A PHASE-FIELD INVESTIGATION OF DOMAIN STRUCTURES IN
FERROELECTRIC BISMUTH FERRITE THIN FILMS

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by
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Abstract

The ferroelectric domain structure of multiferroic BiFeO$_3$ thin films are strongly affected by the electrical boundary conditions. We employ a Ginzburg-Landau-Devonshire phase-field model to investigate the effects of the electrical boundary conditions on domain structure in BiFeO$_3$ thin films. We examine the domain structure under short-circuit and under open-circuit boundary conditions with varying levels of compensation. As the degree of compensation changes, we find a smooth transition between the two types of domain structure. In the open-circuit case, we note small triangular nanodomains at the surface/wall interfaces that may be useful in nanoelectronic applications.

The ferroelectric domain structures of epitaxial BiFeO$_3$ thin films on miscut substrates were studied using a phase-field model. The effects of substrate vicinality towards (100) are considered by assuming charge-compensated surface and film/substrate interface. The predicted domain structures show remarkable agreement with existing experimental observations, including domain wall orientations and local topological domain configurations. The roles of elastic, electric, and gradient energies on the domain structures were analyzed. It is shown that the substrate strain anisotropy due to the miscut largely determines the domain variant selection and domain configurations.
We employ phase-field modeling to explore the elastic properties of artificially-created 1-D domain walls in (001)$_p$-oriented BiFeO$_3$ thin films. The walls are composed of a junction of the four polarization variants, all with the same out-of-plane polarization: a “vortex” is comprised of polarization variants rotating around the junction, and an “anti-vortex” is comprised of two polarization variants pointing towards the junction and two pointing away. It was found that these junctions exhibit peculiarly high electroelastic fields induced by the neighboring ferroelastic/ferroelectric domains. These fields may contribute to the segregation of charged defects and charge carriers to the vortex and anti-vortex cores.

We use a Ginzburg-Landau-Devonshire model to explore localized switching in epitaxial BiFeO$_3$ thin films. We considered switching under a PFM tip for a range of misfit strains as well as in the proximity of a 71° domain wall. We find a strong correlation between the mismatch strain and coercive bias, in good agreement with previous theoretical and experimental results. We also note a large, non-linear change in the piezoresponse near the domain wall.
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Chapter 1: Introduction

1.1 General Background

1.1.1 Ferroics and Ferroelectrics

Ferroics are materials with a spontaneous property, switchable by an applied field, which arises in domains throughout the material. Such a spontaneous property may be called an “order parameter”, and in ferroics the order parameter must have at least two symmetry- and energy-equivalent equilibrium states in the absence of applied fields. The best-known classes of ferroic materials are the ferroelectric, ferromagnetic, and ferroelastic, with spontaneous electric polarization, magnetization, and strain, respectively. Materials which exhibit more than one ferroic order parameter are called “multiferroics”.

Ferroelectrics have historically found broad applications in electronics as sensors, transducers, capacitors, and as pyroelectric materials. All ferroelectrics are also piezoelectric, and many strongly so, which has made them useful in actuators and acoustic devices. Ferroelectrics are generally semiconductors or insulators, as the spontaneous dipole in a ferroelectric conductor would be screened by free charges and thus be unswitchable. In recent years, with advances in thin film technologies, ferroelectric or multiferroics have found new applications in non-volatile ferroelectric
memory, micro-engineered mechanical systems (MEMS), and tunable microwave devices.

1.1.2 Perovskite oxide ferroelectrics

One of the most commonly studied classes of ferroelectrics is the perovskite oxides, with chemical formula $\text{ABO}_3$, where $A$ and $B$ are metal cations with the valence of the $A$ cation ranging from +1 to +3, and the valence of the $B$ cation ranging from +3 to +6. The parent structure is usually the cubic space group $Pm\bar{3}m$, with oxygen anions on the face centers, the $A$ cation on the crystal cell corners, and the $B$ cation at the cell center. At the Curie temperature, a ferroelectric undergoes a phase transition to the ferroelectric material; the $A$ cation and the oxygen anions displace to create a net polarization. A typical ferroelectric perovskite transition is shown in Figure 1.1 for the rhombohedral material $\text{BiFeO}_3$. The paraelectric to ferroelectric transition is also accompanied by a structural transition; an elastic distortion of the unit cell along the direction of polarization. In perovskites, this transition is typically ferroelastic. The coupling between the polarization and the spontaneous strain, $\varepsilon_{ij}^S$, is described through the electrostrictive tensor, $Q_{ijkl}$:

$$\varepsilon_{ij}^S = Q_{ijkl} P_k P_l.$$  \hspace{1cm} (1.1)

Other ferroic transitions may also be present, such as the transition to ferromagnetic or a rotation of the oxygen octahedra, and these may couple with the polarization or spontaneous strain.
Figure 1.1 (a) A cubic perovskite unit cell with $P=0$ (oxygen atoms not shown). The A cation is in the center B-cation cage. (b) Rhombohedral ferroelectric below the Curie temperature. The A cation has moved off-center, with the effect of creating a net polarization. Here we exaggerate the structural transition.

1.1.3 Ginzburg-Landau-Devonshire Theory

In the 1950s, Vitaly Ginzburg and Lev Landau developed a thermodynamic model describing the energy of a system in terms of an order parameter. Above the transition temperature of the system, the material is in the parent (or “reference”) phase, and the order parameter is zero. The Ginzburg-Landau model was later extended to ferroelectrics by Devonshire\(^{2-4}\). For ferroelectrics, the transition temperature is called the Curie temperature and denoted $T_c$. By considering the free energy of the system as a Taylor series expansion about the ($P = 0$) state, we can obtain a polynomial expression for the energy:
\[ f(P) = f(0) + a_i P_i + \frac{1}{2!} b_{ij} P_i P_j + \frac{1}{3!} c_{ijk} P_i P_j P_k + \frac{1}{4!} d_{ijkl} P_i P_j P_k P_l + \cdots \] (1.2)

Where the parameters, \( a_i, b_{ij}, c_{ijk}, \) etc., are related to the free energy by

\[ a_i = \frac{\partial F(P)}{\partial P_i}\bigg|_{P=0}, \quad b_{ij} = \frac{\partial^2 F(P)}{\partial P_i \partial P_j}\bigg|_{P=0}, \quad c_{ijk} = \frac{\partial^3 F(P)}{\partial P_i \partial P_j \partial P_k}\bigg|_{P=0}, \text{ etc.} \]

If we assume that the parent phase is non-polar, then the energy of a polarization \( f(P) \) and its opposite, \( f(-P) \), must be equal, so that the odd parameters must equal zero and thus the odd terms of the equation drop out. For convenience, we also rescale the parameters, and the energy expression becomes:

\[ f(P) = f(0) + \frac{1}{2} a_{ij} P_i P_j + \frac{1}{4} a_{ijkl} P_i P_j P_k P_l + \frac{1}{6} a_{ijklmn} P_i P_j P_k P_l P_m P_n + \cdots, \] (1.3)

where the parameters, \( a_{ij}, a_{ijkl}, a_{ijklmn}, \) etc., are called the Landau parameters, and the above expression for the free energy is known as the Landau or chemical energy for a ferroelectric.

It is usually sufficient to truncate the energy expression at the 4th or 6th-order expansion, however exceptions exist for materials with particularly low symmetry.

Note that the highest-order terms must be positive, in order for the energy function to have stable minima. For simplicity, we consider only the first Landau parameter to be temperature-dependent, according to the Curie-Weiss Law:

\[ a_{ij} = \frac{(T - T_c)}{C}, \] (1.4)

where \( C \) is the Curie constant, which describes the first-order ferroelectric susceptibility of the material. Below the Curie temperature, the first Landau parameter is negative, and the free energy function has multiple energy wells. Above the Curie temperature,
the energy function has only one energy well, at \( P = 0 \). We show a typical energy function for an orthorhombic ferroelectric in Figure 1.2, in which there are four energy-equivalent minima.

Figure 1.2. (a) Characteristic energy landscape for an orthorhombic ferroelectric below \( T_c \), with four energetically-equivalent minima at \(|P_1| = |P_2| \approx 0.35\). (b) Characteristic energy landscape for the same ferroelectric above \( T_c \) with one energy well at \( P_1 = P_2 = 0 \).

The time-dependent Ginzburg-Landau equation, also known as the Allen-Cahn equation\(^6\), describes the temporal evolution of a non-conserved order parameter such as polarization. Using the variational derivative of the energy of the system, the evolution of the system is chosen such that the total energy decreases monotonically with time:

\[
\frac{\partial P_i(x)}{\partial t} = -L \frac{\partial F}{\partial P_i(x)},
\]

where \( L \) is a kinetic parameter related to the interfacial mobility, and \( F \) is the total energy of the system including contributions from the interfacial (gradient) energy density:
\[ f_{\text{interfacial}} = \frac{1}{2} G_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}. \] (1.6)

Here \( G_{ijkl} \) denotes the gradient energy coefficients.

To the Landau energy, we may also add additional energy terms related to the
electromechanical coupling, the electrostatic energy, or any other polarization coupled-
terms. The elastic energy density is defined as a function of elastic strain, \( e_{ij} \):

\[ f_{\text{elastic}} = \frac{1}{2} c_{ijkl} e_{ij} e_{kl} \] (1.7)

which is coupled to the polarization through the stress-free strain, \( e^*_\ell \),

\[ e_{ij} = e_{ij} - e^*_{ij} = e_{ij} - Q_{ijkl} P_k P_l, \] (1.8)

where \( e_{ij} \) is the total strain. The electrostatic energy density is

\[ f_{\text{electric}} = -\frac{1}{2} \varepsilon_r \varepsilon_0 E_i E_i - E_i P_i. \] (1.9)

Here \( E_i \) is the sum of internal and external electric fields along \( x_i \), \( \varepsilon_r \) is the background
dielectric constant, and \( \varepsilon_0 \) is the vacuum dielectric permittivity.

The effects of the elastic and electric fields on polarization in a ferroelectric thin film is
shown in Figure 1.3. Under an applied stress, the ferroelectric domains rearrange to
minimize the elastic energy (Fig 1.3). For a compressive strain, this means minimizing
the elastic footprint of the ferroelectric on the film, and so polarizations out-of-the-
plane of the film are favored (Fig. 1.3(b)). For a tensile strain, in-plane polarizations are
favored (Fig. 1.3(c)).
Figure 1.3. Effects of applied strain on a ferroelectric thin film. (a) A sample domain structure under no applied strain. (b) Under tensile in-plane strain, the polarization will prefer in-plane domain variants. (c) Under compressive in-plane strain, the polarization will prefer domain variants with greater out-of-plane polarization.

Under an electric field (either applied externally or from internal charges), the electric dipoles attempt to align with the electric field (Fig. 1.4). If the electric field is anti-parallel to the polarization direction and of high enough magnitude, a new domain with polarization much closer to parallel to the electric field will nucleate and grow (Fig. 1.4(c)).
Figure 1.4. Effects of applied electric fields on a ferroelectric thin film. (a) A sample domain structure under no applied field. (b) Under a field nearly aligned with the polarization direction, the polarization will be increased in magnitude. (c) If the field is opposite to the polarization, polarization will decrease or re-orient. Under high enough fields, new domains will nucleate and grow with polarization much closer to parallel with the applied field.
1.1.4 Strain-engineering in ferroelectrics

As mentioned previously, the transition from a paraelectric to ferroelectric state is associated with a ferroelastic transition, and the coupling between the polarization and the stress-free strain state is given as $\varepsilon_{ij}^S = Q_{ijkl}P_kP_l$. The strong electromechanical coupling present in many perovskite oxides allows 'strain engineering' of ferroelectrics. Commonly, strain engineering takes the form of thin-film epitaxy, in which a deposited thin film material is in crystallographic alignment with a substrate, constraining the film to have the same in-plane lattice parameters as the substrate. A sufficiently thick substrate will constrain a thin film for the in-plane components of strain. However, the misfit strain carries an associated elastic energy penalty, which scales with both the film thickness and the misfit strain, causing thicker films to often form dislocations to relax the misfit strain. Other approaches to strain engineering, such as making layered or columned heterostructures comprised of different materials, can partially overcome some of the problems associated with dislocation creation in epitaxial thin films.

Strain engineering has been shown to alter the ferroelectric transition temperatures of some ferroelectrics by hundreds of degrees, introduce new ferroelectric phases, and affect the switching properties of ferroelectric thin films.

1.1.5 Bismuth Ferrite

The bulk of this work will be focused on bismuth ferrite ("BFO", chemical formula: BiFeO$_3$). BiFeO$_3$ has been a subject of considerable study since the discovery of high
ferroelectricity in thin film form in 2003 by Wang et al\textsuperscript{16}. It is multiferroic, exhibiting both ferroelectricity ($T_C \approx 830 \, ^\circ C$) and G-type antiferromagnetism ($T_N \approx 310 \, ^\circ C$)\textsuperscript{17}, and at nearly $100 \, \mu C/cm^2$, has the highest currently known ferroelectric polarization\textsuperscript{17,18}. The crystal structure is that of a rhombohedrally-distorted perovskite, with polarization along the pseudocubic cell diagonals, e.g., [111]$_p$, where subscript “p” denotes the pseudocubic perovskite cell axes. As we will deal extensively with the rhombohedral polarization variants, we denote the 8 symmetry-equivalent rhombohedral variants as $r_1^+, r_2^+, r_3^-, r_4^-$, where the x-y components of the $r^+$ variants correspond to the four quadrants of the Cartesian coordinate system, and $r_i^- = -r_i^+$. The unit cell parameters of BiFeO$_3$ are $\alpha_r = 0.6^\circ$ and $a_p = 3.96 \, \text{Å}$ at room temperature.

BiFeO$_3$ is also magnetoelectric\textsuperscript{19}, and the recent discoveries breathed fresh life into the search for room-temperature multiferroics with strong magnetoelectric coupling\textsuperscript{19–22}. At the same time, it has received attention for potential spintronic applications\textsuperscript{23,24} and novel photovoltaic activity in domain walls\textsuperscript{25,26}. Under very strong compressive in-plane strains (~4.5%), BFO becomes strongly tetragonal\textsuperscript{13,27–29} with a $c/a$ ratio of around 1.25. Last, with growing environmental restrictions on Pb-based materials, there is a push to replace the Pb-based ferroelectrics which are currently dominant in some nanoelectric applications\textsuperscript{30,31}, and here BFO shows promise due to its high remanant polarization.

\textbf{1.1.6 Phase-field modeling}
In simulating ferroelectric materials, we have the choice of treating the spatial distribution of the polarization as varying discretely or continuously\textsuperscript{32,33}, as shown in Figure 1.5. By treating the polarization as a continuous variable, varying smoothly between ferroelectric domains, we can solve the time-dependent Ginzburg–Landau equation in Fourier space, reducing spatial derivatives to pointwise linear operations. With periodic boundary conditions, the Fourier transform is exponentially convergent and spectrally accurate, with computational complexity of $O(n \log n)$. This greatly increases the efficiency of these simulations.

Figure 1.5. Diffuse-interface versus sharp-interface models. (a) Diffuse-interface model, in which the field variable transitions smoothly between domains. (b) Sharp-interface model, in which the field variable transitions abruptly between domains. Adapted from Ref. [32].
1.2 Objectives

The goal of this work is to extend the current understanding of relationships between domain structure, boundary conditions, and electrostatic and elastic properties in BiFeO$_3$ thin films, using phase-field simulations. The specific objectives are:

1. To understand the effect of electrical boundary conditions on BiFeO$_3$ thin films, and to explore related
2. To explore the effects of miscut substrates on BiFeO$_3$ thin films, and to understand the domain variant selection observed in experimental studies.
3. To explore topological defects in ferroelectric thin films, and to better understand their stabilities, origin, and potential nanoelectronic applications.
4. To develop a model of BiFeO$_3$ switching under a PFM tip for calibration of PFM studies, and to explore the piezoresponse behavior of domain walls in ferroelectric thin films with a ferroelastic component.

1.3 Thesis structure

The thesis has been organized into seven chapters.

Chapter 1 presents a general background of ferroics, Ginzburg-Landau theory, bismuth ferrite, and other areas of relevance to this work.

Chapter 2 discusses our simulation structure and general methods.
In Chapter 3, we study the effect of electrical boundary conditions and thickness on BiFeO₃ thin films, and present a hypothesis to explain experimental observations of domain structures on rare-earth scandate substrates.

In chapter 4, we apply the phase-field model to BiFeO₃ thin films on miscut substrates, in order to explain the domain structures seen in experiment.

In chapter 5, we explore the electroelastic fields in topological defects in BiFeO₃ thin films. We study the switching behavior, the expected concentration of mobile charge carriers, and the effects of materials parameters on the domain structure.

In chapter 6, we explore the switching behavior of BiFeO₃ thin films under a PFM tip. We consider a range of in-plane strains, and we examine the proximity of a nearby domain wall on the switching behavior and piezoresponse.

In chapter 7, we discuss the conclusions of our work and consider future directions for investigations into BiFeO₃ thin films.
References


Chapter 2: General Methods

2.1 Use of the Semi-Implicit Fourier Spectral Method

Our simulation structure typically consists of a regularly spaced rectangular grid, correlating to the pseudocubic structure of an [001]p-oriented BiFeO3 thin film. As described earlier, we use the time-dependent Ginzburg-Landau (TDGL) equations to describe the temporal evolution of the spatial polarization \( \mathbf{P}(x) = [P_1(x) \ P_2(x) \ P_3(x)] \),

\[
\frac{\partial P_i(x)}{\partial t} = -L \frac{\partial F}{\partial P_i(x)},
\]

(2.1)

where \( L \) is a kinetic parameter related to domain wall motion, \( P_i \) is the polarization field along axis \( x_i \) and \( F \) is the total free energy functional, as given by the spatial integral of the Landau, gradient, electric, and elastic energy densities,

\[
F = \int \left( f_{\text{Landau}} + f_{\text{gradient}} + f_{\text{elastic}} + f_{\text{electric}} \right) dV
\]

(2.2)

To solve the TDGL equation, we employ a semi-implicit Fourier spectral method. Denoting the polarization at timestep \( n \) as \( P^n \), the explicit TDGL equation is discretized as

\[
P_i^{n+1} = P_i^n - L \Delta t \frac{\partial F(P^n)}{\partial P_i}.
\]

(2.3)

We can gain computational stability by treating the gradient energy implicitly. Separating the gradient energy from the other energy terms, the semi-implicit TDGL becomes
\[
\begin{align*}
\frac{\partial F_{\text{gradient}}(P^{n+1})}{\partial P_i} = \frac{\partial F_{\text{not-gradient}}(P^n)}{\partial P_i}, \\
\text{The driving force from gradient energy density reduces to}
\end{align*}
\]

\[
\frac{\partial f_{\text{gradient}}}{\partial P_i} = G_{ijkl} (\nabla)^2 P_k,
\]

where \((\nabla)^2\) are the mixed second partial derivatives. In Fourier space, it becomes much simpler to treat simple spatially-dependent driving forces such as this one, and there the volume integral of the gradient energy driving force reduces to a set of pointwise multiplications, as in

\[
\mathcal{F} \left\{ \frac{\partial F_{\text{gradient}}}{\partial P_i} \right\} = G_{ijkl} k_j k_l \tilde{P}_k,
\]

where \(\mathcal{F}\{P_i\} = \tilde{P}_i\) signifies the Fourier transform of \(P_i\), and \(k_i\) is the Fourier-space vectors along axis \(i\). Thus, we can transform the entire semi-implicit TDGL as

\[
\tilde{P}_{i}^{n+1} + L \Delta t G_{ijkl} k_j k_l \tilde{P}_k = \tilde{P}_{i}^n - L \Delta t \mathcal{F} \left\{ \frac{\partial F_{\text{not-gradient}}(P^n)}{\partial P_i} \right\},
\]

and the timestepping procedure becomes a set of linear equations.

### 2.2 Energy terms

We re-define the individual energy terms here. For BiFeO\(_3\), the Landau energy is derived from a 4\(^{th}\)-order Taylor expansion of the bulk/chemical energy with respect to polarization, and is described as

\[
f_{\text{Landau}} = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2),
\]

where \(\alpha_{ij}\) are the phenomenological Landau coefficients for a stress-free system.
For a cubic system, the gradient energy density is of the form

\[
f_{\text{gradient}} = \frac{1}{2} G_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + G_{12} (P_{1,1} P_{2,2} + P_{2,2} P_{3,3} + P_{1,1} P_{3,3}) \\
+ \frac{1}{2} G_{44} \left[ (P_{1,2} + P_{2,1})^2 + (P_{2,3} + P_{3,2})^2 + (P_{1,3} + P_{3,1})^2 \right] \\
+ \frac{1}{2} G_{m44} \left[ (P_{1,2} - P_{2,1})^2 + (P_{2,3} - P_{3,2})^2 + (P_{1,3} - P_{3,1})^2 \right],
\]

which is the cubic form of the general gradient energy equation, \(f_{\text{gradient}} = \frac{1}{2} G_{ijkl} P_{i,j} P_{k,l}\).

Here \(P_{i,j} = \partial P_i / \partial x_i\), and \(G_{ijkl}\) is the gradient energy coefficient, where \(G_{ijkl}\) is related to \(G_{mn}\) by Voigt’s notation. Due to a lack of experimental data on the gradient energy coefficients, we typically employ isotropic values for \(G_{mn}\), where \(G_{11} = 2 G_{44} = 2 G_{m44}, G_{12} = 0\). The elastic energy density is given by

\[
f_{\text{elastic}} = \frac{1}{2} c_{ijkl} e_{ij} e_{kl} = \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0),
\]

where \(c_{ijkl}\) is the elastic stiffness tensor, \(e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0\) is the elastic strain, and \(\varepsilon_{ij}^0\) and \(\varepsilon_{ij}\) denote the eigenstrains (stress-free strain) and the total strains, respectively. The standard notation for repeated indices is used, where \(i, j, k, l = 1, 2, 3\), and the film-substrate interface is assumed to be coherent. The eigenstrains are derived from the spontaneous ferroelectric structural transition by the electrostrictive equation, \(\varepsilon_{mn}^0 = Q_{mноп} P_o P_p\), where \(Q_{mноп}\) are the electrostrictive coefficients.

Lastly, the electric energy density is given by

\[
f_{\text{electric}} = -E_i \left( \frac{1}{2} \varepsilon_b e_0 E_i + P_i \right),
\]
where $\varepsilon_0$ is the vacuum dielectric permittivity, and $\varepsilon_b$ is the background dielectric constant and $E_i$ is the total electric field, including contributions from both the inhomogeneous polarization distribution and any applied electric field.

For a thin film simulation, the simulation grid dimensions are typically much larger along $x_1$ and $x_2$ (length and width) than $x_3$ (height). The out-of-plane axis is divided into three parts: substrate, film, and vacuum, where only the film portion has a non-zero order parameter, as shown in Figure 2.2. The substrate is used to apply elastic boundary conditions to the bottom of the film. It is allowed to elastically deform down to the bottom boundary of the simulation box, where it is held fixed, as described further in the appendix and in previous literature. The simulation grid size $\Delta x$ is related to the real size by $L_0 = \Delta x = \sqrt{G_{110}/\alpha_0}$, where $\alpha_0 = |\alpha_1| T$, where $T$ is the temperature of the simulation. The vacuum portion of the simulation acts as a barrier between the top and bottom of the film, as Fourier transforms performed on the simulation grid implicitly assume periodic boundary conditions.
Figure 2.1. Schematic diagram of a thin film structure, with the film and thicknesses shown as $h_f$ and $h_s$, respectively. Reproduced with modification from Li et al.\textsuperscript{2}

2.3 Further reading

For further treatment of the individual energy terms and their numerical implementation, we refer the reader to previous publications: elastic\textsuperscript{2}, gradient\textsuperscript{2,3}, and electric\textsuperscript{4,5}, while a more general introduction to the semi-implicit Fourier spectral method for phase-field applications can be found in the work of Chen and Shen\textsuperscript{6}. We provide a more detailed mathematical description of the elastic equations of the substrate in Appendix A, and in Appendix B we outline programming changes which led to greater computational efficiency.
References


Chapter 3: The Effect of Electrical Boundary Conditions and Film Thickness on BiFeO₃ Film Domain Structures

3.1. Introduction

It has long been known that electrical boundary conditions strongly influence the domain structure of ferroelectric thin films\(^1\)–\(^4\). Uncompensated thin films tend to prefer domain structures which favor in-plane variants\(^5\), or domain structures with alternating out-of-plane variants, reducing the concentration of bound charge on the surfaces. Recently, Y.H. Chu et al demonstrated the ability to control the concentration of \(71^\circ\) versus \(109^\circ\) domain walls by altering surface compensation via the buffer electrode thickness\(^1\). Such domain wall control is particularly interesting in BiFeO\(_3\) thin films, which spontaneously form high densities of twinning domain walls exhibiting functional magnetic\(^6,7\), conducting\(^8\), and photocurrent\(^9\) behavior. In order to elucidate how electrical boundary conditions influence the domain structure and domain wall type, we employ a phase-field model.

We compare our results to \((001)_{p}\)-oriented BiFeO\(_3\) films grown by molecular beam epitaxy onto \((101)_{O}\)-oriented TbScO\(_3\) substrates (\(O\) indicates orthorhombic indices). In this system, elastic strains are minimal due to the low mismatch strain of TbScO\(_3\) and BiFeO\(_3\) at room temperature (~0.15%), improving the focus on the electrical boundary effects. Previous work by Folkman et al indicates that BiFeO\(_3\) films deposited on TbScO\(_3\) tend to form only two ferroelastic variants\(^2,10\), here as \(r_{1}^{+/-} = \pm[111]_{p}\) and \(r_{4}^{+/-} = \pm[1\bar{1}1]_{p}\). The exact mechanism
for this variant selection is unknown, although it has observed in BiFeO3 thin films on other rare-earth scandates, and has been ascribed broadly to the substrate anisotropy\textsuperscript{10-12} Earlier work by Streiffer et al\textsuperscript{13} indicates a limited number of elastically favorable domain walls for \( r_1 \) and \( r_4 \), as summarized in Fig 3.1. The domain wall type corresponds to a given set of elastic and electric boundary conditions. In the case of \( r_1/r_4 \) domain variants, a domain structure with 71° domain walls has uniform surface charge distribution, requiring that the surfaces be compensated, as seen in Figure 3.1(a). The 109° and 180° domain walls typically occur in systems with insufficiently charge-compensated surfaces, and their alternating out-of-plane polarizations serve to reduce the local concentration of bound charge (Fig 3.1(b,c)).
Figure 3.1. Elastically favorable twin domain structures for $r_1/r_4$ domain variants for (a) 71° polarization rotation, forming $\{101\}_p$-oriented walls, (b) a 109° polarization rotation, forming $\{010\}_p$-oriented walls, and (c) 180° polarization change, forming $\{-110\}_p$ walls. The 109° and 180° domain walls produce alternating bound charges, which relaxes the electrical energy from open-circuit boundary conditions.
3.2 Specific methods

We employ the general methods described in Chapter 2. In order to reproduce the experimentally-observed preference for \( r_1/r_4 \) variants\(^2,10 \), we set the initial polarizations as small, randomly distributed \( r_1 \) and \( r_4 \) ferroelectric variants, and we increase the electrostrictive shear term \( Q_{44} \) by a factor of 3. By increasing \( Q_{44} \), we increase the tendency of the system to retain only these two ferroelastic variants, and increase the effective thickness of the film. We use a simulation size of \( 128\Delta x \times 128\Delta x \times 32\Delta x \). The gradient energy terms are taken as \( G_{11} = 0.3, G_{12} = 0.3, G_{44} = 0.15, G_{m44} = 0.15 \), which for a cell width of 1 nm, corresponds to a gradient energy density of 9.8 mJ/m\(^2\) for a 71° domain wall. We use a film thickness of 14\( \Delta x \), and a substrate thickness of 14\( \Delta x \), which is allowed to elastically deform to the bottom surface of the film. We assumed a temperature of \( T = 298 \) K. The materials constants used are taken from the literature\(^14 \).

We employ two sets of electrical boundary conditions\(^5 \), short-circuit and open-circuit. Under short-circuit boundary conditions, the electric potential on both film surfaces is set to zero. Under open-circuit boundary conditions, the depolarization field at the interfaces is uncompensated, such that the electric displacements at the interfaces are set to zero. In our simulations, the domain structures are generally head-to-tail and uncharged, and the major contribution to any electric energy comes from external electric fields such as the depolarization field. Accordingly, changing the dielectric constant can serve as a proxy for
changing the compensation on the surfaces, and acts as a way to scale the surface contributions to the electric energy for the open-circuit case.

### 3.3 Results and Discussion

The domain structure for the open-circuit films under a range of dielectric constants is presented in Figure 3.2. For the case of $\varepsilon_r=50$, Fig. 3.2(c), the simulation forms paired $r_1^+/r_4^-$ or $r_1^-/r_4^+$ domains; i.e., 109° walls. The alternating out-of-plane polarization reduces the bound charge density at the surfaces and the associated electrostatic energy and is observed in other open-circuit ferroelectric thin films such as PbTiO$_3$\textsuperscript{15}. As the dielectric constant increases, the electric interactions become weaker, and the film begins to form 71° walls (Fig. 3.2(b,c)), with the 71° domain wall aligned along the (101)$_p$ plane so as to minimize strain and electric energy, in good agreement with both theoretical predictions\textsuperscript{13} and experiment\textsuperscript{1,16}. This domain structure is identical to the domain structure we see under short-circuit boundary conditions.

In addition, under sufficiently low dielectric constant, the film forms 71°, of $r_1^+/r_3^-$ or symmetry-equivalent pairs (not shown here). These structures are also seen in simulations of very thin films, and are discussed later.
Figure 3.2. Domain structures under different background dielectric constants: (a) $\varepsilon_r=50$, (b) $\varepsilon_r=250$, and (c) $\varepsilon_r=500$. As the dielectric constant increases, the effective electrical interactions decrease, and the film transitions from 109° domain walls (a), to mixed 71° and 109° domain walls (b), to only 71° domain walls (c). The different ferroelectric rhombohedral variants are shown in different colors, i.e., dark blue=$r_1^\uparrow([111])$, light blue=$r_1^\downarrow([-1-1-1])$, orange=$r_4^\uparrow([-1-1])$, yellow=$r_4^\downarrow([-1-1])$.

In addition, we examined the effects of the film thickness for simulations with a background dielectric constant of $\varepsilon_b = 100$. For thicker films, we increased the in-plane number of gridpoints, so that the length:height ratio of the simulation was always at least 3.
We present the domain structures in Figure 3.3. The effects of increasing film thickness are somewhat similar to those of relaxing the electrical interactions. The thinnest films (Fig. 3.3(a)) have domain structures comprised of regions of 71° pairs of alternating $P_3$: e.g., pairs of $r_1^+/r_3^-$, $r_2^+/r_4^-$, etc., with (110)- and (110)-oriented walls. In this case, the initial starting polarization of $r_1/r_4$ was insufficient to maintain a domain structure made up of only $r_1/r_4$ variants. As the films become thicker (Fig. 3.3(b,c)), the domain structure transitions to $r_1/r_4$ 109° domain walls. At even greater thicknesses, we see a mix of 109°, 71°, and 180° domain walls between the $r_1/r_4$ variants, which make up about 95% of the film. On the top and bottom surfaces, we see the same +/- $P_3$ 71° domain pairs observed in the thinnest film.

Figure 3.3. Domain structures with varying thicknesses. (a) The film thicknesses are (a) 7 $\Delta x$, (b) 21 $\Delta x$, (c) 42$\Delta x$, and (d) 80 $\Delta x$. The domain variants are colored respectively as $r_1^+/r_3^-$: dark and light blue, $r_2^+/r_2^-$: red and pink, $r_3^+/r_3^-$: dark and light green, $r_4^+/r_4^-$: orange and yellow and orange.
In these simulations, all three types of the expected $r_1/r_4$ domain walls – 71°, 109°, and 180° - are present. In addition, other 71° domain walls are also sometimes present, such as $r_1^+\!/r_3^-$, where only $P_3$ varies. In practice, fully open-circuit conditions at the film surface exposed to atmosphere are unlikely due to ionic adsorbates such as $\text{OH}^-$ and $\text{H}^+$ which compensate exposed film surfaces. Because the open-circuit domain structure of Fig. 3.2(b) is observed experimentally, these simulations suggest little or moderate surface charge compensation is present during MBE growth, and the domain structure is retained after exposure to ambient conditions.

Figure 3.4. (a) Side view of open-circuit BiFeO$_3$ simulation, with vertical 109° domains running along the [100]$_p$ direction. Note the small triangular domains at alternating domain wall/substrate interfaces. (b) Cross section dark field TEM image of a 20nm BiFeO$_3$ film on insulating TbScO$_3$ with the beam along the [100]$_p$, with small triangular domain marked. (c) Enlarged cross-section of (a), showing the triangular domains at the interfaces.
Within the striped domain structure of the open circuit case, we note triangular nanodomains at the junctions between domain walls and film surfaces [Fig 3.4(a)], shown in greater detail in Fig 3.4(c). These nanodomains have been experimentally observed in high-resolution TEM images of film/substrate interfaces in BiFeO$_3$ on TbScO$_3$ [Fig 3.4(b)]. Their formation is due to a minimization of the electric energy density (equation 3.3) at the domain wall edge. For a given pair of ferroelastic variants, there is only one favorable $109^\circ$ domain wall orientation, due to the elastic conditions described by Streiffer et al – in this case, (010)$_p$.

Between the two possible $109^\circ$ pairings of $r_1/r_4$, neither pairing has a change in $P_2$ between the variants. In other words, a film consisting of one of these pairs will have a near-constant $P_2$.

However, the sign of $P_3$ switches across the $109^\circ$ domain wall, changing the sign of the bound charge at the surface and setting up electric fields near the surfaces which run along with and alternate in sign with $x_2$. Where these electric fields runs antiparallel to $P_2$, the electric energy is increased (Fig 3.5(b)). Where they run parallel to $P_2$, the electric energy is decreased. The high-energy regions can be relaxed somewhat by the introduction of nanodomains with a reversed $P_2$, aligned with the local electric field [Fig 3.5(c, d)].
Figure 3.5. Schematic diagram of domain structures in open-circuit film (a,c) with corresponding electric energy calculated from phase-field simulation (b,d) in arbitrary units. The domain structure with simple stripes, (a) leads to the creation of large in-plane electric fields and high electric energies at some of the wall / film boundaries, (b). To reduce the bound charge, small triangular domains form, (c), with the resulting electric energy shown in (d) in arbitrary units. (Reprinted with adaptation from C.T. Nelson et al\textsuperscript{2}).

To test this, we took the simulation results from the open-circuit simulation and changed the electrical boundary conditions, compensating the top surface. The triangular nanodomains disappeared, while the 109° domain walls remained. This is in good agreement
with experimental data\textsuperscript{2}, which shows no triangles on the top surface, likely due to post-deposition compensation by adsorbed ions.

In experiment, the triangular nanodomains are rotated 180° relative to the nearby large domain, i.e., $r_1^-$ near $r_1^+$, as in Fig 3.4(c). However, our simulation results show a 71° relation, i.e., a $r_4^+$ nanodomain adjacent to a $r_1^+$ macrodomain. The reason for the discrepancy is unclear.

Also of note is the wall orientation for the 71° relation, a (0\overline{1}1) wall separating $r_1^+$ ([111]) and $r_4^+$ ([\overline{1}11]) domains. Since the polarization change is not parallel to the plane of the wall, the domain wall is electrically charged. However, this charge is of opposite sign to the bound charge at the nearby film interface, so that the charge from the domain wall is substantially compensated. This implies that partial compensation at the interface, either by charged defects or by an induced electric dipole in the substrate, may favor the 180°-related nanodomains.

We also present a hypothesis for the domain variant preference for BiFeO$_3$ thin films on rare-earth scandates, as follows. Streiffer \textit{et al} demonstrated that there are a limited number of elastically-allowed domain variants for a rhombohedral ferroelectric thin film. For each of the three types of domain walls – 71°, 109°, and 180° – there are domain structures that reduce the electrostatic energy under open-circuit boundary conditions, where adjacent domains have alternating $P_3$. For 71°, these are the $r_1^+/r_3^-$ and symmetry-equivalent pairs, and the domain walls are $\sim (P_1P_20)$. Streiffer notes that these 71° walls are unlikely to be seen in thin films, as they do not serve to relax any substrate misfit strain, although they have been observed in first-principles, open-circuit simulations\textsuperscript{17}. The 109° walls are (010)- or (100)-oriented, depending on
the components of polarization involved. Last, all 180° walls have alternating $P_3$ between adjacent domains, and there are six possibilities for the wall orientation among the $\{1\bar{1}0\}$-oriented planes, irrespective of which ferroelectric variants are involved.

The choice of “best” domain structure to relieve the depolarization field will be governed by the competition or cooperation between domain wall and elastic energies. Typically, the domain wall energy in ferroelectrics increases with increasing degree of changing polarization, i.e., $f_{110} \text{wall} < f_{109} \text{wall} < f_{180} \text{wall}$.

Each of the allowed open-circuit domain structures has a markedly different relationship with the substrate. The charge-compensating 109° and 71° walls are associated with a “puckered” domain structure, in which the plane of the wall alternates spatially between being stressed down and up, creating strain in the substrate. That is, for 109° walls, the puckering is a strain along the $x_3$ direction of the wall: for 109° walls, either $(100)_p$ for $r_1/r_4$ or $r_2/r_3$ pairs, or $(010)$, for $r_1/r_2$ pairs or $r_3/r_4$ pairs, and the associated strains are $e_{23}$ and $e_{13}$, respectively. For 71° walls, as mentioned previously, the walls are $(\bar{1}10)$- or (110)-oriented. For sufficiently thin films, the elastic energy is dominated by that of the substrate, which can restrict the ability of the film to form the puckered domain structure; the energy associated with the eigenstrain is not strong enough to overcome the stiffness of the substrate. Moreover, rare-earth scandates such as TbScO$_3$ and GdScO$_3$ are orthorhombic or monoclinic$^{18-20}$, and have different elastic stiffnesses associated with out-of-plane domain puckering along $(100)_p$, $(010)_p$, $(1\bar{1}0)_p$ or $(110)_p$. If the stiffness anisotropy is sufficiently large, one type of 109° or 71° walls will be preferred above the rest.
On the other hand, 180° domain structures are elastically neutral (neglecting electrostriction within the wall itself). The strain profile is similar to that of a single domain, with no out-of-plane stresses, and it will have a misfit strain associated with the $\epsilon_{12}^0$ component of eigenstrain. If the elastic energy associated with puckering is higher than the domain wall energy difference, then a 180° domain structure may be preferred. In our simulation, the substrate and film have the same cubic elastic constants and therefore, we are currently unable to test this hypothesis ourselves. However we note recent work by Johann et al.\textsuperscript{12} indicate that BiFeO$_3$ thin films on GdScO$_3$ and SmScO$_3$ transition from a flat domain structure to puckered above a critical thickness (around 26 nm).

In short, as ferroelectric films become even thinner, we can expect to see the substrate play a bigger role in governing the domain structure of the ferroelectric. These affects, however, are not limited to only in-plane substrate properties, but also the out-of-plane as well, for cases where the domain structure induces an out-of-plane effect in the substrate. Therefore, out-of-plane anisotropies in the elastic properties of the substrate should play a role in the domain structure and preferred domain variants.
3.4 Summary

In summary, we present a phase-field model for the investigation of the electrical effects in ferroelectric BFO thin films. We find that these boundary conditions strongly influence the domain structures. Particularly interesting is the open-circuit case, where small nanodomains form at the interfaces between film surfaces and 109° domain walls. As these nanodomains represent back-switched regions along $x_2$, they may be useful in controlling the in-plane switching properties of BiFeO$_3$ thin films. In addition, we discuss the effect of substrate stiffnesses on the preferred open-circuit domain structure. We hypothesize that substrate stiffness anisotropies can change the domain structure by allowing some “puckering” 71° or 109° domain structures to be preferred over others.
References


Chapter 4: Phase-field Simulation of Domain Structures in

Epitaxial BiFeO$_3$ Films on Vicinal Substrates

4.1 Introduction

Domain wall orientations and domain structure strongly influence the ferroelectric properties of BiFeO$_3$ thin films. Domain walls can act as pinning sites that reduce remnant polarization$^{1,2}$, and domain structure plays a role in ferroelectric fatigue. For instance, it has been shown that thin films consisting of only two polarization variants separated by 71° appear to have longer lifetimes than BiFeO$_3$ thin films with four variants$^{1,3}$. Previous experimental work shows that substrate vicinality can influence the polarization symmetry; by depositing BiFeO$_3$ on a SrTiO$_3$ substrate miscut towards (100)$_p$, the number of preferred ferroelectric variants may be reduced from eight to two$^{3-9}$. The domain structure changes from a mosaic pattern [Fig 3.1(a)], consisting of mixed {101}$_c$ and {100}$_c$ domain walls, to a striped pattern with predominantly {101}$_c$-oriented walls [Fig 3.1(b)]; i.e., 71° domains. It has been suggested that the growth kinetics and substrate step morphologies may cause the reduced symmetry and variant selection$^{3,7}$. However, the substrate miscut will also introduce anisotropy to the strain in a (001)-oriented BiFeO$_3$ film imposed by a (001)-oriented cubic substrate, which is otherwise isotropic. Therefore, the main objective of this work is to employ the phase-field method to explore the possibility that substrate strain
anisotropy alone is sufficient to produce the observed domain variant selection, domain wall orientations, and domain patterns under a short-circuit boundary condition.

Figure 4.1. PFM-style images of simulation of (a) (001)$_p$-oriented BiFeO$_3$, and (c) miscut BiFeO$_3$. PFM images of (b) (001)$_p$-oriented BiFeO$_3$, and (d) miscut BiFeO$_3$. In (a) and (b), there is a mixture of all four ferroelastic variants. The white regions represent two in-plane variants ($r_1$ and $r_4$), while the lightly- and darkly-colored regions represent the $r_2$ and $r_3$ variants, respectively. In the images of miscut films, (c) and (d), the dark- and light-striped regions are mixed $r_1/r_4$ domains with 71° domain walls. (Fig 3.1(b) and 3.1(d) reprinted with permission from H.W. Jang, et al$^{20}$).

4.2 Specific Methods

We introduce two rectangular coordinate systems: a global system, with orthogonal axes $x'_i$, with $x'_1$ and $x'_2$ in the plane of the film, and a local system based on the pseudocubic crystal cell, with axes $x_i$, where $x_2=x'_2$, and $x_1$ and $x_3$ are related to $x'_1$.
and $x'_3$ by a rotation about $x'_2$ by the transformation $x'_i = a_{ij}x_j$ with transformation matrix given below in equation (3.4). The spatial polarization $P' = [P'_1 P'_2 P'_3]$ describes a domain structure with polarization components in the global axes. The temporal evolution of the global polarization is determined by the time-dependent Ginzburg-Landau (TDGL) equation,

$$\frac{\partial P'_i(x)}{\partial t} = -L \frac{\partial F}{\partial P'_i(x)}$$

where $F$ is the total free energy and $L$ is a kinetic coefficient related to domain wall mobility. The free energy $F$ is the sum of the Landau, gradient, elastic, and electrostatic energies in global coordinates. It should be noted that when we consider the elastic effect, we assume the film is coherent with the substrate, with misfit strains in the $x'_1$-$x'_2$ plane of the film. The mathematical expressions for the Landau, electric, and gradient energies are described in Chapter 2 and in Ref. [10–14], and the corresponding coefficients are listed in Ref. [20], as found in the literature\textsuperscript{15,16}.

The elastic energy density is given in the global system by

$$f_{\text{elastic}} = \frac{1}{2} c'_{ijkl} e'_{ij}e'_{kl} = \frac{1}{2} c'_{ijkl} \left[ \varepsilon'_{ij} - (e^0_{ij})' \right] \left[ \varepsilon'_{kl} - (e^0_{kl})' \right]$$

where $c'_{ijkl}$ is the elastic stiffness tensor in global coordinates, $e'_{ij} = \varepsilon'_{ij} - (e^0_{ij})'$ denotes the elastic strain in global coordinates, and $\varepsilon'_{ij}$ and $(e^0_{ij})'$ denote the total and stress-free strains in the global coordinate system, respectively.
The stress-free strain term derives from the ferroelectric structural transition and is given by

\[
(\varepsilon_{ij}^0)' = a_{im}a_{jn}(Q_{mnp}P_nP_p).
\]  

(4.3)

We consider a substrate miscut towards [100]_p. The transformation matrix corresponds to a counterclockwise rotation about the x'_2 axis,

\[
a_{\text{miscut along (100)}} = \begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta 
\end{pmatrix},
\]  

(4.4)

where \( \theta \) is the degree of rotation from the [001]_c axis.

We use a semi-implicit Fourier spectral method to solve Eq. (1)\textsuperscript{10,12,17}. We use a simulation size of \( 128\Delta x \times 128\Delta x \times 32\Delta x \) under periodic boundary conditions, with film and substrate thicknesses of both \( 14\Delta x \). The grid spacing \( \Delta x \) is related to the real value of the grid size through the domain wall energy: we choose \( \Delta x = \frac{1}{2} l_0 \), where \( l_0 = \sqrt{G_{110}/\alpha_0} \), using gradient energy coefficients of \( G_{11}/G_{110} = 0.3 \) and \( G_{44}/G_{110} = G_{m44}/G_{110} = 0.15 \). If \( l_0 \) is 2.0 nm, then \( G_{11} \) corresponds to \( 4.73 \times 10^{-10} \) C\(^2\)m\(^4\)N, and the bulk domain wall energy is about 0.020 Jm\(^{-2}\) for 71° domain walls. We assumed an isotropic background dielectric constant of 50, and a temperature of \( T = 298 \)K. \( \Delta t / t_0 = 0.08 \).

We start the simulation with small random polarization values. We set the initial \( P_3 \) to be positive, since existing experimental observations show that the direction of the
P₃ polarization component for all variants are all out-of-plane, due to a small built-in voltage resulting from the difference between the film/surface and the film/substrate interface. We employ short-circuit electric boundary conditions on both film surfaces, \( \varphi_{top} = \varphi_{bottom} = 0 \), so that the polarization charges at the surfaces are assumed to completely compensated, and there is no applied voltage.

### 4.3 Results and Discussion

We compare an (001)ₜ-oriented film and a film with 4° miscut towards [1̅00]ₜ, with the bi-axial strain of a coherent BiFeO₃ film on a SrTiO₃ substrate, \( \varepsilon'_{11} = \varepsilon'_{22} = -1.5\% \). In good agreement with experiment⁴, the (001)ₜ-oriented film has all four ferroelastic variants present, while the miscut film has broken polarization symmetry, i.e., preferring only two ferroelastic variants, \( r_1 \) and \( r_4 \), as shown in Fig. (4.1(c)). The polarizations within these two variants are related by 71°, and they form striped domain patterns with domain walls along (101)ₜ. The (001)ₜ-oriented film contains all four ferroelastic variants in a mosaic pattern, with a mixture of 71° and 109° domain walls in the expected \( \{101\}_t \) and \( \{100\}_t \) domain wall orientations¹⁸. It should be noted that the only difference between the simulation conditions for the (001)ₜ-oriented film and the miscut film is the direction of the biaxial strain with respect to the film. It has been previously suggested that the formation of two variant domain structures might be due to the presence of surface ledges during film growth⁵. The present simulation results
demonstrate an alternative mechanism for the formation of two-variant domain structures in a miscut thin film.

To better understand the mechanism for the polarization variant selection, we analyzed the effect of various energetic contributions by deliberately eliminating one or more of them, i.e., we conducted phase-field simulations of domain structure formation in a BiFeO$_3$ film grown on a miscut substrate by excluding either the electric energy or the elastic energy, or both. (It should be noted that these are not intended to reproduce any real, physical state of BiFeO$_3$ thin films, but simply serve as a model for discovering the energetic origin of the domain preference). As expected, we found that when both elastic and electric energy are excluded, all polarization domains are degenerate, i.e., all ferroelastic variants are equally favored [Fig. 4.2(d)]. This follows from the fact that the Landau and gradient energies are degenerate and isotropic for all ferroelectric variants, and do not vary with film orientation. Likewise, including the electric energy alone has little effect on the variant degeneracy [Fig. 4.2(b)]. We note that excluding the elastic energy contribution leads to vertical domain walls, which minimizes the gradient energy relative to tilted domain walls, which are typically caused by elastic energy minimization [Fig. 4.2(b,d)].

When elastic energy is included, the substrate miscut has a marked effect on the polarization variant selection. The film retains the experimentally-observed $r_1$ and $r_4$ striped domain pattern, as seen in Fig. 4.2(a). Excluding just the electrostatic interactions has little effect on the two-variant striped domain patterns [Fig. 4.2(c)].
Figure 4.2. Domain structures of miscut BiFeO$_3$ with different energy components included: (a), with all energy forms included, (b), with electric but not elastic energy, (c), with elastic but not electric energy, (d), with neither elastic nor electric energy. The elastic energy drives the symmetry non-degeneracy, and only the simulations which include elastic energy term, (a) and (c), form striped domain structures consisting of only two variants.

The elastic strain energy effect can be understood by examining the local strains, imposed from the global strains under the standard second-rank tensor transformation, $\varepsilon = a\varepsilon'a^{-1}$:

$$
\varepsilon = \begin{pmatrix}
\varepsilon'^{11}_1 \cos^2 \theta + \varepsilon'^{33}_3 \sin^2 \theta & 0 & (\varepsilon'^{11}_1 + \varepsilon'^{33}_3) \cos \theta \sin \theta \\
0 & \varepsilon'^{22}_2 & 0 \\
(\varepsilon'^{11}_1 + \varepsilon'^{33}_3) \cos \theta \sin \theta & 0 & \varepsilon'^{11}_1 \cos^2 \theta + \varepsilon'^{33}_3 \sin^2 \theta
\end{pmatrix}. \quad (4.5)
$$
The relevant term here is the shear strain along the miscut direction, \( \varepsilon_{13} = (-\varepsilon_{11}' + \varepsilon_{33}') \cos \theta \sin \theta \), which indicates that the global strains contribute to a non-zero local \( \varepsilon_{13} \). This \( \varepsilon_{13} \) term is negative for compressive global in-plane strains and positive for tensile strains. Thus, under sufficiently large \( \varepsilon_{11}' \), two polarization variants will be favored to relax the elastic energy: \( r_1 \) and \( r_4 \) for compressive strains, or \( r_2 \) and \( r_3 \) for tensile strains (Fig. 4.3)

\[ + (\varepsilon_{11} = \varepsilon_{22}) \]

\[ - (\varepsilon_{11} = \varepsilon_{22}) \]

\[ + (\varepsilon_{11} = \varepsilon_{22}), - (\varepsilon_{11} = \varepsilon_{22}) \]

Figure 4.3. Schematic of ferroelastic variant formation for (a,b) (001)\(_p\)-oriented and (c,d) miscut substrates. For an (001)\(_p\)-oriented substrate, all four ferroelastic variants are degenerate under both (a) tensile, and (b) compressive strain. For the miscut substrate, mismatch strain will be along the global \( x_1'\times x_2' \) plane, which in the local system translates to include a shear strain. A tensile strain favors in-plane variants (those tilted towards the global \( x_1'\times x_2' \) plane), (c), while a compressive strain favors out-of-plane variants, (d).
To test this, we examined the effect of varying strains on the miscut film, once again including all the energy terms. As previously shown, the \( r_1 \) and \( r_4 \) variants are strongly preferred under a strong compressive strain of \(-1.5\%\), as seen in Fig. 4.4(a). However, at 0.0\% strain, all four ferroelastic variants become stable again despite the presence of a miscut substrate (Fig. 4.4(b)). Likewise, with a strong tensile strain of +1.5\%, the \( r_2 \) and \( r_3 \) variants become strongly favored, Fig. 4.4(c). As this is a combination of two variants separated by a 71° in-plane rotation, the domain structure forms stripes similar to the compressively strained film.

![Figure 4.4](image1.png)

Figure 4.4. Domain structures of miscut BiFeO\(_3\) simulations under different substrate strains. (a) \( \epsilon’_{11} = \epsilon’_{22} = -1.5\%\), (b) \( \epsilon’_{11} = \epsilon’_{22} = -0.0\%\), (c) \( \epsilon’_{11} = \epsilon’_{22} = +1.5\%\). When the miscut film is sufficiently strained, two ferroelastic variants become favored, and the variants line up in a striped domain structure, as seen with compressive strain with \( r_1/r_4 \) variants, (a), and with tensile strain with \( r_2/r_3 \) variants, (c). Under weak strain, (b), all four variants are present.
The strain we used may appear high; in experiment, misfit strain often decreases as the film thickness increases, due to relaxation from dislocations. However, during initial growth the film is coherent, and the initial domain structures will correlate with the coherent strain. As the film thickens and relaxes, the domain structure will change only if the new domain pattern has a lower energy. Thus, while the misfit strain at the beginning of film growth may be substantially stronger than that at the end, it may still dominate the domain structure formation if the energy cost of switching is too high.

### 4.4 Summary

In summary, we use a Ginzburg-Landau-Devonshire phase-field model to describe the evolution of ferroelectric and ferroelastic domain structures BiFeO$_3$ thin films. We find that the domain structures of BiFeO$_3$ thin films are strongly dependent on the combination of orientation and strain. Furthermore, a small degree of miscut is sufficient to cause a degeneracy of favored ferroelectric variants for strong-strain substrates such as SrTiO$_3$, due to the elastic effects from the substrate mismatch. Due to the importance of strain in breaking polarization symmetry in miscut films, we expect that the degree of miscut needed to produce domain non-degeneracy will depend strongly on the magnitude of the misfit strain.
References


20. The parameters used in the simulations, in SI units (where the temperature $T$ is in K): $\alpha_1 = 4.9 \times 10^5$, $\alpha_{11} = 6.50 \times 10^8$, $\alpha_{12} = 1.0 \times 10^8$, $Q_{11} = 0.032$, $Q_{12} = -0.016$, $Q_{44} = 0.02$, $c_{11} = 3.00 \times 10^{11}$, $c_{12} = 1.62 \times 10^{11}$, $c_{44} = 0.691 \times 10^{11}$. 

50
Chapter 5: Phase-field Simulations of Switching Under a Piezoforce Microscopy Tip in BiFeO$_3$ Thin Films

5.1. Introduction

In the last few decades, Piezoforce Microscopy has emerged as a powerful tool for probing and manipulating electromechanical phenomena in ferroelectric thin films. Piezoforce Microscopy (PFM) is a variant of Atomic Force Microscopy in which a conductive tip is used to measure the displacements in the top surface of a material during the application of an applied bias. Under an applied field, the converse piezoelectric effect induces a strain in the material, which shifts the cantilever position and is measured optically. As the piezoelectric effect is modified by the local polarization direction and magnitude in the material, the resulting displacement provides information about the domain structure.

Piezoforce microscopy has been used recently to examine the ferroelectric size effect in BiFeO$_3$ thin films$^1$ and the evolution of domain populations in PbZr$_x$Ti$_{1-x}$O$_3$ thin films with respect to Zr content$^2$, as well as to understand changes in hysteretic behavior in polycrystalline PbZr$_{0.7}$Ti$_{0.3}$O$_3$ bilayer systems$^3$. PFM also has demonstrated promise for clarifying the switching dynamics of ferroelectric thin films around charged defects$^4$, dislocations, and domain walls$^5$–$^7$, as well as for the intrinsic switching dynamics in the absence of defects$^8$. However, spatial resolution is typically limited to
about 10-50 nm, depending on the probe size and local electronic environment\textsuperscript{9}.

Additionally, although both phenomenological\textsuperscript{10-13} and analytical\textsuperscript{4,14,15} theory have both been well-developed for PFM studies, these theories are partially limited in their ability to dynamically model the nanometer-scale switching phenomena. In applying the phase-field model to the same problems, we can help clarify the phenomena underlying observed PFM measurements, guiding the interpretation of future PFM work.

Currently, there has been little work on phase-field simulations of the switching response in BiFeO\textsubscript{3} thin films under a PFM tip. This work will use a phase-field model to explore such responses under a range of in-plane strains and near a 71° domain wall, stopping to explore interesting phenomena we find along the way.

Other work: Ferroelastic backswitching in 71 domains\textsuperscript{16} Strain dependence of coercivity in BiFeO\textsubscript{3} thin films\textsuperscript{17} Previous in-plane switching in phase-field simulations of BFO thin films\textsuperscript{7} Previous observations of nucleation biases as related to tip size or proximity to a wall\textsuperscript{4}

\section*{5.2 Methods}

\subsection*{5.2.1 Numerical methods and energy model}

As before, we apply the time-dependent Ginzburg-Landau equations to solve the evolution of polarization over time in a thin film:
\[
\frac{\partial P_i(x)}{\partial t} = -L \frac{\partial F}{\partial P_i(x)}, \quad i = 1, 2, 3, \tag{5.1}
\]

where \(F\) is the total free energy, \(P_i(x)\) is the \(i\)th component of the spatial polarization distribution, and \(L\) is a kinetic parameter related to domain wall mobility. We use the standard notation for repeated indices, where \(i, j, k, l = 1, 2, 3\). Here the total free energy is defined as the sum of the Landau, gradient, elastic, and electric energies,

\[
F = \int (f_{\text{Landau}} + f_{\text{gradient}} + f_{\text{elastic}} + f_{\text{electric}}) dV, \tag{5.2}
\]

where \(dV\) is over the volume of the film. We use a fourth-order Landau-Devonshire polynomial\(^\text{18}\) for the Landau energy, and the coefficients employed are \(\alpha_1 = 8.78 (T - 830) \times 10^5, \alpha_{11} = 4.71 \times 10^8, \alpha_{12} = 5.74 \times 10^8\). The gradient energy is

\[
f_{\text{gradient}} = \frac{1}{2} G_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}, \tag{5.3}
\]

For a cubic system, where \(G_{ijkl} = G_{jikl} = G_{ijlk}\), and the energy equation in Voigt notation is of the form

\[
f_{\text{gradient}} = \frac{1}{2} G_{11} (p_{1,1}^2 + p_{2,2}^2 + p_{3,3}^2)
+ G_{12} (p_{1,1}p_{2,2} + p_{2,2}p_{3,3} + p_{1,1}p_{3,3})
+ \frac{1}{2} G_{44} \left[ (p_{1,2} + p_{2,1})^2 + (p_{2,3} + p_{3,2})^2 + (p_{1,3} + p_{3,1})^2 \right]
+ \frac{1}{2} G_{44}' \left[ (p_{1,2} - p_{2,1})^2 + (p_{2,3} - p_{3,2})^2 + (p_{1,3} - p_{3,1})^2 \right], \tag{5.4}
\]
The coefficients employed are isotropic, and the normalized gradient energy coefficients are given as \( G_{11} = 0.6, G_{12} = 0.0, G_{44} = G'_{44} = 0.3 \).

The elastic energy is given as a function of the elastic strain, \( e_{ij} \), and the elastic stiffness tensor, \( c_{ijkl} \),

\[
f_{\text{elastic}} = \frac{1}{2} c_{ijkl} e_{ij} e_{kl}. \tag{5.5}\]

This is coupled to the polarization through the stress-free strain, \( e^s_{ij} \),

\[
e_{ij} = e_{ij} - e^s_{ij} = e_{ij} - Q_{ijkl} P_k P_l, \tag{5.6}\]

where \( e_{ij} \) is the total strain and \( Q_{ijkl} \) is the electrostrictive coefficients. The elastic constants employed are taken from the literature\(^1\): \( Q_{11} = 0.035, Q_{12} = -0.0175, Q_{44} = 0.02015, c_{11} = 3.02 \times 10^{11}, c_{12} = 1.62 \times 10^{11}, c_{44} = 0.68 \times 10^{11} \).

The mathematical expressions for the electric energy contribution is provided in previous publications\(^{20,21}\):

\[
f_{\text{electric}} = -E_i \left( \frac{1}{2} \varepsilon_b \varepsilon_0 E_i + P_i \right). \tag{5.7}\]

Here \( E_i \) is the total electric field, \( \varepsilon_0 \) is the vacuum dielectric permittivity, and \( \varepsilon_b \) is the isotropic background dielectric constant. We employ a background dielectric constant of \( \varepsilon_b = 10 \).

We use a system size of \( 200\Delta x \times 200\Delta x \times 50\Delta x \), where \( \Delta x \) is size of the cubic simulation grid. We use a substrate thickness of \( 30\Delta x \) and a film thickness of \( 14\Delta x \). The system is periodic in the \( x_1 \) and \( x_2 \) directions, and we solve equation (5.1) with the semi-implicit Fourier method. We assume that the temperature \( T = 300K \). The real size of
the simulation grid size are related by \( L_0 = \Delta x = \sqrt{G_{110}/\alpha_0} \), where \( \alpha_0 = |a_1|_{T=300K} \). As mentioned previously, we used a normalized gradient energy coefficient of \( G_{11}/G_{110} = 0.6 \), which, if \( L_0 = 1 \text{nm} \), corresponds to a domain wall energy density of roughly 0.11 \( \text{J/m}^2 \) for a 71° domain wall and a gradient energy coefficient of \( G_{11} = 4.23 \times 10^{-10} \).

Additionally, in these simulations we apply a bias under a PFM tip. Here we approximate the potential on the top surface of the film as a Lorentzian distribution,

\[
\varphi(x, y) = \varphi_0 \left( \frac{\gamma^2}{(x-x_0)^2 + (y-y_0)^2 + \gamma^2} \right),
\]

where \( \varphi_0 \) is the applied bias directly under the tip, \((x_0, y_0)\) is the tip location on the top surface of the film, and \( \gamma \) is the half-width, half-maximum of the applied potential. We use \( \gamma = 7 \Delta x \), half of the film thickness.

### 5.2.2 Calibration of the initial domain structure

For simulations which start from a pre-set domain structure, it is important to carefully calibrate that domain structure before beginning measurements. Generally, the thin film domain structure should typically be stable to perturbations, as well as be relaxed with respect to variations in system (or domain) width. For example, if we desired to simulate the PFM switching properties in a tetragonal film of PbTiO\(_3\) under 0.0% in-plane strain, we might naively begin from a single \( c^+ \) domain, with polarization uniformly oriented parallel to \([001]_p\). Upon applying a bias great enough to induce nucleation and switching, we would see not only the expect \( c^- \) domains growing through
the thickness of the film, but $a$ domains nucleating and growing through the film both laterally and vertically, until they had formed domains stretching through the entire length of the film. Logically, this would be expected, as the preferred domain structure for PbTiO$_3$ at 0.0% is an $a/c$ mix, and the $a$ domains are necessary for ferroelastic relaxation via twinning. However, the absence of these domains during the initial switching simulation can greatly modify the coercive field and switching behavior, thus being deleterious to what might otherwise be a successful comparison with experiment.

Accordingly, we explore how domain widths affect the energy in the film for the systems to which we will apply a biased PFM tip. First, we explore the energy difference associated with a change in domain width of a typical 71° domain pair ($r_1/r_4$), oriented with the domain wall at (101). To do this, we take 2-D slices across the domain wall (with dimensions along [010] and [001]), and set the initial domain structure to the expected domain wall orientations. We periodically apply small perturbations to the polarization, and we allow the system to evolve until the free energy has stopped decreasing (typically, to within 1 part in $10^6$). As the initial domain structure is close to that of the preferred structure and the simulation is two-dimensional, these simulations are very quick. Using an automated script to generate the necessary input files and collect the data, we can run hundreds of these simulations on a typical new PC within a 24-hour period.

The results for the 71° domain pairs are shown below. In Figure 5.1(a), we show the sensitivity of energy in a system to the domain width for a range of strains. Each
curve is baselined to zero, that is, we show the change in energy relative to the
minimum energy width for that strain. We observe that most of the strains exhibit a
greater energy penalty for domains that are too narrow than too wide. In addition, the
preferred domain width is greater as the in-plane strain decreases. This is expected, as
these domain pairings relax the misfit strain caused by the $\epsilon_{12}^0$ component of
eigenstrain. This eigenstrain depends on the in-plane polarization, which increases
with greater tensile strain or decreases with greater compressive strain.
Figure 5.1. (a) Side view of the starting domain structure during calibration, and (b) final domain structure after relaxation. (c) Change in average energy versus domain width. With decreasing in-plane strain, the film becomes less sensitive to the domain width.
However, we note that the energy differentials observed here are relatively small compared to the energy change between different strains. For instance, the minima of the curves for 0.0% and -0.5% strain are separated by a normalized energy of about 0.04, 10x the range of Figure 5.1(a). Thus, we pick our domain width to be $100\Delta x$, which is close to the energy minima for each of the strains.

Experimental measurements show similar ferroelastic 71° domain pairs have a width of about 200-400 nanometers in 150 nm thick films\(^7\) on SrTiO\(_3\) substrates ($\varepsilon_{11} = \varepsilon_{22} \approx -1.5\%, \varepsilon_{12} = 0.0\%$), or similarly for 120 nm thick films\(^{23,24}\) on DyScO\(_3\) substrates ($\varepsilon_{11} = -0.35\%, \varepsilon_{22} = -0.48\%, \varepsilon_{12} = 0.0\%$). Thus, the experimental domain widths are still 2-4x as wide as the preferred widths observed here. However, our films are about 1/10\(^{th}\) of the thickness of the experimental films, and we have observed a widening of the preferred domain width with increasing film thickness (data not shown here).

### 5.3 Results and Discussion

#### 5.3.1 Switching near a 71° domain wall

It will be useful to define some terms as spatial reference points; here we denote the spatial location along [100] of the top of the wall as $w_{top}$, and the location of the bottom of the wall as $w_{bottom}$. As the wall is tilted towards (101), we expect that a tip bias on the +[100] side of $w_{top}$ will interact with more surface area of the wall, and thus,
have stronger interactions with the wall, than a similar applied tip bias on the opposite side. The values of $w_{top}$ and $w_{bottom}$ are related here by $w_{bottom} = w_{top} + 5$, showing that the domain wall is not truly (101)-oriented, but canted vertical. This is due to the gradient energy, which attempts to minimize the domain wall area.

In Figure 5.2, we present the hysteresis loops for the polarization versus the tip location. Measurements are given in normalized units, where the normalization constants are $p_0 = 0.52$, $a_0 = |\alpha_1|_{T=300K}$, and $V_0 = a_0 p_0 L_0$. The polarization is given as the average $P_3$ in the film under the center of the tip. For comparison, we also show the hysteresis loop for case of the tip far away from the wall on each plot. First, we observe that for all three tip locations near the wall, the nucleation field is lower than for the tip located far from the wall. Furthermore, although we see backswitching in each case, the switched domains closer to the wall show a greater resistance to backswitching. Far from the domain wall, the backswitching occurs at about -1.0 V/$V_0$, while the backswitching at the domain wall is reduced by about -0.5 V/$V_0$. We observe that the switching directly at $w_{top}$ and $w_{top} - 7\Delta x$ is hindered. Although nucleation and growth start at much lower voltages (-1.5 V/$V_0$), domain growth is hindered. The domain structure from the top shows a greater degree of twist on the negative side of the wall than on the positive side, which correlates with the hindered switching and implies the possibility of an electromechanical damping of switching. The switching at $w_{top} + 7\Delta x$, however, is the shape of a classic hysteretic loop, and the polarization switching there occurs even more sharply than for the case far from the domain wall.
Figure 5.2. Polarization-voltage hysteresis loops and side view of domain structures at $\varphi = 3.0V/V_0$. The domain structures are for the tip at (a) $w_{\text{top}} - 7\Delta x$, (c), $w_{\text{top}}$ and (e), $w_{\text{top}} + 7\Delta x$. Tip locations are noted by arrows on the top surface, and the colors of the polarization variants are given as yellow=$r_4^-$, dark green=$r_3^+$, red=$r_2^+$, light blue=$r_1^-$. The normalized hysteresis loops are given for the tip at (b) $w_{\text{top}} - 7$, (d) $w_{\text{top}}$, (f) $w_{\text{top}} + 7$.

We present the loop of the tip far from the wall on each graph for comparison.
In Figure 5.3, we present the displacement hysteresis loops. The displacement in the hysteresis loops is defined as the displacement directly under the tip during switching. We note that each of the loops has a different remanent displacement after switching, indicating that the wall moves during switching. In addition, the first two cases ($w_{top}, w_{top} - 7\Delta x$) show damped $u_3$ responses to the applied potential during switching. The tip located at the $w_{top} + 7\Delta x$ shows a greater piezoresponse during switching than either these two cases or the case of switching far from the wall, corresponding well with the sharp polarization switching observed in Figure 5.2.
Figure 5.3. Displacement versus applied potential loops for various locations around the domain wall. The normalized hysteresis loops are given for the tip at (a) \( w_{top} - 7 \), (b) \( w_{top} \), (c) \( w_{top} + 7 \). We present the loop of the tip far from the wall on each graph for comparison.
A comparison of the displacements versus tip location for unipolar excursions of the applied bias is shown in Figure 5.4. The x-axis is aligned such that the zero point is at $w_{top}$. The curves are for the biases between -3.0 and +3.0 V, in increments of 1.0 V. We remove points for which nucleation has occurred, i.e., these are the non-switching displacements. In the plot of $u_1$, we note a jump in the region between $w_{top}$ and $w_{bottom}$ by the domain wall. Additionally, this is the region in which we observe the greatest change in $u_3$. The peak of the zero-bias curve is at $w_{bottom}$ (i.e., $\mathbf{= 5}$), and the curves shift towards the left as the bias increases. The region around $w_{top}$ also shows a greater piezoresponse for negative biases (Figure 5.4(c), orange line).
Figure 5.4. Displacements as a function of tip location for unipolar bias excursions, for (a), $u_1$ component of displacement, (b), $u_2$ component of displacement, and (c), $u_3$ component of displacement. We exclude points where opposite domains have nucleated.
We also show the nucleation bias versus tip location in Figure 5.5. As with much of the other data, the extreme is in the positive region. The nucleation bias has a minimum of $1.45 \frac{V}{V_0}$ between 3 and 4 grid points on the soft side of the wall, compared to a maximum of 3.35 far away from the domain wall. We note that the minima occurs between $w_{top}$ and $w_{bottom}$. The curve is nearly symmetrical, and is similar to that observed in other theoretical work\(^4\).

Figure 5.5. Nucleation bias versus tip location across a domain wall. The x-axis is centered such that the top of the domain wall is at zero.

5.3.2 The effects of in-plane strain

We also study the effect of the in-plane strain on the PFM switching far from a domain wall. We find that the nucleation bias increases with decreasing in-plane strain, in good agreement with previous experimental and theoretical results for ferroelectric thin films\(^{25-30}\). We present the coercive field as a function of in-plane strain for a PFM tip.
far from a domain wall in Figure 5.6. Between -1.5% strain and +1.5% strain, the coercive bias drops by almost a factor of four, to about 1.1 V/V₀. The change in coercive bias per change in strain is greatest for more positive strains.

Figure 5.6. Nucleation bias versus mismatch strain.

In Figure 5.7, we present the change in displacement for a unipolar excursion bias applied for a tip far from the domain wall. While the out-of-plane piezoresponse changes linearly with the in-plane strain (Fig 5.7(c)), the in-plane piezoresponses change non-linearly, peaking between -0.5% and -1.0% strain (Fig 5.7(a,b)). We note that the displacement magnitudes are different between the u₁ and u₂ graphs (Fig 5.7(a) and (b)) indicating that the domain structure still affects the degree of absolute displacement, even far from a domain wall. In addition, the piezoresponses increase in all three direction with an increase in strain.
In Figure 5.8, we see the polarization and displacement hysteresis loops with regard to the in-plane strain. We note that the more-compressive strain has both a higher remanent polarization and coercive field, as is common in ferroelectrics. The more-compressive strains also backswitch more easily; although this may be related to the size of the switched region. For a given applied bias, the switched region is smaller for the more-compressive strains, and thus may be relatively quicker to backswitch. Future work might examine the causes of backswitching, and the relative strength of the elastic and gradient energies in driving the domain wall movement.

We see that the less-compressive strains have a more traditional hysteresis loop and sharper transitions during initial switching. These strains form simple 71° domains during switching, e.g., a $r_3^+$ domain in an $r_1^-$ region, or a $r_2^+$ in an $r_4^-$ region. However, as the strain becomes increasingly negative, we see more complex domain structures emerge, such as topological defects of head-to-head domains as observed in experiment and previous simulations\textsuperscript{31}. These domains are caused by the in-plane electric fields around the PFM tip, the strength of which will be related to the tip width, which governs the lateral change in applied potential. These structures are more dominant with negative mismatch strain because of the effect of the substrate strain on the Landau energy minima. With compressive strain, the in-plane energy minima move closer together and have lower energy barriers to formation, such that it becomes more energetically favorable to create in-plane variants to compensate the in-plane fields. Additionally, we observe a correlation between the presence of these in-plane variants
and the hindered switching in the more-compressive strain cases, and we hypothesize that the two may be connected.
Figure 5.7. Displacements as a function of in-plane strain for unipolar bias excursions, for (a), $u_1$ component of displacement, (b), $u_2$ component of displacement, and $u_3$ component of displacement. We exclude points where opposite domains of $P_3$ have nucleated.
Figure 5.8. Polarization and strain hysteresis loops for a range of misfit strains. (a) The hysteresis loop for the normalized polarization versus normalized applied bias, and (b) the hysteresis loop for normalized $u_3$ displacement versus normalized applied bias.
5.4 Summary

We examine the effects of substrate strain and proximity from a 71° domain wall on the switching properties of BiFeO$_3$ thin films. We find lower nucleation biases near the domain walls and at higher in-plane strains, and note a propensity for backswitching in all films at the thickness we used. Additionally, we note a very non-linear change in piezoresponse around the domain wall with respect to the tip location and the applied potential. These results may help guide future PFM measurements around 71° domain walls.
References


Chapter 6: Electroelastic Fields in Artificially Created Vortex

Cores in Epitaxial BiFeO$_3$ Thin Films

6.1 Introduction

It has recently been discovered that some types of domain walls in BiFeO$_3$ may be conductive$^1$, and Balke et al.$^2$ demonstrated the possibility of writing conductive domain channels into BiFeO$_3$ thin films through the introduction of topological defects in the domain structure. Using SPM writing of domains, and by varying the applied bias and the raster speed, they were able to create domain structures in which four domain variants met at along the [001] axis. The possibility of writing and erasing conductive nanochannels into a ferroelectric film is intriguing. Here we will use the phase-field model examine the electroelastic fields at these topological defects. While the transition between two domains is called a domain wall, we will call the intersection of more than two domains a “junction”, and a 1-D domain junction a “core”.

Figure 6.1. A top-down schematic diagram of the (a) vortex and (b) anti-vortex cores, showing the relative directions of polarization in the four surrounding domains. Each of the domains has a positive out-of-plane polarization. (c), Perspective view of the starting simulation domain structure. (d) In-plane PFM of vortex and anti-vortex domain structure in 150 nm BiFeO$_3$ thin films, showing the domain structure for experimental vortex cores (adapted from Ref. [2]).

In this paper, we examine two types of domain cores which run parallel to the [001]$_p$ direction. These are the intersections of the four $r^+$ variants: in the “vortex”, the in-plane polarizations of the surrounding domains rotate around the core (Fig. 6.1(a)), whereas the “anti-vortex” is comprised of the same four $r^+$ variants, arranged such that
the in-plane polarizations alternate between pointing towards or away from the core (Fig. 6.1(b)). In experiment, these domain structures were constructed in BiFeO$_3$ films using SPM tip$^{2,3}$. Previously, we examined the conductive properties of the cores by their relation to the thermodynamic equilibrium concentrations of oxygen vacancies, holes, and electrons in lightly-doped materials$^2$. As oxygen vacancies are well-known to be shallow wells for electrons in many perovskite oxides, and oxygen vacancies are coupled with strain through a positive Vegard stress coefficient, control of the elastic fields in BiFeO$_3$ thin films may offer some control of the conductance. Here we employ phase-field modeling to study the elastic fields at the cores.

### 6.2 Specific methods

We employ the general methods described in Chapter 2. The elastic and Landau parameters used are listed in ref. [12], as found in the literature$^4$. We used a simulation size of $128 \Delta x \times 128 \Delta x \times 32 \Delta x$, with both film and substrate thicknesses set at $14\Delta x$. We used a normalized gradient energy coefficient of $G_{11}/G_{110} = 0.6$, which, if $\Delta x = L_0 = 1$nm, corresponds to a domain wall energy density of roughly $0.11 \text{ J/m}^2$ for a $71^\circ$ domain wall and a gradient energy coefficient of $G_{11} = 4.23 \times 10^{-10} \text{ C}^{-2} \text{ m}^4 \text{ N}$.

We assumed a background dielectric constant of $\varepsilon_b = 50$ with short-circuit boundary conditions on the top and bottom surfaces of the film, that is, the electric potential was specified at the surfaces. We assumed $T = 300K$, and we set the initial domain structure in rectangular domains similar to the experimental vortex/anti-vortex
structure, and then allowed the structure to evolve until the polarization ceased changing.

In some of the simulations, we applied a tip bias to the top surface of the films to explore the properties of the vortex cores under a bias. The bias was applied in a Lorentz distribution,

$$\varphi_L(x, y) = \varphi_0 \left( \frac{y^2}{r^2 + y^2} \right), \quad (6.1)$$

where $\varphi_0$ is the applied bias directly under the tip, $r$ is the lateral distance away from the tip center, and $\gamma$ is the half-width, half-maximum of the applied potential. We applied voltage at a rate of 0.05 V / 100 timesteps, up to sweeps of +/- 6 V for the vortex and anti-vortex cores, and up to +/- 4 V for the domain wall and domain center. Here $\gamma = 7$, half the thickness of the film.

### 6.3 Results and Discussion

#### 6.3.1. Vortex domain structure and strain properties

Fig. 6.2 shows the domain structure and the associated domain wall structure after polarization evolution has become negligibly small. We see that the domain structure at the top surface of the vortex core exhibits a twist opposite to the polarization rotation direction. Likewise, the top surface of the anti-vortex shows a “pinched” domain structure, where the outward-pointing domain variants grow at the expense of the inward-pointing domains, in agreement with experimental observations.$^2$
(Fig. 6.1(d)). These effects are reversed at the bottom surfaces. These “twist” and “pinch” effects are caused by the domain walls twisting away from their preferred $\langle 1 \ 0 \ 1 \rangle$ orientations$^5$ to become parallel to $[0 \ 0 \ 1]$ near the cores. A cross-section across half the thickness of the film would show the four domain walls meeting at about 90° angles and running along the $[1 \ 0 \ 0]$ and $[0 \ 1 \ 0]$ axes. At the top and bottom of the film, however, the distortion results in the modified wall structure. For example, a wall between $r_1^+$ and $r_4^+$ with a preferred orientation of $\langle 1 \ 0 \ 1 \rangle$ will have an orientation of $\langle 1 \ 0 \ 0 \rangle$ at a core. For the vortex cores, this results in a clockwise rotation at the top of the film and a counter-clockwise at the bottom of the film.
Figure 6.2. (a) Perspective view of the relaxed simulation domain structure, and (b) a top-down view of the domain walls at the vortex (left) and anti-vortex (right). Note that the domain wall twist at the vortex and the pinch at the anti-vortex vary through the height of the film, as each of the domain walls rotate to become parallel with [0 0 1] near the core.

The vortex cores exhibit a high degree of in-plane elastic tensile strain ($\varepsilon_1 \approx 0.7\%$, $\varepsilon_2 \approx 1.1\%$), while the out-of-plane direction is compressively strained.
(ε₁ ≈ −0.4%), leading to volumetric expansion of the unit cell of about 1.4% along nearly the entire height of the core (Fig 4c). The anti-vortex core exhibits much weaker volumetric compressive strains of about −0.1% (ε₁ ≈ −0.3%, ε₂ ≈ −0.6%, ε₃ ≈ 0.9%). The average out-of-plane polarization at the vortex core is 1.25 p₀ and 1.42 p₀ at the anti-vortex core, compared to 1.13 p₀ in the middle of a domain, while the in-plane polarizations at the cores are suppressed. The increased polarization at the cores is partially due to the fact that the core is the intersection of four domain walls between polarization variants with only +P₃ in common. We note that the increased P₃ is energetically expensive at the vortex core, given the local in-plane tensile strain. The strain properties of the cores are presented in Figure 6.3.
Figure 6.3. Components of total strains, (a), \((\varepsilon_{11} + \varepsilon_{22})/2\), (b), \((\varepsilon_{33})\), (c) \((\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})\), and (d), \((|\varepsilon_{12}| + |\varepsilon_{23}| + |\varepsilon_{13}|)\), looking across [110], with the vortex core visible on the left and the anti-vortex core on the right. Domain walls are visible on the sides and in the middle. The high in-plane expansion and out-of-plane compression of the vortex core is visible, with the resulting volumetric strain shown in (c). In (d), we note a decreased shear strain along the entire length of the vortex core, and mixed regions of high and low shear strain in the anti-vortex core.
6.3.2 Underlying mechanisms

The interesting properties of the cores come from their symmetry-breaking or symmetry-enforcing structures. Each core type has its own local symmetry: in international notation, the anti-vortex core has symmetry $mm2$, with mirror planes at $(110)$ and $(1\overline{1}0)$, while the vortex core has a symmetry of $4$. Recall that under stress-free conditions, BiFeO$_3$ exhibits a ferroelastic elongation of the crystal cell along the polarization direction and a contraction in perpendicular directions. In the domains surrounding the vortex core, the in-plane components of polarization are parallel to the core; so that with respect to the core, each domain has a negative $\varepsilon_{12}^0$ (Fig 6.4a). That is, each of the neighboring domains exerts a tensile stress on the vortex core along the respective $\{110\}$ direction (Fig 6.4b). Furthermore, at the center of the vortex core, the rotational symmetry is broken, and the shear strains ($\varepsilon_{12}, \varepsilon_{23}, \varepsilon_{13}$) are suppressed (Fig 6.3(d)).

Figure 6.4. (a) Diagram of the in-plane lattice distortions due to eigenstrains in the domains around the vortex core, and (b) resulting in-plane stresses exerted upon the core.
To test this hypothesis, we examined the volumetric strain at the cores and at the middle of a domain over a range of in-plane strain. Under a compressive strain, the polarization will rotate towards the plane of the film\(^4\), which should decrease the \(\varepsilon_{12}^0\)-related stresses around the vortex core. This was verified by our simulations, which showed a much greater change in volumetric strains over a range of mismatch strains from -1.0% to +1.0% at the vortex cores (see Fig. 6.5): a change of 1.8% for the vortex core, 1.1% for the anti-vortex core, and 0.95% for the middle of a domain. If vortex/anti-vortex domain pattern was written with a tip in our simulations, instead of generated from a preset domain structure, then these changes would be somewhat offset by changes in the equilibrium domain width, which would compensate the changes in in-plane stress somewhat.
Figure 6.5. Effect of mismatch strain on the local volumetric strain ($\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}$) at a vortex core (blue diamonds), anti-vortex core (red circles), and in the middle of a domain (green triangles). The volumetric strain of the vortex core is much more sensitive to changes in the applied strain, presumably due to the effect of the applied strain on the in-plane polarizations and eigenstrains.

Similarly, for the anti-vortex core, the in-plane polarization components in the surrounding domains point towards the core, resulting in a net in-plane compression and out-of-plane expansion of the core. In addition, the anti-vortex core also experiences the effects of the $\varepsilon_{13}^0$ shear strain component, which adds a thickness-dependent effect, and thus the properties show more variability through the thickness of the film. Overall, the anti-vortex core exhibits a more compressive in-plane strain.
compared to that of the vortex core, and $P_3$ is likewise higher here. The anti-vortex core also exhibits very high $\varepsilon_{12}$ at the top surface.

### 6.3.3 Charged defect estimates

We will use Vegard’s Law to approximate the effect of oxygen vacancy concentration on strain. Other oxides are estimated$^{6,7}$ to have Vegard tensors between 0.18 and 0.28 $[m^3/m^3]\cdot[\text{atoms/atom}]^{-1}$, and we estimate the oxygen vacancy formation volume for BiFeO$_3$ to be around 0.23 $[m^3/m^3]\cdot[\text{atoms/atom}]^{-1}$. Therefore, we estimated$^3$ the change in conductivity near the cores by examining the thermodynamic equilibrium concentrations of electrons ($n$), holes, and oxygen vacancies ($N_{V^+}$).

$$N_{V^+}(x) = N_{V^+_0} \exp \left[ \frac{\bar{\sigma}^V_{ij}(x)/\rho - e\varphi(x)}{k_B T} \right] ;$$

(6.2)

and

$$n(x) = n_0 \exp \left[ -\frac{q\varphi(x)}{k_B T} \right] ,$$

(6.3)

where $\bar{\sigma}^V_{ij}$ is the Vegard stress tensor for oxygen vacancies, $\sigma_{ij}$ is the stress, $\rho$ is the number of atoms per unit volume in the material, $e$ is the elementary charge, $q$ is the charge of the hole or electron ($\pm e$), $\varphi$ is the electrostatic potential, $k_B$ is the Boltzmann’s constant, and $N_{V^+_0}$ and $n_0$ are the bulk concentrations of the oxygen vacancies and electrons, respectively.
We can obtain the local concentration of defects relative to the bulk concentration from the exponential terms, \( \frac{N^V_1(x)}{N^V_{0}} = \exp \left[ \frac{\left( \overline{\mu}^V_{i,1}(x)/\rho - e\varphi(x) \right)}{k_B T} \right] \), and

\[
\frac{n(x)}{n_0} = \exp \left[ -\frac{q\varphi(x)}{k_B T} \right].
\]
The results indicate a propensity for hole segregation at the anti-vortices and electron and oxygen vacancy segregation at the vortices, as presented below in Table 6.1.
Table 6.1. Electroelastic fields and carrier segregations at the topological defects.
To show the distribution of the strain tensor trace, potential, and electric field trace in the domain structures, we present Figure 6.6. In the trace of the electric fields, we note the strongest electric fields are seen at the surface, due to the discontinuity of polarization there. This is partly a numerical artifact, but the in-plane differences in the electric field as a function of distance from the vortex or anti-vortex cores can still be seen. In the trace of the strain tensor, we note the symmetry patterns around the vortex and anti-vortex cores. The extension of the strain from the anti-vortex along the <110> directions. This agrees with our argument that the $\varepsilon_{12}^0$ component of the eigenstrain is responsible for the properties of the cores.
Figure 6.6 (a) Domain structure after relaxation, for reference, (b) the trace of the electric field, (c) trace of the strain tensor, and (d) electric potential.
We examined the effects of an applied bias on the domain structure for unipolar bias excursions under a PFM tip in both the positive and negative directions. We present the evolution of the electroelastic fields for a positive excursion bias in Figure 6.7.

The control case is the middle of a domain, and exhibits switching behavior similar to a traditional ferroelectric hysteresis loop. Along the domain wall, switching begins earlier, but saturates at about the same applied potential as the control case. The anti-vortex starts switching the earliest of any of the domains. Indeed, in simulations with decreased gradient energy, we see nucleations of $P_3^-$ domains at the surfaces of the anti-vortex, even under no applied bias. However, it takes more applied potential to finish switching for the anti-vortex than in either the domain wall or the control case. During switching, all three of these also undergoes through a change in the trace of the average strain, of about 0.2%.

The anti-vortex switches in steps, first with nucleation and lateral growth at around 1.3 V, but saturates at a partially-switched state until the bias is increased to about 4.5 V. Notably, the average potential within the film remains nearly constant as the potential on the top surface is increased, and at the same time, the average strain trace declines steadily. We posit that the electric energy within the vortex core is converted to mechanical energy. I.e., an increase in applied potential is screened by the changes in polarization in the nearby domains via the electrostriction. We show later that the electrostrictive coefficient $Q_{44}$ has a strong effect on the potential at the vortex core. Furthermore, the electromechanical coupling is verified by an examination of the domain structure of the vortex core under positive applied bias (not shown). As the bias increases, the characteristic "twist" associated with the vortex
domain structure unwinds. When the twist is gone, that is, when a top view of the domain walls on the top surface shows the walls to be parallel to the in-plane crystal axes, nucleation occurs. The strong coupling between strain and potential is also seen in the negative bias excursion for the vortex cores (Fig. 6.8), where the strain trace at the vortex core shows a 50-100% increase in sensitivity to applied potential compared to the domain wall and control cases (Fig 6.8(c)), while the average potential decreases about 33-50% as quickly (Fig 6.8(a)).
Figure 6.7. Evolution of electroelastic fields at the defects as a function of tip potential for a positive excursion, for (a) average polarization, (b) strain trace, and (c) potential.
Figure 6.8. Evolution of electroelastic fields at the defects as a function of tip potential for a negative excursion, for (a) average polarization, (b) strain trace, and (c) potential.
We also examine the effect of modified materials parameters on the electroelastic fields. In particular, we look at doubling and halving the electric constant \((\varepsilon_b = 25, \varepsilon_b = 100)\), the normalized gradient energy coefficient \(g_{11} = 0.30, g_{11} = 1.20\), or the shear component of the electrostrictive coefficient \((q_{44} = 0.0403, q_{44} = 0.010075)\). Our reasoning as as follows: we examine the background dielectric constant because it may affect the electric potential at the cores, and the value employed for BiFeO\(_3\) under Landau theory has varied somewhat in the literature\(^8,9\). We also examined the effect of decreasing the background dielectric constant \(\varepsilon_b\) to 10; however, the vortex domain structure was unstable with this value and reverted to a simple striped two-variant domain structure. For this case, we hypothesize that either the topological defects need to be further apart, or that screening of the potential by free charges is necessary to stabilize the domain structure.

The reasoning for examining the effect of \(q_{44}\) and \(g_{ij}\) is as follows. A cubic substrate could apply \(e_{11}, e_{22},\) and \(e_{12}\) strains on a BFO thin film. However, as BFO is rhombohedral, the only one of these strains which can be alleviated via the domain structure is \(e_{12}\), and this alleviation occurs by twinning of domain variants pairs with different \(e_{12}^0\), such as \(r_1/r_2\) or \(r_2/r_3\). Thus, the equilibrium domain width in a short-circuit BFO thin film will be dominated by the interplay between the shear electrostrictive coefficient \(q_{44}\), which governs the amount of \(e_{12}\) generated, and the gradient energy coefficients \(g_{ij}\), which affects the domain wall energy. The electrostrictive coefficient \(q_{44}\) is also responsible for the elastic fields at the topological defects, as explained earlier and in the literature\(^10,11\). Considering the domain width which gives us the minimum energy in the film, tests of the initial set of materials parameters indicate a preferred domain width of about \(85\Delta x\) for a pair of \(r_1^+/r_4^+\) stripes, which is a low-energy domain structure.
which is able to compensate the long-range strains imposed by the substrate. This is somewhat far from the initial width of $32\Delta x$ we used. Therefore, to further validate our results, we also repeated the above set of modified-materials-parameters simulations for a doubling of the system and domain sizes in the x-y directions. We expect that wider domains will enhance the effect of the topological defects by increasing the range over which the electrostrictive effects can build up.

The stress and electric potential data are taken as averages in a $2\Delta x \times 2\Delta x$ area around the vortex and anti-vortex cores through the thickness of the film, as well as through the middle of a domain for a control. We find good translation of results between the regular and increased system size simulations: the potentials at both core types are roughly doubled in the larger simulations, while the stress is about 2-10x greater in the larger system for the anti-vortices, but unchanged for the vortex cores. The control cases show no change for the change in system size, as expected for a relaxed state. Because of good translation of results between the regular and larger systems, we will present only the data for the larger system size (Table 6.2 and 6.3).
<table>
<thead>
<tr>
<th></th>
<th>anti-vortex</th>
<th></th>
<th>vortex</th>
<th></th>
<th>control</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi$</td>
<td>$\sum \sigma_{ii}$</td>
<td>$\phi$</td>
<td>$\sum \sigma_{ii}$</td>
<td>$\phi$</td>
<td>$\sum \sigma_{ii}$</td>
</tr>
<tr>
<td>No change</td>
<td>-0.19</td>
<td>-5.15E+08</td>
<td>0.05</td>
<td>9.45E+09</td>
<td>0.00</td>
<td>4.02E+08</td>
</tr>
<tr>
<td>$\varepsilon_b = 25$</td>
<td>-0.20</td>
<td>-3.08E+08</td>
<td>0.05</td>
<td>9.49E+09</td>
<td>0.00</td>
<td>5.95E+08</td>
</tr>
<tr>
<td>$\varepsilon_b = 100$</td>
<td>-0.18</td>
<td>-6.06E+08</td>
<td>0.05</td>
<td>9.39E+09</td>
<td>0.00</td>
<td>2.92E+08</td>
</tr>
<tr>
<td>$g_{11} = 0.3$</td>
<td>-0.12</td>
<td>-1.38E+09</td>
<td>0.08</td>
<td>9.40E+09</td>
<td>0.00</td>
<td>3.76E+08</td>
</tr>
<tr>
<td>$g_{11} = 1.2$</td>
<td>-0.18</td>
<td>3.00E+08</td>
<td>0.04</td>
<td>9.00E+09</td>
<td>0.00</td>
<td>4.23E+08</td>
</tr>
<tr>
<td>$q_{44} = 0.0101$</td>
<td>-0.05</td>
<td>1.41E+09</td>
<td>0.01</td>
<td>6.55E+09</td>
<td>0.00</td>
<td>2.85E+08</td>
</tr>
<tr>
<td>$q_{44} = 0.0403$</td>
<td>0.01</td>
<td>-7.79E+08</td>
<td>0.34</td>
<td>9.04E+09</td>
<td>0.00</td>
<td>8.37E+08</td>
</tr>
</tbody>
</table>

Table 6.2: Electric potential and the trace of the stress tensor, for the vortex, anti-vortex, and the control case, simulated for under a variety of different parameters.
The case of “no change” refers to using the original materials parameters, as given in the Methods section. We note first that the control has relatively low values of potential and stress, which produces relative concentrations close to unity for all three types of defects, as expected. We will now ignore the control case and focus our remaining comments on the cores.

We find that the results vary little with respect to the background dielectric constant, at least, within the range of values examined here. Changes to the gradient energy coefficient cause moderate changes in electroelastic fields; the drop of about 0.1 V between the lower and upper values for $g_{11}$ translates into an increase by a factor of $\sim 10^2$ in the concentrations of the oxygen vacancies or holes. Last, a drop in $q_{44}$ does lead to the expected drop in segregation-inducing fields. However, we note an anomalously high potential for the vortex when $q_{44}$ is doubled. As $q_{44}$ is related to the degree of domain wall twist at the vortex cores via the ferroelastic distortion, and twisted domain walls are charged, we expect that the increase in potential is caused by the increased domain wall twist. This also agrees with observations of the vortex core under an applied tip bias, in which applying a negative bias increased the (counterclockwise) domain twist, while a positive bias decreased it. Under the application of a negative applied bias, the core twists in order to form a compensating positive potential. In this case, we see the same stronger-than-usual counterclockwise twist on the top surface of the vortex cores, still accompanied by a strong positive potential, but it is a side effect of an increased $q_{44}$, rather than compensation for an applied bias.
Generally, the anti-vortex is characterized by a low electric potential, which will lead to a competition between segregation of holes and oxygen vacancies, with holes dominant due to the low or negative stresses. The vortex, characterized by low but positive potentials and high positive stresses, will be characterized by a cooperative segregation of electrons and oxygen vacancies. The values here produce estimates of $10^1 - 10^3$ relative concentrations for holes at the anti-vortex. For the vortex cores, if we assume moderate cooperation between the electrons and oxygen vacancies such that the positive potential is completely screened by the electrons and the stress is completely screened by the oxygen vacancies, we arrive at estimates of about $10^1 - 10^3$.

### 6.4 Summary

We conducted phase-field simulations to study the properties of a pair of topological defects in (001)$_p$-oriented BiFeO$_3$ thin films, the “vortex” and “anti-vortex” cores. We found that the vortex core is characterized by a strong tensile volumetric strain with repressed shear strains, while the anti-vortex core is characterized by a compressive volumetric strain and a mix of both enhanced and repressed shear strains. We hypothesize that the elastic fields at the cores are largely governed by the elastic properties of the nearby domains.
References


12. The parameters (in SI units, where the temperature T is in °C) are as follows:
   \[ \alpha_1 = 8.78 \times 10^5, \alpha_{11} = 4.71 \times 10^8, \alpha_{12} = 5.74 \times 10^8, Q_{11} = 0.035, Q_{12} = -0.0175, Q_{44} = 0.02015, c_{11} = 3.02 \times 10^{11}, c_{12} = 1.62 \times 10^{11}, c_{44} = 0.68 \times 10^{11} \].
Chapter 7: Conclusions and future work

7.1 Conclusions

In this thesis, we applied phase-field model to study the ferroelectric domain structures of BiFeO$_3$ thin films. The specific contributions were as follows:

1. The effects of film thickness and the electrical interactions in BiFeO$_3$ thin films were studied. We find a strong correlation between the domain structure and the electrical compensation. With greater thicknesses or electrical compensation, we find that the strain energy dominates in the formation of the domain structure.

2. It was shown that films deposited on vicinal substrates are effected by the misfit strain, which contributes a shear strain to the film. This offers additional ways to influence the domain structure in films, and provide guidance for strain engineering of these films.

3. An investigation of vortex domain structures shows the electroelastic properties are controlled by the electrostrictive shear coefficient and in-plane polarization. The vortex and anti-vortex are expected to be significantly more conductive than the bulk ferroelectric, due to local accumulations of charge carriers caused by the strong electroelastic fields.

4. Switching under a PFM tip was explored under a range of in-plane strains and in the proximity of a 71° wall. As has been found in other ferroelectric thin films$^{1,2}$, the coercive field is strongly affected by the in-plane strain. Additionally, the 71° wall can
acts as a nucleation center or pinning center, depending on the location of the PFM tip relative to the wall.

7.2 Future work

7.2.1 Charged defects

In chapter 5, we examined the effects of electroelastic fields on the expected carrier segregation in BiFeO3 thin films. However, it is desirable to incorporate charged defects such as electrons, holes, and oxygen vacancies into the evolution of the system, rather than estimate them from thermodynamic equilibrium equations at the end of the simulations. Additionally, the model would ideally not just calculate the quasi-steady state concentrations of electrons and holes, but solve the free energy functional with respect to these, so that the entire energy of the system was minimized.

7.2.2 Domain wall energies

Although there is a little data about the domain wall energies in BiFeO3, the gradient energy coefficients for BiFeO3 are currently unexplored. These play a significant role in determining the domain wall energies in phase-field calculations, which in turn influence the domain structure. More careful comparison between experiment, Landau-based theory, as well
as other theoretical calculations is needed to properly understand the properties of domain walls in BiFeO$_3$ thin films in different systems.

### 7.2.3 Substrate conditions

It is well-understood that very thin films are very strongly influenced by the elastic and misfit properties of the substrate. For many of the possible domain structure - substrate combinations, the interactions are dominated by in-plane properties of the materials. However, we note that some types of domain structures are not flat in the film plane, but puckered, as with the $r_1^+/r_4^-$ pairing in BiFeO$_3$ thin films. Similarly, flexoelectricity in thin films is also often related to an out-of-plane component of strain. To date, we are unaware of any work which explores the effects of out-of-plane elastic properties of the substrate. Such work could aide our understanding of open-circuit domain structures and guide the development of nanoelectronics for flexoelectric applications.

### 7.2.4 Backswitching

As we observed in Chapter 5, backswitching can cause the hysteresis loops in very thin ferroelectric films to strongly differ from that of bulk. Future work should examine the causes of backswitching in, as well as the relative strength of the elastic and gradient energies in driving the domain wall movement during backswitching.
7.2.5 Electromechanical or ferroelectric screening of switching

We have observed several types of topological defects: vortex and anti-vortex cores, as well as head-to-head domains under a PFM tip. Each of these has significantly different switching characteristics under a PFM tip than bulk, and in particular, the vortex and head-to-head structures exhibit resistance to switching after nucleation.
References


Appendix A: Comments on Efficient Fortran Programming

A.1 Introduction

In the course of research, we found that the algorithms and programming used could be improved significantly, and that their inefficiency hindered our research. We rewrote the code for efficiency and clarity, according to the guidelines that we outline here. The principles underlying many of these changes are well-known for programming, and they will not come as a surprise to seasoned programmers. Many of these principles are based on computational practices: how arrays are laid out in memory, how the processor retrieves data from arrays in memory, and how the processor executes instructions on arrays, while others are considerably more basic. We found that implementing these principles in our code resulted in speed improvements of 5-10x.

A.2 Algorithmic efficiency for polynomials

Nested polynomials are quicker to compute than distributed polynomials. For instance, consider these two ways of performing the following multiplication, where \( i = 1,2,3 \):

\[
d = a \times b_i
\]

Distributed polynomial (3 multiplications, 2 additions):

\[
d = a b_1 + a b_3 + a b_2
\]

Nested polynomial (1 multiplications, 2 additions):

\[
d = a(b_1 + b_3 + b_2)
\]

Both methods involve two additions, however, the number of multiplications for the distributed polynomial scales with the number of terms of \( b_i \). Thus, use nested polynomials when possible.

A.3 Loop optimization by the compiler

There are many ways in which loops can be re-arranged within a program so as to execute them more quickly and efficiently (loop unrolling, loop blocking, etc.). With proper coding, the compiler can perform many of these for the programmer, abstracting the difficult
work away from the programmer. Here, we outline how the programmer can aid the Fortran compiler in optimization. First, though, here is the compile tag which instructs the compiler to attempt to optimize the code:

-O"#"

where “#” is a number referring to the optimization level. For instance, “-O0” is zero-th level optimization, i.e., no optimization at all. The Intel Fortran compiler has four levels of optimization (O0, O1, O2, O3), which are related to the degree to which the compiler will change the code from its as-written state. Higher levels of optimization will cause the code to take longer to compile, but often result in greater speed improvements. However, the programmer should generally check that the level of optimization does not change the results of the program, running test cases to verify.

We move on to helping the compiler optimize the code. Generally, the bulk of the computational time for scientific computing is spent in loops, and the foremost issue in loop optimization is loop dependency. The compiler needs to be able to determine that calculations performed in a loop are independent: that is, that an operation on one part of an array within the loop is not dependent on other parts of the array. If the order in which the loop is performed affects the results, then the loop is dependent. For arrays $a$, $b$, and $c$, here is an example of an independent loop:

```fortran
  do i=1,n
    a(i)=b(i)*c(i)
  end do
```

And an example of a dependent loop:

```fortran
  do i=2,n
    a(i)=a(i-1)*b(i)
  end do
```

The second loop is dependent, as each member of the array $a$ depends on another member of the same array.

Although these two loops have a similar number of mathematical operations, the independent loop can typically be much more quickly calculated. During execution, arrays can be retrieved from memory in segments, perhaps 8 or 16 members of each array at a time. With an independent loop, these members can be retrieved together, the operation performed
across all of these members, and then the batch of results is returned to memory. However, for a dependent loop, each loop step requires the computer to fetch a single member of the each of the right-hand side arrays, perform the operation, then return the result to memory. This is repeated across each member of the arrays. The additional ‘fetches’ result in wasted computational time.

A modern compiler such as the Intel Fortran compiler can usually determine dependency for simple loops. If the instructions within the loop are complex, however, the programmer may aid the compiler by instructing it to treat the loop as independent. This is done by inserting the following tag on an empty line directly before the loop:

```fortran
!HPF$   INDEPENDENT
```

We also recommend that the programmer avoid using if-then statements within loops, as this can interfere with the compiler’s ability to determine loop dependency. Instead, one can use the “where” or “forall” constructs, which were introduced in Fortran 90. The proper usage of these constructs is outlined on the IBM website for Fortran 95[1].

Last, for Fortran 90 and later, the syntax for many array operations has been considerably simplified considerably, such that do loops are often no longer necessary. Using the new syntax makes the code easier to read, as well as implicitly informing the compiler of the array operation’s independence. For operations over entire arrays of the same size, we can rewrite the operations as if the arrays were single variables. For instance, consider the multiplication

\[
c(i,j,k) = a(i,j,k) \ast b(i,j,k)
\]

Where \(i = 1, \ldots, x0\), \(j = 1, \ldots, y0\), and \(k = 1, \ldots, z0\). Under the old syntax, this would require three nested loops,

```fortran
do i=1,x0
  do j=1, y0
    do k=1,z0
      c(i,j,k) = a(i,j,k) * b(i,j,k)
    enddo
  enddo
enddo
```

Using the new syntax, we can rewrite this as simply

\[
c = a \ast b
\]
Furthermore, we can specify operations over part of an array index as “start number : end number”, or over an entire index with just “:”. For example, suppose we only wanted to calculate the previous multiplication for first five members of the first index (i = 1, ..., 5), the second member of the second index (j = 2), and for all members of the last index, (k = 1, ..., z0), we would write the code as

\[ c(1:5, 2:2, :) = a(1:5, 2:2, :) * b(1:5, 2:2, :) \]

I note that many of these array practices - simplified syntax, using “where” or “forall” constructs, or declaring loop dependencies - may also help the compiler perform automatic parallelization. I refer the reader to the Intel Fortran compiler handbook[2], which explains multi-threading parallelization by an Intel compiler in further detail.

**A.4 Nested Loop direction**

When it is necessary to construct nested loops, we would like the order of array operation to match the array layout in memory. This speeds the retrieval of the array data from memory during program execution. In Fortran, arrays are laid out in memory such that the first index varies fastest, whereas in C this is reversed. That is, for an array \( a(i,j) \), where \( i=1,2,3, \) and \( j=1,2, \) the sequential layout of the array in memory is outlined in Table A.1,

<table>
<thead>
<tr>
<th>Memory location relative to 1\textsuperscript{st} array member</th>
<th>Fortran</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0</td>
<td>a(1,1)</td>
<td>a(1,1)</td>
</tr>
<tr>
<td>+1</td>
<td>a(2,1)</td>
<td>a(1,2)</td>
</tr>
<tr>
<td>+2</td>
<td>a(3,1)</td>
<td>a(2,1)</td>
</tr>
<tr>
<td>+3</td>
<td>a(1,2)</td>
<td>a(2,2)</td>
</tr>
<tr>
<td>+4</td>
<td>a(2,2)</td>
<td>a(3,1)</td>
</tr>
<tr>
<td>+5</td>
<td>a(3,2)</td>
<td>a(3,2)</td>
</tr>
</tbody>
</table>

Table A.1. Outline of the layout of array members in memory for Fortran and C.

Thus, a nested loop operating over this array in Fortran should iterate over the second index in the outer loop and over the first index in the inner loop: “first index varies fastest”. Likewise, the reverse should be true for nested loops in C: “last index varies fastest”.

**A.5 Documentation and commenting**

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It is universally acknowledged among programmers that the first rule of programming is to always document your code. It is also highly recommended that the programmer not make exceptions to this rule, as it is nearly always easier to document your code as you write it than to return to it later. Documenting the code immediately also helps the programmer not to forget or procrastinate.

However, I would take this further. For scientific programming, I recommend three parts of code documentation, addressing the following questions:

1) What equation(s) are you solving, and why?
2) What algorithm or method are you using to solve these equations? Write down the steps or references that take you from the equations to the algorithm.
3) In the code, what do your variables and functions do?

Typically, the third part is handled via in-code commenting, as well as by making sure that the naming convention used is both easy to understand and well-documented.

All together, these comprise the information that is necessary for someone else to follow your work. It allows them to understand the purpose of your program, to check that your proposed methods are scientifically sound and that your algorithms are appropriate, and to easily examine how you executed those methods within your program.

A.6 Streamlined programming

Last, we might find that some calculations are unnecessary, or can be simplified. Let’s consider three cases:

1) A calculation is needed only rarely. For instance, we might output simulation results after every 100 timesteps, but we also want to output some data which would be unnecessary to compute in the normal process of the simulation. In this case, we would obviously want to only calculate this data for output, rather than at every timestep.
2) A calculation is needed often, but remains the same throughout the simulation. For instance, we might have an array that is specific to a particular simulation, and which is used at each timestep of the simulation, but remains the same from one timestep to the next. We can reduce computation by calculating the array once during the simulation setup and storing it for later use. This comes with a trade-off, however, as it costs extra memory, but the simulations I were generally speed-limited rather than memory-limited.
3) A calculation can be simplified or truncated. For instance, our code has the capability of handling a Landau energy expansion up to the 8th order. However, the simulations in this work used only a 4th-order Landau expansion for BiFeO3. Previously, the program still calculated energy contributions from all terms up to 8th-order, even if the higher-order coefficients were defined as nil. Therefore, the code was rewritten so that the calculation is only performed for non-zero terms.

A.7 Conclusions and Future work

By rewriting our Fortran code in accordance with the principles outlined here, we were able to increase simulation speeds by a factor of 5-10x. In addition, there may still room for significant refinement in some parts of the code. The author is of the opinion that another 2x increase of speed can be obtained by further trimming unnecessary calculations, even without parallelization of the code. All together, these improvements allow us to simulate larger systems, to run test cases much more quickly, and to incorporate other physical effects into our model.
References

Appendix B: An Introduction to the Solution of Plate

B.1 Introduction

We solve the displacement, \(u_k\), defined in a rectangular grid of size \(n_x \times n_y \times n_z\), where \(n_x, n_y\) and \(n_z\) denote the number of gridpoints along directions \(x_1, x_2,\) and \(x_3\) respectively. The grid is continuous in the \(x_1\) and \(x_2\) directions, but discontinuous in the \(x_3\) direction, with discontinuities at the top and bottom surfaces. We define the height of the bottom and top surfaces as \(h_0\) and \(h_1\), respectively.

We refer the reader to work by Li et al\(^1\) for a previous description of the plate solution, and to as Barber and Ting\(^2\) for an introduction to the Stroh formalism for general anisotropy. This work draws heavily from the prior works, and is meant to be an introductory re-explanation.

We will denote the derivative operator as \(\frac{\partial}{\partial x_i}\) or \(\partial_i\). We use the Einstein notation, in which we sum over repeated indices; for example, \(a_{ij}b_j = a_{i1}b_1 + a_{i2}b_2 + a_{i3}b_3\).

For other details about notation, please see the legend.

This guide is broken into four parts:

1. Define the body force equation in terms of a set of 1-D differential equations.
2. Find the set of general solutions for each of the 1-D problems.
3. Apply the boundary conditions to each 1-D problem to get the complete solution.
4. Combine the \( n_x \times n_y \) set of solutions to recover the solution of the entire system.

B.2: Define the body force equation in terms of a set of 1-D differential equations

The displacement \( u_i \) satisfies the condition of body force = 0. That is, the net force along any direction \( i \) is 0:

\[
\frac{\partial \sigma_{ij}}{\partial x_j} = c_{ijkl} \frac{\partial u_k}{\partial x_l \partial x_j} = 0 \quad (B.1.1)
\]

Let’s rewrite the derivative operator \( \frac{\partial}{\partial x_i} \) as \( \partial_i \). Thus, we rewrite equation 1 as

\[
c_{ijkl} \partial_j \partial_i u_k = 0. \quad (B.1.2)
\]

Following the notation of Barber and Ting\(^2\), it is helpful to break up the fourth-rank elastic tensor \( c_{ijkl} \) into parts:

\[
\begin{align*}
Q_{ik} &= c_{i1k1}; \\
Y_{ik} &= c_{i1k2}; \\
E_{ik} &= c_{i1k3}; \\
T_{ik} &= c_{i2k2}; \\
F_{ik} &= c_{i2k3}; \\
G_{ik} &= c_{i3k3}. \\
\end{align*}
\quad (B.1.3)
\]
Note that the elasticity tensor $c_{ijkl}$ satisfies the symmetry relation: $c_{ijkl} = c_{jilk} = c_{klij} = c_{ijkl}$, which implies: $c_{i2k1} = (Y_{ik})^T$; $c_{i3k1} = (E_{ik})^T$; $c_{i3k2} = (F_{ik})^T$. Thus all 9 of these 3x3 matrices are accounted for.

Let us denote a 3x3 matrix made up of $Q_{ik}$ as $Q$. So we further rewrite equation 1 as:

\[
\begin{align*}
(Q \partial_1 \partial_1 + Y \partial_1 \partial_2 + E \partial_1 \partial_3 + 
Y^T \partial_2 \partial_1 + T \partial_2 \partial_2 + F \partial_2 \partial_3 + 
E^T \partial_3 \partial_1 + F^T \partial_3 \partial_2 + G \partial_3 \partial_3) u & = 0. 
\end{align*}
\]

(B.1.4)

In the planes of the film ($x_1, x_2$), the spatial functions $u_k(x)$ is continuous and defined. For those directions, we can transform $u_k(x)$ into Fourier space: $u_k(x_1, x_2, x_3)$ becomes $\tilde{u}_k(k_1, k_2, x_3)$. The differential operators in these directions also transform, becoming linear products of $i = \sqrt{-1}$ and the Fourier-space vectors: $\partial_1 = ik_1$, $\partial_2 = ik_2$.

Let’s break up equation (1.4) by contribution from the remaining differential operator, $\partial_3$ (here $\partial_3$ is highlighted for clarity):

\[
\begin{align*}
\left[ (Q \partial_1 \partial_1 + Y \partial_1 \partial_2 + Y^T \partial_2 \partial_1 + T \partial_2 \partial_2) + (E \partial_1 + F \partial_2 + E^T \partial_1 + F^T \partial_2) \partial_3 \right] \tilde{u} & = 0. 
\end{align*}
\]

(B.1.5)

Defining

\[
W = Q \partial_1 \partial_1 + Y \partial_1 \partial_2 + Y^T \partial_2 \partial_1 + T \partial_2 \partial_2,
\]

and
\[ R = E \partial_1 + F \partial_2, \]  
(B.1.7)

we have now a \( n_x \times n_y \) set of one-dimensional, second-order differential equations:

\[ G \partial^2_3 \tilde{u} + (R + R^T)\partial_3 \tilde{u} + W \tilde{u} = 0. \]  
(B.1.8)

There is one of these problems for each of the k-space vectors.

**B.3: Find the set of general solutions for a 1-D problem.**

In 1-D, we might solve a single equation of the form

\[ ay'' + by' + cy = 0, \]

using its characteristic equation of

\[ ar^2 + br + c = 0. \]

By finding the roots of the above characteristic equation \((r_1 \text{ and } r_2)\) using the quadratic equation, we would have the general solution,

\[ y(x) = d_1 e^{r_1 x} + d_2 e^{r_2 x}, \]

where \(d_1\) and \(d_2\) are unspecified in the case of a general solution, or are constrained to specific values in the presence of boundary conditions. In our case, the problem is multi-dimensional; i.e., the displacement \( \tilde{u} \) is a vector, even though we are solving it along only one direction, \( x_3 \), so the structure of the solution is still similar. The form of a solution is

\[ \tilde{u} = a e^{p x_3}, \]  
(B.2.1)

So that, substituting the solution form into equation (1.8) yields the equation
\[
(Gp^2 + (R + R^T)p + W)ae^{px_3} = 0,
\]

Or equivalently, since \( e^{px_3} \neq 0 \), we obtain the characteristic equation:

\[
(Gp^2 + (R + R^T)p + W)a = 0. \tag{B.2.2}
\]

We solve this equation, finding the roots. In 1-D we use the quadratic equation to solve a 2nd-order polynomial; in multiple dimensions the analogue of the quadratic equation is the non-linear eigenvalue problem. With a 2nd-order differential equation in 3 dimensions, we expect 6 solutions.

A normal eigenvalue problem has the form: \( Bx = \lambda x \), or, equivalently, \( Bx - \lambda x = 0 \), or \( (B - \lambda I)x = 0 \), where \( I \) is the identity matrix. Our non-linear eigenproblem is simply equation 2.2.

We can convert our nonlinear eigenproblem to an ordinary linear eigenproblem by doubling the size (i.e., by “zooming out”, so that the vector size doubles and we construct matrices corresponding to our problem out of \( W, R, G \)). Let us define a new vector, \( b \), as some linear combination of \( a \) and \( p \). For later convenience, we pick \( b \) such that it is related to the out-of-plane stresses, \( \sigma_{l3} \), by \( \sigma_{l3} = be^{px_3} \). Since \( \sigma_{l3} = c_{l3kl} \frac{\partial u_k}{\partial x_l} \), after transforming \( u_k(x) \) into Fourier space \( \tilde{u}_k(k,x_3) \), and using the short form of equations (1.3), it becomes

\[
\tilde{\sigma}_{l3} = (E^T \partial_1 + F^T \partial_2 + G \partial_3)\tilde{u},
\]

Because the form of the solutions is \( v = ae^{px_3} \), by (1.6), and (1.7) we have:

\[
\tilde{\sigma}_{l3} = (E^T_{lk} \partial_1 + F^T_{lk} \partial_2)a_k e^{px_3} + pG_{lk}a_k e^{px_3} = (R^T + pG)ae^{px_3} = be^{px_3}.
\]

Thus:
\[ b = (R^T + pG)a \]  \hspace{1cm} \text{(B.2.3)}

Substituting (2.3) into (2.2), the new linear eigenvalue problem in terms of \( b \) and \( a \) becomes:

\[ pb + (Rp + W)a = 0. \]  \hspace{1cm} \text{(B.2.4)}

If we rearrange equations (2.3) and (2.4) so that all the terms of \( p \) are on the right-hand side, and put them into matrix form, they become:

\[
\begin{pmatrix}
-R^T & I \\
-W & 0
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix} =
\begin{pmatrix}
P & 0 \\
R & I
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
\]  \hspace{1cm} \text{(B.2.5)}

Furthermore, recall \( p \) is a scalar, so we can commute it with the matrix \( \begin{pmatrix} P & 0 \\ R & I \end{pmatrix} \) on the RHS, and invert and carry that matrix over to the LHS:

\[
\begin{pmatrix}
P & 0 \\
R & I
\end{pmatrix}
\begin{pmatrix}
G^{-1} & 0 \\
-RG^{-1} & l
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix} =
\begin{pmatrix}
P & 0 \\
R & I
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
\]  \hspace{1cm} \text{yields}

\[
\begin{pmatrix}
-G^{-1}R^T \\
-RG^{-1}
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix} =
\begin{pmatrix}
P & 0 \\
R & I
\end{pmatrix}
\begin{pmatrix}
a \\
b
\end{pmatrix}
\]  \hspace{1cm} \text{(B.2.6)}

We solve this linear eigenvalue problem using a numerical solver. Since \( R \) and \( W \) are dependent on the Fourier-space vector \( k = [k_1 \ k_2] \), we must solve this for each \( k \), so that we have \( n_x \times n_y \) sets of eigenvectors and eigenvalues.
B.4: Applying the boundary conditions.

For a given $k$-vector, we will have 6 eigenvectors and eigenvalues. Letting $m$ and $n$ range from 1 to 6, we’ll call the $m$th eigenvector of equation (2.4) $\xi_m = \begin{pmatrix} \alpha_m \\ \beta_m \end{pmatrix}$, or in tensor notation,

$\alpha_m = \alpha_{mk}, \beta_m = \beta_{mk}, \xi_m = \xi_{mn},$ where subscript $k = 1, 2, 3$, so that $\xi_{mn} = \alpha_{mk}$ for $n = k,$

and $\xi_{mn} = \beta_{mk}$ for $n = k + 3$.

The eigenvalues are denoted $\rho_m$. Thus, the six solutions of the displacement are:

$$\tilde{u}_m = \tilde{u}_{mk} = \alpha_{mk} e^{\rho_m x_3} \quad (B.3.1)$$

And denoting the scalar linear combination terms as $d_m$, the complete solution is a linear combination of the six solutions:

$$d_m \tilde{u}_{mk} = \sum_{m=1}^{6} d_m \alpha_{mk} e^{\rho_m x_3} \quad (B.3.2)$$

It only remains to find the linear combination of the solutions which satisfies the boundary conditions.

Example (corresponding to the thin film solution):
Let \( u_k = g_k \) on the bottom surface and \( c_{i3kl} \frac{\partial u_k}{\partial x_l} = \sigma_{i3} = h_i \) on the top surface. Like \( u_k \), these boundary conditions will be transformed into Fourier-space in the \( x_1 \)-\( x_2 \) plane:

\[
\tilde{g}_k(k_1, k_2), \tilde{h}_l(k_1, k_2). 
\]

Then a linear combination of the solutions must satisfy:

\[
d_m \alpha_m e^{\rho_m x_3} |_{x_3=0} = \tilde{g}, \tag{B.3.3}
\]

on the bottom surface, and

\[
d_m c_{i3kl} \frac{\partial (\alpha_m e^{\rho_m x_3})}{\partial x_l} = d_m \beta_m e^{\rho_m x_3} |_{x_3=h_i} = \tilde{h}, \tag{B.3.4}
\]

on the top surface, by equation (2.2). This gives us a set of 6 linear equations:

\[
\alpha_{mk} e^{\rho_m h_0} d_m = \tilde{g}_k \tag{B.3.5a}
\]

\[
\beta_{mk} e^{\rho_m h_1} d_m = \tilde{h}_k \tag{B.3.5b}
\]

Solving equations (3.5) by matrix inversion gives us \( d_m \).

**B.4: Combine the \( n_x \times n_y \) set of solutions to recover the solution of the entire system.**

After performing this for each Fourier space vector, we have the complete solution-of-plate for the displacement, still transformed into Fourier space in the \( x_1 \) and \( x_2 \) directions. To recover the complete real-space solution, we collect all the 1-D solutions into a 3-D array, and then perform inverse Fourier transforms on the \( x_1 \)-\( x_2 \) planes, taking \( \tilde{u}_k(k_1, k_2, x_3) \Rightarrow u_k(x_1, x_2, x_3) \).
B.5: Summary

The general algorithm is thus:

1. Setup:

   For each vector \( \mathbf{k} = [k_1 \ k_2] \) in Fourier space:

   a. Develop the \( 6 \times 6 \) matrix
      \[
      \begin{pmatrix}
      -G^{-1}R^T & G^{-1} \\
      RG^{-1}R^T - W & -RG^{-1}
      \end{pmatrix}
      \].

   b. Solve the matrix to find the 6 eigenvalues and eigenvectors that give the specific solutions.

2. Apply the boundary conditions (e.g., at a given timestep):

   a. Transform the boundary conditions into Fourier space.

   For each vector \( \mathbf{k} = [k_1 \ k_2] \) in Fourier space:

   b. Find the linear combination terms, \( d_m \), that will give us the solution that satisfies the boundary conditions.

   c. Get the total 1-D solution as the linear combination of the specific solutions.

3. Collect all the 1-D solutions into a 3-D matrix.

4. Perform inverse Fourier transforms on the \( x_1 \cdot x_2 \) planes to recover the solution in real space.
B.6: Notes

On other uses for this solution-of-plate algorithm:

1. The solution-of-plate may also be applied to other thin film problems, such as finding the electric potential or electric field meeting an arbitrary surface potential or electric field. The solutions would be the 1-D specific solutions satisfying electrostatic equilibrium equation\(^3\):

\[
D_{i,i} = 0,
\]

Where \(D\) is the electric displacement.

On the practical use of the solution-of-plate in phase-field simulations (or any simulation where the solution will need to be calculated multiple times):

1. We recommend that, at a minimum, the \(6 \times 6 \times n_x \times n_y\) eigenvectors and \(6 \times n_x \times n_y\) eigenvalues be stored.

2. If desired, the \(6 \times 6 \times n_x \times n_y\) matrix \((\xi_{mn}e^{pm_{x3}|at\ b.c.})^{-1}\) may also be stored, to simplify the calculation of the linear combination terms,

\[
d_m = (\xi_{mn} e^{pm_{x3}|at\ b.c.})^{-1}(b.\ c.)_n. \text{ Otherwise, } n_x \times n_y \text{ inversions of the } 6 \times 6 \text{ matrices will be needed at each timestep.}
\]

3. Indeed, if space is quite freely available, one may also store the entire set of solutions at each gridpoint; the \((6 \times 3 \times n_x \times n_y \times n_z)\) matrix corresponding to \(a_{mk}e^{pm_{x3}}\), to cut down on computation even further.
2-D Fourier-transform

\[ a(x_1, x_2, x_3) \xrightarrow{\text{becomes}} \tilde{a}(k_1, k_2, x_3) \]

Vector notation:

\[ \mathbf{u} = u_k \]

Fourier-space vector:

\[ \mathbf{k} = [k_1 \ k_2] \]

The general solution:

\[ \mathbf{u} = d_1 \alpha_1 e^{\rho_1 x_3} + d_2 \alpha_2 e^{\rho_2 x_3} + \cdots = \sum_{m=1}^{6} d_m \alpha_m e^{\rho_m x_3} \]

The form of a specific solution:

\[ \alpha e^{\rho x_3} = \alpha_k e^{\rho x_3} \]

Elasticity tensor:

\[ c_{ijkl} \]

Differential operators:

\[ \frac{\partial}{\partial x_i} = \partial_i \quad \text{and} \quad \frac{\partial u_k}{\partial x_i} = \partial_i u_k = u_{k,i} \]

Displacement:

\[ u_k \]

Stress:

\[ \sigma_{ij} = c_{ijkl} \frac{\partial u_k}{\partial x_l} \]

Operate over 1,2,3:

\[ i,j,k,l \]

Operate over 1,..,6:

\[ m,n \]

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References and Recommended reading


VITA

Ben Winchester was born in Gainesville, Florida, on March 31, 1983, the fourth child of Brian Winchester and Deborah Collier. He grew up in north central Florida, where he graduated from high school in 2000 and subsequently attended a few years of community college in his hometown, focusing his studies on Computer Science. In 2003, he moved to Wilmore, Kentucky, to study at Asbury College. After graduating from Asbury in 2006 with a B.A. in Computational Science, he enrolled in the Ph.D. program in the Department of Material Science and Engineering at Pennsylvania State University, spending the next six years of his life working towards his doctorate degree.

Benjamin authored and co-authored six publications during his graduate career. After finishing at Pennsylvania State University, he joined Sandia National Laboratories in Albuquerque, New Mexico, to study grain growth using the phase-field model.