curvature at the tip. When the growing front of the martensite plate crosses the triple junction, the martensite plate penetrates into the grain and is aligned with the favored orientation. However, the coarsening of the blue variant in the direction perpendicular to the habit plane is momentarily arrested by the modified local energy around the plate, and gives rise to a cascade of pairing red variants, i.e. autocatalysis phenomenon. It should be noted that branched martensite plates are hardly found due to the limitations of the 2D model that allows only two different twin-related variants. The branched martensite plates are only found when the grain boundary is located in between the orientations of the postcursors in the neighbor grains (see inset in Figure 4.3b). This is different to the richer accommodated patterns consisting of all 24 K-S orientation variants widely observed in the experiments for other Fe-based alloys [UYU02]. Figure 4.1f illustrates the morphology of full martensite after long-time simulation. The alternative alignments of twinning related red and blue martensites are in agreement with the kink solution of the solitary wave in Ref. [GB91]. The width and energy density of the twin boundary shown in Figure 4.1f correspond to about 2-3 nm and $0.45 J/m^2$, respectively. Although the simulated twin boundary energy density accords well with that of stationary analysis, the width of the twin boundary in simulation shows 3 times broader than that of several atomic diameters observed from TEM image. It is the inherent consequence of the diffuse interfaces utilized in Landau modeling. In this work, the gradient coefficient was selected by considering a compromise between the twin boundary width and the size of the grains.

Figure 4.1: (a) Spatial distribution of the grain orientation angle as indicated in each grain (b)-(f) Martensitic nucleation and growth in polycrystals, as shown by the deviatoric strain e_2 at 275K under an applied stress $\sigma_{app} = 50MPa$, at time steps of 800, 12000, 92000, 94800 and 104000, respectively. The red and blue domains represent two martensite variants while the green domain is austenite. The grain boundaries are displayed in white.

Figure 4.2: Martensitic nucleation and growth in polycrystals, as shown by the deviatoric strain e_2 at 275K under an applied stress $\sigma_{app} = 500MPa$ at time steps of 800 (a), 5200 (b), 6400 (c), 8000 (d), and 28000 (e), respectively. The red and blue domains represent two martensite variants while the green domain is austenite. The grain boundaries are displayed in white.

4.3.2 Heterogeneous Nucleation under the Applied Stress of 500 MPa

The martensitic nucleation under $\sigma_{app} = 500 \text{ MPa}$ shows similar features (Figure 4.2b) at the early stages of the simulation: the tweed pattern develops within the grains and strain distortions appear at grain boundaries, but both occur more rapidly because of the higher stresses. The accumulation of the deviatoric strain raised by the local stress is supposed to smear out or weaken the effect of postcursors. At the same time, the interplaying of elastic transformation energy and lattice curvature drives the 'twinned' strain distortion to split into 'diploes' (indicated by the arrows in Figure 4.2-b) and be located at the triple junctions and high angle grain boundaries, both of which serve as the preferential sites for martensitic nucleation and growth, as shown in Figure 4.2c. Three martensite plates (marked (1), (2) and (3) in Figure 4.2d) are nucleated at the triple junctions, and grow into the twins aligned with their optimum twinning orientations in individual grains. For instance, the pairs of needle-like martensites in the grains with the orientation $\theta = 22.5^\circ$ (i.e. the grains in yellow in Figure 4.2a) align along the 67.5° with respect to the horizontal axis of global reference. A different scenario is found in the twinned martensite plates marked (4) in Figure 4.2d. They nucleate and grow assisted by the high angle grain boundaries, and the leading plate in red propagates beyond the neighbor triple junction without changing orientation apparently. However, it accommodates itself later to match the surrounding grain misorientation by subtly rotating the residing twin boundary to form the full martensitic morphology (Figure 4.2f).

4.3.3 The Effect of Applied Stress on Heterogeneous Nucleation at Grain Boundaries

In Figure 4.3, the deviatoric strain as a function of the distance to a high angle grain boundary is plotted for different applied stresses and times at $T = 275 \text{ K}$. Although the high angle grain boundaries can be considered analogous to 2D planar defects in Refs. [CK90, GB91], we must clarify that our modeling has its root in the dynamical nucleation developed by Clapp [Cla93], Cao [CKG90, CK90] and Gooding et al. [GB91]. The hyperbolic-type profiles of the deviatoric strain are consistent with the analytical results of Cao [CK90] who introduced a predefined stress field as a martensite embryo for twin. The deviatoric strains raised by the small local stresses rapidly accumulate within the first hundreds of steps (see inset of Figure 4.3 with $\sigma_{app} = 20 - 100 \text{ MPa}$). However, they are one to two orders of magnitude smaller than the threshold of 'spinodal strain' to serve as steady martensite embryos or form stable martensite variants. The strain profile with $\sigma_{app} = 500 \text{ MPa}$ and at normalized time $t^* = 6400$ (in the direction perpendicular to the twin plane 4# in Figure

4.2d) exhibits the oscillation between the positive/negative deviatoric strains of two rectangular martensite variants, demonstrating that the local stress has driven the martensitic nuclei into stable plates. Beyond the analytic solution, our results prove that the spatiotemporal evolution is greatly dependent on the strain gradient. In contrast to the predefined stress solution [CK90], the asymmetry of the profile with $\sigma_{app} = 500MPa$ and at $t^* = 2800$ indicates that the strain distortion undergoes the curvature driving modulation (through either strain gradients or displacement gradients) and is concentrated at the triple junction. As a result, more martensites nucleate at the triple junctions under $\sigma_{app} = 500MPa$ (see martensites 1# – 3# in Figure 4.2d) than at high angle grain boundaries. All the above findings reveal that intragranular nucleation around grain boundaries prevails those under small applied stress, whereas nucleation at triple junctions and high angle grain boundaries is dominant under moderate applied stress. These results support the argument of Clapp [Cla73], who stated that high angle grain boundaries are the favored nucleation sites if the free surface and incoherent grain boundaries are absent. It should be further emphasized that the triple junctions are more suitable nucleation sites than high angle grain boundaries in the case of the relative large local stresses.

4.3.4 The Effect of Quenching Temperatures on Heterogeneous Nucleation at Grain Boundaries

The effect of quenching temperature on the Landau energy landscape and the transformation pathways is addressed in Figure 4.4, which illustrates the morphology of the principal martensitic plates at different temperatures under $\sigma_{app} = 100MPa$. When quenching the system to a low temperature $T = 250K < T_c$, the martensite plates prefer to form and grow at the triple junctions prior to the boost of homogeneous decomposition inside grains. Quenching to $T_c < T = 275K < M_s$, in contrast, leads to a diversity of the martensitic nucleation sites depending on the localized geometric, energetic and kinetic conditions, when the stress fields localized at the postcursors, grain boundary and triple junctions are comparable in complexity and magnitude. The groups of stripe-like martensites nucleate to grow intragranularly following the tracks of postcursors. On the contrary, the red variant nucleates at the high angle grain boundary, proceeds along the pretrained postcursors after crossing the grain boundary, but leaves with a kink; while the blue martensite plate nucleated at the triple junction accommodates itself to match the optimal orientations in the neighboring grains. The later morphology at the very high-angle grain boundary (see the top-right inset in Figure 4.4b) is consistent with the coarse lenticular martensites observed in Fe-based materials [UYU02]. On quenching to $T = M_s = 295K$, the morphology

Figure 4.3: Evolution of the deviatoric strain e_2 as a function of the distance to a high angle grain boundaries at the time step of 800 under different applied stresses $\sigma_{app} = 20, 50, 100$ and 500 MPa , respectively, and at later times of 2800 and 6400 steps with $\sigma_{app} = 500 \text{ MPa}$.

exhibits a heterogeneous structure containing austenite-martensite alternated stripes in the grains (Figure 4.4c). This process takes place via the nucleation and growth relying on the preexisting postcursors with a morphology much like the stress-induced martensite at room temperature ($T > M_s$) for certain cubic-to-monoclinic II SMAs [US13]. Note that since the symmetry breaking of cubic-to-monoclinic II transformation contains the elements of cubic-to-tetragonal one, a specific 2D projection of the microstructure of cubic-to-monoclinic II in a fine wire sample could sustain the lamella features in tetragonal alloys [LXC14]. The formation of a single martensite variant in equilibrium with the austenite is energetically allowed at M_s , and even at higher temperature, if the local stress is above a threshold. Nevertheless, it is constrained by geometrical compatibility in 3D bulk materials. So far, our simulations have demonstrated that the martensitic nucleation modes (sites) are sensitive to the quenching temperature. The primary nucleation sites vary from triple junctions to high angle grain boundaries to postcursors as the quenching temperature increases. Thus, it can be inferred that a continuous cooling to a lower temperature is perfectly adequate to yield the formation of stable martensite plates at the triple junctions, as proven in Figure 4.4d.

4.3.5 Phase Diagram of Nucleation Modes

Most of the discoveries by our simulations can be summarized in the phase diagram of nucleation modes for the Fe-Pd ferroelastics presented in Figure 4.5. The phase diagram has a look similar to a conventional TTT diagram, and conveys the information about the principally favored mode of martensitic nucleation under particular combination of quenching temperature and applied stress. It is still noteworthy that the nucleation and growth of martensite are actually governed by the local stress rather than by the applied stress. However, the applied stresses can be easily used to control processing in an industrial environment. The phase diagram manifests that nucleation at the postcursors dominates at high quenching temperatures. As the quenching temperature decreases or the applied stress increases, nucleation at the postcursors is replaced by four distinct mixed modes, namely, grain boundary + postcursor, triple junction + postcursor, hybrid (i.e. all sorts of nucleation sites are possible) and triple junction + grain boundary. Only the postcursors can develop themselves to a type of nucleation sites, while the grain boundaries and triple junctions have to cooperate to become viable nucleation sites, as shown in Figure 4.5. It is worth pointing out that our results have been obtained assuming that the material was elastic and continuous. Thus, other aspects associated with grain boundary nucleation such as plasticity, incoherent interfaces and defect cores have not been considered. The incorporation of these issues into the simulation will be necessary to include more physics in the model and enhance the

Figure 4.4: Morphology of the initial stabilized martensitic plates in polycrystals undergoing isothermal transformation after quenching to 250K(a), 275K(b) and 295K(c) and continuous cooling at the rate of 0.01K/step from 300K to 100K(d), as shown by the deviatoric strain e_2 under an applied stress $\sigma_{app} = 100MPa$

predictive capabilities of this strategy.

Figure 4.5: Phase diagram of the nucleation modes of martensite in the Fe-Pd ferroelastic polycrystals.

4.4 Conclusion

In summary, we investigate the dynamical nucleation of martensite in polycrystals by means of Lagrange-Rayleigh dynamics and Landau energetics. Avoiding the details of the defect cores, the simulations capture the heterogeneous processes of dynamical martensitic nucleation under the local stress field, and are able to predict the phase diagram of martensitic nucleation sites. Exemplified in the Fe-Pd ferroelastic polycrystals, the phase diagram illustrates that postcursors, high angle grain boundaries and triple junctions serve as the preferential heterogeneous nucleation sites depending on the loading and cooling conditions.

The information, presented in the form of a phase diagram like Figure 4.5, specify how the quenching temperature and applied stress conditions can be combined to activate particular mechanisms of martensitic nucleation and growth, leading to complex microstructures in order to meet microstructural design goals.

Chapter 5

Displacive-Diffusive Model Integrated with CALPHAD Technique

Metallographic information is still a basis for interpreting and modeling various phenomena and metallography provides an important testing ground for models.

-Mats Hillert 1999

Quantitative Landau modeling coupled with computational thermo-kinetics is capable of simulating microstructure evolution over the arrays of composition, heat treatment and processing. It opens up a new way of prediction and control of microstructure and properties, by doing so, upgrades the traditional 'trial-error' method towards orientated alloys design.

5.1 CALPHAD and Computational Thermodynamics

The microstructure development in a real processing is always influenced by the cooperation and/or competition between displacive and diffusional transformations. Despite the physics robustness of Landau theory in modeling many displacive phase transformations in solids, it should be coupled with other advanced techniques in order to predict the microstructure evolution in real alloy systems subjected to real processing [Ste09, GBTF00]. To quantitatively (or semi quantitatively) control the microstructure, the precise thermodynamic and kinetic inputs are vital to a Landau simulation for displacive-diffusive coupled phase transformation [ZSD⁺15]. In contrast to Landau polynomial served as grand potential in theoretical analysis, the Gibbs energy is widely applied for engineering use, because both temperature and pressure, as independent thermodynamic variables of Gibbs energy, can be feasibly

controlled in industry. Among various integration of models at different scales for the (semi-) quantitative simulation, the phase field modeling coupled with CALPHAD (Calculation of PHase Diagram) technique has achieved great success [CMWW04, WZP⁺08, EBS06]. The CALPHAD technique is a sub-discipline of computational materials science [Xio15]. By simultaneously evaluating thermochemistry properties of each phase and information of phase diagram to obtain database with mathematical models containing self-consistent parameters, the CALPHAD technique provides reliable thermodynamic data and phase diagram information for practical processes and helps to get deeper insights into the physical metallurgical mechanisms of the materials behaviors via computer calculation/simulation.

The scientific foundation of CALPHAD technique is that a phase diagram manifests the equilibrium thermodynamic properties of the system. Various thermodynamic variables can be expressed as functional of the Gibbs energy of the system and/or individual phases. Although several earlier works of binary and ternary phase diagrams had been glittering with the wisdom of Van Laar [VL08], Wagner [WMW52], Meijering [Mei59], Kubaschewski [OC65], et al., the representation of phase diagram of multicomponent and multiphase system and the prediction of thermodynamic properties in a space of complicated processing variables by 'hand construction' was undoubtedly a nightmare before the prevailing of computer simulations. Initiated by Kaufman [KRSJ67] and Ansara [ABKS78] who introduced the concept of lattice stability in calculating phase diagrams and consolidated by Hillert's effort on the comprehensive thermodynamic theories of phase diagram, phase equilibria and phase transformation [Hil80, Hil07], significant advances of CALPHAD technique have been achieved over the past decades, including the design of high efficient algorithm and robust software to optimize and derive thermodynamic parameters, proposition of thermodynamic reasonable models, assessment of self-consistent databases for multicomponent systems, and tons of calculations upon powerful computing engine and databanks to improve understanding of various industrial and technological processes. Served as the roadmap for materials research, CALPHAD technique helped to discover the cobalt based super alloy [SOO⁺06], select the most promising composition candidates for lead-free solders [ZT02], accelerate the data mining of new generation of databanks extending from conventional thermodynamic properties to all physics properties and so forth. Nowadays CALPHAD technique has gained rebirth with the name of Computational Thermodynamics and has made a major breakthrough being considered as one of the most successful tools for materials design and acted as core fundamental infrastructure for Integrated Computational Materials Engineering (ICME) [SP12] to integrate with other computational techniques such as first principles calculations, phase field modeling, molecular dynamic simulations and so on.

In this chapter, the strategic work that couples CALPHAD technique with Landau model

is devoted. More specific, the Compound Energy Formalism (CEF) [Hil01, LFS07] based Gibbs energy and atomic diffusion mobility models for diffusive transformation are incorporated to IRS based Landau model developed in previous chapters for displacive transformation. In the sections follow, the integrated model is applied to the simulations of microstructure and composition evolution in hypothetical dislocation-free steels resulting from the Quenching and Partitioning(Q&P) process.

5.2 Thermo-Kinetic Model in CALPHAD Technique

Different from the energy expression in Landau model and most of phase field models (except for the multi-phase-field model), the Gibbs energy is individually modeled for each phase in CALPHAD technique and the total Gibbs energy of a system is expressed as the phase fraction weighted summation of Gibbs energy of individual phases, i.e.

$$G^{system} = \sum_{\theta} \phi_{\theta} G^{\theta}. \quad (5.1)$$

The ϕ_{θ} and G^{θ} are phase fraction and Gibbs energy of θ phase, respectively. The Gibbs energy of a phase, G^{θ} , is an extensive property, depending on the amounts of the constituents in the phase. In CALPHAD community, modeling a composition dependent property is more convenient to use the molar Gibbs energy, G_m , defined in Eq. (5.2), and gives the size of the system as the total amount of components, N , which is the sum of moles of all components N_i

$$G^{\theta} = N G_m^{\theta}, N = \sum_i N_i, x_{ci} = \sum_i N_i / N. \quad (5.2)$$

In general, the molar Gibbs energy of a phase is expressed as

$$G_m^{\theta} = G_m^{\theta \text{ } srf} + G_m^{\theta \text{ } id} + G_m^{\theta \text{ } ex} + G_m^{\theta \text{ } phys} \quad (5.3)$$

where the superscript *srf* stands for 'surface of reference'. This term represents the Gibbs energy of an unreacted mechanical mixture of the end-member species. The temperature dependence of the molar Gibbs energy of each end-member phase (pure substance or stoichiometric compound) relative to a selected reference state (conventionally the room temperature 298.15K and 1atm) is derived from the Kirchhoff's law of heat capacity, and described by a power series

$$G_m^{\theta \circ} = G_m^{\theta - SER \circ} + a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 \dots \quad (5.4)$$

The temperature coefficients in molar Gibbs energy for most solution and stoichiometric compounds are accessible from the SGTE handbook [Din91].

The second term on the right hand side of Eq.(5.3), $G_m^{\theta id} = -TS_m^{\theta id}$, is the Gibbs energy contributed from the entropy of ideal mixing. In (sub) regular solution model, the energy contribution from the entropy of ideal configuration mixing reads $G_m^{\theta id} = RT \sum_i x_{ci} \ln x_{ci}$ by using Stirling's approximation. $G_m^{\theta phys}$ represents the energy contribution due to a physical model. In specific, the magnetic energy contribution in CALPHAD technique is written as functions of composition-dependent variables like the Curie temperature T_c and the average Bohr magneton number $\bar{\beta}^\theta$ [HJ78]

$$G_m^\theta = RT \ln [\bar{\beta}^\theta(x_{ci}) + 1] f\left(\frac{T}{T_c(x_{ci})}\right) \quad (5.5)$$

where the Curie temperature T_c will be substituted by Neel temperature T_N if the material is anti-ferromagnetic. T_c and $\bar{\beta}^\theta$ for different phases are described as functions of composition by using the Redlic-Kister polynomial. The term with pre-superscript 'ex' stands for the excess Gibbs energy that describes the remaining part of the real Gibbs energy of the phase when aforementioned three terms have been subtracted. In CALPHAD technique, the (sub) regular solution model is not sufficient to describe the phase with ordering, which leads to the development of CEF [Hil01] for solution phase. The CEF is to describe the thermodynamic properties of a particular phase with different sublattices, which was proposed by Hillert and has been widely applied to various phases (e.g. metallic, aqueous solution, and ionic crystals) so as to handle different problems (e.g. eutectoid transformation, uphill diffusion, order-disorder transformation, etc.). In each sublattice, the lattice sites are crystallographically equivalent. The structure of a phase is represented with formula like $(A, B, C)_k(D, E, F)_l$, where A, B and C mix in the first sublattice while D, E , and F in the second one. The coefficients k and l are the stoichiometric coefficients of two different sets of lattice sites. Specifically in Fe-C binary system, $(Fe)_{0.5}(C, V_A)_{0.5}$ is used to represent FCC structured austenite and $(Fe)_{0.25}(C, V_A)_{0.75}$ is adopted for BCC/BCT structured martensite, V_A is vacancy in the interstitial sublattice II. With the definition, the conception of site fraction in each sublattice $y_i^{(s)}$ is indicated as the i^{th} component in s^{th} sublattice. Intuitively, we have

$$\sum_i y_i^{(s)} = 1 \quad (5.6)$$

e.g. $y_C^{II} + y_{V_A}^{II} = 1$ holds for FCC and BCC phases in Fe-C system. Since the molar fraction

x_{ci} in metallic system is linked to site fractions using

$$x_{ci} = \frac{\sum_s a_s y_i^{(s)}}{\sum_i \sum_s a_s y_i^{(s)}} = 1, \quad (5.7)$$

the molar Gibbs energy of θ phase with two sublattices in CEF reads

$$G_m^\theta = \sum_i \sum_j y_i^I y_j^{II} G_{i,j}^{\circ,\theta} + RT(a \sum_i y_i^I \ln y_i^I + b \sum_j y_j^{II} \ln y_j^{II}) + {}^{ex}G^\theta \quad (5.8)$$

with the excess molar Gibbs energy expressed as

$$\begin{aligned} {}^{ex}G^\theta &= \sum_m y_m^{II} \sum_{i,j>i} y_i^I y_j^I \sum_v L_{i,j}^{v,\theta,I} (y_i^I - y_j^I)^v \\ &+ \sum_i y_i^I \sum_{m,n>m} y_m^{II} y_n^{II} \sum_v L_{m,n}^{v,\theta,II} (y_m^{II} - y_n^{II})^v \\ &+ \sum_{i,j} \sum_{m,n} y_i^I y_j^I y_m^{II} y_n^{II} L^{rec} \end{aligned} \quad (5.9)$$

where y_i^I is site fraction of element i in I^{th} sublattice; $L_{m,n}^{v,\theta,II}$ represents the v^{th} order interaction parameter between elements m and n in the sublattice II of θ phase, and L^{rec} is reciprocal parameter.

With the thermodynamic models and database [Gus85], the full calculated phase diagram of Fe-C binary system is shown in Figure 5.1, which includes the stable phases of Liquid, FCC-Austenite, BCC-Ferrite, metastable cementite, metastable equilibrium between Austenite and Ferrite (dashed lines in orange and light blue), and the composition dependent T_0 temperatures where the Austenite and Ferrite (BCT martensite) have the same Gibbs energy. In the sections of this chapter, except the multicomponent model in 5.7, the chemical energy of ferrite and martensite in steel are modeled by a same sublattice model with same thermodynamic parameters. The vertical dashed lines show the nominal mass fractions of the two representative carbon steels with the experimental data in literature [TMR15, TMH⁺14], which will serve as the objective alloys in our simulations.

Figure 5.2 depicts the Gibbs energy of austenite and ferrite (martensite) at three characteristic temperatures, i.e. room temperature to which the steels are quenched, the onset temperatures of MT in two steels, where 578K corresponds to the steel with composition of Fe-0.59 wt% C and the 478K for Fe-0.59 wt% C [VB12]. Drawing a common tangent joining the Gibbs energy curves of austenite and ferrite at each temperature, the metastable

Figure 5.1: Calculated phase diagram of Fe-C binary system. The dashed lines in orange and light blue indicate the metastable equilibrium between austenite and ferrite (martensite); dotted line in red indicates T_0 temperature associated with diffusionless transformation.

equilibrium compositions of austenite and ferrite can be obtained as the dashed lines in orange and light blue indicate. If the formation of cementite is ignored, it is obvious that the phase constitution is austenite + ferrite at all three characteristic temperatures. Thus, both austenite and ferrite (martensite) will resist in real microstructure and the partitioning of carbon between austenite and ferrite (martensite) is thermodynamically allowed.

5.3 Diffusion Potential and Chemical Mobility

Utilizing the mathematical expressions of Gibbs energy, the real time diffusion potential as the driving force of diffusional phase transformation can be extracted for microstructure simulation. Instead of the conventional strategy of extracting the chemical driving force from CALPHAD technique by directly subtracting two molar Gibbs energy of phases (which is viewed as the integral driving force to describe net driving force in entire phase transfor-

Figure 5.2: Calculated chemical molar Gibbs energy of austenite and ferrite(martensite) at three characteristic temperatures. The calculated Gibbs energy and driving forces are used to calibrate the Landau energy densities for MT in section 5.4

mation), the diffusion potential (differential driving force) as the functional of the real time chemical potentials is extracted from the sublattice based CEF model to serve as inputs to Landau modeling of mixed microstructure. The chemical potential is generally defined as

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}. \quad (5.10)$$

In a (sub) regular solution model, the chemical potential of a component using the molar Gibbs energy G_m^θ must sum over the partial derivatives ergodically with respect to all the components:

$$\mu_i^\theta = G_m^\theta + \left(\frac{\partial G_m^\theta}{\partial x_i} \right)_{T, P, x_{j \neq i}} - \sum_j \left(\frac{\partial G_m^\theta}{\partial x_j} \right)_{T, P, x_{k \neq j}} \quad (5.11)$$

The second summation on the right-hand-side is the Lagrangian constraint due to the mass conservation expressed in constituent fractions [ZSD⁺15]. Thus, the diffusion potential in a

phase for two components can be written as a difference between two chemical potentials, i.e.

$$\tilde{\mu}^\theta = \mu_i^\theta - \mu_j^\theta = \left(\frac{\partial G_m^\theta}{\partial x_i} \right)_{T,P,x_{j \neq i}} - \left(\frac{\partial G_m^\theta}{\partial x_j} \right)_{T,P,x_{k \neq j}} \quad (5.12)$$

Similarly, with the constraint of site fractions in Eq.(5.6), the chemical potential of an end-member K in θ phase is linked with the molar Gibbs energy G_m^θ by

$$\mu_K^\theta = G_m^\theta + \sum_s \left(\frac{\partial G_m^\theta}{\partial y_i^{(s)}} \right)_{T,P,y_{j \neq i}} - \sum_s \sum_j \left(\frac{\partial G_m^\theta}{\partial y_j^{(s)}} \right)_{T,P,y_{k \neq j}} \quad (5.13)$$

Since the end-member K is a compound with fixed stoichiometry, the molar Gibbs energy of the end-member can be connected with the chemical potential of components in sublattice s .

$$G_m^K = \sum_s a_s \mu_i^{(s)} \quad (5.14)$$

Given the CEF model of austenite by the sublattices $(Fe)_{0.5}(C, V_A)_{0.5}$, the Gibbs energy of end-member $Fe_{0.5}C_{0.5}$ is equal to

$$G_m^{Fe_{0.5}C_{0.5}} = 0.5\mu_{Fe} + 0.5\mu_C \quad (5.15)$$

Another constraint relevant to diffusion potentials is the internal equilibrium among different sublattices, which requires the diffusion potential is independent on which sublattice is used in calculation, such that

$$\tilde{\mu} = \mu_i^{s1} - \mu_j^{s1} = \mu_i^{s2} - \mu_j^{s2} \quad (5.16)$$

With the previous definitions, we can derive the diffusion potential of austenite and ferrite (martensite) in binary Fe-C system. The unified sublattice expression for both phases can be written as $(Fe)_k(C, V_A)_l$. Since the composition of Fe is not independent in this binary system, the diffusion potential is determined based on the basic independent variable of

carbon composition x_{cC} . For ferrite (martensite), a set of determinative equations is

$$\begin{aligned}\tilde{\mu}_C^{BCC} &= \mu_C^{BCC} - \mu_{Fe}^{BCC} = \mu_C^II - \mu_{Fe}^I \\ &= \frac{1}{0.75} \left[\left(\frac{\partial G_m^{BCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \left(\frac{\partial G_m^{BCC}}{\partial y_{VA}^II} \right)_{y_C^II} \right] \\ &\quad - \frac{1}{0.25} \left\{ G_m^{BCC} + \left(\frac{\partial G_m^{BCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \sum_{i=C,VA} \left[y_i^II \left(\frac{\partial G_m^{BCC}}{\partial y_i^II} \right)_{y_j^II} \right] \right\};\end{aligned}\quad (5.17)$$

$$y_C^II + y_{VA}^II = 1;$$

$$x_{cC}^{BCC} = \frac{y_C^II}{3 + y_C^II}$$

Similarly, the diffusion potential of the austenite reads,

$$\begin{aligned}\tilde{\mu}_C^{FCC} &= \mu_C^{FCC} - \mu_{Fe}^{FCC} = \mu_C^II - \mu_{Fe}^I \\ &= \frac{1}{0.5} \left[\left(\frac{\partial G_m^{FCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \left(\frac{\partial G_m^{FCC}}{\partial y_{VA}^II} \right)_{y_C^II} \right] \\ &\quad - \frac{1}{0.5} \left\{ G_m^{FCC} + \left(\frac{\partial G_m^{FCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \sum_{i=C,VA} \left[y_i^II \left(\frac{\partial G_m^{FCC}}{\partial y_i^II} \right)_{y_j^II} \right] \right\}\end{aligned}\quad (5.18)$$

$$y_C^II + y_{VA}^II = 1$$

$$x_{cC}^{FCC} = \frac{y_C^II}{1 + y_C^II}$$

It is noted that the energy density in Landau potential presents the energy per volume (area), thus the diffusion potentials derived from CALPHAD database should be divided by mole volume when they enter the Landau model. It means

$$\begin{aligned}\tilde{\mu}_C^{BCC} &= \frac{1}{0.75V_m} \left[\left(\frac{\partial G_m^{BCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \left(\frac{\partial G_m^{BCC}}{\partial y_{VA}^II} \right)_{y_C^II} \right] \\ &\quad - \frac{1}{0.25V_m} \left\{ G_m^{BCC} + \left(\frac{\partial G_m^{BCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \sum_{i=C,VA} \left[y_i^II \left(\frac{\partial G_m^{BCC}}{\partial y_i^II} \right)_{y_j^II} \right] \right\}; \\ \tilde{\mu}_C^{FCC} &= \frac{1}{0.5V_m} \left[\left(\frac{\partial G_m^{FCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \left(\frac{\partial G_m^{FCC}}{\partial y_{VA}^II} \right)_{y_C^II} \right] \\ &\quad - \frac{1}{0.5V_m} \left\{ G_m^{FCC} + \left(\frac{\partial G_m^{FCC}}{\partial y_C^II} \right)_{y_{VA}^II} - \sum_{i=C,VA} \left[y_i^II \left(\frac{\partial G_m^{FCC}}{\partial y_i^II} \right)_{y_j^II} \right] \right\}\end{aligned}\quad (5.19)$$

The diffusion potential of the system is evaluated via

$$\tilde{\mu}_C(x_{cC}, \mathbf{r}, t) = \frac{e_{OP}(\mathbf{r}, t)}{e_{OP}^0} \tilde{\mu}_C^{BCC}(x_{cC}, t) + \left(1 - \frac{e_{OP}(\mathbf{r}, t)}{e_{OP}^0}\right) \tilde{\mu}_C^{FCC}(x_{cC}, t) \quad (5.20)$$

where, the e_{OP}^0 is equilibrium OP strain indicated by the transformation strain, while e_{OP} is the spatiotemporal evolving OP strain.

Figure 5.3 compares the diffusion potentials of individual phases calculated from commercial software Thermo-Calc and the in-house codes with the parameters from Fe-C thermodynamic database. It is clear that our in-house code well represents the diffusion potentials. The developed calculation engine of thermodynamics embedded in the in-house codes of MTs to simulate the diffusive-displacive coupled transformation will be elaborated in the following subsections.

Figure 5.3: The calculated diffusion potential of representative alloys (in symbols) compared with the results from calculation by Thermo-Calc software.

A (semi-)quantitative Landau modeling of displacive-diffusive coupled phase transformation also requires accurate chemical mobilities entering Cahn-Hilliard equation. The chemical mobility is the functional of the atomic mobility. The latter can be directly extracted from multicomponent and multiphase diffusion kinetic database. In a natural way, it bridges the computational diffusion kinetics and the Landau modeling of phase transformation. In computational diffusion kinetics, atomic mobility can be expressed as

$$M_i^\theta = \frac{M_i^{\theta 0}}{RT} \exp\left(-\frac{Q_i^\theta}{RT}\right) \quad (5.21)$$

The $M_i^{\theta 0}$ is a frequency factor, and the activation energy Q_i^θ is written in CALPHAD fashioned Redlich-Kister polynomial as

$$Q_i^\theta = \sum_p x_p Q_i^\theta + \sum_p \sum_{q>p} x_p x_q \left[\sum_{r=0,1,2} {}^r Q_i^{p,q} (x_p - x_q)^r \right] \quad (5.22)$$

for (sub)regular solution model, and

$$Q_i^\theta = \sum_j \sum_m y_j^I y_m^{II} Q_i^{\theta-j,m} + \sum_j \sum_{k>j} \sum_m y_j^I y_k^I y_m^{II} \left[\sum_{r=0,1,2} {}^r Q_i^{\theta-j,k} (y_j^I - y_k^I)^r \right] \\ + \sum_j \sum_m \sum_{n>m} y_j^I y_m^{II} y_n^{II} \left[\sum_{r=0,1,2} {}^r Q_i^{\theta-m,n} (y_m^{II} - y_n^{II})^r \right] \quad (5.23)$$

Table 5.1: The calculated chemical potentials and diffusion potentials (J/mol) of BCC(martensite) and FCC(austenite) phases in two objective Fe-C alloys at different temperatures

Cwt.%	Potential Name		Values	
		298.15K	452.95K	578.15K
0.59	$\mu_{C.BCC}$	83238.62	70371.54	59450.16
0.59	$\mu_{Fe.BCC}$	-8213.18	-13375.61	-18674.90
0.59	$\tilde{\mu}_{BCC}$	91451.80	83747.14	78125.06
0.59	$\mu_{C.FCC}$	29516.28	21336.58	14206.28
0.59	$\mu_{Fe.FCC}$	-2836.82	-9332.61	-15678.98
0.59	$\tilde{\mu}_{FCC}$	35353.10	30669.18	29885.26
1.07	$\mu_{C.BCC}$	84959.09	72985.27	62786.36
1.07	$\mu_{Fe.BCC}$	-8282.53	-13480.96	-18809.38
1.07	$\tilde{\mu}_{BCC}$	93241.62	86466.23	81595.74
1.07	$\mu_{C.FCC}$	32574.76	25159.59	18647.63
1.07	$\mu_{Fe.FCC}$	-2961.29	-9487.78	-15858.99
1.07	$\tilde{\mu}_{FCC}$	35536.05	34647.37	34506.62

for the CEF sublattice model. The chemical mobilities M_{kj}^θ in single phase are related to atomic mobility M_i^θ via the equations

$$\begin{aligned} M_{kj}^\theta &= \frac{1}{V_m} \sum_l (\delta_{jl} - x_{cj}) (\delta_{lk} - x_{ck}) x_{cl} M_l^\theta \\ M_{kj}^\theta &= \frac{1}{V_m} \sum_l (\delta_{jl} - u_{cj}) (\delta_{lk} - u_{ck}) u_{cl} M_l^\theta + \frac{1}{V_m} \sum_{l \notin S} \delta_{jl} y_{VA}^H u_{cl} M_l^\theta \end{aligned} \quad (5.24)$$

where δ_{jl} and δ_{lk} are the Kronecker delta. In binary Fe-C system, M_{CC}^θ is served as the exclusive independent variables. Therefore,

$$\begin{aligned} M_{CC}^{FCC} &= \frac{1}{V_m} (x_{cFe}^2 x_{cC} M_C^{FCC} + x_{cC}^2 x_{cFe} M_{Fe}^{FCC}) \approx \frac{1}{V_m} x_{cFe}^2 x_{cC} M_C^{FCC} \\ M_{CC}^{BCC} &= \frac{1}{V_m} (x_{cFe}^2 x_{cC} M_C^{BCC} + x_{cC}^2 x_{cFe} M_{Fe}^{BCC}) \approx \frac{1}{V_m} x_{cFe}^2 x_{cC} M_C^{BCC} \end{aligned} \quad (5.25)$$

In a structural and compositional non-uniform system, the same relation between M_{kj} and M_i should hold for entire system, while the atomic mobility is spatiotemporally dependent and coupled with the OP strain in displacive transformation via

$$M_l = M_l^{BCC} + M_l^{FCC} - (M_l^{BCC})^{e_{OP}/e_{OP}^0} (M_l^{FCC})^{(1-e_{OP}/e_{OP}^0)} \quad (5.26)$$

Thus, the approximated chemical mobility in Landau modeling is expressed as

$$\begin{aligned} M_{CC} &= \frac{1}{V_m} (x_{cFe}^2 x_{cC} M_C + x_{cC}^2 x_{cFe} M_{Fe}) \\ &\approx \frac{1}{V_m} x_{cFe}^2 x_{cC} M_C = \frac{1}{V_m} x_{cFe}^2 x_{cC} \left[M_C^{BCC} + M_C^{FCC} - (M_C^{BCC})^{e_{OP}/e_{OP}^0} (M_C^{FCC})^{(1-e_{OP}/e_{OP}^0)} \right] \end{aligned} \quad (5.27)$$

5.4 Coupled Model and Semi-quantification

In this section, the Landau model in chapter 3 is further developed by adding the energy contributions of chemistry. The coupled model is designed to simulate the microstructure of steel and its evolution in polycrystals. In this displacive-diffusive coupled model, the symmetry adapted deviatoric strain e_2 , spatiotemporal distribution of the carbon composition x_{cC} and grain orientations η_i are selected as field variables. With the field variables, one can

distinguish the domains of martensite variants and austenite by a combination of strain and composition. The total free energy of the system is expressed as

$$F = \int d\vec{r} (f_{el} + f_{ch} + f_{grain} + f_{cpl} + f_{gradc} + f_{grade}) \quad (5.28)$$

and is composed of the non-linear elastic free energy $-f_{el}$, the chemical free energy $-f_{ch}$, the grain boundary energy f_{grain} , the coupling energy contributions $-f_{cpl}$ and the chemical (f_{gradc}) and elastic (f_{grade}) gradient energy [BA06, BA07]. According to the nonlinear Landau model in chapter 3, the square-to-rectangular MT is described by a 2-4-6 Landau polynomial with the primary OP of deviatoric strain e_2 , i.e.

$$f_{el} = (c_{11} + c_{12}) [e_1 - \kappa_{1c}x_c - \kappa_{12}e_2^2]^2 + 2c_{44}e_3^2 + (c_{11} - c_{12})e_2^2 + Be_2^4 + Ce_2^6 \quad (5.29)$$

here, the influences of OP strain and composition on the bulk dilatation are taken into consideration that become significant when the directions of habit planes deviate from those of twin planes.

In our model, the diffusion potential detailed in the section 5.3 instead of $\frac{\delta f_{ch}}{\delta x_{cC}}$ enters the Cahn-Hilliard equation to solve the diffusion of carbon, thus the expression of chemical energy in CALPHAD is not necessary explicitly given here. The grain boundary energy has the same expression as that in chapters 3 and 4, which is no longer repeated here. However, for a semi-quantitative simulation, an appropriate normalization factor of $m = 0.01$ is multiplied in front of f_{grain} to correctly describe the small value of the grain boundary energy density around $1.0J/m^2$ [RSM⁺13].

Besides the above energy contributions, various coupling effects are included in our coupled model. Although the continuous grain boundary model in chapter 3 successfully described the grain boundary nucleation assisted with gradient of OP strain in polycrystals, the grain boundary relaxation of the localized strain is not included. In this chapter, an additional coupling term between shape function of grain boundaries and strain gradient $\frac{a_1}{2}(\nabla e_2)^2 \sum_i^Q (\nabla \eta_i)^2$ is incorporated in Landau free energy. (Figure 5.4 illustrates the simu-

lated morphology of polycrystals by using the shape function of grain boundaries $\sum_i^Q (\nabla \eta_i)^2$.) The starting point of incorporating this dual-gradient term is based on the experimental discovery that the coupling of strain gradient and grain orientation does effect on the mechanical properties by our colleagues. To ensure the formal integrity of the coupling effect, a conventional coupling between strain itself and shape function of grain orientation is also taken, namely, $\frac{a_0}{2}e_2^2 \sum_i^Q (\nabla \eta_i)^2$, which has ability to account for suppression effect of grain bound-

Figure 5.4: The morphology of grain boundary represented by the shape functions $\sum_i^Q (\nabla \eta_i)^2$

ary on MT in some nano-sized polycrystals. The solute drag effect at the grain boundary is simplified as $\kappa_{cg}x_{cC}mf_{grain}$, and the coupling between elastic distortions and composition is introduced as $\kappa_{ce}e_2^2x_{cC}^2$ with a 2-2 fourth order power function appropriate for all the crystallographic symmetry. Therefore, a complete nonlinear Landau energy for the displacive-diffusive coupled phase transformation can be written in

$$F = \int dr \left\{ \begin{aligned} & (c_{11} + c_{12}) [e_1 - \kappa_{1c}x_c - \kappa_{12}e_2^2]^2 + 2c_{44}e_3^2 + (c_{11} - c_{12}) e_2^2 + Be_2^4 \\ & + Be_2^6 + f_{ch} + mf_{grain} + \frac{g_e}{2}(\nabla e_2)^2 + \frac{g_c}{2}(\nabla x_{cC})^2 + \frac{a_0}{2}e_2^2 \sum_i^Q (\nabla \eta_i)^2 \\ & + \frac{a_1}{2}(\nabla e_2)^2 \sum_i^Q (\nabla \eta_i)^2 + \kappa_{cg}x_{cC}mf_{grain} + \kappa_{ce}e_2^2x_{cC}^2 \end{aligned} \right\} \quad (5.30)$$

With the function of Landau free energy, the semi-quantification of Landau free energy for MT in steel was carried out. From thermodynamics of MT, the martensitic nucleation in steel is no longer attributed to the acoustic lattice softening of the phonons with a small wave vector, which was evidenced by the negative temperature dependence of elastic constants. The temperature dependence of the bulk and shear moduli of BCC iron was measured by

Dever et al. [Dev72] and shown in Figure 5.5 accompanying with the linear fitting. The similar temperature dependence of elastic moduli was found in low carbon steel by Fukuhar et al. [FS93]. With the two sets of experimental data assessed, the approximate linear expressions of symmetry adapted elastic moduli are given in Table 5.2. These expressions directly enter Landau free energy to serve as materials parameters in front of the square terms of the symmetry adapted strains in Eq.(5.29).

Table 5.2: The temperature dependent moduli by linear fitting

	$C_{11} + C_{12}$	$C_{11} - C_{12}$	C_{44}
Fe-0.59wt.C	$392.6 - 0.0456T$	$169.0 - 0.0436T$	$92.23 - 0.0442T$
Fe-1.07wt.C	$389.6 - 0.0456T$	$166.3 - 0.0436T$	$89.23 - 0.0442T$

Figure 5.5: Temperature dependence of the bulk and shear moduli of BCC iron

Except for the square terms in Landau free energy, the material parameters of anharmonic terms were determined by calibrating the driving forces at three characteristic temperatures, i.e. onset temperatures of MT, room temperature (see Figure 5.3). It is known that the MT in steel starts below the T_0 temperature, which means there is a driving force to trigger MT. In CALPHAD type thermodynamic model, the concept of lattice stability is implied in the Gibbs energy functions. Therefore, the difference of Gibbs energy between austenite and martensite derived from CALPHAD technique on the one hand triggers the structural MT, on the other hand, the real diffusion potential drives the diffusive transformation. With this concept, the free energy density of martensite at the quenching temperature in Landau polynomial should be equal to the difference of Gibbs energy between austenite and martensite with a given composition in CALPHAD. It needs to emphasize that the renormalization of

the Landau potential for MT at each time step is still open, although the seamless integration with CALPHAD technique in our model ensures the real time diffusion potential in each grid in simulation box and at each time step can be calculated. To semi-quantitatively describe the driving force of MT, the material coefficients of anharmonic terms in Eq.(5.30) were adjusted to determine the Landau free energy. The values of energy wells on Landau energy surface were calibrated against the thermodynamic driving forces at M_s and room temperatures, and the transformation strains indicated by energy wells were adjusted in accordance with experiments data. Figure 5.6 shows the normalized Landau free energy of Fe-0.59wt% C and Fe-1.07wt% C with a normalized energy density factor of $2.52 \times 10^{11} J/m^2$ and $2.06 \times 10^{11} J/m^2$, respectively, at room, M_s , and partitioning temperatures.

Figure 5.6: Normalized Landau free energy at room, M_s , and partitioning temperatures, which are calibrated with thermodynamic database. The upper panel is the energies of Fe-0.59wt% C alloy, and the bottom panel is for Fe-1.07wt% C

The numerical procedures for simulating MT have been detailed in section 3.3 by solving the general equation of motion Eq.(3.8). For displacive-diffusive coupled transformation, the Cahn-Hilliard equation is used to monitor the spatiotemporal redistribution of carbon element with the chemical mobility associated with the atomic mobility from kinetic database of CALPHAD method. The chemical mobility in Eq.(5.31) varies with coordinates and time,

rather than a constant in most of conventional phase field modeling.

$$\frac{\partial x_{cC}(\vec{r}, t)}{\partial t} = \nabla M_C(\vec{r}, t) \nabla \left(\frac{\delta F(\vec{r}, t)}{\delta x_{cC}(\vec{r}, t)} - g_c \nabla^2 x_{cC}(\vec{r}, t) \right) \quad (5.31)$$

The numerical treatment of explicit finite difference in time and semi-implicit spectral scheme in space is widely accepted in computer simulation of Cahn-Hilliard equation. To overcome the time-step constraint, a term $0.5g_c \mathbf{k}^4 \hat{x}_{cC}(\mathbf{k}, t)$ was added to both sides of equation in the conventional first-order semi-implicit Fourier spectral scheme [ZCST99], which leads to

$$\begin{aligned} \hat{N}L &= \mathcal{F} \left(\frac{\delta F(\vec{r}, t)}{\delta x_{cC}(\vec{r}, t)} \right) \\ (1 + 0.5\Delta t g_c \mathbf{k}^4) \hat{x}_{cC}^{(n+1)}(\mathbf{k}, t) &= (1 + 0.5\Delta t g_c \mathbf{k}^4) \hat{x}_{cC}^{(n)}(\mathbf{k}, t) \\ &+ \Delta t i \mathbf{k} \mathcal{F} \left\{ M_C(\vec{r}, t) \mathcal{F}^{-1} \left(i \mathbf{k} \left[\hat{N}L + g_c \mathbf{k}^2 \hat{x}_{cC}^{(n)}(\mathbf{k}, t) \right] \right) \right\} \end{aligned} \quad (5.32)$$

where $\mathcal{F}$ and $\mathcal{F}^{-1}$ denote Fourier and inverse Fourier transformations, respectively.

5.5 Microstructure Evolution

5.5.1 Grain Boundary Nucleation and Growth

To examine the martensitic nucleation and growth assisted with grain boundary, a 2D bicrystal benchmark containing two grains of $\theta = 0$ and $\pi/6$ was firstly employed, as is shown in Figure 5.7a. The two grains are separated by a flat grain boundary with the normalization factor of $m = 0.01$ for grain boundary energy. Although the grain boundary nucleation can be realized without the coupling term in chapter 4, the coupling gradients representing the strain relaxation at grain boundary was added to facilitate the nucleation of martensite. The dual-gradient coupling coefficient was set at $a_1=0.7$, while the direct coupling was set $a_0=0$, which avoids the inhibition of grain boundary nucleation. The value of dilatation coupling coefficient κ_{12} between e_1 and e_2 was set to 1.25. The random fluctuations of displacement following the Gaussian distribution were incorporated at the initial stage. Figure 5.7 illustrates the temporal evolution of martensite variants as the results of isothermal simulation after quenched the Fe-0.59% C alloy to the room temperature. At the room temperature lower than the M_s , the nucleation of martensites can occur due to the lowered stability of the austenite with respect to the martensite. It is clear that two types of martensite variants, represented in red and blue, promptly nucleate at the grain boundary preceding those in bulk counterpart. The phenomenon originates from the reduced nucleation barrier for the formation of martensites at grain boundary due to the coupling between the grain boundary and the non-local strain gradient, which accounts for the extra relaxation

of misfit strain. The simulation results prove the MT occurs at grain boundaries without continuous cooling or external loading. Though some pre-existing nuclei are in fact allowed in grain interior, they are unable to form the stable nuclei for MT in comparison with the grain boundary nucleation. Evolving with time, the martensites no longer grow paralleling. Some of them promptly penetrate inside the grains, thus in turn trigger the autocatalysis phenomena as is detailed in chapter 4.

Figure 5.7: Martensitic nucleation and growth of Fe-0.59% C steel at 298K against grain boundary without external loading. (a) Bicrystals morphology (b-d) Microstructure evolution. The twin-related martensite variants are in red and blue, and the retained austenite is in green.

The orientations of the twin boundaries between two neighboring martensite variants in the $\theta = 0$ grain interface are aligned to $\pm\pi/4$, which follows the kinematic compatibility to achieve strain accommodation by the formation of twins with plane normal of $\langle 11 \rangle$. However, the invariant plane normals deviate from the $\langle 11 \rangle$ orientations (as was interpreted in chapter 3, the orientations of twin plane and invariant plane coincide with each other in 2D square-to-rectangular case). It is due to the effect of the coupling between dilatational strain e_1 and deviatoric strain e_2 . The orientations of twin planes in the $\theta = \pi/6$ grain are evidenced aligning $5\pi/12$ and $11\pi/12$ with respect to the horizontal X axis, as was predicted by kinematic compatibility condition in polycrystals in chapter 3.

Figure 5.8: The comparison of martensite morphology with different values of dilatation coupling $\kappa_{12} =$ (a) 0, (b) 1.25, (c) 3.25, (d) 4.25

5.5.2 Effect of Lattice-mismatch-induced Strains

Figure 5.8 compares the simulated morphology of the martensites and retained austenite with different values of the coupling coefficient κ_{12} . If $\kappa_{12} = 0$, the morphology in Figure 5.8a exhibits perfect domain walls lying in square $\{11\}$ planes to minimize dilatational and shear energy. A long time simulation leads to a full martensitic microstructure. When κ_{12} is larger than 0, there is a competition between the driving force favoring the transformation and the coherency stress arising out of the volume change. Thus, the full martensite microstructure is no longer favored, see Figure 5.8(b) and (c). With an increasing value of κ_{12} , an increasing phase fraction of austenite (represented in green) is retained after quenching, and the orientation of invariant plane deviates more from the $\{11\}$ plane. In Figure 5.8(d), the simulated zig-zag morphology well represents widely observed microstructure in the Fe-Ni alloys, which was also evidenced in the Q&P steel after tempering [TMR15].

Figure 5.9 compares the microstructures between our simulation for the Fe-1.07wt% C and the SEM image of Fe-1.07wt% C-2.2Si-2.9Mn steel (quenched to 17°C followed by the partitioning) [TMR15]. The orientation of the invariant plane can be inspected by defining

Figure 5.9: The simulated mixed microstructure of martensite and retained austenite in Fe-1.07wt% C steel is compared with experimental observation in Fe-1.07wt% C-2.2Si-2.9Mn steel [TMR15]

an angle ϕ with respect to the Y axis, such that

$$\frac{\partial^2 e_i}{\partial x^2} = e_i'' \cos^2 \phi, \quad \frac{\partial^2 e_i}{\partial y^2} = e_i'' \sin^2 \phi \quad (5.33)$$

Base on the St. Venant's compatibility, there is

$$\frac{\partial^2 e_1}{\partial x^2} + \frac{\partial^2 e_1}{\partial y^2} - \frac{\partial^2 e_2}{\partial x^2} + \frac{\partial^2 e_2}{\partial y^2} = 0 \quad (5.34)$$

If $e_1 - \kappa_{1c}x_c - \kappa_{12}e_2^2$ is not equal to zero, e_1 fails to be vanishing, so that martensites and austenite would lead to different values of e_1 and e_2 from those of equilibrium. If we admit the jumps of e_1 and e_2 across the invariant interface but keep the displacement continuous as the kinematic compatibility enforced, the St. Venant's compatibility gives

$$\delta e_1 \cos^2 \phi + \delta e_1 \sin^2 \phi - \delta e_2 \cos^2 \phi + \delta e_2 \sin^2 \phi = 0 \quad (5.35)$$

which will be satisfied if

$$\cos 2\phi = \frac{\delta e_1}{\delta e_2} \quad (5.36)$$

In this case, the values of e_1 and e_2 lead to the $\phi \approx \pm\pi/6$ or $\phi \approx \pm\pi/3$. The included angle between two types of invariant planes Ψ shows the angle of $\pi/6$, which is consistent with $\pi/6$ the observed in the SEM image.

5.5.3 Carbon Redistribution in As-quenched Microstructure

The short-range diffusion of carbon from martensite to austenite in Fe-0.59wt% C is clearly observed in Fig. 5.10(b); especially, the carbon element is segregated at the martensite / austenite (α'/γ) interfaces colored in yellow and orange. Simulation confirms that diffusion potential at the room temperature provides chemical driving force to diffusion. However, the atomic diffusion mobility of carbon in martensite is about seven orders of magnitudes greater than that in austenite. The synergy of diffusion potential and chemical mobility led to a strong redistribution of carbon characterized in its segregation at α'/γ interfaces. Therefore, it has demonstrated that the partitioning or compositional redistribution of carbon in Q&P steels is the inherent behavior of the diffusion, and is nothing special in comparison with the ordinary diffusional transformations, which are all governed by diffusion potential and chemical mobility. The only peculiarity is the effect of short-range diffusion or relaxation of carbon is smeared out in the displacive MT, which was hardly to be detected until the maturity of 3DAP technique.

Figure 5.10: (a) The as-quenched mixed microstructure of martensite and austenite and (b) carbon distribution in Fe-0.59wt% C alloy at 298K

Recently, Toji et al. [TMH⁺14] adopted 3DAP to study the carbon partitioning in Q&P steel with the composition Fe-0.59wt%C-2.0Si-2.9Mn, and presented a direct atomic scale evidence of carbon partitioning from martensite to austenite without the presence of bainite transformation. In their 3DAP observation, the carbon concentration fluctuated in the range between 1.5 at.% and 4.5 at.% in the as-quenched sample, giving the average carbon concentration of 2.77 at.%, in good agreement with the bulk carbon content of the steel (2.7 at.%).

Figure 5.11: (a) The simulated profiles of local transformation strain and carbon content across the twin boundary in Fe-0.59wt% C. The composition profile of carbon well represents the (b) 3DAP mapped local distribution of carbon elements in as-quenched Fe-0.59wt%C-2.0Si-2.9Mn steel [TMH⁺14]

Several carbon-enriched regions in the C atom map were not able to be unambiguously identified as austenite or martensite in experiments, thus were inferred as the regions of carbon segregation at dislocations or boundaries.

Figure 5.11(a) displays the calculated composition profile of carbon across the α'/γ interface corresponding to the martensite variants in the inset of Figure 5.10(b). The carbon composition range of 2.2 at.% $\sim$ 4.2at.% revealed by simulation is in good agreement with the results in experiments. The twin boundary region is evidenced with the width of 10nm, which also coincides with the experiments. However, the variation of composition in experimental atom mapping is more diffuse in comparison with that in the simulated profile. In Figure 5.11(a), the carbon elements are preferentially segregated in the region of twin boundary and have the highest contents at the center of the twin boundary, which support the deduction that the carbon-enriched regions in the C atom map are indeed the twin boundaries. The simulation results of segregation further manifest the fact that carbon elements undergo a diffusion from martensite to austenite. It is because our Landau model has soliton-based kink solutions, characterized by the alternation of two types of martensites with the twin boundary being mathematically treated as a special austenite. The conclusion will be verified in the following simulations for the true partitioning at higher temperature. Similarly, Figure 5.12 shows the as-quenched mixed microstructure of martensite and retained austenite, carbon redistribution and the profiles of deviatoric strain and composition of Fe-1.07wt% (5.0 at%)C.

Figure 5.12: (a) The simulated mixed microstructure of martensite and austenite, (b) the local distribution of carbon, and (c) the profiles of local transformation strain and carbon content across the twin boundary in Fe-1.07wt% C.

5.5.4 Carbon Redistribution after Partitioning

In order to analyze the carbon diffusion between martensite and austenite during the partitioning process, the microstructure evolution of Fe-1.07wt% C alloy at 673K is simulated by an isothermal relaxation for 1.0×10^5 time steps as analog of partitioning. The simulated as-quenched mixed microstructure is selected as the initial microstructure, which

contains about 50% retained austenite and 50% as-quenched martensite. To readily enhance the resolution of the carbon redistribution in the following simulations of partitioning, the initial mixed microstructure was generated being subjected to a longer evolution to form coarse martensites. In Figure 5.13, a small number of tempered martensites are generated against the stable nuclei in austenite with the widths of martensite plate smaller than those of as-quenched martensite (circled in black). However, in most of the austenite regions without stable nuclei, no tempered martensite is formed after a long-time calculation. The formation of tempered martensite was evidenced by experimental results of our colleagues [dDCDKM⁺15] for other Q&P steels, but was not confirmed by the experiments for the Fe-1.07wt%C-2.9%Mn-2.2%Si alloy, in which the volume fraction of austenite was essentially not changed by holding the quenched specimens at 673K up to 3000s and many carbides were raised inside the martensites during the partitioning. Since the formation of carbide has not been taken into consideration in our simulation for simplicity, the formation of trace tempered martensite is the inevitable result at the temperature of 673K lower than T_0 temperature.

Figure 5.13: The microstructure (upper panel) and carbon distribution (bottom panel) in Fe-1.07wt% C alloy during the partitioning at 673K at 10^3 , 5.0×10^4 , 1.0×10^5 time steps

Figure 5.14 illustrates the profile of carbon distribution after partitioning at 673K for 10^5 steps corresponding to the region of martensite and retained austenite indicated by arrow.

Compared with the as-quenched carbon distribution shown in Figures 5.11 and 5.12 characterized by the short-range relaxation and segregation of carbon at twin boundaries, a relative long-range diffusion of carbon is evidenced by a clear inhomogeneity between austenite and martensite. The composition of carbon in martensite is 0.8wt.%, in comparison with 1.3-1.5wt.% in austenite near the interface. However, the composition of carbon in austenite far beyond the interface keeps the same value as the alloy composition, i.e. 1.1wt.%. In this way, remarkable pileups of carbon in the vicinity of the martensite/austenite(α'/γ) interface inside the austenite region can be observed. All these phenomena presented in our simulation results were found in experiments by Toji et al. [TMR15] However, pileups region in Figure 5.14 shows a width about $0.02\mu m$, which is one order of magnitude smaller than that of experiments. It is due to the short simulation time compared with real partitioning time of 300s. The diffusion will propel the front of pileups penetrating into the bulk austenite in a relatively long time partitioning. Most noteworthy is that our simulations neither incorporated an arbitrary energy contribution, nor did constrained carbon equilibrium(CCE) model [SMDCS03], but only employed the diffusion potential with the CALPHAD database. Therefore, the carbon partitioning is indeed an ordinary diffusion dominated by diffusion potential and chemical mobility without any other constraint. The independence of carbon partitioning on martensite volume fraction, discovered in experiments, is in essence consistent with inherent feature of diffusion potential model. Such learnt conclusion that bulk carbon content doesn't exert influence on carbon partitioning based on the EPMA and 3DAP experiments is in fact only suitable for the partitioning for time in several seconds. In a long-time annealing, the energy difference between phases with different chemical potentials/carbon contents indeed drives the partitioning towards the full equilibrium state.

5.5.5 Effect of Continuous Cooling

Figure 5.15 compares two sets of simulation results to reveal the effect of continuous undercooling. The Fe-0.59wt% C alloy is chosen as objective material. The figures in upper panel reveal the MT was triggered by a step varying driving force. The simulation was carried out by directly quenching austenite to 290K followed by 1000 steps of relaxation, and then continuous cooling at a rate of 0.13K per 100 steps from to 290K and 210K. The snapshots of microstructure in bottom panel depict the MT by directly quenching the austenite to 290K followed by long time isothermal relaxation. It is obviously that the volume fraction of martensite increases with decreasing quenching temperature, consistent with the trend of the observed phase fraction in optical micrographs [TMR15]. Moreover, a continuous varying driving force can further accelerate the MT. It is worthy of noting that the phase fraction

Figure 5.14: The local composition profile of carbon derived from the simulation for Fe-1.07wt% C alloy after an isothermal relaxation at 673K for 1.0×10^5 time steps

in our simulation fails to be quantitatively compared with the results of the experiments, because the time limitation of simulation.

5.6 Extend to Multicomponent System

To extend the application of our model to the multicomponent alloys, we have to implement a pseudo-ternary approximation for the multicomponent and multiphase thermo-kinetic database to overcome the disadvantage in solving the multicomponent diffusion equations, while effectively describe the effect of alloying elements.

Figure 5.15: The microstructure evolution of Fe-0.59wt% C under a continuous cooling condition (upper panel) compared with those of isothermal relaxation (bottom panel)

5.6.1 Pseudo-ternary Approximation

A pseudo-ternary system of steel Fe-M'-C is described as $(Fe, M')_m(C, V_A)_n$ to represent multicomponent Q&P steels by using CEF in the framework of CALPHAD. The M' represents the equivalent transition metal element. The CEF describes the Gibbs energy of the austenite or martensite phase by using

$$G^\Phi = \sum_{i=Fe, M'; j=C, V_A} y_i y_j G_{i,j}^\Phi + RT \left[m \sum_{i=Fe, M'} (y_i \ln y_i) + n \sum_{j=C, V_A} (y_j \ln y_j) \right] \\ + m y_{Fe} y_{M'} \left(\sum_{j=C, V_A} L_{Fe, M'}^j y_j \right) + n y_C y_{V_A} \left(\sum_{i=Fe, M'} L_{C, V_A}^i y_i \right) \quad (5.37)$$

To account for the effect of alloying elements, an equivalent weight fraction is introduced. In this work, both CSM1 (Steel produced by Centro Svil. Mater.) and TKSE1 (Steel produced by ThyssenKrupp) steels are selected to validate the pseudo-ternary description for the multicomponent steel. Take CSM1 steel as an example, the Mn is selected as equivalent

element, such that

$$\begin{aligned} w_{Mn'} &= \lambda_{Mn} w_{Mn} + \lambda_{Si} w_{Si}, \\ x_{Mn'} &= \lambda_{Mn} x_{Mn} + \lambda_{Si} x_{Si} \frac{M_A^{Si}}{M_A^{Mn}}; \\ \lambda_{Mn} &= 1, \\ \lambda_{Si} &= -0.4 \end{aligned} \quad (5.38)$$

where λ is equivalent coefficient, w and x are weight and mole fractions.

While for TKSE1 steel, the Si element equivalent is adopted because Si is a major alloying element,

$$\begin{aligned} w_{Si'} &= \lambda_{Si} w_{Si} + \lambda_{Mn} w_{Mn} + \lambda_{Cr} w_{Cr} + \lambda_{Al} w_{Al}; \\ \lambda_{Al} &= \lambda_{Si} = 1, \\ \lambda_{Cr} &= 0.1, \\ \lambda_{Mn} &= -0.5 \\ x_{Si'} &= \lambda_{Si} x_{Si} + \lambda_{Mn} x_{Mn} \frac{M_A^{Mn}}{M_A^{Si}} + \lambda_{Cr} x_{Cr} \frac{M_A^{Cr}}{M_A^{Si}} + \lambda_{Al} x_{Al} \frac{M_A^{Al}}{M_A^{Si}} \end{aligned} \quad (5.39)$$

With the definition of the equivalent element, the thermodynamic database should be re-assessed by calibrating the phase diagram and M_s temperature. The upgrading of thermodynamic model for martensite is following the strategy of Ghosh and Olson [GO94a, GO94b]. The Gibbs energy of martensite can be derived from the critical condition for $f_{cc} \rightarrow b_{cc}$ transformation via:

$$G_M = G_A + V_m(\Delta g_{ch} + g_{el} + \frac{2\sigma}{nd} - W_{fr}) = G_F + V_m(g_{el} + \frac{2\sigma}{nd} - W_{fr}) \quad (5.40)$$

where G_M and G_A are Gibbs energy of martensite and austenite. Δg_{ch} is the chemical Gibbs energy difference between ferrite and austenite, g_{el} is strain energy per unit volume, σ is interface energy, n is the number of close-packed planes comprising the nucleus thickness, d is the spacing between close-packed planes, and W is interface frictional work. W can be described as the function of shear modulus χ , i.e.

$$\begin{aligned} W &= K^\chi \chi(x_j, T) \\ \chi(x_j, T) &= 10^{10} \times \left(9.2468 + \sum x_j \left(\frac{d\chi}{dx_j} \right) \right) [1 - 7.9921 \times 10^{-7} T^2 + 3.317 \times 10^{-10} T^3] \end{aligned} \quad (5.41)$$

where the constant 9.2468 is the reference shear modulus of pure iron in austenitic state, and the summation term is shear modulus contribution that changes austenite to martensite.

By adding the contributions from elastic strain, interfaces and friction into Gibbs energy, and then fitting both thermodynamic and phase transformation data from experiments and literature, the parameters in our thermodynamic model for martensite are optimized.

Figure 5.16 illustrates the calculated composition dependence of the M_s temperature in comparison with assessed M_s temperature of TKSE1 steel from experiments.

Figure 5.16: The calculated metastable isopleth of M/A transus

The calculated isopleths by using the assessed thermodynamic database of pseudo-ternary Fe-M'-C are shown in Figure 5.17. The temperatures of austenite-ferrite transition have been adopted as the fitting property. The results in Figure 5.17 represent the transition temperatures in good comparison with the results calculated with full multicomponent thermodynamic database by using Thermo-Calc software. In Fig.5.17(b), the calculated equilibrium transition temperature is also compared with experimental A_{c3} temperature in non-equilibrium condition. The developed thermodynamic database is going to be updated as the accumulating experimental data such as the phase fraction at different processing.

With the updated thermodynamic description, the Landau modeling for a multicomponent system can be straightforwardly carried out by the method in this chapter with a full Landau potential of

$$\begin{aligned}
 F = \int dr \{ & \frac{c_{11} + 2c_{12}}{3} [e_1 - \kappa_{1c}x_{cC} - \kappa_{1M}x_{cM'} - \kappa_{12} (e_2^2 + e_3^2)]^2 + 2c_{44} \sum_{i=4}^{4-6} e_i^2 \\
 & + \frac{c_{11} - c_{12}}{2} (e_2^2 + e_3^2) + \frac{1}{6\sqrt{6}} (c_{111} - 3c_{112} + 2c_{123}) e_3 (e_3^2 - 3e_2^2) + C(e_2^2 + e_3^2)^2 \\
 & + G_{ch} + \kappa_{ce} (e_2^2 + e_3^2) (x_c^2 + x_M^2) + \frac{g_e}{2} [(\nabla e_2)^2 + (\nabla e_3)^2] + \frac{g_c}{2} [(\nabla x_c)^2 + (\nabla x_M)^2] \}
 \end{aligned}
 \quad (5.42)$$

Figure 5.17: The calculated isopleth by using the pseudo-ternary database a) CSM1 and b) TKSE1 steels

and Cahn-Hilliard equation for multicomponent system is given by

$$\frac{\partial^2 c_i(\vec{r}, t)}{\partial t^2} = \nabla \left(L_{ij} \nabla \frac{\delta F}{\delta c_j} + L_{ii} \nabla \frac{\delta F}{\delta c_i} \right) \quad (5.43)$$

where,

$$\begin{aligned} L_{ii}^n &= \frac{1}{V_m^n} \{ (1 - x_i) x_i M_i - x_i [(1 - x_i) x_i (M_i - M_n) - x_i x_j (M_j - M_n)] \} \\ L_{ij}^n &= \frac{1}{V_m^n} \{ -x_i x_j M_j - x_j [(1 - x_i) x_i (M_i - M_n) - x_i x_j (M_j - M_n)] \} \end{aligned} \quad (5.44)$$

are chemical mobility and M_i is the atomic mobility, x_i is the composition of species i .

Chapter 6

Multi-field Model Incorporating Dislocations

-Origin of the Martensitic Morphology in Steels

The greatest shortcoming is that the dislocation density tensor, no matter whether introduced through differential geometry or in the conventional way, measures the average dislocation density only and therefore, regards the internal mechanical state utmost incompletely.

-Ekkehard Kröner 1999

In chapter 5, the simulated zig-zag patterns of martensite plates have always been observed in nickel carbon steel. However, the martensites in low- and medium-carbon steels showing up different morphology have not been correctly simulated. In the perspective of PTMC [Bha03], the $\{225\}_{fcc}$ habit plane in low- and medium-carbon steels is not an undistorted habit plane in the strictest sense, while $\{259\}_{fcc}$ habit plane in nickel steels is less distorted than $\{225\}_{fcc}$. Experimental results reveal the varying trend of habit plane $\{111\}_{fcc} \rightarrow \{225\}_{fcc} \rightarrow \{259\}_{fcc}$ with increasing carbon content as well as a decreasing of dislocation density [Nis12]. To this end, it is a manifest that the configuration and evolution of dislocations in solid crystals play a critical role in the development of various martensitic morphology. Numerous research works on dislocations have been carried out in different perspectives of energetics, kinematics and dynamics. Among them, the continuum theories of dislocations found by Kröner [Kro71] and Kosevich et al. [Kos64] and consolidated by Le[LS96, KL08], Acharya [Ach01], Berdichevsky [Ber06], and Gurtin [Gur02], et al. adopted the variables of dislocation density tensors as the functional of plastic deformation to describe the dislocation patterning. For example, Kratochvíl and Sedláček et al. formulated the Eulerian and the Lagrangian frames based on the dislocation density tensor to

evolve the dislocation patterning [KS03]. Rickman and Viñals [RV97] developed a general phase-field formalism of the dislocation patterning by minimizing the free energy to obtain the time-evolving dislocation density tensor, without considering the specific crystal structural symmetry. Limkumnerd and Sethna [LS06] proposed an elasto-plastic Landau model in mesoscale to investigate the evolution of dislocations into sharp dislocation walls. The time evolution of the system was implemented by using motion equations with the free energy of the system written in pure plastic distortion tensor. The dislocation density tensor was expressed in plastic distortion tensor by definition. The approach allows to study dislocation motion by pure glide and a combination of glide and climb at different temperatures. These models incorporated the concepts of incompatibility, energy minimization and energy dissipation in solid crystals, showing many common ingredients between the continuum theories of dislocations and the nonlinear Landau model. The high similarity inspires the initiatives of integrating these two theories to shed light on the physical mechanisms of the interplaying of dislocations and phase transformations, which gives rise to the formation of microstructure. Recently, Gröger utilized Kröner's continuum theory to deal with the formation of distinct microstructure in a MT affected by the dislocations [GLS08, GLS10]. The presence and evolution of dislocations were depicted as the response to the nonlocal coupling of the incompatibility field and the OP strains. The incompatibility was explicitly written as the dual-curl of elastic strain tensor and related to the gradients of the scalar dislocation density. Minimizing the free energy subject to the incompatibility constraint for a given distribution of dislocations generated a localized stress field that exerted effects on the formation of martensite variant. Combining the methods of Gröger and Limkumnerd allows us to propose the Landau model of MT with dislocations in Lagrange dynamics in this chapter. Instead of the explicitly embedding incompatibility into TDGL equation in Gröger's work, our model characterizes in the usage of the underdamped general equation of motion with basic variables of displacements or velocities. So it also avoids the derivation of the complex incompatibility tensor when the model is extended to 3D.

6.1 Continuum Theory of Dislocations

The dislocation deformation viewed in macroscopic continuum has a general property that there is a certain finite displacement increment $\bar{\mathbf{b}}$ with the same magnitude and direction as one of the lattice vectors when calculating the net displacement $\mathbf{u}$ along a passage round any closed contour L , which encloses the dislocation line with the direction unit vector $\boldsymbol{\tau}$, see Figure 6.1.

The property of a single dislocation with Burgers vector $\bar{\mathbf{b}}$ can be described as the integral

Figure 6.1: Schematic drawing of edge and screw dislocations and dislocation elements

of displacement gradient,

$$\oint_L du_k = \oint \frac{\partial u_k}{\partial x_m} dx_m = -b_k \quad (6.1)$$

The equation implies that the increment $\bar{b}$ with the magnitude and direction equal to lattice vector can be viewed as an additional displacement generated by a particular deformation different from the elastic and other intrinsic distortions. In continuum model of dislocation, the overall effect of distortion/displacement doesn't destroy the continuity of the material. Such that the dislocation can be introduced into the defect-free medium by keeping the curl of the of total distortion field vanishing. Provided that dislocation is created by plastic deformation only, and the geometrically linear approximation is adopted for deformation, we have

$$\mathbf{F} - \mathbf{I} = \nabla \mathbf{u} = \nabla (\mathbf{u}^{el} + \mathbf{u}^{pl}) \quad (6.2)$$

Thus, the curl-free condition of the deformation gradient is equivalent to

$$\nabla \times \varpi = \nabla \times (\varpi^{el} + \varpi^{pl}) = 0 \quad (6.3)$$

where ϖ denotes the unsymmetrical distortion tensor of displacement gradient in this chap-

ter, i.e.

$$\varpi_{mk} = \frac{\partial u_k}{\partial x_m}, \varepsilon_{mk} = \frac{1}{2} (\varpi_{km} + \varpi_{mk}) \quad (6.4)$$

Utilizing Stokes' theorem, $dx_m \sim \epsilon_{ilm} df_i \frac{\partial}{\partial x_l}$, the integral round the contour L can be transformed into a surface integral S_L with the unit surface f_i . Thus, Eq.(6.1) is rewritten as

$$\oint_L du_k^{pl} = \oint_L \varpi_{mk}^{pl} dx_m = \oint_{S_L} \epsilon_{ilm} \frac{\partial \varpi_{mk}^{pl}}{\partial x_l} df_i = -b_k \quad (6.5)$$

Here, the integral over the surface has nonvanishing values only along the singular dislocation line, such that the integral must be solved by mean of delta function.

$$\epsilon_{ilm} \frac{\partial^2 u_k^{pl}}{\partial x_m \partial x_l} = -\tau_i b_k \delta(\xi) \quad (6.6)$$

Now we derive the force on the dislocation due to the local elastic stress created by external loading. Let an element dislocation τdl be displaced by an amount $\delta \mathbf{x}$, the area change of the dislocation loop is

$$\delta \mathbf{s} = \delta \mathbf{x} \times \tau dl, \quad i.e. \quad \delta s_k = \epsilon_{klm} \delta x_l \tau_m dl \quad (6.7)$$

In general, the work δW done by elastic stress in an infinitesimal displacement can be expressed as

$$\delta W = \int \sigma_{ik} \delta \varepsilon_{ik}^{pl} dV = \int f_l \delta x_l dl \quad (6.8)$$

In the case of slip, the very elastic stress creates the displacement increment (Burgers vector) of $\bar{\mathbf{b}}$ between both sides of the slip plane. Therefore, the work is

$$\delta W = b_i \delta \int \sigma_{ik} ds_k = b_i \int \sigma_{ik} \epsilon_{klm} \delta x_l \tau_m dl \quad (6.9)$$

Substituting the expression of unit area Eq.(6.7) into Eq.(6.9), the Peach-Koehler equation is derived

$$f_l = \epsilon_{lkm} \sigma_{ki} b_i \tau_m, \quad \mathbf{f} = (\boldsymbol{\sigma} \cdot \mathbf{b}) \times \boldsymbol{\tau} \quad (6.10)$$

Again with the property of the discontinuity represented by $\bar{\mathbf{b}}$ on an arbitrarily chosen surface spanning the dislocation loop, the displacement gradient and strain tensors due to the

dislocation are written in a form similar to the strain kinematic compatibility (Eq. 2.72) in conventional phase field method but including a delta singularity.

$$\begin{aligned}\varepsilon_{ik}^{pl} &= \frac{1}{2} (n_i b_k + n_k b_i) \delta(\xi) \\ \varpi_{ik}^{pl} &= n_i b_k \delta(\xi)\end{aligned}\quad (6.11)$$

where n_i is the component of slip plane normal.

Except for the above variables are in common with elasticity, several variables frequently used in continuum theory of dislocations are introduced. One is the dislocation density tensor describing the distribution of dislocation

$$\epsilon_{ilm} \frac{\partial \varpi_{mk}^{pl}}{\partial x_l} = -\rho_{ik} \quad (6.12)$$

An integral of ρ_{ik} over a surface S spanning any contour is equal to sum of the Burgers vectors $\bar{\mathbf{b}}$ for all the dislocation lines embraced by the contour

$$\int_{S_L} \rho_{ik} ds_i = b_k \quad (6.13)$$

With Eqs. (6.11) and (6.12), the dislocation density tensor of a single dislocation reads

$$\rho_{ik} = \tau_i b_k \delta(\xi) \quad (6.14)$$

The dislocation density tensor ρ_{ik} served as the state function is independent of whether the dislocations are at rest or motion. To describe the time evolution of the dislocation, the dislocation flux density tensor has to be introduced as follow

$$-j_{ik} = \frac{\partial \varpi_{ik}^{pl}}{\partial t} \quad (6.15)$$

By applying right-hand rule $n_i = (-\boldsymbol{\tau} \times \delta \mathbf{x})_i$, we can derive the flux density tensor for an isolate dislocation

$$\begin{aligned}j_{ik} &= -\frac{\partial \varpi_{ik}^{pl}}{\partial t} = -\frac{\partial n_i b_k \delta(\xi)}{\partial t} = -\frac{\epsilon_{ilm} \partial x_l \tau_m b_k \delta(\xi)}{\partial t} = \epsilon_{ilm} \rho_{lk} v_m \\ &= \frac{\epsilon_{ilm} \tau_l \partial x_m b_k \delta(\xi)}{\partial t} = \epsilon_{ilm} \tau_l v_m b_k \delta(\xi)\end{aligned}\quad (6.16)$$

where v is the velocity of the moving dislocation line. It is worthy of note that the trace of j_{ik} is proportional to the component of the velocity of dislocation along the normal of its slip plane. If the trace of $j_{kk} = 0$, the motion of the dislocation is conservatively slipping on the slip plane without any inelastic volume changes generated. Otherwise, the motion contains a non-conservative, vacancy/interstitial diffusion (climb) piece.

With the fundamental variables, the complete set of dynamic equations of elastic continuum with dislocations can be obtained. Generally, the plastic deformation is performing after the elastic deformation, thus, the sum of elastic displacement gradient ϖ_{ik}^{el} due to the transformation and the plastic displacement gradient ϖ_{ik}^{pl} originating from the motion of dislocations contribute the total displacement gradient ϖ , reads

$$\varpi_{ik} = \varpi_{ik}^{el} + \varpi_{ik}^{pl} \quad (6.17)$$

which is also valid in a system undergoing MT accompanying with dislocation evolution. Substituting the Eq.(6.17) into the definition of Eq.(6.15), the rates change of the elastic deformation is related with the dislocation flux density and the spatial derivative of velocity.

$$\frac{\partial \varpi_{ik}^{el}}{\partial t} = \frac{\partial \dot{u}_k}{\partial x_i} + j_{ik} \quad (6.18)$$

Moreover, differentiating with respect to time for Eq.(6.14) and to spatial coordinates for Eq.(6.15) give rise to a compatibility equation relating two tensors describing the evolution of dislocations.

$$\frac{\partial \rho_{ik}}{\partial t} + \epsilon_{ilm} \frac{\partial j_{mk}}{\partial x_l} = 0 \quad (6.19)$$

Eqs. (6.12) (6.18) and (6.19) coupled with the general equation of motion (3.8) constitute the complete set of dynamic equations of elastic continuum with dislocations [LL86].

6.2 Coarse-grained Model

In coarse-grained model of dislocation, the microscopic details associated with the crystal structure are taken into account by averaging in a mesoscale cell. Each mesoscopic cell contains a large number of crystal dislocations. The vector sum of microscale Burgers vectors $\bar{\mathbf{b}}$ within the mesoscale cell leads to net Burgers vector $\mathbf{B}$ served as one of the basic variables in coarse-grained dislocation model. If a finite number of discrete slip systems with specific $\bar{\mathbf{b}}$ are considered, the net Burgers vector $\mathbf{B}$ is expressed as

$$\mathbf{B} = \sum_s N^s \mathbf{b}^s \quad (6.20)$$

where N^s is the number of dislocations line with the Burgers vector $\bar{\mathbf{b}}^s$ in the slip system s . The density of net Burgers vector can be approximated by a Nye tensor field α_{ik} that is continuous throughout the entire space [Nye53]. The Nye tensor is formally similar to

Figure 6.2: Schematic illustration of the mesoscopic cell is represented in the entire solid black square, in which many crystallographic FCC unit cells are outlined in grey ; the slip planes (dotted lines in blue and red) correspond to two $\{110\}$ slip systems.

the dislocation density ρ_{ik} representing the net length of all dislocation lines per area of the mesoscale cell in this work.

$$\nabla \times \varpi^{pl} = \epsilon_{ilm} \frac{\partial \varpi_{mk}^{pl}}{\partial x_l} = -\alpha_{ik} = \sum_s D^s \tau_i^s b_k^s \quad (6.21)$$

where D^s is the scalar dislocation density representing the number of dislocation lines of slip system s per unit area. In line with α_{ik} , the mesoscale flux density tensor $\mathbf{J}$ is defined as

$$J_{ik} = \sum_s D^s \epsilon_{ilm} \tau_l^s v_m^s b_k^s \quad (6.22)$$

In our coarse-grained model coupling MT and dislocations, the complete set of dynamic equations, i.e. Eqs. (3.8), (6.12), (6.18) and (6.19), is not rigidly followed for simplicity. The general equation of motion is still used to evolve the total displacement and to dissipate

the excess energy towards the stress equilibrium state. The evolved displacements give rise to the updated total strain and displacement gradient in each time step. To overcome the difficulty evolving J_{ik} by using α_{ik} via Eq. (6.19), the evolution of plastic strain/deformation is realized via a phenomenologically overdamped equation detailed in the following paragraph, and the compatibility of $\mathbf{J}$ and $\boldsymbol{\alpha}$ is satisfied via the Peach-Koehler force.

In a system with finite discrete slip systems which are independent with each other, the Nye tensor is only dependent on the spatial temporal evolution of scalar dislocation density. Following the strategy of [GLS08], only the motion of crystal dislocations by glide in their corresponding slip planes is considered. The evolution of the scalar dislocation density is

$$\frac{\partial D^{s\pm}(\vec{r}, t)}{\partial t} = -L \nabla \cdot (\mathbf{F}_{glide}^{s\pm}(\vec{r}, t) D^{s\pm}(\vec{r}, t)) \quad (6.23)$$

where, $\mathbf{F}_{glide}^{s\pm}$ is the glide component of the Peach-Koehler force on the crystal dislocations with the densities $D^{s\pm}$ in the mesoscopic cell. Its value varies with position coordinates $\vec{r}$ and time t . Since the elastic stress tensor at arbitrary time and coordinates is evaluated via the general equation of motion, the components of the Peach-Koehler force on each crystal dislocation with the Burgers vector $\bar{\mathbf{b}}^s$ can be calculated via Eq. (6.10) [HL82, HB11]. Then, the $\mathbf{F}_{glide}^{s\pm}$ is determined by projecting the Peach-Koehler force on the corresponding slip plane

$$\mathbf{F}_{glide}^{s\pm} = (\mathbf{F}_{PK}^{s\pm} \cdot \mathbf{b}_0^{s\pm}) \mathbf{b}_0^{s\pm}, \quad \text{with} \quad \mathbf{b}_0^{s\pm} = \mathbf{b}^{s\pm} / |\mathbf{b}^{s\pm}| \quad (6.24)$$

The scalar dislocation densities with positive/negative Burgers vectors in each slip systems evolve independently following Eq. (6.23). To be consistent with evolution of α_{ik} , the plastic displacement gradient calculated with the definition of Eq. (6.15) but substituting the j_{ik} with mesoscale dislocation flux density tensor J_{ik} . This equation is exactly same as the conventional dynamic equation of plasticity

$$\frac{\partial \varepsilon^{pl}(\vec{r}, t)}{\partial t} = \sum_s \dot{\gamma}^s \frac{1}{|2\mathbf{b}^s|} (\mathbf{n}^s \otimes \mathbf{b}^s + \mathbf{b}^s \otimes \mathbf{n}^s) \quad (6.25)$$

Because there is

$$J_{ik} = - \sum_s D^s \frac{\partial n_i^s b_i^s}{\partial t} = \sum_s D^s \epsilon_{ilm} \tau_l^s v_m^s b_k^s \quad (6.26)$$

in our model, the specific slip system of dislocation with predefined $\bar{\mathbf{b}}$ and τ ensures the direction vectors of tensor J_{ik} and α_{ik} automatically satisfying compatibility Eq. (6.19). The self-consistence of the magnitudes of J_{ik} and α_{ik} can be achieved if the velocity of dislocation line v^s is assumed to be proportional to Peach-Koehler force. Same as the strategy of

Limkumnerd[LS06], we construct a flow rule of velocity for crystal dislocation and average dislocation in each mesoscale cell, which reads

$$\begin{aligned} \mathbf{v}^s &= L \mathbf{F}_{PK}^{s\pm} \\ \bar{\mathbf{V}} &= L \sum_s D^s \mathbf{F}_{PK}^{s\pm} \end{aligned} \quad (6.27)$$

Substituting the Peach-Koehler force into Eq. (6.26), $\|\mathbf{J}\| \propto (\mathbf{F}_{PK}^s \cdot \mathbf{b}_0^s)$ is same as that for α_{ik} evidenced in Eq.(6.23), if and only if L in Eqs. (6.26) and (6.27) has the same value for time evolution. A degenerated way is to directly evolve Eq. (6.25) for plastic strain, provided that $\dot{\gamma}^s = L$, which is widely used in phase field modeling. With the plastic strain/displacement gradient, the elastic strain in each time step, calculating with Eq. (6.17), will enter the general equation of motion for iteration of total displacement.

In comparison is the strain-based method developed by Gröger [GLS08, GLS10], in which the introduction of incompatibilities allows the coupling to dislocation behavior via a Nye tensor, and then the incompatibilities enter the long-range kernel of OP strains and evolve with OP strains to represent the microstructure of martensites and dislocations. It has advantages of clear physical picture but fails to describe the stress free state inside the martensite after the coupled transformation.

6.3 Simulations Procedures

In the chapter, except the single dislocation benchmark (subsection 6.4.1), the proposed model is exemplified in the 2D simulations for the coupled transformation in Fe-0.59wt%C and Fe-1.07wt%C steels. In the simulations, the X axis of simulation box coincides with the [100] direction of the crystal with the grain orientation of $\theta = 0$, and the Y axis is parallel to the [010] direction. The lattice directions in the grain with the grain orientation of $\theta = \pi/6$ are anticlockwise rotated by $\pi/6$. The benchmarks in this chapter only involve the edge dislocations with the dislocation lines along the Z axis perpendicular to the paper. In this 2D plane strain problem, the strain components relative to the third dimension vanish, however, the stress component of σ_{33} exists with the expression

$$\sigma_{33} = \frac{C_{12}}{C_{11} + C_{12}} (\sigma_{11} + \sigma_{22}) \quad (6.28)$$

And the Peach-Koehler force in 2D is simplified as

$$F_{PKk}^{s\pm} = \mp \epsilon_{jk} \sigma_{jl} b_l^s \quad (6.29)$$

in the numerical implementation of Eqs. (6.23) and (6.24). For simplicity, we consider only two slip systems in a FCC austenite with the Burgers vectors of $\frac{1}{2} \langle 110 \rangle$, which are evidenced as the active mode of glide accounting for plastic deformation in experiments [MHF⁺06, IMTK11]. Since each slip system contains crystal dislocations with positive and negative Burgers vectors, the scalar densities of these dislocations have to be treated separately. For specific, four independent scalar dislocation densities correspond to the Burgers vectors of $\mathbf{b}^{1\pm} = \pm 1/2[110]$ and $\mathbf{b}^{2\pm} = \pm 1/2[\bar{1}10]$, respectively. Figure 6.2 shows the schematic illustration of the dislocation configuration used in our benchmarks. In numerical simulations, most of the materials and simulation parameters are chosen the same as those in chapter 5. The scalar dislocation density ranging 0 to $6 * 10^{15} m^{-2}$ is given with different values for simulations. The Onsager coefficient in L in overdamped equations is set to 1. Other parameters will be given in the discussion of the microstructure results.

6.4 Microstructure Simulations

6.4.1 Evolution of Single Edge Dislocation

In order to demonstrate that our model is capable of describing the internal stress field around individual net dislocations by solving the set of modified motion equations, a benchmark for the stress field evolution with a single edge dislocation was carried out. The edge dislocation embedded in an isotropic austenite has dislocation line along the Z axis perpendicular to the paper, and Burgers vector directs toward the X axis. From the Figure 6.3 (a) and (b), the overall distribution of the calculated stress field around the edge dislocation is similar to that derived from the isotropic elasticity [HL82, HB11]. However, the stress fields of the dislocations will be altered when the evolution of dislocation is coupled with MT, especially when dislocations are located at interfaces, such as grain boundaries, habit planes, etc., where the stresses raised by MT cannot be thoroughly eliminated. Figure 6.3(c) and (d) show the morphology of martensites represented by the deviatoric strain e_2 and the deviatoric stress σ_2 undergoing a square-to-rectangular MT. The characteristic deviatoric strain e_2 of the lattice caused by an edge dislocation in the middle of the block is similar to the strain based TDGL results of [GLS08, GLS10]. However, our simulated stress field shows the internal stress is only accumulated around the dislocation, while a stress-free state is found in the interior parts of the perfectly formed martensite variants. It significantly differs from the strain-based scenario [GLS08].

Figure 6.3: Stress fields of (a) σ_{xx} and (b) σ_{yy} around one edge dislocation with its dislocation line perpendicular to paper and Burgers vector parallel to the X axis in austenite; (c) martensitic microstructure coupled with single dislocation represented by deviatoric strain e_2 ; (d) the corresponding deviatoric stress σ_2

6.4.2 MT with Dislocations

Figure 6.4 illustrates two physical scenarios of MT coupled with dislocations in steels. Figure 6.4(a-c) depicts the martensitic nucleation and growth against the dislocations, leaving the grain boundary nucleation playing secondary role. In the simulation, the scalar dislocation density is assumed to $6 * 10^{14} m^{-2}$ in accordance with the experiments [MSO⁺05, MNM03, RGFS06]; a smaller coupling coefficient κ_{12} is set to 1.25 for such MT with small dilatation volume change, as the low/medium carbon Fe-C alloys without substitutional elements. The motion of dislocations provides additional plastic strains superposition to the eigen-elastic strains, which might be generated accompanying with the precursors at the early stage of MT. The total strain promptly exceeds the 'strain spinodal' on the nonlinear

nonlocal energy surface, such that the intragranular nucleation precedes the grain boundary nucleation as is shown in Figure 6.4(b). Finally, the mixed microstructure with martensite and retained austenite is formed and characterized by the rougher twin boundary compared with sharp interface discovered in SMA. It is the most remarkable difference on morphology of martensites between SMAs and steels. A few of noticeable retained austenites represented in green are found to locate at twin boundaries, inside the martensite variants and in the regions surrounded by martensite package, as is shown in Figure 6.4(c).

Figure 6.4: MT in polycrystalline Fe-0.59wt.%C alloy coupled with the evolution of dislocation (scalar dislocation density $6 * 10^{14} m^{-2}$) with $\kappa_{12} = 1.25$ (a-c) and $\kappa_{12} = 4.0$ (d-f).

Figure 6.4(d-f) depicts another scenario of the grain boundary nucleation and growth surpassing the dislocation nucleation due to the large lattice-misfit strain introduced by $\kappa_{12} = 4.25$. In this simulation, the effect of dilatational volume change on the martensite morphology is also evidenced by the higher volume fraction of retained austenite and the butterfly like martensite variants in the grains, as apparently seen from the simulated microstructure of Fe-1.07wt.% C in Figure 6.5(d-f). Although the alloying elements are not included in simulation, the simulated microstructure well represents the typical appearance of martensites in high alloying steels, which implies that the alloying elements play their rules more via the geometry rather than the chemistry. The similar stories are also found in

the simulation results of Fe-1.07wt.%C alloy, see Figure 6.5.

Figure 6.5: MT in polycrystalline Fe-1.07wt.%C alloy coupled with the evolution of dislocation (scalar dislocation density $6 * 10^{14} m^{-2}$) with $\kappa_{12} = 1.25$ (a-c) and $\kappa_{12} = 4.25$ (d-f).

The magnified simulated microstructure of Fe-0.59wt.%C alloy is compared with the EBSD images of the martensite blocks and variants in Fe-0.0026wt.%C [MTK⁺03] and Fe-0.18wt.%C in Figure 6.6, where the rough twin boundaries between blocks are consistent with the twin boundaries in our simulation. What is noteworthy lies in that the 24 K-S variants appear generally in Fe-C alloy to form four sets of three composite blocks. Such three blocks in experiments correspond to three correspondence variants in Landau or phase field modeling for cubic-to-tetragonal MT, which are exactly derived from the Bain correspondence. In degenerated 2D case, only two martensite variants with opposite deviatoric strain, i.e. red and blue domains, exist in our simulation results. To account for the 24 K-S variants associated with the orientation relationship and the rigid body rotation of Bain strains, viz. to take slip martensite into simulation, the specific information of the dislocation reactions in particular slip systems should be incorporated to evaluate the contribution of plastic strain to MT, which is yet been realized in current coarse-grained dislocation model.

Figure 6.7(a) shows the simulated mixed microstructure of Fe-1.07wt.%C alloy after isothermal relaxation of the austenite at the quenching temperature to generate the marten-

Figure 6.6: (a) The simulated martensitic microstructure of Fe-0.59wt.%C alloy is compared with EBSD image of martensite variants in (b) Fe-0.0026wt.%C [MTK+03] and (c) Fe-0.18wt.%C steels

site and retained austenite. As is mentioned in previous paragraph, the effect of substitutional alloying elements to the orientation of habit plane is equivalently introduced by setting lattice misfit strain, here $\kappa_{12} = 4.25$. It is compared with the SEM microstructure image of Fe-1.07wt.%C-2.2Si-2.9Mn alloy subjected to the processing of water quenching and subsequent partitioning at 673K for 300s. The partitioned microstructure is used for validation since the domain boundaries in as-quenched microstructure are too ambiguous to be identified. Due to the formation of carbides inside the martensite in experiments does not ruin the overall shape of martensite, we utilized the partitioned microstructure as reference. In Figure 6.7(a), the two intersecting martensite variants in red with the crossing angle of $\pi/3$ is in good agreement with the observed martensite in Figure 6.7(b). Besides the plate martensites, a few of isolated martensites in small size are embedded in the austenite matrix. The trace of retained austenite is also found inside the martensite plate. Both of these microstructure features, indiscernible in the dislocation-free simulations, were readily identified in both simulations and experiments [TMR15].

To study the carbon partitioning behavior with dislocation, the isothermal relaxation of the coupled fields at 673K is implemented to represent the microstructure evolution of the as-quenched Fe-1.07wt.%C alloy followed by the partitioning. Due to the absence of the carbides and other diffusional phase transformations, the growth of the martensite cannot be retarded or halted at the very temperature lower than T_0 . In the simulated microstruc-

Figure 6.7: (a) The simulated mixed microstructure of martensite + retained austenite in as-quenched Fe-1.07wt.%C alloy with lattice misfit strain $\kappa_{12} = 4.25$ in comparison with (b) SEM image of martensite variants in Fe-1.07wt.%C-2.2Si-2.9Mn alloy [TMR15].

ture in Figure 6.8(a), a larger amount of retained austenite [in green in Figure 6.5(f)] are transformed into tempered martensite after the isothermal simulation for 60000 steps, leaving the retained austenite surrounded by the twins. Different from the tempered martensite with smaller size in dislocation-free simulation, the tempered martensites in Figure 6.8(a) have no significant distinctions in size and distribution from quenched martensites. Figure 6.8 (b) shows the distribution of carbon after partitioning. In contrast to the clear outlines of iso-composition planes aligning with the twin boundaries in the dislocation-free simulation, the distribution of carbon undergoing a dislocation involved diffusional phase transformation shows no distinctive shapes of iso-composition contours. Except for the clear evidence that the carbon element diffuses from martensite to austenite, the carbon elements more likely reside themselves in regions with higher dislocation density. In a region with coarse martensites separating the austenite [marked in a circle in Figure 6.8(a)], the carbon exhibits a similar distribution as that in the dislocation-free transformation. As is shown in the inset of Figure 6.8(b), the carbon content inside the martensite is lower than that of interface and the austenite. Figure 6.8(c) quantitatively describes the spatial distribution of carbon along the arrow direction. The values of composition in individual phases are in good agreement with the experimental results from EPMA and 3DAP [TMR15, TMH⁺14]. At the four interfaces indicated by green dashed lines, the segregation of carbon elements are noticeable in line with what were observed in the as-quenched microstructure. However, the pile-ups are not clearly shown in our simulated profile. The composition and the deviatoric strain are no

longer homogeneous inside the martensites due to the existence of dislocations, which has also been evidenced by experiments.

6.4.3 Limitation of the Model

Although our multi-fields model has ability to represent the stress field of dislocation and account for many experimental observations in viewpoint of interplaying of dislocation and transformation strain, our modified coarse-grained dislocation model is yet embryonic. The greatest shortcoming is that the Nye tensor measures the average dislocation density only and therefore regards the internal mechanical state utmost incompletely. Many features, like more complicated cross slip systems, dislocation tangling, yield surfaces, nucleation of new dislocations, etc., which are known to be macroscopically important in real materials, have been ignored in our model. While, it does incorporate the geometric constraints, long-range elastic interaction, and energetics driving the dislocation dynamics, but the dynamics remains suffering from many hypothesis. Therefore, it is yet developed into a mature method in comparison with the strain based dynamics driven by minimizing energy with a clear statement of incompatibility in geometry.

Figure 6.8: (a) The simulated mixed microstructure of Fe-1.07wt.%C alloy quenched to room temperature followed by partitioning at 673K for 60000 time steps. (b) The carbon distribution under the same conditions as (a). (c) The local composition profile of carbon corresponding to the region in the inset of (b). The simulation is implemented with lattice misfit strain $\kappa_{12} = 4.25$.

Chapter 7

Conclusions and Future Works

If we knew what it was we were doing, it would not be called research, would it?

-Albert Einstein

7.1 Conclusions

This thesis has provided deeper insights into the physical essentials of the various models of MTs and the Landau model of MT has been extended to be used in practical applications of engineering materials.

The comparison of the current models of MT led to the conclusion that, the models, rather than being isolated, share many common ingredients while cast their pronounced individual distinctiveness, and none of them is applicable to every aspect of the MT.

- Regarding the physical essentials of MT models
 - (1) All the models are common in energy minimization, either explicitly or implicitly;
 - (2) PTMCs and phase field models have a foundation on rigid body mechanics, while the Landau model is rooted in wave mechanics and crystal lattice dynamics;
 - (3) The microelasticity phase field and Landau models resort to Green's function based long-range integral kernel in Fourier space to represent the symmetry constraint on martensite microstructure, while the PTMC and thermomechanical phase field directly handle the kinematic compatibility and transformation strain in coordinate space;
 - (4) The Landau model equipped with finite strains, anharmonic and nonlocal energy in the linearized tensor space, and inertial dynamics is the most complete from the physics viewpoint and has ability to capture the complete dynamic behaviors of martensites.
- Regarding the application capabilities among the models,

(1) in thermodynamics, the PTMC and phase field methods- in contrast with the Landau model- has been widely used to study MTs coupled with various effects, including grain boundaries and dislocations. They also have advantages in describing habit plane, internal twinning and slip martensite. In this respect, the development of Landau model falls behind them.

(2) in dynamics, the Landau model is able to tackle all dynamics, ranging from inertial to full dissipative and from TDGL to statics, as such the phenomena due to the dynamics can readily be captured by Landau modeling. In contrast, the PTMC and phase field methods are only sufficient in statics and dissipative dynamics for the equilibrium microstructure and properties governed by dissipative dynamics.

To widen the applications of Landau model, it has been extended to analyze martensitic nucleation and growth in polycrystals, coupled with diffusional transformations (through integration with CALPHAD technique), and to incorporate the influence of dislocations. The new model has been used to provide a deeper understanding of the complex microstructure evolution during MTs in steels. In particular, the following objectives have been achieved:

- A modified Landau model was developed to describe the MTs in polycrystals based on the Lagrange-Rayleigh dynamics with the Landau energetics. The stress term in the dissipative force equation was reformulated in terms of the functional of local Landau energy with respect to global displacement gradients. The key microstructural features and their response to the external loads were in agreement with experimental observations and satisfied the kinematic compatibility condition in CM-PTMC. Therefore, the physical consistence between Landau model and CM-PTMC was identified and verified.

- The updated model was successfully applied to the martensitic nucleation problem in polycrystals. The simulated results manifest that the MT undergoing a non-classical transformation path led to a new classical 'C-shaped' relationship between the nucleation modes and the processing parameters such as external loading and temperature. It implied that the classical transformation path indeed corresponds to a thermodynamic limit of the non-classical paths.

- An attempt of semi-quantitative description for the displacive-diffusive coupled transformation was made by integrating the nonlinear-nonlocal Landau model with CALPHAD technique. The Landau free energy and the corresponding driving force were quantified from the CALPHAD type thermodynamic database, whereas the chemical mobility were expressed in the functions of atomic mobility that was again from the diffusion kinetic database. With the correct diffusion potential and real chemical mobility, the mechanism of partitioning of carbon in steels was proven an ordinary diffusion event governed by the diffusion potential and chemical mobility, which varied spatially and temporally. The carbon diffused

from martensite to austenite as a natural result of the difference of the mobilities between two phases.

- A simplified dislocation model based on the continuum theory was seamlessly 'embedded in' the Landau model of MTs. Together with the diffusional transformation model as a whole, the multi-field model succeeded in simulating the dissipative MT in steel rather than be limited in the SMAs or for functionalities only. Based on the simulations, the irregularities of microstructure, as rough twin boundaries and retained austenite within the martensite in steels was attributed to the effect of dislocations.

7.2 Future Works

The following tasks are proposed in the further

- Development of the Bales-Gooding dynamic model with 3D long-range compatibility kernel and 3D simulations for real materials with the combination of Landau energetics and Bales-Gooding dynamics.
 - Simulations of cubic-monoclinic II MTs by inertial dynamics.
 - Extension of displacive-diffusive coupled transformation model to multicomponent and multiphase system.
 - Incorporation of nucleation of dislocations, slip systems, dislocation tangling to the developed dislocation model in continuum theory.

Appendix A

Compatibility Kernel of Cubic-Tetragonal MT

Table A.1: Compatibility kernel of cubic-to-tetragonal MT on special planes and directions

	U_{22}		U_{23}		U_{23}	
$k_x \neq 0,$ $k_y \rightarrow 0,$ $k_z \rightarrow 0$	$\frac{k_x^2}{2(k_y^2 + k_z^2)}$	$\frac{N_y^2 N_z^2 k_x^2}{2(N_y^2 + N_z^2)}$	$\frac{\sqrt{3}k_x^2}{2(k_y^2 + k_z^2)}$	$\frac{\sqrt{3}N_y^2 N_z^2 k_x^2}{2(N_y^2 + N_z^2)}$	$\frac{3k_x^2}{2(k_y^2 + k_z^2)}$	$\frac{3N_y^2 N_z^2 k_x^2}{2(N_y^2 + N_z^2)}$
$k_y \neq 0,$ $k_x \rightarrow 0,$ $k_z \rightarrow 0$	$\frac{k_y^2}{2(k_x^2 + k_z^2)}$	$\frac{N_x^2 N_z^2 k_y^2}{2(N_x^2 + N_z^2)}$	$-\frac{\sqrt{3}k_y^2}{2(k_x^2 + k_z^2)}$	$-\frac{\sqrt{3}N_x^2 N_z^2 k_y^2}{2(N_x^2 + N_z^2)}$	$\frac{3k_y^2}{2(k_x^2 + k_z^2)}$	$\frac{3N_x^2 N_z^2 k_y^2}{2(N_x^2 + N_z^2)}$
$k_z \neq 0,$ $k_x \rightarrow 0,$ $k_y \rightarrow 0$	$\frac{2k_z^2}{(k_x^2 + k_y^2)}$	$\frac{2N_x^2 N_y^2 k_z^2}{(N_x^2 + N_y^2)}$	$\frac{3(k_x^2 - k_y^2)}{(k_x^2 + k_y^2)}$	3	0.5	0.5
$k_x \neq 0,$ $k_y \neq 0,$ $k_z \rightarrow 0$	$\frac{1}{2} \left(\frac{k_y^2}{k_x^2} + \frac{k_x^2}{k_y^2} \right) - 1$		$\frac{\sqrt{3}}{2} \left(\frac{k_y^2}{k_x^2} - \frac{k_x^2}{k_y^2} \right)$		$\frac{3}{2} \left(\frac{k_y^2}{k_x^2} + \frac{k_x^2}{k_y^2} \right) + 5$	
$k_x \neq 0,$ $k_z \neq 0,$ $k_y \rightarrow 0$	$12 \left(\frac{k_x^2}{k_z^2} + \frac{4k_z^2}{k_x^2} + 7 \right)$		$-\frac{\sqrt{3}}{2} \left(\frac{k_x^2}{k_z^2} + 3 \right)$		$\frac{1}{2} \left(\frac{3k_x^2}{k_z^2} + 1 \right)$	
$k_z \neq 0,$ $k_y \neq 0,$ $k_x \rightarrow 0$	$\frac{1}{2} \left(\frac{k_x^2}{k_z^2} + \frac{4k_z^2}{k_x^2} + 7 \right)$		$\frac{\sqrt{3}}{2} \left(\frac{k_x^2}{k_z^2} + 3 \right)$		$\frac{1}{2} \left(\frac{3k_x^2}{k_z^2} + 1 \right)$	

Appendix B

Compatibility Kernel of Cubic-Trigonal MT

In cubic-to-trigonal MT, the non-OPs e_1 , e_2 , and e_3 can be written in terms of OPs shear strains

$$e_{i=1,2,3} = \sum_{s=4,5,6} N_{is} e_s \quad (\text{B.1})$$

where, the matrix of N_{is} is

$$\begin{pmatrix} N_{14} & N_{15} & N_{16} \\ N_{24} & N_{25} & N_{26} \\ N_{34} & N_{35} & N_{36} \end{pmatrix} = \begin{pmatrix} \frac{(k_x^2 - k_y^2 - k_z^2)}{2\sqrt{3}O_4} & \frac{(k_y^2 - k_z^2 - k_x^2)}{2\sqrt{3}O_5} & \frac{(k_z^2 - k_x^2 - k_y^2)}{2\sqrt{3}O_6} \\ \frac{(k_x^2 + k_y^2)}{(2k_z^2 + k_x^2 - k_y^2)} & \frac{- (k_x^2 + k_y^2)}{(2k_z^2 - k_x^2 + k_y^2)} & \frac{- (k_x^2 - k_y^2)}{(2k_z^2 + k_x^2 + k_y^2)} \\ \frac{2\sqrt{2}O_4}{2\sqrt{6}O_4} & \frac{2\sqrt{2}O_5}{2\sqrt{6}O_5} & \frac{2\sqrt{2}O_6}{2\sqrt{6}O_6} \end{pmatrix} \quad (\text{B.2})$$

The harmonic energy of non-OP strains is reformulated as

$$\hat{f}_{non-OP} = \sum_{i=1,2,3} \frac{A_i}{2} |\hat{e}_i(k)|^2 = \sum_{l,l'=4,5,6} \frac{A_1}{2} U_{l,l'}(k) \hat{e}_l(k) \hat{e}_{l'}^*(k) \quad (\text{B.3})$$

Therefore, the compatibility kernel is derived

$$U_{l,l'}(k) = \frac{v}{A_1} \sum_{i=1,2,3} A_i N_{il} N_{il'} \quad (\text{B.4})$$

Following the strategy in Subsection 2.4.11, the values of compatibility kernel at special points in Fourier space are listed in Table B.1.

Table B.1: Compatibility kernel of cubic-to-trigonal MT on special planes and directions

	$k_x \neq 0,$ $k_y \rightarrow 0,$ $k_z \rightarrow 0$	$k_y \neq 0,$ $k_x \rightarrow 0,$ $k_z \rightarrow 0$	$k_z \neq 0,$ $k_x \rightarrow 0,$ $k_y \rightarrow 0$	$k_x \neq 0,$ $k_y \neq 0,$ $k_z \rightarrow 0$	$k_x \neq 0,$ $k_z \neq 0,$ $k_y \rightarrow 0$	$k_z \neq 0,$ $k_y \neq 0,$ $k_x \rightarrow 0$
N_{14}	$\frac{k_x^2}{2\sqrt{3}k_yk_z}$	$\frac{-k_y}{2\sqrt{3}k_z}$	$\frac{-k_z}{2\sqrt{3}k_y}$	$\frac{k_x^2 - k_y^2}{2\sqrt{3}k_yk_z}$	$\frac{k_x^2 - k_z^2}{2\sqrt{3}k_yk_z}$	$\frac{-1}{2\sqrt{3}} \left(\frac{k_y}{k_z} + \frac{k_z}{k_y} \right)$
N_{15}	$\frac{-k_x}{2\sqrt{3}k_z}$	$\frac{k_y^2}{2\sqrt{3}k_xk_z}$	$\frac{-k_z}{2\sqrt{3}k_x}$	$\frac{k_x^2 - k_y^2}{2\sqrt{3}k_xk_z}$	$\frac{-1}{2\sqrt{3}} \left(\frac{k_x}{k_z} + \frac{k_z}{k_x} \right)$	$\frac{k_y^2 - k_z^2}{2\sqrt{3}k_xk_z}$
N_{16}	$\frac{-k_x}{2\sqrt{3}k_y}$	$\frac{-k_y}{2\sqrt{3}k_x}$	$\frac{k_z^2}{2\sqrt{3}k_xk_y}$	$\frac{1}{2\sqrt{3}} \left(\frac{k_x}{k_y} + \frac{k_y}{k_x} \right)$	$\frac{k_z^2 - k_x^2}{2\sqrt{3}k_xk_y}$	$\frac{k_z^2 - k_y^2}{2\sqrt{3}k_xk_y}$
N_{24}	$\frac{k_x^2}{2\sqrt{2}k_yk_z}$	$\frac{k_y}{2\sqrt{2}k_z}$	0	$\frac{-k_x^2 - k_y^2}{2\sqrt{2}k_yk_z}$	$\frac{k_x^2}{2\sqrt{2}k_yk_z}$	$\frac{k_y}{2\sqrt{2}k_z}$
N_{25}	$\frac{-k_x}{2\sqrt{2}k_z}$	$\frac{-k_y^2}{2\sqrt{2}k_xk_z}$	0	$\frac{k_x^2 + k_y^2}{2\sqrt{2}k_xk_z}$	$\frac{-k_x}{2\sqrt{2}k_z}$	$\frac{-k_y^2}{2\sqrt{2}k_xk_z}$
N_{26}	$\frac{-k_x}{2\sqrt{2}k_y}$	$\frac{k_y}{2\sqrt{2}k_x}$	0	$\frac{1}{2\sqrt{2}} \left(\frac{k_y}{k_x} - \frac{k_x}{k_y} \right)$	$\frac{-k_x}{2\sqrt{2}k_y}$	$\frac{k_y}{2\sqrt{2}k_x}$
N_{34}	$\frac{k_x^2}{2\sqrt{6}k_yk_z}$	$\frac{-k_y}{2\sqrt{6}k_z}$	$\frac{2k_z}{2\sqrt{6}k_y}$	$\frac{k_y^2 - k_x^2}{2\sqrt{6}k_yk_z}$	$\frac{k_x^2 + 2k_z^2}{2\sqrt{6}k_yk_z}$	$\frac{1}{2\sqrt{6}} \left(\frac{2k_z}{k_y} - \frac{k_y}{k_z} \right)$
N_{35}	$\frac{-k_x}{2\sqrt{6}k_z}$	$\frac{k_y^2}{2\sqrt{6}k_xk_z}$	$\frac{2k_z}{2\sqrt{6}k_x}$	$\frac{k_x^2 - k_y^2}{2\sqrt{6}k_xk_z}$	$\frac{1}{2\sqrt{6}} \left(\frac{2k_z}{k_x} - \frac{k_x}{k_z} \right)$	$\frac{2k_z^2 + k_y^2}{2\sqrt{6}k_xk_z}$
N_{36}	$\frac{-k_x}{2\sqrt{6}k_y}$	$\frac{-k_y}{2\sqrt{6}k_x}$	$\frac{-k_z^2}{2\sqrt{6}k_xk_y}$	$\frac{-1}{2\sqrt{6}} \left(\frac{k_x}{k_y} + \frac{k_y}{k_x} \right)$	$\frac{-2k_z^2 - k_x^2}{2\sqrt{6}k_xk_y}$	$\frac{2k_z^2 + k_y^2}{2\sqrt{6}k_xk_y}$

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