Ferroelectric Thin Film Nanocomposite and Bilayer Characterization through Simulation using the Phase Field Method

by

Blaine Geddes, B.Sc., B.Sc.E.E., M.A.Sc.

A thesis submitted to the Faculty of Graduate studies and Research in partial fulfillment
of the requirements for the degree of Doctor of Philosophy.

Ottawa-Carleton Institute for Mechanical and Aerospace Engineering

Carleton University

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Abstract

Ferroelectric thin film bilayers and nanocomposites are investigated by computer simulation using the phase field method and analytically using thermodynamic models. Domain structures under applied electric field and hysteresis loops are generated by the phase field model for bilayer, porous and nanocomposite ferroelectric thin films. Perovskite materials which undergo a cubic to tetragonal ferroelectric phase transformation, specifically PbTiO_3 , PZT ($\text{PbTi}_x\text{Zr}_{(1-x)}\text{O}_3$), and BaTiO_3 , are considered. The results show that bilayer, porous, and nanocomposite structures can stabilize a polydomain structure.

Thermodynamic theory is reviewed and an analytical model based on available Ginzburg-Landau-Devonshire thermodynamic models is developed and applied to the bilayer systems. Excellent agreement is demonstrated between the hysteresis loops obtained using the analytical model and the simulated hysteresis loops for the bilayer systems.

The nanocomposite structure with weak dielectric inclusion in a ferroelectric matrix is demonstrated through simulation to offer a significant dielectric constant enhancement for both lead titanate and barium titanate by stabilizing a polydomain structure with a significant fraction of in-plane domains present over a wide range of applied electric field. The nanocomposite thin film structure, where the inclusions may be simply voids of controlled size, shape and distribution, is believed to represent a novel technique for

engineering high dielectric constant thin film devices using common perovskite materials. The significant increase in dielectric constant combined with the simplicity of the structure and the fact that common materials are employed make it potentially of strong industrial significance.

The inverse structure of a ferroelectric inclusion in a dielectric matrix is also considered and is shown to not have strong dielectric constant enhancement or tunability properties.

Acknowledgement

I acknowledge the contribution of all researchers in this field before me whose insight and ideas collectively form the great assembly of knowledge without which this meager work would not have been possible. Specifically, I acknowledge the effort, wisdom, and insight of Dr. Andrei Artemev for his many years of work on the physics of phase transformations and the phase field model which laid the foundation for this study.

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List of Symbols

- α : Coefficients in the GLD potential function polynomial
- β : Dimensionless gradient tensor
- δ : Variational derivative or impulse function
- χ : Electric susceptibility
- χ_0 : Electric susceptibility in the paraelectric phase well above the Curie temperature
- ϵ : Strain or strain tensor
- ϵ_0 : Electric permittivity of free space
- ϵ_r : Relative permittivity
- ϵ_{ij}^0 : Stress free transformation strain tensor
- $\bar{\epsilon}_{ij}$: Homogeneous (average) strain tensor
- Φ : Thermodynamic potential
- λ_{ijkl} : Young's modulus tensor
- λ : Electrostatic energy to chemical energy ratio
- θ : Shape function describing a domain of transforming particles.
- σ : Stress or stress tensor or charge density
- σ_{ij}^0 : Fictitious stress corresponding to that stress required to elastically produce the equivalent of ϵ_{ij}^0
- ζ : Mechanical to chemical energy ratio
- B_{ij} : Dimensional gradient tensor
- B : Magnetic field
- C : Capacitance
- D : Electric displacement
- d : Converse piezoelectric coefficients
- E : Electric field
- F : Free energy
- k : Magnitude of the wave vector or dielectric constant
- $\mathbf{k}$: wave vector
- P : Polarization

P_0 : Spontaneous polarization of the ferroelectric

p : Pressure

q : Electrostrictive tensor

T : Temperature

T_c : Curie temperature

U : Energy

u : Displacement or displacement tensor

V : volume

1.0 Introduction

Ferroelectrics are a class of materials that exhibit a state of reversible spontaneous electrical polarization in the absence of any applied electrical field. The polarization is reversed by applying a suitably oriented electrical field. The spontaneous polarization arises due to a phase change in the crystal in which charge is offset from its equilibrium position to rest in a new equilibrium that leaves the crystal polarized. A net dipole moment can only occur through mechanical strain in the crystal, so the polarization is linked to a mechanical strain, which is the phenomenon known as the piezoelectric effect if the strain is linearly proportional to polarization and electrostriction if it is proportional to the square of polarization. To be piezoelectric, a material must have an asymmetric crystal structure, i.e., lacking a center of inversion, which all ferroelectrics have in their ferroelectric state, although they may not be piezoelectric in their paraelectric (non-polar) phase. Physically the piezoelectric effect is merely electrostriction in a polarized crystal such that the square law effect appears approximately linear.

The phase change of a ferroelectric occurs at a temperature point known as the Curie temperature. Above the Curie temperature a ferroelectric material is in its paraelectric phase, where it exhibits no ferroelectric behavior. Cooling below the Curie temperature results in a phase change that produces a spontaneous polarization.

The ferroelectric phase transformation can be categorized as one of two types, order-

disorder or displacive. Displacive transformations occur in crystals which are centrosymmetric in their paraelectric phase and the phase transformation consists of charge displacement to produce a dipole moment in each unit cell. In an order-disorder transformation, each unit cell has multiple stable states of net dipole moment. Random occupation of the states in the paraelectric phase ensures no net macroscopic dipole moment, but the phase transformation results in shifts of charge in each cell such that the dipoles align and the crystal becomes polarized. There are two key distinguishing features of the two types of transformations. The first is that the displacive transformation is associated with a crystal that is non-piezoelectric in its paraelectric state, whereas an order-disorder transformation is typically, but not necessarily, associated with a crystal that is non-centrosymmetric, and therefore is usually piezoelectric, in its paraelectric state*. The second is that ferroelectrics of the order-disorder type tend to have lower dielectric constants as a consequence of the physics of the transformation³.

The spontaneous polarization of the ferroelectric can be controlled with an applied electrical field, which can shift the energy balance so as to cause some alignment of the net polarization vector with the applied field. Contiguous regions within the material having a common electrical polarization orientation are called domains. For a given strain orientation of a region of crystal, the corresponding electrical polarization can have one of two values of 180° opposing states of polarization.

* Tri-glycine sulphate is a notable exception, being centrosymmetric (therefore non-piezoelectric) in its paraelectric phase, but transforming by an order-disorder type of transformation³.

Although the spontaneous polarization of a ferroelectric crystal may be altered by the application of an electric field, the material will have some tendency to remain in its current state of polarization, therefore an energy barrier must be surmounted to change polarization, leading to a hysteresis behavior of the material's polarization versus applied electric field. Since the hysteresis phenomenon is analogous to the hysteresis effect of the magnetic moment which occurs in ferromagnetic materials in response to an applied magnetic field, such materials are termed “ferroelectrics”, despite the fact that they are electrically insulative dielectric materials and in general do not contain any iron.

Of the 32 crystal classes, twenty are piezoelectric. Of these, eleven are pyroelectric, meaning that the crystal is polarized in the absence of an electrical field over some temperature range. The additional requirement defining a ferroelectric is that the spontaneous polarization be reversible. Relatively few pyroelectrics are also ferroelectric. The ferroelectrics can be divided into two broad classifications. The first are orthorhombic or tetragonal crystals in their paraelectric phase and the second are cubic in their paraelectric phase. A common class of ferroelectrics of the second type are perovskites. The ferroelectric phase transformation in perovskites is displacive.

Perovskites¹, are ceramic materials of the chemical formula ABO_3 , where A and B are cations. $BaTiO_3$ is industrially one of the most widely used and most broadly studied perovskite ferroelectric materials, being used heavily as a dielectric material in electrical

¹ The original perovskite was $CaTiO_3$ first discovered in the Ural mountains of Russia in 1839 and named for the Russian mineralogist Perovski.

capacitors. PbTiO_3 and PbZrO_3 are also common ferroelectric materials. PZT, a common piezoelectric material for transducers, is a solid state solution of PbTiO_3 and PbZrO_3 . The solution is identified by weight fraction and denoted as $\text{Pb}_x\text{Zr}_{(1-x)}\text{TiO}_3$. BaTiO_3 and PbTiO_3 have a cubic crystal structure in their paraelectric phase and transform to a tetragonal ferroelectric phase. PZT at a weight fraction of PbTiO_3 above about 50% is also cubic in its paraelectric phase and transforms to tetragonal as a ferroelectric. The research of this work deals mainly with the modeling and domain structures of thin film ferroelectrics that undergo a cubic to tetragonal ferroelectric phase transformation such as BaTiO_3 , PbTiO_3 , and PZT. In particular the domain structure and behaviour of bilayer structures, which is simply a stack of two thin films of dissimilar ferroelectric materials, and ferroelectrics with dielectric inclusions will be considered.

BaTiO_3 has three distinct ferroelectric states distinguished by their crystal structures. Below about 120°C and above about 0°C it is tetragonal. From 0°C to about -90°C it is orthorhombic and below -90°C it is rhombohedral. The paraelectric phase for BaTiO_3 and all other perovskites is cubic, which is a non-piezoelectric phase due to the fact the crystal is centrosymmetric. An elongation of the unit cell along one Cartesian cube axis with corresponding contraction along the other two axes, results in the tetragonal structure. An elongation along a face diagonal of the cube produces the orthorhombic crystal structure and an elongation along the cube diagonal results in a rhombohedral crystal. Since the tetragonal crystal structure of BaTiO_3 is its state at room temperature, it is the primary structure of interest.

The cubic to tetragonal transition for PbTiO_3 occurs at a much higher temperature of around 479°C . The only ferroelectric crystal structure of PbTiO_3 is tetragonal. The high dielectric constants of PbTiO_3 and BaTiO_3 in their paraelectric phase can be understood on the basis of the large size difference between the relatively large barium or lead atoms compared to the relatively small titanium atom, allowing the titanium atom plenty of room within the unit cell (Figure 1.1) to be displaced, hence it can "rattle around" in response to an applied electrical field. The titanium atom also exists in a $4+$ oxidation state, which allows small movements of the titanium ion to result in large changes in polarization.

PbZrO_3 is unique in that its behavior is antiferroelectric rather than ferroelectric. An antiferroelectric material is one which exhibits a ferroelectric-like phase transition as it is cooled below some transition temperature where the crystal undergoes a distortion and loss of symmetry, but which has no spontaneous polarization in the low symmetry phase. The effect can be understood, on the basis of offsetting dipole moments within the molecule produced by the phase change, which exactly cancel leaving no net dipole moment.

Figure 1.1: Barium titanate perovskite crystal structure

An intriguing application of ferroelectrics is for use in a nonvolatile random access electrical memory cell (NVRAM) for computer data storage, where the retained state of polarization of the ferroelectric is exploited as the bit storage mechanism. Achieving competitive densities with a ferroelectric memory cell requires that the individual bit cell be a small region within a thin film that is generally grown heteroepitaxially on a substrate. Information is written to the cell by inducing polarization using an electric field applied between the surface of the film and the substrate, therefore in order that a region of the film have utility as a memory device it must have a polarization component perpendicular to the substrate. For maximal information storage a structure consisting exclusively of vertically oriented domains (c-domains) is ideal. Inhibiting the growth of exclusively c-domains in the presence of an applied electrical field normal to the film is the mechanical constraint of elastic strain at the interface with the substrate, therefore polydomain structures will generally develop that consist of some pattern of horizontally

polarized (a-domains) alternating with c-domains. A comprehensive understanding of the domain morphology that develops in a thin film as the film undergoes its ferroelectric phase transition is vital to engineering the film characteristics so as to maximize the density of regions with a polarization component orthogonal to the substrate and to achieve a reasonably uniform and fine scale distribution of domain types, such that no large region of the crystal is c-domain deficient.

Bilayer ferroelectric materials and other types of ferroelectric composites have potential in engineering high dielectric constant materials for high value capacitors in the form of thin films deposited on a substrate. A bilayer and certain ferroelectric composite structures can have the effect of stabilizing a polydomain structure within the material which can lead to an enhanced dielectric constant. The phenomenon of enhanced dielectric constant is due to the relative ease of migration of domain walls in response to an applied field. Electric susceptibility is by definition: $\partial P / \partial E$, so if the domain structure can be engineered so as to produce a relatively large polarization change for a comparatively small change in the applied field, then the electric susceptibility will have been increased. A material with finely dispersed 180° domains and mobile domain walls will readily permit the conversion of a region of one domain orientation into its polar opposite, thus it will allow a large polarization change for a small change in applied field, hence a high dielectric constant.

A porous ferroelectric can have the same property of polydomain structure stabilization

leading to a high dielectric constant. The stabilizing effect is due to the depolarizing fields created by the internal free surfaces, which for spherical void inclusions will have a continuously changing orientation over the surface of the sphere, which will promote both normal and in-plane components of polarization. The air inclusion will have the lowest depolarizing field of any dielectric inclusion, therefore it can be expected to offer the most dielectric constant enhancement. The further interesting property of the porous ferroelectric material is that the air entrainment may simultaneously reduce the dielectric loss, making it a material with the potential for simultaneously enhancing dielectric constant while reducing the loss tangent, material properties which are normally mutually exclusive. The competing effect to the loss tangent reduction by the insertion of air is the effect of energy expenditure in moving the domain walls of the ferroelectric, an effect not easily quantified by the techniques used in this study, so it is unclear which effect will dominate and the degree to which an air entrained ferroelectric will have a lower loss tangent and whether it will have a lower loss tangent at all.

Stabilizing a polydomain structure within a ferroelectric should lead to a substantial increase in the dielectric constant, perhaps an order of magnitude, which would be significant in engineering high value small form factor capacitors for electrical filters or electrical energy storage. If air entrainment of the ferroelectric can lead to a lowering of the loss tangent and the material retains a dielectric constant enhancement into the microwave frequency region, then such a material can be very significant for engineering microwave components, for example miniaturizing radio frequency filters. Depositing a

porous ferroelectric material as a thin film between metal plates could result in a large value capacitor in two respects: capacitance scales inversely with the plate spacing, so the thin film has a natural capacitance increase associated with it; and the dielectric constant enhancement effect of the domain stabilized porous ferroelectric increases the capacitance in direct proportion to any increase in dielectric constant.

Stabilizing a domain structure during switching could lead to nonlinearities in the polarization versus applied field curve, which would create a tunable device that has a dielectric constant that is a function of the applied field. A device with a voltage controlled dielectric constant would have applications in engineering tunable filters or integrated tuning elements for voltage controlled oscillators.

1.1 The hysteresis loop

Ferroelectrics may be succinctly characterized by their hysteresis loops of polarization versus applied electric field. A sinusoidal time varying electrical signal is applied to the ferroelectric sample while polarization is recorded. Polarization can only be observed indirectly. A standard circuit structure that enables the measurement of polarization is the Sawyer-Tower^[1] circuit illustrated in Figure 1.2. The x-sweep of the oscilloscope in x-y mode is driven directly by the voltage on the device under test. The voltage on the series capacitor is representative of the polarization within the capacitor under test and governs the y-sweep of the plot. That the series capacitor voltage is proportional to the polarization of the ferroelectric sample is simply understood by noting that $V_1 = V - V_x$.

Since V_x varies in proportion to the polarization of the ferroelectric, V_1 must also vary according to the polarization of the ferroelectric.

As with ferromagnetic materials, the energy dissipated in cycling the field applied to the material is determined as the area within the hysteresis loop and the electric susceptibility for a given applied field is determined as the instantaneous slope of the P vs. E curve, hence the hysteresis loop captures both dielectric constant and energy loss in a cycle within a single graph. Figure 1.3 shows a representative hysteresis loop with the switching point (coercive field) denoted as $\pm E_c$.

Figure 1.2: Sawyer Tower circuit for determining polarization versus applied electric field

Figure 1.3: Representative ferroelectric polarization versus electric field hysteresis loop

The objectives for engineering a memory device and for engineering a high dielectric constant material are conflicting. A ferroelectric memory device ideally requires a sharp switching transition and broad enough hysteresis loop to be noise immune. The domain structure should be quite uniform throughout the film with a strong normal component to polarization (c-axis). In-plane domains (a-axis; Figure 1.4) contribute nothing to bit storage as they have an electrically neutral orientation with respect to a switching voltage applied to the surface of the film, whereas the opposite is desired of a memory device.

The typical perovskite ferroelectric has a dielectric constant measured perpendicular to its polarization vector that is much larger than the dielectric constant measured aligned with its polarization, therefore in engineering a high dielectric constant material a predominantly a-domain structure is ideal as the c-domain has a relatively low dielectric constant. In terms of the hysteresis loop, a high dielectric constant material requires a

narrow loop, ideally having zero width, and a steep linear response of polarization versus applied electrical field over a broad range of electric field. For high frequency use, the hysteresis loop of the high dielectric constant material should not appreciably widen as frequency is increased, which implies that the material must have excellent charge mobility.

Figure 1.4 Tetragonal domain types

A common figure of merit for expressing dielectric loss is the loss tangent, which mathematically is determined as the reactive component of electric permittivity divided by the real component of permittivity. Physically, loss in a dielectric or ferroelectric is related primarily to the energy expenditure in displacing ions in the crystal to change the crystal's polarization state. The conductivity of typical ferroelectric and dielectric materials is very low, therefore conduction losses are a negligible component of the dielectric loss. Dielectric loss will typically begin to increase at some high frequency, while dielectric constant will be reduced. At low frequencies ions in the crystal have time to adjust positions in response to the applied field, but as frequency is increased, the lag between polarization and applied field increases, with the result that ions in the crystal

are continuously "chasing" the electric field. The lag means a drop in $\partial P / \partial E$ (electric susceptibility) and a dissipation of energy in shifting charge which never fully aligns with the applied field.

The characterization of a dielectric using a hysteresis loop is predominantly a low frequency technique, due to limitations of the test apparatus. At microwave frequencies resonant structures would be used for measurement of dielectric losses.

1.2 Thermodynamic theory of ferroelectrics

Structural phase transformations can be classified as being either first or second order. A first order phase transformation is an abrupt transition of the crystal symmetry and is characterized by a temperature hysteresis effect and a discontinuity in some measured parameter as the material undergoes a distortion of its crystal lattice. A second order phase transformation is a continuous transition of the crystal symmetry over a range of temperatures and is characterized by a gradual change in the material properties. The ferroelectric phase transitions in barium titanate are first order³. The phase transitions in lead titanate and lead zirconate are weakly first order¹⁵. For a solution of lead titanate and lead zirconate (PZT) at concentrations removed from the pure extremes, the phase transition becomes predominantly second order¹⁵.

The behavior of a ferroelectric material is a property of the thermodynamics of the material, therefore fundamental to building a comprehensive predictive model is an accurate thermodynamic model. The model can be developed by mathematically relating the potential function to measurable properties such as spontaneous polarization, electric susceptibility, or electrostrictive coefficients. The principles involved in developing a quantitative thermodynamic potential model are the same regardless of whether the phase transition is first order or second order, but the shape of the potential function at the Curie temperature depends on the order of the phase transition.

The Gibbs change in free energy for a process at fixed temperature is given as:

$$d\Phi = dH - TdS \quad [1.1]$$

Since no chemical reaction occurs during the ferroelectric phase change, the enthalpy component is composed of only the pressure-volume change of the crystal and the applied electric field interaction with the polarization of the crystal, therefore the Gibbs free energy change, or differential thermodynamic potential, for a constant pressure, constant applied field and constant temperature ferroelectric can be written as:

$$d\Phi(v, P, S) = pdv - EdP - TdS \quad [1.2]$$

For the case of variable temperature and fixed entropy, the Gibbs thermodynamic potential differential becomes:

$$d\Phi(v, P, T) = pdv - EdP - SdT \quad [1.3]$$

Polarization is a conveniently observed property of the ferroelectric and may be regarded as the order parameter for developing an approximation to the thermodynamic potential. For an unclamped crystal with no applied stress, the $p \cdot dv$ term disappears. If temperature is assumed to be fixed, then the thermodynamic potential can be reduced to a function of polarization alone. In general the thermodynamic potential function is unknown, but like any unknown function can be represented as a Taylor series expansion in the independent variable of polarization about some equilibrium polarization P_0^{4*} .

* If the expansion is at T_c , then P_0 is zero for a centrosymmetric crystal.

$$\Phi(\mathbf{P}) = \Phi(\mathbf{P}_0) + \Phi' \mathbf{P} + 1/2 \cdot \Phi'' \mathbf{P}^2 + 1/6 \cdot \Phi''' \mathbf{P}^3 \dots \quad [1.4]$$

Since the polarization of a electric dipole has two opposite states and each state must have equivalent electrical energy this excludes all odd order terms from the expansion, else positive and negative polarizations along the same axis would have different thermodynamic potentials. The assumption here is an unclamped crystal, so the strain effect does not contribute to the free energy, and therefore is not explicitly included in equation 1.4. In the phase field model of the material (Chapter 2), the effect of strain is separately accounted for using microelasticity theory, where the polarization is the order parameter and the transformation strains are proportional to the square of polarization.

Ferroelectrics for which the spontaneous polarization is linearly proportional to the order parameter are termed proper ferroelectrics, as distinct from the much less common improper ferroelectrics in which the spontaneous polarization is proportional to some other physical quantity or to the order parameter raised to some higher power⁴. In general strain in a ferroelectric is proportional to polarization squared, so most ferroelectrics are proper ferroelectrics, but improper ferroelastics.

Dropping the odd terms and recognizing the derivatives may be expressed as arbitrary functions of temperature allows the thermodynamic potential to be rewritten as a function of polarization but generalized to recognize the coefficients as temperature dependent.

$$\Phi(\mathbf{P}) = \Phi_0 + \alpha_1(T) \mathbf{P}^2 + \alpha_{11}(T) \mathbf{P}^4 \dots \quad [1.5]$$

The functions of temperature $\alpha_1(T)$ and $\alpha_{11}(T)$ may each be expanded in their own Taylor series producing the following expansions as functions of temperature:

$$\alpha_1(T) = \alpha_1(T_c) + \alpha_1'(T-T_c) + 1/2 \cdot \alpha_1''(T-T_c)^2 \quad [1.6]$$

$$\alpha_{11}(T) = \alpha_{11}(T_c) + \alpha_{11}'(T-T_c) + 1/2 \cdot \alpha_{11}''(T-T_c)^2 \quad [1.7]$$

The constant term on the $\alpha_1(T)$ expression, $\alpha_1(T_c)$, must vanish at the Curie temperature. To envision the rationale for this, consider the situation of $\alpha_1(T)$ being positive (Figure 1.5). A positive value of $\alpha_1(T)$ at the transition temperature would imply an increase in the thermodynamic potential for small values of P , because $\alpha_1(T)$ is the quadratic term coefficient and the quadratic term dominates over all higher power terms for small values of P , but an increase in the thermodynamic potential for the development of some small amount of polarization is inconsistent with a driving force for a phase change at the transition temperature. For $\alpha_1(T)$ being negative, the thermodynamic potential would decrease for a small disturbance of polarization from the equilibrium value, which would mean that the Curie temperature point would represent a metastable state and the crystal would then have to have a non-zero polarization in its paraelectric phase. Since the case of a non-zero polarization can not correspond to the paraelectric state of the crystal, $\alpha_1(T)$ must vanish at the Curie temperature, for which the necessary and sufficient condition is that $\alpha_1(T_c)$ be zero.

Thermodynamic potential versus order parameter is illustrated in Figure 1.5 for the two cases of a positive and negative constant term in the quadratic term coefficient ($\alpha_1(T_c)$ of equation 1.7) and for both first order and second order phase transitions. At exactly the transition temperature the curve flattens as $\alpha_1(T_c)$ vanishes for both first and second order phase transitions. At temperatures slightly above T_c , the potential function describing a first order phase transition will have three local minima, one at zero, and one at each of the positive and negative spontaneous polarizations of the ferroelectric state at higher energies, which collapse to only the two minima at $\pm P_0$ at a temperature slightly below the Curie temperature, thus supporting an instantaneous jump in polarization from the non-polar phase. As the temperature is lowered from T_c , the P_0 minima become lower in energy. The corresponding potential function describing the second order phase transition will have only the single minimum at a temperature above the Curie temperature with similarly two local minima developing as the temperature is lowered below the Curie temperature. Whether the type of phase transition is first order or second order is merely a subtlety affecting only the coefficients in the polynomial model, but does not affect the structure of the model or its method of derivation.

Figure 1.5: Thermodynamic potential versus polarization for both positive and negative second order terms and the curve shapes for both first order and second order transitions

Reducing the expansion of equation 1.6 to its minimal form by truncating the expression to retain only the first term, which is typical of the thermodynamic potential functions in the literature⁴, yields the following result for the coefficients:

$$\alpha_1(T) = \alpha_1'(T-T_c)$$

$$\alpha_{11}(T) = \alpha_{11}(T_c)$$

Applying these to the thermodynamic potential functions yields an approximation for the thermodynamic potential function where only the quadratic term has a temperature dependence and the expression has the following form:

$$\Phi(\mathbf{P}) = \Phi_0 + \alpha_1'(T-T_c) \cdot \mathbf{P}^2 + \alpha_{11}(T_c) \cdot \mathbf{P}^4 \dots \quad [1.8]$$

Higher order terms are simply constants of the same form as $\alpha_{11}(T_c)$, so extending to the sixth order term and abbreviating $\alpha_{11}(T_c)$ as simply the constant α_{11} and α_1' as simply α_1 yields:

$$\Phi(\mathbf{P}) = \Phi_0 + \alpha_1(T-T_c) \cdot \mathbf{P}^2 + \alpha_{11} \cdot \mathbf{P}^4 + \alpha_{111} \cdot \mathbf{P}^6 \dots \quad [1.9]$$

For the case of an applied electric field, an energy term would be added to the thermodynamic potential function to reflect the energy of interaction of the material polarization with the applied field. The thermodynamic potential function expansion would then become:

$$\Phi(\mathbf{P}) = \Phi_0 + \alpha_1(T-T_c) \cdot \mathbf{P}^2 + \alpha_{11} \cdot \mathbf{P}^4 + \alpha_{111} \cdot \mathbf{P}^6 - \mathbf{E} \cdot \mathbf{P} \quad [1.10]$$

Polarization is a vector quantity so it must have three orthogonal components in a Cartesian system. If each of these components were independent, then equation 1.10 would be sufficient to describe a sixth order thermodynamic potential, however polarization is linked to mechanical strain and a strain along one axis of the unit cell implies a contraction on the other two due to a Poisson effect, therefore, in the case of a cubic to tetragonal transformation, a polarization along one axis tends to inhibit polarization on the other two axes. The effect can be captured mathematically by introducing cross terms into the thermodynamic potential equation, with a term in each

power of P for each possible combination of orthogonal polarizations. The complete expansion then becomes:

$$\begin{aligned}\Phi(\mathbf{P}, T) = & \Phi_0 + \alpha_1 \cdot (T - T_c) \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{12} \cdot (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] \\ & + \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2) - E_i P_i\end{aligned}\quad [1.11]$$

The concept may be extended to higher order, with an eighth order expansion becoming:

$$\begin{aligned}\Phi(\mathbf{P}, T) = & \Phi_0 + \alpha_1 \cdot (T - T_c) \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{12} \cdot (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] + \\ & \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2) \\ & + \alpha_{1111} \cdot (P_1^8 + P_2^8 + P_3^8) + \alpha_{1112} \cdot [P_1^6 \cdot P_2^2 + P_1^6 \cdot P_3^2 + P_2^6 \cdot P_1^2 + P_2^6 \cdot P_3^2 + P_3^6 \cdot P_1^2 + P_3^6 \cdot P_2^2] \\ & + \alpha_{1123} \cdot [P_1^4 \cdot P_2^2 \cdot P_3^2 + P_2^4 \cdot P_1^2 \cdot P_3^2 + P_3^4 \cdot P_1^2 \cdot P_2^2] - E_i P_i\end{aligned}\quad [1.12]$$

The expression of thermodynamic potential as a polynomial in the form of equation 1.11 or 1.12 is known as a Ginzburg, Landau, Devonshire model after those who pioneered the theory.

1.2.1 Applied Stress

To model a ferroelectric material under stress that undergoes a phase transformation, Equation 1.12 could be modified to effectively reinsert the $p \cdot dV$ term of equation 1.3 and introduce the electrostrictive strain energy term. Then 1.12 would become:

$$\begin{aligned}
\Phi(P,T) = & \Phi_0 + \alpha_1 \cdot (T-T_c) \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) \\
& + \alpha_{12} \cdot (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] \\
& + \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2) + \alpha_{1111} \cdot (P_1^8 + P_2^8 + P_3^8) \\
& + \alpha_{1112} \cdot [P_1^6 \cdot P_2^2 + P_1^6 \cdot P_3^2 + P_2^6 \cdot P_1^2 + P_2^6 \cdot P_3^2 + P_3^6 \cdot P_1^2 + P_3^6 \cdot P_2^2] \\
& + \alpha_{1123} \cdot [P_1^4 \cdot P_2^2 \cdot P_3^2 + P_2^4 \cdot P_1^2 \cdot P_3^2 + P_3^4 \cdot P_1^2 \cdot P_2^2] - E_i P_i + \frac{1}{2} \epsilon_{ij} \sigma_{ij} + q_{ijkl} P_k P_l \sigma_{ij} \quad [1.13]
\end{aligned}$$

The tensor q_{ijkl} is the electrostrictive tensor relating polarization to strain.

1.2.2 Piezoelectricity and electrostriction

Piezoelectricity is defined as the property of a crystal to generate an electrical field that is linearly proportional to a strain in the crystal. Electrostriction is that phenomenon of strains which are proportional to the square of an applied field.

$$\epsilon_{ij} = d_{kij} E_k + q_{kl ij} E_k E_l, \quad [1.14]$$

where d_{kij} describes the converse piezoelectric effect and $q_{kl ij}$ is the tensor of electrostrictive coefficients.

Although converse piezoelectricity and electrostriction are considered to be distinct, converse piezoelectricity arises only because of electrostriction, and is really just

electrostriction in a spontaneously polarized crystal. Consider that polarization is approximately linearly related to the applied electrical field with the proportionality constant being the electric susceptibility, therefore the strain tensor could equivalently be written in terms of polarization using different coefficient tensors as:

$$\epsilon_{ij} = d'_{kij}P_k + q'_{klj}P_kP_l \quad [1.15]$$

Let the spontaneous polarization be P_0 and the modification to P_0 caused by some external field be ΔP , then consider a simple one dimensional electrostriction.

$$\begin{aligned} \epsilon &= q'(P_0 + \Delta P)^2 \\ &= q'(P_0^2 + 2P_0\Delta P + \Delta P^2) \end{aligned} \quad [1.16]$$

Since ΔP is just χE , and considering only strains caused by the field E , equation 1.16 could instead be written in terms of the true electrostrictive coefficient as:

$$\epsilon = q(P_0E + E^2) \quad [1.17]$$

An impartial observer would say that there is a strain component linear in the applied field of qP_0E and another related to the square of the field as qE^2 , and ascribe qP_0 to the converse piezoelectric effect, but the physical reality is that it is all electrostriction. Obviously the converse also applies and piezoelectricity is just converse electrostriction

in a polarized crystal.

1.3 Electric susceptibility and the Curie-Weiss law

A critical parameter describing a dielectric material is its electric susceptibility, χ defined as $\partial P/\partial E$, which may be derived from the thermodynamic potential function. From equation 1.11 for a ferroelectric in its ferroelectric state,

$$\partial\Phi/\partial P = E,$$

Differentiating with respect to P gives:

$$\partial\Phi^2(P)/\partial P^2 = \partial E/\partial P, \quad [1.8]$$

$$\text{so } \chi = 1/(\partial\Phi^2(P)/\partial P^2) \quad [1.19]$$

The phase transformation temperature where the ferroelectric transforms from its paraelectric state to its ferroelectric state is known as the Curie temperature, denoted as T_c in equations 1.11 and 1.12. The electric susceptibility of a ferroelectric in its paraelectric state rises as temperature is lowered approaching the Curie temperature. The onset of the transformation to the ferroelectric state causes the ions to become highly mobile as they are shifting to their displaced polarized positions from their neutral locations, which allows any applied field to easily alter the crystal polarization, leading to a high $\partial P/\partial E$ or high electric susceptibility. The behavior follows the Curie-Weiss law for temperatures above the Curie temperature:

$$\chi = \frac{\chi_0}{T-T_c} \quad [1.20]$$

χ_0 is the electric susceptibility value far above the transition temperature, also known as the Curie-Weiss constant.

For temperatures below the Curie temperature, electric susceptibility is given as the reciprocal second derivative of thermodynamic potential with respect to polarization (equation 1.19), while for temperatures above the Curie temperature, the Curie-Weiss law (equation 1.20) applies.

Electric susceptibility is occasionally referred to as dielectric stiffness, following the mechanical analogy with Young's modulus. Electric field takes the analogous role of applied stress, while the material polarization is the impressed electrical strain. Dielectric stiffness relates electric field and polarization as Young's modulus relates stress and strain*.

* electric susceptibility relates a change in polarization to a change in applied electric field whereas Young's modulus relates a change in stress to a change in strain, so more properly electric susceptibility would be analogous to compliance.

1.4 Applications of ferroelectrics

The dominant industrial ferroelectric compounds are BaTiO_3 and PZT. The main use of BaTiO_3 is as the dielectric material in electrical capacitors where it is used as a simple dielectric. Its ferroelectric properties are incidental. PZT is the dominant material used in piezoelectric transducers, where it is valued for its high piezoelectric coefficients rather than its ferroelectricity. The following describes some of the most common applications of ferroelectrics, but most of these do not exploit the reversible spontaneous polarization property directly. The main exception is ferroelectric memories, where the hysteretic behavior is fundamental to the operation of the device.

1.4.1 Ferroelectric memories

Conceptually, a ferroelectric memory cell may be constructed by simply substituting the dielectric in the capacitor of a dynamic random access memory (DRAM) cell with a ferroelectric material. A 1T-1C DRAM cell is shown in Figure 1.6. The FET has very high impedance in its off state and the capacitor has low internal leakage, so a charge placed on the capacitor can remain for some relatively "long" time (typically milliseconds). Because of the finite leakage, regular refresh is required. A refresh cycle consists of reading the memory element by addressing its word line and bit line, then allowing the current to flow from the capacitor into some load resistor. The voltage

developed across the load indicates the state of the memory and that value is written back to the element to refresh its state. The circuitry to perform the refresh operation is normally included in the DRAM chip. Any normal read operation is destructive so the state of the memory must be restored after reading.

Figure 1.6: 1T-1C DRAM cell element⁵¹

If the dielectric material of the capacitor were replaced with a ferroelectric material and a bipolar voltage that exceeded the coercive field of the ferroelectric were available to be applied to the plates, then the ferroelectric could be toggled between its two polarization states. The polarization of a ferroelectric will remain in the absence of an applied field, so such a memory element would be non-volatile, would not require refresh, and the read operation would be non-destructive.

The competing non-volatile memory technology is electrically erasable programmable read-only memory (EEPROM). If the EEPROM is programmed by writing large blocks of data at once, then it is called a Flash EEPROM. EEPROM uses an active element for

storage rather than a capacitor. In a typical EEPROM cell, the active device is a unique type of dual gate FET where one gate is fully insulated (floating gate). The other gate is the control gate and performs the function of controlling the conductivity of the channel region as in a standard single gate FET. Schematically the floating gate FET is illustrated in Figure 1.7. For relatively low voltages applied to the control gate, as would be applied in its read-only mode, the conductivity of the channel is dependent on the charge on the floating gate. The floating gate becomes charged by applying an elevated voltage to the control gate. At a sufficient potential between the control gate and the channel, the control gate can dominate the behavior of the device, so that the channel becomes conducting or is pinched-off independent of the state of charge of the floating gate. The floating gate is separated from the channel by only a very thin oxide layer, so electrons can jump on or off the floating gate during programming. Once programmed, the floating gate maintains its charge indefinitely and it is this charge that defines the stored state of the memory. The obvious drawbacks to Flash as non-volatile storage are that a high programming voltage is required and an active element is required as the storage element, versus simply a capacitor as is the case for DRAM.

Figure 1.7: Floating gate MOSFET used as the storage element in Flash EEPROM⁵¹

1.4.2 Piezoelectric transducers

The piezoelectric property of ferroelectrics is exploited in acoustic transducers. The piezoelectric effect is the development of an electrical field in the material in response to a mechanical strain, which enables its use as an acoustic detector. The application of an electrical field also results in a mechanical strain for a piezoelectric material, which is known as the converse piezoelectric effect and enables the use of the material as an acoustic transmitter. A common application is the transducers used for ultrasound imaging, which are typically PZT because of its relatively high piezoelectric response.

Surface acoustic wave (SAW) filters use a piezoelectric substrate. The substrate is excited by an electrical signal applied to interdigital electrodes of specific spacing so as to achieve a resonance effect for the center frequency of the filter. The length, spacing, and number of electrodes determine the frequency response of the filter. The acoustic wave that is propagated through the filter is detected by a set of electrodes at the output of the SAW device and converted back to an electrical signal. SAW devices have a finite impulse response characteristic identical to that of a tapped delay line digital filter structure. SAW filters are used at HF and VHF frequencies where sampling rates would prohibit the use of digital filters.

The piezoelectric effect in ferroelectrics also enables their use in sensors such as accelerometers and displacement gauges. Piezoelectrics can also be used as actuators.

The control valve in an inkjet printer head is a piezoelectric material as are some newer fuel injectors for diesel engines. Atomic force microscopes typically use piezoelectric actuators for precise positioning of the sample in the x-y plane while scanning and in the z plane to maintain constant force between the probe tip and the sample. The piezoelectric can provide very accurate fine scale positioning that is proportional to an electrical signal, which makes control relatively simple.

All ferroelectrics have a strong piezoelectric characteristic in their poled state, but it is important to note that not all piezoelectrics are ferroelectric. A common example of a non-ferroelectric piezoelectric is quartz, which is used for its piezoelectric properties in engineering electromechanically resonant crystals for frequency control.

1.4.3 Capacitors

The electrical capacitor industry uses large quantities of barium titanate because of its high dielectric constant. The fact that barium titanate is a ferroelectric is not directly fundamental to choosing it, but its low cost, high dielectric constant and the established infrastructure built around it make it a preferred capacitor dielectric material for ceramic film capacitors.

Exploiting the ferroelectric property as a matrix for containing dielectric (non-

ferroelectric) inclusions that may stabilize a domain structure for certain sizes and distribution of inclusions such that the dielectric constant increases is a topic that is investigated by this thesis research. If such an effect can be demonstrated for barium titanate films, the implications for the electrical capacitor industry are significant.

1.4.4 Ferroelectric liquid crystals (FLC)

Liquid crystal molecules exist which have both chirality and spontaneous polarization. Their ferroelectric property allows them to be easily switched in orientation by an applied electrical field. Their optical chirality allows them to be oriented so as to control the passage of plane polarized light, which is the basic principle behind liquid crystal displays. FLC based LCD displays offer advantages of speed and resolution over non-ferroelectric LCDs.

1.5 Thin film effects

For incorporating in an integrated circuit, ferroelectrics in the form of a thin film are required. Thin films show phenomenon not observed in bulk form. Thin film specific effects include capacitance reduction due to a low permittivity interfacial layer at the surface contacts, proportionally large domain wall energy, which can result in domain pinning, and the ferroelectric limit below which ferroelectricity vanishes. For epitaxially grown films, lattice mismatch at the film to substrate interface produces elastic strain effects that strongly influence the domain structure. The same interfacial effects influence the domain structure in bilayer systems. Any surface interfacial effects become proportionally more significant as the film thickness shrinks.

1.5.1 Surface interfacial layer

When a ferroelectric material is metallized, the contact between the ferroelectric and the metal creates a Schottky barrier analogous to that which forms between a semiconductor and a metal³⁸. When a metal and a semiconductor are brought into contact, a junction is formed due to a difference in the Fermi energy levels in each material. The Fermi level is the electron energy level at which 50% of the electrons can be expected to have lower energy and 50% can be expected to have higher energy⁴⁸. The Fermi levels will not abruptly transition at the contact surface, but will transition over some region of space, leading to a polarization at the junction. The separation of charge becomes a junction

capacitance. The electrical potential necessary to overcome the junction potential is known as the Schottky barrier.

The junction capacitance is analogous to the depletion region capacitance in a semiconductor p-n junction. The metal-semiconductor junction has rectifying properties just like the p-n junction. Metal-semiconductor diodes are known as Schottky diodes and have the advantage of a low forward voltage drop and faster switching because of their reduced parasitic capacitance. Their disadvantages are relatively high leakage currents and low reverse voltage ratings.

Titanate Ferroelectrics act as weak natural semiconductors due to impurity substitution throughout the crystal and oxygen deficiencies primarily at the surface. Impurities typically result in a p-type semiconductor characteristic because the substitution is usually of a lower valence atom. Na^+ substitutes for Pb^{2+} , Fe^{3+} substitutes for Ti^{4+} . Oxygen deficiency creates an n-type characteristic by removing the electron receiving oxygen atom³⁸.

For a parallel plate capacitor the capacitance scales in direct proportion to the plate area and inversely to the thickness.

$$C = \frac{k \cdot A \cdot \epsilon_0}{d}$$

For bulk dielectric materials that have been metallized the junction is very narrow, on the order of only a few atomic layers, therefore the capacitance is large and typically can be ignored. As the thickness of the dielectric is made very small, the junction capacitance can become significant. A thin film capacitor can be modeled as three capacitive elements in series; the junction capacitance, C_j , at both surfaces and the capacitance of the dielectric, C_d . The net capacitance is:

$$\frac{1}{C} = \frac{1}{C_j} + \frac{1}{C_d} + \frac{1}{C_j}$$

In bilayer and multilayer ferroelectric thin film structures, a parasitic capacitance can be expected to form at the interface between the layers, so the overall capacitance of the heterostructure will be reduced.

1.5.2 Domain walls and the ferroelectricity limit

The energy of the domain wall sets a limit on the fineness of the domain structure. A spontaneously polarized structure in zero field must be electrically neutral overall and, in the absence of surface energy effects, would be electrically neutral on the scale of

individual unit cells. Preventing such an atomically fine dispersion of randomly oriented dipoles is the surface energy associated with the lattice distortion that accompanies polarization. Domains represent an energy minimum that allows macroscopic electrical neutrality while tolerating some surface energy at the domain interface.

The interface region between domains has a finite thickness as the polarization vector gradually adjusts over some finite length scale. In experimental studies on PbTiO_3 single crystals, 90° domain walls have been determined to be approximately 1.0 ± 0.3 nm thick³⁸. The mobility of 90° domains is higher than the mobility of 180° domains, which is intuitively obvious from the fact that to migrate the 180° domain wall requires complete inversion of the polarization vector, whereas to migrate 90° domain walls requires only 90° rotation of the polarization vector.

The finite domain wall thickness and the surface energy of the domain interface implies that a size limit exists below which ferroelectricity vanishes. This limit is known as the superparaelectric limit (SPE). First principles studies suggest that the SPE should be on the order of 2.4 nm for films sandwiched between conducting electrodes³⁹. In support of such a small SPE, experimental studies on $\text{Pb}_{0.2}\text{Zr}_{0.8}\text{TiO}_3$ films have demonstrated stable ferroelectricity on films as thin as 4 nm⁴⁰.

The energy of domain walls also contributes to reduced domain mobility in extremely thin films or very small volumes leading to the idea of domain pinning in very small regions as could occur within a nanocomposite material. The concept is consistent with the observation of the scaling of coercive field with domain size. Experiments establish that the logarithm of the coercive field rises approximately linearly with a logarithmic reduction in thickness of the film³⁸.

1.6 Phase Field Modeling of ferroelectrics

Modeling the ferroelectric phase transformation and the domain evolution can be done by accounting for all energy effects, and determining the state of minimum energy. The components which comprise the energy of a crystal undergoing a ferroelectric phase transformation are the chemical energy as described by the Devonshire polynomial² expansion of thermodynamic potential, elastic strain energy developed internally in the crystal due to the evolution of its domain structure, the electric field effect of dipole interaction between the developing domains, and the surface energy between domains.

Chemical energy is a purely homogeneous effect of the bulk crystal independent of domain morphology and can be described by the Ginzburg, Landau, Devonshire polynomial expansion². Elastic strain energy and electrical dipole interaction energy are field effects and depend on the state of the domain structure of the entire body, therefore determining the strain and dipole interaction energies requires the solution of differential equations in three dimensions at each chosen point in time during the transformation process. Surface energy is only locally dependent on domain morphology and is determined through a gradient expression.

In this work a phase field model (PFM) is adapted to ferroelectric modeling. The PFM is a computational technique originally developed for modeling phase transformations in solids for the purpose of predicting the evolution of the phase fields and has been broadly applied to the study of solidification problems. If the effects of elastic strain energy are

incorporated as would occur in physical phase transformations then it can be used to predict domain evolution in a solid state phase transformation such as the martensitic transformation, where each of the domains represents a unique geometric variant of the transformation⁵⁶. In a solid state phase transformation, strain energy is a dominant effect and is incorporated in the PFM using microelasticity theory⁵, where each strain variant of the transformation is represented by an order parameter and the order parameter is merely an arbitrary quantity with some defined association to the phase transformation strains.

In extending the PFM to modeling the ferroelectric phase transformation, the additional complexity of electrical interaction between domains must be considered. The problem of solving for the force field due to the distributed dipoles of the domains can be approached in manner analogous to that of microelasticity theory as both elastic strain energy and electric dipole interaction energy are defined by very similar differential equations. The electrical variants of the transformation may be represented by their polarizations. For a ferroelectric transformation, polarization and strain are linked, therefore the polarization can take the role of the order parameter in describing both the electrical and mechanical artifacts of the phase transformation. The electrical field effect is the dominant effect, being so dominant for the perovskite ferroelectrics of PbTiO_3 , PbZrO_3 and BaTiO_3 considered here that elastic strain energy becomes almost negligible by comparison, although elastic strain effects can have significant influence on the domain structure evolution in some circumstances⁴⁹.

The fourth energy component to be considered is gradient energy, or the energy of the transition between domains, which is a surface energy effect due to the misalignment of transformed crystal regions at a domain boundary. The gradient energy term is difficult to quantify, but is typically very small relative to the other transformation driving forces.

The PFM is similar to other numerical computational techniques, such as the finite element method, in that it requires the body being modeled to be subdivided into smaller regions (elements). The PFM solves an energy minimization problem for the entire assembly of elements using Fourier transforms to perform calculations in both real space and reciprocal space. The PFM recursively applies the time dependent Ginzburg-Landau equation to update the transformation state, where the update to the order parameter (polarization) at each time step is equated to the negative of the variational derivative of free energy with order parameter.

$$\frac{\partial P}{\partial t} = \frac{-\delta F}{\delta P}$$

The free energy is determined as the sum of chemical energy, strain energy, dipole interaction energy and surface energy at each step in time. After some number of iterations the total energy state should converge to its equilibrium value and the output of the model is the polarization state. The advantage of the PFM is several orders of magnitude improvement in execution speed relative to a finite element method based

approach.

Since the PFM uses a Fourier based mathematical approach, it is inherently periodical so the system modeled is not a single system in isolation, but an infinity of such systems with each confronting its image in each dimension. The elements are simple cubic elements. Cartesian axes are used. The natural system size is an integral power of 2 in each dimension, due to the nature of the fast Fourier transform, but the dimensions are not constrained to be equal.

Establishing a length scale for the domain structures produced by the PFM is only crudely approximate as there is no absolute reference of size in the model. The only size reference is to compare the structures produced to some known real structures and infer a length scale by comparison. For ferroelectric domains the most convenient point of reference is the estimated domain wall widths. By noting domain wall widths produced in simulation and comparing with predicted or measured domain wall widths, a grossly approximate estimate of the size of a cube element may be determined, from which the system size can be approximated to within a factor of a few times.

1.6.1 Alternative modeling techniques

The PFM is very computationally efficient compared to other modeling techniques, but it has the drawbacks of periodical boundary conditions; Fourier transform constrained system sizes (powers of two) in which the surfaces must all be flat and at right angles;

and time and length scales which can be only vaguely inferred. The PFM also assumes fluctuations in strain and polarization decay to zero at its boundaries, which will be violated somewhat for all systems with a domain structure. Systems with large inclusions are likely to have significant fluctuations in strain and polarization at the system boundaries.

The PFM is a mesoscale technique in which the elements are assumed large enough that fluctuations on a unit cell level are insignificant but the elements are small enough that they represent domains with sufficient resolution. Combining this with the upper limit on system size for reasonable computational cost arrives at a narrow range of system sizes for which the PFM is applicable.

Atomistic modeling is applicable to the modeling of effects on a smaller scale than PFM. For modeling a single molecule or a unit cell, the low level first principles (ab initio) technique of density functional theory (DFT) in which each electron orbital is modeled can be applied. DFT is computationally very expensive and is limited to a few atoms or tens of atoms. At a higher level, simplified models of individual atoms are used to form the elements of the model and the system can be some assembly of unit cells. Two main approaches are used for multi unit cell models, the shell model and the effective Hamiltonian⁴¹.

The shell model captures the atom as a massive core surrounded by a massless sphere of charge linked to each other by springs. All charges in the model interact for as many atoms as are modeled. Input parameters on which the simplified parameters are based can be derived from DFT. The shell model approach has been used to correctly predict phase diagrams, predict surface properties and examine ferroelectric superlattices in perovskite materials⁴¹. The system size is limited by what is computationally reasonable, which makes modeling a system large enough to predict domain evolution challenging.

The effective Hamiltonian approach uses the Hamiltonian principle of classical mechanics in modeling the atom. The starting point is determining the sum of kinetic and potential energies of the atoms, which can also be determined using DFT. The effective Hamiltonian technique has been applied to the study of the ferroelectric phase transitions in BaTiO₃, PbTiO₃ and to the study of the phase boundaries in PZT, where it confirms experimental results and provides some insight on fluctuations and their dynamics and stability⁴³. The effective Hamiltonian approach is limited to system sizes similar to that of shell models and is not suitable for modeling domain evolution or domain mobility.

Finite element analysis can be used to determine strain and electrostatic field in continuum bodies and it does not suffer from the limitations of the phase field model in that the object shape and boundary conditions may be arbitrary, voids can be easily incorporated, and there is no implied condition of zero surface fluctuations in the field

quantities. However, finite element analysis for mesh sizes comparable to what is feasible with PFM is orders of magnitude more computationally expensive. A single or a few solutions for an instant in time could be performed, but temporal evolution applying the Ginzburg-Landau equations would be prohibitive for similar system sizes.

Finite element analysis has been used to model polycrystalline ferroelectrics under electrical and mechanical load under the assumption of some imposed very simplified and artificial random domain structure⁴⁴. The system size used by Pathak and McMeeking was small compared to PFM works and the domains were coarse (6 elements representing plus and minus for each orthogonal polarization direction). The thermodynamics of the phase transition was not modeled as the interest of the researchers was domain mobility of an established domain structure. Despite the limitations, the FEM reproduced well qualitative features of ferroelectric switching⁴⁴.

1.7 Experimental works

Ferroelectric thin films have been imaged by atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM), but obtaining complete three dimensional maps of the through thickness domain structure is challenging. X-ray diffraction can more easily provide relative domain fraction balances, but without details of structure or size⁹. Domain structures have been mapped experimentally in PZT for films as thin as 70 nm using piezoforce microscopy (PFM) and show the presence of "herringbone" domain structures with widths as small as about 8 nm⁶. HRTEM images in 450 nm single crystal PZT films show clearly c/a twinned domain structures (Figure 1.8)⁷.

Figure 1.8: Schematic representation of a domain structure map obtained on a 450 nm PZT (Zr/Ti = 40/60) film on a Ti substrate by HRTEM imaging⁷

PFM imaging is a variant of AFM in which the conductive probe tip has a voltage applied. Any converse piezoelectric effect in the sample in response to the applied voltage will be registered as a variation in surface topography as the sample is scanned. For a film of a tetragonal ferroelectric of known orientation, three PFM scans will record polarization. One vertical scan determines P_z and two orthogonal lateral scans will determine P_x and P_y , which is sufficient for a topographic map of the domain structure.

A PFM study applied to imaging PZT thin films from 100 nm to 300 nm thick on a GaN substrate shows domain structures that depend on the sample thickness, being strongly a-domain oriented for the thinner films and c-domain oriented for the thicker films⁸. Another PFM study⁴⁵, imaged nanograins of PbTiO_3 with an average diameter as small as about 40 nm and found that they contain a domain structure of predominantly 90° a-domains with c-domains being absent in the 40 nm particles. These were not thin films, but rather discrete particles prepared by chemical solution deposition on a Pt/Ti/SiO₂/Si substrate. Images of nanograins as small as 20 nm were attempted, but it was inconclusive whether they were multidomain or single domain due to the limit of resolution of the PFM technique. The probe tip used had a radius of about 10 nm. Images of the larger grains, greater than about 60 nm in size, show a varied multidomain structure including both a-domains and c-domains.⁴⁵

Contradicting the result of small nanograins being predominantly 90° a-domains is the

work of reference 46, where a similar experiment was carried out on nanograins also using chemical solution deposition on a Pt/TiO₂/SiO₂/Si substrate which found that 180° domains dominated in isolated nanograins, but in dense polycrystalline films 90° domains dominated. The technique was able to measure grains as small as about 12 nm diameter and 4 nm height. Below about 20 nm diameter, the grains showed no piezoelectric effect, indicating this may be a size limit.

Figure 1.9 Topographic domain images. "(a) shows 11 PTO grains of sizes between 100 down to 20 nm indicated by the circles. In the line scan over the grain denoted with an arrow, shown at the bottom, the size of the grains can be determined. In the PFM images (b) in-plane and (c) out-of-plane piezoresponse the grain of the size of 20 nm is not visible leading to the assumption they do not have any permanent polarization"⁴⁶

A study on 0.5 - 2.0 μm BaTiO₃ films heteroepitaxially grown on MgO using chemical vapor deposition showed a domain structure that varies through the film thickness⁴⁷. The samples were sectioned and polished to produce a domain dependent surface topography.

AFM was used to image the sections to obtain a series of through thickness pictures of the domain morphology. The film was polydomain with an area fraction of about 0.5 c-domain near the surface transitioning to predominantly a-domain near the substrate. The dominance of the a-domains at the substrate implies a tensile strain against the MgO substrate. Domain dimensions as small as 15 nm were clearly resolved. The study exemplifies the difficulty in obtaining a three dimensional image map of domains in thin films. Surface topography alone is insufficient as the domain structure can vary greatly through the film thickness. It also demonstrates the important role of elastic interactions in influencing domain morphology.

The virtual approach of software based modeling, despite its limitations and approximations, can provide a useful qualitative assessment of the domain structures that develop especially in difficult to fabricate materials such as composites. Film thickness, inclusion size, or volume fractions for composites are easily varied. Relative strengths of electrical, mechanical, and thermodynamic effects are easily adjusted, so that a prediction of the approximate effect can be obtained prior to depositing and imaging real samples.

1.7.1 Depositing Thin Films

Thin film deposition technologies include chemical vapor deposition (CVD), chemical solution deposition, sputtering and pulsed laser deposition (PLD). Sputtering and PLD are known as physical vapor deposition (PVD) technologies. Sputtering has two main variants, DC sputtering and RF sputtering. Only RF sputtering is suitable for dielectric

materials.

Sputtering involves bombarding a target with ions to eject atoms from the material. The impinging ion imparts energy to the surface atoms via elastic collision, causing some of the atoms of the target to be ejected. The sputtering gas is typically an inert gas such as argon. DC sputtering involves holding the target at a high negative DC potential with respect to the substrate in an environment of high vacuum. The sputtering gas is admitted between the substrate and the target, so it becomes ionized by the glow discharge of electrons from the target knocking loose electrons of the gas. The resulting positive ions of the sputtering gas are accelerated towards the target by electrostatic force. The collisions with the target allow atoms of the target to be dislodged. Some of the dislodged atoms have momentum in the direction of the substrate and will reach the substrate growing a film one atom at a time. The drawback of DC sputtering is that the cathode must be a conductor in order to allow glow discharge, therefore it is not useful for the sputtering of dielectric materials.

RF sputtering circumvents the problem of requiring a conductive cathode target. With an oscillating field applied of sufficient frequency, electrons oscillating in the glow region can acquire enough energy to cause ionizing collisions. Electrons are more mobile than the atoms of the target, so the target still acts as a cathode, providing the source of electrons to knock electrons free from the gas and the process is then the same as DC sputtering.

Sputtering is a relatively low deposition rate process, but the yield can be improved by introducing a magnetic field. The process is then referred to as magnetron sputtering. The magnetic field alters the path of electrons from the cathode causing them to follow a bent or helical path which results in more collisions with gas molecules and improves sputtering yields.

A technology similar to sputtering is pulsed laser deposition (PLD), where instead of an ion stream bombarding the target, a laser beam is focused on the target, which results in a complex discharge consisting of electrons, ions, atoms, molecules, and clusters of molecules from the target. The plume of particles expands in the vacuum. Some of the particles settle on the substrate. The basic setup is conceptually simple, consisting of only a target, a focused laser beam, and a substrate contained within a vacuum chamber.

Chemical vapor deposition involves introducing reactants as gases to a heated chamber and allowing them to react over the substrate. A product of the reaction is a solid that is deposited on the substrate. Volatile byproducts are typically produced also which are removed by gas flow. CVD may be carried out at atmospheric pressure or at some much lower pressure. Variants of CVD exist which employ additional means to increase the reactivity of the precursors. Plasma enhanced CVD uses a plasma to enhance the chemical reactivity of the gases. Hot wire enhanced CVD uses a hot filament to enhance

the reactivity of the gases.

Chemical solution deposition involves up to four basic steps: (1) the synthesis of the precursor solution, (2) deposition by spin casting or dip coating (3) low temperature heat treatment for drying, pyrolysis of unwanted organics, and the formation of an amorphous film (4) a higher temperature heat treatment for crystallization and densification of the coating. Sol-gel is one of the most common types of chemical solution deposition. The process starts with a liquid solution (the sol) which reacts to produce a colloid of dispersed particles in the solvent, which ultimately become linked together as a polymer in solution (the gel). Drying drives off the solvent. Firing is often done to further improve the mechanical properties of the film. Sol-gel uses organic solvents. Metal organic decomposition (MOD) is a variant on the sol-gel process where the solvent is a metal organic compound which reacts to ultimately deposit the metal or some compound of the metal on the film.

1.8 Objectives of this research

This work focuses on applying the phase field model to simulate domain structure, hysteresis behaviour, and electric susceptibility in ferroelectric bilayer thin films and nanocomposite (matrix with spherical inclusion) ferroelectric films to test the hypothesis that the dielectric constant may be enhanced in such bilayer and composite structures.

The materials that are modeled are $\text{Pb}_{0.5}\text{Zr}_{0.5}\text{TiO}_3$, PbTiO_3 , and BaTiO_3 , although, as is typical of computational materials science, the results are expected to be of a general and qualitative nature.

2.0 The Phase Field Model

The PFM is a well known computational method and has been applied to the study of a variety of problems including solidification^{54,55}, phase transformations^{5,55}, phase transformations with inclusions⁵⁶, and to the study of domain structures in ferroelectrics^{49,52,53,57,58}. The phase field model (PFM) as adapted to the modeling of ferroelectric phase transformations predicts the temporal evolution of the spontaneous polarization vector, by applying the time-dependent Ginzburg-Landau (TDGL) kinetic equation:

$\partial P_i / \partial t = -L \cdot \delta F / \delta P_i$, where L is the kinetic coefficient, P_i is the polarization vector, and

F is the free energy

Computationally, the essence of the model consists of simple recursion. The variational derivative of the free energy expression with respect to polarization produces a rate of change vector for the polarization which is integrated over the simulation time step to produce an increment vector for the polarization. The update to P allows a new free energy term to be computed, which is then differentiated to produce another incremental rate of change for P and so on. Assuming constant applied fields, the program continues recursively until equilibrium is established where energy values may be observed to have converged to some relatively static level.

The model can also be used with dynamic fields, in which case equilibrium is never

completely established, instead the energy values are constantly adapting to a varying field. It is this approach that is most convenient for obtaining a simulated hysteresis loop, but the caveat is that inaccuracies can be introduced because only one iteration of the TDGL kinetic equation is performed for each update to the applied field, so for any value of the stimulus, the system can not fully settle.

For modeling ferroelectrics, the polarization vector acts as the order parameter describing the transformation. A phase transformation is said to be proper if some observable parameter is linearly proportional to the order parameter. For a ferroelectric phase transformation the key parameter is polarization, so for a proper ferroelectric, polarization is linearly proportional to the order parameter. Since the order parameter is a parameter of atomic rearrangement that is not easily directly quantified, the polarization may be taken directly as the order parameter in the thermodynamic model. In perovskite ferroelectrics, the strain is related to polarization squared, so with respect to strain the perovskite ferroelectric phase transformation is improper.

A strong component of driving force in solid state phase transformations is elastic strain energy, so a domain morphology will tend to evolve that is most optimally strained under the influence of the stress field in the surrounding matrix. Gradient (interfacial) energy, and the applied stress or overall boundary constraints also influence the morphology. To model a ferroelectric transformation the additional complexity of electric dipole interactions must be taken into account. The electric field effect is typically much larger

than the elastic strain energy effect, so it is mandatory that it be included in the model.

The four energy effects included in the PFM are: elastic strain energy, dipole-dipole interaction energy, gradient energy, and chemical energy. The derivation of the equations describing these energies are discussed below.

2.1 Derivation of the Elastic Strain Energy Expression

The original development of the elastic strain energy expression from microelasticity theory is contained in reference 5. The following is based on that derivation, expounding upon some points where that detail was merely implied in the original work.

2.1.1 Basic Assumptions and Method

The physical foundation for the development of the elastic strain energy equations of the computational model is based on a set of fairly simple principles of a multiphase mixture applied in a set of simple thought experiment steps. Two key assumptions in this model should be noted:

- 1) Homogeneous elastic modulus. All regions of the sample and all phases of the

multiphase mixture must have the same elastic modulus.

- 2) The average length dimensions of all particles are small compared to the overall system dimensions.

Consider some volume of crystal of parent phase and imagine the transformation to occur by the following steps.

Step 1. Arbitrarily choose a particle of the parent phase and cut this particle from the parent phase. If it is large enough such that its surface area to volume ratio is sufficiently small, the interfacial energy associated with this can be neglected and the system energy remains unaffected.

Step 2. Let the particle transform to its new phase in the absence of any boundary constraints. This will result in a strain for the new phase relative to the untransformed parent phase, but this strain will be stress-free, hence it will have no strain energy. Let this shape transformation be described by a strain tensor, ϵ_{ij}^0 .

Step 3. Apply a boundary stress to the transformed particle such that its original shape is restored. The strain associated with this will be exactly the negative of the homogeneous transformation strain of Step 2 and by Hooke's law, the stress required will be

$\sigma_{ij} = -\lambda_{ijkl} \cdot \epsilon_{kl}^0$, where λ_{ijkl} is the general 81 component elastic modulus tensor. The strain energy stored in the particle becomes:

$\Delta U_{\text{self}}(\mathbf{p}) = 1/2 v_p \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0$, where v_p is the volume of the particle.

Now suppose we have multiple particles all of the same size and shape. Since the particles are identical, all particles of like geometric variant of the phase transformation will have the same restoration strain energy*.

So, letting $V_p = N_p v_p$, where N_p is the number of particles of any one geometric variant (the pth variant), V_p would be the total volume of all particles of that variant, and the energy of that variant becomes:

$$\Delta U_{\text{self}} = 1/2 V_p \lambda_{ijkl} \epsilon_{ij}^0(\mathbf{p}) \epsilon_{kl}^0(\mathbf{p}),$$

where $\epsilon_{ij}^0(\mathbf{p})$ is the transformation strain tensor for the pth phase transformation variant.

The total energy will be a summation over all variants. For the general case, a number of variants of six could independently represent any final morphology. Three variants represent the three orthogonal principal strains and three variants represent shear strains on each of the faces of the cube.

$$\Delta U_3 = 1/2 \sum_p V_p \lambda_{ijkl} \epsilon_{ij}^0(\mathbf{p}) \epsilon_{kl}^0(\mathbf{p})$$

While it is not mathematically necessary that all particles have the same size and shape, it is much more convenient to divide some macroscopic body into identical uniform particles, which is the approach taken in the application of the model within this work, hence the term particle should be interpreted as the basic uniform entity or cell assembled with all other identical cells to comprise the whole body, rather than some arbitrary shape.

Step 4. Install the restored particles, with their surface traction still applied, back into the original matrix. This is a zero energy step as they all fit exactly in their original holes.

Step 5. Weld the particles on the matrix so that the system is again a single crystal.

Step 6. Remove the traction stress that is holding the particle shape. This will result in relaxation of the particle as some of its strain energy is transferred to the surrounding crystal. A balance will be achieved at the point of balance of forces where the matrix exerts a force on the particle equal and opposite to that of the particle on the matrix.

2.1.2 Relaxation Energy

Elastic strain energy may be obtained by expanding an expression for strain energy in a power series in the strain tensor with truncation after the second term. This would be a polynomial of three terms. For any elastic material not complicated by a transformation, there is no stress if no strain exists, since $\sigma_{ij} = \partial U / \partial \epsilon_{ij}$, the linear term of this expansion will be non-existent¹⁰. In the case of an unrestrained transformed particle, there is a stress-free transformation strain, which leads to the presence of a linear term in the relaxation energy formula.

The particle's relaxation energy power series expansion is then expressed as:

$$U = -\sigma_{ij}^0 \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}.$$

The term, σ_{ij}^0 , is the stress which would be required to produce the stress-free transformation strain if the particle were being mechanically forced to its deformed shape rather than being deformed as a consequence of a phase transformation with chemical driving energy. Therefore, $-\sigma_{ij}^0$ is the stress required to squeeze the transformed particle back to its untransformed original shape. The strain is measured from the initial untransformed shape of the particle, to which it is squeezed by the application of the imaginary stress.

If the particle relaxes only slightly in the matrix, it will experience only a small strain and the relaxation energy will be approximately $-\sigma_{ij}^0 \epsilon_{ij}$ (negative energy is energy given up by the particle to the matrix). If it relaxes fully to its stress-free transformed state, then the energy it gives up will be:

$$\begin{aligned} U &= -\sigma_{ij}^0 \epsilon_{ij}^0 + 1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \\ &= -1/2 \sigma_{ij}^0 \epsilon_{ij}^0. \end{aligned}$$

Graphically this is depicted below. The relaxation energy of the particle is the area of the triangle under the linear stress-strain curve minus the area of the $\sigma^0 \epsilon_{ij}$ rectangle. For very

small strains, this can be approximated as work done under constant stress and is equal to $-\sigma_{ij}^0 \epsilon_{ij}$. For full relaxation of the particle, i.e. to a strain equal to the stress-free transformation strain ϵ_{ij}^0 , it becomes simply the negative of the area under the stress-strain curve ($-1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0$).

Figure 2.1 Graphical depiction of the relaxation energy of the transformed particle as it is released into the matrix. For any given relaxation ϵ_1 , the relaxation energy is given by the shaded region.

For the matrix, its energy is also given as:

$$U = -\sigma_{ij}^0 \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl},$$

but in the case of an untransformed matrix particle, its stress free transformation strain is non-existent, which removes the linear term, so this reduces to:

$$U = 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl},$$

which is simply the area of the triangle under its linear stress-strain curve.

The power series expansion for strain energy simply extends only to the second order term because of the assumption of linear elastic behavior. If the material were to be modeled as non-linear, higher order terms in this expansion would be required.

The total energy of the system after relaxation of the particle is the sum of the shape restoration energy of step 3 and the relaxation energy:

$$U_{\text{elast}} = \Delta U_3 + \Delta U_{\text{relax}} = \frac{1}{2} \sum_p V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) + \int_v [-\sigma_{ij}^0 \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}] dV$$

σ_{ij}^0 in the above equation refers to the stress applied to a particle of a given orientation variant to restore its shape. For a cluster of p particles, this could be expressed as $\sum \sigma_{ij}^0(p) \theta_p(r)$, where $\sigma_{ij}^0(p)$ is the restoration stress for the p th type of particles (i.e. one of the p variants) and $\theta_p(r)$ is the shape function describing all of the p th type particle variants within the matrix. The shape function takes the value of unity within a transforming particle of the p th type and zero outside of this type of particle. The summation is taken over all variants. Expressing the relaxation energy where multiple transforming particles of multiple variants are involved then results in:

$$\Delta U_{\text{relax}} = \int_v [\sum -\sigma_{ij}^0(p) \theta_p(r) \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}] dV \quad (2.1)$$

Solving this equation is non-trivial as it requires the evaluation of the elastic strain field throughout the volume. However, it may be simplified somewhat by decomposing the elastic strain field into two constituent fields, a homogeneous strain field and a

heterogeneous strain field, such that the total field is the sum of the two.

$$\varepsilon_{ij}(r) = \bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(r)$$

The homogeneous strain is defined as a macroscopic strain that is constant throughout the volume of the body. The heterogeneous strain field does not affect the macroscopic crystal shape and its integral over the body volume will be zero.

Substituting $\varepsilon_{ij}(r)$ in component form (homogeneous + heterogeneous) in equation 2.1 and expanding yields:

$$\Delta U_{\text{relax}} = \int_V [\Sigma - \sigma_{ij}^0(p) \theta_p(r) (\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(r)) + 1/2 \lambda_{ijkl} (\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(r)) (\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl}(r))] dV$$

$$\Delta U_{\text{relax}} = \int_V [\Sigma - \sigma_{ij}^0(p) \theta_p(r) \bar{\varepsilon}_{ij} + 1/2 \lambda_{ijkl} \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl}] dV + \int_V [\Sigma - \sigma_{ij}^0(p) \theta_p(r) \delta\varepsilon_{ij}(r) + 1/2 \lambda_{ijkl} (\delta\varepsilon_{ij}(r) \delta\varepsilon_{kl}(r) + 2\delta\varepsilon_{ij}(r) \bar{\varepsilon}_{kl}(r))] dV$$

$$= U_{\text{homogeneous}} + U_{\text{heterogeneous}}$$

where:

$$U_{\text{homogeneous}} = \int_V [\Sigma - \sigma_{ij}^0(p) \theta_p(r) \bar{\varepsilon}_{ij} + 1/2 \lambda_{ijkl} \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl}] dV$$

With the average strain being constant, its integration is trivial. Recognizing the integral of the shape function over volume as simply the total volume of the pth type particles, yields:

$$U_{\text{homogeneous}} = \Sigma -\sigma_{ij}^0(p) \bar{\epsilon}_{ij} V_p + 1/2 \lambda_{ijkl} \bar{\epsilon}_{ij} \bar{\epsilon}_{kl} V \quad (2.2)$$

$U_{\text{heterogeneous}}$ can be rearranged as follows:

$$\begin{aligned} U_{\text{heterogeneous}} &= \int_V \left[\Sigma -\sigma_{ij}^0(p) \theta_p(r) \delta \epsilon_{ij}(r) + 1/2 \lambda_{ijkl} (\delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r) + 2 \delta \epsilon_{ij}(r) \bar{\epsilon}_{kl}) \right] dV \\ &= \int_V \left[\Sigma -\sigma_{ij}^0(p) \theta_p(r) \delta \epsilon_{ij}(r) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r) + \lambda_{ijkl} \delta \epsilon_{ij}(r) \bar{\epsilon}_{kl} \right] dV \\ &= \int_V \left[\delta \epsilon_{ij}(r) (\Sigma -\sigma_{ij}^0(p) \theta_p(r) + \lambda_{ijkl} \bar{\epsilon}_{kl}) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r) \right] dV \end{aligned} \quad (2.3)$$

The relaxation of the particles will equilibrate at a total energy minimum, which may be found by setting the derivatives with respect to strain and displacement of the functions to

0. The total energy is $\Delta U_3 + \Delta U_{\text{relax}}$, but ΔU_3 is a constant. Therefore its derivative is 0.

Setting derivatives with respect to both average strain and displacement to 0 yields:

$$\partial U_{\text{hom}} / \partial \bar{\epsilon}_{ij} = 0; \quad \partial U_{\text{heterogeneous}} / \partial u_i = 0.$$

$$\text{From 2.2, } \partial U_{\text{hom}} / \partial \bar{\epsilon}_{ij} = -\Sigma V_p \sigma_{ij}^0(p) + V \lambda_{ijkl} \bar{\epsilon}_{kl} \quad (2.4)$$

$$\text{Setting this to zero results in } \lambda_{ijkl} \bar{\epsilon}_{kl} = \Sigma w_p \sigma_{ij}^0(p) \quad (2.5)$$

where $w_p = V_p / V$ = volume fraction of all transforming particles of the pth variant.

Exploiting this result by substituting in equation 2.3 simplifies the heterogeneous relaxation energy to:

$$\begin{aligned}
U_{\text{heterogeneous}} &= \int_v [(-\sum_p (\sigma_{ij}^0(p) \delta \epsilon_{ij}(r) (\theta_p(r) - w_p)) + \frac{1}{2} \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r))] dV \\
&= \int_v [(-\sum_p (\sigma_{ij}^0(p) \delta \epsilon_{ij}(r) (\theta_p(r) - w_p)) + \frac{1}{2} \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r))] dV \\
&= \int_v [(-\sum_p (\sigma_{ij}^0(p) \delta \epsilon_{ij}(r) \Delta \theta_p(r) + \frac{1}{2} \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r))] dV \quad (2.6)
\end{aligned}$$

where $\Delta \theta_p(r) = \theta_p(r) - V_p/V$

From 2.5 and given that $\sigma_{ij}^0(p) = \lambda_{ijkl} \epsilon_{ij}^0$, we can write:

$$\bar{\epsilon}_{ij} = \sum_p w_p \epsilon_{ij}^0$$

Substituting in equation 2.2, simplifies the homogeneous energy expression as:

$$U_{\text{homogeneous}} = - \sum_p \sum_q \lambda_{ijkl} w_p \epsilon_{ij}^0 \epsilon_{kl}^0 V_q + \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q$$

where the summations are performed twice over all variants in the system, p and q.

$$\begin{aligned}
U_{\text{homogeneous}} &= - \sum_p \sum_q \lambda_{ijkl} w_p \epsilon_{ij}^0 \epsilon_{kl}^0 V_q + \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q \\
&= - \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q \quad (2.7)
\end{aligned}$$

2.1.3 Heterogeneous Strain energy

By applying the infinitesimal strain approximation from elasticity theory, an approximate expression for the variation of heterogeneous strain with respect to displacement may be determined.

Applying the Lagrangian infinitesimal strain relation,

$$\delta\epsilon_{ij} = \frac{1}{2}(\partial u_i/\partial r_j + \partial u_j/\partial r_i) \quad (2.8)$$

allows the product of differential strain elements to be expressed in terms of displacement.

$$\begin{aligned} \delta\epsilon_{ij}\delta\epsilon_{kl} &= [\frac{1}{2}(\partial u_i/\partial r_j + \partial u_j/\partial r_i)] [\frac{1}{2}(\partial u_k/\partial r_l + \partial u_l/\partial r_k)] \\ &= [1/4(\partial u_i\partial u_k/\partial r_j\partial r_l + \partial u_j\partial u_k/\partial r_i\partial r_l + \partial u_i\partial u_l/\partial r_j\partial r_k + \partial u_j\partial u_l/\partial r_i\partial r_k)] \end{aligned}$$

Because of the symmetry of the tensors, this equates to:

$$\delta\epsilon_{ij}\delta\epsilon_{kl} = \partial u_k\partial u_i/(\partial r_l\partial r_j) \quad (2.9)$$

Substituting 2.9 and 2.8 in 2.6 gives:

$$U_{\text{heterogeneous}} = \int_V [-\sum_p \sigma_{ij}^0(p) [\frac{1}{2}(\partial u_i/\partial r_j + \partial u_j/\partial r_i)] \Delta\theta_p(r) + \frac{1}{2}\lambda_{ijkl}\partial u_k\partial u_i/(\partial r_l\partial r_j)] dV$$

Recognizing again the symmetry of the tensors, reduces this to:

$$U_{\text{heterogeneous}} = \int_V \left[- \sum_p \sigma_{ij}^0(p) \partial u_i / \partial r_j \Delta \theta_p(r) + \frac{1}{2} \lambda_{ijkl} \partial u_k \partial u_l / (\partial r_i \partial r_j) \right] dV \quad (2.10)$$

The first variation of the heterogeneous relaxation energy may be simply written as:

$$\delta U_{\text{heterogeneous}} = \int_V \delta \left[- \sum_p \sigma_{ij}^0(p) \partial u_i / \partial r_j \Delta \theta_p(r) + \frac{1}{2} \lambda_{ijkl} \partial u_k \partial u_l / (\partial r_i \partial r_j) \right] dV$$

The function of interest in the variation is the displacement tensor, so the variation may be written as:

$$= \left(\int_V \left[- \sum_p \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r) + \frac{1}{2} \lambda_{ijkl} (\partial \delta u_k / \partial r_l) \partial u_l / \partial r_i + \frac{1}{2} \lambda_{ijkl} (\partial u_k / \partial r_l) \partial \delta u_l / \partial r_i \right] dV \right)$$

Since the tensors are symmetric, this equates to:

$$= \left(\int_V \left[- \sum_p \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r) + \lambda_{ijkl} (\partial \delta u_k / \partial r_l) \partial u_l / \partial r_i \right] dV \right)$$

Integration by parts,

$$\int_0^L w dv = - \int_0^L v dw + wv \Big|_0^L$$

may be applied to each term of the $\delta U_{\text{heterogeneous}}$ expression. This gives:

$$\int_v \left[\sum_p \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r) \right] dV = - \sum_p \sigma_{ij}^0(p) \Delta \theta_p(r) \delta u_i \Big|_a^b + \int_v \sum_p \sigma_{ij}^0 \partial (\Delta \theta_p(r)) / \partial r_j \delta u_i dV$$

and

$$\int_v [\lambda_{ijkl} (\partial u_k / \partial r_l) \partial \delta u_i / \partial r_j] dV = \lambda_{ijkl} (\partial u_k / \partial r_l) \delta u_i \Big|_a^b - \int_v [\lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) \delta u_i] dV$$

The expression for $\delta U_{\text{heterogeneous}}$ can be simplified by assuming that the variation in strain, $\delta u_i = 0$, vanishes at the surface of the body, which is a consequence of the assumption that the heterogeneous strain field does not affect the macroscopic crystal shape. This is not strictly true and variations in the local heterogeneous strain field will exist. Variations in the strain field near the surface of the cube are minimized by using the largest number of cells practicable in the cube.

By setting $\delta u_i = 0$ at the surface, δu_i evaluated over the limits of the system will be zero and the expression reduces to:

$$\delta U_{\text{heterogeneous}} = \int_v \left[\sum_p \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j \right] \delta u_i dV - \int_v [\lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l)] \delta u_i dV$$

Dividing both sides by δu_i gives:

$$\delta U_{\text{heterogeneous}} / \delta u_i = \int_v \left[\sum_p \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j \right] dV - \int_v [\lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l)] dV$$

From the total energy minimum criterion, $\delta U_{\text{heterogeneous}}/\delta u_i = 0$, therefore:

$$\begin{aligned} \int_V [\Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j] dV &= \int_V [\lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l)] dV \\ \Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j dV &= \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) dV \end{aligned} \quad (2.11)$$

This is the fundamental equation defining heterogeneous strain throughout the body volume.

A convenient technique for solving any differential equation is the application of the Fourier transform, defined as:

$$f(\mathbf{k}) = \int_V [f(r) e^{-i\mathbf{k}r}] dV, \text{ where } \mathbf{k} \text{ is the wave vector and } f(\mathbf{k}) \text{ becomes the transformed function in wave vector space.}$$

Let $v(\mathbf{k})$ be the transform of $u(r)$, i.e.

$$v(\mathbf{k}) = \int_V [u(r) e^{-i\mathbf{k}r}] dV$$

and apply the Fourier transform to equation 2.11. This produces the following result:

$$-i \Sigma_p \sigma_{ij}^0 k_j \Delta \theta_p(\mathbf{k}) = \lambda_{ijkl} k_j k_l v_l(\mathbf{k}) \quad (2.12)$$

Note the Fourier transform of $du(r)/dr = ikv(\mathbf{k})$ and the Fourier transform of

$$d^2u(r)/dr^2 = -k^2v(\mathbf{k}) \text{ and } i = \sqrt{-1}.$$

The unknown function of interest is $v(\mathbf{k})$, so solving for $v(\mathbf{k})$, yields the following:

$$v_i(\mathbf{k}) = -i \sum_p \sigma_{ij}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \quad (2.13)$$

Writing the heterogeneous strain energy expression, 2.10 in Fourier transform space gives the following:

$$U_{\text{heterogeneous}} = \int_V \left[-i \sum_p \sigma_{ij}^0(p) k_j v_i(\mathbf{k}) \Delta \theta_p(\mathbf{k}) - \frac{1}{2} \lambda_{ijkl} k_j v_i(\mathbf{k}) k_l v_k^*(\mathbf{k}) \right] dV$$

The differential volume element is dV or dr^3 . In wave vector space, the differential element is $dk/2\pi$, so expressing this fully in k space gives the following:

$$U_{\text{heterogeneous}} = \int_k \left[-i \sum_p \sigma_{ij}^0(p) k_j v_i(\mathbf{k}) \Delta \theta_p(\mathbf{k}) - \frac{1}{2} \lambda_{ijkl} k_j v_i(\mathbf{k}) k_l v_k^*(\mathbf{k}) \right] d^3k / (2\pi)^3 \quad (2.14)$$

This can be rewritten by substituting the expression for $v(\mathbf{k})$ of equation 2.13 in equation 2.14.

$$U_{\text{heterogeneous}} = \int_k \left[-i \sum_p \sigma_{ij}^0(p) k_j \left(-i \sum_q \sigma_{jk}^0(q) k_k \Delta \theta_q(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \Delta \theta_p(\mathbf{k}) \right] d^3k / (2\pi)^3 - \int_k \left[\frac{1}{2} \lambda_{ijkl} k_j k_l \left(i \sum_p \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(i \sum_q \sigma_{ij}^0(q) k_i \Delta \theta_q(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \right] d^3k / (2\pi)^3 \quad (2.15)$$

Since $(\lambda_{ijkl} k_j k_l) (\lambda_{ijkl} k_i k_l)^{-1} = \mathbf{I}$, the second term of 2.15 reduces to:

$$- \frac{1}{2} \int_k \left[\left(i \sum_p \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(i \sum_q \sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) \right] d^3k / (2\pi)^3$$

rearranging gives:

$$\frac{1}{2} \int_k \left[\left(\sum_p \sum_q \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(\sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) \right] d^3k / (2\pi)^3$$

The first term of equation 2.15 rearranges to:

$$- \int_k \left[\sum_p \sum_q \sigma_{ij}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right] \left(\sigma_{jk}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) d^3k / (2\pi)^3$$

Adding the two rearranged terms of equation 2.15 gives simply:

$$- \frac{1}{2} \int_k \left[\left(\sum_p \sum_q \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(\sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) \right] d^3k / (2\pi)^3 \quad (2.16)$$

The total relaxation energy is the sum of the homogeneous and heterogeneous components. Adding 2.7 and 2.16 gives:

$$U_{\text{relax}} = - \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q +$$

$$- \frac{1}{2} \int_k \left[\left(\sum_p \sum_q \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(\sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) \right] d^3k / (2\pi)^3$$

The total elastic energy is the sum of the strain energy that restored the particle to its original shape (ΔU_3 ; equation 2.0) and the relaxation energy above.

$$U_{\text{elast}} = \frac{1}{2} V \sum_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) - \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q +$$

$$- \frac{1}{2} \int_k \left[\left(\sum_p \sum_q \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) \left(\sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) \right) \right] d^3k / (2\pi)^3 \quad (2.17)$$

$\Delta\theta_p(r)$ is defined as follows: $\Delta\theta_p(r) = \theta_p(r) - V_p/V$

So, the Fourier transform of $\Delta\theta_p(r)$ is:

$$\int_V [(\theta_p(r) - V_p/V) e^{ikr}] dV$$

If $k=0$, this reduces to:

$$\int_V (\theta_p(r) - V_p/V) dV$$

$$= V_p - V_p$$

$$= 0$$

For $k \neq 0$,

$$\Delta\theta_p(r) = \int_V (\theta_p(r) - V_p/V) e^{ikr} dV$$

$$= \int_V \theta_p(r) e^{ikr} dV$$

which is simply the definition of $\theta_p(\mathbf{k})$. Therefore, 2.17 can be written in terms of $\theta_p(\mathbf{k})$

with the 0th term excluded from the integration.

$$\begin{aligned} U_{\text{elast}} = & \frac{1}{2} \sum_p V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) - \frac{1}{2} V \sum_p \sum_q \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q + \\ & - \frac{1}{2} \int_k \left[\left(\sum_p \sum_q \sigma_{jk}^0(p) k_j \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \right) (\sigma_{ij}^0(q) k_j \theta_q(\mathbf{k})) \right] d^3k / (2\pi)^3 \end{aligned} \quad (2.18)$$

The stress-free transformation strain tensor, ϵ^0_{ij} is some function of the order parameter. For a phase transformation that is proper with respect to strain, this is a simple linear function. For the perovskite ferroelectrics considered here, the strains are proportional to the square of polarization. In general they take the general form of the electrostrictive relation, $\epsilon^0_{ij} = q_{ijkl} \cdot P_i P_j$, where P is the spontaneous polarization of the phase transformation. For the cubic to tetragonal transformation in ferroelectric perovskites, the shear strains and electrostrictive tensor cross-terms are zero, so ϵ^0_{ij} is a diagonal matrix and the expression can be simplified as $\epsilon^0_{ii} = a_{ij} \cdot P_j^2$, and $\epsilon^0_{ij} = 0$, for $i \neq j$.

2.2 Electric Dipole interaction Energy

The spontaneous polarization of the phase transformation creates a localized electric field which affects the formation of other polarized regions of the crystal. The effect is analogous to elastic coupling of the strain field, but instead of mechanical coupling through the elastic modulus of the material, the field effect is coupled through the electric susceptibility of the material. As with elastic coupling driving the formation of the most favorably oriented geometric variants that minimize strain energy, the electric coupling drives the formation of the most favorably oriented electric dipole moments so as to minimize the dipole interaction energy.

The interaction energy of a system of dipoles is typically determined by finding the fields contributed by each dipole then determining the energy effect of a single dipole in the field. The analysis is repeated for each dipole in the system and the energy effects are integrated. This approach determines the correct total field composed of both homogeneous and heterogeneous components and can be developed as follows.

Consider that charge separation on an atomic scale due to the ferroelectric phase transition is small relative to the lattice parameter, so that the far field approximation for the electric field due to a dipole may be applied. The far field (short dipole) approximation has a $1/r^3$ dependence rather than $1/r^2$ as for isolated point charges⁵⁹. It is

most conveniently expressed in radial coordinates as follows:

$$E_r = \frac{1}{4\pi\chi\epsilon_0} \frac{2p \cdot \cos\theta}{r^3} \quad (2.19)$$

$$E_\theta = \frac{1}{4\pi\chi\epsilon_0} \frac{p \cdot \sin\theta}{r^3} \quad (2.20)$$

$$E_\phi = \frac{1}{4\pi\chi\epsilon_0} \frac{p \cdot \sin\phi}{r^3} \quad (2.21)$$

where ϵ_0 = permittivity of free space

χ = electric susceptibility

Figure 2.2: Far field approximation for the electric field of a dipole expressed in radial coordinates

The energy stored in a dipole is given as $\frac{1}{2}E_i D_i$. For a region of space containing multiple dipoles, the energy contribution of a single dipole is determined as the electric field due to all other dipoles evaluated at the location of the single dipole multiplied by the dipole moment of the single dipole. The total energy is the summation of all single dipole to electric field interactions evaluated for each dipole in the system.

$$\sum_{i=1}^N \sum_{k=1}^N \frac{1}{2} D_i E_k \quad (2.22)$$

Where:

E_k is the electric field due to the kth dipole resolved at the point of the ith dipole

D_i is the electric displacement of the ith dipole

N is the total number of dipoles in the system

$D_i = \epsilon_0 E_a + P_i$. For no applied field, $D_i = P_i$, therefore the energy expression becomes:

$$\sum_{i=1}^N \sum_{k=1}^N \frac{1}{2} P_i E_k \quad (2.23)$$

Substituting equations 2.19, 2.20, and 2.21 in 2.23 gives the total energy expression in terms of the polarization. The problem with this approach is that it contains both a homogeneous field component and a heterogeneous field component. In the phase field model, the homogeneous field component is already contained in the Ginzburg-Landau-Devonshire thermodynamic equation, so to use equations 2.19-2.23, the homogeneous field component, i.e. that due to the spontaneous polarization of the ferroelectric, must be separated and subtracted, which adds significant complexity to the method.

The more direct method of arriving at a set of equations describing the dipole-dipole interaction is to start with Maxwell's equations of electrostatics.

$$\nabla \times \mathbf{E} = \frac{-\partial \mathbf{B}}{\partial t} = 0 \quad [2.24]$$

$$\nabla \cdot \mathbf{D} = 0 \quad [2.25]$$

Any uniform polarization will automatically satisfy Maxwell's equations, so the solution to Maxwell's equations will be only the heterogeneous field and not the homogeneous field which is already accounted for by the thermodynamic model.

$$\nabla \cdot \mathbf{D} = \nabla \cdot \epsilon_0 \mathbf{E} + \nabla \cdot \mathbf{P} = 0 \quad [2.26]$$

$$\epsilon_0(\nabla \cdot \mathbf{E}) = -\nabla \cdot \mathbf{P} \quad [2.27]$$

In Fourier transform space, $\text{Div}(\mathbf{A}) = \mathbf{k} \cdot \mathbf{A}$, where $\mathbf{k}$ is the wave vector, therefore in

Fourier space,

$$\epsilon_0(\nabla \cdot \mathbf{E}) = -\nabla \cdot \mathbf{P}$$

$$\epsilon_0 \mathbf{k} \cdot \mathbf{E}(\mathbf{k}) = -\mathbf{k} \cdot \mathbf{P}(\mathbf{k})$$

$$\mathbf{E}(\mathbf{k}) = \frac{-\mathbf{k} \cdot \mathbf{P}(\mathbf{k})}{\epsilon_0 |\mathbf{k}|} \quad [2.28]$$

The energy of dipoles in an electric field is given by:

$$-\frac{1}{2} \int_V \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) dV \quad [2.29]$$

From the definition of an inverse Fourier transform,

$$\mathbf{P}(\mathbf{r}) = \int \mathbf{P}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \frac{d^3 \mathbf{k}}{2\pi^3} \quad [2.30]$$

$$\mathbf{E}(\mathbf{r}) = \int \mathbf{E}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \frac{d^3 \mathbf{k}}{2\pi^3} \quad [2.31]$$

Substituting 2.30 and 2.31 in 2.29, then applying 2.28, yields a k-space expression for the dipole interaction energy in terms of the polarization.

$$U(\mathbf{r}) = \frac{1}{2} \int_V \frac{\mathbf{k} \cdot \mathbf{P}(\mathbf{k})}{\epsilon_0 |\mathbf{k}|} e^{i\mathbf{k} \cdot \mathbf{r}} \int \mathbf{P}(\mathbf{k}') e^{i\mathbf{k}' \cdot \mathbf{r}} \frac{d^3 \mathbf{k}}{2\pi^3} \frac{d^3 \mathbf{k}'}{2\pi^3} dV \quad [2.32]$$

From the definition of a Fourier transform,

$$E(k) = \int E(r) e^{-ikr} d^3r, \quad [2.33]$$

which vectorizes by multiplication by the unity wave vector as:

$$E(k) = \frac{\mathbf{k}}{k} \int E(r) e^{-ikr} d^3r, \quad [2.33a]$$

and the fact that the Fourier transform of a sinusoid is an impulse,

$$\delta(k-k') = \int e^{ik'r} e^{-ikr} d^3r, \quad [2.34]$$

allows 2.32 to be re-written as:

$$U(r) = -\frac{1}{2} \iint \frac{\mathbf{k}P(k)}{\epsilon_0 k} P(k') \delta(k'-k) \frac{d^3k}{2\pi^3} \frac{d^3k'}{2\pi^3} \frac{\mathbf{k}}{k} \quad [2.35]$$

Recognizing the integral of the impulse function as unity, simplifies 2.35 to:

$$U(r) = -\frac{1}{2} \int \frac{\mathbf{k}P(k)}{\epsilon_0 k} P(k') \frac{d^3k}{2\pi^3} \frac{\mathbf{k}}{k} \quad [2.36]$$

2.3 Gradient Energy

At the interface between domains, surface energy arises due to the misalignment of the adjoining regions of crystal. The magnitude of the interface energy within the solid is far less than for a free surface at the boundary of a solid, but the effect is large enough to affect the domain morphology. The interface energy is proportional to the gradient of polarization, therefore it is also known as gradient energy and is greater for a narrow domain wall and less for a wide domain wall.

Mathematically it is:

$$E_s = \int_{\text{vol}} B_{ij} (\nabla_i P_j)^2 \quad [2.37]$$

where E_s is surface energy and B_{ij} is the gradient energy coefficient.

B_{ij} is a matrix with all terms assumed to be equivalent, which is commonly the case in the literature¹¹. Some justification for a reduced weighting of the diagonal terms of B_{ij} could be argued as changes in polarization at right angles to the direction of domain transition should give rise to the largest offset of atomic bonds at the interface, while axial changes in polarization should have a much smaller affect on atomic displacement at the interface, however estimates of gradient energy are only approximate and the complexity of introducing more than one gradient energy value were not explored as the impact on the overall energy balance is likely to be very marginal.

Expanding the expression and letting the single gradient scalar be G gives:

$$U_s = \int_{\text{vol}} G \cdot [(dP_x/dx)^2 + (dP_y/dy)^2 + (dP_z/dz)^2 + (dP_x/dy)^2 + (dP_x/dz)^2 + (dP_y/dx)^2 + (dP_y/dz)^2 + (dP_z/dx)^2 + (dP_z/dy)^2] dV \quad [2.38]$$

2.4 Chemical Energy

Chemical energy is quantified by the thermodynamic potential function, the derivation of which is described in section 1.2. The sixth order model as used in this work is of the form:

$$\begin{aligned}\Phi(P,T) = & \alpha_1 \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{12} \cdot (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] \\ & + \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2),\end{aligned}\quad [2.39]$$

which is equivalent to equation 1.11, except that the electric field interaction term ($E \cdot P$) is removed, leaving only purely chemical energy as dipole interactions are separately accounted for.

By simple extension of the principles of the derivation of the sixth order model, an eighth order model may be generated:

$$\begin{aligned}\Phi(P,T) = & \alpha_1 \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{12} \cdot (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] + \\ & \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2) + \alpha_{1111} \cdot (P_1^8 + P_2^8 + P_3^8) + \\ & \alpha_{1112} \cdot (P_1^6 \cdot P_2^2 + P_1^6 \cdot P_3^2 + P_2^6 \cdot P_1^2 + P_2^6 \cdot P_3^2 + P_3^6 \cdot P_1^2 + P_3^6 \cdot P_2^2) + \\ & \alpha_{1123} \cdot (P_1^4 \cdot P_2^2 \cdot P_3^2 + P_2^4 \cdot P_1^2 \cdot P_3^2 + P_3^4 \cdot P_1^2 \cdot P_2^2)\end{aligned}\quad [2.40]$$

The physics dictate that at least the α_1 term be temperature dependent due to the Curie-

Weiss law, but often to achieve a better fit over a broader temperature range without resorting to a higher order model, additional coefficients are made temperature dependent. The coefficients for the barium titanate sixth order and eighth order models for the tetragonal phase, as available in the literature¹²⁻¹⁴ are given in Tables 3.1-3.3. The sixth order widely cited Bell and Cross model is used for this work (Table 3.1).

Similarly, a thermodynamic model can be developed for PZT¹⁵⁻¹⁹. The coefficients for PZT are dependent on the zirconate to titanate ratio. The coefficients for 50% PZT are contained in Table 3.4.

2.5 Dimensionless Units

The model operates on dimensionless units, where the elastic strain, gradient, and electrostatic energy terms are expressed as functions of the chemical energy. The input parameters controlling the energy values are λ , the electrostatic to chemical energy ratio, ζ , the elastic strain to chemical energy ratio, and β_{ij} the gradient coefficient tensor. Polarization is normalized as a ratio of P_0 , the spontaneous polarization and the applied field E is normalized as a fraction of P_0 divided by the electric permittivity of the material.

Adjusting either λ or ζ allows convenient control over the strength of electrical and mechanical energies respectively while leaving all other parameters unchanged, thus the effects are easily separated and the effect of variation in either parameter simulated in isolation.

$$\lambda = \frac{P_0^2}{4\pi \cdot \epsilon_0 \epsilon_r \Delta f}$$

$$\zeta = \frac{U_{\text{elast}}}{\Delta f} \quad U_{\text{elast}} = \frac{1}{2} \epsilon_{ij}^0 \sigma_{ij}$$

ϵ_{ij}^0 = Stress-free transformation strains corresponding to the spontaneous polarization P_0

$$\sigma_{ij} = \lambda_{ijkl} \epsilon_{kl}^0$$

Δf = Change in free energy of the phase transformation at the temperature of the simulation.

P_0 = Equilibrium spontaneous polarization

$$\epsilon_0 = \text{Permittivity of free space} = 8.85 \times 10^{-12} \frac{\text{C}^2}{\text{N} \cdot \text{m}^2}$$

ϵ_r = Background (non-ferroelectric) relative permittivity of the material

The gradient coefficient tensor describes the strength of gradient energy in dimensionless units. Relative to its dimensional counterpart (2.3), it is defined as:

$$\beta_{ij} = \frac{B_{ij}}{\Delta f l_0^2}$$

The gradient tensor is not well quantified. For this work it is set to:

$$\beta_{ij} = \begin{bmatrix} 2 & 2 & 2 \\ 2 & 2 & 2 \\ 2 & 2 & 2 \end{bmatrix}$$

Dimensionless electric field:

$$E_{\text{dimensionless}} = \frac{\epsilon_r \epsilon_0 E}{P_0}$$

Dimensionless polarization:

$$P_{\text{dimensionless}} = \frac{P}{P_0}$$

3.0 Thermodynamic Models

As described in 1.2, Ginzburg, Landau, Devonshire theory allows the thermodynamic potential for a ferroelectric material, to be quantified as a function of polarization (P) and temperature (T), in the form of a Taylor series expansion^{2,4,12}. Truncating the series to sixth order results in the following thermodynamic potential function:

$$\begin{aligned}\Phi(P,T) = & \alpha_1 \cdot (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} \cdot (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} \cdot (P_1^6 + P_2^6 + P_3^6) + \\ & \alpha_{12} \cdot (P_1^2 \cdot P_2^2 + P_1^2 \cdot P_3^2 + P_2^2 \cdot P_3^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2 + P_3^2) + P_2^4 \cdot (P_1^2 + P_3^2) + P_3^4 \cdot (P_1^2 + P_2^2)] + \\ & \alpha_{123} \cdot (P_1^2 \cdot P_2^2 \cdot P_3^2)\end{aligned}\quad [3.1]$$

Where: P_i are the Cartesian components of the Polarization vector on each of the cubic [100] directions and the α terms are the coefficients of the model. Consistent with the approach of Bell and Cross¹², α_1 , α_{11} , and α_{111} are allowed to linearly vary with temperature and take the form of

$$\alpha = \alpha'(T - T_o)$$

T_o is the transition temperature for Curie-Weiss behavior, which is equivalent to the Curie temperature for a second order ferroelectric phase transition.

The first derivative of thermodynamic potential with respect to the polarization vector gives the applied electric field. Below the Curie temperature the ferroelectric will have a spontaneous polarization in the absence of an applied electric field. Differentiating [3.1]

with respect to P_1 gives the following general result for E_1 .

$$\begin{aligned} \frac{\partial \Phi(P,T)}{\partial P_1} = & 2\alpha_1 \cdot P_1 + 4\alpha_{11} \cdot P_1^3 + 6\alpha_{111} \cdot P_1^5 + \\ & 2\alpha_{12} \cdot (P_1 \cdot P_2^2 + P_1 P_3^2) + 4\alpha_{112} \cdot P_1^3 \cdot (P_2^2 + P_3^2) + 2\alpha_{112} \cdot P_2^4 \cdot P_1 + 2\alpha_{123} \cdot (P_1 P_2^2 P_3^2) \\ = E_1 \end{aligned} \quad [3.2]$$

Equating the field to zero and solving for the polynomial roots at various temperature values allows a curve of predicted spontaneous polarization versus temperature to be developed.

In the tetragonal phase, the only component of spontaneous polarization is along the axis of tetragonal elongation (c-axis). Setting $P_2=P_3=0$ reduces [3.2] to the c-axis result for the electric field.

$$\begin{aligned} \frac{\partial \Phi(P,T)}{\partial P_1} = & 2\alpha_1 \cdot P_1 + 4\alpha_{11} \cdot P_1^3 + 6\alpha_{111} \cdot P_1^5 \\ = E_1 \end{aligned} \quad [3.3]$$

P_1 is the value of measured spontaneous polarization on the cubic [100] axis for the tetragonal phase. Since the polarization is spontaneous, the applied electric field is zero. Therefore, the coefficients chosen for the model should produce a zero result for equation 3.3 over the entire range of temperature and c-axis spontaneous polarization in the tetragonal phase state.

Considering P_2 to be the axis of spontaneous polarization and setting P_1 and P_3 to zero in equation 3.2 yields an expression for a-axis electric field, which also must equate to zero. By immediate inspection, equation 3.2 will be zero if $P_1=0$, therefore the a-axis field condition is automatically satisfied by the chosen polynomial.

For the orthorhombic phase, the spontaneous polarization vector is oriented along [110] directions with respect to the original cubic cell, so $P_1=P_2$; $P_3=0$ and equation 3.2 for the c-axis electric field reduces to the following:

$$\begin{aligned} \frac{\partial \Phi(P,T)}{\partial P_1} = & 2\alpha_1 \cdot P_1 + 4\alpha_{11} \cdot P_1^3 + 6\alpha_{111} \cdot P_1^5 + \\ & 2\alpha_{12} \cdot (P_1 \cdot P_2^2) + 4\alpha_{112} \cdot P_1^3 \cdot P_2^2 + 2\alpha_{112} \cdot P_2^4 \cdot P_1 \\ = & E_1 \end{aligned} \quad [3.4]$$

To determine the a-axis electric field, consider the equivalent case of $P_1=0$ and the field defined by $P_2=P_3 \neq 0$. Again, by inspection, equation 3.2 can be immediately observed to evaluate to 0, so this condition is automatically satisfied by the choice of a polynomial with no linear term.

From the definition of electric susceptibility of $\chi = \partial P / \partial E$, the electric susceptibility is simply determined as:

$$\frac{\partial^2 \Phi(P,T)}{\partial P_1^2} = 1/\chi_1 \quad [3.5]$$

The generalized second derivative of thermodynamic potential from equation 3.1 is as follows:

$$\frac{\partial \Phi^2(P,T)}{\partial P_1^2} = 2\alpha_1 + 12\alpha_{11} \cdot P_1^2 + 30\alpha_{111} \cdot P_1^4 + 2\alpha_{12} \cdot (P_2^2 + P_3^2) + 12\alpha_{112} \cdot P_1^2 \cdot (P_2^2 + P_3^2) + 2\alpha_{112} \cdot P_2^4 + 2\alpha_{123} \cdot (P_2^2 P_3^2) \quad [3.6]$$

Applying the conditions of the spontaneous polarization state for each of the orthorhombic and tetragonal phase regions for both the c-axis and a-axis yields the following expressions for $1/\chi$.

Tetragonal phase c-axis ($P_2=P_3=0; P_1 \neq 0$):

$$\frac{\partial \Phi^2(P,T)}{\partial P_1^2} = 2\alpha_1 + 12\alpha_{11} \cdot P_1^2 + 30\alpha_{111} \cdot P_1^4 \quad [3.7]$$

Tetragonal phase a-axis ($P_1=P_3=0; P_2 \neq 0$):

$$\frac{\partial \Phi^2(P,T)}{\partial P_1^2} = 2\alpha_1 + 2\alpha_{12} \cdot P_2^2 + 2\alpha_{112} \cdot P_2^4 \quad [3.8]$$

Orthorhombic phase c-axis ($P_1=P_2 \neq 0; P_3=0$):

$$\frac{\partial \Phi^2(P,T)}{\partial P_1^2} = 2\alpha_1 + 12\alpha_{11} \cdot P_1^2 + 30\alpha_{111} \cdot P_1^4 + 2\alpha_{12} \cdot P_2^2 + 12\alpha_{112} \cdot P_1^2 \cdot P_2^2 + 2\alpha_{112} \cdot P_2^4 \quad [3.9]$$

Orthorhombic phase a-axis ($P_2=P_3 \neq 0; P_1=0$):

$$\frac{\partial \Phi^2(P,T)}{\partial P_1^2} = 2\alpha_1 + 2\alpha_{12} \cdot (P_2^2 + P_3^2) + 2\alpha_{112} \cdot P_2^4 + 2\alpha_{123} \cdot (P_2^2 P_3^2) \quad [3.10]$$

The final condition to be satisfied is a free energy balance at the phase transition temperature. Since the primary consideration here is the low temperature tetragonal and high temperature orthorhombic regions, the cubic to tetragonal free energy balance condition can be ignored. Alternately imposing the conditions of polarization vector orientations for each of the tetragonal and orthorhombic states on equation 1 and equating the two results produces equation 3.11.

$$\begin{aligned} \alpha_1 \cdot P_{1t}^2 + \alpha_{11} \cdot P_{1t}^4 + \alpha_{111} \cdot P_{1t}^6 = \\ \alpha_1 \cdot (P_1^2 + P_2^2) + \alpha_{11} \cdot (P_1^4 + P_2^4) + \alpha_{111} \cdot (P_1^6 + P_2^6) + \\ \alpha_{12} \cdot (P_1^2 \cdot P_2^2) + \alpha_{112} \cdot [P_1^4 \cdot (P_2^2) + P_2^4 \cdot (P_1^2)] \end{aligned} \quad [3.11]$$

where: $P_{1t} = [100]$ polarization in the tetragonal phase state;
 $P_1=P_2 = [100]$ and $[010]$ (relative to cubic crystal) polarizations in the orthorhombic phase.

A given set of coefficients can be tested against the model, by substituting them in equations 3.3 and 3.4 with the condition of zero electric field then solving for the roots of the polynomial. The polarization values which satisfy 3.3 and 3.4 under the zero field condition should also be consistent with experimentally determined values of spontaneous polarization, satisfy 3.11 at the known transition temperature, and produce electric susceptibility values that are reasonably consistent with experimental data.

3.1 Barium titanate models.

Merz²⁰ produced a comprehensive study of the electrical properties of barium titanate in his 1949 paper. He later revised the data in his 1953 paper²¹ with the discrepancy attributed to the use of inferior quality crystals in the previous experiments, however only his polarization data was affected for which he claimed a scaling of previous results by a factor of about 1.7-1.8 times²¹. In 1958 Meyhofer²² produced plots of electric susceptibility for the tetragonal phase state substantially in agreement with the Merz data of 1949 (Figures 3.1 and 3.2).

Both Merz and Meyerhofer used crystals grown by the Rameika method³⁰. Johnson measured dielectric constant in the tetragonal region in crystals grown by a top seeded solution growth technique and obtained quite different results from Merz and Meyerhofer²³. Johnson also obtained a higher Curie temperature of about 132°C versus 120°C obtained by measurements on the Rameika grown crystals. The higher Curie temperature for melt grown barium titanate over the flux grown crystals of the Rameika method was corroborated by other researchers^{27,31}, however no consistent set of independent single crystal dielectric constant measurements was found in the literature for the melt grown crystals.

Huibregtse and Young²⁵, generated coefficients for a reduced version of equation 3.1, by fitting the equations at specific temperature points. Buessem, Cross, and Goswami²⁴

produced a set of coefficients modified from the Huibregtse and Young values, but they do not explain the procedure of their modification. Bell and Cross¹² used the Buessem, Cross, Goswami coefficients and extended them to add the α_{123} term to build a full sixth order model consistent with equation 3.1.

Figure 3.1: Electric Susceptibility and Polarization data from Merz 1949²⁰.

Figure 3.2: Updated tetragonal phase region polarization data from Merz 1953²¹. Merz specifies a scaling factor of 1.7-1.8 for his previous polarization data (Figure 3.1) to correct the measurements.

Figure 3.3: A-axis and c-axis electric susceptibility measurements from Meyerhofer²²

$\alpha_1 = 3.34 \times 10^5(T-108)$	VmC^{-1}
$\alpha_{11} = 4.69 \times 10^6(T-120) - 2.02 \times 10^8$	Vm^5C^{-3}
$\alpha_{111} = -5.52 \times 10^7(T-120) + 2.76 \times 10^9$	Vm^9C^{-5}
$\alpha_{12} = 3.23 \times 10^8$	Vm^5C^{-3}
$\alpha_{112} = 4.47 \times 10^9$	Vm^9C^{-5}
$\alpha_{123} = 4.91 \times 10^9$	Vm^9C^{-5}

Table 3.1: Bell and Cross model coefficients (T in °C)¹².

$\alpha_1 = 4.124 \times 10^5 (T-115)$	VmC^{-1}
$\alpha_{11} = -2.097 \times 10^8$	Vm^5C^{-3}
$\alpha_{111} = 1.294 \times 10^9$	Vm^9C^{-5}
$\alpha_{12} = 7.974 \times 10^8$	Vm^5C^{-3}
$\alpha_{112} = -1.950 \times 10^9$	Vm^9C^{-5}
$\alpha_{123} = -2.500 \times 10^9$	Vm^9C^{-5}
$\alpha_{1111} = 3.863 \times 10^{10}$	$Vm^{13}C^{-7}$
$\alpha_{1112} = 2.529 \times 10^{10}$	$Vm^{13}C^{-7}$
$\alpha_{1112} = 1.637 \times 10^{10}$	$Vm^{13}C^{-7}$
$\alpha_{1112} = 1.367 \times 10^{10}$	$Vm^{13}C^{-7}$

Table 3.2: Li, Cross, and Chen model Coefficients (T in °C)¹³.

$\alpha_1 = 3.61 \times 10^5 (T-391)$	VmC^{-1}
$\alpha_{11} = 4.0 \times 10^6 \cdot T - 1.83 \times 10^9$	Vm^5C^{-3}
$\alpha_{111} = -3.2 \times 10^7 \cdot T + 1.39 \times 10^{10}$	Vm^9C^{-5}
$\alpha_{12} = 6.7 \times 10^6 \cdot T - 2.24 \times 10^9$	Vm^5C^{-3}
$\alpha_{112} = -2.2 \times 10^9$	Vm^9C^{-5}
$\alpha_{123} = 5.51 \times 10^{10}$	Vm^9C^{-5}
$\alpha_{1111} = 4.84 \times 10^{10}$	$Vm^{13}C^{-7}$
$\alpha_{1112} = 2.53 \times 10^{11}$	$Vm^{13}C^{-7}$
$\alpha_{1122} = 2.80 \times 10^{11}$	$Vm^{13}C^{-7}$
$\alpha_{1123} = 9.35 \times 10^{10}$	$Vm^{13}C^{-7}$

Table 3.3: Wang et al. 8th Order Model (T in Kelvin)¹⁴.

Figures 3.4 and 3.5 show the c-axis and a-axis, respectively, electric susceptibility result of the Bell and Cross model plotted against the measured data of Merz. The polarization data was obtained from the model by imposing the condition of zero electric field and determining the roots of equations 3.3 and 3.4.

Recently an eighth order model has been proposed¹³. By the same technique of deriving

the predicted spontaneous polarization of the model by determining the roots of the polynomials obtained from the first derivatives of the free energy expression, and substituting in the second derivative expression, the predicted values of electric susceptibility versus temperature may be determined. The c-axis and a-axis susceptibilities for the eighth order model are shown in Figures 3.6 and 3.7 respectively.

An alternate sixth order model has been proposed by Quoc and Srinivas²⁹, but when evaluated for self consistency by determining the polynomial roots as above and calculating electric susceptibility using the model's own polarization, the model was found to fail, producing results very much inferior to the results of the Bell and Cross and the Li, Chen and Cross models, despite the claim of Quoc and Srinivas of a superior fit and their complex optimization algorithm.

The Bell and Cross sixth order thermodynamic model of barium titanate provides a reasonably accurate self consistent model for the electric behavior over the tetragonal and orthorhombic phase fields that is in good agreement with the experimentally determined values of Merz. The eighth order model of Li, Chen, and Cross offers a minor improvement primarily in improving the electric susceptibility fit in the orthorhombic phase, with only a slight improvement in the tetragonal phase region.

Figure 3.4: C-axis electric susceptibility predicted by the Bell & Cross model for the tetragonal and orthorhombic phases overlaid on the data of the Merz measurements.

Figure 3.5: A-axis electric susceptibility predicted by the Bell & Cross model for the tetragonal and orthorhombic phases overlaid on the data of the Merz measurements.

Figure 3.6: C-axis electric susceptibility predicted by the Li, Cross, and Chen model overlaid on the Merz experimental data.

Figure 3.7: A-axis electric susceptibility predicted by Li, Cross, and Chen model overlaid on the Merz experimental data.

Figure 3.8: Spontaneous polarization versus temperature for the Merz data and the sixth and eighth order models.

3.2 PZT Thermodynamic Model

PZT is a crystal formed of the two perovskites lead zirconate (PbZrO_3) and lead titanate (PbTiO_3). The crystal is both piezoelectric and ferroelectric and exhibits increasing dielectric constant as the zirconate fraction is increased. The phase diagram is shown in Figure 3.9. The P_c region represents the paraelectric cubic phase. F_t is the ferroelectric tetragonal phase field and F_r is ferroelectric rhombohedral. The rhombohedral region is split into two phase fields, a rhombohedral high temperature and a rhombohedral low temperature. The distinction is due to a tilt of the oxygen atoms on their polar axis at low temperatures, which must be accounted for in the thermodynamic model.

In references 15-19, a comprehensive thermodynamic model is developed covering all phase regions and compositions and including dielectric stiffness terms, oxygen tilt angle and electrostriction terms. For the purposes of this work, our interest is primarily in modeling the tetragonal phase field at close to room temperature and only the electrical effect (governed by the dielectric stiffness terms) of the thermodynamic model is of interest, as the mechanical strain effects are incorporated separately through a microelasticity model.

Figure 3.9. PZT Phase Diagram³²

The paraelectric-ferroelectric phase transition in PZT is only weakly first order for compositions near the concentration extremes of the phase diagram¹⁵, i.e. near either pure lead zirconate or pure lead titanate. For intermediate compositions the phase transition is predominantly second order.

For the rhombohedral phase $P_1^2 = P_2^2 = P_3^2 \neq 0$ in equation 3.2 and the spontaneous polarization can be determined as the roots of:

$$\begin{aligned}
\frac{\partial \Phi(P,T)}{\partial P_1} &= 2\alpha_1(T-T_0) \cdot P + 4\alpha_{11} \cdot P^3 + 6\alpha_{111} \cdot P^5 + \\
&\quad 4\alpha_{12} \cdot P^3 + 10\alpha_{112} \cdot P^5 + 2\alpha_{112} \cdot P^5 + 2\alpha_{123} \cdot P^5 \\
&= E_1 = 0
\end{aligned} \tag{3.12}$$

In the tetragonal phase, the only component of spontaneous polarization is along the axis of tetragonal elongation (c-axis). Setting $P_2=P_3=0$ reduces [3.2] to the c-axis result for the electric field.

$$\begin{aligned}
\frac{\partial \Phi(P,T)}{\partial P_1} &= 2\alpha_1(T-T_0) \cdot P + 4\alpha_{11}(T-T_c) \cdot P^3 + 6\alpha_{111}(T-T_c) \cdot P^5 \\
&= E_1 = 0
\end{aligned} \tag{3.13}$$

Very little experimental data is available on spontaneous polarization versus temperature, but a few researchers have published experimental results of the measurement of electric susceptibility versus temperature³³⁻³⁵ either for polycrystalline bulk PZT or c-axis oriented epitaxial films.

To validate the model of Huan, et al¹⁵⁻¹⁹, spontaneous polarization values over temperature were determined as roots of equation 3.12 or equation 3.13, depending on the phase field for the given composition. These polarization values were then used to calculate electric susceptibility according to equation 3.5 and compared against available experimental results.

The coefficients for PZT are dependent on the zirconate to titanate ratio. For 50% PZT (the composition used for the simulations of this work), the coefficients of the sixth order standard model¹⁶ for the tetragonal phase are repeated below. Coefficients for other compositions are contained in reference 16.

$\alpha_1 = 1.33 \times 10^5(T-392.6)$	VmC^{-1}
$\alpha_{11} = 4.764 \times 10^7$	Vm^5C^{-3}
$\alpha_{111} = 1.336 \times 10^8$	Vm^9C^{-5}
$\alpha_{12} = 1.735 \times 10^8$	Vm^5C^{-3}
$\alpha_{112} = 6.128 \times 10^8$	Vm^9C^{-5}
$\alpha_{123} = -2.894 \times 10^9$	Vm^9C^{-5}

Table 3.4 Huan et al 6th order model for 50% PZT

Figures 3.10-3.14 show the available results for various compositions of $PbZr_xTi_{(1-x)}O_3$ plotted against the prediction of the model. The best fits were obtained for the 70% zirconate epitaxial thin film samples of Takayama/Tomita³⁴ and the 50% bulk polycrystalline samples of Whatmore-Clarke³⁵, however the 52% epitaxial thin film samples of Kanno, Yokoyama, Kotera, Wasa³³ were a substantially poorer fit. For the Takayama data, although the fit of the rhombohedral composition of $x=0.7$ was quite good, the fit for tetragonal compositions of $x=0.4$ and $x=0.23$ was quite divergent particularly at high temperatures. The pattern in this set of data is a diminishing quality of fit as the zirconate fraction is reduced and as temperature is increased.

The Kanno data was obtained on an epitaxial thin film of c-axis oriented PZT grown by rf

magnetron sputtering on an MgO substrate. The Takayama data was similarly obtained on an epitaxial thin film of c-axis oriented PZT grown by rf magnetron sputtering on an MgO substrate, however when overlaid, the two sets of experimental curves are inconsistent.

The model is a reasonable fit for the available experimental data, but given the lack of data and the inconsistencies of similarly grown samples, a conclusive view on the validity of the 6th order GLD model can not be drawn. For two cases the model is a very good fit. In one case the sample was a bulk polycrystal and in the other it was a sputtered c-axis oriented thin film, so no statement can be made on the accuracy of the model for single crystal data relative to polycrystalline data.

Figure 3.10: Takayama/Tomita³⁴ Measurements vs. Huan/Furman/Jang/Cross GLD model¹⁵⁻¹⁹ for $x=0.4$ and $x=0.7$ ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$).

Figure 3.11: Whatmore-Clarke Measurements³⁵ vs. Huan/Furman/Jang/Cross GLD model¹⁵⁻¹⁹ for $x=0.9$ ($\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$).

Figure 3.12: Zhuang, Haun, Jang, Cross measurements³⁶ vs. Haun, Furman, Jang, Cross GLD model¹⁵⁻¹⁹ for 50% PZT.

Figure 3.13: Kanno,Yokoyama, Kotera, Wasa measurements³³ of $x=0.52$ PZT vs. Haun, Furman, Jang, Cross GLD model¹⁵⁻¹⁹ for 52% PZT.

Figure 3.14: Takayama/Tomita Measurements³⁴ vs. Huan/Furman/Jang/Cross GLD model¹⁵⁻¹⁹ for $x=0.23$ $(\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3)$.

4.0 Ferroelectric Bilayers

A thin film bilayer system is a stack of two thin films of different ferroelectric materials. The systems considered here are primarily a $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PZT) on PbTiO_3 (PTO) bilayer system with a 50% volume fraction for each of the layers, and a BaTiO_3 on PbTiO_3 system also with a 50% volume fraction for the layers.

A field applied normal to the plane of the film will tend to induce a polarization aligned with the field (c domains), which may exist as either a single uniform polarization state throughout the film (monodomain), or as a state of mixed, oppositely oriented domains with 180 degree polarization vectors (180 degree polydomain). The idealized assumption for analysis of the bilayer is that no in-plane (a domains) exist.

For a system of two different ferroelectrics, the bilayer stack exhibits electrical interactions between the layers which can result in the stabilization of a polydomain structure in one of the layers (stronger ferroelectric layer) over a broad range of applied electric field. The dominant effect in shaping the domain structure is the electrical field effect, although the mechanical effect of elastic strain energy is also a factor.

The electrical model of the ferroelectric bilayer with a fixed external voltage source is shown in Figure 4.1. The surface charge density (σ) is the polarization of the dielectric material. The electric field across the dielectric is given simply by the surface charge

density divided by the permittivity of free space (ϵ_0)* as all internal dipole fields within the dielectric can be considered as canceled by the adjoining end to end dipoles, leaving only the unpaired free charges at the surface.

Each layer of the bilayer supports a different electric field owing to the unique spontaneous polarization of each of the layers. By Kirchoff's law, the summation of the voltages on the two layers balances the applied voltage.

For characterizing the switching behaviour, two cases of domain structure are significant:

(a) polydomain in the stronger (higher value of spontaneous polarization) ferroelectric layer with a monodomain structure in the weaker ferroelectric layer, and (b) a monodomain structure in both layers.

* σ in units of C/m^2 and ϵ_0 in units of $N\cdot m^2/C^2$ gives the field in units of Newtons/Coulomb = Joules per Coulomb-meter = Volts/meter.

$$V = E(h_1 + h_2) = E_1 h_1 + E_2 h_2 \text{ (Kirchoff's Law)}$$

$$\alpha = \frac{h_2}{h_1 + h_2}$$

$$E = E_2 \alpha + E_1 (1 - \alpha) \quad [4.1]$$

Figure 4.1: Electrical Model of the Bilayer System.

The field E_1 of Figure 4.1 can be derived from first principles of charge separation by the superposition of two electric fields. The first field is due to the difference of the net charge at the top metal plate and the net charge at the layer 1 to layer 2 interface. The second field is due to the net charge at the bottom metal plate relative to a fictitious ground plane imagined to exist at the position of the top metal plate. The concept is illustrated in Figure 4.2.

$$E = \frac{(\sigma_0 - \sigma_1) - (\sigma_1 - \sigma_2)}{2\epsilon_0}$$

$$E = \frac{0 - (\sigma_2 - \sigma_0)}{2\epsilon_0}$$

$$\begin{aligned}
 E_1 &= \frac{(\sigma_0 - \sigma_1) - (\sigma_1 - \sigma_2)}{2\epsilon_0} + \frac{0 - (\sigma_2 - \sigma_0)}{2\epsilon_0} \\
 &= \frac{(\sigma_0 - \sigma_1)}{\epsilon_0} \quad [4.2]
 \end{aligned}$$

Figure 4.2: Derivation of the electric field by superposition

The field E_2 can be similarly derived.

$$\begin{aligned}
 E_2 &= \frac{(\sigma_1 - \sigma_2) - (\sigma_2 - \sigma_0)}{2\epsilon_0} + \frac{(\sigma_0 - \sigma_1) - 0}{2\epsilon_0} \\
 &= \frac{(\sigma_0 - \sigma_2)}{\epsilon_0} \quad [4.4]
 \end{aligned}$$

The total field is the sum of the two multiplied by their respective thickness fractions.

$$E = E_2\alpha + E_1(1-\alpha)$$

$$E = \frac{(\sigma_0 - \sigma_2)\alpha}{\epsilon_0} + \frac{(\sigma_0 - \sigma_1)(1-\alpha)}{\epsilon_0} \quad [4.5]$$

4.1 Case 1: Monodomain -polydomain bilayer

For the case of a bilayer ferroelectric consisting of the weak ferroelectric layer in the monodomain state and the strong ferroelectric in the polydomain state, the field in the strong ferroelectric may be approximated as zero as it can readily adjust its polarization to match the external polarization by simply adapting its ratio of positive to negative domain polarization. Migrating a domain boundary to expand or contract one monodomain region is significantly lower in energy than the event of nucleating a new domain within a region with dissimilar electrical domain.

Let α represent the thickness fraction of the strong layer (layer 1). Setting the field in the strong ferroelectric to zero, E_1 in equation 4.1, results in $E = E_2 \cdot (1 - \alpha)$ and $\sigma_0 = \sigma_1$.

Recognizing that polarization is surface charge density gives:

$$E = \frac{(\sigma_0 - \sigma_2)\alpha}{\epsilon_0} = \frac{(\sigma_1 - \sigma_2)\alpha}{\epsilon_0} = \frac{\Delta P \alpha}{\epsilon_0} \quad [4.6]$$

The electric field in the ferroelectric is given as the derivative of Ginzburg-Landau free energy polynomial expansion with respect to polarization.

$$\frac{\partial \Phi_2}{\partial P_2} = E_2 = \frac{\Delta P}{\epsilon_0} \quad [4.7]$$

For a given applied field E , the unknowns are the surface charge densities, σ_0 and σ_1 , which can be determined from equations 4.6 and 4.7. The approach taken is to fix the

applied voltage, which fixes ΔP for a given thickness, then the solution to the differential equation involving the thermodynamic potential derivative $(\partial\Phi_2/\partial P_2)$ in equation 4.7 gives P_2 (σ_2). Thermodynamic potential is described by a Landau expansion of the form of equation 3.1. P_1 is then known given P_2 and ΔP .

The electric field in the strong layer remains approximately zero regardless of the applied field and regardless of the layer thickness fractions, hence its effective dielectric constant approximates infinity. The dielectric constant of the bilayer stack is determined by the change in polarization of the stack for a given change in an applied field.

$$\chi = \frac{\partial P}{\partial E} \cdot \frac{1}{\epsilon_0} \quad [4.8]$$

The polarization of the stack is the average polarization of the two layers determined as:

$$P = \alpha P_2 + (1-\alpha)P_1 \quad [4.9]$$

The dielectric constant of the weak layer remains approximately constant and independent of the layer thickness fraction. The polydomain (strong ferroelectric) layer behaves as an infinite capacitance while the monodomain layer exhibits a capacitance that scales inversely with its thickness fraction. The composite structure behaves as a pair of capacitors in series, so the net result is exactly the same as if the weak ferroelectric layer were deposited alone without the influence of a second ferroelectric layer. Therefore the

polydomain layer has approximately no impact on the capacitance of the composite structure, thus rendering the bilayer structure not particularly useful for enhancing capacitance. The effect on the dielectric constant is somewhat artificial. The dielectric constant "appears" to be enhanced due to fact that one of the layers is made very thin, while capacitance is measured across more widely separated plates, thus there is an apparent enhancement effect on the dielectric constant as illustrated in Figure 4.3, but under the idealized assumptions used here for analysis, no real improvement in the dielectric constant occurs, furthermore such a device is unlikely to have any utility as the layer of strong ferroelectric is simply playing an electrical role that is equivalent to a metal plate.

The composite dielectric constant becomes approximately:

$$\chi = \frac{\chi_2}{\alpha}$$

Figure 4.3: Electric susceptibility of a PTO/PZT_{x=0.5} ferroelectric bilayer in a monodomain/polydomain state. α represents the thickness fraction of the weak ferroelectric (PZT) layer.

4.2 Case 2: Monodomain-monodomain bilayer

The situation where the bilayer system consists of a monodomain microstructure in both layers is governed by a system of three equations in three unknowns, the two differential thermodynamic equations, one for each layer, and the equation for the applied field as a function of the polarizations of each layer. For a given applied field E , the unknowns are the surface charge densities σ_0 , σ_1 , and σ_2 or equivalently the polarizations for the surface charge densities on the dielectrics.

$$E = \frac{(\sigma_0 - \sigma_2)\alpha}{\epsilon_0} + \frac{(\sigma_0 - \sigma_1)(1-\alpha)}{\epsilon_0} \quad [4.10]$$

$$\frac{\partial \Phi_1}{\partial P_1} = E_1 = \frac{(\sigma_0 - \sigma_1)}{\epsilon_0} \quad [4.11]$$

$$\frac{\partial \Phi_2}{\partial P_2} = E_2 = \frac{(\sigma_0 - \sigma_2)}{\epsilon_0} \quad [4.12]$$

Solving these three equations (4.10 - 4.12) for the bilayer composed of $\text{PZT}_{x=0.5}$ and PbTiO_3 , then calculating the electric susceptibility for each layer shows that the dielectric behavior is quite constant and independent of the thickness fraction. The susceptibility of the PZT layer is reduced to a value very close to the susceptibility of the strong lead titanate layer. The bilayer assembly does not exhibit any anomaly or spike for any value of the thickness fraction in contrast to the behaviour noted for the $\text{BaTiO}_3/\text{SrTiO}_3$ system

in reference 37. However in that work, the SrTiO_3 layer was above its Curie temperature (105 K) in its paraelectric phase, so the bilayer consisted of a ferroelectric/paraelectric composite.

The thermodynamic models for PZT follow those of references 15-19 and the system is assumed to be at room temperature.

4.3 Analytical hysteresis loops

An idealized dielectric polarization versus applied electric field plot may be developed analytically by considering only the effect of electrical polarization and chemical free energy using equations 4.10-4.12 for the dual monodomain layers or the simpler versions as equations 4.6 and 4.7 for the polydomain/monodomain layers. Mechanical strain energy effects and gradient energy effects are secondary, in general negligible, and therefore ignored in the idealized analysis.

The solution to the equations for the monodomain-monodomain case may be simplified by starting with a forced value of $\sigma_0 - \sigma_1$, the differential equation 4.11 is then solved for the polarization in layer 1, which for the Ginzburg-Landau model is simply the exercise of determining the roots of the polynomial. The external surface charge density σ_0 is then known from the value of P_1 and the forced charge density difference. The layer 2 polarization is determined by iteration of equation 4.12 to find a P_2 value that satisfies the differential equation. Substitution of the charge density values in equation 4.10 then gives the external applied electric field.

For the polydomain-monodomain case, the solution is substantially simpler as no iterative process is necessary. The ΔP value is similarly chosen as the independent variable, and the roots of equation 4.7 give the polarization of layer 2. Using the P_2 value and the known ΔP , both P_1 and σ_0 are then known.

The plot of the average polarizations versus applied electric field gives a characteristic S shaped curve for both the polydomain-monodomain system and for the fully monodomain system. A superposition of the curves for $\text{Pb}_{0.5}\text{Zr}_{0.5}\text{TiO}_3/\text{PbTiO}_3$ $\alpha=0.5$ is shown in Figure 4.4. The S-curves are symmetrical with a center of inversion at the origin. The S shape implies multiple stable solutions are possible in each case for small values of the electric field. Minimization of the overall system free energy will dictate whether the system takes on a polydomain structure in the strong ferroelectric layer or a monodomain structure in both layers. At very high applied fields the system will be fully poled and monodomain. As the field is reduced, the system will revert to polydomain in the strong ferroelectric layer at the point of a change of inflection in the thermodynamic potential function for the chemical free energy, analogous to the mechanism of spinodal decomposition, where the transition to negative curvature of the free energy function promotes a drift of equilibrium composition for small fluctuations due to random thermal noise on localized regions.

For the strong ferroelectric layer, PbTiO_3 , setting $\frac{\partial^2 \Phi}{\partial P_1^2} = 0$ results in a

P_1 value = $\pm 0.523 \text{ C/m}^2$ and a $P_{\text{avg}} = \pm 0.522 \text{ C/m}^2$, which is annotated in Figure 4.4 as $\pm E_c$.

Since the coercive field value (E_c) that would force the monodomain structure in the

strong ferroelectric layer to breakdown and the layer to adopt a polydomain structure is beyond the field at which a polydomain structure is stable, it can be expected that this system will never switch to the polydomain state once poled to the fully monodomain state. The hysteresis loop will become a simple broad square loop with switching points at the nose of the monodomain-monodomain S-curve as indicated in Figure 4.5. The coercive field is approximately 80 MV/m which is near the limit of the dielectric breakdown strength for PZT (~ 120 MV/m) and would require large voltages applied across the thin film device, with a 1 micron film requiring an 80 V coercive field.

Figure 4.4: $\text{Pb}_{0.5}\text{Zr}_{0.5}\text{TiO}_3/\text{PbTiO}_3$ $a=0.5$ bilayer system polarization versus applied electric field.

Figure 4.5: Hysteresis Loop $\text{Pb}_{0.5}\text{Zr}_{0.5}\text{TiO}_3/\text{PbTiO}_3$ $\alpha=0.5$

Figure 4.6 shows the polydomain-monodomain curve superimposed on the monodomain-monodomain curve for a $\text{BaTiO}_3/\text{PbTiO}_3$ bilayer system also with a layer thickness fraction (α) of 0.5. For the $\text{BaTiO}_3/\text{PbTiO}_3$ system the coercive field which forces a switch from the fully monodomain state to the polydomain-monodomain state occurs well within the region of a stable polydomain-monodomain structure, therefore the hysteresis loop would be a narrow double loop as depicted in Figure 4.7 if the material were able to sustain the large coercive electric field of approximately 580 MV/m. Since a

field of that magnitude is beyond the dielectric strength of the material (~ 100 MV/m), it can be expected that this system can never be truly fully poled and will exist only in its monodomain-polydomain state.

Figure 4.6: BaTiO₃/PbTiO₃ bilayer system polarization versus applied electric field.

Figure 4.7: BaTiO₃/PbTiO₃ theoretical hysteresis loop shape

4.4 General hysteresis loop shapes

Following the above thermodynamic analysis, representative theoretical P vs. E curves are shown in Figure 4.8. Critical points, a, b, c, d, that define the shape of the resulting hysteresis loop are indicated in Figure 4.8a. Point a is the point at which the polydomain-monodomain state switches to a monodomain-monodomain state on increasing field. Point b is the point at which the opposite switch occurs on decreasing field. Points c and d are the points at which the curves lose stability for the polydomain-monodomain (S-P) system and for the monodomain-monodomain system (S-S) respectively. Three types of loops can result depending on the location of point b and the maximum field that the material can sustain.

If point b lies between c and d then the switch to S-P does not occur on decreasing field, therefore a single broad loop will be the result (outer loop Figure 4.8b). If point b lies between c and a then a double loop feature will be the result (Figure 4.8c). If the maximum field that the material can sustain is below point a then the double loop feature does not appear and the result is a single narrow loop (inner loop Figure 4.8b).

a

b

c

Figure 4.8: Representative bilayer system hysteresis loops⁴⁹

4.5 Simulation Results

Simulations were performed using the phase field model (PFM) to predict the microstructure developed in thin film bilayers. Thermodynamic parameters for a Ginzburg-Landau-Devonshire 6th order model corresponding to $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PZT) on PbTiO_3 (PTO) at 20° C with equal thickness of each layer were used.

The ratio of electrostatic energy to the phase transformation free energy change (λ) and the ratio of elastic strain energy to the phase transformation free energy change (ζ) were varied. Although the parameters used describe with reasonable accuracy a PZT on PTO system, by varying the electrical energy/chemical energy and strain energy/chemical energy ratios, the behaviour of the system is distorted. The modification is for the purpose of separately understanding the effects of mechanical energy and electrical energy in shaping the equilibrium morphology of the bilayer structure.

At very low values of ζ the microstructure consists of lamellar domains of 180° polarization variants which extend through both layers as shown in Figure 4.9, where the vertical direction is normal to the film and a pronounced step with some small region of a-domains is evident at the boundary between layers. From an electrical energy standpoint, each ferroelectric layer naturally prefers a different ratio of 180° domain fractions because of the unique spontaneous polarization of each layer. With the low value of ζ , the mechanical energy cost of the stepped change in domain thickness is low,

therefore the electrical effect dominates and the result is lamellar through thickness aligned domains with a relatively sharp step in domain thickness at the interface between the films.

As ζ increases (right image of Figure 4.9), the mechanical energy of the stepped structure becomes sufficient that the system loses its dual polydomain stability and the overall bilayer polarization state is electrically accommodated by a monodomain structure in the weak ferroelectric layer with a polydomain structure in the strong ferroelectric layer. By breaking into a monodomain-polydomain system, all interfacial energy effects are removed within the monodomain layer, thus strain energy is minimized within that layer. The polydomain layer assumes a columnar domain structure as the columnar domain shape offers more enclosed volume for less surface energy cost than the lamellar shape. Since domain walls have a finite thickness where one polarization variant gradually adapts to its 180° degree opposite variant, the domain wall has an elastic strain energy cost. The energy associated with the domain wall places a limit on the fineness of the domain structure.

As ζ is increased further to 1.5, the system reverts to a through thickness aligned lamellar domain structure, but with no abrupt step at the film boundary and an approximately uniform thickness in both layers as shown in Figure 4.10. The constant thickness domain has an electrical cost due to the fact that the different ferroelectric layers have unique spontaneous polarizations, but the mechanical energy cost is minimal.

Additional simulations were performed with the value of λ reduced to 6, but negligible difference in microstructure was observed. The electrical energy effect is substantially greater than the mechanical energy effect such that a 50% reduction in electrical energy still leaves it dominant.

$\lambda = 12, \zeta = 0.25$

$\lambda = 12, \zeta = 0.5$

Figure 4.9: Transition from stepped lamellar to columnar with increasing ζ

$$\lambda = 12, \zeta = 1.5$$

Figure 4.10: Lamellar domain structure of $\zeta=1.5$

The simulations show that the morphology is strongly determined by the relatively small contribution to total energy of elastic strain. For very low stiffness materials, the films equilibrate with a lamellar structure with the lamellae aligned between films but with different thicknesses, due to the different spontaneous polarizations of each of the ferroelectric layers, because that is the structure which minimizes the electrical energy contribution to the free energy. At high mechanical strain the structure is again lamellar, but the thickness is quite uniform in both ferroelectric layers. The system pays an electrical energy cost to have uniform lamellae in each layer, but this cost is offset by a savings in strain energy where no gradation of polarization is required at the interface to accommodate a stepped domain. At intermediate values of mechanical strain energy, the

system breaks into a monodomain-polydomain columnar structure where the strong ferroelectric layer becomes polydomain. The polydomain-monodomain structure represents an energy compromise solution where the electrical energy penalty is due to the non-ideal monodomain structure of the strong layer, and the mechanical energy penalty is strain associated with the domain wall of the columnar domains.

In the work of reference 49, the subject of domain morphologies in thin film bilayers was addressed through phase field modeling. Part of that study considered a pair of bilayer systems with different electrical to chemical energy ratio (λ), while the electrical to mechanical energy ratio (ξ) was held fixed, i.e. both systems had the same chemical energy but one system had relatively high electrical and mechanical energy compared to the other. The domain morphologies developed in the two systems were similar but with the notable difference that the high λ , ξ system produced sharper corners on its closing domains (Figure 4.11), likely attributable to its relatively low chemical energy cost. The low cost of chemical energy in the system would mean that domain wall energy is lower as the system could more easily afford to deposit some paraelectric phase material in the domain wall.

Figure 4.11 Domain morphologies in bilayer films⁴⁹. Left: $\lambda = 60$, $\xi = 125$. Right: $\lambda = 250$, $\xi = 125$.

4.5.1 Results with surface contacts modeled

The simulation results discussed above were run with no external applied field and the inherent periodical boundary conditions of the PFM (Figure 4.12), which yields a surface charge due to the polarization difference in the layers. The polarization difference at the interface becomes equivalent to an applied electrical field that evolves with time as the average polarization in each layer changes with the evolving domain structure.

To remove the effect of the "floating" external electric field that changes as the domain structure evolves, the program was modified to introduce a cancellation field by creating an image charge field that mirrors the charges of the evolving dipoles within an extended computational volume (figure 4.13). By canceling the uncompensated surface charges of the polarized films, the external field can be controlled, producing a more accurate computational result. The cost is increased computation due to the doubling of the computational volume.

Figure 4.12: Periodical Boundary Conditions

Figure 4.13: Extended computational volume element for implementing zero potential on the substrate surfaces

With the zero potential on the film surfaces implemented, the simulations result in an entirely in-plane domain structure as no external field is present to align growing domains, therefore a small bias field is required. At low applied field strengths, the external field is insufficient to maintain a monodomain state in the strong layer and the microstructure is lamellar and dual polydomain, but as the field is increased, at some field strength magnitude, a monodomain state can be stabilized in the strong layer leaving only the weak ferroelectric layer with a polydomain structure (Figure 4.14), which is typically columnar.

Varying the strength of the bias field while keeping λ and ζ fixed can result in switching the polydomain film from a 180° columnar type of structure to a c-a rounded plate-like domain structure as indicated in Figure 4.15, however the energy difference between the two structures is quite small and therefore both can be stable under the same conditions, making the equilibrium microstructure path dependent. For the same applied field and fixed λ and ζ , both structures were observed depending on the seed value used to generate pseudo-random noise or the initial state.

For very high levels of applied field, the polydomain state of the weak layer also breaks down to become monodomain and the bilayer is simply fully monodomain. The field level at which this occurs is ζ dependent. For a high ζ value (relatively large elastic strain energy) the bilayer becomes fully monodomain at a lower applied field strength. Due to the finite domain wall thickness, any polydomain structure will have some

associated elastic strain energy, therefore if the strain energy effect is increased, the system will favor coarsening the domain structure at some lower level of applied electric field.

Figure 4.14: Transition from a dual lamellar polydomain bilayer film domain structure (lower micrographs) to a monodomain/polydomain columnar domain structure on increasing field strength (upper micrographs)

Figure 4.15: Microstructure cross sections transitioning from columnar to c-a.

4.5.2 Hysteresis Loop Simulations

Using the PFM and applying a sinusoidal electrical field to the ferroelectric bilayer with conductive surface contacts, and recording polarization versus applied field, a hysteresis loop may be developed. Figure 4.16 shows such a loop for a 50% $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PZT) on PbTiO_3 . The simulated loop is overlaid on a calculated result determined from the principles described in sections 4.1 and 4.2. The fit is clearly quite close, which tends to validate the assumption of the polydomain layer adapting its polarization with approximately zero energy expenditure and therefore supporting no electrical field within the layer. Similar closeness of fit between PFM simulated and analytically obtained loops was observed for the bilayer systems studied in reference 49.

Figure 4.16: Calculated versus simulated hysteresis loops for a PZT/PbTiO₃ bilayer

5.0 Porous and nanocomposite thin film simulation results

Simulations were performed using the phase field model (PFM) to predict the domain structure developed in nanocomposite thin films where the nanocomposite consists of ferroelectric and dielectric materials. Two types of nanocomposite films were studied. The first consisted of a ferroelectric matrix with a spherical dielectric inclusion. The second was the inverse system of a dielectric matrix with ferroelectric inclusion. The most interesting system electrically is the porous ferroelectric, which is the limiting case of a dielectric inclusion in a ferroelectric matrix, where the inclusion is simply an air cavity.

The dielectric was modeled by continuously forcing the polarization calculated for the dielectric region to zero within the PFM iteration loop, hence the region is forced to have zero ferroelectric susceptibility but because a "background" electric susceptibility is inherent in the way the material is modeled, the dielectric constant of the dielectric material is not 1.0, as would be the value for air, but instead the dielectric constant has a value of around six times for both the lead titanate and barium titanate models. The inclusion region is elastically equivalent to the matrix, so mechanically it behaves like the surrounding matrix. Therefore, due to limitations of the model, the porous film that is the main subject of study is neither electrically or mechanically equivalent to air and is more accurately described as a type of nanocomposite film which consists of low dielectric

constant spherical inclusions that are rigidly attached to the matrix.

The limitation of the model is not a fundamental limitation as the phase field model has been applied to the modeling of voids in elastic bodies⁵⁰. Appropriate modifications could be incorporated to elastically decouple the inclusion from the matrix, accurately treating it as a void. This was not used because of the simulation time penalty involved, but the necessary changes to the PFM implementation used in this research work were created and the concept was validated. A full model of a porous structure would also require that the pores be modeled as air with a dielectric constant of 1.0 which would mean modeling a material with an inhomogeneous electric susceptibility in addition to modeling the mechanical effect of the elastic discontinuity of the void.

The other type of nanocomposite film considered is one with a spherical ferroelectric particle embedded within a dielectric matrix. The situation is the inverse of the one above, with the matrix having the low dielectric constant and the rigidly attached particle being ferroelectric.

Metal contacts were modeled for all simulations as described in section 4.4.1.

Thermodynamic models for PbTiO_3 and BaTiO_3 were used as described in Chapter 3. λ and ζ values of 12 and 2.2 respectively were used and believed to be approximately correct for lead titanate. For barium titanate λ and ζ are estimated to be about 3 and 2.2 respectively, although BaTiO_3 simulations were run for λ of both 12 and 3.

The temperature for all simulations was 20°C. The approximate length scale for the total size of the cubic systems is on the order of 150 nm (based on the chosen value of the gradient coefficient tensor and experimental work on measured domain wall thickness). In all domain structure plots, the x-direction is normal to the plane of the film and is the direction of the applied field.

Uncompensated charges are present on the free surface of any polarized dielectric where some component of polarization is normal to the surface. As demonstrated by the domain structure simulations where the results for unmetallized ferroelectric stacks having bound surface charges were clearly different than for simulated metallized surfaces where the surface charges were compensated by the source of applied electric potential on the metal plates (section 4.4.1), these surface charges can influence the development of the electrical domain pattern in the films. The effect is such that a polydomain structure is favored by the presence of the bound charge, which leads to the idea of deliberately introducing voids or non-ferroelectric inclusions to the ferroelectric for the purpose of stabilizing a polydomain state. A stable polydomain state is normally present in a bilayer film at relatively low levels of applied electrical field and is stable in a single layer ferroelectric only at much lower levels of applied electric field.

On the steep portion of the hysteresis loop P vs E curve for the ferroelectric a large fraction of in-plane domains are present. The richly polydomain state may either be dominant as a stable structure for that level of applied field or exist as an unstable

intermediate state during switching. Since $\partial P/\partial E$ is highest for the steep part of the P vs. E curve, and electric susceptibility is defined as $\partial P/\partial E$, a balanced polydomain state for a ferroelectric can typically be expected to have a higher dielectric constant than a ferroelectric in a monodomain state. The effect may also be understood on the basis of polarization mobility where the gradual change in polarization at the domain wall may be relatively easily shifted from one 180° orientation to another and the domain wall migrated, whereas a fully monodomain state requires a much greater driving force to completely invert its polarization, because a domain of the polar opposite state must first be nucleated. The conversion of polar opposite domains is further enhanced if some substantial fraction of in-plane domains are present. Therefore a possible avenue to engineering a high dielectric constant material is to exploit the effect of induced voids in stabilizing a polydomain state, especially a polydomain state that includes a significant fraction of in-plane domains.

The countervailing effect of the void is to dilute the permittivity of the material by introducing air with a dielectric constant comparable to that of vacuum or 1.0, which can be approximately expected to reduce the permittivity in simple proportion to the volume fraction of the pores. Stabilizing a domain structure in the film can be expected to have a much larger effect and may be very non-linear as a function of the film porosity. At a certain level of film porosity, void size, and distribution, a stable domain structure up to a certain coercive field strength can be expected to persist, which should substantially increase the dielectric constant of a typical ferroelectric.

To examine the effects of voids, a spherical inclusion was created in a cube of length 64 on a side. The spherical region was electrically modeled as low dielectric constant material by overriding the polarization evolution for that region, setting it to zero. Mechanically the sphere remained a solid with elastic properties equivalent to the matrix, but the mechanical effects are believed to be insignificant and dominated by the electrical effect. The results confirm that the spherical void modeled in this way has the effect of stabilizing a polydomain structure.

In Figure 5.1 central cross sections are shown, with arrows indicating the directions of polarization within each domain, for systems containing spherical void radii of 24 and 16, each located at the cube center, in a PbTiO_3 cube of size $64 \times 64 \times 64$. To produce a partially poled structure, the applied electrical field was set to a dimensionless value of $E=0.00001$ (≈ 150 kV/m) on the x-axis for each case. The void of radius 16 produced domains that were predominantly aligned with the field (90% volume fraction), about 3% oriented 180° to the applied field, and the balance in-plane domains. The void simulation for the radius 24 sphere produced quite different volume fraction results, with far fewer domains aligned with the applied field (approximately 59%) and a much larger volume fraction of in-plane domains (19%). When the applied field was removed, a stable polydomain state remained in each case.

For an applied field that is normal to the film, the polarization surface charge induced on the interior of the spherical void surface creates an electric field component that is in the plane of the film, therefore it tends to stabilize in-plane domains. The void also tends to promote a polydomain structure in order to minimize charge on its surface. Polarization vectors that are tangential to the void surface will eliminate any charge at the surface, therefore a domain structure that is maximally tangential to the void will tend to develop in zero field and be quite stable with respect to changes in the applied field. Both effects cause the void to stabilize in-plane domains.

Figure 5.1: Central cross sections of a 64x64x64 cube with a spherical void at the center; left: radius 16 sphere; right: radius 24 sphere. Applied field on x-axis. Arrows indicate directions of polarization.

5.1 Hysteresis loops of the porous ferroelectric

Figure 5.2 shows a hysteresis loop obtained with a radius 24 spherical void inserted in a 64x64x64 cube (22% void volume fraction) of PbTiO_3 . A sinusoidal electric field was applied as stimulus in simulation. As indicated in the domain structure plots of Figure 5.1, the larger volume fraction void greatly enhances the fraction of in-plane domains over a broader range of applied field than a smaller void. The same polydomain stabilization effect can be inferred from the hysteresis loop, where the switching is not abrupt as in the solid material, but follows a shallower discontinuous slope, evidently due to the void inducing a stability to the polydomain structure.

Figure 5.2: Hysteresis loop for a radius 24 void in a 64x64x64 cube of PbTiO₃. Measured susceptibilities from the simulation data at various points are as indicated. The theoretical susceptibility of PbTiO₃ based on the thermodynamic model used is 66.

The region of switching where steps appear (labeled A on Figure 5.2) was further investigated by simulating at fixed static levels of applied field. Figure 5.3 shows this switching region. The electric field levels over which the switching occurs are reduced relative to Figure 5.2 where sinusoidal stimulus was used. The effect is attributable to a lag in the simulated domain structure which requires time to stabilize, thus, for a continuously changing applied field, it is constantly chasing the field. Two steps are evident in Figure 5.3, which correspond to states in which a polydomain structure is

somewhat pinned.

The steps of figure 5.3 correspond to quasi-stable states. Once the material has acquired this state, the region of stability is large and very linear. Schematically these are drawn as dotted lines on Figure 5.2. Figure 5.5 shows the effect of "retracing" the applied field on the steps for the radius 24 spherical void in the 64x64x64 cube. The electric susceptibility ($\partial P/(\epsilon_0 \partial E)$) measured in this state is approximately 400 on the upper & lower slopes, and slightly less on the middle slope, while the electric susceptibility of the fully poled material is only in the range of 50-100 depending on the field in which it is measured (Figure 5.2). The theoretical electric susceptibility for PbTiO_3 based on the thermodynamic model used in simulation at 20°C is 66.

Figure 5.4 shows the domain structure within a stable intermediate slope of Figure 5.2 (radius 24 inclusion) and within a similar stable slope for a radius 20 inclusion at the point of zero applied electric field. Clearly the patterns are similar. Note the dominance of in-plane domains.

Figure 5.3: Polarization versus applied field in the switching region ("A" Figure 5.1) for a radius 24 spherical void in a 64x64x64 cube.

Figure 5.4: Domain structure plots at $E=0$ for the intermediate stable slope for radius 20 sphere (left) and radius 24 sphere (right). The patterns are remarkably similar for both inclusion sizes and over a range of applied fields. Note that domains are predominantly in-plane. Arrows indicate the directions of polarization.

Figure 5.5: Dielectric constant enhancement in the stabilized switching region of a porous ferroelectric (void radius = 24)

Smaller void volume fractions produce sharper switching transients, so the region of high polydomain stability during switching is more difficult to induce. Figure 5.6 shows the intermediate states of high polydomain stability for a radius 22 spherical void in the same 64 cube (17% volume fraction) of PbTiO_3 . The middle stability region has a dielectric constant of about 60% of that of the two symmetrically offset stability regions. Similar measurements for a radius 20 void in the 64 cube (13% volume fraction) indicate similar dielectric constants for three stable states, but with the void size reduced to 16

(6.5% volume fraction) no region of intermediate polydomain stability could be detected on the hysteresis loop.

Figure 5.6: P vs. E for the intermediate stable polydomain regions (void radius = 22).

Figure 5.7 shows the domain structure at three orthogonal cross-sections through the center of the cube for a radius 22 void. The domain structure corresponds to a stable point on the P vs. E curve of Figure 5.6 at about 22 MV/m (point A), but very similar domain structures are present at all points along the indicated line with electric susceptibility of approximately 230. The domain structure consists almost exclusively of in-plane components of polarization (a-domains). The c-domains account for only about a 3.5%

volume fraction.

Figure 5.7: Central cross-sections of the cube showing domain morphology for a radius 22 spherical void in an applied field in the x direction of 22 MV/m. Almost all domains are in-plane and of a single variant (77% -y, 4.5% +y). Arrows within the domains indicate the direction of the polarization vector.

5.1.1 BaTiO₃ hysteresis loops

Figure 5.8: BaTiO₃ hysteresis loops for dielectric inclusions of radii 16, 24 and 28.
 $\lambda=12, \zeta=2.2$

Figure 5.8 shows the effect on the hysteresis loop of changing the inclusion radius from 16 to 28 while using the barium titanate thermodynamic model, but keeping the electrical to chemical and mechanical to chemical energy ratios at 12 and 2.2 respectively. Figure 5.9 shows the same result for the radius 28 and radius 24 inclusions with the electrical to chemical energy ratio reduced to 3, which is a value estimated to be more correct for BaTiO₃, based on the calculated free energy change and the calculated spontaneous polarization value (0.266 C/m²) of the thermodynamic models of chapter 3. The effect of reducing the strength of the electrical effect is to broaden the loop, because with a

reduced electrical strength, the material has less incentive to switch in response to the applied field, so it remains more mechanically pinned at greater applied field strengths.

Figure 5.9: BaTiO₃ hysteresis loops for dielectric inclusions of radii 24 and 28. $\lambda=3$, $\zeta=2.2$

The notable difference in the hysteresis loops from the results for lead titanate is the lack of a pronounced step feature during switching. Clearly the switching slope is reduced as the inclusion size increases, but it is not clear from the dynamic simulation plot whether the transition states on the switching slope are stable, or just slow to adapt to the changing field. To determine whether they are stable, additional simulations were run

with a static field.

Figure 5.10 shows polarization versus time as the result of using a starting structure corresponding to the state at point A of Figure 5.9, then fixing the field to a small negative value. In response, the polarization settles to a value of about -0.067 C/m^2 , which is intermediate between the switched extremes. Figure 5.12 shows the equilibrium domain structure. Using other values of static applied negative field causes the polarization to reach the same final state. Static values of positive field caused the structure to drift to a symmetrical positive state, demonstrating that the material behaves very similarly to PbTiO_3 .

Figure 5.10: Polarization versus time for the radius 28 spherical inclusion in BaTiO_3 as a result of using a fixed negative applied field and the starting state of point A in Figure 5.9. A stable point is reached just as is the case for PbTiO_3 .

Figure 5.11 shows the P versus E plot obtained by using an intermediate stable state for the system with radius 24 inclusion as a starting point and applying a sinusoidal stimulus with fixed dc offset. A complete cycle of the sine wave was not applied therefore the loop is not "closed". The electric susceptibility measured from the curve is approximately 240, which is about 2-4 times the value simulated for the same radius 24 inclusion as indicated in Figure 5.9.

Figure 5.11: P vs E for a small applied field starting from the stable polarization state of Figure 5.10. Only a part cycle sinusoidal stimulus was used. Measured $\chi \approx 240$.

Figure 5.12: Equilibrium domain structure corresponding to the polarization of Figure 5.10. About 50% of the domains are in-plane. Arrows within the domains indicate the direction of the polarization vector.

5.2 Elastic energy effect

The energy of the electric field dipole interactions is far greater than the energy of the elastic strain field, but the effect of elastic strain energy in stabilizing a polydomain structure in the porous ferroelectric is not negligible. Figure 5.13 shows the effect of varying the strength of elastic strain energy on the shape of the hysteresis loop for the case of the spherical cavity of radius 24. Strain energy strength is controlled in simulation through the parameter ζ , which sets the relative strength of strain energy to chemical energy. A value of ζ of 0.2 is unrealistically low for the perovskite materials considered, while $\zeta=2.2$ is estimated to be approximately correct for PbTiO_3 .

The sharper switching transition for the low strain energy material shows the role of elastic energy in pinning domains. The migration of a domain wall requires that some region of the crystal be converted to another domain orientation, which would strain that region of crystal relative to its neighbors, therefore a mechanically stiffer material can be expected to exhibit reduced domain mobility.

Since the void is artificially modeled with an elasticity equivalent to that of the matrix and is effectively "welded" to the matrix, it may also contribute to increasing the resistance of the material to domain wall motion, but the effect should be far less within

the void region than within the matrix because the void does not support a domain structure and the effect of the elasticity of the inclusion in pinning domains can only be present at the boundary. The void is also forced to be in its paraelectric phase so it is mechanically neutral with respect to any orientation that an adjoining piece of crystal may adopt. For these reasons it is believed that the effect of modeling the cube of material as an elastic continuum is quite realistic despite the marked effect shown by the change of elasticity in Figure 5.13.

Figure 5.13: The effect of elastic energy. With negligible elastic energy ($\zeta=0.2$), no switching shoulder is evident on the hysteresis loop (spherical void radius = 24 in PbTiO_3).

5.3 Ferroelectric particle in a dielectric matrix

The inverse system of a ferroelectric inclusion in a very weak dielectric matrix was also investigated. Figure 5.14 shows a P vs. E plot for a PbTiO_3 radius 28 spherical inclusion in a $64 \times 64 \times 64$ non-ferroelectric matrix (35% volume fraction ferroelectric). Like the previous dielectric inclusion simulations, the simulation was run by continuously overriding the calculated polarization value for the non-ferroelectric region to set it to zero, hence the matrix becomes non-ferroelectric, with the inherent "background" dielectric constant. Mechanically, the inclusion and matrix are equivalent, so the composite modeled is one with an inclusion rigidly attached to a matrix that has a dielectric constant equal to the modeled background constant or about 6.

The electric susceptibility in the linear range of the P vs E curve has a value of only around 9 which is well below the theoretical value of 66 for lead titanate predicted by the same thermodynamic model and below the value expected of a material composed of lead titanate proportionally diluted by a material of electric susceptibility of 0. Although the curve shows some nonlinearity at its extremes, the field strengths of several GV/m would be well beyond the breakdown strengths of any real material, therefore nonlinearity in the curve could not be exploited to produce a tunable device.

The ferroelectric inclusion does transition through richly varied stable polydomain states,

but the surrounding matrix remains fully monodomain and the dielectric constant remains quite constant over the linear region shown in Figure 5.14. Figure 5.15 shows an example of the polydomain microstructure at zero field.

Figure 5.14: P vs E for a radius 28 PbTiO_3 inclusion in a weak dielectric (non-ferroelectric) 64x64x64 matrix.

Figure 5.15: Central cross section domain structure plots corresponding to point A in Figure 5.14.

6.0 Conclusions

Composite ferroelectric thin films consisting of low dielectric constant inclusions embedded in a ferroelectric matrix have been demonstrated through simulation to offer a significant increase in the dielectric constant of the composite over that of the homogeneous ferroelectric by stabilizing a polydomain state, in particular an in-plane domain state, in the ferroelectric. The a-axis domains have a greater dielectric constant than the c-axis domains and are more easily re-oriented to align with the applied field as the energy barrier that must be surmounted to flip a domain 90° is generally less than that to flip a domain 180° .

The inclusion could also be imagined to be a void with a dielectric constant of 1.0, which would make the structure a porous film. A possible additional benefit of the porous structure is reduced loss tangent which would enable its use at high frequencies. A downside of the porous structure is the impact on the structural integrity of the film of removing 22% or more of the material. A technique for modifying the phase field model to accept elastic voids was investigated and implemented for verification, but not implemented to model a porous ferroelectric because of the computational penalty.

The inclusion promotes an in-plane domain structure in the ferroelectric through two mechanisms. The first is that distribution of charge on the surface of the spherical

inclusion creates an in-plane component of electric field which stabilizes a corresponding component of polarization. The second is the formation of closing domains, as tangential as possible to the sphere surface, in the ferroelectric material around the sphere to minimize surface charge on the sphere. The polydomain stabilization effect of the inclusion was found to be so strong as to prohibit complete poling to a 100% monodomain state even in fields well in excess of the dielectric breakdown strength of the material.

The dielectric constant increase was determined by simulation to be approximately between about four and eight times in lead titanate and between about two and four times in barium titanate for inclusion volume fractions that are about 22% or more and inclusion diameters that are 75% or more of the film thickness. The dielectric constant increase is over a range of applied field that is a significant fraction of the dielectric breakdown strength of the material. Barium titanate is dominant in the electrical capacitor industry and is commonly used in the form of a thin film, so the increase in dielectric constant over such a significant range of applied field has strong industrial merit and the technology is potentially patentable and valuable. The fabrication of devices to test the simulation result would be a very worthy research project, but was beyond the scope of this research.

In one respect, a real void should have a stronger polydomain stabilization effect than that of the simulated inclusion because the simulated inclusion is subject to the inherent

background (non-ferroelectric) dielectric constant of the material whereas a real void is air with a dielectric constant of 1.0. In another respect, a real porous material cannot be expected to be fabricated with nearly as perfect a uniformity and distribution of voids as the simulated material, which should detract from the polydomain stabilization effect, so the overall effect on dielectric constant that can be realized is uncertain.

The simulated hysteresis loops of the dielectric inclusion in the ferroelectric matrix were complex loops consisting of intermediate stabilized states, which is a type of ferroelectric hysteresis loop not known to have ever been observed experimentally in any material nor to have been postulated to exist by any previous analytical work. Enhanced dielectric constant in the intermediate states may be not the only useful artifact of such a novel characteristic. The multiple stable switching levels suggest that such a material may be used to make a multi-state memory element, allowing an effective ferroelectric memory density increase of two times for a material with four stable states.

Bilayer devices structured of $\text{PbTiO}_3/\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ were simulated and found to not have a dielectric constant higher than the homogeneous film of a single material because the system is of a type in which the layers are simply both monodomain for all stable points on the hysteresis loop. In general, the system of dielectric inclusions in a ferroelectric film were found to be more effective at stabilizing a polydomain structure than the ferroelectric bilayer system, in that a high percentage of in-plane domains can be stabilized by the presence of the inclusion, whereas the bilayer system stabilizes

primarily a mixture of 180° domain types.

The analytically derived hysteresis loop for $\text{PbTiO}_3/\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ based on established thermodynamic models and the simplifying assumption of a uniaxial polarization vector in the polydomain layer was found to be in excellent agreement with the simulated hysteresis loops, thus validating the analytical approach. A bilayer consisting of $\text{PbTiO}_3/\text{BaTiO}_3$ was also analyzed but not simulated. The analysis shows a narrow double hysteresis loop, but with the secondary loops beyond the dielectric breakdown strength of the material.

The three types of bilayer system hysteresis loops shown in Figure 4.8 degenerate to only two basic types. The type depends on the location of the point of loss of stability of the dual monodomain state on decreasing field. If the point b of Figure 4.8 is below the field strength at which a polydomain-monodomain structure is stable, then the loop becomes a simple broad loop, otherwise a double loop exists consisting of a relatively narrow loop centered at zero field with smaller secondary loops at much higher field strengths. If the field strength at which the secondary loop would appear is beyond the dielectric breakdown strength of the material, then it will not be observed experimentally.

The simulation of a ferroelectric composite consisting of a dielectric matrix and a ferroelectric inclusion of PbTiO_3 showed the structure to have negligible hysteresis and to

not offer the same dielectric constant enhancement as the inverse system. Although a polydomain state can be stabilized within the inclusion, and a dielectric constant increase realized as a result, the overall dielectric constant of the system is significantly lower than if PbTiO_3 were used homogeneously.

The PbTiO_3 inclusion in the dielectric matrix system had high linearity in its polarization versus applied field, therefore it is not useful as a tunable device. The idea of adding ferroelectric particles to a dielectric matrix may have merit for the purpose of engineering a composite with a dielectric constant that is controlled by the volume fraction of ferroelectric, but the simulations indicate that a dielectric constant higher than that of the ferroelectric alone can not be achieved.

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