MORRISON, PHILLIP DEAN. Development of a Thermo-Magneto-Mechanical Free-Energy Model for the Ferromagnetic Shape-Memory Material Ni-Mn-Ga. (Under the direction of Stefan Seelecke.)

The objective of this research is to develop a mathematical model for NiMnGa that correctly simulates its behavior under applied heat, stress, and magnetic field. The need for such a model is motivated by a NiMnGa-based microactuator design that incorporates a permanent magnet and Joule heating. The actuator utilizes both first-order phase transitions between martensite and austenite and second-order phase transitions between ferro- and paramagnetism in the material.

The model presented here is a multi-scale free-energy model based on the theory of thermally-activated processes. Within the model, a Helmholtz free-energy landscape is constructed in which paraboloidal energy wells representing magnetic martensite and austenite variants of the material are separated by activation barriers. Applied stresses and magnetic fields are accommodated within the Gibbs free-energy equations to determine driving forces between variants. These are then employed in a Boltzmann distribution equation to determine phase-fraction evolution of the material and its corresponding macroscopic properties.

To help orient the reader, an introduction to the constitutive behaviors of the material is provided. Advantages to the modeling approach are then discussed and the model equations are developed. Model data is compared to measured data for a wide variety of experiments to demonstrate the fidelity of the model. Similarities and discrepancies between these are noted and improvements to the model are suggested.
Development of a Thermo-Magneto-Mechanical Free-Energy Model for the Ferromagnetic Shape-Memory Material NiMnGa

by
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The objective of the research described herein is to develop a thermo-magneto-mechanical free-energy model for the ferromagnetic shape-memory alloy NiMnGa. This model accurately reproduces a wide variety of material behavior and has potential for proper rate dependence and the simulation of inner hysteresis loops. Because it is formed at the mesoscale, the model remains connected to microscale physics while efficiently reproducing macroscale behavior.

The following chapter provides a brief introduction to ferromagnetic shape-memory alloys. It highlights some of the experimental and theoretical work on the subject and discusses a number of difficulties encountered when integrating the material into actuators. An actuator design is then introduced that overcomes some of these difficulties, leading to a motivation for the research.

1.1. Background

Ferromagnetic shape-memory alloys (FSMAs) are a member of a class of substances known as “smart materials.” Among these, some of the most well known are piezoelectrics, magnetostrictives, and conventional shape-memory alloys (SMAs). Piezoelectric materials generate a potential difference in response to applied stress. These materials also frequently exhibit the converse piezoelectric effect, by which they strain in response to an electric field. These strains are typically on the order of 0.1%.

Under the influence of an applied magnetic field, the magnetization direction of a magnetostrictive material may be caused to rotate. Due to magnetoelastic coupling within the material, this may produce strains of up to 0.2%.

SMAs strain by twin- and phase-boundary motion in response to stress and heat. These materials are capable of repeated strains on the order of several percent. While actuation
frequencies for piezoelectrics and magnetostrictives are in the kHz range, SMAs, which require time to heat up and cool down, can achieve frequencies of only a few Hz.

Similar to magnetostrictive materials, FSMAs are ferromagnetic and strain in response to a magnetic field. Unlike magnetostrictives, magnetic-field-induced strain in FSMAs results from twin-boundary motion. As with SMAs, this allows FSMA actuators to exhibit very large strokes. Because they do not depend on heating to function, however, FSMAs are also capable of actuation frequencies approaching those of piezoelectric and magnetostrictive materials.

Ferromagnetic shape-memory alloys, then, have potential to be the best of both worlds: large strain and high actuation frequency. It is for this reason ferromagnetic shape-memory materials are of academic interest. The most studied of these, and among the most promising, is nickel-manganese-gallium (NiMnGa). This material, however, is plagued by a number of problems that have slowed its adoption into actuators. Like most smart materials, it can be expensive and difficult to machine. Unlike most smart materials, it is quite brittle, requires large magnetic fields for actuation, and the strain it produces may be suppressed by stresses as small as a few MPa.

1.1.1. Experimental Results

Experimental study of the phase transitions exhibited by NiMnGa dates back until at least 1984 (Webster, et al., 1984). By 1991, it was known that phase transitions in the material could be induced mechanically and thermally (Kokorin, et al., 1992). It was also shown that three varieties of martensite could occur based on applied stress and temperature: a five-layer-modulated (5M) tetragonal, a seven-layer-modulated (7M) orthorhombic, and a non-modulated (NM) tetragonal. By 1995, the focus of research had largely shifted to the ferromagnetic nature of the material and the effect of stoichiometry on its mechanical and magnetic properties (Chernenko, et al., 1995). This work resulted in the discovery of

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1 Researchers would later clarify the large role played by stoichiometry in this regard (Richard, et al., 2006).
NiMnGa alloys that remain martensitic – and may, therefore, be actuated – at room temperature.

Researchers also began to discuss the possibility of magnetic-field-induced phase transitions. In 1996, Ullakko, et al., demonstrated magnetic-field-induced strain in the 5M structure of approximately 0.2% (Ullakko, et al., 1996). By prestressing the material, this value was gradually extended to nearly 6% in 1999 and 2000 (Tickle, et al. 1999, Tickle and James, 1999, Murray, et al., 2000), the approximate theoretical limit for five-layer martensite. Two-way actuation of the material was accomplished by incorporating a bias stress (Murray, et al., 2000) or a perpendicular magnetic field (Sozinov, et al., 2001).

In the 7M structure, magnetic-field-induced strains approaching the theoretical limit of 10% were demonstrated by 2003 (Sozinov, et al., 2003). Researchers also demonstrated that full-stroke actuation frequencies approaching 2 kHz may be possible for certain actuator configurations (Marioni, et al., 2003).

1.1.2. Modeling Efforts to Date

A large number of models exist that describe some aspect of NiMnGa behavior. We mention here only what are, in our opinion, some of the highlights. Because of their relevance to the subject of the thesis, each of the models reviewed predicts the magnetization or strain response of the material to one or more applied forces. Models dealing with phenomena otherwise related to NiMnGa, such as the effect of stoichiometry on the material’s physical parameters, will not be discussed.

Following the demonstration of magnetic-field-induced strain in NiMnGa, researchers immediately began to investigate how to reproduce the effect mathematically. Early attempts to model the behavior of NiMnGa include O’Handley, 1998, Likhachev and Ullakko, 1999, and Tickle, et al., 1999. The model by O’Handley was phenomenological in nature and made a number of qualitative and quantitative predictions. It separately considered the behavior of materials having strong, weak, and intermediate anisotropy relative to their Zeeman energies and was the first to explain some of the nonlinearities seen in experimental data.
The model by Likhachev and Ullakko was constructed based on a strain dependence of magnetization. It treated the effect of an applied magnetic field as equivalent to an additional stress (“magnetostress”) and exhibited some quantitative agreement between predicted and measured magnetization and strain-magnetic field curves.

The model by Tickle, et al. minimized a micromagnetic energy functional and incorporated the effect of demagnetization in addition to that of applied stress and magnetic field. The model provided qualitative reproductions of experimental data but was quantitatively inaccurate in some cases and, like the O’Handley model, did not reproduce hysteresis.

More recent modeling efforts include Hirsinger and Lexcellent, 2003, and Kiefer and Lagoudas, 2004. Both of these models incorporate internal variables and produce quantitatively accurate results, including hysteresis. The model by Kiefer and Lagoudas incorporates energy dissipation effects as per the Second Law of Thermodynamics. The Hirsinger-Lexcellent model distinguishes between hysteretic and anhysteretic material behavior.

A model described in Faidley, 2006, is unique among those listed here in that it simulates the actuation of the material in the collinear stress-field configuration. Like the other models, however, it reproduces only stress-strain, strain-magnetic field, and magnetization-magnetic field behavior.

During the literature review, only Buchelnikov and Bosko, 2003, was revealed to simulate thermal aspects of the material behavior. This model was thermodynamic in nature and incorporated a number of energy terms similar to those that appear in this paper. Although the model demonstrated some quantitative agreement with experimental data, it appears the model was not pursued further as no additional papers on it were published.

1.2. Motivation

The ability of ferromagnetic shape-memory alloys to exhibit large strokes at high frequencies makes them promising actuator candidates, particularly in MEMS devices where the force output of these materials significantly exceeds that of conventional electromechanical
The inclusion of electromagnets capable of generating the necessary magnetic fields, however, typically makes actuators utilizing the magnetic shape-memory effect difficult to miniaturize. As an example of this, see Figure 1.1, which shows part of an experimental setup for measuring magnetic-field-induced strain. Here, it can be seen that the sample of NiMnGa is dwarfed by the electromagnet used to actuate it. Not shown here is the spring that would typically be used to apply a compressive bias stress.

Figure 1.1: Electromagnet necessary for NiMnGa actuation (adapted from Couch, 2006).

Recently, Kohl, et al. have proposed a thin-film actuator design that avoids the need for an electromagnet by utilizing a small permanent magnet and the conventional temperature-induced shape-memory effect coupled with a ferro- to paramagnetic transition above the Curie temperature (Kohl, et al., 2003, Kohl, et al., 2004). This actuator is shown schematically in Figure 1.2(a). It is built around a thin-film NiMnGa cantilever, heated by passing electrical current through it. The cantilever is anchored, and the permanent magnet held in place, by a small, gallows-shaped structure. A mirror may be attached to the free end of the cantilever, as in Figure 1.2(b), and coupled with a laser to produce an optical microscanner. As the figures show, this configuration results in an actuator comparable in size to the NiMnGa sample.
At first glance, the design’s reliance on heating and cooling to create motion would appear to significantly limit the bandwidth of the device, as in the case of conventional shape-memory alloy actuators. In reality, due to the thinness of the cantilever beam and the close proximity of the phase transition temperatures and Curie point, the device can reach actuation frequencies approaching 100 Hz. This may be seen in the transfer function of Figure 1.3.

This and other experiments effectively demonstrate the design’s potential. However, a number of questions regarding its properties remain. What physical parameters of the system limit its scanning angle and actuation frequency? How nearly should the Curie point and austenite-martensite transition temperatures be placed to achieve an ideal balance between stroke and bandwidth? Is there an optimal shape and size for the cantilever?
In order to resolve questions such as these, and to allow for control of the nonlinear, hysteretic microactuator system, a mathematical model of the material behavior is required. Such a model could be employed within a finite-element simulation to optimize the actuator design and form the basis for its control algorithm.

A first attempt at simulating the behavior of the Kohl actuator was made in Lee and Seelecke, 2005. Here, the authors amended their model for conventional shape-memory alloys to include ferromagnetism and a ferro- to paramagnetic transition at the Curie temperature. Although this effort yielded some useful results, a model in which the ferromagnetism and shape-memory effect are fully coupled is required to better understand the system’s properties.

1.3. Research Objective

Presently, we know of no model capable of reproducing the entire range of behaviors exhibited by NiMnGa in both its martensitic and austenitic states. Such a model could be used to explain and optimize the behavior of the Kohl actuator. More generally, a NiMnGa model that incorporates the temperature effects would contribute to a better understanding of the material and allow for the NiMnGa-actuator design space to be more thoroughly explored.

The objective of this research is to begin development of a full thermo-magneto-mechanical model for NiMnGa. Although some refinement of the model will still be required upon completion of the project, it is expected that the model described here should effectively reproduce the quality of most of the stress-, magnetic-field-, and temperature-dependent constitutive behaviors of the material. Where sufficient experimental data is available to properly calibrate the model, it should also be capable of providing meaningful quantitative results.

Because the properties of NiMnGa vary substantially from one stoichiometry to the next, a secondary objective of this work is to produce a model that does not require a complex system-identification process. For this reason, the model will be based on physical
parameters of the material and will not incorporate, for example, look-up tables or other purely numerical representations of material behavior. The model formulation must be kept simple, with future real-time control applications in mind.

1.4. Thesis Outline

The thesis is divided into five chapters as follows:

Chapter 1 summarizes experimental and theoretical research on NiMnGa and describes an actuator design that avoids some of the weaknesses of conventional NiMnGa actuators. The research objective is then stated with regard to this design, and the structure of the thesis is presented.

Chapter 2 introduces the constitutive behaviors of NiMnGa and includes a brief introduction to ferromagnetism. The properties of austenitic and martensitic NiMnGa at scales ranging from crystallographic to macroscopic are discussed. The behavior of mixed samples of martensite and austenite is then described.

Chapter 3 outlines the modeling approach employed in this paper and introduces the constitutive model equations. The issue of how the model should be scaled is also addressed.

Chapter 4 discusses model calibration and the effect of various parameters on model behavior. Model data is then compared to data from a wide range of experiments and similarities and discrepancies are noted.

Chapter 5 summarizes the paper and draws conclusions regarding the strengths and weaknesses of the model in its current form. Future work for the purposes of improving the model is also suggested.
CHAPTER 2
MATERIAL BEHAVIOR

The following chapter introduces the constitutive behaviors of the ferromagnetic shape-memory alloy NiMnGa. To familiarize the reader with the magnetic energy terms that are largely responsible for this behavior, a discussion of physical concepts relevant to ferromagnetic materials is first presented. The properties of NiMnGa are then built up gradually from the crystallographic to macroscopic scale. Because it is not realistic to study primitive lattice cells of the material in isolation, the discussion of unit-cell behavior may be considered little more than a thought experiment. Its purpose is to help elucidate observations of the material in larger quantities. In general, the martensite and austenite phases are considered separately. Their combined behavior is discussed in the final section.

2.1. Primer on Ferromagnetism

Ferromagnetism is the phenomenon by which certain materials exhibit magnetization in the absence of an external magnetic field. It results from a combination of four magnetic energy terms: anisotropy energy, magnetostatic or stray-field energy, exchange energy, and Zeeman energy. Each of these energies will be discussed individually before considering how they combine to create magnetic domains and ferromagnetism.

When discussing magnetic phenomena, the term “anisotropy energy” is used in reference to a number of different effects. Stress anisotropy refers to a variation in the magnetization direction of a material that results from an applied stress. It is due to magnetoelastic coupling within the material. Shape anisotropy, as its name implies, depends on the shape of a sample and is largely a function of magnetostatic energy, discussed below.

The type of anisotropy in which we’re most interested is specifically referred to as magnetocrystalline anisotropy. It is due to a spin-orbit coupling within the material (Van Vleck, 1937) that links its magnetization direction and crystal structure. The two types of magnetocrystalline anisotropy relevant here are uniaxial and cubic anisotropy. Uniaxial anisotropy describes a material that has a single preferred axis of magnetization, known as its
“easy axis.” To rotate the magnetization vector off of this axis requires energy. It is this energy to which we refer when using the term “anisotropy energy.” Because the anisotropy-energy function has even symmetry, the magnetization vector can point in either direction along an easy axis – we’ll refer to these as its “easy directions” – without incurring an energy penalty.

For a uniaxial anisotropic material, the directions orthogonal to its easy axis are referred to as “hard axes.” The “easy”/”hard” nomenclature reflects the fact that the material is easier to magnetize (i.e., requires a smaller magnetic field) in some directions than in others.

Cubic anisotropy describes a material that has three orthogonal easy axes and six easy directions. Cubic anisotropic materials possess an “intermediate axis” along each of the cube’s minor diagonals and a hard axis along each of its major diagonals.

The magnetostatic or stray-field energy is the classical magnetic energy that causes the north pole of one bar magnet to be attracted to the south pole of another. It is frequently illustrated using magnetic field lines that originate at the magnet’s north pole and terminate on its south pole. This energy is minimized when the material emits no magnetic field. The term stray-field energy is preferred to magnetostatic energy here because of the picture it evokes, that being one of magnetic field lines escaping from the material, the magnitude of the energy increasing with the density of field lines and the extent to which they reach.

The exchange energy carries with it a very short-range force that is frequently approximated as extending only to the nearest neighbors of a crystal cell. It is quantum-mechanical in nature and is minimized when nearby cells are magnetized in the same direction. Unlike anisotropy, the exchange energy has odd symmetry and is maximized when the magnetization vectors of neighboring cells are anti-parallel.

Zeeman energy occurs only in the presence of an external magnetic field. It is the potential energy of a magnetic dipole within the field and is minimized when the magnetization of a material aligns with the field direction. Like the exchange energy, the Zeeman energy has odd symmetry.
Magnetic domain formation is one of the identifying traits of ferromagnetic materials. It occurs when large regions of material known as magnetic domains are magnetized in the same direction. Because the domains are fixed to easy axes of the material, such a configuration minimizes both exchange and anisotropy energy within the domain.

Magnetic domains are bounded by domain walls, regions over which the magnetization vectors gradually rotate from the direction of one domain to the next. Seen at the top of Figure 2.1 is one type of domain wall referred to as a Bloch wall. Here, the magnetization vectors rotate in a plane orthogonal to the plane of magnetization. Alternatively, the magnetization vectors within the wall may rotate within the plane of magnetization. This is known as a Néel wall and appears at the bottom of Figure 2.1. Because the magnetization vectors in a Néel wall are in-plane, they result in reduced stray-field energy and so typically occur throughout thin samples or at the surface of thicker samples. Bloch walls typically occur, otherwise.

**Figure 2.1:** 180° Bloch (top) and Néel (bottom) domain walls (adapted from Fukumoto, 2005).

The anti-parallel domains seen in Figure 2.1 are characteristic of a uniaxial anisotropic material. The magnetization vectors within the domain wall are rotated off of the material’s easy axis and, therefore, possess anisotropy energy. Because the domain-wall vectors are not in perfect alignment with their neighbors, they also possess exchange energy. The width of
the domain walls – typically quite small in comparison to that of the domains – results from a competition between these energy terms: the anisotropy energy favors thin walls in which very few magnetization vectors deviate from the easy axis; the exchange energy favors thick walls in which neighboring vectors are rotated only slightly from each other. We will refer to the sum of these energies for all domain walls within a sample as the “domain-wall energy.”

While the size of domain walls is dictated by the anisotropy and exchange energies, the size of the domains in the absence of an external magnetic field result from a competition between the domain-wall energy and the stray-field energy. This is illustrated in Figure 2.2, where the partition of a bar magnet into magnetic domains reduces the stray-field energy but requires domain walls, increasing the domain-wall energy. Here, field lines represent the magnitude of the stray-field energy, arrows indicate the magnetization direction of each domain, and domain walls are represented simply as lines.

![Figure 2.2: Reduction of stray-field energy with the addition of magnetic domains.](image)

The application of an external magnetic field introduces Zeeman energy into the system and reduces the energy of domains magnetized in the direction of the field with respect to those magnetized in other directions. In response to this, the aligned domains grow at the expense of misaligned domains. This is shown in Figures 2.3(a) and (b) for materials exhibiting uniaxial and cubic anisotropy, respectively. Because domain-wall and stray-field energy remain factors, domain-structure rearrangement occurs via both domain wall nucleation/annihilation and domain-wall motion. Note that, due to the domain-size imbalance
they exhibit, the domain structures at the bottom of each figure possess more stray-field energy than their counterparts at the top. Note also in Figure 2.3(b) that the magnetization of domains that are neither parallel nor anti-parallel to the applied field will rotate slightly so as to better align with the field. This is the result of a competition between the anisotropy and Zeeman energies.

![Figure 2.3](image)

**Figure 2.3:** Magnetic domain growth with applied magnetic field for (a) uniaxial and (b) cubic anisotropic materials.

As opposed to magnetization vector rotation, domain-structure rearrangement is inelastic. Because of this, the magnetic domain structure will not be fully restored upon removal of the field. The extent to which a ferromagnetic material’s structure is restored is dependent on the nature of the material. If most of the domain structure is restored, the material is referred to as magnetically “soft.” If very little of the structure is restored, the material is described as magnetically “hard.” Iron is one example of a magnetically soft material. Neodymium-iron-boron (NdFeB) is magnetically hard. A representative magnetization curve for each type of material is shown in Figure 2.4.
Figure 2.4: Magnetization curves shown schematically for (a) magnetically soft and (b) magnetically hard materials.

Under application of a sufficiently large magnetic field, both soft and hard materials will be driven into a state of magnetic saturation. This occurs when one magnetic domain grows to fill the entire sample. A further increase in the magnetic field at this point has no effect on the magnetization. If the magnetic field is removed, the magnetization of the material will decrease from its saturation magnetization, $M_s$, to its remanent magnetization, $M_r$. As is seen in Figure 2.4(b), these values may be quite similar for magnetically hard materials. The coercive field, $H_c$, is the magnetic field necessary to return the sample to zero magnetization after it has been saturated.

2.2. The Crystallographic Unit Cells of NiMnGa

The crystallography of NiMnGa in its various phases is the subject of much research, most of which is beyond the scope of this paper. Although three separate martensite phases – a five-layer-modulated (5M) tetragonal, a seven-layer-modulated (7M) orthorhombic, and non-modulated (NM) tetragonal – have been discovered, only the first is of interest here. It is in this phase that the material’s properties are considered the most promising, and it is on this phase that most of the research on NiMnGa is conducted. And although the structure of 5M martensite is technically monoclinic, it is very nearly tetragonal and for our purposes we may neglect the differences between the two. In this paper, then, we will consider that NiMnGa occurs in only two phases: a cubic austenite and a tetragonal martensite. An in-depth discussion of the crystallography of martensitic NiMnGa appears in Ge et al., 2007.
The crystallographic unit cell of austenitic NiMnGa is represented in Figure 2.5(a). The cell is cubic in shape, with each side having equal length $a$. The austenitic unit cell also exhibits cubic anisotropy. This results in six magnetic variants of the cell, one for each of the cell’s easy directions. The magnetic variants of austenitic NiMnGa are shown in Figure 2.5(b).

![Figure 2.5](image)

**Figure 2.5:** (a) The crystallographic unit-cell of austenitic NiMnGa and (b) its magnetic variants.

The magnetic behavior of an austenitic cell is summarized in Figure 2.6. When the cell is subjected to a small magnetic field perpendicular to its magnetization direction, its magnetization vector will begin to rotate. As the magnitude of the field is increased, the vector will eventually flip to a neighboring easy direction. The magnetization vector will remain in the new orientation after the field is removed.

![Figure 2.6](image)

**Figure 2.6:** Response of austenitic unit cell to small perpendicular magnetic field.

Upon cooling, cubic austenite transforms into tetragonal martensite, having two long sides of length $a'$ and a short side of length $c$. This is shown in Figure 2.7(a). In reality, these lengths differ by only a few percent. The effect is exaggerated here for clarity.

The reduction in symmetry from austenite to martensite produces three mechanical variants, referred to as martensite “twins.” Each twin has its short side $c$ oriented along a different
crystallographic axis of the material. Because martensitic NiMnGa exhibits uniaxial anisotropy, it possesses only one easy axis, parallel to \( c \), and two easy directions for each martensite twin. This results in a total of six magneto-mechanical variants, seen in Figure 2.7(b).

![Figure 2.7](image)

**Figure 2.7:** (a) The crystallographic unit-cell of martensitic NiMnGa and (b) its magneto-mechanical variants.

When a magnetic field is applied perpendicular to a martensitic cell’s direction of magnetization, the vector will rotate toward the field. If the magnitude of the field is increased, the vector will rotate further, but will not flip to the opposite easy direction. When the field is removed, the vector will return to its original orientation.

![Figure 2.8](image)

**Figure 2.8:** Response of martensitic unit cell to small perpendicular magnetic field.

### 2.3. Magnetic Domain Structure

Magnetic domain formation for a single-twin sample of martensitic NiMnGa is typical of uniaxial anisotropic materials. The domain structure for a twin having its easy directions to the left and right is shown in Figure 2.9. Here, the magnetization vectors of individual cells are represented as arrows and domain walls are again represented as lines. Figure 2.9(a)
shows the domain structure under no applied magnetic field. In Figure 2.9(b), an intermediate magnetic field is applied upward along a hard axis, causing the magnetization vectors to rotate with the field slightly. In Figure 2.9(c), a small magnetic field applied to the right, causing the domain magnetized to the right to grown at the expense of the domain magnetized to the left.

**Figure 2.9:** Magnetic domain structure of a single-twin sample of martensitic NiMnGa under (a) no magnetic field, (b) an intermediate field directed along a hard axis, and (c) a small field directed along the easy axis.

The magnetization curves for martensitic NiMnGa along the easy axis (light gray) and a hard axis (dark gray) are shown in Figure 2.10, with the current domain structure represented for several points along each curve. As can be seen from the figure, the material may be saturated in either direction, but the mechanisms by which this occurs are different. Along a hard axis, the magnetization vectors gradually rotate with the field until those of both domains align with it. Along the easy axis, the aligned domain grows until it constitutes the entire sample. From the slopes of the respective curves – known as the hard- and easy-axis magnetic susceptibilities – it is clear that saturation along a hard axis requires a significantly greater magnetic field than saturation along the easy axis. The small width of the easy-axis curve indicates that martensitic NiMnGa is a magnetically soft material.
Figure 2.10: Easy-axis and hard-axis magnetization curves shown schematically for a sample of martensitic NiMnGa.

Experimental evidence of the domain structure of austenitic NiMnGa is presently lacking. It likely resembles that of other cubic anisotropic materials. For reference, the domain structure in a thin film of iron, which exhibits cubic magnetic anisotropy, is shown in Figures 2.11. For thicker samples of material, the domain structure becomes noticeably more complex.

Figure 2.11: Magnetic domain structure in an iron film (from Schneider et al., 1996).
2.4. Magneto-Mechanical Behavior

When multiple twin variants occur within a sample of martensitic NiMnGa, they are separated by a “twin boundary.” The structure of the twin boundary is shown in Figure 2.12, with magnetization vectors indicated by arrows. From the figure, the source of the name “twinning” becomes clear: structurally, the variants on one side of the boundary are mirror images of those on the other. As before, the difference in length between the long and short sides has been exaggerated in Figure 2.12(a). When the sides are given the proper ratio, as in Figure 2.12(b), it becomes evident that the twin boundary is simply an array of deformed martensite cells. The easy axes of neighboring twins are also nearly perpendicular. This fact will allow us to make a clear distinction between easy-axis and hard-axis martensite twins in an applied magnetic field.

![Figure 2.12: Twin-boundary structure for (a) exaggerated and (b) proportionate martensite twin sizes.](image)

When we look at the magnetic domain structure of a multiple-twin sample of martensitic NiMnGa, we see something resembling the micrograph in Figure 2.13(a). Here, domains appear as a series of alternating horizontal and vertical bands. They form a step-like pattern due to the presence of two martensite twins: one whose easy axis is oriented along the horizontal and one whose easy axis is oriented along the vertical. The martensite twins are visible as diagonal layers running from the bottom-left to top-right of the figure. The twin layers are separated by structures known as “twin boundaries.” A schematic illustration of the multiple-twin structure is shown in Figure 2.13(b). The effect of a small applied magnetic field directed to the right is shown in Figure 2.13(c). Because multiple twins are now present, such a field is along the easy axis for some layers and along a hard axis for others. As a result, the field will cause both magnetization-vector rotation and domain-wall motion. As is
shown in the figure, the domain walls from one twin layer to the next will typically remain linked. This process is discussed in O’Handley, et al., 2003.

Figure 2.13: Martensite twin variant and magnetic domain structure shown via (a) micrograph and (b) schematic; (c) schematic illustration of the structure with an applied magnetic field to the right. (Micrograph taken from Ge, 2007).

Because their magnetization vectors are rotated off of the easy axis, the hard-axis layers possess some non-zero anisotropy energy. This creates an energy difference over the twin boundary referred to as a “driving force.” If the driving force is sufficiently large, the twin boundaries will move so as to grow the easy-axis twin layers at the expense of the hard-axis twin layers. This is analogous to the motion of domain walls under the application of a magnetic field. Twin-boundary motion is seen in Figure 2.14, where dark gray diagonal bands indicate one twin and light gray bands indicate another.

Figure 2.14: Twin-boundary motion (taken from Straka et al., 2004).
Because martensite twins have different dimensions, twin-boundary motion causes a sample to strain macroscopically. The different sizes of martensite twins also allows for twin-boundary motion to be caused by the application of stress. A compressive stress, for example, energetically favors the martensite twin having its short axis most nearly oriented along the direction of the stress.

When twin-boundary motion is caused by the application of a magnetic field, the resultant strain is referred to as magnetic-field-induced strain (MFIS). It is frequently represented via a strain-vs.-magnetic field plot, such as that shown in Figure 2.15(a). If we imagine the dark bands in Figure 2.14 correspond to twins having positive strain, while the light bands correspond to twins having negative strain, we can roughly locate images A-F on the strain-magnetic field curve.

![Figure 2.15: A schematic illustration of (a) magnetic-field-induced strain and (b) the magnetic-field-induced shape-memory effect.](image)

From Figure 2.15(a), it is clear that, once MFIS has reached its maximum value, reversal of the magnetic field has no effect on the strain. This is because the positive and negative magnetic fields favor the same twin variant. A perpendicular magnetic field may be used to return the sample to its previous strain value, but more frequently a perpendicular compressive bias stress is employed. In this scenario, the material is placed under a constant compressive that favors one twin, while the magnitude of a magnetic field favoring another twin is varied. When the magnetic field is large, it is capable of overcoming the compressive stress and moving twin boundaries so as to grow field-favored twin layers. When the magnetic field is small, the compressive stress is sufficient to overcome it and move twin boundaries to enlarge stress-favored twin layers. This reversible process is known as the
magnetic-field-induced shape-memory effect. It is the subject of a majority of the papers published on NiMnGa and other ferromagnetic shape-memory alloys. The strain-magnetic field curve it produces is shown in Figure 2.15(b). Because energy is required to initiate twin-boundary motion, the curve exhibits a large hysteresis. Arrows in the figure indicate the direction in which the hysteresis loop is traversed.

2.5. Material Response to Increasing Temperature

As the temperature of a ferromagnetic material increases, its spontaneous magnetization decreases in the manner shown in Figure 2.16. The temperature at which the material attains zero magnetization is referred to as its Curie temperature. At this temperature, the material undergoes a phase transition into the paramagnetic state. Because the transition is second-order, no hysteresis is seen when the material is allowed to cool back into a ferromagnetic state.

![Figure 2.16: Schematic illustration of spontaneous magnetization as a function of temperature.](image)

Upon heating, martensitic NiMnGa also undergoes a first-order phase transition into austenite. This is due to entropic stabilization of the material’s austenite phase with respect to its martensite phase that results from an increase in the temperature of the sample. Because the austenite’s magnetic and structural properties both differ from those of the martensite, the phase transition affects both the magnetization and strain of the material.

Both twinned martensite (FCT) and austenite (FCC) may be identified in the micrograph of Figure 2.17(a). This heterogeneous mixture of twins and phases is represented schematically...
in Figure 2.17(b). Here, austenite is shown in solid white. Martensite may be recognized by its magnetic domains, shown in various shades of gray. The structure that separates austenite from martensite is referred to as a “phase boundary.”

![Figure 2.17: Heterogeneous mixture of austenitic and martensitic NiMnGa shown via (a) micrograph and (b) schematic. (Micrograph taken from Sullivan, et al., 2004.)](image)

In a manner analogous to that of domain walls and twin boundaries, the motion of phase boundaries may be induced by energetically favoring one phase over the other. If heat is applied, the phase boundaries will encroach upon the martensite, increasing the presence of austenite. Allowing the sample to cool restores the martensite. The phase boundaries may also be forced to recede by the application of a suitable stress or magnetic field.
CHAPTER 3
MODEL DEVELOPMENT

The following chapter discusses the modeling approach employed in this paper and introduces the constitutive model equations. The issue of how to properly scale the model is also addressed.

3.1. Modeling Approach

The modeling approach taken here is based on that outlined in R. C. Smith, et al., 2006, which has previously been applied to piezoelectrics (Smith, et al., 2003a), magnetostrictives (Smith, et al., 2003b), and conventional shape-memory alloys (Seelecke, 2002).

In the model, a Helmholtz free-energy landscape is constructed for mesoscale volume elements with temperature, strain, and magnetization as order parameters. The landscape includes energy wells representing all relevant martensite and austenite variants. Phase transformations resulting from temperature changes and applied stresses and magnetic fields follow from a system of evolution laws based on the Gibbs free energy equations and the theory of thermally-activated processes. The relevant phase fractions are then used to determine the macroscopic strain and magnetization of a sample of NiMnGa by a standard averaging procedure.

This modeling approach has a number of advantages over competing models. Because it functions at the mesoscopic scale, it effectively reproduces macroscopic behavior while remaining connected to microscale physics. The model also incorporates physical parameters of the material, has potential for rate dependence, and can be used to simulate inner hysteresis loops.

3.2. The Free-Energy Landscape for NiMnGa

We begin development of the model by introducing a free-energy landscape for NiMnGa. For the sake of clarity, we will describe this landscape in terms of corresponding unit-cell
states. As we will see, such a perspective does not accurately reflect the mechanisms responsible for variant transformation. A number of amendments to the energy picture will, therefore, be required. These will be discussed in Section 3.4.

To keep the model simple, we will restrict magnetic field application and magnetization measurement to the $x$ axis and stress application and strain measurement to the $y$ axis. We will also assume that these axes coincide with the crystallographic axes of the unit cells. The coordinate system employed is visible in Figure 3.1(a). The locations of several martensite variants within the coordinate system also appear in the figure. Because one of the twins discussed in Chapter 2 (having magnetization vectors into and out of the page) can be favored by neither our applied stress nor magnetic field, it is neglected. As seen in the figure, our selection of coordinate system also creates degeneracy between the two martensite variants that are magnetized vertically.

![Figure 3.1](image-url)

**Figure 3.1:** (a) Coordinate system and (b) Helmholtz energy landscape for martensitic NiMnGa.

In total, two martensite twins and three distinguishable magneto-mechanical states remain. The top twin, which is given positive strain in our coordinate system, is commonly referred to as “martensite plus;” it is the easy-axis twin, denoted $e$, in this configuration. Its magnetic variants will be referred to as easy-left, $el$, and easy-right, $er$, in reference to their magnetization directions. The degenerate state, which has negative strain, is known as “martensite minus”; it is the hard-axis twin, $h$, in this configuration.
In terms of the energy landscape, the variants shown represent all possible magneto-mechanical states for a martensitic unit cell in the absence of applied stresses and magnetic fields. Because the cell states are metastable, they are depicted as energy wells in Figure 3.1(b). A given cell, then, can be thought of as populating the well corresponding to its current state. An energy barrier (also known as an “activation barrier”) resides between each pair of wells. Due to thermal activation, the strain and magnetization of each cell will vary about the strain and magnetization minima of the well in which it resides. If the level of thermal activation is sufficiently large, the energy of the cell will exceed that of the barrier. When this occurs, the cell will immediately transition between states (Levitas, 1995).

It was mentioned in Chapter 2 that martensite initially exhibits elastic strain under the influence of stress. In terms of the energy landscape, this is depicted in Figure 3.2(a) for a small compressive stress. Here, the landscape shifts about the strain axis in reaction to the stress, causing a small change in the strain minimum of each well and the strain of any cells that populate it. The energy difference between the $h$ and $e$ wells – commonly referred to as a “driving force” – and the shape of the $h$-$e$ barrier are also affected. As a result, the likeliness of $e$-to-$h$ transitions increases while that of $h$-to-$e$ transitions decreases. The magnetic analog of this effect is shown in Figure 3.2(b), where an applied magnetic field to the right changes the magnetization minimum of each well, encouraging transitions from $er$ to $el$ and discouraging $el$-to-$er$ transitions.
Figure 3.2: Gibbs energy landscapes for martensitic NiMnGa under the application of a small (a) stress and (b) magnetic field and a (c) large stress and (d) magnetic field.

If the applied stress or magnetic field is further increased, it will at some point elevate an energy well minimum to the height of a neighboring barrier. This is shown in Figure 3.2(c) for an applied stress and Figure 3.2(d) for an applied magnetic field. In the former case, the stress forces transitions from the easy-axis wells to the hard-axis well. In the latter, transitions from \( h \) to \( el \) or \( h \) to \( er \) variants result. Because the relevant energy barrier in each case has been completely negated, the transitions now occur regardless of the level of thermal activation.

Transitions from \( h \) to \( el \) or \( h \) to \( er \) may also be brought about magnetically if the applied field can create a sufficient driving force between the \( h \) and \( el \) or \( er \) wells. A magnetic-field-induced \( h \)-to-\( er \) transition is represented in Figure 3.3(a). Note that reversal of the magnetic
field here would only force transition from the $er$ to the $el$ state. To restore the cell back to the $h$ state, a compressive stress is required. Also, observe the large change in the magnetization minimum of the $h$ well. This reflects that the magnetization vector of the hard-axis twin rotates due to the applied field prior to transition.

![Figure 3.3: An h-to-e transition resulting from applied (a) magnetic field and (b) stress.](image)

For comparison, Figure 3.3(b) shows a stress-induced $h$-to-$e$ transition. Because there is no applied magnetic field in this case, neither the $el$ nor $er$ variant is energetically favored. As a result, the cell will transition with equal probability into either state.

To incorporate austenite into the energy landscape, we take an approach similar to that taken for the martensite. We again see that a number of austenite variants do not factor into the model. Because of the higher symmetry of austenite, no one variant can be favored over any of the others by stress. Only the austenite variants having magnetization to the left and right can be favored by the magnetic field. As a result, we are left with a total of two magneto-mechanical austenite variants. These are added to the coordinate system and energy landscape in Figure 3.4(a). The austenite energy wells are depicted in Figure 3.4(b) at a temperature that brings them level with their martensite counterparts. The austenite energy wells, and their associated magneto-mechanical states, we refer to as austenite-left, $al$, and austenite-right, $ar$. 
It was previously mentioned that the austenite phase is entropically stabilized by heat. As a result, the energy of austenite with respect to that of martensite is temperature-dependent. The magnetization of the material is also temperature-dependent, decreasing quickly as the material approaches its Curie temperature. These effects are illustrated in Figure 3.5, where an increase in temperature now energetically favors the austenite wells over the martensite wells, forcing transitions from the latter to the former. A gradual merger of the $er$ and $el$ wells and $ar$ and $al$ wells is also evident, as seen in the decrease of the magnetization minima of each well and in the decrease of the height of $er\leftrightarrow el$ and $ar\leftrightarrow al$ energy barriers. If the temperature further increases to the Curie point for one of the phases, total negation of an energy barrier will result. The left-right wells will then merge and any material in the phase will become fully paramagnetic. In general, the Curie temperatures of the martensite and austenite are not the same.
3.3. Free Energy Equations

We will now begin to formulate the model mathematically. To this end, we will first derive an expression for the Helmholtz energy of each well. Applied stresses and magnetic fields will then be incorporated within the Gibbs free energy equations, derived from the Helmholtz energy by means of a Legendre transformation. As before, we will fully introduce the martensite before discussing the austenite.

To express the Helmholtz energies, we must first locate the energy wells within our coordinate system. We may rely on the lattice parameters to find values for the remnant strains of the easy- and hard-axis variants relative to that of the austenite. As Figure 3.6 illustrates, we have that $\varepsilon_{ra} = 0$, $\varepsilon_{re} = +1.82\%$, and $\varepsilon_{rh} = -3.92\%$ for the strain minima of the austenite, easy-axis martensite, and hard-axis martensite wells, respectively.
Figure 3.6: Relation between lattice constants for martensite and austenite (from Straka, 2007).

Physical arguments may be used to locate the magnetization minima of the wells. Because the $h$ well corresponds to the hard-axis twin, we expect that it should be centered about zero magnetization. The $el$ and $er$ wells correspond to variants that are fully magnetized to the left or right. They must, therefore, be located at $\pm M_{\text{sat}}$, the saturation magnetization for martensite. The austenite wells will then be located at $\pm M_{\text{sat}}$, the saturation magnetization for austenite. Both saturation values are temperature-dependent and will need to be found from experimental data.

Regarding the shape of the wells, paraboloids have previously been employed in similar models with success (see references in Section 3.1). We expect that the curvatures of the wells should incorporate physical parameters of the material. Along the strain axis, the curvatures will be proportional to the Young’s modulii for hard- and easy-axis martensite, $Y_h$ and $Y_e$, and austenite, $Y_a$. This may be understood intuitively by considering that, as the Young’s modulus and therefore the curvature of the well increases, more energy will be required to effect a similar change in strain. A similar argument may be used to yield an inverse proportionality between the curvature of the $h$ well along the magnetization axis and the hard-axis magnetic susceptibility, $\chi_h$. With this, we arrive at for each of the energy wells
\[
\psi_h = \frac{1}{2} Y_h (\varepsilon_h - \varepsilon_{rh})^2 + \frac{1}{2} \frac{\mu_h}{\chi_h} M_h^2 \\
\psi_{er} = \frac{1}{2} Y_e (\varepsilon_e - \varepsilon_{re})^2 + \frac{1}{2} \lambda_e (M_{er} - M_{sm})^2 \\
\psi_{el} = \frac{1}{2} Y_e (\varepsilon_e - \varepsilon_{re})^2 + \frac{1}{2} \lambda_e (M_{el} + M_{sm})^2 \\
\psi_{ar} = \frac{1}{2} Y_a \varepsilon_a^2 + \frac{1}{2} \lambda_a (M_{ar} - M_{sa})^2 \\
\psi_{al} = \frac{1}{2} Y_a \varepsilon_a^2 + \frac{1}{2} \lambda_a (M_{al} + M_{sa})^2
\]

(3.1)

where \(M_h, M_{er}, M_{el}, M_{ar},\) and \(M_{al}\) are the magnetization minima of the corresponding wells and \(\varepsilon_h, \varepsilon_e,\) and \(\varepsilon_a\) are the strain minima of the hard-axis, easy-axis, and austenite wells, respectively. Unlike the remnant strains and saturation magnetizations, these values will depend on the applied stress and magnetic field. The \(\frac{1}{2}\) coefficients in front of each quadratic term ensure an integral relationship between the free energy and its corresponding force. Note, for instance, that the derivative of the first term in each equation with respect to strain results in an expression for Hooke’s Law. In general, a magnetoelastic coupling constant would also appear here. For NiMnGa, however, its value is negligible (Hečko, 2005).

Note also the presence of a \(\lambda\) in front of the quadratic magnetization terms for the left and right easy-axis martensite and austenite wells. To clarify the absence of a magnetic susceptibility term in each of these equations, a distinction must be made between the mechanisms responsible for varying magnetization within each of these wells and that for the hard-axis martensite well. Whereas, for hard-axis martensite, magnetization changes as the result of a rotating magnetization vector, a change in the magnetization of easy-axis martensite or austenite results from a redistribution of cells between left and right variants. None of the individual easy-axis or austenite cells can have any magnetization value other than the saturation value for its phase. In other words, we have that \(M_{er}\) and \(M_{el}\) equal \(M_{sm}\) and \(-M_{sm}\), respectively, \(M_{ar}\) and \(M_{al}\) equal \(M_{sa}\) and \(-M_{sa}\), respectively, and the curvatures \(\lambda_e\) and \(\lambda_a\) are infinite. Such a non-physical scenario leads us to question the idea of formulating the energies in terms of unit-cell states. To resolve the problem, we must consider the behavior of quantities of material much larger than that unit cells. This will be discussed...
further in Section 3.4. Deriving expressions for the energy barriers will be left until Section 3.5. For now, we will simply remove the terms containing $\lambda$’s and consider the effect of applied stresses and magnetic fields.

The stress- and magnetic-field-dependent Gibbs energy equations derive from the Helmholtz equations by means of Legendre transforms,

\[
\begin{align*}
g_h &= \frac{1}{2} Y_h \left( \varepsilon_h - \varepsilon_{rh} \right)^2 + \frac{1}{2} \frac{\mu_0}{\chi_h} M_h^2 - \sigma \varepsilon_h - \mu_0 H M_h, \\
g_{cr} &= \frac{1}{2} Y_c \left( \varepsilon_c - \varepsilon_{rc} \right)^2 - \sigma \varepsilon_c - \mu_0 H M_{cr}, \\
g_{el} &= \frac{1}{2} Y_e \left( \varepsilon_e - \varepsilon_{re} \right)^2 - \sigma \varepsilon_e - \mu_0 H M_{el}, \\
g_{ar} &= \frac{1}{2} Y_a \varepsilon_a^2 - \sigma \varepsilon_a - \mu_0 H M_{ar} + \beta(T), \\
g_{al} &= \frac{1}{2} Y_a \varepsilon_a^2 - \sigma \varepsilon_a - \mu_0 H M_{al} + \beta(T) .
\end{align*}
\]

We may calculate the strain and magnetization minima in terms of the applied stress and magnetic field as

\[
\begin{align*}
\varepsilon_h &= \varepsilon_{rh} + \frac{\sigma}{Y_h} M_h = \chi_h H, \\
\varepsilon_c &= \varepsilon_{rc} + \frac{\sigma}{Y_c} M_{cr} = M_{sm}, \\
\varepsilon_e &= \varepsilon_{re} + \frac{\sigma}{Y_e} M_{el} = -M_{sm}, \\
\varepsilon_a &= \varepsilon_{ra} + \frac{\sigma}{Y_a} M_{ar} = M_{sa}, \\
\varepsilon_a &= \varepsilon_{ra} + \frac{\sigma}{Y_a} M_{al} = -M_{sa}
\end{align*}
\]

where the easy-axis martensite and austenite wells have been assigned the saturation magnetizations for their respective phases, as was previously discussed. The temperature-dependent $\beta$ term in the austenite-well equations reflects the difference in entropy between the martensite and austenite phases. If we assume this term is linear in $T$, we have that

\[
\beta(T) = S_0 + S_{rel} T ,
\]
where $S_0$ is the entropy difference between martensite and austenite at absolute zero and $S_{rel}$ is the difference in the entropy change per unit temperature of each,

$$S_{rel} = \left( \frac{dS}{dT} \right)^{\text{aust}} - \left( \frac{dS}{dT} \right)^{\text{mart}}.$$  \hspace{1cm} (3.6)

Because austenite is less stable than martensite at low temperatures and more stable at high temperatures, we expect that the value for $S_0$ should be greater than zero and that for $S_{rel}$ should be less than zero. These values may be estimated from the austenite-to-martensite and martensite-to-austenite transition temperatures, $T_{am}$ and $T_{ma}$.

### 3.4. Model Scale

We now deviate somewhat from our discussion of free energies to reconsider the mechanisms responsible for variant transformation: the motion of phase boundaries, twin boundaries, and magnetic domain walls. In so doing, we will rescale the model in terms of mesoscopic elements. These will be tied to microscopic behavior but capable of explaining macroscopic observations.

Figure 3.7 provides a schematic representation of the microstructure of a heterogeneous sample of NiMnGa. Here, slabs of austenite, shown in solid white, are separated from martensite by a series of phase boundaries. Twin boundaries appear within the martensite slabs, partitioning these into alternating easy- and hard-axis twin layers. Within each twin layer, magnetic domains are visible, separated by horizontal or vertical magnetic domain walls. Magnetic domains also permeate the austenite. These are not shown in the figure.
Figure 3.7: Interface types within a heterogeneous sample of NiMnGa.

There are a number of features in this figure that demand further discussion. First, it can be seen that all of the interfaces shown in the figure – phase boundaries, twin boundaries, and magnetic domain walls – are depicted as straight lines. This reflects the experimental observation that, under normal circumstances, each of these interfaces will remain coherent. Because of this, the cell-by-cell transition referred to above, which would require interfaces to contort awkwardly, will not occur. Rather, each interface will move in a direction approximately normal to its cross section, and some minimum volume of cells proportional to the cross-sectional area of the interface will transition simultaneously.

What we now see is a hierarchy of transformation. Motion of a domain wall will cause a large number of unit cells to transition from one magnetic variant to another. Motion of a twin boundary will force cells constituting a mixture of magnetic variants to transition from one martensite twin to another. Motion of a phase boundary will cause a transition to or from a mixture of twin variants.

From these considerations, we conclude that the elements of interest to us are not the individual unit cells but rather the slices of material adjacent to each interface, which we will call domain elements, twin-layer elements, and phase elements. In order for an interface to

\[2\] For conventional shape memory alloys, twin and phase boundaries have been described as “often close to being atomically sharp” (Ren and Truskinovsky, 2000).
move, it must be energetically beneficial for these much larger quantities of material; and it is these quantities that will be affected each time interface motion occurs.

Because we cannot know the size of each and every interface, we resolve to describe the affected quantities in an average sense and denote them as $V_{de}$, $V_{te}$, and $V_{pe}$: the volumes of the domain element, twin-layer element, and phase element, respectively. (Although $V_{de}$ for easy-axis martensite and austenite will, in general, be different, we find no experimental justification for distinguishing one from the other.) Rather than attempt to count individual cells of each variant, we instead find phase fractions, $x$, which are the number of cells of a given variant divided by the total number of cells. To allow us to make predictions regarding unpopulated twins and phases and to prevent divide-by-zero errors, we renormalize these as

$$x_{elf} + x_{erf} = 1$$
$$x_{alf} + x_{arf} = 1$$
$$x_{ef} + x_{hf} = 1$$
$$x_m + x_a = 1$$

(3.7)

where the “f” in the subscript indicates that the value is expressed as a fraction of its phase or twin layer. To determine the absolute phase fractions, we multiply the renormalized fractions,

$$x_h = x_{hf} \cdot x_m$$
$$x_{er} = x_{erf} \cdot x_{ef} \cdot x_m$$
$$x_{el} = x_{elf} \cdot x_{ef} \cdot x_m$$

(3.8)

$$x_{ar} = x_{arf} \cdot x_a$$
$$x_{al} = x_{alf} \cdot x_a$$

The concepts discussed in this section are summarized in Table 3.1.
Table 3.1: Physical mechanisms responsible for variant transition and the volumes for which transition occurs.

<table>
<thead>
<tr>
<th>Physical Mechanism</th>
<th>Resulting Transitions</th>
<th>Relevant Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain-wall motion within easy-axis martensite twin</td>
<td>$er \leftrightarrow el$</td>
<td>Volume of a domain element, $V_{de}$</td>
</tr>
<tr>
<td>Domain-wall motion within austenite phase</td>
<td>$ar \leftrightarrow al$</td>
<td>Volume of a domain element, $V_{de}$</td>
</tr>
<tr>
<td>Twin-boundary motion</td>
<td>$h \leftrightarrow e$</td>
<td>Volume of a twin-layer element, $V_{te}$</td>
</tr>
<tr>
<td>Phase-boundary motion</td>
<td>$a \leftrightarrow m$</td>
<td>Volume of a phase element, $V_{pe}$</td>
</tr>
</tbody>
</table>

The mesoscopic volumes in the rightmost column serve to discretize the model. They also scale the effect of thermal activation. This will be investigated further in Chapter 4.

3.5. Phase Fraction Evolution

We will now discuss the behavior of mesoscopic quantities of material. From considerations in the previous section, we may conclude that the energy of an easy-axis twin-layer element should have the form

$$g_e = x_{eff} g_{er} + x_{eff} g_{el} + E_{int}, \quad (3.9)$$

where the first two terms on the right-hand side of the equation are simply a weighted average of the energies of the component domain elements. The last term represents an interaction energy that emerges only when the material is allowed to congregate into mesoscopic quantities. To justify its presence, we reconsider the easy-axis magnetization curve of the material, shown in Figure 3.8. We have previously noted that this curve is the result of a transition of material between the $er$ and $el$ wells. The question then becomes, why does the material transition gradually, as seen by the finite slope of the curve? In the context of our energy picture, why should the material not transition suddenly as the height of the $er$ or $el$ energy well approaches that of the barrier?
Figure 3.8: Easy-axis magnetization curve for NiMnGa (from Straka, 2007).

This thought experiment reinforces the need for an $E_{int}$ term to regulate the rate at which material transitions between the $er$ and $el$ wells. As to resolving the form of this term, we take clues from the physical process that occurs when the material is saturated along its easy axis. This process involves two mechanisms that are, thus far, unaccounted for in our energy picture: the nucleation and annihilation of domain walls and the expansion of stray magnetic fields as domains grow large. The finite slope of the easy-axis magnetization curve, then, represents a shifting balance between domain-wall energy and stray-field energy as Zeeman energy increases due to application of a magnetic field. Rather than incorporate exact expressions for each of these energies in our $E_{int}$ term, we aim only to find an expression with the proper quality. This is shown in Figure 3.9.

Figure 3.9: Variation of $E_{int}$ as a function of $x_{erf}$.

The important feature here is that the energy is minimized at $x_{erf} = ½$ and is symmetric about this point. The equation for the plot is
\[ E_{\text{int}} = -C_{\text{dim}} x_{\text{erf}} (1 - x_{\text{erf}}) + \frac{C_{\text{dim}}}{4}, \]  

(3.10)

where \( C_{\text{dim}} \) is the domain-imbalance constant for martensite and the \( C_{\text{dim}} / 4 \) term ensures that the energy minimizes to zero. (Note that \( E_{\text{int}} \) could just as easily have been expressed in terms of \( x_{\text{elf}} \).) In order for this term to have the desired effect – that is, to regulate the easy-axis transitions – it must also factor into the driving force between the \( \text{er} \) and \( \text{el} \) wells. To determine the change in energy that results from a change in the \( x_{\text{erf}} \) phase fraction, we differentiate \( E_{\text{int}} \) with respect to the phase fraction,

\[ \frac{dE_{\text{int}}}{dx_{\text{erf}}} = C_{\text{dim}} (2x_{\text{erf}} - 1), \]  

(3.11)

and add this to the driving force from \( \text{er} \) and \( \text{el} \). If formulated in terms of the easy-axis magnetization, this expression becomes essentially identical to that typically used to represent demagnetization.

Using a similar line of reasoning, we can motivate the need for a domain-imbalance term for austenite, as well as twin-imbalance and phase-imbalance energy terms. We formulate these in terms of \( C_{\text{dia}}, C_{\text{ti}}, \) and \( C_{\text{pi}} \) to give driving forces between each pair of wells of

\[
\begin{align*}
F_{\text{er} \leftrightarrow \text{el}} &= \pm \left( g_{\text{er}} - g_{\text{el}} + C_{\text{dim}} (2x_{\text{erf}} - 1) \right) \\
F_{\text{ar} \leftrightarrow \text{al}} &= \pm \left( g_{\text{ar}} - g_{\text{al}} + C_{\text{dia}} (2x_{\text{arf}} - 1) \right) \\
F_{h \leftrightarrow \epsilon c} &= \pm \left( g_{h} - g_{a} + C_{\text{ti}} (2x_{\text{hcf}} - 1) \right) \\
F_{a \leftrightarrow \epsilon m} &= \pm \left( g_{a} - g_{m} + C_{\text{pi}} (2x_{\text{afl}} - 1) \right)
\end{align*}
\]  

(3.12)

where the right-hand side takes the positive for the forward transition (e.g., \( \text{er} \rightarrow \text{el} \)) and the negative for the backward transition.

To make these values meaningful, we must now derive an expression for the height of the energy barriers. Previous versions of the model, such as that for conventional shape-memory alloys (Seelecke, 2002), possessed one fewer order parameter, allowing for the use of convex parabolas rather than paraboloids for the energy wells. In this case, the energy barrier was
found by connecting the energy wells with a concave parabola and enforcing first-order continuity between it and the wells at transition points.

The use of paraboloidal energy wells, however, complicates things. In three dimensions, the energy barriers are saddle-shaped, and transitions do not occur over the top of the barriers but over saddle points, the lowest-energy maxima encountered in traversing the width of the saddle. Rather than find a saddle equation for each barrier and determine the lowest-energy path between each pair of wells at any given time, we approximate the barrier height by drawing analogies to the parabolic case. Shown in Figures 3.10(a) and 3.10(b) are the two parameters on which we base the approximation. The $\Delta g_0$ parameter is the height of the energy barrier in the absence of any applied forces. The $F_{cr}$ parameter, referred to as the critical driving force, is the driving force at which the barrier height is completely negated. In the two-dimensional case, it can be shown that $F_{cr}$ is equal to $4\Delta g_0$.

![Figure 3.10](image-url)  
**Figure 3.10:** Definition of the (a) energy barrier at zero driving force and (b) critical driving force.

Physically, the energy barrier between any two wells $\alpha$ and $\beta$, $\Delta g_{\alpha\beta}$, should never become negative. Beyond $F_{cr}$, we also expect that it should increase linearly with the driving force, $F_{\alpha\beta}$. This gives us the piecewise expression
The relationshi p is shown graphically in Figure 3.11, where first-order continuity at the critical driving forces is evident. A more in-depth derivation of (3.13) can be found in Kim and Seelecke, 2007.

![Figure 3.11: Relationship between $\Delta g_0$ and the driving force.](image)

Because they represent different physical processes (i.e., the movement of domain walls, twin boundaries, and phase boundaries), the $\Delta g_0$ will be different for each transition,

$$
\Delta g_0 = \begin{cases} 
\Delta g_{0,se} & \text{for } er \leftrightarrow el \text{ and } ar \leftrightarrow al \\
\Delta g_{0,eh} & \text{for } h \leftrightarrow e \\
\Delta g_{0,pb} & \text{for } a \leftrightarrow m
\end{cases}.
$$

These may be given values by finding the critical driving forces, $F_{cr}$. If we assume vanishing thermal activation, the critical driving forces will be recognizable in the data as the point at which transition occurs.
For the case of twin-boundary motion, the critical driving force coincides with the twinning stress. It is a simple matter to find the driving force at this stress and divide this value by 4 to yield $\Delta g_{0, tb}$. Alternatively, we could find the barrier height using the switching field – defined as the magnetic field at which twin-boundary motion occurs in the absence of applied stress – or at any combination of forces that results in twin-boundary motion.

In the case of domain wall motion, an analogous force is provided by the coercive field, $H_c$. For phase boundary motion, there is no convenient reference point at which to define $\Delta g_{0}$, so we may instead use half of the width of the hysteresis in an austenite-martensite stress-strain curve, $\sigma_{w/2}$. Example equations for our $\Delta g_0$’s incorporating the above quantities are

$$\Delta g_{0, dw} = \frac{F_{cr, el \rightarrow er}}{4} = g_{el}(H_c) - g_{er}(H_c) = \frac{1}{4} \left( 2 \mu_0 M_{sm}^* H_c \right)$$

$$\Delta g_{0, tb} = \frac{F_{cr, e \rightarrow rh}}{4} = g_{e}(\sigma_{rw}) - g_{h}(\sigma_{rw}) = \frac{1}{4} \left( \frac{1}{2} \sigma_{rw}^2 \left( \frac{1}{Y_h} - \frac{1}{Y_e} \right) + \sigma_{rw} (\epsilon_{rh} - \epsilon_{re}) \right)$$

$$\Delta g_{0, pb} = \frac{F_{cr, a \rightarrow sm}}{4} = g_{h}(\sigma_{w/2}) - g_{a}(\sigma_{w/2}) = \frac{1}{4} \left( \frac{1}{2} \sigma_{w/2}^2 \left( \frac{1}{Y_h} - \frac{1}{Y_a} \right) + \sigma_{w/2} \epsilon_{rh} \right)$$

where $M_{sm}^*$ is the saturation magnetization of martensite at the temperature at which $H_c$ was measured. Although the barriers to domain-wall motion will in general be different in martensite and austenite, no experimental justification for distinguishing the value of one from the other has been found.

Employing our $\Delta g_0$’s within (3.13), we now use the Boltzmann distribution equation to calculate the probability of an element transitioning between variants,
\[ P_{\text{er} \rightarrow \text{rel}} = \frac{1}{\tau_x} \exp \left( -\frac{\Delta g_{\text{er} \rightarrow \text{rel}} V_{\text{de}}}{k_B T} \right) \]
\[ P_{\text{ar} \rightarrow \text{al}} = \frac{1}{\tau_x} \exp \left( -\frac{\Delta g_{\text{ar} \rightarrow \text{al}} V_{\text{de}}}{k_B T} \right) \]
\[ P_{\text{hr} \rightarrow \text{c}} = \frac{1}{\tau_x} \exp \left( -\frac{\Delta g_{\text{hr} \rightarrow \text{c}} V_{\text{lc}}}{k_B T} \right) \]
\[ P_{\text{me} \rightarrow \text{a}} = \frac{1}{\tau_x} \exp \left( -\frac{\Delta g_{\text{me} \rightarrow \text{a}} V_{\text{pc}}}{k_B T} \right) \]  \hspace{1cm} (3.16)

where \( \tau_x \) is an “attempt frequency” that dictates the rate-dependence of the behavior. It must be estimated from experimental data that includes a time component (such as maximum-frequency or creep experiments). Notice the position of the mesoscopic-element volumes in these equations. As a given volume increases, a greater temperature will be necessary to cause the same transition probability. In this way, the element volumes scale the effect of thermal activation on the material.

Once we know the transition probabilities, we can determine the phase fraction rates of change as
\[ \dot{x}_{\text{er}} = x_{\text{elf}} P_{\text{el} \rightarrow \text{er}} - x_{\text{er}} P_{\text{er} \rightarrow \text{rel}} \]
\[ \dot{x}_{\text{ar}} = x_{\text{al}} P_{\text{al} \rightarrow \text{ar}} - x_{\text{ar}} P_{\text{ar} \rightarrow \text{al}} \]
\[ \dot{x}_{\text{hr}} = x_{\text{hlf}} P_{\text{h} \rightarrow \text{c}} - x_{\text{hr}} P_{\text{c} \rightarrow \text{h}} \]
\[ \dot{x}_{\text{m}} = x_{\text{ma}} P_{\text{m} \rightarrow \text{a}} - x_{\text{m}} P_{\text{a} \rightarrow \text{m}} \]  \hspace{1cm} (3.17)

where the first term on the right-hand side of each equation represents the phase fraction gained from the neighboring well and the second term represents the fraction lost to the neighboring well.

The absolute phase fractions may then be used to determine the macroscopic strain and magnetization,
\[ \langle \varepsilon \rangle = x_{\text{a}} \varepsilon_{\text{a}} + x_{\text{h}} \varepsilon_{\text{h}} + x_{\text{c}} \varepsilon_{\text{c}} \]
\[ \langle \mathbb{M} \rangle = (x_{\text{ar}} - x_{\text{al}}) M_{\text{a}} + x_{\text{h}} M_{\text{h}} + (x_{\text{er}} - x_{\text{el}}) M_{\text{el}} \]  \hspace{1cm} (3.18)
where the macroscopic values are simply the weighted averages of all component elements.

3.6. Model Implementation

The model is implemented using Matlab and Simulink. The differential equations (3.17) are integrated numerically using ode45 (Dormand-Prince). The Matlab code for the model appears in Appendix 1. A screen capture of the Simulink model appears in Appendix 2.
CHAPTER 4
MODELING RESULTS

This chapter discusses calibration of the model and the effect of various parameters on its
behavior. Data from the model is compared to data from a wide range of experiments and
similarities and discrepancies are noted.

4.1. Model Calibration

The model described here simulates a wide variety of material behavior. As a result, a large
number of parameters are required for its execution. In other materials, some of these would
be considered “known” parameters, such as the saturation magnetization or Young’s
modulus. However, in NiMnGa, many of these parameters vary significantly with
temperature (discussed in Section 4.5), stoichiometry, and even from sample to sample (see
Straka, et al., 2003). Little about a given piece of material can be simply assumed.

In calibrating the model to a given experiment, some of the model parameters will be
measurable from the experiment, itself. A greater number of them will not. In many cases,
these hidden parameters will have little effect on the simulation of the experiment. The
saturation magnetization, for instance, need not be known to simulate thermal superelasticity.
In some cases, however, a given parameter will not be measurable from an experiment but
will strongly affect it. As an example of this, consider the magnetic-field-induced shape-
memory effect. It is seen experimentally as a sharp increase in strain with an increasing
magnetic field. An important factor in the occurrence of this effect is the hard-axis magnetic
susceptibility. If the susceptibility is too large, the magnetization vector of the hard-axis
variant will rotate too easily there will be little energetic benefit for the sample to transition
into the easy-axis variant. But while the magnetic susceptibility largely scales the driving
force between the easy- and hard-axis variants and strongly affects the stress at which the
magnetic-field-induced shape-memory effect is blocked, it can not be measured directly from
a strain-magnetic field plot.
In this paper, we will adopt the following approach in calibrating the model: for a given experiment, we will determine as many of the model parameters as possible from the experiment, itself; those parameters that may not be taken directly from the experiment will generally be taken from other experiments performed by the same research group on a sample of the same stoichiometry (here, the research group of Straka and Heczko and the material Ni_{49.7}Mn_{29.4}Ga_{21.2}); if the necessary experiments have not been performed, or if the indirect effects of a parameter on the experiment lead us to conclude that its value must differ from that measured elsewhere, we will note this and justify the parameter value we select.

Calibration of model parameters from an experiment is demonstrated in Figure 4.1. In the figure, we see a stress-strain curve for martensitic NiMnGa. A large magnetic field of constant magnitude is applied. The driving force generated by the field is sufficient to cause hard-axis-to-easy-axis transition of the material at low stress. As the stress increases, it overcomes the magnetic field and eventually causes the reverse transition, closing the hysteresis loop. This effect may be referred to as “magnetosuperelasticity.”

**Figure 4.1:** Calibration of model parameters from a magnetosuperelastic stress-strain curve. (Data taken from Straka, 2007.)
From the figure, we see that a number of model parameters may be taken from the experiment. In linear regions (i.e., regions where the material is not transitioning), the slope of the stress-strain curve should be equal to the Young’s modulus of the material. As the figure shows, this value is generally different for the hard- and easy-axis martensite variants. Tracing the linear portion of the hard-axis variant back to zero stress, we find the difference in the remnant strains of the two twins. We may draw a vertical line at half this value to indicate the point at which half of the material has transitioned from one variant to the other. By our definition, the critical driving force is the driving force that results in transition of half of the material, so the intersections between our line and the stress-strain curve allow us to determine $\Delta g_{0.5b}$. We calculate the slope of the curve at the critical points to estimate $C_{ti}$.

Although most of the model parameters are scalars, the magnetization of the material must be described accurately as a function of temperature, and so its saturation values are determined from an exponential-curve fit. At the inset of Figure 4.2, we see the magnetization-temperature curve for our material at a large applied field, capable of magnetically saturating the material. At 308 K on the curve, a sudden change in the magnetization occurs. Because the sample is cooled during the experiment, this point represents a phase transition of the material from austenite to martensite.
In general, the saturation magnetizations of austenite and martensite will not be the same. Data from pre- and post-transition portions of the curve must therefore be fit separately. The results of both fits are shown in Figure 4.2.

Table 4.1 lists a number of experiments from which some of the model parameters may be obtained. This list is not exhaustive.
Table 4.1: A list of experiments that may be used to determine model parameters.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Stress vs. strain at $H &gt; H_{sw}$ to show full hysteresis curve</td>
</tr>
<tr>
<td>(2)</td>
<td>Stress vs. strain at $T &gt; T_{m,a}$ to show full hysteresis curve</td>
</tr>
<tr>
<td>(3)</td>
<td>Strain vs. magnetic field at $\sigma &gt; \sigma_{tw}$ to show full hysteresis curve</td>
</tr>
<tr>
<td>(4)</td>
<td>Strain vs. temperature at $\sigma &gt; \sigma_{tw}$ or $H &gt; H_{sw}$ to show full hysteresis curve</td>
</tr>
<tr>
<td>(5)</td>
<td>Magnetization vs. magnetic field for all three phases</td>
</tr>
<tr>
<td>(6)</td>
<td>Saturation magnetization and low-field magnetization vs. temperature</td>
</tr>
<tr>
<td>(7)</td>
<td>Time-dependent data for all transition types</td>
</tr>
<tr>
<td>(8)</td>
<td>In-situ microphotography for all transition types</td>
</tr>
</tbody>
</table>

Table 4.2 gives the full list of model parameters and outlines which of the above experiments may be used to find them. Experiments (1) and (2) yield most of the structural data necessary to calibrate the model while experiments (5) and (6) provide most of the relevant magnetic data. Some parameters may be approximately obtained from a given experiment, such as the austenite-martensite transition temperatures from experiment (4). In reality, because martensite is stabilized by a compressive stress or a large magnetic field, the transition temperatures seen here will deviate slightly from their true values. The attempt frequency, $\tau_x$, and element volumes may only come from experiments of types (7) and (8), respectively. Data of this type is generally unavailable, so values for these parameters are estimated based on measurements of similar materials and experience with other models of this type (see references in Section 3.1).
Table 4.2: A complete list of model parameters and the experiments from which they may be obtained.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sources</th>
<th>Parameter</th>
<th>Sources</th>
<th>Parameter</th>
<th>Sources</th>
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<tr>
<td>$Y_h$</td>
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<td>$\chi_h$</td>
<td>(5)</td>
<td>$C_{dim}$</td>
<td>(5)</td>
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<td>(5), (6)</td>
<td>$C_{dia}$</td>
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<td>(2)</td>
<td>$M_{sa}$, $M_{sa}(T)$</td>
<td>(5), (6)</td>
<td>$C_{ri}$</td>
<td>(1), (3)</td>
</tr>
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<td>$T_{a,m}$</td>
<td>(~4), (6)</td>
<td>$C_{pi}$</td>
<td>(2)</td>
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<tr>
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<td>$T_{m,a}$</td>
<td>(~4), (6)</td>
<td>$V_{de}$</td>
<td>(8)</td>
</tr>
<tr>
<td>$F_{cr}^{(tw)}$</td>
<td>(1), (3)</td>
<td>$F_{cr}^{(dw)}$</td>
<td>(6)</td>
<td>$V_{te}$</td>
<td>(8)</td>
</tr>
<tr>
<td>$F_{cr}^{(pt)}$</td>
<td>(2)</td>
<td>$\tau_x$</td>
<td>(7)</td>
<td>$V_{pc}$</td>
<td>(8)</td>
</tr>
</tbody>
</table>

4.2. Model Walkthrough

To help the reader become oriented with the behavior of the model, a simulation of the magnetic-field-induced shape-memory effect (MFI SME) will be described in detail. In this simulation, a constant compressive stress of 1.5 MPa is applied. The magnetic field is then cycled between $-7 \times 10^5$ A/m and $7 \times 10^5$ A/m, resulting in the hysteresis curves shown in Figure 4.3.

![Figure 4.3: Model simulation of the magnetic-field-induced shape-memory effect.](image)

The process by which these curves are created may be better understood by decoupling the forcing functions and order parameters. Figure 4.4 shows the model inputs (top row) and
outputs (middle row) as functions of time. The relevant phase fractions appear at the bottom of the figure.

The material is initially in the hard-axis state. From time 0 to 5, no magnetic field is applied and the compressive stress of the material increased to 1.5 Mpa. From this point on, the stress is held constant. At time 5, the magnetic field begins to increase. This results in a slow, linear increase in the magnetization due to vector rotation of the hard-axis variant. No change in the strain is seen.

Around time 7, both the magnetization and strain of the sample increase suddenly. From the bottom of Figure 4.4, we can see that this change is the result of a full transition of material from the $h$ to $er$ variant. The current field is sufficient to cause magnetic saturation of the easy-axis twin, so neither strain nor magnetization further increase.

![Figure 4.4: The magnetic-field-induced shape-memory effect as viewed in time and by phase fraction.](image-url)
Beginning at time 10, the magnetic field begins to decrease. As the field’s value nears zero, it becomes unable to counteract the compressive stress. The stress causes the material to transition completely back into the hard-axis variant prior to time 15. As before, magnetization of the sample now results from vector rotation within the hard-axis variant.

As the field becomes increasingly negative after time 15, we again see a full hard-to-easy-axis-twin transition. This occurs at approximately time 17. Because the material has transitioned into the $el$ variant, the magnetization now attains its negative saturation value.

At time 20, the magnetic field begins to increase from its most negative value. By time 25, the magnetic field has returned to zero value and the compressive stress has once again caused all of the material to transition back into the hard-axis variant.

Let us now reconsider the experiment in the context of the energy landscapes previously described. Figure 4.5 shows the Gibbs energies (top row), driving forces (middle row), and phase fractions (bottom row) in terms of the relevant magnetic (left column) and structural (right column) variants. As a reminder, the Gibbs energy of each variant corresponds to the minimum of its corresponding energy well. In the middle row, the dashed line represents the relevant critical driving force. It takes either of two values based on which transition is the next to occur. Because the driving forces between the $el$ and $er$ variants grow much larger than the critical forces, a rescaled version of the $er-el$ driving-force plot appears at its inset. The inputs and outputs are as before.
Figure 4.5: The magnetic-field-induced shape-memory effect in terms of the driving forces.

In the figure, we see that from time 0 to 5, while the compressive stress is being applied, the energy of the easy-axis variant increases, while that of the hard-axis variant decreases. This is due to the compressive stress favoring the twin having smaller strain in the direction of the stress. It results in a large increase in the driving force from \( e \rightarrow h \). As the \( er \) and \( el \) variants...
are structurally the same, the compressive stress has no effect on the driving force between them.

As the magnetic field begins to increase at time 5, the driving force between $er$ and $el$ decreases rapidly due to the effect of the Zeeman energy; the driving force overcomes the $er$-$el$ energy barrier almost immediately. However, because no material is currently in the easy-axis-twin state, there is initially no increase in the $er$ phase fraction.

Because the easy-axis twin may more readily magnetize itself in the direction of the applied magnetic field, the driving force from $e$ to $h$ also decreases, reaching the critical force at around time 7. When this occurs, all of the material in the $h$ well immediately spills out. Because the critical force between $er$ and $el$ variants has already been exceeded, this material spills completely into the $er$ variant.

Although the driving force between $e$ and $h$ continues to decrease as the field increases, it does so at a decreasing rate. In terms of the energy landscape, this is due to the magnetization minimum of the $h$ well moving increasingly near to that of the $er$ well, thus reducing the effect of the Zeeman energy. Physically, this reflects the equilibrium state of the magnetization vector rotating toward the field. Eventually, the magnetization minimum of the $h$ well reaches the saturation value at approximately time 8 and the driving force from $h$ to $e$ ceases to increase.

As the magnetic field starts to decrease beginning at time 10, the process essentially proceeds in reverse. However, here the relevant critical driving force is that required for transition from the $e$ to $h$ well. This is attained around time 14, causing a full transition of the material back into the hard-axis variant.

At time 15, the magnetic field begins to grow increasingly negative. This favors the easy-axis twin, as before, but now causes the driving force between the $er$ and $el$ wells to grow largely positive. When the magnetic field becomes sufficiently large at about time 17, the material in the $h$ well spills back out of it and into the $el$ well. This material returns to the $h$ well after the magnitude of the field has decreased, at time 24.
4.3. Effect of Model Parameter Variation

A number of the parameters specific to the model correspond to quantities that, while they are based in physical processes, are not intuitive in their physical effect on the material. For this reason, the variation of these parameters will be demonstrated here.

Figure 4.6 shows model data for three different experiments. In the first, a sample of martensite composed entirely of the easy-axis twin is subjected a cyclical magnetic field. In the second experiment, identical to that described in Section 4.2, a fully martensitic sample is placed under a compressive stress and then subjected to a cyclical magnetic field. In the final experiment, a sample of material is heated into an austenitic state and then subjected to varying amounts of compressive stress.
Figure 4.6: Effect of energy barriers on model output.

In each of the experiments in Figure 4.6, the data incorporate a change in the height of the most relevant energy barrier. The first experiment shown in Figure 4.6 simulates transition of material between the \(er\) and \(el\) wells. The manner in which this process occurs is influenced by the barrier to domain-wall motion for martensite, \(\Delta g_{0,dwm}\). In the second experiment, material transforms from the easy- to hard-axis twin and back. The barrier to twin-boundary motion, \(\Delta g_{0,\text{tb}}\), is considered here. In the final experiment, temperature causes the sample to
move into the austenite state while a large stress forces it back into martensite. The barrier to phase-boundary motion, $\Delta g_{0,pts}$, regulates the process.

From the figure, it is seen that in all cases an increase in the relevant energy barrier results in a widening of the hysteresis. In other words, a greater driving force is required to induce transformation. This result may be further clarified by referring back to the middle row of plots in Figure 4.5. Here, the increase in the height of the energy barriers acts to move the critical driving forces apart, separating the transitions in terms of the applied forces.

The effect of an increase in the relevant imbalance constants of each of the three experiments is shown in Figure 4.7. Because their energy barriers are the same, each pair of curves has the same approximate width and crosses the other at its middle, where the driving force is zero. The slopes of the curves, however, vary noticeably. This reflects how the various imbalance terms energetically reward configurations in which phase fractions are similar and punish configurations where one phase fraction is much greater than the other.
The effect of the element volumes is demonstrated in Figure 4.8. As each of these volumes decreases, the hysteresis exhibited by the material may also be seen to decrease. This results from a relative increase in the thermal activation of the material. The random thermally-induced vibrations that for large quantities of material are mostly self-negating may significantly impact the energy of smaller quantities of material. At very small element volumes, the phase transition comes to resemble a diffusive process and the hysteresis disappears.
The effect of the relaxation time, $\tau_x$, may only be seen when its order of magnitude is comparable to the period with which the material is actuated. To demonstrate this, Figure 4.9 shows the second experiment above with an enlarged relaxation time. It can be seen from that figure that, as the relaxation time approaches the actuation period, the material struggles to keep up with the forcing function. In terms of this experiment, the magnetic field is being varied so quickly that domain-wall motion lags behind, causing the hysteresis to widen as a result of the inertia of the material.
4.4. Comparison to Experimental Data

To demonstrate the flexibility of the model, we now compare model output to experimental data from a wide range of experiments. As discussed in Section 4.1, parts of the model are calibrated based on the experiment to which it is being compared. However, it is important to note that the resulting parameter values should be considered “best guesses” only, and no optimization to the experimental data is performed.

4.4.1. Magnetization as a Function of Magnetic Field and Temperature

Figure 4.10(a) shows the response of the material in its martensite and austenite phases to a cyclical magnetic field. The model output for this scenario is shown in Figure 4.10(b). From the figure, it may be seen that the model correctly reproduces magnetization curves of the material for each of the three structural variants.
Figure 4.10: (a) Experimental and (b) model magnetization data for easy- and hard-axis martensite and austenite. (Data taken from Straka, 2007).

Figure 4.11(a) shows model predictions for the variation in magnetization with temperature. At small fields, the magnetization is seen to increase suddenly as the material transitions from martensite to austenite. This is due to the larger magnetic susceptibility of the material in its austenite state. As the field grows larger, however, eventually a decrease in magnetization is seen during the phase transition. This is caused by the larger saturation magnetization of martensitic NiMnGa.

Figure 4.11: (a) Model output for magnetization vs. temperature at several applied fields and (b) relevant locations on the magnetization curve.
To help explain the effect, Figure 4.11(b) shows a magnified region of the magnetization curve from Figure 4.10(b), with the magnetization of the material at each of the relevant fields highlighted. In the figure, an arrow indicates the direction of change of the magnetization as it transitions from martensite to austenite. The figure shows that, at the small fields employed, the magnetization of austenite is greater than that of martensite. At the largest field, capable of saturating the material in both phases, the magnetization of martensite is greater.

We were unable to locate comparable experimental data for the material, finding only the magnetization-temperature curve shown in Section 4.1. However, a similar curve for NiMnGa of a different stoichiometry appears in Marioni, et al., 2005. It is reproduced in Figure 4.12. The figure indicates that the magnetization-temperature data yielded by the model is qualitatively correct.

![Figure 4.12: Magnetization-temperature curve from Marioni, et al., 2005.](image)

### 4.4.2. Magnetic-Field-Induced Strain as a Function of Compressive Stress

The magnetic-field-induced shape-memory effect was described in detail in Section 4.2. Figure 4.13 demonstrates how the effect responds to variations in compressive bias stress. At
very low values of stress, the material easily transitions from the hard- to easy-axis twin at large magnetic fields but struggles to transition back when the magnitude of the field is decreased. As the stress grows large, the magnetic field can no longer cause a full transition into the easy-axis twin before the magnetization of the hard-axis twin saturates.

Figure 4.13: Measured variation in magnetic-field-induced shape-memory effect as a function of compressive stress (taken from Straka, 2007).

From the figure, it may be seen that the transition is blocked at approximately 2 Mpa. This value is smaller than that typically seen for these materials (see, for example, Heczko, et al., 2000). As a result, to ensure good agreement between the model and experimental data, here
it was necessary to decrease the martensitic saturation magnetization in the model by approximately 10%. This reduces the driving force at a given field value and causes a corresponding decrease in the blocking stress.

**Figure 4.14:** Modeled variation in magnetic-field-induced shape-memory effect as a function of compressive stress.

It can be seen from Figure 4.14 that, with the change noted above, the model obtains good qualitative and quantitative agreement with the experimental data. This idea is reinforced by Figure 4.15, in which the maximum strains and reversible strokes experimentally obtained at
each of the compressive stresses are compared to corresponding values generated by the model.

![Graph showing maximum strain and reversible strain](image.png)

**Figure 4.15:** Comparison of experimental and model data for maximum and reversible MFI strain as a function of compressive stress. (Experimental data taken from Straka, 2007.)

### 4.4.3. Stress-Strain Behavior under the Application of a Magnetic Field and Heat

In Figure 4.16, the stress-strain curve for the material in a magnetic field of 0.6 T is shown. This effect was previously referred to magnetosuperelasticity and was described in Section 4.1. Here, a very good agreement between model and experiment is visible.
Figure 4.16: Comparison of experimental and model stress-strain curves at 0.6 T. (Experimental data taken from Straka and Heczko, 2003.)

To demonstrate the fidelity of the model, its output is now compared to stress-strain data at a number of other magnetic fields without recalibration. The results may be seen in Figure 4.17. In general, the model agrees well with data at all fields. The largest deviation between model and experimental data occurs at 0.9 T. This is a result of the model hard-axis magnetization saturating at a lower field than the material in the experiment.
Thermal superelasticity is demonstrated in Figure 4.18. Similar to the magnetosuperelastic case, the material undergoes a large deformation under the influence of stress that is completely recovered when the stress is removed. Unlike the magnetic case, the mechanism responsible here is a transition from martensite into austenite. As a result, the material does not realize a 6% strain, but one of slightly less than 4%, the difference in remnant strains between hard-axis martensite and austenite.
As before, there is good agreement between the model and experimental data. Analogous to an increase in the magnetic field shown in Figure 4.17, a further increase in the temperature here would move the hysteresis curve away from the origin.

4.4.4. Strain as a Function of Temperature under the Application of a Magnetic Field

To see the material transition between the easy-axis martensite and austenite phases, a magnetic field must be employed in addition to heat. This is shown in Figure 4.19, where a constant magnetic field creates a driving force from austenite to easy-axis martensite. As the temperature is increased, the material undergoes a full transition into austenite. When the temperature is allowed to cool, the magnetic field forces the material back into easy-axis martensite.
Figure 4.19: Comparison of experimental and model data for variation in strain as a function of temperature at constant magnetic field. (Experimental data from Straka, 2007).

The model again produces a quantitatively accurate depiction of the effect.

4.5. Open Problems

Although the model correctly reproduces most of the behavior exhibited by the material, model data deviates significantly from experimental data under certain conditions. As an example of this, consider the plot shown in Figure 4.20(a). Here, the temperature of a sample is varied under application of several constant compressive stresses. Because the hard-axis martensite variant is of smaller strain in the direction of the compressive stress, it is initially favored. As the temperature increases, however, the austenite is stabilized and eventually a transition from hard-axis martensite to austenite occurs. When the temperature cools, the material transitions back.
Figure 4.20: (a) Experimental and (b) model data for variation in strain as a function of temperature at constant compressive stress. (Experimental data taken from Heczko and Straka, 2004).

The model output for this scenario is shown in Figure 4.20(b). A number of discrepancies between it and the experimental data are visible. First, the model shows significant decrease in the maximum strain of the material with compressive stress that does not appear in the experimental data. This is due to an incorrect model value for the Young’s modulus of the austenite which, from the data shown in Figure 4.18, was estimated to be 3.75 GPa. Stresses of 30 Mpa and 60 Mpa would have a noticeable effect on such a soft material, causing elastic strains of 0.8% and 1.6%, respectively. From the experimental data, then, it seems as if this sample must actually be much stiffer, and that proper function of the model could be restored by simply recalculating the Young’s modulus of austenite from its stress-strain curve.

In fact, the Young’s modulus of the material is strongly dependent on temperature, softening in the vicinity of the phase transformation (Heczko and Straka, 2004). A number of other physical parameters also vary strongly with temperature, including saturation magnetization, magnetic susceptibility, lattice size, twinning stress, etc. (see Heczko and Straka, 2003, and Straka, et al., 2006). In order to correctly reproduce material behavior at a range of temperatures, the variation of each of these should be accounted for in the model.

Another discrepancy visible here, and throughout the rest of the experiments, is the general smoothness of the experimental curves as compared to the sharp transitions exhibited by the model. The sharpness of the model data results from the model’s assumption that the material
is essentially homogeneous and sees no local variations in stress or magnetic field. Therefore, when one element attains the driving force necessary to transition, all other elements of that type do also. This behavior is regulated somewhat by the introduction of imbalance constants, which force the material to transition more gradually. However, it is believed that, excepting the domain-imbalance constant for which the stray-field energy provides a known source, these constants are simply substitutes for the heterogeneity of the material that is truly responsible.

The heterogeneity of NiMnGa is the topic of Marioni, et al., 2004. How it may be incorporated into models such as this one is discussed in Zhong, 2003.
CHAPTER 5
CONCLUSIONS

The objective of this research was to develop a free energy model for NiMnGa capable of simulating the behavior of the material under variations in stress, magnetic field, and temperature. In Chapter 1, the material was introduced, a number of experimental and theoretical results were noted, and the need for such a model was motivated.

Chapter 2 discussed the mechanisms responsible for the constitutive behaviors of ferromagnetic shape-memory alloys such as NiMnGa. The energy terms that contribute to magnetic domain development and ferromagnetism were introduced and the properties of the material at scales ranging from crystallographic to macroscopic were discussed.

Chapter 3 outlined the modeling approach and considered the scale at which the model functions. The Gibbs and Helmholtz energy landscapes relevant to the material were introduced and the model equations were stated.

In Chapter 4, model calibration was discussed and demonstrated. A model simulation of the magnetic-field-induced shape-memory effect was described in depth and the effect of various parameters on model function was shown. The model was then compared to experimental data and the results were discussed.

The model was shown to produce quantitatively accurate depictions of a number of experiments. These include the variation of magnetization with changes in magnetic field and temperature, the variation of magnetic-field-induced strain as a function of compressive bias stress, superelastic stress-strain behavior in a constant magnetic field and at austenitic temperatures, and the variation of strain with temperature in a constant field.

In simulating the variation of strain with temperature under constant stress, it was found that the model possessed a number of shortcomings. The most noteworthy of these were the model’s inability to allow for variations in physical parameters with temperature and its assumption of perfectly homogeneous material. Future work on the model should address each of these.
REFERENCES


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Schneider, M., Müller-Pfeiffer, St., and Zinn, W. Magnetic force microscopy of domain wall fine structures in iron films, *Journal of Applied Physics* 79(11), 8578-8583, 1996.


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APPENDICES
This function simulates the behavior of the material within the Simulink model:

```matlab
function [f] = FSMAmodel(x_hf, x_erf, x_a, x_arf, sigma, H, T, t)
% x_hf:     hard-axis twin phase fraction of martensite (martensite minus)
% x_erf:    magnetization right phase fraction of easy-axis twin
% x_a:      austenite phase fraction
% x_arf:    austenite right phase fraction of austenite
% sigma:    applied stress in Pa
% H:        applied magnetic field in A/m
% T:        temperature in K
% t:        time in s (passed into function for debugging purposes only)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Set model constants and parameters
% k_B = 1.3806503e-23;  % Boltzmann's constant in m^2*kg/(s^2*K)
mu_0 = pi*4e-7;       % vacuum permittivity in N/A^2
Y_h = 3.1e9;          % Young's modulus along hard axis for mart. in Pa
Y_e = 375e6;          % Young's modulus along easy axis for mart. in Pa
Y_a = 3.5e9;          % Young's modulus for austenite in Pa
chi_h = 1.0749;       % hard-axis magnetic susceptibility in a.u. at 297K
epsilon_rh = -0.0392; % remnant strain for hard-axis twin at 297K in a.u.
epsilon_re = 0.0182;  % remnant strain for easy-axis twin at 297K in a.u.
epsilon_ra = 0;       % remnant strain for austenite at 323K in a.u.
M_sm0 = 7.203e5;      % saturation magnetization for mart. at 0K in A/m
M_sa0 = 5.727e5;      % saturation magnetization for aust. at 0K in A/m
sigma_tw = 0.7e6;     % mean twinning stress in Pa
dsiga = 9.4e6;        % half of diff. b/w phase transition stresses in Pa
V_pe = 1e-22;         % phase element volume in m^3
V_le = 1e-23;         % layer element volume in m^3
V_de = 1e-24;         % domain element volume in m^3 for mart. and aust.
tau_x = 5e-3;         % attempt frequency in 1/s
H_c = 8e3;            % coercive field for el <-> er transition in A/m
C_dim = 5.5e4;        % domain imbalance constant for martensite in J/m^3
C_dia = 4e3;          % domain imbalance constant for austenite in J/m^3
C_ti = 5e3;           % twin-imbalance constant in J/m^3
C_pi = 3e5;           % phase-imbalance constant in J/m^3
T_a2m = 308;          % austenite-to-martensite transition temp. in K
T_m2a = 317;          % martensite-to-austenite transition temp. in K

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find x_m, x_ef, x_elf and x_alf and ensure all phase fractions have
% reasonable values
```
% \[ x_{hf} = \min(\max(x_{hf}, 0), 1); \]
% \[ x_a = \min(\max(x_a, 0), 1); \]
% \[ x_{ef} = 1 - x_{hf}; \]
% \[ x_m = 1 - x_a; \]
% \[ x_{erf} = \min(\max(x_{erf}, 0), 1); \]
% \[ x_{elf} = 1 - x_{erf}; \]
% \[ x_{arf} = \min(\max(x_{arf}, 0), 1); \]
% \[ x_{alf} = 1 - x_{arf}; \]
%
%
% Calculate \( M_s(T) \) values for martensite and austenite
%
Bm = 0.6563*8.02e3;
Cm = 90.6629;
M_sm = M_sm0 + Bm*(1-exp(T/Cm));
if (M_sm < 0), M_sm = 0; end
%
Ba = 8.2328e-5*8.02e3;
Ca = 27.2795;
M_sa = M_sa0 + Ba*(1-exp(T/Ca));
if (M_sa < 0), M_sa = 0; end
%
%
% Find strain, magnetization coordinates for bottom of each energy well
%
epsilon_h = epsilon_rh + sigma/Y_h; % hard-axis twin strain minimum
epsilon_e = epsilon_re + sigma/Y_e; % easy-axis twin strain minimum
epsilon_a = epsilon_ra + sigma/Y_a; % austenite strain minimum
M_h = chi_h*H;  % hard-axis twin (martensite minus) magnetization minimum
%                 easy-axis magnetization minima assumed +/- M_sm
%                 austenite magnetization minima assumed +/- M_sa
if (abs(M_h) > M_sm)
  M_h = sign(M_h)*M_sm; % ensure we saturate properly
end
%
%
% Estimate \( dg_0 \) for magnetic and structural transitions
%
F_c = 2*mu_0*H_c*5.8e5; % 5.8e5 = \( M_s \) @ 297K
dg_0_dwm = F_c/4; % activation barrier for martensite domain-wall motion
dg_0_dwa = dg_0_dwm; % activation barrier for austenite domain-wall motion
%
F_tw = 1/2*sigma_tw^2*(1/Y_e - 1/Y_h) + sigma_tw*(epsilon_re-epsilon_rh);
dg_0_tb = F_tw/4; % activation barrier for twin-boundary motion
%
F_pt = 1/2*dsigma^2*(1/Y_a - 1/Y_h) + dsigma*(epsilon_ra-epsilon_rh);
\[ dg_0_pb = F_{pt}/4; \] % activation barrier for phase-boundary motion

% \%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find Gibbs energy of each well
% \sf_e = -C_{dim}x_{erf}*(1-x_{erf}) + C_{sfm}/4; \% Easy-axis stray-field energy
\[ d_{sfe} = C_{dim}*(2*x_{erf}-1); \% d(sf_e) / d(x_{erf}) for pl <-> pr transitions \]
\[ \sf_a = -C_{dia}x_{arf}*(1-x_{arf}) + C_{sfa}/4; \% Austenite stray-field energy \]
\[ d_{sfa} = C_{dia}*(2*x_{arf}-1); \% d(sf_a) / d(x_{arf}) for al <-> ar transitions \]
\[ ti = -C_{ti}x_{hf}*(1-x_{hf}) + C_{ti}/4; \]
\[ d_{ti} = C_{ti}*(2*x_{hf}-1); \]
\[ d_{pi} = C_{pi}*(2*x_{a}-1); \]
\[ S_{rel} = -1.4e5; \% per-K relative change in entropy b/w aust., martensite \]
\[ S_0 = -1/2*S_{rel}*(T_m2a+T_a2m); \]
\[ beta = S_0 + S_{rel}*T; \% should equal zero at T = (T_a2m + T_m2a) / 2 \]
\[ g_h = 1/2*Y_h*(epsilon_h-epsilon_rh)^2 + 1/2*mu_0/chi_h*(M_h)^2 - sigma*epsilon_h - mu_0*H*M_h; \]
\[ g_er = 1/2*Y_e*(epsilon_e-epsilon_re)^2 - sigma*epsilon_e - mu_0*H*M_sm; \]
\[ g_el = 1/2*Y_e*(epsilon_e-epsilon_re)^2 - sigma*epsilon_e + mu_0*H*M_sm; \]
\[ g_e = x_{erf}*g_er + x_{elf}*g_el + \sf_e; \% Energy of easy-axis-twin layers \]
\[ g_h = x_{hf}*g_h + x_{elf}*g_e + ti; \% Energy of martensite phase \]
\[ g_m = x_{arf}*g_ar + x_{alf}*g_al + \sf_a + beta; \% Energy of austenite phase \]

% \%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find transition probabilities
% \% for magnetic transitions from the er well to the el well
\[ F = g_{er} - g_{el} + d_{sfe}; \]
\[ if (F < -4*dg_0_dwm) \]
\[ dg = -F; \]
\[ elseif (F > 4*dg_0_dwm) \]
\[ dg = 0; \]
\[ else \]
\[ dg = 1/dg_0_dwm*(F/4-dg_0_dwm)^2; \]
\[ end \]
\[ P_{er2el} = 1/tau_x*exp(-(dg*V_de/(k_B*T))); \% reverse transition \]
\[ F = g_{el} - g_{er} - d_{sfe}; \]
\[ if (F < -4*dg_0_dwm) \]
\[ dg = -F; \]
\[ elseif (F > 4*dg_0_dwm) \]
\[ dg = 0; \]
\[ else \]
\[ dg = 1/dg_0_dwm*(F/4-dg_0_dwm)^2; \]
\[ end \]
\[ P_{el2er} = \frac{1}{\tau_x} \exp(-\frac{dg V_{de}}{(k_B T)}) \]

\% for magnetic transitions from the ar well to the al well
\n\[ F = g_{ar} - g_{al} + d_{sfa} \]
\nif (\( F < -4dg_0_{dwa} \))
\[ dg = -F \]
elseif (\( F > 4dg_0_{dwa} \))
\[ dg = 0 \]
else
\[ dg = \frac{1}{4dg_0_{dwa}}(F/4-dg_0_{dwa})^2 \]
end
\n\[ P_{ar2al} = \frac{1}{\tau_x} \exp(-\frac{dg V_{de}}{(k_B T)}) \]
\% reverse transition
\n\[ F = g_{al} - g_{ar} - d_{sfa} \]
\nif (\( F < -4dg_0_{dwa} \))
\[ dg = -F \]
elseif (\( F > 4dg_0_{dwa} \))
\[ dg = 0 \]
else
\[ dg = \frac{1}{4dg_0_{dwa}}(F/4-dg_0_{dwa})^2 \]
end
\n\[ P_{al2ar} = \frac{1}{\tau_x} \exp(-\frac{dg V_{de}}{(k_B T)}) \]
\% for structural transitions from the e wells to the h well
\n\[ F = g_{e} - g_{h} - d_{ti} \]
\nif (\( F < -4dg_0_{tb} \))
\[ dg = -F \]
elseif (\( F > 4dg_0_{tb} \))
\[ dg = 0 \]
else
\[ dg = \frac{1}{4dg_0_{tb}}(F/4-dg_0_{tb})^2 \]
end
\n\[ P_{e2h} = \frac{1}{\tau_x} \exp(-\frac{dg V_{le}}{(k_B T)}) \]
\% reverse transition
\n\[ F = g_{h} - g_{e} + d_{ti} \]
\nif (\( F < -4dg_0_{tb} \))
\[ dg = -F \]
elseif (\( F > 4dg_0_{tb} \))
\[ dg = 0 \]
else
\[ dg = \frac{1}{4dg_0_{tb}}(F/4-dg_0_{tb})^2 \]
end
\n\[ P_{h2e} = \frac{1}{\tau_x} \exp(-\frac{dg V_{le}}{(k_B T)}) \]
\% for structural transitions from the m wells to the a well
\n\[ F = g_{m} - g_{a} - d_{pi} \]
\nif (\( F < -4dg_0_{pb} \))
\[ dg = -F \]
elseif (\( F > 4dg_0_{pb} \))
\[ dg = 0 \]
else
\[ dg = \frac{1}{4dg_0_{pb}}(F/4-dg_0_{pb})^2 \]
end
\n\[ P_{m2a} = \frac{1}{\tau_x} \exp(-\frac{dg V_{pe}}{(k_B T)}) \]
% reverse transition
F = g_a - g_m + d_pi;
if (F < -4*dg_0_pb)
    dg = -F;
elseif (F > 4*dg_0_pb)
    dg = 0;
else
    dg = 1/dg_0_pb*(F/4-dg_0_pb)^2;
end
P_a2m = 1/tau_x*exp(-(dg*V_pe/(k_B*T)));
%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find time rate of change for each phase fraction
% x_hf_dot = x_ef*P_e2h - x_hf*P_h2e;
x_erf_dot = x_elf*P_el2er - x_erf*P_er2el;
x_a_dot = x_m*P_m2a - x_a*P_a2m;
x_arf_dot = x_alf*P_al2ar - x_arf*P_ar2al;
%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find macroscopic strain and magnetization values
% epsilon = x_m*(x_hf*epsilon_h + x_ef*epsilon_e) + x_a*epsilon_a;
M = x_m*(x_hf*M_h + x_ef*(x_erf-x_elf)*M_sm) + x_a*(x_arf-x_alf)*M_sa;
%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Find time rate of change for each phase fraction
% db = [g_h; g_e; g_er; g_el]; % values of interest (for debugging purposes)
f = [x_hf_dot; x_erf_dot; x_a_dot; x_arf_dot; epsilon; M; t; db];
end