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# Phase-field approach to surface-induced phase transformations and dislocations

by

Mahdi Javanbakht

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Major: Mechanical Engineering

Program of Study Committee: Valery I. Levitas, Major Professor Pranav Shrotriya Baskar Ganapathysubramanian

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Ames, Iowa

2013

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## DEDICATION

I would like to dedicate this thesis to my dear Imam, Hazrat Sahib Al-Zaman Mahdi (A. S.), and to my mother and father for all the sacrifices and prayer they made for me.

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#### CHAPTER 1. Introduction

#### Martensitic phase transformations

Martensitic phase transformations play a very important part in material science, being responsible for formation of unique microstructure, mechanical properties, and material phenomena in steels, shape memory alloys and ceramics. Martensitic phase transformation is the first-order, displacive, and diffusionless transformation. During cooling or mechanical loading, crystal lattice of the cubic phase, austenite (A), transforms to the lower-symmetry lattice of martensite (M). Due to symmetry of the crystal lattice, there is always a finite numbers of crystallographically equivalent martensitic variants  $M_i$  (Fig.1.1). Typical microstructure during transformation consists of a fine mixture of martensitic variants and residual austenite (Fig.1.1). The width of each martensitic variant plate is of the order of magnitude of several to several tens of nanometers and is determined by the interplay of elastic energy of internal stresses and interfacial energy between both martensite and austenite and martensitic variants.

#### Martensitic phase transformations and plastic deformation

Various material phenomena related to martensitic PTs and plastic deformation due to twinning and dislocations are of fundamental and technological importance. Examples are: heat and thermomechanical treatment of material to obtain desired structure and properties; pseudoelasticity, pseudoplasticity, one- and two-way SME in SMAs; transformation-induced plasticity (TRIP); synthesis of materials under high pressure and



Figure 1.1 Scheme of phase transformation of cubic austenitic crystal lattice into three crystallographically equivalent and symmetry-related tetragonal lattices of martensitic variants. Martensitic microstructure in a sample is shown in the lower left corner.

high pressure with large plastic deformations, e.g., during ball milling; and PTs during friction, surface treatment, and projectile penetration. Even in bulk materials, nucleation of martensite, twin, or dislocation is a nanoscale phenomenon. Typical structure after PT represents nanotwinned martensite. A semicoherent phase interface has a width of 1 nm and possesses dislocations, which determine interface mobility and martensite morphology. With development of the nano science and technology, PT and plasticity are studied in nano particles, films, and wires, for smart nanosystem applications. The current trend in the synthesis of materials with high strength and ductility is based on a combination of nanograined or nanotwinned materials with PTs. The main challenges in the above problems are the lack of a deep understanding of the basic physics and mechanics of the interaction between PTs and plasticity at the nanoscale, because of luck of the corresponding theory and simulation techniques.

Application of stresses causes transformation between martensitic variants and changes the resultant deformation. The evolution of a multivariant martensitic nanostructure and microstructure during PT determines deformational properties of materials and the possibility of actuation and/or energy absorption. Utilization of PT-related phenomena leads in a number of cases to the unique mechanical properties that combine high strength with high plasticity, which in some cases is reversible, and consequently high energy absorption. Since PT parameters can be controlled e.g., by alloying or plastic deformationmechanical properties can be controlled as well. PT causes plastic deformations even in SMAs, which are assumed to deform elastically. Dislocations are accumulated during cycling, leading to residual strain and spoiling pseudoelastic properties. Accommodation of transformation strain in some steels is accompanied by large plastic deformation even without external stresses. Dislocations generated in a weaker austenite are inherited by growing martensite, which leads to arrest of martensitic growth and morphological transition from plate to lath martensite (Fig. 1.2)<sup>59</sup>.

#### Phase field theory of multivariant phase transformations

There are a number of continuum theories that determine parameters of nanostructure during phase transformations<sup>1-5</sup>, assuming some geometry. Alternatively, a phasefield or Ginzburg-Landau (GL) approach was broadly applied to model the evolution of nanostructure without a priori geometric assumptions and the simulation of various aspects of multi-variant martensitic  $PTs^{6-37}$ . The key advantage of the phase-field approach is that the computation of the microstructure evolution proceeds without additional efforts being required to guess a possible scenario and to track multiple interfaces.



Figure 1.2 TEM micrograph of lath martensite microstructure in Ferrium C69 steel showing dislocation substructure associated with plastic accommodation during martensitic growth.

The phase-field approach plays a unique role, being intermediate between the atomistic and continuum thermodynamic approaches. While resolving detail at the nanoscale (e.g., interface width and the thickness of transformed surface layer are of the order of 1 nm), it allows us to consider samples and process time much larger than in atomistic simulations. It also allows loading with a realistic strain rate. On the other hand, it contains much more information and requires more theoretical effort than traditional thermodynamic approaches, because thermodynamic potential in the phase-field approach is determined for all intermediate states between phases and at interfaces. Despite the significant progress in GL simulation<sup>6-37</sup>, it is based on models that contain a minimum of physics – i.e., just conceptual ideas that lead to first-order PT. Such models have been called by Krumhansl<sup>19</sup> **pedagogical** models. Namely, the local thermodynamic potential G has minima corresponding to A and M<sub>i</sub>, and isotropic gradient energy without coupling between martensitic variants is used. Thus, this method represented a more

numerically convenient approach for evolution of martensitic microstructure rather than physically based modeling; a lot of basic physics and mechanics have to be included. Recently, significant basic and applied interest arose in phase transformations in nanosize samples – i.e., in nanoparticles, nanowires, and nanofilms, as well as in nanograined polycrystalline materials (Figs.1.3, 1.4, 1.5, and 1.6), see<sup>38-41</sup>. In this case, surface-induced pre-transformation and transformation phenomena, interface and surface tension, and scale effect play essential roles, changing thermodynamics, kinetics, and nanostructure. Comprehensive study of a combination of multiple nonlinearities and phenomena (large elastic, transformation strains and rotations; multivariant phase transformations; twinning; nonlocal interaction; surface tension; variable surface energy) will definitely lead to the discovery of new nanostructures, mechanisms, phenomena, and qualitative and quantitative regularities of interaction between phase transformations and surface effects at the nanoscale. As an example, one of the remarkable recent efforts in the literature is related to studying of nanotwinned materials, in particular copper, that exhibit a combination of high strength (~ 1GPa) and elongation (up to 0.14)<sup>42, 43</sup>, see Fig.1.5. In principle, nanograins with nanotwinned structure can be created as a result of martensitic phase transformations. All these motivated us to study the phase transformations and surface effects at the nanoscale.



Figure 1.3 Martensite in nanocrystalline NiTi shape memory alloy<sup>40</sup>.



Figure 1.4 Tensile stress strain curves of nanostructured TiNi shape memory wire obtained by cold drawing to different degrees of reduction in cross sectional area during drawing<sup>44</sup>.

Recently, in <sup>45-47</sup>, a sophisticated thermodynamic Gibbs potential is developed that allowed us to describe some conceptually important features of known experimental stress-strain curves for shape-memory alloys, steel, and ceramics. Namely, the transformation strain tensor is independent of temperature (in agreement with crystallographic theory<sup>48</sup>), phase transformation starts at nonzero tangent elastic moduli, temperature dependence of stress hysteresis is controlled and can be negligible, and all thermomechanical properties of A and martensitic variants  $M_i$  are introduced into the theory for arbitrary symmetry of  $M_i$ . Large-strain formulation and simulations are presented in <sup>49</sup>. The importance of dynamics is demonstrated in<sup>50</sup>. The threshold-type (athermal) interface friction is introduced in<sup>54, 55</sup>, which allowed us to describe multiphase stationary microstructures and the theory was extended for a microscale in<sup>56</sup>. Examples of the phase field simulations are presented in Fig.1.7. Newly, a more sophisticated PF theory to PTs is presented in<sup>51, 52</sup> which represents a correct surface tension at interfaces, introduces a new gradient term to control martensite-martensite interface energy, and



Figure 1.5 (a) TEM image of the microstructure of Cu sample after tensile straining showing nanotwins and dislocations; (b) tensile stress-strain curve for nano-twinned Cu with 20-100nm twin spacing, a nanocrystalline Cu (mean grain size ~ 30nm), and a coarse-grained polycrystalline Cu (mean grain size>  $100\mu m$ )<sup>43</sup>.

suggests a noncontradictory expression for variable surface energy. Also, the external surface layer is introduced in<sup>53</sup> and the effect of the width of the external surface layer and internal stresses on surface-induced pretransformation and phase transformations (PTs) are revealed.

The evolution of martensitic microstructure is described in terms of the evolution of the *n* order parameters  $\eta_i$  associated with  $i^{th}$  martensitic variant  $M_i$ . Each order parameter  $\eta_i$  varies from 0, corresponding to A, to 1, corresponding to  $M_i$ . The local Helmholtz free energy depends on elastic strain, temperature, and all order parameters  $\eta_i$ . In addition to the local contribution, the Helmholtz energy includes a part depending on the gradient of the order parameter  $\nabla \eta_i$ , which is concentrated at the finite-width interface between phases and reproduces the interface energy. The evolution of the order parameters and multivariant martensitic microstructure is described by *n* Ginzburg-Landau equations, which represent the linear relationships between the rate of change of the order parameters,  $\dot{\eta}_i$ , and generalized thermodynamic forces conjugate to them.

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Figure 1.6 Nucleation of martensite phase near surface with edges in a sample under tensile stress is shown. Atoms detected as martensite are larger sphere. Nucleation sites are emphasized by circles or pointed out by arrows. In the 1D model they are typically found at the corner edges of the specimen, whereas in the 3D model they exist everywhere. The 2D model shows the importance of free surface most intuitively. All of the nucleation sites in 2D model are found on free surfaces<sup>41</sup>.

#### Phase field theory of dislocations

There are significant achievements in the large scale simulation of dislocations based on the PFA<sup>12, 37, 47, 60-67</sup>. However, the PFA to dislocations developed in<sup>37, 12</sup> is based on a formalism similar to the PFA for martensitic PTs developed in<sup>16</sup> and shares a similar shortcomingnamely, that the equilibrium values of the Burgers vector and the plastic strain depend on the stress. There are a number of additional drawbacks<sup>69</sup>. Some of them were resolved in<sup>69</sup>, including large-strain formulation, stress-independent Burgers vector, objective (i.e., independent of the numerical mesh) dislocation height,



Figure 1.7 Examples of the phase field simulations of martensitic nano- and microstructure. (a) Formation of the stationary multivariant nanostructure (four internally twinned nanograins) after introduction of an athermal threshold in the GL theory ( $^{54, 55}$ ); (b) Distribution of M<sub>2</sub> in a cubic sample for dynamic problem ( $^{50}$ ); (c) Stress-induced martensite in the polycrystalline sample based on the microscale theory ( $^{56, 57}$ ); (d) barrierless nucleation at two dislocation dipoles; (e) barrierless surface-induced nucleation.

and lack of artificial stress oscillations. Dislocation reactions, such as the combination and dissociation of complete dislocations into partial dislocations have been addressed  $in^{60-68}$ but with the drawbacks mentioned above.

#### Interaction between PT and dislocations

The interaction between PT and dislocations is the most basic problem in the study of martensite nucleation and growth<sup>26, 28, 29, 70-73</sup>. There are a number of analytical treatments based on PFA to PT<sup>74-76</sup>, followed by numerical 2-D<sup>28, 77</sup> and advanced 3-D <sup>12, 78</sup> simulations. Dislocations are introduced through their stationary stress field rather than as an evolving phase field. Recently<sup>79</sup>, a simplified PFA for PT and dislocation was developed, in which, dislocations were located at the moving phase interface only. PFA for martensitic PT with continuum dislocation theory is presented in<sup>80</sup>, but we are interested in discrete dislocations. Both approaches<sup>79, 80</sup> have all drawbacks of the approaches to PT and dislocations mentioned above. In<sup>69</sup>, some problems on interactions between PT and dislocations using a simplified version of PFA are solved.

#### Thesis organization

In chapter 2, the PF theory for multivariant martensitic phase transformations is advanced in three directions: the potential is developed that introduces the surface tension at interfaces; a mixed term in gradient energy is introduced to control the martensitemartensite interface energy independent of that for austenite-martensite; and a noncontradictory expression for variable surface energy is suggested. In chapter 3, an in-detail study of martensite–martensite interface energy and width is presented and the effect of the martensite-martensite interface energy and grain size on the stationary and nonstationary nanostructure inside the transforming grain embedded in the austenitic matrix is determined. Also, the effect of finite element discretization on the interface energy and width is studied. In chapter 4, the external surface layer as a transition between external and internal phases is included in GL theory, and the effect of the width of this layer and internal stresses on surface-induced pretransformation and phase transformations (PTs) are revealed. In chapter 5, the PF theory to dislocations is conceptually advanced in the following directions: (a) Large strain formulation is developed. (b) A new local potential is developed to eliminate stress-dependence of the Burgers vector and to reproduce desired local stress-strain curve, as well as the desired, mesh-independent, dislocation height for any dislocation orientation. (c) A new gradient energy is defined to exclude localization of dislocation within height smaller than the prescribed height but does not produce artificial interface energy and dislocation widening. In chapter 6, PF theory to coupled evolution of martensitic phase transformations (PTs) and dislocation is developed, and the following problems are studied: hysteretic behavior and propagation of an austenite (A) – martensite (M) interface with incoherency dislocations for temperatureinduced PT; evolution of phase and dislocation structures for stress-induced PT, and the growth and arrest of martensitic plate for temperature-induced PT.

#### **Experimental Observation**

Here, we present some experimental observations, which can be explained with our simulations.

1. It is known that in polycrystalline sample not all austenite transforms to martensite (Fig.1.8)<sup>12</sup>. We found also that residual austenite remains in single crystalline sample as well, see Figs.2.1, 3.1, 3.9, and 3.11.

2- For relatively large  $M_i$ - $M_j$  interface energy, martensite-martensite interface splits producing region of austenite between martensitic variants and the triple junction of two martensitic variants and austenite, see Fig.2.1. Such a mechanism of a barrierless austenite nucleation at  $M_i$ - $M_j$  interface was observed experimentally in <sup>58</sup>, see Fig.1.9.

3. For the transforming grain embedded in austenitic matrix, for very high overcooling the nanostructure in Figs. 3.9 and 3.11 resembles the alternating twin structure predicted by crystallographic theory and observed experimentally, see Fig.1.10 in<sup>48</sup>.



Figure 1.8 Microscope image of full phase transformation, it is indicated that the specimen contains a combination of martensite and residual austenite<sup>12</sup>.



Figure 1.9 Optical micrograph, the triple junction among martensitic phases and austenite  $^{58}$ .

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Figure 1.10 A high resolution transmission electron micrography of fine twinning in  $NiAl^{48}$ .

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# CHAPTER 2. Surface tension and energy in multivariant martensitic transformations: phase-field theory, simulations, and model of coherent interface

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#### Abstract

The Ginzburg-Landau theory for multivariant martensitic phase transformations is advanced in three directions: the potential is developed that introduces the surface tension at interfaces; a mixed term in gradient energy is introduced to control the martensite-martensite interface energy independent of that for austenite-martensite; and a noncontradictory expression for variable surface energy is suggested. The problems of surface-induced pretransformation, barrierless multivariant nucleation, and the growth of an embryo in a nanosize sample are solved to elucidate the effect of the above contributions. The obtained results represent an advanced model for coherent interface.

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## Introduction

Phase-field or Ginzburg-Landau (GL) modeling represents a unique approach for simulation of various aspects of stress-induced multivariant martensitic phase transformations (PTs)<sup>1</sup>. Recently<sup>2</sup>, we developed a much more sophisticated Landau potential to make the theory conceptually consistent with known experimental data for shapememory alloys, steel, and ceramics. The athermal resistance to interface motion is introduced<sup>3</sup>, and the theory is extended for large strain<sup>4</sup>, dynamics<sup>5</sup>, and microscale<sup>6</sup>. In these approaches and below, each of the n-order parameters  $\eta_i$  varies from 0 (corresponding to A) to 1 (corresponding to martensitic variant M<sub>i</sub>). This part of our work advances the GL approach in three directions.

a) Since the thickness of martensitic variants is of the order of 1 nm and they possess sharp tips, surface tension should play a significant role in the nucleation and evolution of martensitic nanostructure. However, we are not aware of any publications on this topic. We introduce proper terms in the energy potential, resulting in an expression for the surface tension for multivariant PTs that are thermodynamically consistent and consistent with a sharp-interface limit. The nontrivial points in this consideration are that even for negligible small strains we have to use a large strain formulation, consider the gradient of the order parameters with respect to a deformed configuration, and introduce the ratio of mass densities in the nondeformed and deformed states  $\rho_0/\rho$  in some terms. Note that even for liquid-liquid and liquid-solid interfaces, for which expressions for surface tension have been known for decades, they are not completely consistent with a sharpinterface limit because they result in additional hydrostatic pressure<sup>7</sup>. Inconsistency with a sharp-interface approach means that a theory contains internal contradictions. We resolved this problem for liquid-liquid and liquid-solid interfaces as well.

b) Differences in the surface energies of different phases result in surface-induced phenomena – e.g., surface premelting, ordering or disordering, and barrierless nucleation<sup>8</sup> - however, it was not considered for martensitic PTs. The main drawback of previous works is that the utilized expression for surface energy  $q(\eta) = a + b\eta^2$  allows for a solution for the homogeneous parent phase ( $\eta = 0$ ) but does not allow for a homogeneous solution for the product phase – i.e., the product phase always has a surface structure toward the alternative phase, even when this phase is completely unstable. This also leads to unphysical regions in the phase diagram<sup>8</sup>. Here, we derive the expression for  $q(\eta)$  that does not possess the above problems, generalize it for multivariant PTs, and study surface-induced pretransformation and barrierless nucleation of multiple martensitic variants.

c) The current form of the gradient energy results in the energy  $E_{MM}$  of the  $M_i$ - $M_j$ interface to be twice of energy  $E_{AM}$  of A- $M_i$  interface (see below), while in reality it is independent of the energy of the A- $M_i$  interface and is significantly larger. We generalize the expression for gradient energy by introducing the products  $\nabla \eta_i \cdot \nabla \eta_j$  in order to be able to control the energy of  $M_i$ - $M_j$  interface independently. The resultant GL equations became coupled through Laplacians, in addition to traditional coupling.

Combining all of the above advancements, the coupled system of time-dependent GL equations for all order parameters, the continuum mechanical equations, and the boundary conditions are formulated. The finite element method (FEM) approach, algorithm, and subroutines are developed using the COMSOL code<sup>9</sup>. Model problems of surface-induced pretransformation, barrierless multivariant nucleation, and nanostructure evolution in a nanosize sample are solved, and the effect of the above contributions is elucidated. The obtained results represent a more detailed, flexible, and precise model for coherent solid-solid interface than current phenomenological models<sup>10</sup>.

We designate contractions of tensors  $\mathbf{A} = \{A_{ij}\}$  and  $\mathbf{B} = \{B_{ji}\}$  over one and two indices as  $\mathbf{A} \cdot \mathbf{B} = \{A_{ij} B_{jk}\}$  and  $\mathbf{A} : \mathbf{B} = A_{ij} B_{ji}$ , respectively. The subscripts s, e, and t mean symmetrization and elastic and transformational strains;  $\mathbf{I}$  is the unit tensor;  $\overset{\circ}{\nabla}$  and  $\nabla$  are the gradient operators in the undeformed and deformed states; and  $\otimes$  designates a dyadic product.

# Model

Let us define the Helmholtz free energy per unit undeformed volume  $\psi = \psi(\boldsymbol{B}, \eta_i, \nabla \eta_i, \theta)$ , where  $\boldsymbol{B} = 0.5(\boldsymbol{V} \cdot \boldsymbol{V} - \boldsymbol{I})$  is the finite strain measure,  $\boldsymbol{V}$  is the left stretch tensor, and  $\theta$  is the temperature. Traditional thermodynamic procedure for the thermodynamic potential depending on  $\nabla \eta_i$  and linear relationships between thermodynamic forces and fluxes leads to

$$\boldsymbol{\sigma} = \frac{\rho}{\rho_0} \boldsymbol{V} \cdot \frac{\partial \psi}{\partial \boldsymbol{B}} \cdot \boldsymbol{V} - \sum_{i=1}^n \frac{\rho}{\rho_0} \left( \boldsymbol{\nabla} \eta_i \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \right)_s; \qquad \frac{1}{L} \frac{\partial \eta_i}{\partial t} = -\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \eta_i} |_{\boldsymbol{B}} + \boldsymbol{\nabla} \cdot \left( \frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \right),$$
(1)

where L is the kinetic coefficient,  $\boldsymbol{\sigma}$  is the true Cauchy stress tensor, and  $\partial \psi / \partial \eta_i$  is calculated at  $\boldsymbol{B} = const$ . While theory was developed for large strains similar to<sup>4</sup>, to make it more accessible we simplify it for small elastic and shear transformation strains and rotations but keep finite volumetric transformation strain, where necessary. This is the minimum requirement for the correct introduction of surface tension. For this case, kinematics looks like the following

$$\boldsymbol{\varepsilon} = (\stackrel{\circ}{\boldsymbol{\nabla}} \boldsymbol{u})_s, \quad \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_t,$$
(2)

where  $\boldsymbol{u}$  is displacement,  $\boldsymbol{\varepsilon} = 1/3\varepsilon_0 \boldsymbol{I} + \boldsymbol{e}$  is the total strain tensor, and  $\varepsilon_0$  and  $\boldsymbol{e}$  are the volumetric and deviatoric contributions to strain. Also, for simplicity we assume that  $\psi$  is an isotropic function of  $\boldsymbol{\varepsilon}_e$  and  $\nabla \eta_i$ ,  $\psi = \bar{\psi}(\boldsymbol{\varepsilon}_e, \eta_i, \theta, \nabla \eta_i) = \bar{\psi}(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t, \eta_i, \theta, \nabla \eta_i) = \psi(\varepsilon_0, \boldsymbol{e}, \eta_i, \theta, \nabla \eta_i)$ . Functions  $\psi$  and  $\boldsymbol{\varepsilon}_t$  are accepted in the form

$$\psi = \psi^{e}(\varepsilon_{0}, \boldsymbol{e}, \eta_{i}, \theta) + \frac{\rho_{0}}{\underline{\rho}} \check{\psi}^{\theta} + \psi^{\theta} + \frac{\rho_{0}}{\underline{\rho}} \psi^{\nabla};$$
  

$$\psi^{\theta} = \sum_{k=1}^{n} \frac{1}{3} A_{0}(\theta - \theta_{e}) \eta_{k}^{2}(3 - 2\eta_{k}) - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \eta_{i}^{2} \eta_{j}^{2}(\eta_{i} + \eta_{j}) A_{0}(\theta - \theta_{e});$$
(3)

$$\psi^{\nabla} = \frac{\beta}{2} \left( \sum_{i=1}^{n} |\nabla \eta_i|^2 + b \sum_{i=1}^{n} \sum_{j=1, i \neq j}^{n} \nabla \eta_i \cdot \nabla \eta_j \right); \qquad \frac{\rho_0}{\rho} = 1 + \varepsilon_0; \tag{4}$$

$$\breve{\psi}^{\theta} = \sum_{k=1}^{n} A_0(\theta_e - \theta_c) \eta_k^2 (1 - \eta_k)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} F_{ij}(\eta_i, \eta_j);$$
(5)

$$\boldsymbol{\varepsilon}_{t} = \sum_{k=1}^{n} \boldsymbol{\varepsilon}_{t}^{k} (a\eta_{k}^{2} + (4-2a)\eta_{k}^{3} + (a-3)\eta_{k}^{4}) - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \eta_{i}^{2} \eta_{j}^{2} (\eta_{i}\boldsymbol{L}_{ij} + \eta_{j}\boldsymbol{L}_{ji}), \quad (6)$$

$$F_{ij}(\eta_i, \eta_j) = \eta_i \eta_j (1 - \eta_i - \eta_j) \{ B[(\eta_i - \eta_j)^2 - \eta_i - \eta_j] + C \eta_i \eta_j \} + \eta_i^2 \eta_j^2 (\eta_i + \eta_j) (\bar{A} - A_0(\theta_e - \theta_c)).$$
(7)

Here,  $\mathbf{L}_{ij} = (a-3)\boldsymbol{\varepsilon}_t^j + 3\boldsymbol{\varepsilon}_t^i$ ,  $\psi^e = \frac{1}{2}K\varepsilon_{0e}^2 + \frac{1}{2}\mu \boldsymbol{e}_e:\boldsymbol{e}_e$  is the elastic energy with equal (for compactness) bulk K and shear  $\mu$  moduli;  $\theta_e$  and  $\theta_c$  are the equilibrium temperature and temperature for the loss of stability of A;  $\boldsymbol{\varepsilon}_{ti}$  is the transformation strains of the *ith* variant; i = 0 corresponds to A;  $\beta$  is the gradient energy coefficient; and  $A_0$ ,  $\bar{A}$ , B, C, a, and b are parameters. Then Eq.(31) looks like

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_{st}; \quad \boldsymbol{\sigma}_e = \frac{\partial \psi}{\partial \varepsilon_0} \boldsymbol{I} + \frac{1}{(1 + \varepsilon_0)^{2/3}} \frac{\partial \psi}{\partial \boldsymbol{e}} = K \varepsilon_{0e} \boldsymbol{I} + \frac{\mu}{(1 + \varepsilon_0)^{2/3}} \boldsymbol{e}_e; \quad (8)$$

$$\boldsymbol{\sigma}_{st} = (\psi^{\nabla} + \breve{\psi}_{\theta})\boldsymbol{I} - \beta \sum_{i=1}^{n} (\boldsymbol{\nabla}\eta_{i} \otimes \boldsymbol{\nabla}\eta_{i} + b\boldsymbol{\nabla}\eta_{i} \otimes \sum_{j=1, i \neq j}^{n} \boldsymbol{\nabla}\eta_{j});$$
(9)

$$\frac{1}{L}\frac{\partial\eta_i}{\partial t} = \frac{\rho}{\rho_0} (K\varepsilon_{0e}\boldsymbol{I} + \mu\boldsymbol{e}_e): \frac{d\boldsymbol{\varepsilon}_t}{d\eta_i} - \frac{\rho}{\rho_0}\frac{\partial\psi^\theta}{\partial\eta_i} - \frac{\partial\breve{\psi}^\theta}{\partial\eta_i} + \beta(\boldsymbol{\nabla}^2\eta_i + b\sum_{j=1, i\neq j}^n \boldsymbol{\nabla}^2\eta_j), \quad (10)$$

where  $\sigma_{st}$  is the surface tension. For a single order parameter (,e.g., for liquid-liquid and liquid-solid interfaces) and a phase equilibrium condition,  $\frac{\beta}{2} |\nabla \eta|^2 = \check{\psi}_{\theta}^2$ , and we have

$$\boldsymbol{\sigma}_{st} = \beta |\boldsymbol{\nabla}\eta|^2 (\boldsymbol{I} - \boldsymbol{k} \otimes \boldsymbol{k}); \quad \boldsymbol{k} = \boldsymbol{\nabla}\eta / |\boldsymbol{\nabla}\eta|.$$
(11)

Here,  $\boldsymbol{k}$  is the unit normal to the interface. Thus,  $\boldsymbol{\sigma}_{st}$  represents two equal normal stresses acting along the interface, i.e., like surface tension in the sharp-interface approach. Since  $\beta |\nabla \eta|^2$  is the total  $\eta$ -related energy, its integration along the  $\boldsymbol{k}$  gives the total interface energy, such as for sharp-interface. For liquid-liquid and liquid-solid interfaces<sup>7</sup>,  $\boldsymbol{\sigma}_{st}$ contained extra hydrostatic pressure, which was inconsistent with sharp-interface results. Our approach resolves this problem for these interfaces as well.

Let us discuss obtained equations. The main difference between the current and our previous formulation for energy  $Eq.(7)^{2, 4}$  is in the underlined terms and in using the gradient operator  $\nabla$  with respect to the deformed state. When  $\rho_0 \simeq \rho$ , b = 0, and  $\nabla \simeq \overset{\circ}{\nabla}$ ,  $\psi$  is equivalent to that in<sup>2, 4</sup>. It looks like it is not a significant change, but that is exactly what is necessary (excluding  $b \neq 0$ ) to introduce surface tension for martensitic PT and to make it consistent with a sharp-interface approach. The nontriviality of the results is related to the fact that for small strain it is customary to assume that  $\rho_0 \simeq \rho$  and  $\nabla \simeq \overset{\circ}{\nabla}$ . However, this results in  $\sigma_{st} = 0$ . The point is that even for absolutely negligible strain  $d(\frac{\rho_0}{\rho})/d\varepsilon_0 = 1$ , which results in hydrostatic contribution to surface tension. Also, generalized rate  $\overline{\nabla \eta} = \nabla \dot{\eta} - \nabla \eta \cdot \nabla v$  (where v is the velocity vector), due to convective term, results in additional gradient-related surface tension. Thus, a physical phenomenon (surface tension) is introduced using simply geometric nonlinearities. In addition to the luck of the idea that the finite-strain theory should be used, the reason why the surface tension theory was not developed before is that the finite-strain theory was just developed in<sup>4</sup>. Introducing the product  $\nabla \eta_i \cdot \nabla \eta_j$  allows us to control the width and energy of the  $M_i - M_j$  interface independent of A-M<sub>i</sub> interfaces. This, however, complicates GL Eq.(19) by coupling them through Laplacians. Also, an important consequence of Eq.(19) is that surface tension does not contribute to the driving force for PT directly; rather, it affects the driving force by changing stress distribution. The above equations should be supplemented by the equilibrium equation  $\nabla \cdot \boldsymbol{\sigma} = 0$ .

## Variable surface energy

Variable surface energy generates the boundary conditions

$$\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \cdot \boldsymbol{n} = \frac{\partial \psi^{\nabla}}{\partial \boldsymbol{\nabla} \eta_i} \cdot \boldsymbol{n} = \beta (\nabla \eta_i + b \sum_{j=1, i \neq j}^n \boldsymbol{\nabla} \eta_j) \cdot \boldsymbol{n} = -\frac{dq}{d\eta_i},$$
(12)

which generalize known conditions<sup>8</sup> for the 3D case, multiple order parameters, and mixed terms in the gradient energy. Here,  $\boldsymbol{n}$  is the normal to the boundary. We assume

that in the simplest case  $q(\eta_i)$  depends on single "equivalent" order parameter  $p = (\sum_{i=1}^n \eta_i^2)^{0.5}$ . Then, q(p) has the following properties:  $q(0) = \gamma_A$ ;  $q(1) = \gamma_M$ ;  $\frac{dq(0)}{dp} = \frac{dq(1)}{dp} = 0$ , with  $\gamma$  for the surface energy of phases. The last condition ensures that homogeneous states  $\eta_i = 0$  and  $\eta_i = 1$  satisfy boundary conditions, which was not the case in previous works<sup>8</sup>. The simplest polynomial expression that satisfies the above condition is

$$q(p) = \gamma_A + \Delta \gamma (\bar{a}p^2 + (4 - 2\bar{a})p^3 + (\bar{a} - 3)p^4),$$

where  $0 < \bar{a} < 6$  guarantees the monotonic character of q(p) and  $\Delta \gamma = \gamma_M - \gamma_A$ . It is possible to show that to make a condition of barrierless surface-induced nucleation consistent with a sharp-interface result  $\Delta \gamma > E$ , where E is interface energy, we need to choose  $\bar{a} = 3$ . Then  $q(p) = \gamma_A + \Delta \gamma (3p^2 - 2p^3)$ .

## Examples

We use in the calculations material parameters for cubic to tetragonal PT in NiAl found in<sup>2</sup>,  $L = 2596.5m^2/Ns$ ,  $\Delta \gamma = -0.4J/m^2$ , and b = 0.5, unless otherwise stated. The FEM approach and code COMSOL<sup>9</sup> were used. For plane stress 2D problems, two M<sub>i</sub> are considered with the components of  $\varepsilon_t$  (0.215, -0.078, -0.078) and (-0.078, 0.215, -0.078). A rectangular sample was considered and quadrilateral and triangle Lagrange elements with quadratic approximation were employed.

#### Verification

To test numerical procedure, plane interface propagation was considered. Good correspondence with analytical solutions in<sup>2, 3</sup> was found. To avoid internal stresses,  $\varepsilon_t^y = 0$  was chosen along with  $\varepsilon_t^x = 0.05$  and  $\gamma_t = 0.1$ . For example, for temperature  $\theta = \theta_e = 215K$ , normal  $\sigma_x = 1GPa$ , and shear stress  $\tau = -0.3GPa$  the interface velocity is 993.4 m/s (998.0 in<sup>3</sup>). The energy of the A-M interface is  $E = 0.2244J/m^2$  (0.2244 in

<sup>2</sup>). For the limit case of liquid-liquid interface, jump in pressure  $\Delta p = 2E/r$ , where r is the radius of an interface.

#### Effect of b on M-M energy

The effect of b on the energy  $E_{MM}$  of  $M_j$ - $M_i$  interface was studied. Condition  $\psi^{\nabla} \ge 0$ implies that  $b \le 1$ . We found that  $E_{MM} = kE_{AM}$  with k = 2 for b = 0, k = 1.523for b = 0.5, k = 0.692 for b = 0.9, k = 0.486 for b = 0.95, and k = 0 for b = 1. Interface width reduces with the growth of b to zero at b = 1. Variation of b changes the nanostructure evolution significantly since it changes the energy balance.

#### Surface-induced nucleation for single martenistic variant

For a NiAl single variant, surface-induced nucleation was considered in a  $10 \times 10 nm$ sample for free boundaries and  $\theta = 0K$  (see animation 1 in the supplementary materials <sup>11</sup>). Surface energy was constant everywhere, excluding a 1nm part from each side of the x (symmetry) axis at the right-hand boundary. Only half of the sample is considered. For the case with surface tension, a small surface-induced nucleus appeared and reached stationary shape. Without surface tension, the nucleus slowly grows mostly along the side, and after reaching some size, grows fast under  $40^{0}$  to the y axis and reaches the upper horizontal side. Then the interface reaches the upper corner, after which PT propagates toward the left-hand side and completes in the entire sample. For the same sample at  $\theta = 180K$ , but with  $\gamma = const$  everywhere and a preexisting surface nucleus with  $2 \times 2nm$  size symmetric with respect to the x axis at the right-hand boundary, the nucleus disappears for the case with surface tension (see animation  $2 \text{ in}^{11}$ ). Without surface tension, it almost disappears, but a small value  $\eta = 0.2$  propagates along the vertical side. After it reaches the corner, the completely transformed region propagates from the symmetry axis up and then propagates through the sample as a vertical diffuse interface.

#### Surface-induced nucleation for two martenistic variants

For two variants and a sample with  $100 \times 100 nm$ , the following boundary conditions were applied. Vertical sides are stress-free, zero displacement is applied to the upper horizontal side, and symmetry boundary conditions are used for the x axis. Boundary condition (12) with  $\Delta \gamma \neq 0$  is applied to the right vertical line and with  $\Delta \gamma = 0$  to other lines. The initial conditions are  $\eta_i = 0.001$  and zero stresses in the entire sample. The lowest temperature, when a nontrivial stationary surface-induced nanostructure exists, is 90.5K without surface tension and 81.1K with surface tension [Fig. 2.1(a)] (for b = 0in Eq.(12), it is 87.95K for  $\boldsymbol{\sigma}_{st} = 0$  and 80.90K for  $\boldsymbol{\sigma}_{st} \neq 0$  [Fig. 2.1(d)], and the transformation path is quite different. At 90.4K for  $\sigma_{st} = 0$  and at 81.0K for  $\sigma_{st} \neq 0$ , this nanostructure becomes unstable, and PT spreads in the entire sample with nontrivial path (see animation 3 in the supplementary materials<sup>11</sup>). A wedge-type nanostructure consisting of two variants propagates from the free surface and forms the stationary solutions, which consist of two intersecting  $M_2$  plates inside a  $M_1$  matrix for  $\sigma_{st} = 0$  and four plates forming a quadrilateral shape for  $\sigma_{st} \neq 0$ . Surprisingly, regions of residual A are observed at the intersection of plates, forming a triple junction. Surface tension leads to a curved  $A-M_2$  interface, change in the width of the  $M_2$  plate, and some other details [Figs. 2.1(b) and 2.1(c)].

#### Preexisting embryo with two martenistic variants

The evolution of a preexisting embryo of 2 nm radius with  $\eta_i = 0.1$  at the center of a  $60 \times 60nm$  sample under biaxial tensile stresses of 20GPa at  $\theta = 100K$  and  $\gamma = const$ everywhere was considered [Fig. 2.2 and<sup>11</sup>]. The evolution starts with the splitting of the embryo into two martensitic variants separated by austenite. Without surface tension, new nuclei appear at the surface near the corners and the symmetry axis and grow faster than the preexisting nucleus. With surface tension, such a nucleation occurs at a later stage, martensitic variants grow along the symmetry axis and reach the surface. Thus,



Figure 2.1 Distribution of  $\eta_1 - \eta_2$  for the upper part of a  $100 \times 100nm^2$  sample and variable surface energy at the right vertical line. (a) At the lowest temperature, when stationary surface-induced nanostructure exists at 90.5K without surface tension and 81.1K with surface tension (the 10 nm part of the sample is shown); (b) and (c) stationary nanostructures at 90.5K for  $\boldsymbol{\sigma}_{st} = 0$ and at 81.1K for  $\boldsymbol{\sigma}_{st} \neq 0$ ; (d) At the lowest temperature, when stationary surface-induced nanostructure exists for b = 0 in Eq.(12) at 87.95K for  $\boldsymbol{\sigma}_{st} = 0$  and 80.90K for  $\boldsymbol{\sigma}_{st} \neq 0$ . The variant M<sub>1</sub> (M<sub>2</sub>) correspond to positive (negative) values of  $\eta_1 - \eta_2$  as indicated by the shade (color) box.

the PT paths for the two cases are completely different. A complex multiconnected nanostructure passes through the coalescence stage and finally ends in a single-variant state that is different for the two cases.

Note that various phenomenological models of coherent interface exist (see reviews <sup>10</sup>) based on the theory of thin shell and interface constants that are unknown. As a byproduct of the current work, we obtained a much more detailed, flexible, and precise model of a coherent interface, which takes into account the heterogeneity of all properties and  $\varepsilon_t$ ,  $\sigma_{st}$ ,  $\varepsilon$ , and  $\sigma$  along the interface thickness, as well as heterogeneous surface tension and surface stresses. The importance of finite interface width and surface tension is

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Figure 2.2 Evolution of  $\eta_1 - \eta_2$  for preexisting embryo of 2 nm radius with  $\eta_i = 0.1$  at the center of a  $60 \times 60 nm^2$  sample under biaxial tensile stresses of 20GPa at  $\theta = 100K$  with and without surface tension. Quarter of sample is considered.

demonstrated in the example of the A-M interface, in which  $M_1$  is rotated by  $36.5^0$  to get  $\varepsilon_t^y = 0$  [Fig. 2.3]. In this case, for sharp interface we obtained a stress-free solution. For a diffuse interface and  $\sigma_{st} = 0$ , even while  $\varepsilon_t^y = 0$  everywhere, there is a significant  $\sigma^y$  stress with concentration near the corner. The surface tension  $\sigma_{st}^y$  exceeds this  $\sigma^y$  by a factor of more than 2, and it changes the distribution of  $\sigma^y$ , increasing significantly the tensile stress and moving its concentration to the center of the sample. In general, interface thickness and structure adjust themselves during loading; the interface can appear and disappear, and there are intersecting interfaces, triple junction, and corner points, which are separate problems for the sharp-interface approach.

In summary, GL theory for multivariant PTs is advanced to describe surface tension,  $M_i$ - $M_j$  interface energy, and variable surface energy in a noncontradictory manner. FEM solutions for surface-induced, pretransformation, barrierless, multivariant nucleation, and the growth of the embryo and nucleus in a nanosize sample allowed us to elucidate the effect of the above contributions. Note that for smaller external stresses and transformation strain, the effect of surface tension will be even more pronounced. Stationary multivariant surface structures, residual A in the region of intersection of



Figure 2.3 (a) Plots of component  $\sigma_{st}^y$  of surface tension, as well as total stress  $\sigma^y$  for the case without and with surface tension, along the line passing through the center of a  $10 \times 10 nm^2$  sample. Variant  $M_1$  is rotated by  $36.5^0$  to get  $\varepsilon_t^y = 0$  at the A-M<sub>1</sub> interface; (b) and (c) show the distribution of  $\sigma^y$  for the case without and with surface tension, respectively.

martensitic plates, the junction of three phases, and the nontrivial dynamics of PT are revealed.

Note that the residual austenite observed in NiTi shape memory alloy under conditions when it was completely unexpected<sup>12</sup>, can be at least partially explained by our simulations. The obtained results also represent an advanced model for coherent interface. Similar developments can be applied for various phenomena involving interfaces, such PTs (liquid-liquid, melting, amorphization, evaporation, electromagnetic, and reconstructive PTs), diffusive PTs described by Cahn-Hilliard theory, twinning, dislocations, fracture, grain growth and recrystallization, as well as gradient plasticity and damage.

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# CHAPTER 3. Phase-field approach to martensitic phase transformations: effect of martensite–martensite interface energy

Modified from a paper published in the International Journal of Materials Research Valery I. Levitas<sup>\*</sup> and Mahdi Javanbakht<sup>†</sup>

# Abstract

A generalization of the phase-field theory for multivariant martensitic phase transformations is suggested that allows one to vary martensite–martensite interface energy independent of energy for austenite–martensite interface. The finite element method is utilized to solve the coupled phase-field and elasticity equations. Width and energy of the austenite–martensite interfaces are determined. Splitting of the martensite-martensite interface into two austenite-martensite interfaces, leading to barrierless austenite nucleation, is obtained. The effect of the martensite–martensite interface energy and grain size on the stationary and non-stationary nanostructure inside the transforming grain embedded in the austenitic matrix is determined. Some nano-structures differ essentially from the prediction of crystallographic theory. Relationships between the number of twins in grain vs. grain size and width of twin vs. its length are found. Two unexpected stress-relaxation mechanisms at the boundary of transforming grain are revealed.

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# Introduction

Martensitic phase transformations play a very important part in materials science, being responsible for formation of unique microstructures, mechanical properties, and material phenomena in steels, shape memory alloys and ceramics. Martensitic phase transformation is a first-order, displacive, and diffusionless transformation. During cooling or mechanical loading, the crystal lattice of the cubic phase, austenite (A), transforms to the lower-symmetry lattice of martensite (M). Due to symmetry of the crystal lattice, there is always a finite number of crystallographically equivalent martensitic variants  $M_i$ . The typical microstructure during transformation consists of a fine mixture of martensitic variants and residual austenite. The width of each martensitic variant plate is of the order of magnitude of several to several tens of nanometers and is determined by the interplay of elastic energy of internal stresses and interfacial energy between both martensite and austenite and martensitic variants. There are a number of continuum theories that determine the parameters of such a nanostructure<sup>1-4</sup>, assuming some geometry. Alternatively, a phase-field or Ginzburg–Landau (GL) approach was broadly applied to model the evolution of nanostructure without a priori geometric assumptions <sup>6-13</sup>. However, some basic mechanics and physics are still missing in the phase-field equations. Recently, in<sup>14-16</sup>, we developed a sophisticated thermodynamic Gibbs potential that allowed us to describe some conceptually important features of known experimental stress-strain curves for shape-memory alloys, steel, and ceramics. Namely, the transformation strain tensor is independent of temperature (in agreement with crystallographic theory<sup>17</sup>), phase transformation starts at nonzero tangent elastic moduli, temperature dependence of stress hysteresis is controlled and can be negligible, and all thermomechanical properties of A and martensitic variants  $M_i$  are introduced into the theory for arbitrary symmetry of  $M_i$ . Large-strain formulation and simulations are presented in<sup>18</sup>. The importance of dynamics is demonstrated in<sup>19</sup>. The threshold-type (athermal) interface friction is introduced in<sup>20, 21</sup>, which allowed us to describe multiphase stationary microstructures. The interface tension is introduced in<sup>22, 23</sup>. Surface-induced phenomena caused by the reduction in surface energy during transformation are described in<sup>22, 23</sup> and the theory was extended for a microscale in<sup>24</sup>.

The evolution of martensitic microstructure is described in terms of the evolution of the *n* order parameters  $\eta_i$  associated with *i*<sup>th</sup> martensitic variant  $M_i$ . Each order parameter  $\eta_i$  varies from 0, corresponding to A, to 1, corresponding to  $M_i$ . The local Helmholtz free energy depends on the elastic strain tensor, temperature, and all order parameters  $\eta_i$ . In addition to the local contribution, the Helmholtz energy includes a part depending on the gradient of the order parameter  $\nabla \eta_i$ , which is concentrated at the finite-width interface between phases and reproduces the interface energy. The evolution of the order parameters and multivariant martensitic microstructure is described by *n* Ginzburg–Landau equations, which represent the linear relationships between the rate of change of the order parameters,  $\dot{\eta}_i$ , and generalized thermodynamic forces conjugate to them.

One of the remaining problems is related to the current form of the gradient energy,  $\psi^{\nabla} = \frac{\beta}{2} (\sum_{i=1}^{n} |\nabla \eta_i|^2)$ , where  $\beta$  is the gradient energy coefficient. Since  $\psi^{\nabla}$  depends on the single material parameter  $\beta$  only, it is clear that it is impossible to vary the energy  $E_{\rm MM}$  of the martensitic variant  $M_i$  – martensitic variant  $M_j$  interface independent of the energy  $E_{\rm AM}$  of the austenite A – martensitic variant  $M_i$  interfaces. In fact, as will be shown below, for neglected coupling with mechanics,  $E_{\rm MM} = 0.5E_{\rm AM}$ , while in reality energy  $E_{\rm AM}$  is independent of the energy  $E_{\rm MM}$  and may be essentially larger. In this chapter, the expression for gradient energy is generalized by adding the products  $\nabla \eta_i \cdot \nabla \eta_j$  with an additional material parameter b, which allows us to change the energy of the  $M_i-M_j$  interface independently of that for  $A - M_i$  interfaces. This results in more sophisticated GL equations, which become coupled through Laplacian operators, in addition to the usual coupling due to local energy terms. Note that while models with multiple gradient energy parameters had already been introduced for martensitic<sup>14</sup> and ferroelectric transformations<sup>28, 29</sup>, they never were applied for study of  $M_i-M_j$  interface. The finite element method (FEM) approach, algorithm, and subroutines are developed using COMSOL Multiphysics code<sup>25</sup>.

Detailed analytical study of the  $\mathsf{M}_1\text{-}\mathsf{M}_2$  interface has been performed in  $^{7,\ 16,\ 26}$  for the case in which it is described by a single-order parameter that has opposite signs for the two variants. Both elastic stresses and surface tension were neglected. Here, we will numerically study the  $\mathsf{M}_1\text{-}\mathsf{M}_2$  interface for cubic to tetragonal transformation, when each variant is described by a separate order parameter and both elastic stresses and surface tension are taken into account. A coupled system of two GL equations and equations of elasticity theory, suggested in<sup>22</sup>, are used. Solutions are found in a nanosize slab under stress-free boundary conditions and plane stress formulation. The effect of the material parameter b that changes  $M_1-M_2$  interface energy with respect to A - M interface energy is studied in detail, and analytical approximations for  $M_1$ - $M_2$  interface energy and width are obtained. Heterogeneous internal stress fields (both elastic and surface tension) are obtained for the case in which a sharp-interface approach suggests a stress-free solution. For relatively large  $M_1-M_2$  interface energy, barrierless austenite nucleation within the  $M_1-M_2$  interface is obtained in the region of stability of martensite, when temperature reduces to the thermodynamic equilibrium temperature. The width of the austenitic region increases toward the free surface, and triple a junction between austenite and two martensitic variants is observed.

Multivariant nanostructure in a nanograin embedded in austenitic matrix was studied as well. For very large overcooling, it resembles finely twinned structure (in agreement with crystallographic theory<sup>17</sup>). However, the small grain size causes deviation from straight interfaces, the width of martensitic variants varies, and non-complete martensitic variants and broadened interfaces are observed. For smaller overcooling, the nanostructure contains a lot of residual austenite, split  $M_1-M_2$  interfaces and triple junctions, as well as incomplete martensite, and it is much different from the prediction of crystallographic theory. Reduction in martensite-martensite interface energy leads to reduction in twin width, increase in the number of completed variants, reduction of residual austenite, and to sharper interfaces. Some quantitative characteristics of nanostructure as well as specific stress-relaxation mechanisms are found. The effect of the finite element size on the martensite-martensite interface width and energy is studied, and conditions for mesh-independence of the solution are found. It is demonstrated that when element size exceeds the interface width, the obtained nanostructure differs significantly from the correct solution and leads to a wrong conclusion that it is independent of the  $M_1-M_2$ interface energy.

The obtained results represent a more sophisticated and precise model for coherent solid-solid interface than current phenomenological sharp-interface models reviewed in <sup>5, 27</sup>. Our phase-field solution resolves interface structure and heterogeneities of all fields along and across the interface, exhibits heterogeneous elastic stresses and surface tension, and demonstrates the evolution of the interface structure including splitting the interface into two interfaces and the formation of a triple junction as well as the effect of crossing of a free surface.

The chapter is organized as follows. In Section 2, a system of coupled phase-field and elasticity equations is presented and discussed. The numerical procedure is outlined in Section 3. Section 4 contains a description of all our results and concluding remarks are presented in Section 5.

Contractions of tensors  $\mathbf{A} = \{A_{ij}\}$  and  $\mathbf{B} = \{B_{ji}\}$  over one and two indices are designated as  $\mathbf{A} \cdot \mathbf{B} = \{A_{ij} B_{jk}\}$  and  $\mathbf{A} \cdot \mathbf{B} = A_{ij} B_{ji}$ , correspondingly. The subscript s designates symmetrization of a second-rank tensor; the subscripts e and t are utilized for elastic and transformational contributions to the total strain;  $\otimes$  is used for a dyadic product of two vectors;  $\boldsymbol{I}$  is the second-rank unit tensor; and  $\stackrel{\circ}{\nabla}$  and  $\nabla$  designate the gradient operators in the undeformed and deformed states. Some preliminary results have been presented in the short letter<sup>22</sup>.

## System of coupled phase-field and elasticity equations

In this Section, we summarize and discuss the main equations from<sup>22</sup>. The total system of equations is presented in Box 1 for n martensitic variants and specified for 2 variants.

To make the theory from<sup>22</sup> more accessible and to focus on our main problem, we simplify it for small-strain formulation. However, to correctly introduce surface tension we will consider finite displacements and keep some terms, which are usually neglected in small-strain formulation. The motion of the elastic material with phase transformations is described by a vector function  $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$ , where  $\mathbf{r}_0 - \mathbf{r}$  are the positions of material points in the undeformed  $\Omega_0$  and the deformed  $\Omega$  states, respectively; and t is the time. Material in the reference configuration is in the austenitic state. We introduce traditional decomposition Eq. (6) of the strain tensor  $\boldsymbol{\varepsilon} = (\overset{\circ}{\nabla} \boldsymbol{u})_s$  into elastic  $\boldsymbol{\varepsilon}_e$  and transformational  $\boldsymbol{\varepsilon}_t$  parts, where  $\boldsymbol{u}$  is the displacement vector. Eq. (6) also contains decomposition of strain into volumetric  $\varepsilon_0$  and deviatoric  $\boldsymbol{e}$  contributions and an expression for the ratio of the mass density in undeformed  $\rho_0$  and deformed  $\rho$  states in terms of volumetric strain  $\varepsilon_0$ . Transformation strain  $\boldsymbol{\varepsilon}_t$  determines the locally unloaded (i.e., stress-free) state of material point. For phase transformation between austenite A and the *i*<sup>th</sup> martensitic variant  $\mathbf{M}_i$ , the order parameter  $\eta_i$  is unambiguously related to the corresponding transformation strain  $\boldsymbol{\varepsilon}_{ti}$ , which is determined by crystallography. When the order parameter  $\eta_i$  changes between 0 for A and 1 for  $M_i$ , the transformation strain varies between zero and  $\boldsymbol{\varepsilon}_{ti}$ . In general, transformation strain  $\boldsymbol{\varepsilon}_t$  depends on all order parameters  $\eta_i$  and is determined by Eq. (4); *a* is the material parameter.

The Helmholtz free energy per unit undeformed volume  $\psi = \bar{\psi}(\boldsymbol{\varepsilon}_{e}, \eta_{i}, \boldsymbol{\nabla}\eta_{i}, \theta)$ , where  $\theta$  is the temperature, can be presented with the help of kinematic decomposition Eq. (6) and Eq. (4) as  $\psi = \overline{\psi}(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t, \eta_i, \boldsymbol{\nabla}\eta_i, \theta) = \psi(\boldsymbol{\varepsilon}, \eta_i, \boldsymbol{\nabla}\eta_i, \theta)$ . That is, it can be expressed in terms of total strain or elastic strain and different functions of the order parameters, which is convenient in transferring some equations from  $^{22}$ . The Helmholtz free energy consists of four contributions (Eq. (6)): the elastic part  $\psi^e(\varepsilon_0, \boldsymbol{e}, \eta_i, \theta)$ , the thermal part  $\psi^{\theta}$  that is responsible for the driving force for phase transformation, the thermal part  $\frac{\rho_0}{\rho}\breve{\psi}^{\theta}$  that is responsible for the barrier between phases, and the gradient energy  $\frac{\rho_0}{\rho}\psi^{\nabla}$ . Elastic energy Eq. (7) is accepted in the simplest isotropic form with equal bulk K and shear  $\mu$  elastic moduli of phases. Since elastic strains are much smaller than the transformational strains, neglecting anisotropy and change in elastic moduli does not change any conclusion. The thermal part of free energy is divided into two components,  $\psi^{\theta}$  (Eq. (7)) and  $\check{\psi}^{\theta}$  (Eq. (10)), one of them  $\check{\psi}^{\theta}$  is multiplied in Eq. (6) by the density ratio  $\rho_0/\rho$  (the reason will be discussed below). In Eqs. (7)–(11),  $\theta_e$  is the thermodynamic equilibrium temperature for stress-free A and M,  $\theta_{\rm c}$  is the critical temperature at which stress-free A loses its thermodynamic stability; A is the barrier for transformation between martensitic variants, similar to  $A_0(\theta_e - \theta_c)$  for austenite – martensite transformation ( $A_0$  is the material parameter); B and C are parameters that do not affect the phase equilibrium or phase transformation conditions but affect the thermodynamic potential at parameters  $\eta_i$  away from both the A and M<sub>i</sub> minima and the minimum-energy paths between the minima. The gradient energy in Eq. (9), in contrast to known publications<sup>6-13, 18-21</sup>, contains the products  $b \nabla \eta_i \cdot \nabla \eta_j$  with a material parameter b, which allows us to control the energy and width of the  $M_i-M_i$ interface independent of those for  $A-M_i$  interface. Gradient energy depends on two material parameters:  $\beta$ , which is present in all theories, and the new parameter b.

Thermodynamic procedure for the materials with a thermodynamic potential depending on gradient of the order parameters  $\nabla \eta_i$  in the deformed state and linear relationships between generalized thermodynamic fluxes  $\frac{\partial \eta_i}{\partial t}$  and conjugate forces  $X_i$  lead to the expression for the true Cauchy stress tensor  $\boldsymbol{\sigma}$ 

$$\boldsymbol{\sigma} = \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} - \sum_{i=1}^{n} \frac{\rho}{\rho_0} \left( \boldsymbol{\nabla} \eta_i \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \right)_{\mathrm{s}}$$
(1)

and to the generalized Ginzburg–Landau equation

$$\frac{\partial \eta_i}{\partial t} = \chi X_i; \quad X_i = -\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \eta_i} | \boldsymbol{\varepsilon} + \boldsymbol{\nabla} \cdot \left(\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i}\right)$$
(2)

where  $\chi$  is the kinetic coefficient, and the derivative  $\partial \psi / \partial \eta_i$  is calculated at  $\boldsymbol{\varepsilon} = const$ . For the chosen potential, Eq. (31) reduces to Eqs. (15)-(17), in which the stress tensor consists of two parts. The elastic stress  $\boldsymbol{\sigma}_{\rm e}$  is related to elastic strain by Hooke's law Eq.(16). The second contribution  $\boldsymbol{\sigma}_{\rm st}$  (Eq. (17)) is concentrated at the interface (i.e. it is zero if  $\eta_i = 0$  and  $\eta_i = 1$ ) and represents surface tension. There are two reasons for the appearance of the surface tension. The first is because differentiation of the term  $\frac{\rho_0}{\rho} = 1 + \varepsilon_0$  with respect to  $\varepsilon_0$  gives 1 and results in the appearance of hydrostatic pressure  $\psi^{\nabla} + \check{\psi}_{\theta}$  even for negligible strain  $\varepsilon_0$ . That is why the term  $\frac{\rho_0}{\rho} = 1 + \varepsilon_0$ , negligible in small-strain theory, is kept as a multiplier for the selected energy contributions. The second reason is the presence of the gradient energy  $\psi^{\nabla}(\nabla \eta_i)$ . Note that if the energy  $\psi^{\nabla}$  depended on the gradient of  $\eta_i$  in the undeformed state,  $\stackrel{\circ}{\nabla} \eta_i$ , it would not make a contribution to the surface tension. Thus, again even for neglected strains we have to keep the difference between gradients in deformed and undeformed configurations to reproduce the desired surface tension. The criterion for the correct expression for the surface tension  $\ln^{22}$  was that for a single-order parameter it reduces to the biaxial tension along the interface, with the total interface force in each direction equal to the surface tension.

The kinetic Ginzburg–Landau Eqs. (2) for *n* order parameters reduce to Eqs. (19), which for  $b \neq 0$  are coupled through Laplacians in addition to traditional coupling through the local energy terms and transformation strain. The reason that we keep the term  $\frac{\rho_0}{\rho}$ , which is usually neglected in small-strain approximation, is the following. We found that the sum of the first three terms in the right-hand side of Eq. (19) (local contribution to the driving force) have similar magnitude but the opposite sign to the terms with Laplacians. Thus, a small difference in any of the terms can lead to significant change in the total driving force. Another important point that follows from Eq. (19) is that surface tension tensor  $\boldsymbol{\sigma}_{st}$  does not appear in the expression for the driving force  $X_i$ , which depends on elastic stresses only  $\boldsymbol{\sigma}_e$ . However, surface tension indirectly contributes to  $X_i$  by affecting stress distribution.

We have to add traditional equilibrium Eq. (22) to complete the total system of equations. Boundary conditions Eq. (23) for each order parameter correspond to the case in which surface energy for the external surface is independent of  $\eta_i$  – i.e., of phase <sup>22</sup>.

# **Problem formulation**

#### 1. Kinematics

1.1. Decomposition of the strain tensor  $\varepsilon$ 

$$\boldsymbol{\varepsilon} = (\stackrel{\circ}{\boldsymbol{\nabla}} \boldsymbol{u})_{s}; \quad \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_{e} + \boldsymbol{\varepsilon}_{t}; \quad \boldsymbol{\varepsilon} = 1/3\varepsilon_{0}\boldsymbol{I} + \boldsymbol{e}; \qquad \frac{\rho_{0}}{\rho} = 1 + \varepsilon_{0}$$
(3)

1.2. Transformation strain  $\boldsymbol{\varepsilon}_t$ 

$$\boldsymbol{\varepsilon}_{t} = \sum_{k=1}^{n} \boldsymbol{\varepsilon}_{tk} \varphi\left(\eta_{k}\right) - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \eta_{i}^{2} \eta_{j}^{2} \left(\eta_{i} \boldsymbol{L}_{ij} + \eta_{j} \boldsymbol{L}_{ji}\right)$$
$$\boldsymbol{L}_{ji} = (a-3)\boldsymbol{\varepsilon}_{ti} + 3\boldsymbol{\varepsilon}_{tj}; \quad \varphi(\eta_{i}) = a\eta_{k}^{2}(1-\eta_{k})^{2} + (4\eta_{k}^{3}-3\eta_{k}^{4})$$
(4)

For two martensitic variants

$$\boldsymbol{\varepsilon}_{t} = \boldsymbol{\varepsilon}_{t1}(a\eta_{1}^{2} + (4-2a)\eta_{1}^{3} + (a-3)\eta_{1}^{4} - 3\eta_{1}^{3}\eta_{2}^{2} - (a-3)\eta_{1}^{2}\eta_{2}^{3}) + \boldsymbol{\varepsilon}_{t1}(a\eta_{1}^{2} + (4-2a)\eta_{1}^{3} + (a-3)\eta_{1}^{4} - 3\eta_{1}^{3}\eta_{2}^{2}) + \boldsymbol{\varepsilon}_{t1}(a\eta_{1}^{2} + (4-2a)\eta_{1}^{3} + (a-3)\eta_{1}^{3} + (a-3)\eta_{1}^{3$$

$$\boldsymbol{\varepsilon}_{t2}(a\eta_2^2 + (4-2a)\eta_2^3 + (a-3)\eta_2^4 - 3\eta_2^3\eta_1^2 - (a-3)\eta_2^2\eta_1^3)$$
(5)

# 2. Helmholtz free energy and its contributions

$$\psi = \psi^{\mathbf{e}}(\varepsilon_0, \boldsymbol{e}, \eta_i, \theta) + \frac{\rho_0}{\rho} \breve{\psi}^{\theta} + \psi^{\theta} + \frac{\rho_0}{\rho} \psi^{\nabla}.$$
 (6)

2.1. Elastic energy for equal elastic properties of phases

$$\psi^{\mathbf{e}} = \frac{1}{2} K \varepsilon_{0\mathbf{e}}^2 + \mu \boldsymbol{e}_{\mathbf{e}} : \boldsymbol{e}_{\mathbf{e}}$$
<sup>(7)</sup>

2.2. The thermal part of the Helmholtz free energy responsible for the driving force for phase transformation

$$\psi^{\theta} = \frac{1}{3} A_0(\theta - \theta_e) \sum_{k=1}^n \eta_k^2 (3 - 2\eta_k) - A_0(\theta - \theta_e) \sum_{i=1}^{n-1} \sum_{j=i+1}^n \eta_i^2 \eta_j^2 (\eta_i + \eta_j)$$
(8)

For two martensitic variants

$$\psi^{\theta} = \frac{1}{3} A_0(\theta - \theta_e) \{ \eta_1^2(3 - 2\eta_1) + \eta_2^2(3 - 2\eta_2) - 3\eta_1^2 \eta_2^2(\eta_1 + \eta_2) \}$$
(9)

2.3. The thermal part of the Helmholtz free energy responsible for the barrier between phases

$$\breve{\psi}^{\theta} = \sum_{k=1}^{n} A_0(\theta_e - \theta_c) \eta_k^2 (1 - \eta_k)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} F_{ij}(\eta_i, \eta_j)$$
(10)

$$F_{ij}(\eta_i, \eta_j) = \eta_i \eta_j (1 - \eta_i - \eta_j) \{ B[(\eta_i - \eta_j)^2 - \eta_i - \eta_j] + C \eta_i \eta_j \}$$
  
+  $\eta_i^2 \eta_j^2 (\eta_i + \eta_j) (\bar{A} - A_0(\theta_e - \theta_c))$  (11)

For two martensitic variants

$$\breve{\psi}^{\theta} = A_0(\theta_{\rm e} - \theta_{\rm c})\{\eta_1^2(1 - \eta_1)^2 + \eta_2^2(1 - \eta_2)^2\} + \eta_1\eta_2(1 - \eta_1 - \eta_2)\{B((\eta_1 - \eta_2)^2 - \eta_1 - \eta_2) + C\eta_1\eta_2\} + \eta_1^2\eta_2^2(\eta_1 + \eta_2)(\bar{A} - A_0(\theta_{\rm e} - \theta_{\rm c}))(12)$$

2.4. Gradient energy

$$\psi^{\nabla} = \frac{\beta}{2} \left( \sum_{i=1}^{n} |\nabla \eta_i|^2 + b \sum_{i=1}^{n} \sum_{j=1, i \neq j}^{n} \nabla \eta_i \cdot \nabla \eta_j \right).$$
(13)

For two martensitic variants

$$\psi^{\nabla} = \frac{\beta}{2} (|\nabla \eta_1|^2 + |\nabla \eta_2|^2 + 2b\nabla \eta_1 \cdot \nabla \eta_2) = \frac{\beta}{2} (|\nabla \eta_1 + \nabla \eta_2|^2 + 2(b-1)\nabla \eta_1 \cdot \nabla \eta_2)$$

# 3. Stress tensor

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\rm e} + \boldsymbol{\sigma}_{\rm st} \tag{15}$$

3.1 Hooke's law for elastic stresses

$$\boldsymbol{\sigma}_{\mathrm{e}} = \frac{\partial \psi^{\mathrm{e}}}{\partial \boldsymbol{\varepsilon}} = K \varepsilon_{0\mathrm{e}} \boldsymbol{I} + 2\mu \boldsymbol{e}_{\mathrm{e}}$$
(16)

3.2. Interface tension tensor

$$\boldsymbol{\sigma}_{\rm st} = (\psi^{\nabla} + \breve{\psi}_{\theta})\boldsymbol{I} - \beta \sum_{i=1}^{n} (\boldsymbol{\nabla}\eta_{i} \otimes \boldsymbol{\nabla}\eta_{i} + b\boldsymbol{\nabla}\eta_{i} \otimes \sum_{j=1, i \neq j}^{n} \boldsymbol{\nabla}\eta_{j})$$
(17)

For two martensitic variants

$$\boldsymbol{\sigma}_{st} = \left[ \frac{\beta}{2} ((\boldsymbol{\nabla}\eta_1 + \boldsymbol{\nabla}\eta_2)^2 + 2(b-1)\boldsymbol{\nabla}\eta_1 \cdot \boldsymbol{\nabla}\eta_2) + A_0(\theta_e - \theta_c) \{\eta_1^2(1-\eta_1)^2 + \eta_2^2(1-\eta_2)^2\} + \eta_1\eta_2(1-\eta_1-\eta_2) \{B((\eta_1-\eta_2)^2 - \eta_1-\eta_2) + C\eta_1\eta_2\} + \eta_1^2\eta_2^2(\eta_1+\eta_2)(\bar{A} - A_0(\theta_e - \theta_c)) \right] \boldsymbol{I} - \beta \{\boldsymbol{\nabla}\eta_1 \otimes \boldsymbol{\nabla}\eta_1 + \boldsymbol{\nabla}\eta_2 \otimes \boldsymbol{\nabla}\eta_2 + b(\boldsymbol{\nabla}\eta_1 \otimes \boldsymbol{\nabla}\eta_2 + \boldsymbol{\nabla}\eta_2 \otimes \boldsymbol{\nabla}\eta_1)\}$$
(18)

# 4. Ginzburg–Landau equations

$$\frac{1}{\chi}\frac{\partial\eta_i}{\partial t} = \frac{\rho}{\rho_0}\boldsymbol{\sigma}_{\rm e}:\frac{d\boldsymbol{\varepsilon}_t}{d\eta_i} - \frac{\rho}{\rho_0}\frac{\partial\psi^\theta}{\partial\eta_i} - \frac{\partial\breve{\psi}^\theta}{\partial\eta_i} + \beta(\boldsymbol{\nabla}^2\eta_i + b\sum_{j=1,i\neq j}^n \boldsymbol{\nabla}^2\eta_j), \quad i = 1,...,n$$
(19)

For two martensitic variants

$$\frac{1}{\chi} \frac{\partial \eta_{1}}{\partial t} = \frac{\rho}{\rho_{0}} \{\{2a\eta_{1} + 3(4 - 2a)\eta_{1}^{2} + 4(a - 3)\eta_{1}^{3} - 2(a - 3)\eta_{1}\eta_{2}^{3} - 9\eta_{1}^{2}\eta_{2}^{2}\}\boldsymbol{\sigma}_{e}:\boldsymbol{\varepsilon}_{t1} + \{6\eta_{1}\eta_{2}^{3} + 3(a - 3)\eta_{1}^{2}\eta_{2}^{2}\}\boldsymbol{\sigma}_{e}:\boldsymbol{\varepsilon}_{t2}\} - \frac{\rho}{\rho_{0}}\frac{1}{3}A_{0}(\theta - \theta_{e})\{6\eta_{1}(1 - \eta_{1}) + 2\eta_{1}\eta_{2}^{2}(1.5\eta_{1} + \eta_{2})\} + \eta_{1}\eta_{2}(1 - \eta_{1} - \eta_{2})\{B(2(\eta_{1} - \eta_{2}) - 1) + D\eta_{2}\} + 2\eta_{1}\eta_{2}^{2}(1.5\eta_{1} + \eta_{2})(\bar{A} - A_{0}(\theta_{e} - \theta_{c})) + \beta(\boldsymbol{\nabla}^{2}\eta_{1} + b\boldsymbol{\nabla}^{2}\eta_{2}) \tag{20}$$

$$\frac{1}{\chi} \frac{\partial \eta_2}{\partial t} = \frac{\rho}{\rho_0} \{\{2a\eta_2 + 3(4-2a)\eta_2^2 + 4(a-3)\eta_2^3 - 2(a-3)\eta_2\eta_1^3 - 9\eta_2^2\eta_1^2\}\boldsymbol{\sigma}_{e}:\boldsymbol{\varepsilon}_{t2} + \{6\eta_2\eta_1^3 + 3(a-3)\eta_2^2\eta_1^2\}\boldsymbol{\sigma}_{e}:\boldsymbol{\varepsilon}_{t1}\} - \frac{\rho}{\rho_0}\frac{1}{3}A_0(\theta-\theta_e)\{6\eta_2(1-\eta_2) + 2\eta_2\eta_1^2(1.5\eta_2+\eta_1)\} + \eta_2\eta_1(1-\eta_2-\eta_1)\{B(2(\eta_2-\eta_1)-1) + D\eta_1\} + 2\eta_2\eta_1^2(1.5\eta_2+\eta_1)(\bar{A}-A_0(\theta_e-\theta_e)) + \beta(\boldsymbol{\nabla}^2\eta_2 + b\boldsymbol{\nabla}^2\eta_1) \}$$
(21)

#### 5. Equilibrium equation

$$\nabla \cdot \boldsymbol{\sigma} = 0 \tag{22}$$

#### 6. Boundary conditions for the order parameters

$$\boldsymbol{n} \cdot \boldsymbol{\nabla} \eta_i = 0, \quad i = 1, ..., n \tag{23}$$

## Numerical procedure

*Material parameters.* We will consider cubic-to-tetragonal phase transformation in NiAl alloy. We will use the following material parameters determined and/or collected from the literature in <sup>15, 16, 21, 30</sup>:

$$A_{0} = 4.40 \quad MPa \, K^{-1}, \quad \bar{A} = 5.32 \quad GPa, \quad \theta_{e} = 215 \quad K, \quad \theta_{c} = -183 \quad K, \quad a = 2.98,$$
  

$$B = 0, \quad D = 0.5 \quad GPa, \quad \beta = 5.18 \times 10^{-10} \quad N, \quad \chi = 2600 \quad (Pa \cdot s)^{-1},$$
  

$$K = 112.62 \quad GPa, \quad \mu = 71.5 \quad GPa.$$
(24)

In our plane stress 2-D FEM simulations, we included two of the three possible martensitic variants with the following transformation strains <sup>15, 17</sup>:  $\varepsilon_{t1} = (0.215; -0.078; -0.078)$ ,  $\varepsilon_{t2} = (-0.078; 0.215; -0.078)$ . Let us determine the range of variation of parameter *b* from the condition  $\psi^{\nabla} \ge 0$  for all arguments in Eq. (14). It is clear that at the  $M_i - M_j$ interface one has  $\nabla \eta_i \cdot \nabla \eta_j \le 0$ , because for transition from  $\eta_i = 1$  and  $\eta_j = 0$  to  $\eta_i = 0$ and  $\eta_j = 1$  across an interface,  $\eta_i$  reduces and  $\eta_j$  increases. Since we can choose  $\nabla \eta_i$ arbitrarily to ensure that  $\psi^{\nabla} \ge 0$  for all arguments, we choose  $\nabla \eta_i = -\nabla \eta_j$ . Then, one has  $\psi^{\nabla} = -\beta(b-1)|\nabla \eta_i|^2$  and condition  $\psi^{\nabla} \ge 0$  implies  $b \le 1$ . Note that for b = 1, a sharp-interface solution with  $\nabla \eta_i = -\nabla \eta_j$  is  $\eta_i = H(\xi)$ , which gives zero energy  $\psi$ . Here H is the Heavyside step function and  $\xi$  is the local coordinate along the normal to an interface with  $\xi = 0$  at the interface. Indeed,  $\psi^{\nabla} = 0$  because of b = 1, and all other energy contributions, being finite at any point, produce zero interface energy due to zero interface width. Thus, for the thermodynamic parameters for which martensitic variants are stable or metastable, for b = 1 the sharp  $M_i - M_j$  interface represents the minimum interface energy solution. Numerical results below confirm that with  $b \to 1$  the width and energy of the  $M_i - M_j$  interface tends to zero. We will focus below on the case  $b \ge 0$  for which the energy of the  $M_i - M_j$  interface is less than or equal to the doubled energy of the A - M interface.

In the current study, the FEM is utilized, which is implemented in COMSOL code using the arbitrary Lagrangian–Eulerian approach<sup>25</sup>. The complete system of equations describing the phase transformation has a similar mathematical structure to the coupled equations of diffusion and elasticity (or thermoelasticity). The order parameters can be treated as concentrations of different species;  $\varepsilon_t$  is a counterpart of concentration strain with sophisticated dependence on concentrations; Ginzburg–Landau equations are similar to diffusion equations with complex stress- and concentration-dependent sources  $-\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \eta_i}|_{\mathcal{E}}$  and cross-effect between diffusion of different species in Fick's law. Thus, the GL equations are programmed and solved using Transient Diffusion equations in deformed configuration. Elasticity equations are solved statically with the help of a Structural Application module. Triangle Lagrange elements with quadratic approximation of the displacements and order parameters have been used. Since for  $\eta_i$  corresponding to A and  $M_i$  extrema  $\partial \eta_j / \partial t = 0$  according to GL Eq. (21), we always include in the initial condition small deviations from these extrema to avoid a stacking system in them.

We will determine below the width  $\Delta_{\rm MM}(0) = 2.07$  nm and energy  $E_{\rm MM}(0) = 0.5034$  Jm<sup>-2</sup> of M<sub>i</sub>-M<sub>j</sub> interface for b = 0. The maximum surface tension stress  $\sigma_{\rm st}^y$ 

along the  $M_i - M_j$  interface has an order of magnitude of 1 GPa. Characteristic phase transformation time,  $1/(\bar{A}\chi)$ , has an order of magnitude of 0.1 ps and time step in our problems is of the order of  $10^{-3}$  ps. All size, stress, energy, and time parameters will be normalized by 2.07 nm, 1 GPa, 0.5034 Jm<sup>-2</sup>, and 0.1 ps, respectively. Normalized parameters e.g., E will be designated by bars,  $\bar{E}$ . Temperature is uniform and constant for all calculations. The thermal driving force for phase transformation will be characterized by dimensionless overcooling  $\overline{\Delta \theta} = \frac{\theta_e - \theta}{\theta_e}$ .

To test the numerical procedure, plane vertical interface propagation was considered in a rectangular sample of the size of  $8.12 \times 2.71$ . Good correspondence with analytical solutions in <sup>14-16, 21</sup> was found. To reduce internal stresses and to check the effect of the external stresses, the following components of the transformation strain have been used: along the vertical interface  $\varepsilon_t^y = 0$ ; normal to the interface  $\varepsilon_t^x = 0.05$ ; and shear-strain  $\gamma_t = 0.1$ . For example, for temperature  $\theta = \theta_e = 215$  K, normal  $\sigma_x = 1$  GPa, and shear stress  $\tau = -0.3$  GPa the interface velocity is 993.4 ms<sup>-1</sup> in our calculations and 998.0 in<sup>21</sup>.

To verify the A–M energy, a plane vertical interface propagation was considered in a square sample of the size of  $4.83 \times 4.83$ . The first martensitic variant is considered only – i.e.  $\eta_2 = 0$ . To reduce internal stresses at the vertical A–M interface, crystal lattice of M is rotated by  $36.5^0$  in the right-hand side of the sample to get  $\varepsilon_t^y = 0$ . This leads to the components of  $\varepsilon_{t1}^x = 0.1113$ ,  $\varepsilon_{t1}^y = 0$  and  $\varepsilon_{t1}^{xy} = 0.1305$  in the coordinate system xy. In the left half of the sample, initial conditions  $\eta_1 = 0.001$  correspond to A, and in the right part initial conditions  $\eta_1 = 0.999$  correspond to M<sub>1</sub>. The temperature  $\theta = \theta_e = 215$  K and the stress-free boundary conditions are accepted. The energy of the A–M interface is E = 0.2244 Jm<sup>-2</sup> and equal to the value 0.2244 obtained with analytical expression from <sup>16</sup>.

## Results

#### Description of the problem for martensite-martensite interface

The sample in the initial state has a square shape, with the side of 4.83. In the left half of the sample initial conditions  $\eta_1 = 0.999$  and  $\eta_2 = 0.001$  correspond to  $M_1$ , and in the right part initial conditions  $\eta_1 = 0.001$  and  $\eta_2 = 0.999$  correspond to  $M_2$ . Small initial deviations for  $\eta_i$  from 0 and 1 were used to avoid possible artificial stacking of the system at  $M_i$  minima (as described above), while for this problem it was not necessary. If these variants would transform back to austenite, they will have the geometry shown in Fig. 3.1a. Crystal lattice of the austenite is rotated by  $45^0$ , which leads to the components of  $\varepsilon_{t1}^x = \varepsilon_{t2}^y = \varepsilon_{t2}^x = \varepsilon_{t2}^y = 0.0685$  and  $\varepsilon_{t1}^{xy} = -\varepsilon_{t2}^{xy} = 0.1465$  in the coordinate system xy. External stresses are absent in the deformed state. To avoid rigid-body motion due to numerical errors, one point of the external surface is completely fixed and another one is fixed in the x direction. Initial conditions for stresses are  $\boldsymbol{\sigma} = \boldsymbol{\sigma}_{st}$ . Homogeneous stationary temperature  $\theta = \theta_e$  is accepted.

#### Martensite-martensite interface contours and width

Profiles of the order parameters  $\eta_1$  and  $\eta_2$  vs.  $\bar{x}$  at  $\bar{y} = 4.35$  are shown in Fig. 3.2 for different values of b. Isobands of  $\eta_1 - \eta_2$  in the sample are presented in Fig. 3.1a. It is clear that the width of the  $M_1-M_2$  interface decreases with increasing b and decreasing interface energy. For the case b < 0.8 - i.e., when the energy  $E_{\rm MM}$  of the  $M_1-M_2$  interface is larger than the energy  $E_{\rm AM}$  of the A-M interface, the austenitic region nucleates barrierlessly at the martensite-martensite interface at the bottom part of a sample; the smaller b is, the larger is the austenitic region. Such a nucleation does not require thermal fluctuations and is observed experimentally e.g., in<sup>32</sup>.

Barrierless austenite nucleation within the  $M_1-M_2$  interface starts in the region of stability of martensite ( $\theta > \theta_e$ ), when temperature reduces to the thermodynamic equi-



Figure 3.1 Distribution of  $\eta_1 - \eta_2$  (a), dimensionless surface tension stress  $\bar{\sigma}_{st}^y$  (b), total stress  $\bar{\sigma}^y$  (c), and energy  $\bar{\psi}$  (d) for various parameters *b* (shown at the left) in a sample with two martensitic variants. For small *b*, the austenitic region appears at the interface between martensitic variants, leading to splitting of the martensite-martensite interface into two austenite-martensite interfaces and to a triple-junction point.

librium temperature. Note that similar nucleation was found in 1-D models with a singleorder parameter<sup>16, 26</sup> (so-called soliton splitting). However, in <sup>16, 26</sup> martensitic variants were always separated by the point  $\eta = 0$  corresponding to austenite, which expanded into the finite region while approaching the thermodynamic equilibrium temperature.



Figure 3.2 Profiles of the order parameters  $\eta_1$  and  $\eta_2$  vs.  $\bar{x}$  at  $\bar{y} = 4.35$  for different values of b for the M<sub>1</sub>-M<sub>2</sub> interface.

In the current 2-D simulations with two order parameters, one martensitic variant can transform into another without passing through the austenitic point  $\eta_1 = \eta_2 = 0$ , but still the finite austenitic region  $\eta_1 = \eta_2 = 0$  appears between martensitic variants near one of the free surfaces. Also, 2-D simulations exhibited the variable width of the austenitic region and triple junction between an austenite and two martensitic variants. Note that the appearance of an additional phase inside the interface was suggested and explored in the theory of phase transformation via virtual melting<sup>33, 34</sup>, in which a molten layer appears at the interface between two solid phases. There are different ways to define quantitatively the interface width even for a singleorder parameter<sup>16, 26</sup>; it is not trivial to do this for two order parameters using interface profiles  $\eta_1$  and  $\eta_2$  vs. x. Also, interface width determined with the help of  $\eta_1(x)$  and  $\eta_2(x)$  profiles is not physical because interface width determined using  $\boldsymbol{\varepsilon}_t(x)$  (which is a potentially measured physical parameter) differs significantly. Since transition from  $M_1$  to  $M_2$  occurs by a twinning shear along the interface, we use a profile of the shear component

$$\varepsilon_{t}^{xy} = 0.1465(\{a\eta_{1}^{2} + (4-2a)\eta_{1}^{3} + (a-3)\eta_{1}^{4} - 3\eta_{1}^{3}\eta_{2}^{2} - (a-3)\eta_{1}^{2}\eta_{2}^{3}\} - \{(a\eta_{2}^{2} + (4-2a)\eta_{2}^{3} + (a-3)\eta_{2}^{4} - 3\eta_{2}^{3}\eta_{1}^{2} - (a-3)\eta_{2}^{2}\eta_{1}^{3}\})$$
(25)

to determine the martensite-martensite interface width  $\Delta_{\text{MM}}$  (Fig. 3.3). Thus,  $\Delta_{\text{MM}}(b)$ is defined as a length along which transformation shear varies between -0.99 and 0.99of its maximum magnitude at  $\bar{y} = 4.35$ , where width and interface energy belong to the region of their small variation along the y direction.

For b = 0, we obtained  $\Delta_{\rm MM} = 2.07$  nm, which is used as a parameter for normalization of all spatial dimensions. Since  $\Delta_{\rm MM}(0) = s\sqrt{\beta}$  with some parameter  $s^{16}$ , we obtain from our simulations that  $s = 1.286 \times 10^{-4}$ . Dimensionless interface width  $\bar{\Delta}_{\rm MM}$ vs. b is presented in Fig. 3.4. Approximation of this curve gives the following equation for the interface width

$$\Delta_{\rm MM} = 1.286 \times 10^{-4} \sqrt{\beta} (1 - b^{1.445})^{1/2} \tag{26}$$

#### Martensite-martensite interface energy

Energy of a thermodynamically equilibrium interface between phases for arbitrary y is defined as an excess energy with respect to bulk phases, i.e.

$$E := \int_0^l \psi \mathrm{d}x_0 - \psi_\mathrm{b}l \tag{27}$$



Figure 3.3 Distribution of the shear component of the transformation strain along x for b = 0.5 at  $\bar{y} = 3.86$ , which is used for definition of the martensite-martensite interface width.

where l is the initial width of a sample and integration is performed in an undeformed state. Parameters for the bulk phases (designated with the subscript b) can be taken at the points away from the interface, assuming that they are distributed almost homogeneously and are the same from both sides, which is the case for the examples in this chapter. A more complex situation will be considered elsewhere. We defined  $E_{\rm MM}$  for  $\bar{y} = 4.35$ , which belongs to the region with almost homogeneous energy distribution along the y axis for all b. For b = 0 we obtained  $E_{\rm MM} = 0.4490 Jm^{-2}$ , which is twice of the energy of A–M interface. All energies are normalized by this value. Since  $E_{MM}(0) = z\sqrt{\beta}$ , with some parameters  $z^{16}$ , we obtain from our simulations that  $z = 3.128 \times 10^4$ . Dimensionless energy of the M<sub>1</sub>–M<sub>2</sub> interface  $\bar{E}_{\rm MM}$  vs. b, as well as each energy contribution, are presented in Fig. 3.5. Approximation of this curve gives the following equation for the interface energy

$$E_{\rm MM} = 3.128 \times 10^4 \sqrt{\beta} (1 - b^{1.445})^{1/2} \tag{28}$$



Figure 3.4 Dimensionless martensite-martensite interface width  $\bar{\Delta}_{MM}$  vs. b.

It follows from Eqs. (26) and (28) that

$$E_{\rm MM}(b) = 2.4323 \times 10^8 \Delta_{\rm MM}(b) \tag{29}$$

i.e., energy of the interface is proportional to its width for all b and the ratio  $E_{\rm MM}(b)/\Delta_{\rm MM}(b)$ is independent of b.

Note that for the equilibrium A–M interface described by a single-order parameter and neglected mechanics, analytical solutions give  $\check{\psi}^{\theta} = \psi^{\nabla}$  at each local point<sup>16, 26</sup> (note that  $\psi^{\theta}(\theta_{\rm e}) = 0$ ). In our FEM simulations, while total interface energy  $E_{\rm AM} =$ 0.2245 Jm<sup>-2</sup> coincides with the analytical expression from<sup>16</sup>, the contribution of the gradient energy  $E_{\rm AM}^{\nabla} = 0.1149 \,\mathrm{Jm}^{-2}$  is larger than the contribution of the thermal energy  $E_{\rm AM}^{\theta} = 0.1094 \,Jm^{-2}$ ; elastic energy  $E_{\rm AM}^{\rm e} = 0.0002 \,\mathrm{Jm}^{-2}$  is negligible. In contrast, for the M<sub>1</sub>–M<sub>2</sub> interface described by two order parameters, the contribution  $E_{\rm MM}^{\nabla}$  of the gradient energy  $\frac{\rho_0}{\rho} \psi^{\nabla}$  to the  $E_{\rm MM}$  is essentially larger than the contribution  $E_{\rm MM}^{\theta}$  of the thermal energy  $\frac{\rho_0}{\rho} \check{\psi}^{\theta}$  (Fig. 3.5). Thus, local equality cannot be valid as well. Approximation of the results of the calculation gives



Figure 3.5 Dimensionless total energy of the  $M_1$ - $M_2$  interface  $\bar{E}_{MM}$  vs. b, as well as each energy contribution due to gradient  $\bar{E}_{MM}^{\nabla}$ , thermal  $\bar{E}_{MM}^{\theta}$ , and elastic  $\bar{E}_{MM}^{e}$  energies.

For sharp-interface between twins, elastic energy is supposed to be zero (we obtained this using FEM as well). However, for finite-width interface, elastic energy produces a contribution of 4.0 % for b = 0, 7.1 % for b = 0.75, and 14.5 % for b = 0.99. Local energy  $\psi$  is distributed symmetrically with respect to the y axis with the sharp maximum at x = 0 and almost zero value away from the interface (Fig. 3.1d), because the only possible contribution, elastic energy, is very small outside the interface. For large b, local energy is almost homogeneous along the y axis, with some reduction for small y due to increase in the interface width and tendency to potentially split into two A–M interfaces, but with some concentration at the bottom free surface. For small b, the region with almost homogeneous energy distribution along the y axis reduces with reduction in b. Maximum energy significantly reduces for y near the interface splitting region. After the interface splits into two A–M interfaces, the local energy maximum is shifted to the center of theses interfaces.

Figure 3.1 shows the  $M_1-M_2$  interface width and energy vs. number N of finite elements per interface width (determined by Eq. (26)) for two values of b. It is clear that for more than 6 elements per interface width results are practically independent of the FEM discretization. However, for 3 and fewer elements per interface width, both interface width and energy exceed essentially the correct value, especially for relatively large b. These results allow one to choose proper FEM discretization for the solution of more sophisticated problems with multiple interfaces and complex microstructure and to avoid wrong solutions (see below).



Figure 3.6 The  $M_1$ - $M_2$  dimensionless interface width (a) and energy (b) vs. number N of finite elements per interface width (determined by Eq.(26)) for two values of b.

#### Martensite-martensite interface tension and stresses

Distributions of total, elastic, and surface tension stresses in the y direction in the entire sample and vs.  $\bar{x}$  for  $\bar{y} = 4.35$  are shown in Figs. 3.1 and 3.7. Note that for

sharp-interface and neglected surface tension, total and elastic stresses are zero, which we confirmed by our FEM simulations. In contrast, a finite-width, phase-field solution always results in significant stresses inside and near the interface. Surface tension is localized at the interface and its maximum value increases with growing b. In Fig. 3.1, the total and elastic stresses are significantly larger than the surface tension; they spread significantly outside of the interface (where they are equal due to the absence of surface tension). Since total force in the y direction should be zero (or within computational error), stresses outside the interface are mostly of the opposite sign to those inside the interface; they have smaller magnitude outside the interface. At the same time, at the external (almost) horizontal surfaces total normal stress is zero due to the boundary condition, and thus the elastic normal stress is equal to minus the normal component of the surface tension. A sharp drop in total stresses near the intersection of the interface with the free surface of a sample is visible in Fig. 3.1. In the sharp-interface approach, one would apply concentrated compressive loads equal to the surface tension at the points of intersection of the interface with free surface of a sample. In the phase-field approach there are no external concentrated or distributed loads. Surface tension stress is applied at each point of the interface and zero external normal and shear stresses result in a concentration of elastic stresses and strains in the region where interface crosses the free surface of a sample. For small b, when  $M_1-M_2$  interface splits into two A-M interfaces, surface tension stress is again localized at the interfaces, while total and elastic stresses spread into the austenitic region. There is no stress concentration at the triple junction point (region).

#### Austenite–Martensite interface

The first martensitic variant is considered only – i.e.,  $\eta_2 = 0$ . We start with the rectangular sample of size  $4.83 \times 4.83$  in the austenitic state. To reduce internal stresses at the vertical A–M interface, a crystal lattice of M is rotated by  $36.5^{\circ}$  in the right-hand


Figure 3.7 Distributions of dimensionless total  $\bar{\sigma}^y = \bar{\sigma}^y_{st} + \bar{\sigma}^y_e$ , elastic  $\bar{\sigma}^y_e$ , and surface tension stresses  $\bar{\sigma}^y_{st}$  in the y direction vs.  $\bar{x}$  for  $\bar{y} = 4.35$  and several values of b.

side of the sample to get  $\varepsilon_t^y = 0$  (Fig. 3.8). This leads to the components of  $\varepsilon_{t1}^x = 0.113$ ,  $\varepsilon_{t1}^y = 0$  and  $\varepsilon_{t1}^{xy} = 0.1305$  in the coordinate system xy.

In the left half of the sample initial conditions  $\eta_1 = 0.001$  correspond to A and in the right part initial conditions  $\eta_1 = 0.999$  correspond to M<sub>1</sub>. When conditions for  $\eta_1 = 0.999$  are applied, the right half of the sample deforms to the state shown in Fig. 3.8.

External stresses are absent in the deformed state. To avoid rigid-body motion due to numerical errors, one point of the external surface is completely fixed and another one is fixed in the x direction. Initial conditions for stresses are  $\boldsymbol{\sigma} = \boldsymbol{\sigma}_{st}$ . Homogeneous stationary temperature is  $\theta = \theta_{e}$ . Again, for sharp-interface we obtained a stress-free



Figure 3.8 (a) Plots of the *y*-component of dimensionless surface tension  $\bar{\sigma}_{st}^y$  for the A-M<sub>1</sub> interface, as well as total stress  $\bar{\sigma}^y$  for the case with and neglected surface tension stress, along the line passing through the middle of an initially squared sample with a size of 4.83, shown in (b) and (c)<sup>22</sup>. Variant M<sub>1</sub> is rotated by 36.5<sup>0</sup> to get  $\varepsilon_t^y = 0$  at the A-M<sub>1</sub> interface; (b) and (c) present the distribution of dimensionless total stress  $\bar{\sigma}^y$  for the case without and with surface tension, correspondingly.

solution. For a finite-width interface and  $\sigma_{st} = 0$ , even while  $\varepsilon_{st}^y = 0$  everywhere, there is a significant  $\sigma^y$  stress with concentration near the intersection of the interface and the free surface. Maximum tensile stresses are in the martensite, and compressive stresses are in austenite.

The surface tension stress  $\sigma_{st}^y$  exceeds this maximum value of  $\sigma^y$  by a factor of more than 2. Due to asymmetry of the deformed geometry, there is some asymmetry in surface tension distribution. Surface tension changes the distribution of  $\sigma^y$ , increasing significantly the tensile stress and moving its maximum to the center of a sample. The maximum of compressive stress remains near the lower intersection of the interface and the free surface, in the austenitic region. Note that due to the stress-free boundary condition,  $\sigma^y$  is close to zero at the intersection of the interface and the free surface – i.e., stress concentration is shifted inside the sample. To elucidate the effect of martensite-martensite interface energy and FEM discretization on the nanostructure formation, we consider a square grain with a size of 6.04, in which transformation occurs, embedded in the square matrix with a size of 24.15, which is kept in an austenitic state. The upper and lower external boundaries are fixed in the y direction and free in the x direction. The lower left corner is fixed in the x direction and the vertical sides are stress-free. Displacements are continuous across the surface of the internal square, and the boundary conditions for the order parameters Eq. (23) are applied at this surface. The following initial conditions were applied: all stresses are zero everywhere; in the small square,  $\eta_1 = \eta_2 = 0.999$ . Since we are interested in a stationary nanostructure, such initial conditions for  $\eta_i$  allowed us to avoid consideration of martensite nucleation and led to fast relaxation to the stationary solution. It is known that small grain size and elastic constraint suppresses martensitic phase transformation  $^{35, 4}$ . That is why three large overcoolings,  $\overline{\Delta \theta} = 1.93$ , 2.40, and 4.72, have been studied.

Problems for two different b and two different meshes for each b have been considered: a) for b = 0.25 with 11.4 and 2.4 finite elements per interface width determined by Eq. (26); b) for b = 0.75 with 9.5 and 1.5 finite elements per interface width – according to Fig. 3.6, finer mesh should give a mesh-independent solution, but rougher mesh should increase interface width and energy, and solutions may be wrong.

Results of calculations are presented in Fig. 3.9. First, let us focus on a correct solution for fine mesh. Crystallographic theory and continuum sharp-interface theory suggest an alternate twins solution with plain martensite-martensite interfaces. Results that resemble this solution are obtained under large overcooling only. Small grain size distorts this nanostructure, leading to non-planar interfaces and variable width of martensitic variants, as well as non-complete martensitic variants and broadened interfaces. Most of these distortions are caused by boundary conditions Eq. (23) according to which  $\eta_i$ contour lines should be orthogonal to the sides of an embedded square, which confronts



the  $45^{\circ}$  inclination of martensitic twins that is expected from crystallographic theory.

Figure 3.9 Stationary distributions of  $\eta_1 - \eta_2$  in a square grain with a size of 6.04, in which transformation occurs, embedded in the square matrix with a size of 24.15 (not shown), which is kept in the austenitic state. Results are shown for three different overcoolings  $\overline{\Delta \theta} = 1.93$ , 2.40, and 4.72 (designated at the left), for two different parameters b and two numbers of finite elements per correct interface width N.

Note that the boundary conditions Eq. (23) mean that the surface energy of the bounding small square is independent of  $\eta_i$  – i.e., of phase state. Also, in the region where twins intersect the square boundary, martensite is not complete (i.e.,  $\eta_i < 1$ ), which reduces the energy of internal stresses. Reduction in  $M_1-M_2$  interface energy leads to the expected reduction in the width of twins and an increased number of twins. For lower overcooling, the nanostructure is much different from the prediction of crystallographic theory. It contains a large number of residual austenite, split martensite–martensite interfaces, and triple junctions, as well as incomplete martensite. Reduction in  $M_1-M_2$  interface energy leads to an increase in the number of completed twins, reduction of



residual austenite, and to sharper interfaces.

Figure 3.10 Mesh-dependent distributions of  $\eta_1 - \eta_2$  in a square transforming grain with a size of 6.04, embedded in the square austenitic matrix with a size of 24.15 (not shown). Results are shown for three different overcoolings  $\overline{\Delta \theta} = 1.93$ , 2.40, and 4.72 (designated at the left), for two different parameters b and two numbers of finite elements per correct interface width N.

Note that the residual austenite observed in NiTi shape-memory alloy under conditions when it was completely unexpected<sup>36</sup> can be partially explained by our simulations.

Results for the rough mesh for b = 0.25 are completely different from those for the fine mesh for  $\overline{\Delta \theta} = 1.93$ ; different for  $\overline{\Delta \theta} = 2.40$ ; and quite close for  $\overline{\Delta \theta} = 4.72$ . Results for the rough mesh for b = 0.75 show a smaller number of martensitic variants, either incomplete or complete, than with the correct solution for finer mesh. Note that for  $\overline{\Delta \theta} = 4.72$ , results for rough mesh for b = 0.25 and 0.75 are quite close, while correct solutions for these b's are different, having different width and number of martensitic variants. For the mesh with the size of finite element larger than the correct interface width, solutions for some cases became independent of b (Fig. 3.10). Thus, nanostructures for b = 0.25 and N = 0.95 and for b = 0.75 and N = 0.60 are very close for  $\overline{\Delta \theta} = 2.40$  and 4.72. Nanostructures for b = 0.25 and N = 0.45 and for b = 0.75 and N = 0.30 are very close for  $\overline{\Delta \theta} = 1.93$  as well.

To study the scale effect, we consider the same problem but for system size, which is four times larger than in the previous problem – i.e., transforming square grain with the size of 24.15, embedded in the non-transforming austenitic square matrix with the size of 96.62 (see Fig. 3.11). Mesh-independent solutions for  $\overline{\Delta \theta} = 2.40$  in Figs. 3.9 and 3.11 are completely different, with finer nanostructure for a larger sample. Mesh-independent solutions for  $\overline{\Delta \theta} = 2.40$  in Fig. 3.11 for different *b* are completely different as well.



Figure 3.11 Stationary distributions of  $\eta_1 - \eta_2$  in a square grain with a size of 24.15, in which transformation occurs, embedded in the square matrix with a size of 96.62 (not shown), which is kept in the austenitic state.

Thus, in addition to alternating twins structure and chessboard nanostructure<sup>37, 38</sup>, novel nontrivial nanostructure is revealed. For larger overcooling  $\overline{\Delta \theta} \ge 3.79$ , the solution represents alternating twins for both samples. While the size of a sample increases by a factor of 4, the number of twins increases by a factor of  $2 = \sqrt{4}$ .

Note that usually the width of the twin  $w \sim \sqrt{L}$ , where L is the size of a sample<sup>37, 39</sup>.



Figure 3.12 Relationship between width of the twin w and its length l. Dots are the results of simulation, and the curve is the approximation  $w = l^{0.38}$ .

Then the number of twins in a sample  $n \sim L/w \sim \sqrt{L}$  – i.e., our results correspond to the known relationship. However, in contrast to previous works<sup>37, 39</sup>, the width of the twin w varies within a sample and reduces with reduction of the length of twin l. Figure 3.12 shows the relationship w(l), which can be approximated as  $w = l^{0.38}$ . Eqs. (26) and (28) are approximately applicable for the martensite-martensite interfaces in the central region in Figs. 3.9 and 3.11 for large overcooling and are not applicable for small overcoolings.

Note that the grain increases its size during transformation, causing compressive stresses from the matrix that suppress martensitic transformation. Fine nanostructure at twinned martensite and grain boundary (Figs. 3.9, 3.11, 3.13) contains both convex and concave regions. While concave regions locally reduce expansion of the grain, reducing internal stresses, the convex areas increase grain expansion and internal stresses. Analysis of the nanostructure reveals two stress-relaxation mechanisms at the boundary of transforming grain, as follows. (a) At relatively large overcooling, leading to an alternate twin structure, incomplete martensite ( $\eta_i < 1$ ) is observed at the intersection of twin and grain boundaries. It appears at locally convex parts of the grain boundary only, where the twin boundary increases internal stresses, and does not appear at the concave part, where the twin reduces size and internal stresses.

(b) At relatively small overcooling, significant residual austenite remains between martensitic variants, and twinned martensite has a relatively small intersection area with grain boundary. It is worth noting that only the concave regions of the intersection of twins and grain boundary are observed.

It follows from Fig. 3.11 that rough mesh leads to a completely different nanostructure in comparison with fine-mesh solution for  $\overline{\Delta \theta} = 2.40$  and to larger twin width for  $\overline{\Delta \theta} = 3.79$ . Surprisingly, the mesh-independent solutions for b = 0.75 are very close to the solutions for rough mesh for b = 0. The reason is that if the element size is larger than the correct interface width, it increases interface width and energy and produces a nanostructure corresponding to larger  $M_i - M_j$  interface energy – i.e., to smaller b. An example of the nontrivial evolution of the nanostructure with time for a large sample is presented in Fig. 3.13. nite elements per interface width that produce mesh-independent solution.

### Concluding remarks

In summary, phase-field theory for multivariant martensitic phase transformations is extended for the case in which  $M_i-M_j$  interface energy can be varied independently of the A–M interface energy. This has been done by introducing the product of the gradient energy of different order parameters, which results in coupling of the Ginzburg– Landau equations for the order parameters through Laplacians. Surface tension is also taken into account. FEM and COMSOL code have been utilized for the detailed study 63

of the effect of the material parameter b that characterizes  $M_i-M_j$  interface energy on the solutions and nanostructure evolution. Explicit expressions for the  $M_i-M_j$  interface width and energy are obtained. For relatively large  $M_i - M_i$  interface energy, martensitemartensite interface splits the producing region of austenite and the triple junction of two martensitic variants and austenite. Such a mechanism of a barrierless austenite nucleation at  $M_i$ - $M_j$  interface has been observed experimentally e.g., in<sup>32</sup>. Stationary and non-stationary multivariant nanostructures in a nanograin embedded in austenitic matrix were studied. Only for very high overcooling does it resemble the alternating twin structure predicted by crystallographic theory, but with non-planar interfaces, variable width of martensitic variants, non-complete martensitic variants, and broadened interfaces, caused by the small grain size. For lower overcooling, the nanostructure is much different from the prediction of crystallographic theory. It contains a large amount of residual austenite, split martensite-martensite interfaces, and triple junctions, as well as incomplete martensite. Significant residual austenite between martensitic variants and incomplete martensite at the intersection of twin and grain boundaries (where grain boundary becomes convex) are two main stress-relaxation mechanisms at the boundary of transforming grain. Reduction in the  $M_1-M_2$  interface energy leads to a reduction in the twin width, an increase in the number of completed twins, a reduction of residual austenite, and to sharper interfaces. Relationships between the number of twins in grain and grain size, and between the width of a twin and its length are found. The effect of the finite element size on the  $M_1$ - $M_2$  interface energy and width is studied, and conditions for mesh-independence of the solution are found. Solutions for phase transformation in a nanograin for rough mesh differs significantly from the correct solution for fine mesh. It is demonstrated that when element size exceeds the interface width, the obtained nanostructure is independent of the material parameter b, because  $M_1-M_2$  interface size and energy are determined by the size of the finite element independent of b.

We would like to mention that numerous phenomenological models of coherent inter-

face between phases exist in the literature (see reviews<sup>5, 27</sup>) that are formulated using the theory of thin shell and interface constants that are unknown. In the current work, we obtained a significantly more detailed, flexible, and precise model of a coherent interface, which allows for the non-uniformity of all properties, as well as all types of stresses and strains along the interface and interface thickness. The interface thickness and structure vary during thermomechanical loading. The interfaces can appear and disappear, and they may intersect each other, forming triple-junctions and corner points. While all of these events require separate complex models for the sharp-interface approach, they can be treated without extra effort in the phase-field approach. Also, no new parameters are required for the interface model that are not involved in the phase-transformation model.

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Figure 3.13 Evolution of nanostructure leading to the stationary solutions in Fig. 3.11.

# CHAPTER 4. Surface-induced phase transformations: multiple scale and mechanics effects and morphological transitions

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## Abstract

Strong, surprising, and multifaceted effects of the width of the external surface layer  $\Delta_{\xi}$  and internal stresses on surface-induced pretransformation and phase transformations (PTs) are revealed. Using our further developed phase-field approach, we found that above some critical  $\Delta_{\xi}^*$ , a morphological transition from fully transformed layer to lack of surface pretransformation occurs for any transformation strain  $\varepsilon_t$ . It corresponds to a sharp transition to the universal (independent of  $\varepsilon_t$ ), strongly increasing the master relationship of the critical thermodynamic driving force for PT  $X_c$  on  $\Delta_{\xi}$ . For large  $\varepsilon_t$ , with increasing  $\Delta_{\xi}$ ,  $X_c$  unexpectedly decreases, oscillates, and then becomes independent of  $\varepsilon_t$ . Oscillations are caused by morphological transitions of fully transformed surface nanostructure. A similar approach can be developed for internal surfaces (grain boundaries) and for various types of PTs and chemical reactions.

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## Introduction

Reduction in the total surface energy during phase transformations (PTs) may lead to various surface-induced phenomena—e.g., surface premelting, ordering or disordering, martensitic PT, PT from martensitic variant  $M_i$  to variant  $M_j$ , and barrierless nucleation <sup>1, 2, 3</sup>. Thus, transformation may start from the surface from *stable* in bulk to *metastable* phases at temperature  $\theta$ , which may be far from the thermodynamic equilibrium temperature  $\theta_e$  between phases, namely below  $\theta_e$  for melting and above  $\theta_e$  for martensitic PTs. While some of our results are applicable to most of the above PTs, we will focus on PTs during cooling, which include martensitic PTs. When the thermal driving force  $X = (1 - \theta/\theta_e)/(1 - \theta_c/\theta_e)$  ( $\theta_c$  is the temperature of the loss of stability of the parent phase) for martensitic PT increases and approaches zero, a few nanometers thick transformed layer appears, grows, and looses its thermodynamic stability, and transformation propagates through the entire sample. Phase-field or Ginzburg-Landau (GL) approach is widely used for simulation of the surface-induced PTs<sup>3, 4, 5, 6</sup>. PT in this approach is described in terms of evolution of a single or multiple order parameter(s). The martensitic PT below is described by n order parameters  $\eta_i$  that vary from 0 for austenite A to 1 for martensitic variant  $M_i$ . Melting is described by the same potential for a single order parameter<sup>6</sup>. Significant advances were recently achieved in generalization for multivariant martensitic PTs, formulation of a noncontradictory expression for surface energy versus  $\eta_i$ , coupling to advanced mechanics, and consistent expression for interface tension<sup>5, 6</sup>.

Despite this progress, two major contradictions are present in the current GL approaches to surface-induced phenomena. (a) While the GL approach resolves finite width  $\Delta_{\eta}$  of interfaces that are responsible for PTs, the external surface is sharp, although its width is comparable to  $\Delta_{\eta}$ . (b) A sharp external surface also does not permit a correct introduction of surface tension using the method that we developed for the phase interfaces<sup>5, 6</sup>. The goal of this chapter is to introduce and study the effect of the finite

width of an external surface coupled to mechanics with the help of our further developed GL approach. Thus, a surface (e.g., solid-gas) layer of the width  $\Delta_{\xi}$  is described by a solution of the GL equation for an additional order parameter  $\xi$ . Obtained results (Figs. 4.1-4.6) revealed multiple unexpected effects of the surface layer and mechanics, including morphological transitions in the nanostructure, which drastically change our understanding and interpretation of the transformation behavior and results of measurements. Deformation of the crystal lattice of A into the lattice of  $M_i$  is described by the transformation strain tensor  $\varepsilon_{ti}$ , which in our case is taken for cubic-tetragonal PT in NiAl. To elucidate the effect of internal stress generated by  $\varepsilon_{ti}$  in different materials, we considered transformation strain  $k\varepsilon_{ti}$  with  $0 \leq k \leq 1$ . With increasing X, a stationary nanostructure  $\eta_i(\mathbf{r})$  ( $\mathbf{r}$  is the position vector) varies (Fig. 4.4). The critical surface nanostructure  $\eta_c(\mathbf{r})$  corresponds to the critical driving force  $X_c$  above which the entire sample transforms.

For neglected mechanics, two branches on the curve  $X_c$  versus the dimensionless width of the surface layer  $\overline{\Delta_{\xi}} = \Delta_{\xi}/\Delta_{\eta}$  are obtained [Fig. 4.1b]. For  $\overline{\Delta_{\xi}} \ll 1$ , the effect of the surface layer is negligible and  $X_c$  and  $\eta_c$  are the same as for the sharp surface. However, for some critical and quite small  $\overline{\Delta_{\xi}}^* = 0.166$ , the slope of the curve  $X_c(\overline{\Delta_{\xi}})$  has an unexpected jump and a drastic increase in the critical driving force occurs with increasing  $\overline{\Delta_{\xi}}$ . Critical nanostructure undergoes a morphological transition at this point, from a homogeneous layer along the surface with the maximum value  $\eta_c^{max} \simeq 1$  [as in Figs. 4.2a-b], to a thin strip in the middle of the surface layer with very small  $\eta_c^{max} \simeq 10^{-5}$ . This means that as soon as barrierless nucleation starts from the surface, it spreads over the entire sample.

Allowing for mechanics (i.e., energy of internal stresses) increases  $X_c$  with the increasing magnitude of the transformation strain k, as expected. However, for some critical width  $\overline{\Delta_{\xi}^*}(k)$ , the curve  $X_c(\overline{\Delta_{\xi}}, k)$  for any k reaches the master curve for neglected mechanics  $X_c^0(\overline{\Delta_{\xi}})$  (k = 0) and coincides with it for larger  $\overline{\Delta_{\xi}}$ . A jump in the slope in all



Figure 4.1 (a) Plot of the  $\xi$ -dependent term  $\xi_s^2(1-\xi_s)^2/\Delta_{\xi}$  in GL Eq.(5) vs  $\bar{x} = x/\Delta_{\eta}$  for different  $\Delta_{\xi}$ . (b) Critical thermodynamic driving force  $X_c$  vs  $\overline{\Delta_{\xi}}$  for a single M<sub>1</sub> and different cases: neglected mechanics (GL), coupled GL and mechanics with transformation strain of  $\varepsilon_t/3$ ,  $2\varepsilon_t/3$ , and  $\varepsilon_t$  as well as with variable elastic properties  $[\varepsilon_t, \phi(\xi)]$ , and interface  $\sigma_{\eta}^{st}$  and surface  $\sigma_{\xi}^{st}$  tensions  $[\varepsilon_t, \phi(\xi), \sigma^{st}]$ . The curve  $X_c^0$  is approximated as  $X_c^0 = 1 - 0.267\overline{\Delta_{\xi}}^{-2/3}$ .

curves  $X_c(\overline{\Delta_{\xi}}, k)$  at  $\overline{\Delta_{\xi}^*}(k)$  is accompanied by a morphological transition to very small  $\eta_c^{max} \simeq 10^{-5}$ , as with neglected mechanics. This transition explains the lack of the effect of elastic energy on the critical driving force for PT  $X_c$  for  $\overline{\Delta_{\xi}} > \overline{\Delta_{\xi}^*}(k)$ : because for the critical nanostructure  $\eta_c^{max}$  is very small, then the transformation strain and elastic energy are negligible as well. While for k = 1/3 the critical driving force for PT is practically independent of  $\overline{\Delta_{\xi}} < \overline{\Delta_{\xi}^*}$  (as with neglected mechanics), for k = 2/3 and 1,  $X_c$  surprisingly reduces with increasing  $\overline{\Delta_{\xi}}$  before morphological transition and the curve  $X_c(\overline{\Delta_{\xi}}, k)$  has a  $\nu$ -shape at the morphological transition point  $\overline{\Delta_{\xi}^*}(k)$ . One more finding is that for k = 1, there is oscillation at the curve  $X_c(\overline{\Delta_{\xi}})$  caused by three morphological transitions in the critical nanostructure (Fig. 4.2). We designate the contractions of tensors over one and two indices as  $\mathbf{A} \cdot \mathbf{B} = \{A_{ij} B_{jk}\}$  and  $\mathbf{A} : \mathbf{B} = A_{ij} B_{ji}$ , respectively;  $\nabla$  is the gradient operator in the deformed state.



Figure 4.2 Critical nanostructures for the coupled GL and mechanics with  $\varepsilon_t$  for a single  $M_1$  and some values of dimensionless width of the surface layer  $\overline{\Delta_{\xi}}$ . Three morphological transitions are observed with increasing  $\overline{\Delta_{\xi}}$ .

## Phase-field model

The current model generalizes our recently developed model<sup>5</sup> by including the surface layer. Thus, an additional order parameter  $\xi$  describes a smooth transition between solid ( $\xi = 0$ ) and surrounding ( $\xi = 1$ ), e.g., gas. The full model is presented in the Supplemental Materials<sup>11</sup>. Here, we will discuss the structure of new equations only. The Helmholtz free energy per unit undeformed volume,

$$\psi = \psi^{e} + \frac{\rho_{0}}{\rho} \breve{\psi}^{\theta} + \psi^{\theta} + \frac{\rho_{0}}{\rho} \psi^{\nabla} + \frac{\rho_{0}}{\rho} \psi_{\xi}(\xi, \nabla\xi, \eta_{k});$$
(1)  
$$\psi^{e} = 0.5(1 - \phi(\xi))(K\varepsilon_{0e}^{2} + 2\mu \boldsymbol{e}_{e}:\boldsymbol{e}_{e}); \ \phi(\xi) = \xi^{2}(3 - 2\xi),$$

contains the energy  $\psi_{\xi}(\xi, \nabla \xi, \eta_k)$  for the surface layer and the elastic energy  $\psi^e$  with bulk K and shear  $\mu$  moduli, which smoothly reduce to zero within the surface layer. Here,  $\frac{\rho_0}{\rho}$  are the ratio of mass densities in the undeformed and deformed states,  $\check{\psi}^{\theta}$ ,  $\psi^{\theta}$ , and  $\psi^{\nabla}$  are the contributions to  $\psi$  related to the double-well barrier, thermal energy, and energy related to  $\nabla \eta_i$ ,  $\varepsilon_{0e}$  and  $e_e$  are the elastic volumetric and deviatoric strains. The energy of the surface layer per unit deformed volume is<sup>11</sup>

$$\psi_{\xi} = J\xi^2 (1-\xi)^2 + 0.5\beta_{\xi} (\nabla\xi)^2 =$$

$$q(\eta_i)/\Delta_{\xi} \left( 16.62\xi^2 (1-\xi)^2 + 0.542\Delta_{\xi}^2 (\nabla\xi)^2 \right),$$
(2)

where  $\beta_{\xi}$  and J are the parameters, and  $q(\eta_i)$  is the surface energy of the sharp external surface. Equations (7) and (14) lead to the GL equations for  $\xi$  and  $\eta_i$ :

$$\frac{1}{L_{\xi}}\frac{\partial\xi}{\partial t} = \frac{q(\eta_i)}{\Delta_{\xi}} \left(1.083\Delta_{\xi}^2 \nabla^2 \xi - 66.48\xi(1-\xi)(0.5-\xi)\right) + 1.082\Delta_{\xi} \nabla\xi \cdot \nabla q(\eta_i) \quad (3)$$

$$-\frac{\rho}{\rho_0}\frac{\partial\psi^e}{\partial\xi};$$

$$\frac{1}{L}\frac{\partial\eta_i}{\partial t} = -\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\eta_i}|_{\mathcal{E}} + \nabla \cdot \left(\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\nabla\eta_i}\right),$$
(4)

where L and  $L_{\xi} \gg L$  are the kinetic coefficients. For neglected  $\psi^e$ , Eq.(3) has solution for a stationary surface layer<sup>6</sup>:  $\xi_s = [1 + \exp(5.54x/\Delta_{\xi})]^{-1}$ . For neglected mechanics and a single stationary surface layer orthogonal to x, Eq.(3) simplifies to  $(\bar{\psi}^{\theta} = \check{\psi}^{\theta} + \psi^{\theta})$ 

$$\frac{1}{L}\frac{\partial\eta_i}{\partial t} = \beta \nabla^2 \eta_i - \frac{\partial\bar{\psi}^\theta}{\partial\eta_i} - \frac{33.24}{\Delta_\xi} \frac{\partial q(\eta_i)}{\partial\eta_i} \xi_s^2 (1 - \xi_s)^2.$$
(5)

## **Problem formulation**

Material parameters, initial and boundary conditions are given in<sup>11</sup>. The finite element code COMSOL was utilized for plane stress 2D problems. A rectangular  $25 \times 12.5nm^2$  sample discretized with triangle Lagrange elements with quadratic approximation was treated. All sides are stress-free, excluding zero vertical displacement at the upper and lower horizontal sides. The surface layer was introduced at the right vertical line only. We considered GL equation without mechanics, GL equations with mechanics, for k = 1/3, 2/3, 1, with elastic properties independent of  $\xi$  and without surface stresses, the same with elastic properties dependent on  $\xi$ , and the same with surface stresses.



Figure 4.3 Profiles of the single order parameter  $\eta$  for  $\overline{\Delta_{\xi}} = 0$  and the order parameters  $\eta$  and  $\xi$  for  $\overline{\Delta_{\xi}} = 0.066$  for different cases [described in Fig. 4.1b] vs  $\overline{x}$ .

## Scale effects and morphological transitions

First, the simplest model [Eq.(5)] with neglected mechanics (which is generic for various types of PTs) is analyzed. Since the magnitude of the local contribution of the surface layer to the GL Eq.(5) scales with  $1/\Delta_{\xi}$  [Fig. 4.1a], an increase in  $\Delta_{\xi}$ should suppress nucleation. Also, for  $\overline{\Delta_{\xi}} \ll 1$  the results should coincide with those for the sharp external surface. Both of these predictions are confirmed by numerical simulations [Fig. 4.1b]; however, all other results are counterintuitive and unexpected. The critical thermodynamic driving force for PT  $X_c$  vs  $\overline{\Delta_{\xi}}$  and some corresponding critical nanostructures for single  $M_1$  are presented in Figs. 4.1-4.2, respectively. For neglected mechanics, the numerical solution for  $\xi(x)$  is well described by  $\xi_s(x)$ ; thus simple Eq.(5) is valid. Two branches on the curve  $X_c(\overline{\Delta_{\xi}})$  are obtained [Fig. 4.1b]. For  $\overline{\Delta_{\xi}} \ll 1$ , the effect of the surface layer is negligible;  $X_c$ ,  $\eta_c$ , and interface velocity for  $X > X_c$  are practically the same as for the sharp surface; stationary and nonstationary solutions are independent of y,  $\eta_c^{max} = 1$ , and the width of the transformed surface layer  $\delta_{sl}$  (determined from  $\eta_c = 0.5$ ) is essentially larger than  $\Delta_{\xi}$  (Fig. 4.3; plots in Figs. 4.3-4.5 are for the middle line of the sample). However, above some critical and quite small  $\overline{\Delta_{\xi}}^* = 0.166$ , an unexpected jump to a completely different regime occurs. Critical nanostructure undergoes morphological transition to a thin strip in the middle of the surface layer with very small  $\eta_c^{max} \simeq 10^{-5}$ . Consequently, as soon as surface barrierless nucleation starts, PT spreads over the entire sample; thus, pretransformation does not exist.

The slope of the curve  $X_c(\overline{\Delta_{\xi}})$  has a jump (explained by a morphological transition), and a drastic increase in the critical driving force occurs with increasing  $\overline{\Delta_{\xi}}$ . For coupled GL and mechanics formulation (yet with neglected surface stresses and change in elastic properties),  $X_c$  increases with increasing magnitude of the transformation strain k. This is expected because of the suppressing contribution of the energy of internal stresses. For critical nanostructure, while it is homogeneous along y, the width of the transformed layer  $\delta_{sl}$  decreases with increasing k (Fig. 4.3) and  $\eta_c^{max}$  is becoming smaller than 1. However, for some critical width  $\overline{\Delta_{\xi}^*}(k)$ , the curve  $X_c(\overline{\Delta_{\xi}},k)$  for any k reaches the curve  $X_c^0(\overline{\Delta_{\xi}})$ for k = 0 and coincides with it for larger  $\overline{\Delta_{\xi}}$  [Fig. 4.1b]. That is why we call  $X_c^0(\overline{\Delta_{\xi}})$ the universal (i.e., independent of  $\boldsymbol{\varepsilon}_t$  and internal stresses) master dependence. At  $\overline{\Delta_{\boldsymbol{\xi}}^*}(k)$ a jump in the slope in all curves  $X_c(\overline{\Delta_{\xi}}, k)$  occurs, which is caused by a morphological transition to very small  $\eta_c^{max} \simeq 10^{-5}$ , similar to the case with neglected mechanics. This transition explains the coincidence of the curves for different k, i.e., the lack of the effect of elastic energy on  $X_c$  for  $\overline{\Delta_{\xi}} > \overline{\Delta_{\xi}^*}(k)$ . Indeed, since for the critical nanostructure  $\eta_c^{max}$ is very small, then  $\varepsilon_t$  and elastic energy are negligible as well. This result leads to new intuition for such a complex nonlinear interaction between PT, surface phenomena, and mechanics.

While for  $k = 1/3 X_c$  does not change with the increasing width of the surface layer (like for neglected mechanics), for k = 2/3 and 1,  $X_c$  surprisingly reduces with increasing  $\overline{\Delta_{\xi}} < \overline{\Delta_{\xi}}^*$  and the curve  $X_c(\overline{\Delta_{\xi}})$  has a  $\nu$  shape at the morphological transition point  $\overline{\Delta_{\xi}^*}(k)$  [Fig. 4.1b]. For k = 1, there is also oscillation at the curve  $X_c(\overline{\Delta_{\xi}})$ , caused by three morphological transitions of the critical nanostructure [Fig. 4.2]. Thus, the almost homogeneous along y nanostructure for the sharp surface and  $\overline{\Delta_{\xi}} = 0.066$ changes to three different types of localized structures. Such a structure is a result of competition between a promoting effect of the surface layer and a suppressing effect of elastic stresses; localized structure leads to a reduction in elastic energy. When variable



Figure 4.4 Profiles of the single order parameter  $\eta$  vs  $\overline{x}$  for some values of  $\overline{\Delta_{\xi}}$  for critical nanostructures (solid line) and nanostructures for smaller thermodynamic driving forces (dashed line) for the  $[\boldsymbol{\varepsilon}_t, \phi(\xi), \boldsymbol{\sigma}^{st}]$  model.

elastic properties are included for k = 1, results for small  $\overline{\Delta_{\xi}}$  are similar to that with constant properties; i.e., there are some oscillations in  $X_c(\overline{\Delta_{\xi}})$ . However, a reduction in  $X_c$  with growing  $\overline{\Delta_{\xi}}$  is much smaller, critical  $\overline{\Delta_{\xi}}^*$  for morphological transition to small  $\eta_c^{max}$  is larger, and critical nanostructure is independent of y without morphological transitions below  $\overline{\Delta_{\xi}}^*$ . For the complete model, when, in addition, the interface and surface tensions<sup>7</sup> are taken into account,  $X_c$  increases for all  $\overline{\Delta_{\xi}}$  because of suppressing effect of additional compression stresses on transformational expansion along the surface. Pretransformation starts at X which is significantly smaller than  $X_c$  (especially for small  $\overline{\Delta_{\xi}}$ ) but  $\eta(\mathbf{r})$  did not change substantially, while X increases up to  $X_c$  (Fig. 4.4). Such a low sensitivity of surface nanostructure to the driving force, within some range, may have practical importance. Critical nanostructure is independent of y up to  $\overline{\Delta_{\xi}} < 0.664$ , above which it advances more at the sample center.



Figure 4.5 Evolution of surface nanostructure for  $X > X_c$  and two different values of  $\overline{\Delta_{\xi}}$  for the case with the transformation strain of  $\boldsymbol{\varepsilon}_t$  and a single martensitic variant.

Examples of the evolution of nanostructure for single and two martensitic variants after critical nanostructure loses its stability after a slight increase in X are given in Figs. 4.5-4.6 and in the Supplemental Material<sup>7</sup>. The case with two variants is much more complicated for analysis due to the possibility of reduction of elastic energy by combining variants and additional scale parameters (the width of  $M_1$ - $M_2$  interface). To summarize, very strong and multifaceted effects of the width of the external surface layer  $\Delta_{\xi}$  and internal stresses on surface-induced pretransformation and PT was revealed using our extended phase-field approach. Obtained results change our understanding of surfaceinduced PTs and interpretation of experimental data. For neglected mechanics (which is an acceptable approximation for melting, amorphization, and for small transformation strain components along the surface), thermodynamic conditions for the possibility of surface-induced PT are<sup>2, 3</sup>  $\Gamma = \gamma_M - \gamma_A + E_\eta < 0$ , where  $\gamma$  is the surface energy. Our results show that for the chosen material parameters it is true for quite small  $\Delta_{\eta} \ge 6\Delta_{\xi}$ only. The fact that surface-induced melting was observed for various materials<sup>2, 3</sup> means that the solid-liquid interface is much thicker than the solid-gas interface. For a thinner phase interface, the stationary surface-molten layer cannot exist and surface-induced PT occurs spontaneously in the entire sample after some overheating. The lack of a surfacemolten layer and necessity for overheating was observed for various materials and specific orientations<sup>2, 3</sup> and was usually interpreted as a consequence of  $\Gamma > 0$ . It is known<sup>2, 3</sup> that due to a significant error in determining each of three surface energies in the above criterion, it is difficult to predict *a priori* whether surface melting will occur. The same is valid for other PTs, such as martensitic PTs and amorphization<sup>1</sup>. Our results show



Figure 4.6 Evolution of surface nanostructure for two martensitic variants for different values of  $\overline{\Delta_{\xi}}$  and the same thermodynamic driving force X = 0.7915.

that surface-induced transformation should not necessarily occur at  $\Gamma < 0$  and that  $\overline{\Delta_{\xi}}$  is an additional key parameter that strongly affects surface-induced transformation

and  $X_c$ . While allowing for finite  $\overline{\Delta_{\xi}}$  suppresses surface-induced PT for zero or a small transformation strain, for larger  $\varepsilon_t$  there is a range of  $\overline{\Delta_{\xi}}$  for which an increase in  $\overline{\Delta_{\xi}}$ promotes PT; however, for larger  $\overline{\Delta_{\xi}}$ , PT is again suppressed. Finding ways to control  $\Delta_{\xi}$ (e.g., by changing the composition or the surrounding of the surface layer) will allow one to control the surface-induced phenomena and nanostructures. For example,  $\beta - \delta$  PT at the surface of the  $\beta$  occurs at  $\theta_e$  in the presence of nitroplastiziers only<sup>8</sup>. The revealed low sensitivity of surface nanostructure to the driving force, within some range, may also have practical importance. A similar approach can be developed for internal surfaces (grain boundaries and immobile interfaces inside of composite or multiphase materials) and for various types of PTs (electromagnetic, diffusive-displacive, and amorphization) and chemical reactions. Melting and amorphization at grain boundaries for various materials <sup>1</sup> are corresponding examples.

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## Supplementary materials

We designate contractions of tensors  $\boldsymbol{A} = \{A_{ij}\}$  and  $\boldsymbol{B} = \{B_{ji}\}$  over one and two indices as  $\boldsymbol{A} \cdot \boldsymbol{B} = \{A_{ij} B_{jk}\}$  and  $\boldsymbol{A} : \boldsymbol{B} = A_{ij} B_{ji}$ , respectively. The subscripts *s*, *e*, and *t* mean symmetrization and elastic and transformational strains;  $\boldsymbol{I}$  is the unit tensor;  $\stackrel{\circ}{\nabla}$ and  $\boldsymbol{\nabla}$  are the gradient operators in the undeformed and deformed states;  $\otimes$  designates a dyadic product.

#### Phase-field model

The current model generalizes our recently developed model<sup>5</sup> by including the surface layer. Thus, an additional order parameter  $\xi$  describes a smooth transition between solid  $(\xi = 0)$  and surrounding  $(\xi = 1)$ , e.g., gas. Additional energy term  $\psi_{\xi}(\xi, \nabla \xi, \eta_k)$  and GL equation for  $\xi$  are formulated to ensure coupling between different order parameters  $\eta_i$  and  $\xi$  in a consistent way. Kinematics relationships between displacement  $\boldsymbol{u}$  and strain  $\boldsymbol{\varepsilon} = 1/3\varepsilon_0 \boldsymbol{I} + \boldsymbol{e}$ , decomposition of  $\boldsymbol{\varepsilon}$  and the equilibrium equation are

$$\boldsymbol{\varepsilon} = (\stackrel{\circ}{\boldsymbol{\nabla}} \boldsymbol{u})_s, \quad \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_t, \quad \boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = 0,$$
 (6)

where  $\varepsilon_0$  and  $\boldsymbol{e}$  are the volumetric and deviatoric contributions to strain, and  $\boldsymbol{\sigma}$  is the true Cauchy stress tensor. The Helmholtz free energy per unit undeformed volume  $\psi$  and transformation strain tensor  $\boldsymbol{\varepsilon}_t$  are accepted in the form

$$\psi = \psi^{e}(\varepsilon_{0}, \boldsymbol{e}, \eta_{i}, \theta, \xi) + \frac{\rho_{0}}{\rho} \breve{\psi}^{\theta} + \psi^{\theta} + \frac{\rho_{0}}{\rho} \psi^{\nabla} + \frac{\rho_{0}}{\rho} \psi_{\xi}(\xi, \boldsymbol{\nabla}\xi, \eta_{k});$$
(7)

$$\psi^{\theta} = \sum_{k=1}^{n} \frac{1}{3} A_0(\theta - \theta_e) \phi(\eta_k) - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \eta_i^2 \eta_j^2(\eta_i + \eta_j) A_0(\theta - \theta_e);$$
(8)

$$\psi^{\nabla} = \frac{\beta}{2} \left( \sum_{i=1}^{n} |\nabla \eta_i|^2 + b \sum_{i=1}^{n} \sum_{j=1, i \neq j}^{n} \nabla \eta_i \cdot \nabla \eta_j \right); \tag{9}$$

$$\breve{\psi}^{\theta} = \sum_{k=1}^{n} A_0(\theta_e - \theta_c) \eta_k^2 (1 - \eta_k)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} F_{ij}(\eta_i, \eta_j);$$
(10)

$$\boldsymbol{\varepsilon}_{t} = \sum_{k=1}^{n} \boldsymbol{\varepsilon}_{t}^{k} (a\eta_{k}^{2} + (4 - 2a)\eta_{k}^{3} + (a - 3)\eta_{k}^{4}) - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \eta_{i}^{2} \eta_{j}^{2} (\eta_{i} \boldsymbol{L}_{ij} + \eta_{j} \boldsymbol{L}_{ji}), \quad (11)$$

$$\psi^{e} = 0.5(1 - \phi(\xi))(K\varepsilon_{0e}^{2} + 2\mu \boldsymbol{e}_{e}:\boldsymbol{e}_{e}); \quad \phi(\xi) = \xi^{2}(3 - 2\xi).$$
(12)

Here,  $\frac{\rho_0}{\rho} = 1 + \varepsilon_0$  are the ratio of mass densities in the undeformed and deformed states,  $\boldsymbol{L}_{ij} = (a-3)\boldsymbol{\varepsilon}_t^j + 3\boldsymbol{\varepsilon}_t^i, \ F_{ij}(\eta_i,\eta_j) = \eta_i\eta_j(1-\eta_i-\eta_j)\{B[(\eta_i-\eta_j)^2-\eta_i-\eta_j]+C\eta_i\eta_j\} + \eta_i^2\eta_j^2(\eta_i+\eta_j)(\bar{A}-A_0(\theta_e-\theta_c)), \ \psi^e$  is the elastic energy with equal (for compactness) bulk K and shear  $\mu$  moduli of martensitic variants, which smoothly reduce to zero within the surface layer;

 $\beta$  is the gradient energy coefficient; and  $A_0$ ,  $\bar{A}$ , B, C, a, and b are parameters. For the sharp external surface with the normal  $\boldsymbol{n}$ , the boundary conditions for the order parameters related to the variable surface energy  $q(\eta_i)$  are defined as<sup>5</sup>

$$\frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \cdot \boldsymbol{n} = \frac{\partial \psi^{\nabla}}{\partial \boldsymbol{\nabla} \eta_i} \cdot \boldsymbol{n} = \beta (\nabla \eta_i + b \sum_{j=1, i \neq j}^n \boldsymbol{\nabla} \eta_j) \cdot \boldsymbol{n} = -\frac{\partial q}{\partial \eta_i};$$
$$q(\eta_i) = \gamma_A + \Delta \gamma \phi(p), \qquad p = (\eta_1^2 + \eta_2^2 + \dots + \eta_i^2 + \dots)^{0.5}, \tag{13}$$

where  $\gamma$  is the surface energy and  $\Delta \gamma = \gamma_M - \gamma_A$ . For the finite surface layer, the boundary conditions for  $\eta_i$  correspond to unchanged energy of external surface (q = const in Eq.(13)).

#### Surface layer model

The energy of the surface layer per unit deformed volume is

$$\psi_{\xi} = J\xi^2 (1-\xi)^2 + 0.5\beta_{\xi} (\nabla\xi)^2 = q(\eta_i) / \Delta_{\xi} \left( 16.62\xi^2 (1-\xi)^2 + 0.542\Delta_{\xi}^2 (\nabla\xi)^2 \right).$$
(14)

Eqs.(7), (12), and (14) lead to the GL equations for  $\xi$  and  $\eta_i$ :

$$\frac{1}{L_{\xi}}\frac{\partial\xi}{\partial t} = \frac{q(\eta_i)}{\Delta_{\xi}} \left(1.083\Delta_{\xi}^2 \nabla^2 \xi - 66.48\xi(1-\xi)(0.5-\xi)\right) + 1.082\Delta_{\xi} \nabla\xi \cdot \nabla q(\eta_i)$$
(15)

$$-\frac{\rho}{\rho_0}\frac{\partial\psi^e}{\partial\xi};$$
(16)

$$\frac{1}{L}\frac{\partial\eta_i}{\partial t} = -\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\eta_i}|_{\boldsymbol{\varepsilon}} + \boldsymbol{\nabla}\cdot\left(\frac{\rho}{\rho_0}\frac{\partial\psi}{\partial\boldsymbol{\nabla}\eta_i}\right) = \frac{\rho}{\rho_0}\boldsymbol{\sigma}_e:\frac{d\boldsymbol{\varepsilon}_t}{d\eta_i} - \frac{\rho}{\rho_0}\frac{\partial\psi^\theta}{\partial\eta_i} - \frac{\partial\breve{\psi}^\theta}{\partial\eta_i} + \beta(\boldsymbol{\nabla}^2\eta_i + b\sum_{j=1,i\neq j}^n \boldsymbol{\nabla}^2\eta_j) - \frac{1}{\Delta_{\boldsymbol{\xi}}}\frac{\partial q}{\partial\eta_i} \left(16.62\boldsymbol{\xi}^2(1-\boldsymbol{\xi})^2 + 0.542\Delta_{\boldsymbol{\xi}}^2(\boldsymbol{\nabla}\boldsymbol{\xi})^2\right),$$
(17)

where L and  $L_{\xi} \gg L$  are the kinetic coefficients and  $\partial \psi / \partial \eta_i$  is calculated at  $\boldsymbol{\varepsilon} = const$ . We would like to avoid description of an actual solid-gas PT and want to develop a more generic model of the surface layer. That is why  $\psi_{\xi}$  has the same structure as  $\check{\psi}^{\theta} + \psi^{\nabla}$ for single order parameter  $\eta$ , with  $\beta_{\xi}$  for the gradient energy coefficient and J characterizing the double-well energy barrier. Since for homogeneous states  $\psi_{\xi}(0) = \psi_{\xi}(1) = 0$ , Eq.(14) corresponds to the thermodynamic equilibrium between solid and surrounding. For neglected elastic energy, Eq.(16) has a stationary solution for an equilibrium surface layer<sup>6</sup>:

$$\xi = [1 + \exp(5.54x/\Delta_{\xi})]^{-1}; \quad \Delta_{\xi} = 5.54\sqrt{\beta_{\xi}/(2J)}; \quad E_{\xi} = \sqrt{\beta_{\xi}J/18} = q(\eta_i).$$
(18)

Here the surface layer width is  $\Delta_{\xi} = |x_g - x_s|$ , and  $x_g$  and  $x_s$  are determined from the conditions  $\phi(\xi(x)) = 0.01$  and 0.99 respectively; the surface-layer energy  $E_{\xi}$  should be

equal to the variable surface energy  $q(\eta_i)$  to make the surface layer and sharp surface approaches energetically equivalent. Assuming that  $\Delta_{\xi}$  is independent of  $\eta_i$ , one obtains from Eq.(18)  $\beta_{\xi} = \frac{6E_{\xi}\Delta_{\xi}}{5.54} = 1.083q(\eta_i)\Delta_{\xi}$  and  $J = \frac{16.62q(\eta_i)}{\Delta_{\xi}}$ , which justifies the second part of Eq.(14). For neglected mechanics, the stationary version of Eq.(16) and its solution are independent of  $\eta_i$  and 1-D solution Eq.(18) is valid during evolution of  $\eta_i$  as well. Since the magnitude of the local contribution of the surface layer to the GL for  $\eta$ (the last term in Eq.(17)) scales with  $1/\Delta_{\xi}$ , the driving force  $X_c$  that causes PT should increase with growing  $\Delta_{\xi}$ , which is confirmed by numerical simulations (Fig. 4.1). When mechanics is taken into account but the last term in Eq.(16) is negligible, stationary distribution of  $\eta_i$  affects stationary distribution of  $\xi$  through a change in the size of the sample due to transformation strain. However, stationary distribution of  $\xi$  mapped into the undeformed state remains unchanged. For neglected  $\psi^e$ , Eq.(16) has solution for a stationary surface layer<sup>6</sup>:  $\xi_s = [1 + \exp(5.54x/\Delta_{\xi})]^{-1}$ . For neglected mechanics and single stationary surface layer orthogonal to x, Eq.(17) simplifies to

$$\frac{1}{L}\frac{\partial\eta_i}{\partial t} = -\frac{\partial(\bar{\psi}^\theta + \psi^\theta)}{\partial\eta_i} + \beta \nabla^2 \eta_i - \frac{33.24}{\Delta_{\xi}}\frac{\partial q(\eta_i)}{\partial\eta_i}\xi_s^2(1 - \xi_s)^2$$

where we took into account that for the stationary solution  $\xi_s$  the local and gradient terms in the energy Eq.(14) are equal<sup>9</sup>.

Stresses in <sup>5</sup> are supplemented by the term due to  $\xi$ -related surface stresses  $\sigma_{\xi}^{st}$ :

$$\boldsymbol{\sigma} = \frac{\rho}{\rho_0} \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} - \sum_{i=1}^n \frac{\rho}{\rho_0} \left( \boldsymbol{\nabla} \eta_i \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_i} \right)_s - \frac{\rho}{\rho_0} \left( \boldsymbol{\nabla} \boldsymbol{\xi} \otimes \frac{\partial \psi}{\partial \boldsymbol{\nabla} \boldsymbol{\xi}} \right)_s, \tag{19}$$

which leads to

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{e} + \boldsymbol{\sigma}_{\eta}^{st} + \boldsymbol{\sigma}_{\xi}^{st}; \qquad \boldsymbol{\sigma}_{e} = (1 - \phi(\xi))(K\varepsilon_{0e}\boldsymbol{I} + 2\mu\boldsymbol{e}_{e});$$
(20
$$\boldsymbol{\sigma}_{\eta}^{st} = (\psi^{\nabla} + \breve{\psi}_{\theta})\boldsymbol{I} - \beta \sum_{i=1}^{n} (\boldsymbol{\nabla}\eta_{i} \otimes \boldsymbol{\nabla}\eta_{i} + b\boldsymbol{\nabla}\eta_{i} \otimes \sum_{j=1, i \neq j}^{n} \boldsymbol{\nabla}\eta_{j});$$
$$\boldsymbol{\sigma}_{\xi}^{st} = \psi_{\xi}\boldsymbol{I} - \beta_{\xi}\boldsymbol{\nabla}\xi \otimes \boldsymbol{\nabla}\xi = q(\eta_{i})/\Delta_{\xi} \left( \left(16.62\xi^{2}(1 - \xi)^{2} + 0.542\Delta_{\xi}^{2}(\nabla\xi)^{2}\right)\boldsymbol{I} - 1.083\Delta_{\xi}^{2}\boldsymbol{\nabla}\xi \otimes \boldsymbol{\nabla}\xi \right)$$

To obtain a stationary surface layer,  $\xi = 1$  at the external surface and  $\xi = 0$  at the

distance of  $\Delta_{\xi}$  from the surface and along the entire external surface are applied as the boundary conditions.

#### Material parameters

We will consider cubic-to-tetragonal phase transformation in NiAl alloy. We will use the following material parameters determined and/or collected from the literature in <sup>10</sup>:

$$A_{0} = 4.40MPa K^{-1}, \quad \bar{A} = 5.32GPa, \quad \theta_{e} = 215 K, \quad \theta_{c} = -183 K, \quad a = 2.98,$$
  

$$B = 0, \quad D = 0.5GPa, \quad \beta = 2.59 \times 10^{-10} N, \quad L = 2596.5(Pa \cdot s)^{-1},$$
  

$$K = 112.62GPa, \quad \mu = 71.5GPa.$$
(21)

In our finite element method (FEM) simulations, the components of  $\varepsilon_t$  (0.215, -0.078, -0.078) (for M<sub>1</sub>) and (-0.078, 0.215, -0.078) (for M<sub>2</sub>) are used<sup>10</sup>. Also,  $L_{\xi} = 30000 (Pa \cdot s)^{-1}$ ,  $\Delta \gamma = -0.4 J/m^2$ , and b = 0.5. Calculated width and energy of A-M interface for stressfree conditions are  $\Delta_{\eta} = 1.5065 nm$  and  $E_{\eta} = 0.2245 J/m^2$ .

#### Problem formulation

The FEM code COMSOL was utilized for plane stress 2D problems. Rectangular  $25 \times 12.5 nm^2$  sample discretized with triangle Lagrange elements with quadratic approximation was treated. Length of the sample in the horizontal direction is not important as the same results were obtained after the length was doubled. All sides are stress-free, excluding zero vertical displacement at the upper and lower horizontal sides. Boundary conditions (13) for  $\eta_i$  for sharp interface were applied at the right vertical line only; for other sides, and for all sides for problems with surface layer, q = const in Eq.(13). With a surface layer, a stationary solution for  $\xi$  was first obtained for  $\eta_i = 0$ , which was used as an initial condition. Without a layer, initial conditions are  $\eta_i = 0.001$ . The following models were considered: GL equation without mechanics; GL equations with mechanics,

for k = 1/3, 2/3, 1, with elastic properties independent of  $\xi$  and without surface stresses; the same with elastic properties dependent on  $\xi$ ; and the same with surface stresses.

#### Videos' descriptions

Video 1. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\boldsymbol{\varepsilon}_t$  and interface tension  $\boldsymbol{\sigma}_{\eta}^{st}$  for  $\overline{\Delta_{\xi}} = 0$  after critical nanostructure ( $X_c = 0.6859$ ) loses its stability at slight increase in X (X = 0.6864).

Video 2. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.066$ after critical nanostructure ( $X_c = 0.6646$ ) loses its stability at slight increase in X(X = 0.6658).

Video 3. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.199$ after critical nanostructure ( $X_c = 0.6558$ ) loses its stability at slight increase in X(X = 0.6563).

Video 4. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.332$ after critical nanostructure ( $X_c = 0.6432$ ) loses its stability at slight increase in X(X = 0.6445).

Video 5. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.465$ after critical nanostructure ( $X_c = 0.6420$ ) loses its stability at slight increase in X(X = 0.6432).

Video 6. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\boldsymbol{\varepsilon}_t$ , variable elastic properties and interface  $\boldsymbol{\sigma}_{\eta}^{st}$  and surface  $\boldsymbol{\sigma}_{\xi}^{st}$  tensions ( $\boldsymbol{\varepsilon}_t$ ,  $\boldsymbol{\phi}(\xi)$ ,  $\boldsymbol{\sigma}^{st}$ ) for  $\overline{\Delta_{\xi}} = 0.199$  after critical nanostructure ( $X_c =$ 0.6834) loses its stability at slight increase in X (X = 0.6859). Video 7. Evolution of surface-induced nanostructure for coupled GL and mechanics equations with transformation strain  $\boldsymbol{\varepsilon}_t$ , variable elastic properties and interface  $\boldsymbol{\sigma}_{\eta}^{st}$  and surface  $\boldsymbol{\sigma}_{\xi}^{st}$  tensions ( $\boldsymbol{\varepsilon}_t, \phi(\xi), \boldsymbol{\sigma}^{st}$ ) for  $\overline{\Delta_{\xi}} = 1.66$  after critical nanostructure ( $X_c = 0.8116$ ) loses its stability at slight increase in X (X = 0.8141).

Video 8. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain  $\boldsymbol{\varepsilon}_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0$  and X = 0.7915.

Video 9. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.0166$  and X = 0.7915.

Video 10. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.033$  and X = 0.7915.

Video 11. Evolution of surface-induced nanostructure for two martensitic variants for coupled GL and mechanics equations with transformation strain  $\varepsilon_t$  and constant elastic properties for  $\overline{\Delta_{\xi}} = 0.133$  and X = 0.7915.

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## CHAPTER 5. Advanced phase field approach to dislocation evolution

Modified from a paper published in the Physical Review B, Rapid Communication Valery I. Levitas<sup>\*</sup> and Mahdi Javanbakht<sup>†</sup>

## Abstract

Phase field approach to dislocations is conceptually advanced. Large strain formulation is developed. A local thermodynamic potential eliminates stress-dependence of the Burgers vector and reproduces desired local stress-strain curve, as well as the desired, mesh-independent, dislocation height for any dislocation orientation. A gradient energy contains an additional term, which excludes localization of dislocation within height smaller than the prescribed height but does not produce artificial interface energy and dislocation widening. Problems for nucleation and evolution of multiple dislocations along the single and multiple slip systems, and the interaction of dislocations with an austenite (A) – martensite (M) interface are studied using finite element method (FEM). An unexpected scale effect in the athermal resistance to the A–M interface motion due to nucleated incoherency dislocations is revealed.

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## Introduction

Phase field approach (PFA) to dislocation evolution was developed just during the last decade and it is widely used for the understanding of plasticity at nanoscale, see pioneering papers<sup>1-7</sup> and reviews<sup>8, 9</sup>. It allows one simulation of a coupled evolution of multiple interacting dislocations and stress field, without explicit tracking dislocation lines. Despite significant success, there are still a number of points for essential improvement:

(a) All of the previous studies are based on small strain (i.e., < 0.1) formulation. At the same time, plastic shear  $\gamma$  for n dislocations is on the order of magnitude of n, which is huge for multiple dislocations. Elastic strains may also be finite, because stresses for nucleation of a dislocation are of the order of the theoretical strength. Such strains are present when the core structure should be resolved and short-range interaction of dislocations with solute atoms, other dislocations, and dislocation reactions<sup>1, 5, 8</sup> are studied. In these problems, the dislocation height H is taken as interplanar distance d. For larger-scale simulations<sup>2-4</sup>, shear strain is smeared over  $H \sim 100d$  of interplanar distances (and, consequently, reduced by H/d), which does not allow for representing the dislocation core correctly but does not affect stresses far from dislocations. Even for such simulations, shear strain  $\gamma \sim nd/H$  is finite for n > 0.1H/d. Note that for large strains, spectral methods for the problem solution, developed in <sup>1-9</sup>, are not applicable.

(b) As it was mentioned in<sup>10</sup>, the equilibrium value of the order parameters  $\eta_i$  (and consequently, the Burgers vector) depend on stress tensor  $\boldsymbol{\sigma}$ . While in<sup>5</sup> this dependence was eliminated, the Burgers vector appears and grows starting with zero stresses, similar to the case in all other theories. This causes dissipation even in elastic region, which is contradictory in principle but may be not critical for some cases.

(c) In the models<sup>1-5</sup>, the dislocation height H is not defined by a theory but equal to the mesh size; i.e., the theory is in principle not objective and leads to mesh-dependent

solutions. When we reduced mesh size, keeping dislocation height H, dislocation propagates within the height of one element. The problem is not in the numerical approach but in ill-posed problem formulation, which is similar to the problems for shear band localization<sup>11</sup>. This is because the component of the gradient of the order parameter  $\nabla_n = \mathbf{n} \cdot \nabla \eta$  normal to the dislocation plane, does not contribute to the energy, leading to the lack of intrinsic length in this direction and theoretically zero dislocation height. In addition to catastrophic mesh-dependence typical of ill-posed problems, it leads to high oscillating internal shear stress at the interface  $\Sigma$  (which should be of zero width) between the dislocation band and the rest of the crystal. This causes two opposite effects: artificial nucleation of new dislocations and generation of artificial elastic energy at the interface, which suppresses dislocation motion. Also, there is no description of how to handle dislocations inclined with respect to the mesh.

In this chapter, a new PFA to dislocation evolution is developed. It is objective (wellposed) and based on fully large-strain formulation. Our local thermodynamic potential is designed to eliminate stress-dependence of the Burgers vector and to reproduce desired local stress-strain curve, as well as to obtain the desired, mesh-independent, dislocation height for any dislocation orientation. Our gradient energy contains an additional term, related to  $\nabla_n$ , which excludes localization of dislocation within height smaller than the prescribed height H but disappears at  $\Sigma$ ; thus, it does not produce interface energy and does not lead to a dislocation widening. It is demonstrated that internal stresses at  $\Sigma$  can be made negligible by choosing proper numerical approximation; otherwise, error can be drastic. Problems for nucleation and evolution of multiple dislocations along the single and multiple slip systems, and the interaction of dislocations with an A-M interface are studied using FEM. It was found, in particular, that a sharp A-M interface loses its coherency by nucleating a dozen of dislocations; the stationary spacing between them is in perfect agreement with an analytical solution. For a finite-width A-M interface, described by our PFA for phase transformations<sup>13, 14</sup>, an unexpected scale
effect is revealed. In the absence of dislocations, the A–M interface is stable only at the single critical thermal driving force  $X_c^0$ , and it is almost independent of the interface width  $\Delta_{\xi}$ ; thus, an athermal resistance to the interface motion is absent. Generated incoherency dislocations produce an athermal threshold and hysteresis in the driving force for direct-reverse transformation, which strongly depends on the dimensionless interface width  $\bar{\Delta}_{\xi} = \Delta_{\xi}/H$ . Thus, for very small and large  $\bar{\Delta}_{\xi}$ , an athermal threshold and hysteresis unexpectedly disappear.

We designate contractions of tensors A and B over one and two indices as  $A \cdot B$  and A:B; the transpose of A is  $A^{T}$ , I is the unit tensor, and  $\otimes$  designates a dyadic product; summation is assumed over the repeated indices.

## General relationships

## **Kinematics**

Let  $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$  be the location of a material point  $\mathbf{r}_0$  of a body at time t, and  $\mathbf{r}(\mathbf{r}_0, 0) = \mathbf{r}_0$ . The points  $\mathbf{r}_0$  form the reference (undeformed) configuration  $\Omega_0$  while the points  $\mathbf{r}$  form the actual (deformed) configuration  $\Omega$ . Multiplicative decomposition of the total deformation gradient,  $\mathbf{F} := \partial \mathbf{r} / \partial \mathbf{r}_0 = \nabla \mathbf{r}$ 

$$\boldsymbol{F} = \boldsymbol{F}_e \cdot \boldsymbol{F}_p; \quad \boldsymbol{F}_e := \boldsymbol{R} \cdot \boldsymbol{U}_e := \boldsymbol{V}_e \cdot \boldsymbol{R} \tag{1}$$

into elastic and plastic parts is used; here  $\mathbf{R}$  the orthogonal proper lattice rotation tensor  $(\mathbf{R}^t = \mathbf{R}^{-1}, \text{ det } \mathbf{R}=1)$ ;  $\mathbf{U}_e$  and  $\mathbf{V}_e$  are the the symmetric elastic right and left stretch tensors. Eq.(1) is generally accepted in crystal plasticity<sup>12</sup>. After local reduction of stress tensor to zero and disappearance of elastic strain and rotation (i.e.,  $\mathbf{F}_e = \mathbf{I}$ ), an unloaded configuration, characterized by  $\mathbf{F}_p$ , is designated as  $\Omega_p$ . Important point in unambiguous separation of  $\mathbf{F}_e$  and  $\mathbf{F}_p$  is that  $\mathbf{F}_p$  does not change an orientation of the

crystal lattice. For small strain and rotation approximation,

$$F \simeq I + \varepsilon + \omega;$$
  $F_e \simeq I + \varepsilon_e + \omega_e,$   $F_p \simeq I + \varepsilon_p + \omega_p,$  (2)

where  $\boldsymbol{\varepsilon}$  is the symmetric small strain tensor and its elastic and plastic components, and  $\boldsymbol{\omega}$  is the skew-symmetric small rotation tensor and its elastic and plastic components. Then neglecting product of two small tensors, we obtain

$$\boldsymbol{F} = (\boldsymbol{I} + \boldsymbol{\varepsilon}_e + \boldsymbol{\omega}_e) \cdot (\boldsymbol{I} + \boldsymbol{\varepsilon}_p + \boldsymbol{\omega}_p) \simeq \boldsymbol{I} + \boldsymbol{\varepsilon}_e + \boldsymbol{\omega}_e + \boldsymbol{\varepsilon}_p + \boldsymbol{\omega}_p = \boldsymbol{F}_e + \boldsymbol{F}_p - \boldsymbol{I}$$
(3)

and comparison with Eq.(2) for  $\boldsymbol{F}$  implies

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_p; \qquad \boldsymbol{\omega} = \boldsymbol{\omega}_e + \boldsymbol{\omega}_p, \tag{4}$$

i.e., the multiplicative decomposition of deformation gradient into elastic and plastic parts at large strains reduces to additive decomposition of strain and rotations for geometrically linear case. For a single slip at the  $\alpha^{th}$  slip plane with the unit normal  $\mathbf{n}^{\alpha}$  in the  $\omega^{th}$  slip direction with the Burgers vector  $\mathbf{b}^{\alpha\omega}$ ,  $\mathbf{F}_{p}$  represents a simple shear

$$\boldsymbol{F}_{p} = \boldsymbol{I} + \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha \omega}) = \boldsymbol{I} + \gamma_{\alpha \omega} \boldsymbol{m}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha \omega}), \qquad (5)$$

where  $\gamma_{\alpha\omega} = |\mathbf{b}^{\alpha\omega}|/H_{\alpha}$  is the plastic shear strain in a dislocation band per single dislocation,  $\mathbf{m}^{\alpha\omega}$  is the unit vector in the direction of  $\mathbf{b}^{\alpha\omega}$ ,  $\eta_{\alpha\omega}$  is the order parameter for a dislocation in the  $\alpha^{th}$  plane along the  $\omega^{th}$  slip direction, which varies between 0 and nwhen n dislocations appear;  $\Phi$  is a function to be found, which satisfies the condition  $\Phi(n) = n$ . All parameters  $(\mathbf{n}^{\alpha}, \mathbf{b}^{\alpha\omega}, H^{\alpha}, ...)$  and the gradient operator  $\nabla$  are determined in the undeformed configuration. Thus, the order parameter is unambiguously connected to the magnitude of the Burgers vector  $\mathbf{b}^{\alpha\omega}\Phi(\eta_{\alpha\omega})$  or plastic shear  $\gamma_{\alpha\omega}\Phi(\eta_{\alpha\omega})$ in transitional state between n-1 and n dislocations: when  $\eta_{\alpha\omega}$  varies between n-1and n, the Burgers vector and plastic shear vary between their values for n-1 and ndislocations. We define

$$\dot{\boldsymbol{F}}_{p} = \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha\omega}) = \gamma_{\alpha\omega} \boldsymbol{m}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha\omega}), \qquad (6)$$

$$\boldsymbol{F}_{p}^{-1} = \boldsymbol{I} - \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha \omega}) = \boldsymbol{I} - \gamma_{\alpha \omega} \boldsymbol{m}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha \omega}),$$
(7)

which can be checked by proving that  $\boldsymbol{F}_{p} \cdot \boldsymbol{F}_{p}^{-1} = \boldsymbol{I}$ , since vectors  $\boldsymbol{n}^{\alpha}$  and  $\boldsymbol{b}^{\alpha\omega}$  are mutually orthogonal  $(\boldsymbol{b}^{\alpha\omega} \cdot \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha\omega}) = 0)$ , and plastic velocity gradient

$$\boldsymbol{l}_{p} := \dot{\boldsymbol{F}}_{p} \cdot \boldsymbol{F}_{p}^{-1} = \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha \omega}) = \gamma_{\alpha \omega} \boldsymbol{m}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha \omega}) = \dot{\boldsymbol{F}}_{p}.$$
(8)

When slip occurs simultaneously along several slip planes and systems, an additive decomposition is usually accepted for small strains:

$$\boldsymbol{\varepsilon}_{p} + \boldsymbol{\omega}_{p} = \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \Phi(\eta_{\alpha \omega}), \qquad (9)$$

similar to crystal plasticity. This additivity preserves plastic incompressibility, because volumetric plastic strain

$$\varepsilon_{vp} = (\boldsymbol{\varepsilon}_p + \boldsymbol{\omega}_p) : \boldsymbol{I} = \sum_{\alpha=1}^p \sum_{\omega=1}^{m_\alpha} \frac{1}{H^\alpha} \boldsymbol{b}^{\alpha\omega} \cdot \boldsymbol{n}^\alpha \Phi(\eta_{\alpha\omega}) = 0.$$
(10)

For finite strains, crystal plasticity utilizes additivity of plastic velocity gradients, which we will accept as well:

$$\boldsymbol{l}_{p} := \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \boldsymbol{l}_{p}^{\alpha\omega} = \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha\omega}) = \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \gamma_{\alpha\omega} \boldsymbol{m}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha\omega}).$$
(11)

Thus, in contrast to PFA for martensitic phase transformations and twinning at large strains<sup>17, 15, 18</sup>, in which the finite expression for the transformation strain in terms of the order parameters,  $\boldsymbol{F}_p(\eta_i)$ , were accepted, here we formulate differential Eq.(11) for  $\boldsymbol{F}_p$ , which can be expressed as

$$\dot{\boldsymbol{F}}_{p} := \boldsymbol{l}_{p} \cdot \boldsymbol{F}_{p} = \left[\sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha \omega})\right] \cdot \boldsymbol{F}_{p} = \left[\sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \gamma_{\alpha \omega} \boldsymbol{m}^{\alpha \omega} \otimes \boldsymbol{n}^{\alpha} \dot{\Phi}(\eta_{\alpha \omega})\right] \cdot \boldsymbol{F}_{p}.$$
(12)

Thus,  $\mathbf{F}_p$  as a solution of Eq.(12) does not only depend on the all order parameters but on the entire history of their variation. If, e.g., plastic strain occurs along some single slip system 1 producing  $\mathbf{F}_{p1}$ , then along some single slip system 2 at fixed  $\mathbf{F}_{p1}$  producing  $\mathbf{F}_{p2}$  on the top of  $\mathbf{F}_{p1}$ , and so on, then Eq.(12) can be integrated as

$$\boldsymbol{F}_{p} = \boldsymbol{F}_{pn} \cdot \ldots \cdot \boldsymbol{F}_{p2} \cdot \boldsymbol{F}_{p1}; \qquad \boldsymbol{F}_{pi} = \boldsymbol{I} + \frac{1}{H^{i}} \boldsymbol{b}^{i} \otimes \boldsymbol{n}^{i} \Phi(\eta_{i}).$$
(13)

Indeed, if  $\boldsymbol{F}_{pn}$  varies only while all previous slips are fixed, then

$$\dot{\boldsymbol{F}}_{p} = \dot{\boldsymbol{F}}_{pn} \cdot \ldots \cdot \boldsymbol{F}_{p2} \cdot \boldsymbol{F}_{p1}; \quad \boldsymbol{F}_{p}^{-1} = \boldsymbol{F}_{p1}^{-1} \cdot \boldsymbol{F}_{p2}^{-1} \cdot \ldots \cdot \boldsymbol{F}_{pn}^{-1};$$
$$\boldsymbol{l}_{p} := \dot{\boldsymbol{F}}_{p} \cdot \boldsymbol{F}_{p}^{-1} = \dot{\boldsymbol{F}}_{pn} \cdot \boldsymbol{F}_{pn}^{-1} = \dot{\boldsymbol{F}}_{pn} = \frac{1}{H^{n}} \boldsymbol{b}^{n} \otimes \boldsymbol{n}^{n} \dot{\Phi}(\eta_{n}), \qquad (14)$$

where Eq.(8) was utilized for a simple shear  $\boldsymbol{F}_{pn}$ . The last Eq.(14) can be integrated

$$\boldsymbol{F}_{pn} = \boldsymbol{I} + \frac{1}{H^n} \boldsymbol{b}^n \otimes \boldsymbol{n}^n \Phi(\eta_n), \qquad (15)$$

and it is independent of previous  $F_{pi}$ . Thus, it can be multiplicatively superposed on the deformation gradient due to previous shears. Formally, Eq.(13) can be applied when each shear occurs along the same slip system with increasing number of dislocations. In this case, it transforms to an additive rule, e.g.,

$$\boldsymbol{F}_{p} = \boldsymbol{F}_{p2} \cdot \boldsymbol{F}_{p1} = (\boldsymbol{I} + \frac{1}{H^{i}} \boldsymbol{b}^{i} \otimes \boldsymbol{n}^{i} (\Phi(\eta_{i}) - \Phi(\eta_{i}^{1}))) \cdot (\boldsymbol{I} + \frac{1}{H^{i}} \boldsymbol{b}^{i} \otimes \boldsymbol{n}^{i} \Phi(\eta_{i}^{1})) = \boldsymbol{I} + \frac{1}{H^{i}} \boldsymbol{b}^{i} \otimes \boldsymbol{n}^{i} \Phi(\eta_{i}), \quad (16)$$

because  $\mathbf{n}^i \cdot \mathbf{b}^i = 0$ , i.e., our initial assumption of additivity of shears along the same slip direction is noncontradictory.

In addition, Eq.(11) guarantees plastic incompressibility for any values of the order parameters. Indeed, plastic volumetric strain is  $\varepsilon_{p0} := det \mathbf{F}_p$  and its rate  $\dot{\varepsilon}_{p0} = \mathbf{I}: \mathbf{l}_p = 0$ because  $\mathbf{m}^{\alpha\omega} \cdot \mathbf{n}^{\alpha} = 0$ .

To summarize, Eq.(11) (or Eq.(12)) will be used as our main kinematic relationship.

## Thermodynamics

We will consider an arbitrary volume  $V_0$  of material bounded by a surface  $S_0$  with unit external normal  $\boldsymbol{n}$  in the undeformed configuration. To make derivations compact, we will use the expression for the second law of thermodynamics for an isothermal case for the volume  $V_0$ :

$$\bar{D} = \int_{S_0} (\boldsymbol{v} \cdot \boldsymbol{P} \cdot \boldsymbol{n} + \boldsymbol{\Theta}_{\alpha\omega} \dot{\eta}_{\alpha\omega} \cdot \boldsymbol{n}) dS_0 - \frac{d}{dt} \int_{V_0} (\psi + 0.5\rho_0 \boldsymbol{v} \cdot \boldsymbol{v}) dV_0 - \int_{V_0} \rho_0 \boldsymbol{f} \cdot \boldsymbol{v} dV_0 \ge 0, \quad (17)$$

where  $\overline{D}$  is the global (i.e., for the entire volume) dissipation rate,  $\boldsymbol{v} = \dot{\boldsymbol{r}}$  is the material velocity,  $\boldsymbol{P}$  is the nonsymmetric first Piola-Kirchoff (nominal) stress tensor-i.e., the force per unit area in the undeformed state,  $\rho_0$  is the mass density in the reference state,  $\psi$ is the specific (per unit undeformed volume) Helmholtz free energy, and  $\boldsymbol{f}$  is the body force per unit mass. We included an extra generalized surface forces  $\boldsymbol{\Theta}_{\alpha\omega} \cdot \boldsymbol{n}$  conjugate to  $\dot{\eta}_{\alpha\omega}$  in order to balance terms that appear due to dependence of the free energy on  $\nabla \eta_{\alpha\omega}$ . As it will be seen below, without  $\boldsymbol{\Theta}_{\alpha\omega}$ , Eq.(17) will not applicable for an arbitrary volume. Transforming the surface integral into a volume integral with the help of the Gauss theorem and applying the balance of momentum, one obtains from Eq. (17):

$$\bar{D} = \int_{V_0} \left( \boldsymbol{P} \cdot \dot{\boldsymbol{F}}^T + \boldsymbol{\nabla} \cdot \left(\boldsymbol{\Theta}_{\alpha\omega} \dot{\eta}_{\alpha\omega}\right) - \dot{\psi} \right) dV_0 \ge 0.$$
(18)

Due to arbitrariness of the volume  $V_0$ , Eq. (18) can be localized for an arbitrary point

$$D = \boldsymbol{P} : \boldsymbol{\dot{F}}^{T} + \boldsymbol{\nabla} \cdot (\boldsymbol{\Theta}_{\alpha\omega} \dot{\eta}_{\alpha\omega}) - \dot{\psi} \ge 0, \qquad (19)$$

where D is the local dissipation rate.

Let  $\psi = \bar{\psi}(\boldsymbol{F}_e, \eta_{\alpha\omega}, \boldsymbol{\nabla}\eta_{\alpha\omega})$ -i.e., the free energy is independent of the plastic deformation gradient and the temperature is omitted for compactness. Under superposition of the rigid-body rotation  $\boldsymbol{F}^* = \boldsymbol{Q}\cdot\boldsymbol{F}$ , where  $\boldsymbol{Q}$  is the arbitrary proper orthogonal tensor, one has  $\boldsymbol{F}_e^* = \boldsymbol{Q}\cdot\boldsymbol{F}_e$  and  $\psi = \bar{\psi}(\boldsymbol{Q}\cdot\boldsymbol{F}_e, \eta_{\alpha\omega}, \boldsymbol{\nabla}\eta_{\alpha\omega})$ . Utilizing  $\boldsymbol{Q} = \boldsymbol{R}^T$  and the polar decomposition Eq. (1), one has  $\psi = \bar{\psi}(\boldsymbol{U}_e, \eta_{\alpha\omega}, \boldsymbol{\nabla}\eta_{\alpha\omega}) = \psi(\boldsymbol{E}_e, \eta_{\alpha\omega}\boldsymbol{\nabla}\eta_{\alpha\omega})$ , where  $\mathbf{E}_e = 0.5(\mathbf{U}_e \cdot \mathbf{U}_e - \mathbf{I}) = 0.5(\mathbf{F}_e^T \cdot \mathbf{F}_e - \mathbf{I})$  is the Lagrangian strain tensor. Differentiating Eq.(1), we obtain  $\dot{\boldsymbol{F}}^T = \dot{\boldsymbol{F}}_p^T \cdot \boldsymbol{F}_e^T + \boldsymbol{F}_p^T \cdot \dot{\boldsymbol{F}}_e^T$ . Using

$$\boldsymbol{\nabla} \cdot (\boldsymbol{\Theta}_{\alpha\omega} \dot{\eta}_{\alpha\omega}) = (\boldsymbol{\nabla} \cdot \boldsymbol{\Theta}_{\alpha\omega}) \dot{\eta}_{\alpha\omega} + \boldsymbol{\Theta}_{\alpha\omega} \cdot \boldsymbol{\nabla} \dot{\eta}_{\alpha\omega}, \qquad (20)$$

 $\nabla \dot{\eta}_{\alpha\omega} = \overline{\nabla \eta}_{\alpha\omega}$  and substituting these equations in Eq.(19), one transforms

$$D = \left( \mathbf{P} \cdot \mathbf{F}_{p}^{T} - \frac{\partial \psi}{\partial \mathbf{F}_{e}} \right) : \dot{\mathbf{F}}_{e}^{T} + \left( \mathbf{F}_{e}^{T} \cdot \mathbf{P} : \frac{\partial \mathbf{F}_{p}}{\partial \eta_{\alpha\omega}} + \nabla \cdot \mathbf{\Theta}_{\alpha\omega} - \frac{\partial \psi}{\partial \eta_{\alpha\omega}} \right) \dot{\eta}_{\alpha\omega}$$
$$\left( \mathbf{\Theta}_{\alpha\omega} - \frac{\partial \psi}{\partial \nabla \eta_{\alpha\omega}} \right) \cdot \overline{\nabla \eta_{\alpha\omega}} \ge 0.$$
(21)

Assuming that the dissipation rate is independent of  $\dot{\boldsymbol{F}}_{e}^{T}$  and  $\overline{\boldsymbol{\nabla}\eta_{\alpha\omega}}$ , one obtains the constitutive relationship for stresses and definition of  $\boldsymbol{\Theta}_{\alpha\omega}$ ;

$$\boldsymbol{P} \cdot \boldsymbol{F}_{p}^{T} = \frac{\partial \psi}{\partial \boldsymbol{F}_{e}}; \quad \boldsymbol{\Theta}_{\alpha \omega} = \frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_{\alpha \omega}}.$$
(22)

Then, the dissipation inequality reduces to

$$D = X_{\alpha\omega} \dot{\eta}_{\alpha\omega} \ge 0; \qquad X_{\alpha\omega} := \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} : \frac{\partial \boldsymbol{F}_{p}}{\partial \eta_{\alpha\omega}} + \boldsymbol{\nabla} \cdot \left(\frac{\partial \psi}{\partial \boldsymbol{\nabla} \eta_{\alpha\omega}}\right) - \frac{\partial \psi}{\partial \eta_{\alpha\omega}}, \tag{23}$$

where  $X_{\alpha\omega}$  is the thermodynamic force conjugate to  $\dot{\eta}_{\alpha\omega}$  or the driving force for change in  $\eta_{\alpha\omega}$ . Let us elaborate the transformation work term in Eq.(8) with the help of Eq.(12). Thus, according to Eq.(12)

$$\frac{\partial \boldsymbol{F}_p}{\partial \eta_{\alpha\omega}} = \left[\sum_{\alpha=1}^p \sum_{\omega=1}^{m_{\alpha}} \gamma_{\alpha\omega} \boldsymbol{m}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \frac{\partial \Phi}{\partial \eta_{\alpha\omega}}\right] \cdot \boldsymbol{F}_p.$$
(24)

Then

$$\boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} : \frac{\partial \boldsymbol{F}_{p}}{\partial \eta_{\alpha\omega}} = \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} : \left[ \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \gamma_{\alpha\omega} \boldsymbol{m}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \frac{\partial \Phi}{\partial \eta_{\alpha\omega}} \right] \cdot \boldsymbol{F}_{p} =$$

$$\sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \boldsymbol{n}^{\alpha} \cdot \boldsymbol{F}_{p} \cdot \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} \cdot \boldsymbol{m}^{\alpha\omega} \gamma_{\alpha\omega} \frac{\partial \Phi}{\partial \eta_{\alpha\omega}} = \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \tau_{\alpha\omega} \gamma_{\alpha\omega} \frac{\partial \Phi}{\partial \eta_{\alpha\omega}}; \quad \tau_{\alpha\omega} := \boldsymbol{n}^{\alpha} \cdot \boldsymbol{F}_{p} \cdot \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} \cdot \boldsymbol{m}^{\alpha\omega},$$
(25)

where  $\tau_{\alpha\omega}$  is the resolved shear stress for slip system  $\alpha\omega$ . For small strains and rotations,  $\boldsymbol{P} \simeq \boldsymbol{\sigma}$ , where  $\boldsymbol{\sigma}$  is the true Cauchy stress (force per unit deformed area),  $\boldsymbol{F}_p \simeq \boldsymbol{F}_e \simeq \boldsymbol{I}$ , and  $\tau_{\alpha\omega} = \boldsymbol{n}^{\alpha} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{m}^{\alpha\omega}$  simplifies to the usual resolved stress.

#### Kinetic equations and gradient energy

It is traditional in nonequilibrium thermodynamics that one has to assume a general, nonlinear kinetic equation  $\dot{\eta}_{\alpha\omega} = f(X_{\beta\gamma})$  connecting the slip rate in  $\alpha\omega^{th}$  slip system with the driving force for  $\beta\gamma^{th}$  force–i.e., including cross effects. In the linear approximation  $\dot{\eta}_{\alpha\omega} = L^{\beta\gamma}_{\alpha\omega}X_{\beta\gamma}$ , where  $L^{\beta\gamma}_{\alpha\omega}$  are positive definite kinetic coefficients, which satisfy the Onsager reciprocal relationships  $L^{\beta\gamma}_{\alpha\omega} = L^{\alpha\omega}_{\beta\gamma}$ . We will use usual decomposition of the free energy  $\psi = \psi^l + \psi^{\nabla}$  into local energy  $\psi^l$  and gradient-related  $\psi^{\nabla}$  parts. Gradient energy is localized at dislocation core region, thus contributing to the core energy. We decompose

$$\boldsymbol{\nabla}\eta_{\alpha\omega} = \nabla\eta_{\alpha\omega}^{m}\boldsymbol{m}^{\alpha\omega} + \nabla^{n}\eta_{\alpha\omega}\boldsymbol{n}^{\alpha\omega}; \quad \nabla\eta_{\alpha\omega}^{m} := \boldsymbol{\nabla}\eta_{\alpha\omega}\cdot\boldsymbol{m}^{\alpha\omega}; \quad \nabla\eta_{\alpha\omega}^{n} := \boldsymbol{\nabla}\eta_{\alpha\omega}\cdot\boldsymbol{n}^{\alpha\omega}$$
(26)

into contributions along the slip direction and along the normal to the slip plane. It is generally accepted that free energy should be independent of the contribution  $\nabla \eta^n_{\alpha\omega}$ along the normal to the slip plane, because slip planes do not posses any dislocationrelated energy away from the dislocation cores<sup>1-9</sup>. This distinguishes gradient energy of dislocations from that for martensitic units and twins, because all their interfaces posses energy. As we mentioned in Introduction, this, however, leads to the lack of a characteristic length in the directions  $\mathbf{n}^{\alpha\omega}$ , ill-posed system of evolutionary equations for  $\eta_{\alpha\omega}$ , catastrophic mesh-dependence of the solution. Thus, one has to introduce a characteristic length in the directions  $\mathbf{n}^{\alpha\omega}$  and regularize the problem, still keeping energy of the interface  $\Sigma$  between dislocation band and the rest of the crystal zero. In the approximation of the quadratic form, the simplest expression is

$$\psi^{\nabla} = 0.5 \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \sum_{\varsigma=1}^{p} \sum_{\gamma=1}^{m_{\varsigma}} \left( \beta_{\alpha\omega}^{\varsigma\gamma} \nabla \eta_{\alpha\omega}^{m} \nabla \eta_{\varsigma\gamma}^{m} + M(1 - \bar{\eta}_{\alpha\omega})^{2} \nu_{\alpha\omega}^{\varsigma\gamma} \nabla \eta_{\alpha\omega}^{n} \nabla \eta_{\varsigma\gamma}^{n} \right),$$
(27)

If  $\psi^{\nabla} = 0.5 \nabla \eta_i \cdot \boldsymbol{\beta}_{ij} \cdot \nabla \eta_j$ , where  $\boldsymbol{\beta}_{ij}$  are positive definite gradient-energy second-rank tensors, then, the kinetic equation  $\dot{\eta}_j = L_{ji}X_i$  has the form

$$\dot{\eta}_j = L_{ji} \left( \boldsymbol{P}^{\mathrm{T}} \cdot \boldsymbol{F}_e: \frac{\partial \boldsymbol{F}_p}{\partial \eta_j} - \frac{\partial \psi}{\partial \eta_i} + \boldsymbol{\nabla} \cdot (\boldsymbol{\beta}_{ik} \cdot \boldsymbol{\nabla} \eta_k) \right).$$
(28)

$$\boldsymbol{F}_{p} = \boldsymbol{I} + \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \left[ \phi(\bar{\eta}_{\alpha\omega}) + Int(\eta_{\alpha\omega}) \right],$$
(29)

where  $\phi(\bar{\eta}) = \bar{\eta}^2 (3 - 2\bar{\eta})$ , index  $\alpha$  designates the  $\alpha^{th}$  slip plane with the unit normal  $\mathbf{n}^{\alpha}$  and index  $\omega$  is for  $\omega^{th}$  Burgers vector  $\mathbf{b}^{\alpha\omega}$  in each slip plane;  $\eta_{\alpha\omega}$  is the order parameter for dislocations in the  $\alpha^{th}$  plane along the  $\omega^{th}$  slip direction, which varies between 0 and

*n* when *n* dislocations appear;  $Int(\eta_{\alpha\omega})$  and  $\bar{\eta} := \eta - Int(\eta_{\alpha\omega}) \in [0, 1]$  are the integer and fractional parts of  $\eta_{\alpha\omega}$ .

The Helmholtz free energy per unit undeformed volume is accepted as  $\psi = \psi(\boldsymbol{B}_e, \eta_{\alpha\omega}, \boldsymbol{\nabla}\eta_{\alpha\omega})$ , where  $\boldsymbol{B}_e = 0.5(\boldsymbol{V}_e \cdot \boldsymbol{V}_e - \boldsymbol{I})$ . The thermodynamic procedure similar to that for phase transformations<sup>13, 14, 15</sup> and linear relationships between thermodynamic forces and fluxes result in expression for stresses

$$\boldsymbol{\sigma} = \frac{\rho}{\rho_0} \boldsymbol{V}_e \cdot \frac{\partial \psi}{\partial \boldsymbol{B}_e} \cdot \boldsymbol{V}_e \tag{30}$$

and Ginzburg-Landau equations

$$\frac{1}{L}\frac{\partial\eta_{\alpha\omega}}{\partial t} = \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} : \frac{\partial \boldsymbol{F}_{p}}{\partial\eta_{\alpha\omega}} - \frac{\partial\psi}{\partial\eta_{\alpha\omega}} + \boldsymbol{\nabla} \cdot \frac{\partial\psi}{\partial\boldsymbol{\nabla}\eta_{\alpha\omega}}, \qquad (31)$$

where L is the kinetic coefficient,  $\boldsymbol{\sigma}$  and  $\boldsymbol{P}$  are the true Cauchy stress tensor and the nonsymmetric Piola-Kirchoff stress tensor (force per unit area in the undeformed configuration). We accept the expression for

$$\psi = \psi^{e}(\boldsymbol{B}_{e}) + \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} A_{\alpha} \bar{\eta}_{\alpha\omega}^{2} (1 - \bar{\eta}_{\alpha\omega})^{2} + \frac{\beta}{2} \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \left\{ \boldsymbol{\nabla} \bar{\eta}_{\alpha\omega}^{2} + [M(1 - \bar{\eta}_{\alpha\omega})^{2} - 1] (\boldsymbol{\nabla} \bar{\eta}_{\alpha\omega} \cdot \boldsymbol{n}_{\alpha})^{2} \right\},$$
(32)

as the sum of elastic, crystalline, and gradient energy. The coefficient  $A_{\alpha}$  is a periodic step-wise function of the coordinate along the normal to the slip plane  $\mathbf{n}_{\alpha}$ , which is equal to  $A_{0\alpha}$  within the dislocation band of the height  $H_{\alpha}$  and  $kA_{0\alpha}$  ( $k \gg 1$ ) in a thin boundary layer between dislocations of the width  $w_{\alpha} = pH_{\alpha}$  ( $p \ll 1$ ). This function determines the dislocation height independent of the computational mesh, which makes our equations objective. The  $\eta_{\alpha\omega}$  dependence of  $\mathbf{F}_p$  and the crystalline energy is obtained from conditions that for homogeneous states, the stationary solutions of Eq.(31) are  $\eta_{\alpha\omega} = n$  for any stresses, which provides independence of the Burgers vector of the stress. Another solution results in the equilibrium resolved shear stress  $\tau - \bar{\eta}$  relationship:

$$\tau_{\alpha\omega} = \boldsymbol{n}_{\alpha} \cdot \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} \cdot \frac{\boldsymbol{b}^{\alpha\omega}}{|\boldsymbol{b}^{\alpha\omega}|} = \tau^{c}_{\alpha\omega}(1 - 2\bar{\eta}_{\alpha\omega}), \qquad (33)$$

where  $\tau_{\alpha\omega}^c = A_{\alpha\omega}/3\gamma_{\alpha\omega}$  is the critical shear stress;  $\gamma_{\alpha\omega} = |\mathbf{b}^{\alpha\omega}|/H_{\alpha}$  is the plastic shear strain. Eq.(33), in contrast to previous models, has the following desired features: dislocation does not nucleate (i.e.,  $\bar{\eta}_{\alpha\omega} = 0$ ) for  $-\tau_{\alpha\omega}^c < \tau_{\alpha\omega} < \tau_{\alpha\omega}^c$ , i.e., there is no artificial dissipation in elastic region; after nucleation (i.e.,  $\bar{\eta}_{\alpha\omega} \neq 0$ ), stress reduces monotonously with the increasing  $\bar{\eta}_{\alpha\omega}$ , i.e., material instability will lead to  $\bar{\eta}_{\alpha\omega} \to 1$ .

If M = 0, gradient energy in Eq.(32) coincides with known expressions<sup>2-5</sup>. However, for M = 0, after nucleation, dislocation propagates within band of one finite element high, which is unphysical. An additional term with  $M \ll 1$  penalizes gradients along the normal  $\mathbf{n}_{\alpha}$ , which leads to dislocation propagation within entire band of the height H. It is localized at the propagation front, disappears when dislocation is completed  $(\bar{\eta}_{\alpha\omega} = 1)$ , and does not produce artificial surface energy at the boundary  $\Sigma$ .

Equilibrium equation  $\nabla \cdot \boldsymbol{P} = 0$  is included. Isotropic linear elasticity was used for simplicity in all examples. To resolve a dislocation core and interaction between the phase interface and dislocations, we use  $H^{\alpha} = 2d^{\alpha}$  in all problems. However, for largerscale simulations, one can use  $H^{\alpha} = 100d^{\alpha}$  like in<sup>2-4</sup>. The following parameters for all slip systems have been used in all problems, unless stated differently:  $\beta = 8.76 \times 10^{-11}N$ ,  $A_0 = 1.43 \times 10^9 N/m$ ,  $L = 10^4 (Pa \cdot s)^{-1}$ , M = 0.1,  $\gamma = 0.5$ , k = 100, H = 0.7nm, w =0.1H,  $|\boldsymbol{b}| = 0.35nm$ , shear modulus  $\mu = 71.5GPa$ , and bulk modulus K = 112.6GPa.

In our simplified PFA to interaction of dislocations and phase transformations, we use  $\mathbf{F} = \mathbf{F}_e \cdot \mathbf{F}_t \cdot \mathbf{F}_p$  and all equations and properties for phase transformations from<sup>14</sup>, including equation for transformation deformation gradient  $\mathbf{F}_t$ . It is not our goal here to develop a general theory for interaction of dislocations and phase transformations. However, to make the first step toward such a theory and to illustrate our PFA to dislocations with the nontrivial and challenging problems, we included problems that do not require a general theory for such an interaction. Namely, we consider dislocations either solely in austenite (assuming, e.g., much higher yield strength of martensite) or at the austenite-martensite interface.

## Numerical solutions

FEM approach and code COMSOL with embedded remeshing procedure were used. Plane strain problems for straight edge dislocations are considered. All size, stress, and time parameters are normalized by the dislocation height H,  $\tau_c$ , and characteristic time  $1/(A_0L)$ , respectively. The  $\eta$  profile for a single dislocation practically coincided with an analytical expression from<sup>16</sup>.

#### Parametric study of the accuracy of numerical solution

Comprehensive parametric study of the accuracy of numerical solution was performed. As an example, a rectangle with the size of  $5 \times 21.5$  is considered with the upper side fixed in the y direction and the lower side in both x and y directions; lateral sides are stress-free. Macroscopic simple shear strain is applied: the horizontal displacement  $\bar{u} = 0.4\bar{t}$  is applied at the upper side from  $\bar{t} = 0$  to 5, and then  $\bar{u} = 2$  from  $\bar{t} = 5$ to 10. Multiple potential horizontal dislocation bands are introduced by prescribing corresponding periodic function for the threshold  $A^{\alpha}$ . Initial condition is  $\eta = 0.01$  in a small region at the left side of the bands and zero everywhere else. The material properties are listed above except  $A_0 = 0.36 \times 10^9 N/m$  and  $\gamma = 0.25$ . Unstructured FEM mesh was used.

In Fig. 5.1, distribution of the order parameter and shear stress  $\sigma_{xy}$  at  $\bar{t} = 10$  are presented for the 5<sup>th</sup> degree polynomial in space coordinates for both  $\eta$  and displacements (solid red line, mesh-independent solution), and for the 2<sup>nd</sup> degree polynomial for  $\eta$  and 5<sup>th</sup> degree polynomial for displacements (blue dashed line). Results differ drastically. One of the main natural requirements to the solution is that after passing of dislocations through any chosen region, boundaries of the dislocation bands  $\Sigma$  do not generate internal stresses. For the lower degree polynomial, significant unphysical internal shear stresses (oscillations) at the boundaries  $\Sigma$  are present even after appearance of the



Figure 5.1 Distribution of the order parameter (a) and shear stress  $\sigma_{xy}$  (b) at  $\bar{t} = 10$  in a rectangular sample for the 5<sup>th</sup> degree polynomial in space coordinates for both  $\eta$  and displacements (solid red line, mesh-independent solution), and for the 2<sup>nd</sup> degree polynomial for  $\eta$  and 5<sup>th</sup> degree polynomial for displacements (blue dashed line).

first dislocation. These oscillations produce artificial interface energy, which suppresses propagation of dislocations; that is why solutions for different FEM approximations are very different, including different number of dislocations and, consequently, degree of relaxation of elastic stresses. They cause artificial nucleation of dislocations for other situations. At the same time, for  $5^{th}$  degree polynomial for both fields, internal stresses and oscillations are negligible even after appearance of multiple dislocations. Obtained results illustrate potential danger of obtaining physically wrong solutions unless their correctness is proven.

### Sharp A-M interface and incoherency dislocations

A rectangle with the size of  $7.14 \times 57.14$  was considered with the sharp A–M interface in the middle of it and in the middle of a dislocation band (Fig. 5.2). A misfit (transformation) strain of  $\delta = 0.1$  in the x direction is applied in the upper martensitic half of the sample. The upper and lower sides are fixed in the y direction; all other external stresses are zero. Initial condition was  $\eta = 0.01$  inside the dislocation band. Interface loses its

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Figure 5.2 Stationary distribution of dislocations that appeared at free surface and propagated along the sharp A–M interface with a misfit strain of 0.1 in the x direction. Right symmetric half of a sample is shown.

coherence by nucleating dislocations at the free surface, one by another, which propagate along the interface<sup>16</sup>. In the stationary state, distance between any of two neighboring dislocations is 5, in perfect correspondence with analytical expression  $|\mathbf{b}|/(\delta H)$ . Eleven dislocations produce a step at the free surface with shear strain of  $n\gamma = 5.5$ , which clearly requires large-strain formulation.

## Parallel dislocation system

A rectangle with the size of  $7.4 \times 14.26$  was considered with the upper and lower sides fixed in the y direction and the left bottom corner fixed in both directions. This problem models dislocation activity near the lath martensite unit, which is located at the left side of the sample and possesses transformation shear strain 0.3 (Fig. 5.3 and <sup>16</sup>). Initially, there are no dislocations ( $\eta = 0$ ), except in a small region along the inclined A–M interface with  $\eta = 0.01$ . Elastic stresses lead to nucleation and propagation of parallel dislocations, one after another, with 2 or 3 in each system in the stationary state. Relaxation of elastic stresses leads to straightening of initially curved interface. Dislocations do not move outside the prescribed bands, have clear horizontal boundaries (despite the unstructured FEM mesh), and propagate acceptably quasi-homogeneously



(similar to the problem 1). Moreover, the solution is mesh-independent for more than 6 elements per band.

Figure 5.3 Evolution of a parallel dislocation systems in austenite under prescribed transformation shear strain in the martensitic part of a sample.

### Interaction of the evolving A-M interface and dislocations

Both phase transformation and dislocation evolution are described by a PFA. A sample and boundary conditions are the same as for problem 1. First, stationary solution for the horizontal finite-width A-M interface, described by the order parameter  $\xi$  and located at the center of a sample, was obtained without dislocations, which was taken as an initial condition for a coupled problem with dislocations. Transformation strain of  $\delta = 0.1$  in the x direction is applied in the upper martensitic half of the sample, like for problem 1. A dislocation band is located at the middle of the sample (Fig. 5.4). Initial condition is  $\eta = 0.01$  inside the dislocation band. Various interface widths  $\overline{\Delta}$ 



Figure 5.4 Coupled evolution of the phase transformation order parameter  $\xi$  and corresponding dislocation order parameter  $\eta$  for the interface width  $\bar{\Delta}_{\xi}^* = 7.37$  and the driving force X = 0.008 for initially coherent A-M interface in a half of a sample. Thin band above the sample shows evolution of edge dislocations along the A-M interface. Finally, both martensite and misfit dislocations disappear.

have been obtained by varying the magnitude of the potential barrier  $A_0$  for martensitic transformation (similar to  $A_{\alpha}$  in Eq.(32)).

Coupled evolution of the PT and dislocations for the interface width  $\bar{\Delta}_{\xi} = 7.37$  and the thermal driving force  $X = (1 - \theta/\theta_e)/(1 - \theta_c/\theta_e) = 0.008$  for martensitic PT for initially coherent A-M interface is shown in Fig. 5.4 and <sup>16</sup>; here  $\theta$ ,  $\theta_e$ , and  $\theta_c$  are the temperature, the phase equilibrium temperature for A-M, and the critical temperature for the loss of A stability. While dislocations nucleate from the free surface and propagate, at the central part of the sample the interface broadens and finally material transforms to A. Dislocations stabilize horizontal interface, however, vertical interface propagates into M region, pushing dislocations back. Finally, both martensite and misfit dislocations disappear.

Dependence of the critical driving force  $X_c$  to cause complete transformation in a

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sample vs.  $\bar{\Delta}_{\xi}$  is presented in Fig. 5.5. We considered an A-M interface width range of  $0.49 < \bar{\Delta}_{\xi} < 9.83$ . In the absence of dislocations, the coherent A-M interface is stable only at the specific thermodynamic driving force  $X_c$  and it is almost independent of  $\bar{\Delta}_{\xi}$ . Small nonzero  $X_c^0 \simeq \pm 0.005$  is caused by internal stresses and geometric changes due to transformation strain. In the presence of dislocations and for a range of  $\bar{\Delta}_{\xi}$ , the A-M interface is stabilized within a range of X ( $X_c^A < X < X_c^M$ ); at  $X > X_c^M$ , material transforms to M and at  $X < X_c^A$ , it transforms to A.



Figure 5.5 Critical thermodynamic driving force  $X_c$  to cause complete transformation in a sample vs. relative interface width  $\bar{\Delta}_{\xi}$  for the problem in Fig. 5.4. Middle line is for coherent interface, which does not exhibit any hysteresis. Upper and lower lines are for transformation to M and A, respectively, coupled to dislocations evolution. In the region between these lines interface does not evolve, i.e., dislocations produce scale-dependent hysteresis region.

Thus, incoherency dislocations produce athermal resistance to the interface motion, which is expected. What is surprising is that this athermal threshold is strongly size dependent, with maximum at  $\bar{\Delta}_{\xi} = 4.91$  for transformations in both directions. Hysteresis disappears at the critical  $\bar{\Delta}_{\xi}^* = 7.37$ , which is completely unexpected. Also, for small  $\bar{\Delta}_{\xi}$ , hysteresis reduces to a small value. The asymmetry of the curves in Fig. 5.5 with respect to zero is caused by an asymmetry of the deformed geometry.

To summarize, an advanced PFA to dislocations is developed and a number of problems on dislocation evolution and interaction between phase transformations and dislocations are solved. Strong scale dependence of the athermal threshold for the interface propagation due to generation of dislocation is revealed. A similar approach can be developed for partial dislocations and extended for dislocation reactions, and detailed interactions between phase transformations and plasticity. The support of NSF, ARO, DTRA, and ISU is gratefully acknowledged.

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# CHAPTER 6. Phase field approach to interaction of phase transformation and dislocation evolution

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## Abstract

Phase field approach (PFA) to coupled evolution of martensitic phase transformations (PTs) and dislocation is developed. A fully geometrically nonlinear formulation is utilized. The finite element method (FEM) procedure is developed and applied to study the hysteretic behavior and propagation of an austenite (A) – martensite (M) interface with incoherency dislocations, the growth and arrest of martensitic plate for temperatureinduced PT, and the evolution of phase and dislocation structures for stress-induced PT. A similar approach can be developed for the interaction of dislocations with twins and diffusive PTs described by Cahn-Hilliard theory.

# Introduction

Various material phenomena related to interaction between martensitic PTs and dislocational plastic deformation are of fundamental and technological importance. Examples are: heat and thermomechanical treatment of material to obtain desired structure and

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properties; transformation-induced plasticity<sup>1</sup>; synthesis of materials under high pressure and high pressure with large plastic deformations, e.g., during ball milling<sup>2</sup> and in rotational diamond anvil cell<sup>3, 4</sup>; and PTs during friction, indentation, surface treatment, and projectile penetration. With the development of nano science and technology, PT and plasticity are studied in nano particles, films, wires, and for smart nanosystems. The interaction between PT and dislocations drastically changes PT thermodynamics, kinetics, and microstructure and is the most basic problem in the study of M nucleation and growth kinetics, PT hysteresis and irreversibility, i.e., region of metastability of phases<sup>5, 4</sup>. In particular, M nucleation occurs at various dislocations. Interaction between PT and plasticity is also a key point in developing materials with high strength and ductility<sup>6</sup>, in particular, utilizing transformation toughening.

PFA is broadly used for simulations of PTs<sup>7, 9, 8</sup> and dislocation evolution<sup>10, 11</sup>. There are a few simplified PFA approaches to study the interaction between PT and dislocations. There are a number of analytical treatments of M nucleation on dislocations based on PFA to PT<sup>12</sup>, followed by numerical<sup>13</sup> simulations. Dislocations are introduced through their stationary stress field or are located at the moving phase interface only<sup>14</sup> and therefore do not require additional PFA equations. In<sup>11</sup>, we solved some problems on interactions between PT and evolving dislocations using a simplified version of PFA.

Thus, there currently is no PFA to interaction between PT and evolving dislocations.

Here, a coupled PFA to martensitic PT and dislocation evolution is developed as a combination of the most advanced PFA for PT<sup>9</sup> and dislocations<sup>11</sup> with nontrivial coupling terms. It is based on large strain formulation and utilizes other advantages of<sup>9, 11</sup>: advanced thermodynamic potential that describes some conceptual features of the effect of the stress tensor, reproducing, in particular, the stress-independent transformation strain tensor and Burgers vector and desired local stress-strain curve. Also, the desired, mesh-independent, dislocation height is introduced for any slip orientation, leading to a well-posed formulation. Coupling between PT and dislocations includes nonlinear kinematics and corresponding mechanical driving forces, *inheritance* of dislocation during PT, and the dependence of all material parameters for dislocations on the order parameter  $\eta$  that describes PT, which results also in the extra driving force for PT due to the change in dislocation energy during the PT. FEM procedure is developed and applied to the following problems: (a) Hysteretic behavior and propagation of an A – M interface with evolving incoherency dislocations for temperature-induced PT (i.e., without external stresses). Scale-dependent athermal hysteresis is determined and the mechanism of the interface motion through dislocation obstacles is revealed. These results can be utilized for controlling the region of metastability of phases. (b) Evolution of phase and dislocation structures for *stress-induced* PT. Dislocations are *pushed* by the moving interface for small angles between the slip direction and the interface normal and penetrate through the interface and are *inherited* by the product phase for large angles. (c) M plate growth with the generation of dislocations at its tip. At higher temperature dislocations arrest the plate, exhibiting athermal friction. When this friction can be overcome at lower temperature, the width of the M plate is larger than in the case without dislocations due to stress relaxation.

We designate contractions of tensors A and B over one and two indices as  $A \cdot B$  and A:B; the transpose of A is  $A^{T}$ , I is the unit tensor, and  $\otimes$  is a dyadic product.

## Model

Let the motion of an elastoplastic material with PT be described by equation  $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$ , where  $\mathbf{r}$  and  $\mathbf{r}_0$  are the positions of a material point at time t (deformed configuration V) and  $t_0$  (undeformed configuration  $V_0$ , which is in A state). All equations are considered in  $V_0$ . Multiplicative decomposition of the deformation gradient into elastic,

transformational, and plastic parts is used:  $\mathbf{F} = \partial \mathbf{r} / \partial \mathbf{r}_0 = \mathbf{F}_e \cdot \mathbf{F}_t \cdot \mathbf{F}_p$ . Transformation  $\mathbf{F}_t$ and plastic  $\mathbf{F}_p$  deformation gradients are described as<sup>9, 11</sup>

$$\mathbf{F}_{t} = \mathbf{I} + \boldsymbol{\varepsilon}_{t} (a\eta^{2}(1-\eta)^{2} + (4\eta^{3} - 3\eta^{4})), \qquad (1)$$

$$\dot{\boldsymbol{F}}_{p} \cdot \boldsymbol{F}_{p}^{-1} = \sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \frac{1}{H^{\alpha}} \boldsymbol{b}^{\alpha\omega} \otimes \boldsymbol{n}^{\alpha} \dot{\phi}(\bar{\xi}_{\alpha\omega}).$$
<sup>(2)</sup>

The order parameter  $\eta$  for PT varies from 0 (in A) to 1 (in M); the order parameter  $\xi_{\alpha\omega}$ for dislocations in the  $\alpha^{th}$  plane with the unit normal  $\mathbf{n}^{\alpha}$  along the  $\omega^{th}$  slip direction with the Burgers vector  $\mathbf{b}^{\alpha\omega}$  varies from 0 to n when n dislocations appear;  $Int(\xi_{\alpha\omega}) = n$  and  $\bar{\xi}_{\alpha\omega} := \xi_{\alpha\omega} - Int(\xi_{\alpha\omega}) \in [0, 1]$  are the integer and fractional parts of  $\xi_{\alpha\omega}$ . In Eqs.(1) and (2),  $\boldsymbol{\varepsilon}_t = \mathbf{F}_t(1) - \mathbf{I}$  is the transformation strain, a is the parameter,  $\phi(\bar{\xi}) = \bar{\xi}^2(3 - 2\bar{\xi})$ , and  $H^{\alpha}$  is the dislocation height. For compactness, we consider a single M variant only; generalization for multiple M variants can be done as in<sup>9</sup>. The Helmholtz free energy per unit undeformed volume is accepted as the sum of elastic, thermal, crystalline, and gradient energies related to PT and dislocations:

$$\psi = \psi^e + f + \psi^{\nabla}_{\eta} + \psi_{\xi} + \psi^{\nabla}_{\xi}; \tag{3}$$

$$\psi_{\xi} = \sum_{\alpha=1}^{P} \sum_{\omega=1}^{m\alpha} A_{\alpha}(\eta) \bar{\xi}_{\alpha\omega}^{2} (1 - \bar{\xi}_{\alpha\omega})^{2}; \qquad (4)$$

$$\psi_{\eta}^{\nabla} = 0.5\beta_{\eta} |\boldsymbol{\nabla}\eta|^{2}; \quad \psi_{\xi}^{\nabla} = 0.5\beta_{\xi}(\eta) \times$$

$$\sum_{\alpha=1}^{p} \sum_{\omega=1}^{m_{\alpha}} \left\{ \boldsymbol{\nabla}\bar{\xi}_{\alpha\omega}^{2} + [M(1-\bar{\xi}_{\alpha\omega})^{2}-1](\boldsymbol{\nabla}\bar{\xi}_{\alpha\omega}\cdot\boldsymbol{n}_{\alpha})^{2} \right\};$$

$$f = A_{0}(\theta-\theta_{e})\phi(\eta)/3 + A_{0}(\theta_{e}-\theta_{c})\eta^{2}(1-\eta)^{2}.$$
(6)

Here,  $\theta$ ,  $\theta_e$ , and  $\theta_c$  are the temperature, the A-M equilibrium temperature, and the critical temperature for the loss of A stability, respectively;  $\beta_{\xi}$  and  $\beta_{\eta}$  are the gradient energy coefficients, and  $A_0$  and M are parameters. The coefficient  $A_{\alpha}$ , which determines the nucleation barrier for dislocations, is a periodic step-wise function of the coordinate along  $\boldsymbol{n}_{\alpha}^{11}$ . The thermodynamic procedure similar to that  $\ln^{8, 9, 11}$  results in the elasticity rule for the nonsymmetric Piola-Kirchhoff stress tensor (force per unit area in  $V_0$ )  $\boldsymbol{P} \cdot \boldsymbol{F}_p^T \cdot \boldsymbol{F}_t^T = \frac{\partial \psi}{\partial \boldsymbol{F}_e}$  and expressions for the dissipation rate due to PTs  $D_{\eta} = X_{\eta} \dot{\eta} \geq 0$  and dislocations

 $D_{\xi} = X_{\alpha\omega} \dot{\xi}_{\alpha\omega} \geq 0$ . Then, the simplest linear relationships between thermodynamic forces and rates leads to the Ginzburg-Landau equations

$$\frac{1}{L_{\eta}}\frac{\partial\eta}{\partial t} = X_{\eta} = \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e} : \frac{\partial \boldsymbol{F}_{t}}{\partial\eta} \cdot \boldsymbol{F}_{p} + \boldsymbol{\nabla} \cdot \left(\frac{\partial\psi}{\partial\boldsymbol{\nabla}\eta_{i}}\right) - \frac{\partial\psi}{\partial\eta},$$
(7)

$$\frac{1}{L_{\xi}(\eta)}\frac{\partial\xi_{\alpha\omega}}{\partial t} = X_{\alpha\omega} = \boldsymbol{P}^{T} \cdot \boldsymbol{F}_{e}: \boldsymbol{F}_{t} \cdot \frac{\partial\boldsymbol{F}_{p}}{\partial\xi_{\alpha\omega}} + \boldsymbol{\nabla} \cdot \left(\frac{\partial\psi}{\partial\boldsymbol{\nabla}\xi_{\alpha\omega}}\right) - \frac{\partial\psi}{\partial\xi_{\alpha\omega}}, \quad (8)$$

where  $L_{\xi}$  and  $L_{\eta}$  are the kinetic coefficients. All parameters in the equations for dislocations depend on  $\eta$  according to the rule  $B = B_A + (B_M - B_A)\phi(\eta)$ , where  $B_A$  and  $B_M$ are the values of a parameter in A and M. This leads to contributions of the dislocationrelated terms in Ginzburg-Landau Eq.(7) for PT. In addition, both processes are coupled through the mechanical driving force (stress power) in Eqs.(7),(8) and the evolving stress field.

Slip systems of A  $(\boldsymbol{b}_{A}^{\alpha\omega}, \boldsymbol{n}_{A}^{\alpha\omega})$  and M  $(\boldsymbol{b}_{M}^{\alpha\omega}, \boldsymbol{n}_{M}^{\alpha\omega})$  are different and one needs to include both of them at each point (see Fig.  $6.4 \text{ in}^{16}$  for details). Since all equations are defined in  $V_0$ , one has to pull back  $\boldsymbol{b}_M^{\alpha\omega}$  and  $\boldsymbol{n}_M^{\alpha\omega}$  into the undeformed A state:  $\boldsymbol{b}_{MA}^{\alpha\omega} = \boldsymbol{F}_t^{-1} \cdot \boldsymbol{b}_M^{\alpha\omega}$  and  $\boldsymbol{n}_{MA}^{\alpha\omega} = \boldsymbol{n}_{M}^{\alpha\omega} \cdot \boldsymbol{F}_{t} / |\boldsymbol{n}_{M}^{\alpha\omega} \cdot \boldsymbol{F}_{t}|$ . When a diffuse A-M interface passes through dislocations in A, they are inherited by M and their Burgers vector, and normal to slip plane transforms into  $\boldsymbol{b}_{AM}^{\alpha\omega} = \boldsymbol{F}_t \cdot \boldsymbol{b}_A^{\alpha\omega}$  and  $\boldsymbol{n}_{AM}^{\alpha\omega} = \boldsymbol{n}_A^{\alpha\omega} \cdot \boldsymbol{F}_t^{-1} / |\boldsymbol{n}_M^{\alpha\omega} \cdot \boldsymbol{F}_t^{-1}|$ . However, since all equations are referred to  $V_0$ , pulling  $\boldsymbol{b}_{AM}^{\alpha\omega}$  and  $\boldsymbol{n}_{AM}^{\alpha\omega}$  back into  $V_0$  transforms them back into  $(\boldsymbol{b}_A^{\alpha\omega}, \boldsymbol{n}_A^{\alpha\omega})$ , i.e., no transformation is necessary. When a diffuse interface passes through dislocations in M, they are inherited by A and  $(\boldsymbol{b}_{M}^{\alpha\omega}, \boldsymbol{n}_{M}^{\alpha\omega})$  transform into  $(\boldsymbol{b}_{MA}^{\alpha\omega}, \boldsymbol{n}_{MA}^{\alpha\omega})$ , which one already has, i.e., no transformation is needed. Thus, one has to define at each material point slip systems of A ( $\boldsymbol{b}_{A}^{\alpha\omega}, \boldsymbol{n}_{A}^{\alpha\omega}$ ), and after pulling back into  $V_{0}$ , slip systems of M ( $\boldsymbol{b}_{MA}^{\alpha\omega}$ )  $\boldsymbol{n}_{MA}^{\alpha\omega}$  (see Fig. 6.4c in<sup>16</sup>), neither of which (as well as dislocation height  $H_{\alpha}$ ) depends on  $\eta$ . If inherited dislocations do not belong to the favorable slip system of the given phase, their yield strength is much higher or their motion may be arrested completely  $(L_{\xi}=0)$ . In the particular case when slip systems  $(\boldsymbol{b}_{A}^{\alpha\omega}, \boldsymbol{n}_{A}^{\alpha\omega})$  and  $(\boldsymbol{b}_{AM}^{\alpha\omega}, \boldsymbol{n}_{AM}^{\alpha\omega})$  coincide (i.e., they transform together with the crystal lattice during the PT), only one of them should be taken into account (see Fig.  $6.5 \text{ in}^{16}$ ). This case will be considered in examples.

The equilibrium equation  $\nabla \cdot \boldsymbol{P} = 0$  completes our system. Cubic-tetragonal PT was considered. Isotropic quadratic elastic potential  $\psi^e$  in terms of Lagrangian elastic strain  $\boldsymbol{E}_e = (\boldsymbol{F}_e^T \cdot \boldsymbol{F}_e - \boldsymbol{I})/2$  with shear modulus  $\mu = 71.5GPa$  and bulk modulus K = 112.6GPa(the same for both phases) was used for below. The following parameters for PT and all slip systems have been used in all problems<sup>9, 11</sup>:  $L_{\xi} = 10^4 (Pa \cdot s)^{-1}$ , M = 0.1, H = 0.7nm,  $|\boldsymbol{b}| = 0.35nm$ ,  $\beta_{\eta} = 2.59 \cdot 10^{-10}N$ ,  $L_{\eta} = 2600(Pa \cdot s)^{-1}$ , a = 3,  $\theta_e = 215K$ , and  $\theta_c = -183K$ .

## Numerical solutions

FEM approach and the code COMSOL with the embedded remeshing procedure have been utilized. Plane strain problems and straight edge dislocations are considered below. All size and time parameters are normalized by 1nm and 1ps, respectively. Boundary conditions are  $\nabla \eta \cdot \mathbf{k} = \nabla \xi \cdot \mathbf{k} = 0$ , where  $\mathbf{k}$  is the normal to an external boundary in  $V_0$ . The upper side of a rectangle is fixed in the y direction and the lower side in both directions; lateral sides are stress-free; in problems 1 and 3, shear stress is zero at the upper side. All results are shown in the deformed configuration.

### Propagation of a semicoherent A-M interface.

A rectangle with the size of  $8 \times 24$  is considered. First, a stationary solution for the horizontal diffuse A-M interface was obtained in the middle of the sample without dislocations (Fig. 6.1). Transformation (misfit) strain of  $\delta = 0.1$  in the x direction is applied only. We use  $\beta_{\xi} = 8.76 \cdot 10^{-11}N$ ,  $A_{\alpha} = 1.43GPa$  for A,  $A_{\alpha} = 4.29GPa$ for M, and  $\gamma = |\mathbf{b}|/H = 0.5$ . A dislocation band with the initial condition  $\xi = 0.01$  is located at the initial phase interface. Incoherency dislocations nucleate at the free surface and propagate along the interface. In the stationary state (Fig. 6.1), spacing between dislocations is 3.5, in perfect correspondence with  $|\boldsymbol{b}|/\delta$ . Both stationary solutions for the A-M interface and dislocations are taken as initial conditions for a coupled problem. To avoid the effect of the free surface on the A-M interface, we excluded PT from the two regions of the size of  $8 \times 4$  at both ends of the sample (Fig. 6.1).



Figure 6.1 ((a) Coupled evolution of the PT order parameter  $\eta$  and dislocations for semicoherent A-M interface at time instants shown in the corner. Thin band above the sample shows evolution of dislocations in the slip band along the initial A-M interface. (b) Dependence of the critical dimensionless temperature  $\tilde{\theta}_c$  (athermal friction) to cause interface motion until complete PT on the interface width  $\Delta_{\eta}$ .

Evolution of the PT for  $\Delta_{\eta} = 9.17 \sqrt{\beta_{\eta}/(A_0(\theta_e - \theta_c))} = 1.7$  and the dimensionless temperature  $\tilde{\theta} = (\theta_e - \theta)/(\theta_e - \theta_c) = 0.18$  for semicoherent A-M interface is shown in Fig. 6.1a. Dependence of the critical temperature  $\tilde{\theta}_c$  to cause interface motion until complete PT in a sample vs.  $\Delta_{\eta}$  is presented in Fig. 6.1b. Without dislocations, the coherent A-M interface is stable only at the specific temperature  $\tilde{\theta}_c \simeq 0$ , which is almost independent of  $\Delta_{\eta}$ . A semicoherent A-M interface does not move in the range  $\tilde{\theta}_c^A < \tilde{\theta} < \tilde{\theta}_c^M$ , exhibiting an athermal friction. Interface starts motion (at  $\tilde{\theta} > \tilde{\theta}_c^M$  toward A and at  $\tilde{\theta} < \tilde{\theta}_c^A$  toward M) by penetration between two dislocations that increase spacing between them. After an interface reaches a horizontal sample's surface, it spreads laterally. In some cases, such a penetration occurs in two places simultaneously. Thus, an incoherent interface transforms to a coherent one and leaves dislocations behind. Surprising size dependence of an athermal friction, with maximum at  $\Delta_{\eta} = 4.2$  is revealed. The unexpected point is that the macroscopic parameter  $\tilde{\theta}_c$  strongly depends on the ratio  $\Delta_{\eta}$  of two nanometer size parameters, which are usually considered to be zero. These results can be utilized for controlling the region of metastability of phases and can be transferred into a larger scale sharp incoherent interface model<sup>17</sup>.

#### Interaction of A-M interface with evolving dislocations for stress-induced PT.

We consider a rectangular sample of the size of  $36 \times 15$  that contains a rectangular region of the size of  $30 \times 5.6$  at the center in which all equations are solved and outside of which dislocations are not included; also, outside of the region of the size of  $30 \times 9$ at the center, PT is not included either, and only the elastic problem is solved. A parallel horizontal dislocation system is considered with initial  $\xi = 0.01$ . A horizontal displacement u = 1.4 + t is applied at the upper side from t = 0 to 1.4 and then u = 2.8 from t = 1.4 to 1.7. Material parameters are:  $\beta_{\xi} = 1.09 \cdot 10^{-10} N$ ,  $A_{\alpha} = 1.09 \cdot 10^{-10} N$  $0.894GPa, \gamma = 0.25, A_0 = 4.4MPaK^{-1}, \varepsilon_t^y = 0.1, \varepsilon_t^x = -0.05.$  For PT in shape memory alloys, M has significantly lower yield strength than A; we will study the limit case when dislocation evolution is completely arrested in A by using  $L_{\xi} = L \eta$ . The initial condition for PT corresponds to the sharp vertical A-M interface at the sample's center Stresses relax by the nucleation and propagation of dislocations in M and (Fig. 6.2). the reorientation of the interface (Fig. 6.2). The interface pushes dislocations into the M region and they almost do not penetrate into A. At t = 1.1 both M and A nucleate at the upper right and left corners, respectively. While the A region grows, its interface is getting almost parallel to the slip direction and up to three dislocations are inherited



Figure 6.2 Coupled evolution of phase (right) and dislocation (left) systems in a central  $30 \times 5.6$  part of a rectangular  $36 \times 15$  sample under simple shear for  $\tilde{\theta} = 1.17$ .

and arrested in A at the upper left corner. In the middle of a sample, the M embryo  $(\eta \simeq 0.2)$  appears, in which the dislocations nucleate, since  $L_{\xi} > 0$  in the embryo. After parametric study and course graining, these results can lead to the constitutive equations for inheritance of the plastic strain and dislocation density for sharp interface models<sup>17</sup>.

## Growth and arrest of a matertensitic plate.

A rectangular sample of the size of  $67 \times 20$  is considered. As an initial condition, a martensitic rectangular nucleus of the size of  $5 \times 3$  is located at the lower left corner of the sample. Four dislocation systems inclined at  $\pm 60^{\circ}$  (Fig. 6.3) are included. Material parameters are:  $\beta_{\xi} = 7.5 \cdot 10^{-11} N$ ,  $A_{\alpha} = 0.75 GPa$  for A,  $A_{\alpha} = 2.25 GPa$  for M,  $\gamma = 0.5$ ,  $A_0 = 6MPaK^{-1}$ ,  $\varepsilon_t^y = 0.137$ ,  $\varepsilon_t^x = \gamma_{yx} = 0$ , and  $\gamma_{xy} = 0.259$ .

Without dislocations, the martensitic nucleus disappears at  $\tilde{\theta} < 0.39$ . For  $\tilde{\theta} \ge 0.39$ the M propagates through the entire length of the sample and creates a martensitic plate of the equilibrium width, which increases with increasing  $\tilde{\theta}$  (Fig. 6.3a). For the coupled problem, dislocations nucleate at the tip of the plate and propagate within the sample. At some stage, dislocation of the opposite sign nucleates and remains within the M plate

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for slip plane 1 and 2. For  $\tilde{\theta} = 0.39$ , the M plate is arrested by two dislocations in the middle of a sample. In the region of compressive stresses near dislocations, significant thinning of the plate is observed. This nanostructure remains stable up to  $\tilde{\theta} = 0.49$ , after which growth continues until the right end of the sample with observable thickening. In the slip plane 3, dislocation appears near the M tip, then, with propagation of M plate, it disappears and then dislocations of the opposite sign appear one after another. Since nucleation near the free surface is easier, two pairs of two dislocations of the opposite sign appear. Some of dislocations are inherited by M. Two regions of residual A remain in the regions of compressive stresses near dislocations. Thus, the generation of dislocations produces athermal friction and arrests the plate at small driving force. For the case in study, athermal friction is  $\Delta \tilde{\theta} = 0.1$  (corresponding to undercooling of  $\Delta \theta = 40K$ or energy barrier of 80 MPa), which is smaller than for dislocations within interface in Fig. 6.1. When athermal friction can be overcome at lower temperature, the width of the M plate is larger than in the case without dislocations due to stress relaxation. The obtained results explain the arrest of M by plastic accommodation and possible morphological transition from plate to lath martensite. This transition is technologically important and may be used to control nanostructure and properties by controlling the yield strength<sup>5, 6, 15</sup>, e.g., by alloying.

To summarize, a PFA to coupled martensitic PT and dislocation evolution is developed and a number of model problems for temperature and stress-induced PTs interacting with dislocation evolution are solved. Various experimental phenomena are reproduced and some effects are revealed. These results can be used for the development of the larger-scale models. A similar approach can be developed for the interaction of complete and partial dislocations with twins and diffusive PTs, as well as electromagnetic and reconstructive PTs. Dislocation reactions, especially of inherited dislocations, can be included as well.

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Figure 6.3 Martensitic plate in the intermediate (a, b) and stationary (c, d) states for  $\tilde{\theta} = 0.39$  (left) and  $\tilde{\theta} = 0.49$  (right) for the case without plasticity in a part of a rectangular sample of the size of  $67 \times 20$ . For the case with dislocations, the stationary solutions are shown in the entire sample with four slip planes, in the same scale as in (a)-(d), for  $\tilde{\theta} = 0.39$  (e) and  $\tilde{\theta} = 0.49$  (f).

# Supplementary figures

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Figure 6.4 Schematics for Burgers vectors and normals to slip planes in austenite and martensite in different configurations and their transformations during phase transformations. (a) Two dimensional fcc lattice of austenite with two slip systems  $(\boldsymbol{b}_A^{\alpha\omega}, \boldsymbol{n}_A^{\alpha\omega})$  along the faces in the initial configuration  $V_0$ . (b) Two dimensional bcc lattice of martensite with two slip systems  $(\boldsymbol{b}_{M}^{\alpha\omega}, \boldsymbol{n}_{M}^{\alpha\omega})$  along the diagonals in the transformed configuration  $V_M$  obtained from  $V_0$  after applying transformation deformation gradient  $F_t$ . Slip systems of austenite inherited by martensite ( $\boldsymbol{b}_{AM}^{\alpha\omega} = \boldsymbol{F}_t \cdot \boldsymbol{b}_A^{\alpha\omega}, \, \boldsymbol{n}_{AM}^{\alpha\omega} = \boldsymbol{n}_A^{\alpha\omega} \cdot \boldsymbol{F}_t^{-1} / |\boldsymbol{n}_M^{\alpha\omega} \cdot \boldsymbol{F}_t^{-1}|$ ) are shown as well. (c) Slip systems of martensite inherited by austenite  $(\boldsymbol{b}_{MA}^{\alpha\omega} = \boldsymbol{F}_t^{-1} \cdot \boldsymbol{b}_M^{\alpha\omega}, \, \boldsymbol{n}_{MA}^{\alpha\omega} = \boldsymbol{n}_M^{\alpha\omega} \cdot \boldsymbol{F}_t / |\boldsymbol{n}_M^{\alpha\omega} \cdot \boldsymbol{F}_t|)$  during reverse phase transformation are shown in the reference configuration. Even if material is in the martensitic state, since all calculations are performed in the undeformed state, all slip systems in the configuration  $V_M$  should be pulled back to  $V_0$ with the reverse transformation deformation gradient  $\boldsymbol{F}_{t}^{-1}$ . Since under such operations slip systems of martensite  $(\boldsymbol{b}_{M}^{\alpha\omega}, \boldsymbol{n}_{M}^{\alpha\omega})$  transform to  $(\boldsymbol{b}_{MA}^{\alpha\omega}, \boldsymbol{n}_{MA}^{\alpha\omega})$  and slip system of austenite in martensite  $(\boldsymbol{b}_{AM}^{\alpha\omega}, \boldsymbol{n}_{AM}^{\alpha\omega})$  transform to slip system of austenite in martensite  $(\boldsymbol{b}_{AM}^{\alpha\omega}, \boldsymbol{n}_{AM}^{\alpha\omega})$  transform to slip system of a statement of the statement of tem of austenite in austenite ( $\boldsymbol{b}_{A}^{\alpha\omega}, \boldsymbol{n}_{A}^{\alpha\omega}$ ), Fig. 6.4 c contains all slip systems necessary for solution of the problem, namely  $(\boldsymbol{b}_{A}^{\alpha\omega}, \boldsymbol{n}_{A}^{\alpha\omega})$  and  $(\boldsymbol{b}_{MA}^{\alpha\omega}, \boldsymbol{n}_{MA}^{\alpha\omega})$ .



Figure 6.5 Schematics for Burgers vectors and normals to slip planes in austenite and martensite in the deformed  $V_0$  and transformed  $V_M$  configurations and their transformations during phase transformations for the case when slip system of martensite  $(\mathbf{b}_{M}^{\alpha\omega}, \mathbf{n}_{M}^{\alpha\omega})$  coincide with the transformed slip systems austenite  $(\mathbf{b}_{AM}^{\alpha\omega} = \mathbf{F}_t \cdot \mathbf{b}_A^{\alpha\omega}, \mathbf{n}_{AM}^{\alpha\omega} = \mathbf{n}_A^{\alpha\omega} \cdot \mathbf{F}_t^{-1} | \mathbf{n}_M^{\alpha\omega} \cdot \mathbf{F}_t^{-1} | )$ , i.e.,  $\mathbf{b}_M^{\alpha\omega} = \mathbf{F}_t \cdot \mathbf{b}_A^{\alpha\omega}$  and  $\mathbf{n}_M^{\alpha\omega} = \mathbf{n}_A^{\alpha\omega} \cdot \mathbf{F}_t^{-1} / | \mathbf{n}_M^{\alpha\omega} \cdot \mathbf{F}_t^{-1} |$ . (a) Two dimensional bcc lattice of austenite with two slip systems  $(\mathbf{b}_A^{\alpha\omega}, \mathbf{n}_A^{\alpha\omega})$  along the diagonals in the initial configuration  $V_0$ . (b) Two dimensional bct lattice of martensite with two slip systems  $(\mathbf{b}_M^{\alpha\omega}, \mathbf{n}_M^{\alpha\omega})$  along the diagonals in the transformed configuration  $V_M$ , which coincide with slip systems of austenite inherited by martensite  $(\mathbf{b}_{AM}^{\alpha\omega}, \mathbf{n}_{AM}^{\alpha\omega})$ (c) Slip systems of martensite inherited by austenite  $(\mathbf{b}_{MA}^{\alpha\omega}, \mathbf{n}_{AM}^{\alpha\omega})$  during reverse phase transformation in the reference configuration  $V_0$ . They coincide with the slip systems of austenite in austenite in  $V_0$ , i.e.,  $(\mathbf{b}_A^{\alpha\omega}, \mathbf{n}_A^{\alpha\omega})$ . Thus, the only slip systems necessary for solution of the problem are slip systems of austenite in austenite in  $V_0$ , i.e.,  $(\mathbf{b}_A^{\alpha\omega}, \mathbf{n}_A^{\alpha\omega})$ .

# CHAPTER 7. Conclusion

In summary, to study the multivariant PTs, dislocation evolution, and finally the coupled evolution of multivariant PTs and dislocation, we advanced the phase field theory in the following directions:

1. The Ginzburg-Landau theory for multivariant martensitic phase transformations is advanced in three directions: the potential is developed that introduces the surface tension at interfaces; a mixed term in gradient energy is introduced to control the martensite-martensite interface energy independent of that for austenite-martensite; and a noncontradictory expression for variable surface energy is suggested. The problems of surface-induced pretransformation, barrierless multivariant nucleation, and the growth of an embryo in a nanosize sample are solved to elucidate the effect of the above contributions. The obtained results represent an advanced model for coherent interface.

2. The finite element method is utilized to solve the coupled phase-field and elasticity equations. An in-detail study of martensite-martensite interface energy and width is presented. Splitting of the martensite-martensite interface into two austenite-martensite interfaces, leading to barrierless austenite nucleation, is obtained, which is experimentally observed. The effect of the martensite-martensite interface energy and grain size on the stationary and non-stationary nanostructure inside the transforming grain embedded in the austenitic matrix is determined. Some nano-structures differ essentially from the prediction of crystallographic theory.

3. The external surface layer as a transition between external and internal phases is included in GL theory, and the effect of the width of this layer and internal stresses on surface-induced pretransformation and phase transformations (PTs) are revealed. Using our further developed phase-field approach, we found that above some critical  $\Delta_{\xi}^*$ , a morphological transition from fully transformed layer to lack of surface pretransformation occurs for any transformation strain  $\varepsilon_t$ . It corresponds to a sharp transition to the universal (independent of  $\varepsilon_t$ ), strongly increasing the master relationship of the critical thermodynamic driving force for PT  $X_c$  on  $\Delta_{\xi}$ . For large  $\varepsilon_t$ , with increasing  $\Delta_{\xi}$ ,  $X_c$ unexpectedly decreases, oscillates, and then becomes independent of  $\varepsilon_t$ . Oscillations are caused by morphological transitions of fully transformed surface nanostructure. A similar approach can be developed for internal surfaces (grain boundaries) and for various types of PTs and chemical reactions.

4. The phase field approach to dislocations is conceptually advanced. Large strain formulation is developed. A local thermodynamic potential eliminates stress-dependence of the Burgers vector and reproduces desired local stress-strain curve, as well as the desired, mesh-independent, dislocation height for any dislocation orientation. A gradient energy contains an additional term, which excludes localization of dislocation within height smaller than the prescribed height but does not produce artificial interface energy and dislocation widening. Problems for nucleation and evolution of multiple dislocations along the single and multiple slip systems, and the interaction of dislocations with an austenite (A) – martensite (M) interface are studied using finite element method (FEM). An unexpected scale effect in the athermal resistance to the A–M interface motion due to nucleated incoherency dislocations is revealed.

5. PFA to coupled evolution of martensitic phase transformations and dislocation is developed. A fully geometrically nonlinear formulation is utilized. The finite element method procedure is developed and applied to study the hysteretic behavior and propagation of an (A) - (M) interface with incoherency dislocations, the growth and arrest of martensitic plate for temperature-induced PT, and the evolution of phase and dislocation structures for stress-induced PT. A similar approach can be developed for the interaction of dislocations with twins and diffusive PTs described by Cahn-Hilliard theory.