Flexoelectricity, Strain Gradients, and Singularities in Ferroelectric Nanostructures

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Abstract

The effect of flexoelectricity on the formation and evolution of domain structures in ferroelectric materials is developed by integrating strain gradient theory into a finite element phase field model. Length scales associated with elastic strain gradients and the corresponding polarization gradient across a domain wall are integrated into the time-dependent Ginzburg-Landau theory and numerical simulated. Theoretical relations of a shear strain gradient along an electrode/dielectric interface are first solved and verified numerically using the finite element model. A singularity in the strain gradient induced polarization is shown to occur as the elastic strain gradient length scale approaches a flexoelectric length scale. The theory and finite element modeling is then extended to quantify strain gradient electromechanics near 180° and 90° tetragonal phase domain structures. It is shown that the strain gradient length scale (l₁) strongly influences changes in strain across the domain walls but has a negligible effect on the polarization. Strain gradient effects become negligible when l₁ ≃ 0.1 LP where LP is the polarization domain wall length scale.

1 Introduction

Flexoelectricity is an interesting higher order electromechanical coupling phenomenon that occurs in all insulating solids (Tagantsev, 1986; Resta, 2010; Cross, 2006; Zubko et al., 2013; Yudin and Tagantsev, 2013; Catalan et al., 2004; Kalinin and Morozovska, 2015). This material coupling manifest due to a strain gradient that asymmetrically redistributes charge within a solid creating finite polarization. This effect has been previously studied in biological materials (Deng et al., 2014; Petrov, 2002; KD et al., 2009) and liquid crystals (Castles et al., 2011). Such characteristics in ferroelectric materials provide unique opportunities for sensor development and energy harvesting; however, the magnitude of polarization produced by a strain gradient is small and can be difficult to decouple from piezoelectricity (Jaffe et al., 1971). The smaller coupling is partially limited by the brittle characteristics of many dielectric ceramics and single crystals. Enhancing flexoelectricity generally requires utilizing nanoscale structures (e.g., thin films) to reduce the number of defects leading to improved strength (Zhang and Sharma, 2005; Maranganti and Sharma, 2009; Catalan et al., 2005; Zhu

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et al., 2006; Morozovska et al., 2011; Hong et al., 2010b; Lee et al., 2011; Zubko et al., 2007). Selection of materials with high dielectric constants can also improve the flexoelectric coupling (Ma and Cross, 2005). Ferroelectric materials are one ideal choice due to their high dielectric coefficient although these materials also exhibit complex domain structure evolution in the presence of large stresses and/or electric fields. When significantly large strain gradients are present in ferroelectric materials, potential coupling between domain structure motion and flexoelectricity is of strong interest to understand how to control such effects to enhance the design of nanoscale flexoelectric structures and devices. As such, there has been recent efforts to quantify ferroelectric domain structure evolution when coupled to flexoelectricity (Gu et al., 2014; Ahluwalia et al., 2014) except these models have not included strain gradient length scale relations. Phase field methods using fast Fourier transform (FFT) techniques have also investigated the stability of tetragonal phase domains under different strain fields in nanofilms when flexoelectricity is included in the model (Chen et al., 2015). The method proposed here is distinct from FFT since it uses the finite element method which more easily accommodates complex geometries and boundary conditions that are often relevant to the design of micro and nanoscale adaptive structures.

Flexoelectricity scales inversely with the size of the structure and therefore may become significant at the nanoscale (Tagantsev et al., 2009; Sharma et al., 2007). Its dependence on strain gradients can lead to larger electromechanical coupling in nanoscale structures. For example, the classical St. Venant principle shows how strain gradients depend on geometry from a point load applied to the end of a bar. As the lateral dimension decreases, the stress and strain decays exponentially faster towards some mean value as shown in Figure 1 (Ting, 1996; Timoshenko and Goodier, 1970). Such behavior can have a significant impact on electromechanical coupling and polarization switching in ferroelectric capacitor islands containing different lateral widths (L. Cheng and O. Englander and A. Paravastu and W. Oates, 2011). Figure 1 illustrates this concept where the stress emanating from a point decreases exponentially and inversely proportional to the lateral width of the structure (Ting, 1996). This point load could emanate from a domain wall at a ferroelectric/electrode interface, for example. Geometric effects are further complicated by surface relaxation and interface characteristics which become non-negligible at the nanoscale (Gerra et al., 2005, 2007). Experiments on ferroelectric thin films have demonstrated that giant flexoelectricity can be achieved in sub-micron scale structures (Lee et al., 2011) as well as high resolution mechanical switching of polarization using nanoprobe tip
loading (Lu et al., 2012). These results are promising since strain gradients may be used for novel sensor applications since flexoelectricity occurs in centro-symmetric materials and therefore potentially avoids the temperature limitations of piezoelectricity in ferroelectric materials (Jaffe et al., 1971). However, it should also be noted that the largest flexoelectric coupling has been observed near the Curie temperature (Ma and Cross, 2006). Given these challenges and opportunities, it is important to formulate models that can simulate the complex electromechanical domain structure evolution that include strain gradient coupling in ferroelectric nanoscale structures.

In comparison to flexoelectricity, ferroelectricity is more widely applicable due to its strong electromechanical coupling as demonstrated in a wide variety of applications such as nanopositioning, energy harvesting, structural health monitoring, non-volatile memory, and vibration control (Lines and Glass, 1977; Jaffe et al., 1971; Smith, 2005). Significant progress has been made towards understanding the field-coupled constitutive relations using phenomenological models (J.E.Huber et al., 1999), microscale models (Su and Landis, 2007), coupling with atomistic relations (Völker et al., 2011; Kowalewsky, 2004), and ab initio calculations (King-Smith and Vanderbilt, 1994; Vanderbilt, 2004; Cohen, 1992). Fundamental characterization of these materials has also been instrumental in providing insight into the nonlinear constitutive behavior and origins of ferroelectricity (Lines and Glass, 1977; Lynch, 1996; Pramanick et al., 2011; Jaffe et al., 1971; Cohen, 1992).

Modeling and experimental analysis of strain gradients in elastic and plastic materials has been extensively studied (Maugin, 1980; Fleck and Hutchinson, 1997). Coupled stress theory, a general methodology that includes strain gradients, contains higher order effects but also retains anti-symmetric components associated with rotation gradients within the deformation metric (Mindlin and Tiersten, 1962; Mindlin, 1965). Theoretical models of higher order plasticity effects have been studied by Hutchinson and others (Fleck and Hutchinson, 2001; Gao et al., 1999; Maugin, 2011) and compared with experimental measurements (Nix, 1989; Fleck et al., 1994; Lam et al., 2003) leading to new insights into the size effects in deformation, effective stiffness, and yield stress of materials. Much of this work was focused on improving explanations of plasticity that emanate near localized stress, strain, and strain gradients such as near the triple point of a grain boundary in polycrystalline metals. Less research has focused on coupling this behavior with strain gradients and flexoelectricity in ferroelectric materials at the nanoscale. Recent research has extended strain gradient finite element methods to piezoelectric materials where a variety of stress concentrations from cracks and elliptical holes have been considered (Mao et al., 2016).

As more efforts focus on the development of novel nanoscale structures that induce large strain gradients (Ma and Cross, 2005; Zhang and Sharma, 2005), it is important to quantify higher order electromechanical effects and their interactions with domain structure interactions in ferroelectric compositions. Whereas piezoelectricity is characterized as a bulk material tensor that depends on dipole and quadrupole coupling (Martin, 1972; W. Oates, 2013; Oates, 2014), the relative importance of bulk versus surface flexoelectricity has been debated as these effects are complicated by higher order quadrupole and octupole coupling (Resta, 2010; Tagantsev, 1986; Maranganti and Sharma, 2009). Ab initio calculations have
been made on strontium titanate and barium titanate (Maranganti and Sharma, 2009) illustrating self-consistency among different computational studies (Hong et al., 2010a); however, only reasonable predictions of experimental results on strontium titanate have been achieved (Ma and Cross, 2006). More recent analysis applied to strontium titanate has unified thermodynamic relations between continuum and \textit{ab initio} descriptions of phonon dispersion which has provided insights on the coexistence of flexoelectricity and ferroelectricity (Stengel, 2016).

In this analysis, we extend prior studies in continuum mechanics and phase field models of ferroelectric materials (Chen, 2002; Su and Landis, 2007; L. Cheng and O. Englander and A. Paravastu and 2011; Völker et al., 2011) to include strain gradients, flexoelectric coupling, and its influence on tetragonal phase ferroelectric domain structures. The modeling framework utilizes a finite element methodology that incorporates strain gradients using a Lagrange multiplier method (Shu et al., 1999; Mao et al., 2016). This method improves numerical stability and allows lower order linear interpolation functions ($C_0$ elements) to be used as opposed to higher order interpolation functions that would be necessary to directly quantify second order displacement gradients. Here, the governing equations are first summarized followed by the Lagrange multiplier approximation of strain gradients and flexoelectric coupling. The method is then numerically implemented via the finite element method and results are first compared to theory followed by numerical analysis of ferroelectric domain structure simulations.

The outline of the paper is given as follows. The governing equations are first presented and the finite element formulation is used to quantify flexoelectric coupling to domain structure evolution in Section 2. In Section 3, theoretical verification of the finite element model is summarized which first includes flexoelectricity in the absence of ferroelectric domain structure evolution. Numerical verification focuses on a closed form problem of shear along a linear dielectric-electrode interface. The finite element model is then extended to analyze flexoelectric coupling near 180\degree and 90\degree ferroelectric tetragonal phase domain walls. In Section 4, we provide concluding remarks.

## 2 Governing Equations

The governing equations are formulated in terms of a Lagrangian energy density that contains electromagnetics in free space and in a material plus a stored energy of the solid which describes mechanical energy and stored electrical energy. A detailed review of this approach can be found elsewhere (Nelson, 1979, 1991). Here, we extend the result to explore higher order effects associated with strain gradients and polarization gradients. The Lagrangian is given by

\[ \mathcal{L} = \mathcal{L}_F + \mathcal{L}_I + \mathcal{L}_M \]  

(2.1)

where $\mathcal{L}_F$ is the free space Lagrangian density, $\mathcal{L}_I$ is the interaction term, and $\mathcal{L}_M$ contains kinetic and stored energy of the solid. Using variational methods, Maxwell’s equations, linear momentum of the solid, and a set of equations for the electronic structure is obtained. One example for an idealistic single domain ferroelectric crystal can be found elsewhere (Oates,
2014).

The kinetic and stored energy contained within $L_M$ is denoted by

$$L_M = \frac{\rho}{2} v_i v_i + \sum_\nu \rho_\nu \frac{\dot{y}_\nu^i}{\dot{y}_\nu^i} - \Sigma(E_{IJ}, E_{IJ,K}, \Pi'_I, \Pi'_{IJ})$$  \hspace{1cm} (2.2)

where the first term is the kinetic energy associated with the center-of-mass of a representative volume element, the second term is kinetic energy associated with optical modes, and the last term is the stored energy density. The first two terms associated with kinetic energy will be neglected by focusing on quasi-static processes. The stored energy is defined to be a function of the Lagrangian strain $E_{IJ}$, the strain gradient $E_{IJ,K}$, and order parameters associated with the position of electronic structures relative to its center-of-mass as denoted by $\Pi'_I$ for $\nu = 1, \ldots, n$ particles. We also include a gradient correction term that accommodates diffuse domain wall interfaces which is denoted by $\Pi'_{IJ}$.\%

The strain-displacement relation for small strain is

$$\varepsilon_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i})$$  \hspace{1cm} (2.3)

where $u_i$ is displacement. We introduce a third order tensor for the strain gradient as $\eta_{ijk} \equiv u_{k,ij} = \eta_{jik}$.

The Helmholtz energy function, $\psi = \Sigma - s \theta$, is introduced prior to obtaining a set of balance equations. In this equation, $s$ is entropy and $\theta$ is temperature. Variational methods applied to $\psi$ plus the dissipative potential $\Pi_D = -\beta \dot{P}_i \dot{P}_i$ (while neglecting kinetic energy in the Lagrangian) lead to three sets of governing equations including linear momentum, Gauss’ law, and a phase field equation for the polarization evolution. Gauss’ law and the phase field equation governing polarization evolution are

$$D_{ij} = 0$$

$$\xi_{ji,j} - \eta_i = \beta \dot{P}_i$$  \hspace{1cm} (2.4)

The electric displacement is defined by $D_i = \epsilon_0 E_i + P_i$ where $E_i$ is the electric field and $\epsilon_0$ is free space permittivity. Two thermodynamic variables $\xi_{ji}$ and $\eta_i$ have been introduced in the ferroelectric phase field equation. These two variables and the electric field are determined from the free energy using

$$\eta_i = \frac{\partial \psi}{\partial P_i}, \quad \xi_{ji} = \frac{\partial \psi}{\partial P_{i,j}}, \quad \text{and} \quad E_i = \frac{\partial \psi}{\partial D_i}$$.  \hspace{1cm} (2.5)

Details describing these thermodynamic variables and coupling within the phase field equation can be found elsewhere (Su and Landis, 2007).

The equation for linear momentum includes the Cauchy stress and a higher order hyper-stress that is work conjugate to the strain gradient (Maugin, 2011). We limit the analysis to quasi-static deformation with zero body forces which leads to

$$(\sigma_{ji} - \tau_{kji,k})_{j} = 0$$  \hspace{1cm} (2.6)
where $\sigma_{ji}$ is the Cauchy stress and $\tau_{kji}$ is the hyperstress (Shu et al., 1999). The stress and hyperstress are determined from the free energy function using

$$\sigma_{ij} = \frac{\partial \psi}{\partial \varepsilon_{ij}} \quad \text{and} \quad \tau_{ijk} = \frac{\partial \psi}{\partial \eta_{ijk}}.$$  \hspace{1cm} (2.7)

The work conjugate relations for stress, hyperstress, and the field quantities are determined from the following free energy function. Strain gradient elastic coupling is decomposed into orthogonal components summarized elsewhere (Smyshlyaev and Fleck, 1996). The form of the free energy function is

$$\psi = \frac{c_{ijkl}}{2} \varepsilon_{ij} \varepsilon_{kl} + \mu \left( c_{1} \eta_{ij}^{(1)} \eta_{ij}^{(1)} + c_{2} \eta_{ij}^{(2)} \eta_{ij}^{(2)} + c_{3} \eta_{ij}^{(3)} \eta_{ij}^{(3)} + c_{4} \eta_{ij}^{(H)} \eta_{ij}^{(H)} + c_{5} \eta_{ij}^{(H)} \eta_{ij}^{(H)'} \right) + \cdots$$

$$+ \frac{a_{ij}}{4} P_{i} P_{i} + \frac{a_{ijkl}}{6} P_{i} P_{j} P_{k} P_{l} + \frac{a_{ijklmn}}{2} P_{i} P_{j} P_{k} P_{l} P_{m} P_{n} + \frac{a_{0}}{2} P_{i,j} P_{i,j}$$

$$+ \frac{1}{2\varepsilon_{0}} (D_{i} - P_{i})(D_{i} - P_{i}) - b_{ijkl} \varepsilon_{ij} P_{k} P_{l} + f_{ijkl} P_{i} \eta_{jk}$$

where the first row includes strain energy proportional to the elastic tensor $c_{ijkl}$ and strain gradient energy in the second term. The energy due to strain gradients is approximated using an isotropic shear modulus $\mu$ and a set of length scale parameters $c_{i}$ with $i = 1$ to 5. The length scale parameters have units of length squared. The decomposition of the strain gradient tensor, $\eta_{ijk}$, into $\eta_{ij}^{(\nu)}$ with $\nu = 1, 2, 3,$ and $H$ is given by Smyshlyaev and Fleck (Smyshlyaev and Fleck, 1996). The superscript “H” denotes the hydrostatic term which results in $\eta_{ij}^{H} = 0$ for incompressible solids. The energy associated with domain structure polarization formation is governed by the Landau parameters $a_{ij}$, $a_{ijkl}$, and $a_{ijklmn}$ using a sixth order polynomial expansion on polarization. These higher order tensors will be reduced to a smaller set of parameters governing tetragonal phase lead titanate as given by Pertsev et al. (Pertsev et al., 1998) The diffusive parameter $a_{0}$ controls the width of the transition of polarization across a domain wall. The free energy component associated with vacuum energy is given by the term containing permittivity of free space $\varepsilon_{0}$, the electric displacement, and the polarization. Lastly, electromechanical coupling is introduced within the terms containing the electrostrictive fourth order tensor $b_{ijkl}$ and the flexoelectric fourth order tensor $f_{ijkl}$.

### 2.1 Numerical Implementation

The governing equations are implemented using the finite element software package Comsol 4.3b. A Lagrange multiplier is included in the set of equations to approximate the strain gradient. This approximation is implemented to avoid the use of second order interpolation functions required to directly compute second order displacement gradients. It is stated that there are no known stable $C^{1}$ continuous interpolation functions in the literature (Shu et al., 1999); therefore, the strain gradient is approximated using
\[ \eta_{jk} = \frac{1}{2}(\psi_{jk,i} + \psi_{ik,j}) \]  

where \( \psi_{ij} \) is a second order tensor, not to be confused with the free energy function. This tensor is constrained to be approximately equal to the displacement gradient. An additional equation is added to the set of balance equations given by (2.4) and (2.6) to create this constraint. In the weak form, the approximate displacement gradient tensor is constrained to the “true” displacement gradient using

\[ \int_\Omega (\psi_{ij} - u_{i,j}) \delta \rho_{ij} dV = 0 \]  

(2.10)

where we have defined the Lagrange multipliers as \( \rho_{ij} \) which are analogous to the divergence of the hyperstress \( \rho_{ij} = \tau_{ijk,i} \); see Shu et al. for details (Shu et al., 1999).

The additional weak form of the governing equations implemented in the finite element model include re-writing (2.4) as

\[- \int_\Omega D_i \delta \phi_i dV + \int_\Gamma D_i n_i \delta \phi dS = 0 \]

\[- \int_\Omega (\xi_{ji} \delta P_{i,j} - \eta_i \delta P_i) dV + \int_\Gamma \xi_{ji} n_j \delta P_i dS = \int_\Omega \beta \dot{P}_i \delta P_i dV \]

(2.11)

where the test function \( \delta \phi \) is for the electrostatic potential and the test function \( \delta P_i \) is for the polarization. The outward pointing unit normal is denoted by \( n_i \) in the surface integrals. The boundary conditions include the normal component of the electric displacement across surfaces in the first equation and the microstress \( \xi_{ji} \) must satisfy continuity across surfaces as given by the surface integral in the second equation.

The weak form of the linear momentum equation is

\[ \int_\Omega (\sigma_{ji} \delta u_{i,j} + \tau_{kji} \delta \hat{\eta}_{kji} + \tau_{ikl,i}(\delta \psi_{kl} - \delta u_{k,l})) dV = \int_\Gamma (f_i \delta u_i + n_i r_j \delta \psi_{ij}) dS \]

\[ + \int_\Gamma (n_j r_k - n_j r_k)(\delta \psi_{jk} - \delta u_{k,j}) dS \]  

(2.12)

where the test functions for displacement and the approximated strain are \( \delta u_i \) and \( \delta \psi_{jk} \), respectively. The boundary conditions given on the right hand side as well as numerical implementation of this governing equation are well summarized by Shu et al. (Shu et al., 1999). In the case where the approximate displacement gradient \( \psi_{ij} \) equals the true displacement gradient \( u_{i,j} \), this equation satisfies the equilibrium equation given by (2.6) exactly.

3 Modeling Analysis

The numerical analysis first includes verification of the finite element model with a theoretical flexoelectric solution of shearing along a heterogeneous interface. This problem involves
Figure 2: Boundary value problem of a bi-material slab containing an electrode and dielectric. Shear stress induces polarization through a strain gradient along the interface. In the finite element model, periodic boundary conditions are applied along the sides and the dielectric layer is short circuited.

an elastic top electrode adhered to a dielectric that undergoes in-plane shear loading. Strain gradients develop at the interface due to the mismatch in elastic moduli leading to polarization induced by the strain gradient. This is followed by a two-dimensional, fully-coupled ferroelectric domain structure evolution simulation in the presence of strain gradients that may occur along either twinned 180° or 90° tetragonal domains.

3.1 Shear Strain Gradient Analysis

In the one-dimensional theoretical analysis, a slab of a heterogeneous electrode/dielectric bi-material is sheared to induce shear strain gradients along the interface due to the mismatch in elastic properties. A similar analysis for strain gradient elastic materials is given by Shu et al. (Shu et al., 1999). Here, flexoelectric coupling is included in the dielectric layer to quantify strain gradient induced polarization. A shear stress is applied uniformly to the top electrode as illustrated in Figure 2. The only non-zero strain and strain gradient components are $\varepsilon_{12}$ and $\eta_{221}$, respectively. Key constitutive relations are given as follows while the details of the boundary value problem are summarized in the Appendix.

The constitutive relations involve the shear stress and the shear hyperstress components
\[ \sigma_{12} = 2 \mu_i \varepsilon_{12} \]
\[ \tau_{221} = 2 \mu_1 l_1^2 \eta_{221} + f_{1221} \eta_2 \quad \text{for} \quad x_2 < 0 \]
\[ \tau_{221} = 2 \mu_2 l_2^2 \eta_{221} \quad \text{for} \quad x_2 > 0 \]

(3.1)

where we have assumed isotropic elastic material properties via the shear moduli \( \mu_i \) for the top electrode (material \( i = 2 \)) and the bottom dielectric (material \( i = 1 \)).

There are no gradients in the \( x_1 \) direction, therefore Gauss' law is trivially satisfied. The polarization can be determined from (2.5) and (2.8). Approximations of the free energy are made to formulate a linear constitutive law for the dielectric behavior. We assume linear susceptibility behavior which requires \( a_{ij} = \chi P \delta_{ij} \) where \( \delta_{ij} \) is the Kronecker delta and \( \chi P \) is the dielectric susceptibility. All higher order terms are set to zero requiring all components of \( a_{ijkl} \) and \( a_{ijklmn} \) to be zero. We also neglect polarization gradients and electrostriction by setting the parameters \( a_0 \) and \( b_{ijkl} \) to zero. At equilibrium \( \eta_1 = 0 \), and under short circuit conditions the field is zero requiring \( E_1 = 0 \). This leads to polarization in the \( x_1 \) direction in the dielectric layer to be

\[ P_1 = -\chi P f_{1221} \eta_{221}. \]

(3.2)

As detailed in the Appendix, the final solution for the strain in the bi-layer is

\[ \varepsilon_{12} = \frac{\sigma_{12}^\infty}{2 \mu_1} \left\{ 1 + \frac{(\mu_1 - \mu_2)\tilde{l}_1^2}{\mu_1 l_1 + \mu_2 l_2} e^{x_2/\tilde{l}_1} \right\} \quad \text{for} \quad x_2 < 0 \]
\[ \varepsilon_{12} = \frac{\sigma_{12}^\infty}{2 \mu_2} \left\{ 1 + \frac{(\mu_2 - \mu_1)\tilde{l}_2}{\mu_1 l_1 + \mu_2 l_2} e^{-x_2/\tilde{l}_2} \right\} \quad \text{for} \quad x_2 > 0 \]

(3.3)

where the length scales are given by \( \tilde{l}_1 = \sqrt{2} \sqrt{l_1^2 - l_{flex}^2} \) where \( l_{flex} = \sqrt{\frac{\chi P f_{1221}^2}{4 \mu_1}} \) and \( \tilde{l}_2 = l_2 \sqrt{2} \).

The characteristic length scales \( l_1 \) and \( l_2 \) are assumed to be isotropic and homogeneous by letting \( c_1 = c_2 = c_3 = c_4 = l_1 = l_2 \) in materials \( i = 1, 2 \) and \( c_5 = 0 \) in (2.8).

As was noted in (2.10), we approximate the strain gradient using a Lagrange multiplier constraint. In Figure 3, we illustrate the approximate strain solution versus the direct solution of the strain based on the finite element solution, i.e., \( \varepsilon_{12} \simeq \frac{1}{2} (\psi_{12} + \psi_{21}) \). In Figure 3(a), excellent agreement is shown between the finite element strain and the approximation of the strain using \( \psi_{ij} \). In addition, we show excellent agreement between the finite element solution and the theoretical solution from (3.3). In the limit of zero strain gradient effects, a jump in strain would occur at the interface where \( x_2 = 0 \). Here, a small shift in the slope is observed at \( x_2 = 0 \) due to the difference in shear modulus between the two materials. Figure 3(b) also illustrates good agreement between the theoretical polarization component \( P_1 \) and the corresponding polarization from finite element calculations. The error near the peak polarization was reduced by several mesh refinements near the interface until reasonable agreement was achieved. The parameters used in the simulation are based on representative values for lead zirconate titanate and an iridium oxide top electrode; see Table 1.
Figure 3: Comparison of the finite element solution with theory where the origin is located at the interface. (a) Percent strain solutions are plotted across the interface. The result labeled “Lagrangian” is the approximation of the shear strain given by \( \frac{1}{2}(\psi_{12} + \psi_{21}) \). (b) Polarization \( P_1 \) is plotted across the interface.

Based on the theoretical result, some estimates on enhanced strain gradient induced polarization are worth noting. It is shown that the magnitude of the polarization can become highly sensitive to \( \varepsilon_{12,2} \) as a function of the characteristic length scale parameters. By substituting (3.3) into (3.2), the polarization due to a shear strain gradient is

\[
P_1 = -2\chi_P f_{1212} \varepsilon_{12,2} = -\frac{2\chi_P f_{1212} l_2 \sigma_{12}^\infty}{\mu_1 \sqrt{l_1^2 - l_2^{\text{flex}}}} \left\{ \frac{(\mu_1 - \mu_2)}{\mu_1 l_1 + \mu_2 l_2} \right\}^{x_2/l_1} \]

(3.4)

which illustrates that the polarization may dramatically increase if the intrinsic characteristic length scale approaches the flexoelectric length scale. This relation is also consistent with other results that show the flexoelectric coupling is linear proportional to the dielectric constant.

Table 1: Parameters used in verifying the finite element model with the theoretical shear strain gradient solution. The flexoelectric coefficient \( f_{12} \) is based on values for PZT given by Ma (Ma and Cross, 2006) and \( f_{44} \) was based on a proportional relation for barium titanate between \( f_{12} \) and \( f_{44} \) (Maranganti and Sharma, 2009).

| \( \mu_1 \) | 111 | GPa |
| \( \mu_2 \) | 422 | GPa |
| \( f_{12} \) | 0.66 | pV |
| \( f_{44} \) | 0.3 | pV |
| \( \chi_P \) | 2130 | C/(m·V) |
| \( l_1 = l_2 \) | 100 | nm |
(Tagantsev, 1986). It is important to point out, however, that the flexoelectric characteristic length scale \(l_{\text{flex}}\) is considerably smaller than a typical characteristic length scale of a domain wall which is on the order of 0.5 nm based on DFT calculations (Meyer and Vanderbilt, 2002).

### 3.2 Ferroelectric Domain Structure Simulations

The finite element modeling framework is extended to more complex ferroelectric domain structure problems to investigate the effect of strain gradients on domain structure formation. We investigate 180° and 90° domain walls in tetragonal phase ferroelectrics. In particular, calculations of domain structures in lead titanate are given. We illustrate how the strain gradient length scale plays a role in quantifying changes in strain across tetragonal phase domain walls. This length scale parameter should be carefully considered in comparison with the length scale associated with polarization gradients. Specifically, it is shown that the strain gradient length scale \(l_1\) becomes important once it is approximately 10% of the polarization gradient length scale which is governed by the phase field equation. Conversely, changes to \(l_1\) do not change the polarization despite the amount of electrostrictive coupling considered.

The following set of constitutive relations, based on the work conjugate relations from Section 2, are implemented numerically. The general form of the Cauchy stress and hyperstress are

\[
\begin{align*}
\sigma_{ij} &= c_{ijkl}\varepsilon_{kl} - b_{ijkl}P_kP_l \\
\tau_{ijk} &= 2\mu(c_1\eta_{i,jk} + c_2\eta_{i,jk} + c_3\eta_{i,jk} + c_4\eta_{i,jk}^{(H)}) + f_{ijkl}P_i.
\end{align*}
\]  

(3.5)

Similar to the shear strain gradient problem, the characteristic length scale \(l_1\) is assumed to be isotropic and homogeneous in the ferroelectric material by applying \(c_1 = c_2 = c_3 = c_4 = l_1\) and letting \(c_5 = 0\) in (2.8). These two measures of stress are expanded in component form in the Appendix for the two dimensional deformation simulations presented.

The field relations previously given in (2.5) lead to

\[
\begin{align*}
\eta_i &= a_{ij}P_j + a_{ijkl}P_jP_kP_l + a_{ijklmn}P_jP_kP_lP_mP_n - E_i - b_{ijkl}\varepsilon_{kl}P_j + f_{ijkl}\eta_{jkl} \\
\xi_{ji} &= a_0P_{i,j} \\
D_i &= \epsilon_0E_i + P_i.
\end{align*}
\]

(3.6)

For two dimensional problems considered here, the electronic forces due to the polarization, electric field, strain, and strain gradient include

\[
\begin{align*}
\eta_1 &= a_1P_1 + a_{11}P_1^3 + a_{12}P_1P_2 + a_{112}P_1^3P_2 + a_{111}P_1^5 - E_1 - b_1\varepsilon_{11}P_1 - b_2\varepsilon_{22}P_1 - b_3\varepsilon_{12}P_2 \\
&+ f_{1111}\eta_{111} + f_{1122}\eta_{122} + f_{1221}\eta_{221} + f_{1212}\eta_{212} \\
\eta_2 &= a_1P_2 + a_{11}P_2^3 + a_{12}P_1P_2 + a_{112}P_1^3P_2 + a_{111}P_2^5 - E_2 - b_2\varepsilon_{11}P_2 - b_1\varepsilon_{22}P_2 - b_3\varepsilon_{12}P_1 \\
&+ f_{2112}\eta_{112} + f_{2121}\eta_{211} + f_{2211}\eta_{211} + f_{2222}\eta_{222} \\
\end{align*}
\]

(3.7)
where the Landau coefficients have been simplified to the form given by Pertsev et al. (Pertsev et al., 1998). Several anisotropic flexoelectric components have been neglected by implementing the isotropic form of $f_{ijkl}$; see (4.8) in the Appendix. The microstresses and electric displacement components follow from conventional indicial notation and are omitted for brevity (Su and Landis, 2007). It is important to note the length scale associated with the change in polarization across a domain. This can be estimated by using the lowest order term in the Landau energy and the polarization gradient parameter $a_0$ which leads to (Gao and Suo, 2002)

$$l_P \simeq \sqrt{-\frac{a_0}{a_1}}.$$  (3.8)

We use this length scale for comparison to the strain gradient length scale to quantify its effect on simulating polarization and strain across $180^\circ$ and $90^\circ$ domain walls.

The finite element mesh and initial conditions for the $180^\circ$ and $90^\circ$ domain wall simulations are shown in Figure 4. The same mesh is used for both cases; however, in the $90^\circ$ domain wall model case, the crystal structure defined by the polarization order parameter is rotated $45^\circ$ such that the domain wall remains vertical; see Choudhury et al. (Choudhury et al., 2005) for a description of rotation of the crystal structure. The initial conditions are defined by a sharp change in polarization at the interface contained within the highly refined mesh region. The mesh is highly refined in the region of the domain wall to resolve the domain wall width and changes in fields, stress, and strain across the domain wall. The domain wall width is defined in terms of the change in polarization. It will be shown that the width of strain gradient can be increased by increasing $l_1$ without affecting the polarization; see Figures 8 and 9. Note that this may not be true for all possible values of electrostriction.

The model is simulated in time until the domain structures relax to a quasi-static configuration. For the $180^\circ$ domain wall, the solution is static. This is not the case for the $90^\circ$ domain wall due in part to the zero polarization flux boundary conditions on the top and bottom surfaces. This leads to a domain wall that remains vertical, but propagates horizontally. We quantify the solution when the domain wall enters the highly refined mesh regime such that it can be compared to the $180^\circ$ domain wall.

In both $90^\circ$ and $180^\circ$ domain wall structures, the following boundary conditions are applied. The material is held fixed with zero total displacement on the bottom left corner and zero vertical displacement on the bottom right corner (i.e., roller condition). The geometry for these simulations was $30 \times 8 \, \text{nm}^2$. A relatively small geometry was used in order to ensure high resolution mesh refinement across a domain wall of realistic size (on the order of 0.5 nm). On all four boundaries, the traction and double traction associated with the hyperstress are set to zero. The electric potential is also set to zero on all boundaries as well as the micro-traction associated with the polarization gradient.

Finite element solutions near the domain walls are illustrated in Figures 5 and 6 which show the polarization and strain gradients associated with ferroelectric domain wall structures. All solutions used the material parameter values given in Table 2. The strain gradient length scale was $l_1 = 0.1 l_P$ for the simulations in Figures 5 and 6. A comparison of domain wall lengths
Figure 4: Finite element mesh and polarization initial conditions (arrows) used in simulating the (a) 180° and (b) 90° domain walls.

Figure 5: A representative illustration of solutions for the 180° domain wall. (a) Polarization component $P_2$ in C/m$^2$ and (b) the strain component $\varepsilon_{11}$ in percent strain.

for the 180° and 90° domain walls is illustrated in Figure 7. The domain wall length is fit by adjusting $a_0$ to be approximately equivalent to DFT calculations on lead titanate (Meyer and Vanderbilt, 2002). DFT predictions give a domain wall width of 0.5 ± 0.05 nm which is comparable to the domain wall lengths in Figure 7. The size of the 180° and 90° domain walls are practically the same size which is similar to calculations using DFT; however, this is in contrast to other Ginzburg Landau phase field calculations on barium titanate (Su and Landis, 2007). This difference is further investigated by calculating the domain wall energy.

The domain wall energy for the two domain wall configurations is found to also be comparable to DFT calculations. The finite element results give a 180° domain wall energy of 129 mJ/m$^2$. For the 90° domain wall, the domain wall energy was 29 mJ/m$^2$. Achieving this
domain size and energy required adjustments to the Landau parameters given by Pertsev et al. (Pertsev et al., 1998). The Landau parameter $a_{12}$ was found to be particularly sensitive to $90^\circ$ domain wall energy. Cutting this parameter in half increased the domain wall energy of the $90^\circ$ domain without increasing the energy of the $180^\circ$ domain. It is also important to note that the domain wall energy is predominantly determined by a balance between the Landau energy and the energy due to polarization gradients. Flexoelectric energy had negligible effects on the domain wall energy. Whereas the modifications to the Landau parameters provides reasonable correlation with DFT domain wall sizes and domain wall energy, the spontaneous polarization is 0.47 C/m$^2$ in the phase field calculations as opposed to 0.9 C/m$^2$ from DFT calculations.

A more detailed illustration of the domain structures is shown in Figures 8 and 9 where the strain gradient length scale is varied to determine its influence on the two domain structures. In these plots, the polarization and normal strain component $\varepsilon_{11}$ are plotted across the $180^\circ$ and $90^\circ$ domain walls along the centerline ($x_2$ direction away from the top/bottom surfaces). Given the nominal domain wall length of 0.5 nm, a range of strain gradient length scales from $l_1 = 0$ to $l_1 = 5l_P$ was chosen for comparisons. For both domain structures, the strain gradient length scale has practically no influence on the polarization despite electrostrictive coupling. As expected, for the same polarization gradient, the strain varies significantly. Similarly, the $90^\circ$ domain wall illustrates no differences in polarization as a function of the strain gradient length scale as shown in Figure 9. These effects are plotted over the entire finite element domain in Figures 10 and 11 for the $180^\circ$ and $90^\circ$ domain walls, respectively. As shown, the strain component $\varepsilon_{11}$ clearly becomes more diffuse as the strain gradient length scale increases.

Figure 6: A representative illustration of solutions for the $90^\circ$ domain wall. (a) Polarization component $P_2$ in C/m$^2$ and (b) the strain component $\varepsilon_{11}$ in percent strain.
4 Concluding Remarks

A finite element model has been developed to include strain gradient coupling with flexoelectricity and ferroelectric domain structure evolution. This extends strain gradient elasticity developed by Shu et al. (Shu et al., 1999) who introduced a set of Lagrange multipliers to approximate the strain gradient using linear interpolation functions. This approach was extended...
Table 2: Material parameters used in the flexoelectric phase field simulations. The temperature $T$ was set to 373 K. The strain gradient length scale ($l_1$) is varied relative to the polarization gradient length scale ($l_P$) over the range: $\alpha = [0, 0.1, 0.25, 0.5, 1, 5]$. Given the material parameters, $l_P = 0.17$ nm.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
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<tr>
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<td>GPa</td>
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<td>$c_{44}$</td>
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<td>pV</td>
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<td>pV</td>
</tr>
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<td>V·m$^3$/C</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$8.0(T-475) \times 10^5$</td>
<td>V·m/C</td>
</tr>
<tr>
<td>$a_{11}$</td>
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<td>V·m$^3$/C$^3$</td>
</tr>
<tr>
<td>$a_{12}$</td>
<td>$7.9 \times 10^9$</td>
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</tr>
<tr>
<td>$a_{112}$</td>
<td>$1.3 \times 10^9$</td>
<td>V·m$^9$/C$^5$</td>
</tr>
<tr>
<td>$l_1$</td>
<td>$\alpha l_P$</td>
<td>$-$</td>
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</table>

Figure 9: Illustration of the change in polarization (a) and normal strain component $\varepsilon_{11}$ (b) across a $90^\circ$ domain wall based on the finite element simulation illustrated in Figure 6.

to electrostatic and ferroelectric domain structure problems using the phase field approach to quantify the effect of strain gradients and flexoelectric coupling near heterogeneous interfaces and domain wall structures.

A theoretical solution of shear across a metal/dielectric interface was obtained and com-
Figure 10: $180^\circ$ domain wall simulations illustrating the change in the strain component $\varepsilon_{11}$ across the domain wall. The units are in $\%\varepsilon$. The strain gradient length scale increases from $l_1 = 0.1l_P, 0.5l_P, l_P,$ to $5l_P$ in (a), (b), (c), and (d), respectively.

pared to the finite element model to quantify the effect of a jump in material properties at the interface. Good correlation between theory and finite element calculations was achieved. Furthermore, the theoretical solution illustrated a singularity in polarization as the strain gradient length scale approaches the flexoelectric length scale, $l_{flex} = \sqrt{\chi_P^2 \frac{f_{1212}}{4\mu_1}}$. This length scale is well below any atomic length scale based on typical material properties. However, the prediction is based on phenomenological continuum theory. More comparisons with flex-
Figure 11: 90° domain wall simulations illustrating the change in the strain component $\varepsilon_{11}$ across the domain wall. The units are in $\%\varepsilon$. The strain gradient length scale increases from $l_1 = 0.1l_P$, $0.5l_P$, $l_P$, to $5l_P$ in (a), (b), (c), and (d), respectively.

Dielectric DFT calculations should be done to further understand this material behavior for material optimization.

Tetragonal phase ferroelectric domain structure simulations were also implemented to quantify the effect of strain gradients near twinned domains. It was shown that for a given polarization length scale ($l_P$) determined from the phase field equation, the strain gradient length scale $l_1$ could be increased leading to a diffuse strain gradient across both 180° and 90° domains. This effect produces diffuse strain across the domain wall with an upper limit
of the strain gradient as $l_1 \to 0$. Although electrostriction produces full coupling between strain and polarization, changes to the strain across the domain wall did not lead to changes in polarization. When defining the polarization and strain gradient length scales, one must carefully assess if these parameters are coupled. The origins of the polarization gradient energy have been discussed by Mitsui et al. (Mitsui and Furuichi, 1953) where a summation of dipoles is taken to be equivalent to a Taylor expansion on all derivatives of the polarization. Here, a scalar parameter is applied to approximate this Taylor expansion. In principle, the evolution of the electronic structure can be considered independent of the lattice strain (Nelson, 1979); however, the electrostrictive coupling at the nano and sub-nano length scales will most likely require DFT calculations and comparisons with electron microscopy to identity potential deviations from the phenomenological continuum model.

Appendix

Shear Gradient Boundary Value Problem

The flexoelectric boundary value problem illustrated in Figure 2 is summarized here. Many of the details follow directly from the strain gradient problem previously given by Shu et al. (Shu et al., 1999) and therefore only key distinctions required to incorporate flexoelectricity are given.

The linear momentum equation for this particular boundary value problem requires solving

$$\left(\sigma_{12} - \tau_{221,3}\right)_{,2} = 0 \quad (4.1)$$

where the constitutive relations include

$$\sigma_{12} = 2\mu_i \varepsilon_{12} \quad \text{materials } i=1 \text{ and } 2$$

$$\tau_{221} = 2\mu_1 l_1^2 \eta_{221} + f_{1221} P_1 \quad \text{material 1} \quad (4.2)$$

$$\tau_{221} = 2\mu_2 l_2^2 \eta_{221} \quad \text{material 2}$$

Gauss’ law is automatically satisfied since the boundary conditions are defined for the short circuit case. The remaining equilibrium equation that must be satisfied is the “electronic” force ($\eta_i$) given by the work conjugate relation in (2.5). Under equilibrium conditions, this force is zero.

For the shear problem, a zero electronic force leads to the polarization in the $x_1$ direction

$$P_1 = -\chi P f_{1221} \eta_{221} \quad (4.3)$$

Substitution of this relation into the hyperstress in the flexoelectric material (material 1) gives

$$\tau_{221} = 2\mu_1 \left(l_1^2 - \frac{\chi P f_{1221}^2}{2\mu_1}\right) \eta_{221} = 2\mu_1 l_1^2 \eta_{221} \quad (4.4)$$
where $\mathbf{t}_i^2 = l_i^2 - \frac{\chi P f_{1221}^2}{2\mu_1}$. In the electrode material (material 2), the hyperstress has a similar constitutive relation except the flexoelectric coefficient is zero. Upon substitution of the hyperstress and Cauchy stress constitutive relations into the linear momentum equation (4.1), we must solve

$$\varepsilon_{12,2} - l_i^2 \varepsilon_{12,222} = 0$$

(4.5)

where we have introduced $\eta_{221} = 2\varepsilon_{12,2}$ and $\hat{l}_i = l_i \sqrt{2}$. This final form is equivalent to the boundary value problem given by Shu et al. (Shu et al., 1999) except the characteristic length scale $\bar{l}_i$ contains flexoelectricity. The solution of the strain field and polarization follow directly as given by (3.3) and (3.4).

**Flexoelectric Constitutive Relations**

For two dimensional deformation problems, an isotropic, electrostrictive constitutive relation is implemented. The stress-strain relations under plane strain are

$$\sigma_{11} = c_{1111}\varepsilon_{11} + c_{1122}\varepsilon_{22} - b_1 P_1^2 - b_2 P_2^2$$

$$\sigma_{22} = c_{1122}\varepsilon_{11} + c_{1111}\varepsilon_{22} - b_2 P_1^2 - b_1 P_2^2$$

$$\sigma_{12} = 2c_{1212}\varepsilon_{12} - b_3 P_1 P_2$$

(4.6)

and the hyperstresses are

$$\tau_{111} = 2\mu \sum_p c_p \eta_{111}^{(p)} + f_{1111} P_1,$$

$$\tau_{112} = 2\mu \sum_p c_p \eta_{112}^{(p)} + f_{2112} P_2,$$

$$\tau_{121} = 2\mu \sum_p c_p \eta_{121}^{(p)} + f_{2121} P_2,$$

$$\tau_{122} = 2\mu \sum_p c_p \eta_{122}^{(p)} + f_{1122} P_1,$$

$$\tau_{211} = 2\mu \sum_p c_p \eta_{211}^{(p)} + f_{2211} P_1,$$

$$\tau_{212} = 2\mu \sum_p c_p \eta_{212}^{(p)} + f_{1212} P_1,$$

$$\tau_{221} = 2\mu \sum_p c_p \eta_{221}^{(p)} + f_{1221} P_1,$$

$$\tau_{222} = 2\mu \sum_p c_p \eta_{222}^{(p)} + f_{2222} P_2.$$  

(4.7)

The flexoelectric coupling is assumed to be isotropic which requires

$$f_{ijkl} = f_{12}\delta_{ij}\delta_{kl} + f_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$

(4.8)

where the phenomenological constants $f_{12}$ and $f_{44}$ must be quantified experimentally, or in some cases, they can be determined from first principle calculations (Hong et al., 2010a; Maranganti and Sharma, 2009).

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