January 2014

The Soft Mode Driven Dynamics of Ferroelectric Perovskites at the Nanoscale: an Atomistic Study

Kevin Mccash
University of South Florida, kmccash@gmail.com

Follow this and additional works at: http://scholarcommons.usf.edu/etd

Part of the Condensed Matter Physics Commons, and the Nanoscience and Nanotechnology Commons

Scholar Commons Citation
http://scholarcommons.usf.edu/etd/5269

This Dissertation is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
The Soft Mode Driven Dynamics in Ferroelectric Perovskites at the Nanoscale:

an Atomistic Study

by

Kevin McCash

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

Major Professor: Inna Ponomareva, Ph.D.
Pritish Mukherjee, Ph.D.
Sarath Witanachchi, Ph.D.
Lilia Woods, Ph.D.

Date of Approval:
May 28, 2014

Keywords:
Physics, Ferroelectric, Perovskite, Nanoscale

Copyright © 2014, Kevin McCash
Dedication

For Hattie who made it possible.

For Callan who I hope will be proud I have done it.

For my parents who have always supported and encouraged me.
Acknowledgments

I would like to acknowledge Dr. Inna Ponomareva for her guidance and continual help in completing this work. I would also like to thank my committee members for their encouragement and constructive criticism. Lastly I would like to thank my colleagues Ryan Herchig, Dr. Qingteng Zhang, James Almand, Dr. Brajesh Mani, Dr. Chun-Min Chang and Elena Glazkova for their support and the great deal of time I took from them.

The present work is supported by the Army Research Office under grant No. 57787EL (most of the studies in Chapter 4, some studies in Chapter 5), the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award DE-SC0005245 (some studies in Chapter 5 and studies in Chapter 6). The use of services provided by Research Computing, USF is greatly acknowledged.
# Table of Contents

List of Tables iii
List of Figures iv
Abstract vii

1 Introduction 1
   1.1 Historical Background ............................................. 2

2 Fundamentals of Ferroelectrics 4
   2.1 Thermodynamic Treatment ......................................... 4
   2.2 Phase Transitions .................................................. 5
      2.2.1 Second-Order Phase Transitions ................................. 6
      2.2.2 First-Order Phase Transitions ................................ 7
      2.2.3 The Soft Mode .................................................. 8
   2.3 Ferroelectric Domains ............................................... 10
      2.3.1 The Depolarizing Field ....................................... 10
      2.3.2 Domain Structures ............................................. 12
   2.4 Applications of Ferroelectrics ................................... 14

3 Computational Techniques 16
   3.1 Density Functional Theory ....................................... 17
   3.2 First-Principles-Based Models .................................... 20
      3.2.1 The Effective Hamiltonian .................................... 20
      3.2.2 Local Mode Self Energy ....................................... 22
      3.2.3 Dipole-Dipole Interaction .................................... 23
      3.2.4 Short-Range Interaction ...................................... 23
      3.2.5 Elastic Energy .................................................. 25
      3.2.6 Elastic-Local Mode Interaction ................................. 26
      3.2.7 Necessary Parameters .......................................... 26
   3.3 Monte Carlo and Molecular Dynamics ................................ 26

4 Parameterization of BTO 30
   4.1 Lattice Constant .................................................. 31
   4.2 Eigenvector and Pseudoeigenvector of the Local Mode .............. 32
   4.3 Anharmonic Coefficients of the Local Mode ........................ 34
   4.4 Strain-Local Mode Coupling Coefficients ........................... 35
   4.5 Elastic Stiffness Constants ...................................... 38
# Table of Contents

## 4.6 Harmonic Coefficient and Short-Range Interaction
- Parameters .................................................. 39

## 4.7 Additional Parameters ........................................ 41

## 4.8 Phonon Dispersion ............................................. 43

## 4.9 Transition Temperatures ....................................... 45
- 4.9.1 Spontaneous Polarization ................................. 47

## 4.10 Dynamical Properties ......................................... 48

## 4.11 Conclusions .................................................. 52

## 5 The Soft Mode Dynamics of PbTiO₃ Under Different Mechanical Boundary Conditions ............................... 54
- 5.1 Methodology and Computational Setup ....................... 57
- 5.2 Hydrostatic Pressure ......................................... 60
- 5.3 Uniaxial Stress ............................................... 63
- 5.4 Biaxial Stress ............................................... 68
- 5.5 Non-equilibrium Stresses ..................................... 72
- 5.6 Biaxial Strain ............................................... 74
- 5.7 Soft Mode Dynamics Under Pressure and Stress from Analytical Model ........................................ 79
  - 5.7.1 The Case of Hydrostatic Pressure ....................... 84
  - 5.7.2 The Case of Uniaxial Stress ............................ 86
  - 5.7.3 The Case of Biaxial Stress ............................ 88
- 5.8 Conclusions ................................................ 90

## 6 Mechanisms for Polarization Reversal in Ferroelectric Nanowires ........................................ 91
- 6.1 Computational Method ........................................ 93
- 6.2 Results and Discussion ....................................... 95
- 6.3 Conclusions ................................................ 105

## 7 Concluding Remarks ............................................. 107

References ....................................................... 108

Appendix A Proof of Copyright Permissions ......................... 124

Appendix B Publications ........................................... 126

Appendix C Conference Presentations ................................ 127

About the Author .................................................. End Page
List of Tables

3.1 Parameters necessary to complete the effective Hamiltonian used to model ferroelectricity in the perovskite crystal structure. ........................................ 27

4.1 Components of the normalized eigenvector (GGA) and pseudoeigenvector (LDA) describing the local mode in BTO. .................................................. 35

4.2 $B_{\alpha\beta}$ parameters for BTO using the GGA and the LDA. ....................... 37

4.3 Values of the elastic stiffness constants obtained from DFT. ......................... 39

4.4 Short-range interaction parameters, $j_i$, as well as the quadratic self-energy coefficient $\kappa_2$ in units of $Ha/a_0^2$. ................................................. 41

4.5 Values of the Born effective charge, $Z^*$, static dielectric constant, $\varepsilon_\infty$, the local mode effective mass, $M_u^*$ and the inhomogeneous strain mass $M_{\eta_m}$. ............ 42

4.6 The spontaneous polarization predicted by the “hybrid” parameter set. ... 48

4.7 Frequencies of the soft modes of BTO found by DFPT using the GGA and the LDA. ................................................................. 49

4.8 Values for $B_{\alpha\beta}$ used to tune the dynamical properties of BTO. ............ 51

4.9 Complete sets of effective Hamiltonian parameters for BTO. .......................... 53
List of Figures

1.1 Illustration of BTO showing the cubic unit cell which is made up of two intersecting cubic lattices of barium and titanium and an octahedron of oxygen atoms surrounding one of these sites, the B site in this case. 2

2.1 Second-order phase transition. 6

2.2 First-order phase transition. 8

2.3 Schematic diagram of BTO in the a) centrosymmetric cubic paraelectric phase, b) the polar tetragonal phase in the positive or “up” state and the c) polar tetragonal phase in the negative or “down” state. 9

2.4 Illustration of surface charge with arrows indicating the direction of net polarization and the depolarizing field. 12

2.5 Schematic diagram of a) 90° and b) 180° domain configurations. 13

2.6 90° domains in single crystal BTO from optical birefringence measurements using a polarizing microscope. 14

3.1 Schematic illustration of how the soft mode is described by a collection of local modes. 21

3.2 The independent intersite interactions corresponding to the parameters $j_1$, $j_2$ (first nearest neighbor), $j_3$, $j_4$, $j_5$ (second nearest neighbor), and $j_6$ and $j_7$ (third nearest neighbor). 24

3.3 Flowchart of the MD algorithm. 29

4.1 Total energy of the cubic BTO unit cell as a function of lattice constant using the LDA. 32

4.2 Schematic diagram of perovskite unit cell with the A, B and O atoms represented in shaded, solid and open circles respectively. 34

4.3 Total energy of BTO as a function of local mode for three local mode directions [001], [110], and [111] for BTO. 36

4.4 The $\kappa$ versus $\eta_i$ data collected from DFPT within the LDA for BTO. 38

4.5 The eight local mode configurations used to compute the $j_i$ parameters. 39
4.6 Phonon dispersion curves calculated from first-principles using the LDA to DFT. ........................................... 43

4.7 Example of phonon dispersion curves in BTO calculated using the LDA parameter set. ........................................... 44

4.8 Components of the local mode as a function of temperature for bulk BTO using effective Hamiltonian parameters found from the GGA. ................................. 46

4.9 Components of the local mode as a function of temperature for bulk BTO using effective Hamiltonian parameters found using the LDA. ................................. 46

4.10 Components of the local mode as a function of temperature for bulk BTO using the weighted average of effective Hamiltonian parameters found by using the GGA and the LDA. ........................................... 47

4.11 Frequencies of the $A_1$ and $E$ modes of BTO from the dynamical parameter set. 51

5.1 a) soft mode frequencies as a function of temperature for +2.0 GPa (green), -2.0 GPa (red) and zero applied pressure (blue). ........................................... 61

5.2 The dependence of the soft mode frequency squared on the hydrostatic pressure. ........................................... 62

5.3 The temperature dependence of the Curie-Weiss pressure constant. ................. 63

5.4 (a) soft mode frequencies as a function of temperature for -2.0 GPa (red) of uniaxial stress and zero applied stress (blue). ........................................... 65

5.5 The dependence of the soft mode frequencies squared on the uniaxial stress. ........................................... 66

5.6 The temperature dependence of the Curie-Weiss stress constant for compressive (a) and tensile(b) uniaxial stress. ........................................... 67

5.7 (a) soft mode frequencies as a function of temperature for -2.0 GPa (red) of biaxial stress and zero applied stress (blue). ........................................... 69

5.8 The dependence of the soft mode frequencies squared on the biaxial stress. ........................................... 70

5.9 The temperature dependence of the Curie-Weiss stress constant under compressive (a) and tensile (b) biaxial stress. ........................................... 71

5.10 Comparison of Scenario 1 (red) and Scenario 2 (green) for PTO under 2.0 GPa of tensile uniaxial stress. ........................................... 73

5.11 (a) soft mode frequencies as a function of temperature for -2.5% (red) of biaxial strain and unstrained PTO (blue). ........................................... 75

5.12 The dependence of the soft mode frequencies squared on the strain. ........................................... 76

5.13 The temperature dependence of the Curie-Weiss strain constant. ........................................... 78
6.1 Schematic diagram of the PZT nanowires simulated in this study. .......................... 94
6.2 The normalized number of dipoles in the “up” state, $N_{up}$, for two different field strengths. ................................................................. 96
6.3 Plane averaged cross sections of 18x18 unit cell nanowire showing domain-driven PR from initially “down” polarized state (blue) to the “up” polarized state (red). ................................................................. 96
6.4 Radial and axial switching speeds as a function of applied electric field. ........... 97
6.5 Zero kelvin Gibbs free energy profiles of nanowire with a side length of 4.8 nm for three field strengths. ................................................................. 98
6.6 Temperature dependence of the coercive field for homogeneous PR assuming $\mathcal{E}_{\text{kin}} = \frac{k_B T}{2}$ (solid line) and $\mathcal{E}_{\text{kin}} = \frac{3k_B T}{2}$ (dashed line). ......................... 100
6.7 Fractional transition rates, $n(t)$, for 2.8 MV/cm (panel a) and 4.5 MV/cm (panel b). ................................................................. 101
6.8 The electric field dependence of the inverse switching time for two temperatures with fitting lines. ................................................................. 103
6.9 The field dependence of inverse switching time for nanowires with different lateral size. ................................................................. 105
Abstract

The discovery of ferroelectricity at the nanoscale has incited a lot of interest in perovskite ferroelectrics not only for their potential in device application but also for their potential to expand fundamental understanding of complex phenomena at very small size scales. Unfortunately, not much is known about the dynamics of ferroelectrics at this scale. Many of the widely held theories for ferroelectric materials are based on bulk dynamics which break down when applied to smaller scales. In an effort to increase understanding of nanoscale ferroelectric materials we use atomistic resolution computational simulations to investigate the dynamics of polar perovskites. Within the framework of a well validated effective Hamiltonian model we are able to accurately predict many of the properties of ferroelectric materials at the nanoscale including the response of the soft mode to mechanical boundary conditions and the polarization reversal dynamics of ferroelectric nanowires.

Given that the focus of our study is the dynamics of ferroelectric perovskites we begin by developing an effective Hamiltonian based model that could simultaneously describe both static and dynamic properties of such materials. Our study reveals that for ferroelectric perovskites that undergo a sequence of phase transitions, such as BaTiO$_3$ for example, the minimal parameter effective Hamiltonian model is unable to reproduce both static and dynamical properties simultaneously. Nevertheless we developed two sets of parameters that accurately describes the static properties and dynamic properties of BaTiO$_3$ independently.

By creating a tool that accurately models the dynamical properties of perovskite ferroelectrics we are able to investigate the frequencies of the soft modes in the perovskite crystal. The lowest energy transverse optical soft modes in perovskite ferroelectrics are known to be
cause of the ferroelectric phase transition in these materials and affect a number of electrical properties. The performance of a ferroelectric device is therefore directly influenced by the dynamics of the soft mode. Interestingly, however, little study has been done on the effect of mechanical boundary conditions on the soft modes of perovskites. Understanding the effect of mechanical forces on the soft modes is critical to device applications as complicated growth structures often are the cause of pressures, stresses and strains. Using classical molecular dynamics we study the effect of hydrostatic pressure, uniaxial stress, biaxial stress and biaxial strain on the soft modes of the ferroelectric PbTiO$_3$. The results of this study indicate the existence of Curie-Weiss laws for not only hydrostatic pressure, which is well known, but also for uniaxial stress, biaxial stress and biaxial strain. The mode frequencies are also seen to respond very differently to these mechanical forces and lead to a more complete picture of the behavior of nanoscale ferroelectrics.

One nanoscale geometry of perovskite ferroelectrics is the pseudo one-dimensional nanowire. These structures have very unique properties that are highly attractive for use as interconnects, nanoscale sensors or more directly in computer memory devices. Perovskite nanowires have only recently been synthesized and the techniques are not well developed. While progress has been made towards consistently fabricating uniform, high quality nanowires experimental investigation of their properties is prohibitively difficult. Of immediate interest is the polarization reversal dynamics of ferroelectric nanowires. The reading and writing of bits of information stored in a wire’s polarization state is done by switching the polarization. Again using classical molecular dynamics we study the polarization reversal dynamics in ferroelectric nanowires made of Pb(Ti$_{1-x}$Zr$_x$)O$_3$ disordered alloy. We find that there are two competing mechanisms for polarization reversal and that the interplay of these mechanisms is dependent on electric field strength. The dynamics in nanowires also sheds light on long standing theories about polarization reversal mechanisms in thin film and bulk geometries.
1 Introduction

In recent years ferroelectric materials have garnered a lot of attention owing to their remarkable properties and the numerous possibilities those properties present for novel application. One of the most interesting and often disputed areas of interest within the field of ferroelectrics are the dynamics of such materials at the nanoscale. The accepted theoretical models for ferroelectric materials are often only completely valid in the case of macroscopic, or bulk, configurations. The laws that govern ferroelectrics at this size no longer hold true when the dimensions are effectively limited to two, one or zero [1–4]. These so called “scaling laws” require that special theoretical consideration be given to the properties of ferroelectric materials in the nanoscale.

In general a ferroelectric material is defined as one that exhibits spontaneous electric polarization and at least two stable and switchable polar states [5]. In terms of crystal classifications ferroelectrics must be non-centrosymmetric in order to be polarizable and contain a unique polar axis that allows for the development of spontaneous polarization [5]. These two properties are each required by two other types of phenomenon, piezoelectricity and pyroelectricity. Piezoelectricity is defined as the onset of polarization within a material upon application of mechanical strain [6]. Pyroelectricity is the onset or change in polarization by temperature shifts caused by the separation of charges as a result of spontaneous polarization [5]. All ferroelectric materials are in fact pyroelectric and piezoelectric meaning that ferroelectric crystals are sensitive to both mechanical stress and temperature changes.

Probably the largest class of ferroelectrics is the perovskite oxide. This type of compound has a chemical formula following the general form ABO$_3$ and as such has only 5 atoms per
Figure 1.1: Illustration of BTO showing the cubic unit cell which is made up of two intersecting cubic lattices of barium and titanium and an octahedron of oxygen atoms surrounding one of these sites, the B site in this case.

The simplicity of the crystal structure and chemical composition as well as their practical utility makes theoretical study of perovskite ferroelectrics very attractive for the exploration of dynamic properties. Though the following sections describe the theory of ferroelectrics in general, only perovskite oxides were studied in later sections and general statements about ferroelectrics are only meant to apply to such materials.

1.1 Historical Background

The first ferroelectric ever discovered was named Rochelle Salt after the village in France in which it was first created. Rochelle Salt’s formal name is potassium sodium tartrate tetrahydrate and has the chemical formula NaK\(\text{C}_4\text{H}_4\text{O}_6\cdot\text{4H}_2\text{O}\). Its primitive cell contains 4 stoichiometric formula units totaling 112 atoms. This high level of complexity made any sort of theoretical investigation all but impossible in the 1920’s when Rochelle Salt’s ferroelectricity was first discovered [7–12]. As a result ferroelectricity was thought to have been a “mistake” and not a common phenomenon [5]. This belief changed, however, with the discovery of a new series of ferroelectric materials that were mainly phosphates and arsenates.
like potassium dihydrogen phosphate KH$_2$PO$_4$ and its isomorphs [5]. These crystals were much less complex than Rochelle salt with only 16 atoms per unit cell and allowed for more in depth theoretical investigation into the nature of the phenomenon. The preliminary theory that arose from this investigation relied on the orientation of hydrogen bonds within the molecule to cause the polar instability necessary for ferroelectricity [5]. This theory was over-simplified and it took almost a decade before it was discovered that hydrogen was not required for ferroelectricity to occur. In 1945 during a search for materials with large dielectric constants the compound BaTiO$_3$, or BTO, was found to have a large dielectric constant that increased with temperature. Shortly afterwards ferroelectricity was discovered in this material [13–15] and the polar perovskite oxide was brought into the forefront of ferroelectric research [5].
2 Fundamentals of Ferroelectrics

In this section we introduce the basic physics and concepts of perovskite ferroelectrics and their dynamics. This includes discussions of the thermodynamic treatment of ferroelectric materials, the ferroelectric phase transition, the crystal dynamics that are the cause of ferroelectricity in perovskites and lastly the formation of ferroelectric domains.

2.1 Thermodynamic Treatment

From a fundamental perspective the free energy of a ferroelectric is the sum of two free energy contributions. One is electric, $F_P$, and provides the energy terms for polarization and is a function of macroscopic polarization, temperature and external electric field. The other provides the energy contributions from elastic effects, $F_{\eta P}$, as a result of a ferroelectric material’s piezoelectricity [5]. The free energy, $\mathcal{F}$, can then be written as

$$\mathcal{F} = F_P + F_{\eta P}. \quad (2.1)$$

The free energy of polarization, $F_P$, is a polynomial expansion in terms of the order parameter $P$ (polarization) with an added term to express the influence of an external field, $E$, and is given by

$$F_P = \frac{1}{2} \alpha (T - T_0) P^2 + \frac{1}{4} \gamma P^4 + \frac{1}{6} \delta P^6 + \cdots - E \cdot P, \quad (2.2)$$

where $\alpha$, $\gamma$ and $\delta$ are the expansion coefficients indicating the strength of each order inter-
action. It is often convention to arbitrarily terminate the expansion at the 6th order as the higher order terms provide only small contributions. It is also important to note that only even powers are included due to symmetry considerations of the perovskite structure and that two stable states of polarization can exist. In general all of the coefficients in Eq. (2.2) can be temperature dependent however, only the lowest order coefficient, \( \alpha(T - T_0) \), is taken to depend on temperature [5]. This follows the methodology of Devonshire who assumed that the lowest order term is taken to depend on temperature in the vicinity of the transition temperature [5]. The temperature dependence of the quadratic coefficient also results from mean-field statistical models and has also been observed experimentally [5].

The second term in the total free energy, \( F_{\eta P} \), allows for the inclusion of coupling between the components of the strain tensor, \( \eta_i \), and the polarization, but also includes a quadratic strain term and coupling between stress and strain,

\[
F_{\eta P} = \frac{1}{2} K \eta^2 + Q \eta P^2 + \cdots - \sigma \cdot \eta. \tag{2.3}
\]

The combination of Eq. (2.2) and Eq. (2.3) provides all of the necessary components to describe ferroelectricity in a bulk crystal. The expressions above are written for only one dimension however they could be expanded to include additional dimensions.

This phenomenology is called the Landau-Devonshire model after the individuals that proposed the basic premises used here [5]. This model is able to accurately describe, at least qualitatively, the phase transitions of ferroelectric materials and can be expanded to include additional external constraints making it a valuable tool to understand the basic nature of ferroelectrics.

2.2 Phase Transitions

The ferroelectric phase transition is a complex phenomenon that is critical to the study of ferroelectric materials in general. This is why the phase transition sequence and transition
temperatures are often used as a way to validate new techniques [16,17] and as a result are briefly reviewed here.

### 2.2.1 Second-Order Phase Transitions

Taking Eq. (2.2) for the case when $\gamma$ is positive we can describe the nature of a second-order phase transition. For $T > T_0$ this expression is a linear combination of even functions that are symmetric about $P = 0$. In general this results in only one minima of the free energy associated with zero net polarization (see Fig. 2.1). As the temperature is decreased and approaches $T_0$ the minimum of this function remains the same. Once $T < T_0$ the leading term in $F_P$ becomes negative and the energy landscape changes to a double well configuration as seen in Fig. 2.1a. This new landscape has two minima each corresponding to a different direction of spontaneous polarization. $T_0$, therefore, describes the transition temperature.

The evolution of the free energy in this way is termed a second-order phase transition because the changes in free energy occur continuously as temperature is decreased. The name “second-order” results from there being a discontinuity in the second order derivative
of the free energy or susceptibility. The equilibrium state of a ferroelectric also requires that \( \partial F / \partial P = 0 \). Taking this derivative results in an expression for the electric field \( E \) in terms of polarization taking the form

\[
E = \alpha (T - T_0) P + \gamma P^3 + \delta P^4.
\]  

This equation can be used to obtain an expression for the dielectric susceptibility above the transition temperature \( T_0 \) where \( P = 0 \),

\[
\chi = \left. \frac{\partial P}{\partial E} \right|_{P=0} = \frac{1}{\alpha (T - T_0)}.
\]  

The dielectric susceptibility exhibits a discontinuity at \( T_0 \) as is necessary for a second-order phase transition. This expression is useful as it allows for the calculation of the \( \alpha \) coefficient from experimental measurements [5]. Figure 2.1(c) shows the dielectric susceptibility as a function of temperature as well as its inverse indicating the divergence of \( \chi \) at \( T_0 \).

### 2.2.2 First-Order Phase Transitions

In the case when \( \gamma < 0 \) in Eq. (2.2) the resulting free energy landscape begins with three local minima as seen in Fig. 2.2(a). As the temperature is reduced through the transition the minima corresponding to finite polarization become more favorable. In this case the polarization is discontinuous about the Curie temperature, \( T_C \) indicating a first-order phase transition. There are two notable temperatures for a first-order transition in contrast with the second-order transition. The first, \( T_C \), corresponds to the temperature at which the three local minima of the free energy are energetically degenerate and the second \( T_0 \) is where the quadratic coefficient in Eq. (2.2) turns from positive to negative. It is only for \( T_0 < T_C \) that the ferroelectric minima are thermodynamically favorable [18]. A direct result of this energy landscape evolution is the ability for the low temperature phase to exist at higher
temperatures and conversely the high temperature phase to exist at low temperature as metastable states. This leads to thermal hysteresis meaning that the transition temperature is recorded at a higher value when the sample is heated through the transition point than when cooled.

2.2.3 The Soft Mode

While thermodynamics is a powerful tool in describing the qualitative nature of the phase transitions the physical cause of the ferroelectric phase transition is a much more complicated topic. Ferroelectric phase transitions are usually classified as either the displacive or order-disorder type. In the case of perovskite oxide ferroelectrics the dipole moment of the unit cell is often caused by a polar instability resulting from the “softening” of the lowest energy transverse optical phonon mode(s). The term softening is used in this context to describe a phonon mode that decreases in frequency as it approaches a transition temperature. The converse is also true insomuch as a mode is said to harden if its frequency increases with temperature moving away from the transition. In a purely displacive transition the soft mode

Figure 2.2: First-order phase transition. (a) Free energy as a function of the polarization at \( T > T_C \), \( T = T_C \) and \( T = T_0 < T_C \); (b) Spontaneous polarization \( P_0(T) \) as a function of temperature; (c) Susceptibility \( \chi \).
will have zero frequency at the transition temperature, $T_C$ [5]. Order-disorder transitions also require significant softening of the lowest energy transverse optical phonon modes however, the frequency must only decrease enough to allow for thermal hopping between the two available free energy wells [5].

When the primary modes soften the central atom in the unit cell, the B-site atom, is able to move into the non-centrosymmetric regions of the oxygen octahedron offsetting the charge distribution and causing finite polarization to occur as shown in the diagram in Fig. 2.3. This illustration indicates how the direction of displacement affects the polarization of the unit cell.

In the displacive transition all of the unit cells in the material align in the same direction and the onset of polarization occurs instantly as a first-order phase transition. If however, the modes do not soften completely individual unit cells may have finite polarization in different structurally allowed directions for a short time. These individual dipoles interact electrically and due to long and short range interactions align together into a homogeneous polarization. This is the order-disorder type of phase transition and is said to be of second-order as the finite polarization of an entire ferroelectric increases continuously with decreasing temperature. The electrostatic influence of individual unit cells to align into a homogeneous polarization requires a longer time scale. As the temperature of an order-disorder ferroelectric is decreased from $T_C$ the strength of long-range dipole-dipole interactions increases. As more and more individual dipoles align parallel to each other the net polarization is observed to
increase continuously.

It is often said that a specific perovskite ferroelectric does not behave solely as order-disorder or displacive but usually has some degree of both mechanisms. For this reason ferroelectrics are usually characterized by whichever behavior dominates the phase transition. The classic ferroelectrics BTO and lead titanate, PbTiO$_3$, are examples of mostly displacive ferroelectrics. In contrast the more chemically complicated potassium dihydrogen phosphate, KH$_2$PO$_4$, and sodium nitrite, NaNO$_2$, are of the order-disorder type [5].

In addition to differentiating the types of ferroelectric phase transitions the soft mode dynamics of ferroelectrics have strong implications in terms of device application. The frequencies of the soft modes in perovskite ferroelectrics lie in the terahertz regime and are closely related to the complex dielectric response. In fact the soft modes contribute to the limiting conditions on the operating frequency of any electronic device constructed from a polar perovskite.

### 2.3 Ferroelectric Domains

Up to this point all considerations have been for homogeneously polarized ferroelectrics. To allow for further discussion of ferroelectric materials in realistic scenarios, especially at the nanoscale, it is important to discuss the influence of impurities and surface effects. Of great importance is the cause and properties of ferroelectric domains. As in the case of magnetic domains, ferroelectric domains are regions with the same polarization direction. In a ferroelectric sample more than one domain may form as a result of the strong depolarizing field associated with finite size.

#### 2.3.1 The Depolarizing Field

From a electrostatic point of view the electric displacement field in a ferroelectric, or any dielectric in general, is written as
\[ \mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}. \]  

(2.6)

The polarization, \( \mathbf{P} \), has contributions from both the spontaneous polarization, \( \mathbf{P}_S \), and the polarization induced by an external electric field, \( \mathbf{P}_E \). In the presence of surfaces and defects \( \mathbf{D} \) is not continuous in all space but must satisfy Poisson’s Equation

\[ \nabla \cdot \mathbf{D} = \rho, \]  

(2.7)

where \( \rho \) is the free charge density. By combining Eqs. (2.6) and (2.7) the result is an expression for the electric field in all space, \( \mathbf{E} \), in terms of \( \rho \) and \( \mathbf{P}_S \)

\[ \nabla \cdot \mathbf{E} = \frac{1}{\epsilon \epsilon_0} (\rho - \nabla \cdot \mathbf{P}_S). \]  

(2.8)

The direct result of Eq. (2.8) is that the spontaneous polarization of a ferroelectric must go to zero at the surface of the crystal [5]. Thus \( \nabla \cdot \mathbf{P}_S \neq 0 \) making the \( \mathbf{P}_S \) the cause of the depolarizing field. The depolarizing field is an electric field that points anti-parallel to the polarization vector in an effort to reduce the polarization to zero. The accumulation of surface charge by conduction in a ferroelectric thin film, for instance, could be enough to annihilate the spontaneous polarization. [5].

Another, equivalent, but more schematic explanation of the depolarizing field is achieved using a simplified model for a ferroelectric material. The long range ordering of the dipoles in a ferroelectric material with a given homogeneous polarization forces them into a “head-to-tail” configuration with all of the individual dipole moments pointing in the same direction. However, as the diagram in Fig. 2.4 shows for a thin film of ferroelectric material, at the surface terminations of the sample there are uncompensated charges associated with the surface dipoles. This uncompensated charge results in an electric field that points anti-parallel to the polarization vector. Depending on crystal geometry and the terminating configuration of the crystal the fields at the surface of ferroelectric structures are not necessarily zero but
Figure 2.4: Illustration of surface charge with arrows indicating the direction of net polarization and the depolarizing field. [21]

can have a dramatic effect on the polarization of nanoscale ferroelectrics such as thin films, heterostructures, nanowires or nanodots [20].

The depolarizing field plays an important role in the device application of ferroelectric materials. The most important consequence is the polydomain formation within a ferroelectric crystal.

### 2.3.2 Domain Structures

It is easily seen from Eq. (2.2) that any electric field anti-parallel to the polarization will raise the free energy of a ferroelectric nanostructure. There are two mechanisms that can compensate for this unfavorable increase in energy. The first is formation of domain structures. This happens very quickly upon the onset of polarization in the crystal [5] and is the predominant method of compensation for the depolarizing field. It is possible, however, for free carriers in the ferroelectric to distribute throughout the crystal by means of conduction and compensate for the depolarizing field. This process takes significantly longer than domain formation and usually does not have an appreciable effect on the domain structure due to the immobility of domain walls. Domain walls are the small areas that separate domains from each other and while energetically unfavorable themselves the energy cost to create
domain walls is much lower than the cost of an uncompensated depolarizing field [5].

Depending on the phase of the ferroelectric in question the domains can form many different patterns. Domains are characterized by the angles between neighboring polarization vectors and can form 180°, 90°, 109° or 71° angles depending on the ferroelectric phase, the shape of the sample and the boundary conditions. For example a tetragonal ferroelectric (polarization along the \{001\} crystallographic directions) is most likely to develop a 180° domain structure (see Fig. 2.5b) as the energy cost for such a configuration is lower than for any other type. Figure 2.5 gives a visual depiction for two of the most common domain configurations.

Figure 2.6 shows one of the early birefringence images of 90° domain structures in a BTO single crystal that shows that the domains can form in very regular structures. This is not always the case as the domains that form naturally are often irregular. Those domains found in Fig. 2.6 were formed artificially [22] which is the reason for the orderly pattern that they form.

Polydomain states can also be created by application of external electric fields. This is been known to be the basis behind polarization reversal in ferroelectric samples [5, 23]. As will be seen in Chapter 6 the creation of domains and the motion of domain walls is critical to understanding polarization reversal mechanisms at the nanoscale.
2.4 Applications of Ferroelectrics

Ferroelectric materials have made their way into many device applications over the years but many of these applications did not take advantage of the switchable polarization but rather use other properties such as their large dielectric constants or their pyro- and piezoelectricity [5,24]. These applications included sonar detectors, record player pickups, miniature electromechanical devices, high permittivity capacitors and infrared detectors/imagers [5,18,24].

Ever since the discovery of ferroelectricity at the nanoscale [25–27], new device paradigms for ferroelectrics are being explored as the demand for smaller electronic and device components becomes larger. These new devices include ferroelectric tunnel junctions [28–30], ferroelectric capacitors [31], electrocaloric coolers, phased-array radar, computer memories, or nanoscale sensors [24,32,33]. Electron emission from ferroelectric materials also allows for inexpensive high-power microwave devices and miniature x-ray and neutron sources [33].

The “scaling” laws that apply at the nanoscale can only be overcome or taken advantage of by a thorough understanding of the properties ferroelectrics at small dimensions. As the experimental investigation of these properties can be difficult the use of accurate computer

Figure 2.6: 90° domains in single crystal BTO from birefringence measurements using a polarizing microscope. Reprinted Fig. 7 with permissions from [22]. Copyright 1949 by the American Physical Society
models is necessary to make predictions of how ferroelectrics will operate at small length scales. This work will demonstrate how such computer modeling can be used to achieve fundamental understanding of nanoscale ferroelectrics.
3 Computational Techniques

To use computer models to investigate material properties it is important to fully understand the methodology and techniques that they are based upon. As discussed earlier a thermodynamic treatment of ferroelectrics can produce phenomenological models such as the Landau-Devonshire model that accurately predict some properties of perovskite ferroelectrics in bulk and some nanoscale configurations. In many cases these models are oversimplified and cannot be used to make predictions at the atomistic scale or for dynamical properties. To improve on phenomenological models one can resort to highly accurate quantum mechanical calculations that are atomistic in nature. However, such calculations are computationally expensive and as a result are only useful for small systems of few hundred atoms at most. Typically, these first-principles calculations do not allow for the study of finite temperature properties which further limits their reach. Somewhere in the middle of the two types of simulations are first-principles-based models that require simulation techniques such as classical molecular dynamics (MD) and Monte Carlo (MC) in order to be implemented. MD simulations use Newton’s equations of motion to propagate a system of particles through time and MC simulations use the concepts of probability theory and statistical mechanics to model systems. The interactions between particles are described by first-principles-based methods derive their parameters from first-principles calculations. The biggest advantage of first-principles-based models is that they can tackle much larger systems as compared to first-principles methods, but still offer atomistic resolution.
3.1 Density Functional Theory

Density Functional Theory (DFT) is a widely used approach to finding the ground state properties of an atomic system. DFT is built upon the principles of quantum mechanics [34]. If one only considers the time-independent nonrelativistic Schrödinger equation, $H\psi = E\psi$, it may appear that quantum mechanics provides a very uncomplicated way to uncover the physics of complex configurations of atoms. Indeed, if you are able to write the Hamiltonian $H$ of your system and if you know the eigenstates of that Hamiltonian $\psi$ then it is possible to find the ground state energy $E$. Unfortunately, this is not the case as the interactions of a many electron system require that $\psi$ is a function of all electrons in the system of atoms.

Consider the full form of the time-independent Schrödinger equation

$$\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi. \quad (3.1)$$

Here the Born-Oppenheimer approximation is used to write the Hamiltonian of a $N$ electron system, where the first term is the kinetic energy operator, the second term is the electron-nuclei potential $V(\mathbf{r}_i)$, the third term is the electron-electron potential $U(\mathbf{r}_i, \mathbf{r}_j)$ and $\psi$ is the $N$ electron wavefunction. In principle $\psi$ is a function of the spatial coordinates of each of the $N$ electrons and their spin however it is possible to approximate $\psi$ as a product of individual electron wave functions so that $\psi = \psi_1(\mathbf{r})\psi_2(\mathbf{r}), \ldots, \psi_N(\mathbf{r})$ [34]. This expression is termed the Hartree product and there is very good motivation for approximating the many electron wave function in this way [34]. Even using the Hartree product to approximate $\psi$ Eq. (3.1) is impossible to solve analytically for any real system of many particles as the wave function is not known. The only available and measurable quantity is the electron probability density.

Since electrons are indistinguishable particles we can, however, use the electron density $n(\mathbf{r})$

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}), \quad (3.2)$$
which is closely related to the probability density \([34]\). It was shown in the work of Kohn, Hohenberg and Sham in the 1960’s that the electron density of a system of atoms allows for the calculation of numerous ground state properties \([35–38]\).

The basis of DFT are two theorems proved by Hohenberg and Kohn \([35]\). The first states that the ground state energy from Schrödinger’s equation is a unique functional of the electron density. The second states that the electron density that minimizes the energy of the overall functional is the ground state electron density corresponding to the full solution of the Schrödinger equation \([34]\). This reduces the problem from one with 3N dimensions to one with only three. The problem, however, is that the exact form of the functional is unknown. The work of Kohn and Sham showed that a system of interacting electrons can be “mimicked” by a system of non-interacting electrons.

The ground-state energy functional described by the Hohenberg-Kohn theorems has in principle five parts, three of which can be conveniently written in terms of the single-electron wave functions, \(\psi_i\)

\[
E[\{\psi_i\}] = \frac{\hbar^2}{2m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(r)n(r)d^3r \\
+ e^2 \int \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' + E_{\text{ion}} + E_{\text{XC}}[\{\psi_i\}].
\]  

(3.3)

The terms in Eq. (3.3) include the electron kinetic energies, electron-nuclei, electron-electron and nuclei-nuclei Coulombic interactions and the exchange-correlation (XC) functional. The exchange-correlation energy functional contains the kinetic energy difference between an interacting and non-interacting electron system and includes all the other many-body interactions \([39]\). Kohn and Sham showed that by solving equations having the form,

\[
\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r),
\]  

(3.4)

which are named the Kohn-Sham equations, one could obtain the correct electron density \([34, 36–38, 40]\). Note that the set of equations in Eq. (3.4) involve only single electrons.
(independent electron approximation) which greatly simplifies calculations. The first two terms on the left hand side of Eq. (3.4) are the kinetic energy operator and electron-nuclei Coulombic interaction potential. The third is the Hartree potential that describes the repulsive interaction of a single electron and the total density of all electrons in a system. The Hartree potential also includes an unphysical electron self-interaction since each electron is a part of the electron density. The correction for the self-interaction and other effects are combined together into the the last term of Eq. (3.4), $V_{XC}(r)$. The XC potential is formally defined as the functional-derivative of the XC energy term [34]. By self-consistent calculations the ground-state energy of a system containing an arbitrary number of electrons can now be calculated. The issue lies with the form of the XC functional which is not known.

The two main methods of approximating the XC functional utilize the fact that the functional is known for the case of a uniform electron gas. By setting the XC potential at each point to that of the uniform electron gas for the electron density observed at that point we approximate the XC functional by use of the local density thus the local density approximation or LDA. Another method uses not only the local density but the gradient of electron density at that point in order to include more physical information. This method is termed the generalized gradient approximation or GGA.

In the study of ferroelectrics DFT methods are used to investigate structural and electronic properties [41], phonon modes [42] and domain structure [43], just to name a few. The limitation of these types of calculations is that they are quite computationally taxing. Calculations of more than a few dozen atoms becomes extremely computationally expensive. In addition, incorporating finite temperature is difficult and limits DFT considerations of ferroelectrics to 0 K. The need for a method to conduct large scale calculations at finite temperature becomes obvious.
3.2 First-Principles-Based Models

Quite a few computational models have been created in order to extend the accuracy and information inherent in \textit{ab initio} (latin for “from the beginning” or “from first principles”) calculations to ferroelectrics at finite temperature and with larger numbers of atoms. These include the shell model [44–46], the bond-valence model [47,48] and an effective Hamiltonian model [17,49]. The shell model uses a separation of a charged core and a charged valence “shell” to simulate the individual atoms within a lattice structure [44–46]. The bond-valence model [47,48] is a physical chemistry model that utilizes bond strengths and bond lengths to model the interactions between particles. The third model, which uses an effective Hamiltonian, was utilized during the course of the research detailed later and as a result is considered here in depth.

3.2.1 The Effective Hamiltonian

The effective Hamiltonian approach to model ferroelectric perovskites was first proposed in the mid 1990s by Zhong, Rabe, and Vanderbilt [17,49]. It uses an expansion of the total energy of the cubic perovskite crystal in terms of the soft mode responsible for the ferroelectric phase transition [50]. Both calculations and experimental results indicate that only small displacements in atomic positions from the perfect cubic structure result in the ferroelectric phase in perovskites [17]. As a result the effective Hamiltonian is constructed as a Taylor series in displacements from the ideal cubic paraelectric structure [17].

The phonon dispersion relations for perovskite crystals show that only the lowest energy transverse optical modes and long-wavelength acoustic modes contribute to the ferroelectric phase transition [17]. By neglecting the other mode contributions, which do not affect the ferroelectric properties of the crystal, we reduce the number of degrees of freedom from 15 to only 6 per 5 atom unit cell, three from the soft transverse optical mode and three from the acoustic (strain) mode [17].

It is convenient to describe the soft mode over the whole Brillouin zone in terms of a
collective motion of individual “local modes”, $u_i$, [17] as illustrated in Fig. 3.1 for BTO. This local mode is taken to be centered on either the A or B sites of the ABO$_3$ unit cell which provides the highest possible symmetry [17]. The choice between the two depends largely upon the chemical structure and constituent atoms on those sites. The local mode is defined in terms of ionic displacements so that $v = u \xi$, where $v$ is the ionic displacement and $\xi$ is the eigenvector of the soft mode. The components of the soft mode, $\xi_A$, $\xi_B$, $\xi_\parallel$ and $\xi_\perp$ [17] are obtained using first-principles calculations.

In order to account for long-range Coulombic forces each local mode is considered to have a Born effective charge, $Z^*_u$, which is calculated by $Z^*_u = \sum_i \xi_i Z^*_i$ where $\xi_i$ are the components of the soft mode eigenvector and $Z^*_i$ are the Born effective charges of the atoms on unit cell site $i$. The harmonic interactions between $u_i$ are characterized by long-range Coulombic dipole-dipole interactions and short-range interactions between neighboring sites. Anharmonic effects are also considered and are treated in this model by a so called “local anharmonicity approximation” [17]. Instead of explicitly treating the anharmonic interactions of neighboring cells only the on-site interactions are included but are chosen in such
a way that the anharmonic couplings are completely reproduced about the Brillouin zone center [17].

The ferroelectric phase transition is also a structural one. As as a result it is necessary to model the ferroelectric perovskite not only as an electric entity but an elastic body. For this reason the second set of variables in the effective Hamiltonian is the local elastic strains, $\eta$, which includes contributions from homogeneous and inhomogeneous strain components.

After incorporating all of the approximations above one can construct an effective Hamiltonian with five terms that explicitly depends upon only the local soft mode and the local homogeneous and inhomogeneous strain variables. The effective Hamiltonian, using the notation of Ref. [17], takes the form

$$E^{\text{tot}} = E^{\text{self}}(\{u\}) + E^{\text{dpl}}(\{u\}) + E^{\text{short}}(\{u\}) + E^{\text{elas}}(\{\eta\}) + E^{\text{int}}(\{u\}, \{\eta\}).$$  \hspace{1cm} (3.5)

The terms are the local mode self energy, a long-range dipole-dipole interaction, a short-range interaction between neighboring soft modes, an elastic energy and lastly an energy term describing the coupling between the local strain and the local modes, respectively [17]. Each of these terms is described in more detail below.

### 3.2.2 Local Mode Self Energy

The self energy term in the effective Hamiltonian is the total energy of isolated local modes with amplitude $u_i$ so that $E^{\text{self}} = \sum_i E(u_i)$. The energy of an individual cell is an expansion in terms of the local mode since both harmonic and anharmonic contributions are necessary to describe the ferroelectric phase of the material. The cubic reference structure and symmetry considerations only allow for even powers and the expansion must then take the form [17]

$$E(u_i) = \kappa_2 u_i^2 + \alpha u_i^4 + \gamma(u_{ix}^2 u_{iy}^2 + u_{iy}^2 u_{iz}^2 + u_{iz}^2 u_{ix}^2).$$  \hspace{1cm} (3.6)
The coefficients $\kappa_2$, $\alpha$ and $\gamma$ in Eq. (3.6) are calculated from first-principles.

### 3.2.3 Dipole-Dipole Interaction

The dipole-dipole interaction models the long range Coulombic interactions between individual dipoles $\mathbf{d}_i = Z^* \mathbf{u}_i$ within the perovskite crystal. The $\mathbf{u}$ subscript has been dropped from $Z^*$. This term in the Hamiltonian uses the classical energy of one dipole in the field of another and takes the form of [17]

\[
E_{\text{dpl}}(\{\mathbf{u}\}) = \frac{Z^2}{\varepsilon_\infty} \sum_{i<j} \mathbf{u}_i \cdot \mathbf{u}_j - 3\left(\hat{\mathbf{R}}_{ij} \cdot \mathbf{u}_i\right)\left(\hat{\mathbf{R}}_{ij} \cdot \mathbf{u}_j\right) R_{ij}^3. \tag{3.7}
\]

Here $\varepsilon_\infty$ is the optical dielectric constant determined from first-principles calculations and $R_{ij}$ is the distance between local mode sites. This form of $E_{\text{dpl}}$ is not practical for three-dimensional simulations with periodic boundary conditions so an Ewald construction is used instead [17].

### 3.2.4 Short-Range Interaction

The short-range interaction provides the contributions from the interaction of neighboring local modes. These contributions include all of the electrostatic and orbital interactions not included in the dipole-dipole interaction. This is written as

\[
E_{\text{short}}(\{\mathbf{u}\}) = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha \beta} J_{ij\alpha\beta} u_i\alpha u_j\beta. \tag{3.8}
\]

where the intersite coupling matrix, $J_{ij\alpha\beta}$, is a function of the distance between the local modes, $\mathbf{R}_{ij}$ [17]. It decays rather quickly with increasing $|\mathbf{R}_{ij}|$. Taking advantage of this fact only up to third nearest neighbor interactions are considered [17].
Figure 3.2: The independent intersite interactions corresponding to the parameters $j_1$, $j_2$ (first nearest neighbor), $j_3$, $j_4$, $j_5$ (second nearest neighbor), and $j_6$ and $j_7$ (third nearest neighbor). Reprinted Fig. 2 with permissions from Ref. [17]. Copyright 1995 by the American Physical Society.

\[
J_{ij\alpha\beta} = (j_1 + (j_2 - j_1)|\hat{R}_{ij,\alpha}|)\delta_{\alpha\beta} \quad (3.9a)
\]
\[
J_{ij\alpha\beta} = (j_4 + \sqrt{2}(j_3 - j_4)|\hat{R}_{ij,\alpha}|)\delta_{\alpha\beta} + 2j_5\hat{R}_{ij,\alpha}\hat{R}_{ij,\beta}(1 - \delta_{\alpha\beta}) \quad (3.9b)
\]
\[
J_{ij\alpha\beta} = j_6\delta_{\alpha\beta} + 3j_7\hat{R}_{ij,\alpha}\hat{R}_{ij,\beta}(1 - \delta_{\alpha\beta}) \quad (3.9c)
\]

The first nearest neighbor interaction is governed by Eq. (3.9a), the second nearest by Eq. (3.9b) and the third nearest neighbors by Eq. (3.9c). By only considering up to the third nearest neighbors seven individual parameters denoted as $j_1, \ldots, j_7$ need to be calculated. The $j_i$ values give the interactions between local modes as shown in the schematic in Fig. 3.2

The seven $j_i$ parameters are obtained from first-principles calculations.
3.2.5 Elastic Energy

The elastic energy term of the effective Hamiltonian is the sum of the energy contributions from both homogeneous and inhomogeneous deformations so that

\[ E^{\text{elas}}(\{\eta\}) = E_H^{\text{elas}}(\{\eta\}) + E_I^{\text{elas}}(\{\eta\}). \]  (3.10)

The homogeneous component of the energy is expressed in terms of the elastic stiffness matrix components \( B_{ij} \) which are determined from first-principles. In this case the elastic stiffness can be expressed in energy units as \( B_{ij} = a_{\text{lat}} C_{ij} \) where \( a_{\text{lat}} \) is the equilibrium lattice constant of the material and \( C_{ij} \) are the standard cubic stiffness coefficients [17]. From symmetry considerations the elastic energy from homogeneous strain is given by

\[ E_H^{\text{elas}}(\{\eta\}) = \frac{N}{2} B_{11}(\eta_1^2 + \eta_2^2 + \eta_3^2) + NB_{12}(\eta_1 \eta_2 + \eta_2 \eta_3 + \eta_3 \eta_1) \]
\[ + \frac{N}{2} B_{44}(\eta_4^2 + \eta_5^2 + \eta_6^2). \]  (3.11)

Here \( N \) is the number of unit cells in the simulation supercell and \( \eta \) are the homogeneous components of the strain tensor following the Voigt notation. The homogeneous strain components are responsible for allowing the simulation cell to change in shape and volume which is necessary to accurately model the structural effects of the ferroelectric transition.

The inhomogeneous component of the strain is described in terms of atomic displacements from equilibrium positions in lieu of an expression like Eq. (3.11) [17]. This keeps the acoustic phonon frequencies well behaved throughout the Brillouin zone [17]. A rigorous definition of the inhomogeneous strain energy can be found in Ref. [17] however, it suffices that long-wavelength strain deformations are reproduced via terms corresponding to bond bending, bond correlation, and bond stretching [17].
3.2.6 Elastic-Local Mode Interaction

The last term of Eq. (3.5) models electrostrictive coupling between the strain and local mode variables

\[ E^{\text{int}}(\{u\}, \{\eta\}) = \frac{1}{2} \sum_i \sum_{l \alpha \beta} B_{l \alpha \beta} \eta_l u_\alpha u_\beta. \] (3.12)

Here the on-site interaction is written as the sum of the multiplication of a coupling term, \( B_{l \alpha \beta} \), and permutations of the components of the local strain \( \eta_l \) and the local mode, \( u_\alpha \) over all \( i \) sites. The strain-local mode coupling parameters, \( B_{l \alpha \beta} \), must be determined from first-principles calculations. Conveniently, symmetry forces the fifteen components of the \( B_{l \alpha \beta} \) tensor to collapse to only three independent components \( B_{1 xx}, B_{1 yy}, \) and \( B_{1 yz} \) each corresponding to three separate strain-local mode configurations.

3.2.7 Necessary Parameters

The entire energy surface modeled by this effective Hamiltonian is parameterized by nineteen independent parameters, summarized in Table 3.1. These parameters can be calculated from first principles using different types of exchange-correlation functional or pseudopotentials [16,17,50] or even derived from experimental values [17] as justified by different authors.

3.3 Monte Carlo and Molecular Dynamics

The effective Hamiltonian discussed above can be used in the framework of classical MC or MD simulations. These techniques provide valuable insight into the static and dynamical properties of ferroelectrics at finite temperature [16,50].

The focus of this work is the dynamics of ferroelectric perovskites and therefore the appropriate computational tool is MD. The mechanisms behind MC methods are based in the theories of probability, thermodynamics and statistical mechanics and provide a numerical method to sample the free energy surface of a system. This means that the results obtained
Table 3.1: Parameters of the effective Hamiltonian for perovskite ferroelectrics [17]. The atomic system of units is used here with energy in Hartree, \( Ha \), length in Bohr radii, \( a_0 \), and charge in fundamental charges, \( e \).

<table>
<thead>
<tr>
<th>Interaction Type</th>
<th>Parameter name</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self Energy</td>
<td>( \kappa_2 )</td>
<td>( Ha/a_0^2 )</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>( Ha/a_0^4 )</td>
</tr>
<tr>
<td></td>
<td>( \gamma )</td>
<td>( Ha/a_0^4 )</td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>( Z^* )</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon_\infty )</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Eff. Mass of Local Mode</td>
<td>( M_u^* )</td>
<td>amu</td>
</tr>
<tr>
<td>Eff. Mass of Inhomo. Strain</td>
<td>( M_\sigma^* )</td>
<td>amu</td>
</tr>
<tr>
<td>Short-Range</td>
<td>( j_1 \cdots j_7 )</td>
<td>( Ha/a_0^2 )</td>
</tr>
<tr>
<td>Elastic</td>
<td>( B_{11} )</td>
<td>Ha</td>
</tr>
<tr>
<td></td>
<td>( B_{12} )</td>
<td>Ha</td>
</tr>
<tr>
<td></td>
<td>( B_{44} )</td>
<td>Ha</td>
</tr>
<tr>
<td>Coupling</td>
<td>( B_{1xx} )</td>
<td>( Ha/a_0^2 )</td>
</tr>
<tr>
<td></td>
<td>( B_{1yy} )</td>
<td>( Ha/a_0^2 )</td>
</tr>
<tr>
<td></td>
<td>( B_{4yz} )</td>
<td>( Ha/a_0^2 )</td>
</tr>
</tbody>
</table>

from MC techniques apply to equilibrium configurations and do not provide any insight into the dynamics.

MD allows tracing of the time evolution of the degrees of freedom in the effective Hamiltonian. MD methods utilize the numerical integration of Newton’s equations of motion in order to propagate a system of particles in time and there are many different methods to integrate these equations [51]. In this work the MD calculations were carried out using a predictor-corrector (PC) integrator [51,52]. The PC integration is a two step approach that numerically solves the second-order differential equation

\[
\ddot{x} = f(x, \dot{x}, t) \tag{3.13}
\]

for the coordinate variable \( x \). The predictor step first extrapolates the value of \( x(t + h) \) from the values of \( x \), the velocity \( \dot{x} \) and the acceleration \( \ddot{x} \) at previous times \( t = t, t = t - h \) etc. Here \( h \) is the externally chosen time step of integration. The predictor step is defined as [51]
\[ x(t + h) = x(t) + h\dot{x}(t) + h^2 \sum_{i=1}^{k-1} \alpha_i f(t + [1-i]h) \]  \hspace{1cm} (3.14a) \\

\[ h\dot{x}(t + h) = x(t + h) - x(t) + h^2 \sum_{i=1}^{k-1} \alpha'_i f(t + [1-i]h). \]  \hspace{1cm} (3.14b) \\

Once the value of \( f(t + h) \) is computed from the expected values of \( x \) and \( \dot{x} \) a force calculation is completed using the predicted values. Once the forces on all sites have been calculated the corrector step

\[ x(t + h) = x(t) + h\dot{x}(t) + h^2 \sum_{i=1}^{k-1} \beta_i \ddot{x}(t + [2-i]h) \]  \hspace{1cm} (3.15a) \\

\[ h\ddot{x}(t + h) = x(t + h) - x(t) + h^2 \sum_{i=1}^{k-1} \beta'_i \ddot{x}(t + [2-i]h) \]  \hspace{1cm} (3.15b) \\

is applied to refine the predicted estimates for \( x \) and \( \dot{x} \) from the predictor step.

The values of \( \alpha_i, \alpha'_i, \beta_i \) and \( \beta'_i \) in Eqs (3.14a), (3.14b), (3.15a) and (3.15b) are predetermined coefficients of the Adams-Boshford method used in this PC method [51]. The value of \( k \), which is 4 in this case, determines the order of the expansion and how accurate the integration is. The MD algorithm used in the calculations of this work is detailed in Fig. 3.3.
Figure 3.3: Flowchart of the MD algorithm.
4 Parameterization of BTO

BTO is one of the most studied ferroelectric perovskites and in this Chapter we will describe the parameterization of the effective Hamiltonian of Eq. (3.5) for BTO. Previously the effective Hamiltonian has been parameterized for this material with different levels of success [16,17,50].

In one of the first parameterizations of BTO was completed using the LDA to DFT. Some parameters were deduced from experimental results [17] as some properties of the perovskites are not, according to the authors, reliably reproduced by DFT. This set of parameters successfully reproduced the sequence of phase transitions in BTO, however the transition temperatures were severely underestimated [17]. In a recent effort to improve the accuracy of the parameters for BTO the Wu and Cohen GGA functional [53] was used with DFT [16] to parameterize the material. This set of parameters was shown to greatly improve the accuracy of structural properties such as the $c/a$ ratio of the tetragonal phase and more accurately predicts the cubic-tetragonal transition temperature. In addition a parameterization of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ ferroelectric alloy reproduced both the cubic-tetragonal and tetragonal-orthorhombic transition temperatures in BTO very accurately [54]. This parameter set was obtained using the LDA to DFT but one parameter was tuned to fit the experimental Curie point of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ [54].

The main deficiency with these previous sets of parameters for BTO is that they were calculated and validated to reproduce only static properties, such as transition temperatures, polarization and tetragonality. As a result the dynamical properties of BTO were overlooked
and when tested show very poor agreement with experimental results. As a result at present there is no parameter set for BTO that accurately model both the static properties as well as the dynamical ones. It is our goal here to obtain a set of parameters that are derived entirely from first-principles and that accurately and simultaneously reproduce not only static but dynamic properties of BTO.

We used DFT with the Vienna Ab-Initio Simulation Package or VASP \cite{55, 56} for all calculations. Projector augmented wave (PAW) \cite{57, 58} potentials within the LDA \cite{59} and PBE-GGA \cite{60, 61} functionals were used to carry out all first-principles simulations. The plane wave basis was truncated at 600 eV and a Monkhorst-Pack \cite{62} k-point mesh of 11x11x11 was used in all calculations of a single perovskite unit cell. In the cases when more unit cells are required the corresponding k-point mesh was decreased accordingly.

### 4.1 Lattice Constant

The first step in the parameterization is the calculation of the lattice constant of the cubic perovskite structure. As the effective Hamiltonian assumes the ferroelectricity to be caused by small distortions from a paraelectric cubic state the lattice constant has a large impact on the parameterization.

To determine the cubic perovskite lattice constant a series of total energy calculations on a single BTO unit cell were carried out for different values of lattice constant. As the lattice constant approaches the optimal value the total energy of the unit cell approaches a minimum. Figure 4.1 shows the total energy as a function of the cubic perovskite lattice constant with a fitting polynomial \( E_{\text{lat}} = E_0 + b a_{\text{lat}} + c a_{\text{lat}}^2 + d a_{\text{lat}}^3 \). The fitting equation is minimized to find the value of \( a_{\text{lat}} \). In order to enhance the accuracy a finer set of data, shown near the minima in Fig. 4.1, was collected around the minimum. In the case of BTO the lattice parameter, \( a_{\text{lat}} \), was found to be 4.038 Å and 3.952 Å from the GGA and LDA, respectively. These compare well with the value of 4.009 Å found from experiment however, this value was obtained at temperatures above \( T_C \) \cite{15, 50, 63} and is therefore expected to
Figure 4.1: Total energy of the cubic BTO unit cell as a function of lattice constant using the LDA. The dashed line indicates the polynomial fit used to find the computed ground state lattice constant.

be larger than the 0 K DFT obtained values.

4.2 Eigenvector and Pseudoeigenvector of the Local Mode

The ionic displacements in the perovskite unit cell that give rise to ferroelectricity are characterized by an eigenvector, $\xi_i$, of the unstable phonon mode in the cubic phase. This eigenvector is obtained by diagonalizing the interatomic force constant (IFC) matrix. The IFC matrix can be calculated from either a frozen-phonon method [17, 50] or a linear-response method [64]. Frozen-phonon calculations are carried out by displacing the atoms in the unit cell explicitly and calculating the force on each individual atomic species using the Hellman-Feynman (H-F) theorem [65]. The linear-response method uses forces on individual atoms calculated via density functional perturbation theory, DFPT. Once the IFC matrix is calculated the eigenvalues and their respective eigenvectors can be computed. One of
the eigenvalues of the IFC matrix is triply degenerate and negative and its corresponding eigenvector is taken to represent the ionic displacement associated with the soft mode.

The eigenvector associated with the unstable mode ideally points along the direction to the energy minimum. In some instances the energy landscape is such that the IFC matrix provides a vector that points slightly away from the minimum. When this occurs another method of determining the direction to the minimum must be used. By taking the normalized differences in ionic positions between the ground state and the cubic reference structure one can construct a pseudoeigenvector which provides a more accurate direction to the minimum. The method of choice depends largely on the material and the DFT approximation being used. In the case of BTO we used both the linear-response and pseudoeigenvector methods.

Technically the IFC matrix is computed using algorithms included in the VASP and diagonalized using “in house” codes. The 15x15 IFC matrix has 5 triply degenerate eigenvalues. The negative eigenvalue corresponds to the soft mode and its eigenvector represents the ionic displacements of the local mode.

To construct a pseudoeigenvector we first identify the ground state structure. This can be done by comparison of energies associated with fully relaxed tetragonal, orthorhombic and rhombohedral phases. The structure with the lowest energy is the ground state of the material. By taking the difference between the atomic positions in this phase and the reference cubic structure one can define the direction to the energy minimum. The displacement vector is then normalized to calculate the pseudoeigenvector.

The components of eigenvector, schematically shown in Fig. 4.2, describe how the constituent ions in the perovskite displace from their ideal cubic positions giving rise to charge separation and an electric dipole moment. The components of the eigenvector are given in Table 4.1. Since the titanium ion has the largest displacement we will center the local mode on it (B-site model). $\xi_{\parallel}$ and $\xi_{\perp}$ indicate displacements of oxygen ions that have different symmetry. They are schematically shown in Fig. 4.2. The components of the soft mode eigenvector (from the GGA) and the pseudoeigenvector (from the LDA) for BTO are
Figure 4.2: Schematic diagram of perovskite unit cell with A, B and O atoms represented in shaded, solid and open circles respectively. Arrows indicate magnitude and direction of local mode in the [100] direction. Note that the A and B atoms are displacing anti-parallel to the oxygen atoms so that a local dipole will form from the separation of ionic charge. Oxygen atoms marked as 1 have eigenvector component $\xi_{\parallel}$ and those marked with 2 have eigenvector component $\xi_{\perp}$. Adapted from Fig. 1 with permissions from Ref. [49]. Copyright 1994 by the American Physical Society.

shown in Table 4.1. The pseudoeigenvector technique was used to parameterize BTO using the LDA because it provided more accurate results than the eigenvector. To be more specific the pseudoeigenvector provided more accurate anharmonic coefficients and intersite coupling parameters. The accuracy of these parameters was determined from qualitative and quantitative tests of the self-energy landscape and phonon dispersion curves. Both of these will be discussed in more detail in the following sections. In the case of the GGA the pseudoeigenvector was not used because the eigenvector modeled BTO accurately.

4.3 Anharmonic Coefficients of the Local Mode

The anharmonic parameters $\alpha$ and $\gamma$ in Eq. (3.6) are determined from fitting first-principles total energy data obtained for various amplitudes of the local modes, $u$ as shown in Fig. 4.3. The relationship between the local mode and total energy reveals the characteristic double well profiles associated with ferroelectricity. The displacements from the perfect cubic struc-
Table 4.1: Components of the normalized eigenvector (GGA) and pseudoeigenvector (LDA) describing the local mode in BTO. Other values for the eigenvector determined using Vanderbilt ultrasoft pseudopotentials within LDA (Refs. [50] and [17]) and the Wu and Cohen GGA functional (Ref. [16]).

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Refs. [50] and [17]</th>
<th>Ref. [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_A$</td>
<td>-0.12479835</td>
<td>-0.2571072</td>
<td>0.20</td>
<td>0.166</td>
</tr>
<tr>
<td>$\xi_B$</td>
<td>-0.77191308</td>
<td>-0.7437622</td>
<td>0.76</td>
<td>0.770</td>
</tr>
<tr>
<td>$\xi_\parallel$</td>
<td>0.58289572</td>
<td>0.5161002</td>
<td>-0.53</td>
<td>-0.546</td>
</tr>
<tr>
<td>$\xi_\perp$</td>
<td>0.15621802</td>
<td>0.2391173</td>
<td>-0.21</td>
<td>-0.202</td>
</tr>
</tbody>
</table>

ture, $v_i = u\xi_i$, are determined by scaling the eigenvector component for a given atom, $\xi_i$, by the local mode amplitude $u$. Figure 4.3 gives plots of energy versus local mode for local modes applied along the [001], [101], and [111] crystallographic directions.

The energy versus local mode data is fit using Eq. (3.6) with $\alpha$ and $\gamma$ as the fitting parameters. The value of $\kappa$ is set equal to half of the eigenvalue corresponding to the eigenvector $\xi_i$ as defined in Ref. [50]. From the fits for all three local mode directions the values of $\alpha$ and $\gamma$ are obtained.

The data shown in Fig. 4.3 also predicts a ground state of rhombohedral symmetry so that the polarization vector lies in the [111] crystallographic direction. This finding is in agreement with experiment [17,49,50].

### 4.4 Strain-Local Mode Coupling Coefficients

To calculate the values of $B_{i\alpha\beta}$ we consider how the ground state energy will change with the addition of strain. In order to do this we compute the eigenvalues of the IFC matrix in the presence of strain. We apply small amounts of strain, between -0.005 and 0.005, by altering the values of different components of the strain tensor. The IFC matrix is diagonalized and the $\kappa$ values for each strained unit cell are extracted. The coupling tensor $B_{i\alpha\beta}$ denotes the interaction of strain component $\eta_i$ in the Voigt notation with local mode components in the $\alpha$ and $\beta$ directions. The value of $B_{1xx}$, for instance, describes the coupling of local modes in the [100] direction with non-zero strain in the same [100] direction. The interaction
Figure 4.3: Total energy of BTO as a function of local mode for three local mode directions [001], [100], and [111] for BTO. Solid lines indicate the least squares fit of the data using Eq. (3.6).
Table 4.2: $B_{\alpha\beta}$ parameters for BTO using the GGA and the LDA. Other theoretically calculated values are provided for comparison. The units of strain-local mode coupling constants is $\text{Ha}/a_0^2$.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Refs. [50] and [17]</th>
<th>Ref. [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1xx}$</td>
<td>-2.037244</td>
<td>-2.223106</td>
<td>-2.171400</td>
<td>-1.903834</td>
</tr>
<tr>
<td>$B_{1yy}$</td>
<td>-0.288088</td>
<td>-0.164490</td>
<td>-0.198616</td>
<td>-0.0337637</td>
</tr>
<tr>
<td>$B_{4yz}$</td>
<td>-0.0721142</td>
<td>-0.017530</td>
<td>-0.079755</td>
<td>-0.149733</td>
</tr>
</tbody>
</table>

between local modes that are orthogonal to the direction of applied strain is governed by $B_{1yy}$ and all shear strain with local modes lying in the sheared plane by the value of $B_{4yz}$.

By giving $\eta_l$ a nonzero value the ionic spacing in the lattice will change, altering the internal atomic forces and resulting in a different IFC matrix. This changes the IFC eigenvalue corresponding to the soft mode and shifts the quadratic self-energy coefficient $\kappa$. Taking the second-order derivative of Eq. (3.5) with respect to the local mode we obtain

$$\kappa(\eta_l) = \kappa_0 + B_{l\alpha\beta}\eta_l. \quad (4.1)$$

Here $\kappa_0$ corresponds to the value of $\kappa$ with no strain applied. By computing $\kappa$ under small strains and fitting the data with Eq. (4.1) we obtain the values of $B_{l\alpha\beta}$. To obtain correct values for these parameters only two sets of calculations must be completed. The first are IFC calculations on a strained cubic cell with $\eta_3 \neq 0$. From this calculation the $\kappa$ values for both $B_{1xx}$ and $B_{1yy}$ can be computed from the eigenvalues of the IFC matrix. Two of the negative eigenvalues are degenerate and correspond to the situation where the strained crystallographic directions local mode vector that are perpendicular. The other negative eigenvalue is non-degenerate and corresponds to the situation where strained crystallographic direction and local mode are the same. The value of $\kappa$ is taken as half of these eigenvalues in each case. The same procedure is followed in the second set of calculations however $\eta_5 \neq 0$ and the local mode lies in the x-z plane along the [101] crystallographic direction. The linear fit of this data set is given in Fig. 4.4 and was done by linear regression via Eq. (4.1). The
resulting parameters are shown in Table 4.2 for the GGA and the LDA.

Another method for obtaining the coupling coefficients is to do a series of frozen-phonon calculations with strain applied rather than using DFPT methods. In this technique $\kappa$ is extracted from a linear regression fit of energy versus displacement curves using a quadratic function as the fitting equation. These values for $\kappa$ versus strain can then be fit using the same linear equation as above, Eq. (4.1), to obtain the coupling coefficients from the slope of the corresponding lines. This method however requires many more calculations and fittings to be done which may decrease accuracy in the values of $B_{\alpha\beta}$.

### 4.5 Elastic Stiffness Constants

The elastic stiffness constants, $B_{11}$, $B_{12}$, and $B_{44}$ are the elastic constants of the crystal, $C_{ij}$ expressed in units of energy [17]. The values of the elastic stiffness constants are $B_{ij} = a_{lat}C_{ij}$ and can be directly calculated using DFT. By setting the appropriate options in the VASP
Table 4.3: Values of the elastic stiffness constants obtained from DFT. Other theoretically determined values for the stiffness constants are given for comparison. Units of the stiffness constants are Ha.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Refs. [50] and [17]</th>
<th>Ref. [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{11}$</td>
<td>4.1792</td>
<td>4.90380</td>
<td>4.64</td>
<td>4.657</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>1.5242</td>
<td>1.68847</td>
<td>1.65</td>
<td>1.535</td>
</tr>
<tr>
<td>$B_{44}$</td>
<td>1.8027</td>
<td>1.88034</td>
<td>1.85</td>
<td>1.810</td>
</tr>
</tbody>
</table>

Figure 4.5: The eight local mode configurations used to compute the $j_i$ parameters. Each configuration corresponds to a given nearest neighbor interaction as described in Fig. 3.2. The force on the local mode is calculated for each configuration and fit with quadratic equation to find the harmonic coefficient $\kappa$ in each case. [66]

a series of six finite distortions of the lattice are performed and the elastic constants are derived from the stress-strain relationship. The results are then multiplied by the volume of the cell to get $B_{ij}$ shown in Table 4.3.

4.6 Harmonic Coefficient and Short-Range Interaction Parameters

The harmonic coefficient $\kappa_2$ and the short-range interaction parameters $j_i$ are calculated using nine sets of frozen-phonon calculations with different configurations of local modes. The local mode configurations for each case are given in Fig. 4.5.
Six of these calculations use a cubic supercell with 8 units cells (Fig. 4.5a-f) and the other two use a supercell with 10 unit cells (Fig. 4.5g & h). For each configuration self-consistent energy calculations were performed for local modes of different small amplitudes, \( u \). The force on the local mode is then calculated as:

\[
F_u = \xi_B f_B + \frac{1}{8} \xi_A \sum_{A,NN} f_A + \frac{1}{2} \xi_{\perp} \sum_{||,\perp} \sum_{NN} f_{||,\perp}.
\]

(4.2)

Here the summations over \( NN \) correspond to the nearest neighbors of that site (\( A, B, O_\perp \) or \( O_\parallel \)) and \( f_i \) are the forces on each atom. The choice of \( O_\parallel \) and \( O_\perp \) is determined by the orientation of the local mode \( u \) and the oxygen atoms in the summation. By fitting the forces on the local mode we can calculate the harmonic coefficients corresponding to each configuration. These values of \( \kappa \) are then used to explicitly calculate \( j_i \) and \( \kappa_2 \) using Eqs. (4.3a-h) [17]. The total \( \kappa \) for each configuration includes the long-range dipole-dipole interaction, a self energy contribution from \( \kappa_2 \) and the short range interaction from \( j_i \) such that

\[
k_a = -2.094 \times C + \kappa_2 + 2j_1 + j_2 + 4j_3 + 2j_4 + 4j_6, \quad (4.3a)
\]
\[
k_b = 4.844 \times C + \kappa_2 + 2j_1 - j_2 - 4j_3 + 2j_4 - 4j_6, \quad (4.3b)
\]
\[
k_c = -2.422 \times C + \kappa_2 + j_2 - 2j_4 - 4j_6, \quad (4.3c)
\]
\[
k_d = -2.677 \times C + \kappa_2 - 2j_1 + j_2 - 4j_3 + 2j_4 + 4j_6, \quad (4.3d)
\]
\[
k_e = 1.338 \times C + \kappa_2 - j_2 - 2j_4 + 4j_6, \quad (4.3e)
\]
\[
k_f = 0 \times C + \kappa_2 - 2j_1 - j_2 + 4j_3 + 2j_4 - 4j_6, \quad (4.3f)
\]
\[
k_g = 2.932 \times C + \kappa_2 + j_1 - 2j_5 - 4j_7, \quad (4.3g)
\]
\[
k_h = 0.416 + \frac{\kappa_2}{2} - 2j_7. \quad (4.3h)
\]

The constant \( C \) in Eqs. (4.3a-h) is from the dipole-dipole interaction and is given by \( C = \)
Table 4.4: Short-range interaction parameters, $j_i$, as well as the quadratic self-energy coefficient $\kappa_2$ in units of $Ha/a_0^2$.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref [17]</th>
<th>Ref. [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_2$</td>
<td>0.08295379</td>
<td>0.08726568</td>
<td>0.05680564</td>
<td>0.087822341</td>
</tr>
<tr>
<td>$j_1$</td>
<td>-0.01987689</td>
<td>-0.02282133</td>
<td>-0.02734859</td>
<td>-0.02144619</td>
</tr>
<tr>
<td>$j_2$</td>
<td>-0.02880937</td>
<td>-0.00580198</td>
<td>0.04019616</td>
<td>-0.01161840</td>
</tr>
<tr>
<td>$j_3$</td>
<td>0.00642592</td>
<td>0.00736434</td>
<td>0.00927208</td>
<td>0.00709041</td>
</tr>
<tr>
<td>$j_4$</td>
<td>-0.00594322</td>
<td>-0.00503628</td>
<td>-0.00815037</td>
<td>-0.00628772</td>
</tr>
<tr>
<td>$j_5$</td>
<td>-0.00289927</td>
<td>-0.00393986</td>
<td>0.00580405</td>
<td>0.000</td>
</tr>
<tr>
<td>$j_6$</td>
<td>0.00282799</td>
<td>0.00219405</td>
<td>0.00370472</td>
<td>0.00285057</td>
</tr>
<tr>
<td>$j_7$</td>
<td>0.00713156</td>
<td>0.00396818</td>
<td>0.00185236</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$\frac{Z^{*2}}{\varepsilon_{\infty} a_{1t}^3}$. By solving this set of linear equations for the eight unknowns all of the $j_i$ and the value for $\kappa_2$ can be found. The values for $\kappa_2$ and $j_i$ are found in Table 4.4.

### 4.7 Additional Parameters

There are only five more parameters that are needed to complete the parameterization of BTO. Two of these parameters, $\varepsilon_{\infty}$ and $Z^*$, can be directly obtained from DFT calculations. In the VASP the ion-clamped static dielectric tensor and Born effective charge tensors for each atom can be calculated using DFPT. From these two tensors the value for $\varepsilon_{\infty}$ and $Z^*$ are obtained. The value for $\varepsilon_{\infty}$ is directly taken from the static dielectric tensor whereas the value for $Z^*$ must be calculated using the eigenvector or pseudoeigenvector and the Born effective charges of each atom. This is done by the summation $Z^* = \sum_i \xi_i Z^*_i$.

The last three parameters are the effective masses of the local mode $M^*_u$, the inhomogeneous strain $M^*_\sigma$, and the homogeneous strain $M^*_\nu$. The effective mass of the local mode is calculated from Ref. [64]

$$M^*_u = -\frac{8}{u_0^2 \omega_{A_1}^2} E^0,$$

where $E^0$, $u_0$ and $\omega_{A_1}$ are taken from first-principles calculations and correspond to the minimum ground state energy, the local mode associated with it and the frequency of the
Table 4.5: Values of the Born effective charge, $Z^*$, static dielectric constant, $\varepsilon_{\infty}$, the local mode effective mass, $M_u^*$ and the inhomogeneous strain mass $M_{\eta in}^*$. The Born effective charge has units of e, the static dielectric constant is dimensionless and the effective masses have units of amu.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z^*$</td>
<td>10.201</td>
<td>10.27</td>
</tr>
<tr>
<td>$\varepsilon_{\infty}$</td>
<td>6.890</td>
<td>6.883</td>
</tr>
<tr>
<td>$M_u^*$</td>
<td>36.879</td>
<td>41.648</td>
</tr>
<tr>
<td>$M_{\eta in}^*$</td>
<td>233.19</td>
<td>233.19</td>
</tr>
</tbody>
</table>

lowest energy $A_1$ symmetry phonon mode. Minimizing Eq. (3.6) with respect to the local mode for the rhombohedral phase we find $u_{x,0} = u_{y,0} = u_{z,0} = \sqrt{-\frac{\kappa}{6\alpha+2\gamma}}$ and therefore $u_0^2 = -\frac{2\kappa}{6\alpha+2\gamma}$. Inserting the components of $u_0$ into Eq. (3.6) we obtain $E^0 = -\frac{\kappa^2}{4(\alpha+\frac{1}{2}\gamma)}$. The value of $\omega_{A_1}$ is obtained from first-principles calculations using DFPT. The expression for the effective mass of the local mode in Eq. (4.4) is in contrast to the common method which uses the soft mode eigenvector and the atomic mass, $M_i$, of each constituent atom via the summation $M_u^* = \sum_i (\xi_i)^2 M_i$. Our new technique incorporates the ground state dynamical properties into the parameterization of the perovskite and should increase the accuracy of the $M_u^*$ parameter. The effective mass of inhomogeneous strain ,$M_{\eta in}^*$, allows for the description of the acoustic phonons dynamics. This mass is calculated from $M_{\eta in}^* = \sum_i M_i$ where $M_i$ is the atomic mass of each atom and is independent of any quantities calculated from first-principles . The effective mass of homogeneous strain, $M_{\eta hom}^*$, is an artificial parameter that is user controlled and determines the frequency response of the material. This mass can be changed in order to move the intrinsic frequency to lower or higher values so that it does not interfere with the dynamics that are being studied. The values of $Z^*$, $\varepsilon_{\infty}$, $M_u^*$ and $M_{\eta}^*$ are given in Table 4.5 and complete the parameter set needed for the effective Hamiltonian. Next we will run each parameter set through a series of tests in order to investigate their accuracy in reproducing the properties of BTO.
Figure 4.6: Phonon dispersion curves calculated from first-principles using the LDA to DFT. Notice the additional instability next to the Γ-point \( q=(0,0,0) \) that predicts the local mode stability away from the Γ-point.

### 4.8 Phonon Dispersion

The first check of the parameter set is the calculation of the phonon dispersion for the material. The phonon dispersion curves are calculated by diagonalizing the effective Hamiltonian in reciprocal space. The only portions of the Hamiltonian that affect the phonon behavior are from the self energy up to harmonic order, the dipole-dipole interactions and the the short-range local mode interactions. Therefore, only the values of \( \kappa_2 \), \( j_i \), \( Z^* \), \( \varepsilon_\infty \) and the volume \( a_{lat}^3 \) are necessary to calculate the phonon dispersion relationships. By visually inspecting the calculated dispersion curves one can determine if the phonons are well behaved across the Brillouin Zone. In the case of BTO however the phonons were not well behaved and an additional instability, lower in energy than the Γ-point soft mode instability, were predicted by the parameter sets as shown in Fig. 4.6.

To eliminate the additional instability the high energy phonons must be refit. The high
energy local mode configurations (Fig 4.5b, e and f) are A-site dominated. This means that when the B-site is the centering for the local mode the higher energy configurations are not reproduced well. By calculating the phonons in a 40-atom supercell using DFPT we can extract all of the values for $\kappa$ that are found from the calculations described by Fig. 4.5. The difference between the two techniques, and why the frozen phonon method is preferred is that the phonons calculated from first-principles are not always in the exact configuration that is desired. It is reasonable, however, to extract $\kappa$ for only the highest energy configurations and preserving the lower energy values from the frozen phonon calculations. Once these values are incorporated in the parameter set the phonons behave as they should throughout the Brillouin Zone as shown in Fig. 4.7. Only curves for the parameters obtained using the LDA are shown here however the same instability was seen and corrected for the set obtained using the GGA.

![Figure 4.7: Example of phonon dispersion curves in BTO calculated using the LDA parameter set.](image)

Figure 4.7: Example of phonon dispersion curves in BTO calculated using the LDA parameter set.
4.9 Transition Temperatures

Another test of the parameter set is to check how well the ferroelectric behavior is reproduced by calculating the transition temperatures associated with the material. To compute the transition temperature we use the computational annealing method. The temperature is decreased from above the Curie point down to 5 K in steps of $\Delta T=5$ K. At each step we record the components of the local mode. This process is repeated in the opposite direction as well so that the sample is heated through all of the transition temperatures to see if thermal hysteresis is present. BTO undergoes three structural phase transitions and thus three transition temperatures. From experiment the cubic to tetragonal (C-T) transition occurs 403 K, the tetragonal to orthorhombic (T-O) at 278 K and the orthorhombic to rhombohedral (O-R) at 183 K [17, 67]. The parameter set calculated using the GGA gives the three transition temperatures at 540 K (C-T), 480 K (T-O) and 445 K (O-R) as shown in Fig. 4.8. These are considerably higher than the experimental values. Which is likely to be due to overestimation of the lattice constant by the GGA [17].

In contrast, the transition temperatures for LDA are significantly lower than found by experiment. As seen in Fig. 4.9 the transitions occur at 140 K (C-T), 115 K (T-O) and 100 K (O-R). Again this discrepancy is expected as the equilibrium lattice constant found using the LDA is lower than the experimental value. It is important to note that the choice of MD time step is important in the case of the LDA parameters. We found that a time step greater than 0.2 fs produces an incorrect transition sequence.

As the parameters from the GGA overestimate the transitions and the parameters from the LDA underestimate them we propose to combine the two sets into a hybrid one in order to improve the accuracy. We took the difference between the $T_C$ for the (C-T) transition for both the GGA and the LDA parameters and normalized them to the experimental value. The “hybrid” parameters were then calculated as a weighted average of the GGA and the LDA parameters. We used the expression $x_{\text{hybrid}} = \alpha x_{\text{GGA}} + (1 - \alpha) x_{\text{LDA}}$ where $x$ is a parameter and the weight, $\alpha = 0.649$, to calculate the “hybrid” parameter set. The new
Figure 4.8: Components of the local mode as a function of temperature for bulk BTO using effective Hamiltonian parameters found from the GGA. The transition into each ferroelectric phase coincides with an additional component of the local mode becomes nonzero. The C, T, O and R correspond to the cubic, tetragonal, orthorhombic and rhombohedral phases.

Figure 4.9: Components of the local mode as a function of temperature for bulk BTO using effective Hamiltonian parameters found using the LDA. The transition into each ferroelectric phase coincides with an additional component of the local mode becomes nonzero. The cubic (C), tetragonal (T), orthorhombic (O) and rhombohedral (R) phases are indicated at each corresponding point.
Figure 4.10: Components of the local mode as a function of temperature for bulk BTO using the weighted average of effective Hamiltonian parameters found by using the GGA and the LDA. The transition into each ferroelectric phase coincides with an additional component of the local mode becomes nonzero. The cubic (C), tetragonal (T), orthorhombic (O) and rhombohedral (R) phases are indicated at each corresponding point.

parameters were then tested using the computational annealing approach using 300,000 MD steps of 1 fs and the transition temperatures were found to be 365 K (C-T), 310 K (T-O) and 275 K (O-R) as shown in Fig. 4.10. This “hybrid” parameter greatly improves all of the transition temperatures predicted by the effective Hamiltonian when compared with experimental values.

4.9.1 Spontaneous Polarization

In addition to the transition temperature we also test the parameter set’s ability to reproduce the spontaneous polarization, $P_s$. The values of $P_s$ are given in Table 4.6 for each phase of BTO [67]. The polarization was measured at 315 K, 280 K and 220 K in order to compare them to the experimental values. The error in our calculated values for $P_s$ are reasonable for the tetragonal and orthorhombic phases however there is a large discrepancy for the rhombohedral phase. This may be due in part to poor quality samples that were used in the
Table 4.6: The spontaneous polarization predicted by the “hybrid” parameter set. Experimental values are also given for each phase. All values reported in units of C/m$^2$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>“Hybrid”</th>
<th>Ref. [67]</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0.265</td>
<td>0.27</td>
<td>1.2%</td>
</tr>
<tr>
<td>O</td>
<td>0.347</td>
<td>0.368</td>
<td>5.4%</td>
</tr>
<tr>
<td>R</td>
<td>0.405</td>
<td>0.32</td>
<td>27%</td>
</tr>
</tbody>
</table>

Based on the tests described above we conclude that the “hybrid” set of parameters provides the best overall description of static properties. Compared to other available sets of parameters for BTO the "hybrid" set improves the overall description of transition temperatures and improves the predicted values of spontaneous polarization.

### 4.10 Dynamical Properties

In order to test the accuracy of the dynamical properties of a parameter set we must compute the soft mode frequency. This is done using the technique of Ref. [68] which is described in more detail in Chapter 5. In general the complex dielectric response of BTO is calculated and fit with a damped harmonic oscillator model from which the mode frequencies can be extracted. This calculation is done at low temperature (on the order of 10 K) and is compared to the same frequencies obtained from DFPT on a 5 atom fully relaxed unit cell.

The soft modes in BTO are the lowest energy transverse optical modes which are the $A_1$ (1TO) and $E$ (1TO) modes from the irreducible representation notation [69]. The $A_1$ mode characterizes ionic vibrations along the rhombohedral [111] direction or parallel to the polarization vector while the $E$ mode characterizes ionic vibrations along the [555] direction perpendicular to the polarization vector. The 0 Kelvin frequencies of these modes can be directly calculated using DFPT and the results of those calculations are given in Table 4.7. Note that the frequencies of these two modes are very close together especially when compared to a material such as PbTiO$_3$ where the $A_1$ and $E$ mode frequencies found from
Table 4.7: Frequencies of the soft modes of BTO found by DFPT using the GGA and the LDA. Frequencies are given in THz.

<table>
<thead>
<tr>
<th>Mode</th>
<th>GGA</th>
<th>LDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{A_1}$</td>
<td>4.802</td>
<td>5.507</td>
</tr>
<tr>
<td>$\omega_E$</td>
<td>4.729</td>
<td>4.996</td>
</tr>
</tbody>
</table>

DFPT are approximately 2 THz apart.

The “hybrid” parameter set that provides accurate static properties such as transition temperatures and spontaneous polarization fails to reproduce the dynamic properties very well. Calculating the frequencies predicted by the set we find that $\omega_{A_1}$ and $\omega_E$ are nearly 7 THz. Obviously this is unacceptable for practical use in making any sort of predictions about the dynamics of BTO. Conveniently the effective Hamiltonian gives us the ability to calculate the soft mode frequencies analytically.

To derive the frequencies we look to solve the dynamic equation of motion for the zone-center Hamiltonian given in Eq. (3.6) using energy surface renormalized values of $\alpha$ and $\gamma$ denoted as $\alpha'$ and $\gamma'$ [50]. Expressions for the values of $\alpha'$ and $\gamma'$ are derived in Ref. [50]

\[
\alpha' = \alpha - \frac{1}{24} \left( \frac{C^2}{B} + 4 \frac{\nu_t^2}{\mu_t} \right) \tag{4.5}
\]

and

\[
\gamma' = \gamma + \frac{1}{2} \left( \frac{\nu_t^2}{\mu_t} - \frac{\nu_r^2}{\mu_r} \right). \tag{4.6}
\]

Here $B$ is the bulk modulus, $\mu_t$ is the shear modulus for tetragonal distortions and $\mu_r$ is the shear modulus for rhombohedral distortions [50]. The other variables in Eqs (4.5) and (4.6) ($C$, $\nu_t$ and $\nu_r$) are analogous quantities derived from the strain-phonon coupling constants $B_{\alpha\beta}$ as given in Ref. [50].

The frequencies of the modes can be calculated analytically using a Taylor series expansion of the renormalized Eq. (3.6) about the ground state value of the local mode and then solving the dynamical equation. The expressions for the frequencies are $\omega_{A_1} = \sqrt{\frac{-4\pi}{M_u}}$ and
\[ \omega_E = \sqrt{\frac{2\gamma'\kappa}{3M_u^*(\alpha' + \gamma')}} \]. The \( A_1 \) mode is usually well reproduced since \( M_u^* \) is defined using the \( A_1 \) mode frequency calculated from first principles. The \( E \) mode frequency, in contrast, is not reproduced well because of its dependence on the quartic order coefficients \( \alpha' \) and \( \gamma' \). By adjusting the values of \( \alpha' \) and \( \gamma' \), however, the frequency of the \( E \) mode can be “tuned” to the value that is desired. This is done by shifting the values of the coupling coefficients, \( B_{\alpha\beta} \). This technique was shown to allow first-principles effective Hamiltonian parameters found for PbTiO_3 to give simultaneous description of static and dynamic properties [64].

In the case of the “hybrid” parameters however, we found that neither of our MD calculated frequencies match well. We attempted to tune the \( \alpha' \) and \( \gamma' \) parameters in order to force the frequencies of the modes to match those obtained from DFT. However, it is impossible to find a set of \( \alpha' \) and \( \gamma' \) that reproduce static and dynamical properties simultaneously. We believe that more terms need to be included in the effective Hamiltonian to overcome this issue.

Specifically if \( \alpha' \) and \( \gamma' \) for the GGA set are tuned to reproduce dynamical properties the tetragonal and orthorhombic phases become unstable. At low temperature BTO no longer remains in a homogeneously polarized state, instead falling into a domain pattern. The transition temperatures are also altered and become very close to each other in contrast with the experimentally known behavior. This makes the parameter set from the GGA unsuitable for use in modeling dynamical properties. In the case of the parameters obtained using the LDA changing the values of \( B_{\alpha\beta} \) completely eliminates the tetragonal and orthorhombic phases of BTO leaving only one phase transition into the rhombohedral phase at 280 K. While this behavior is not the desired outcome some information may still be gleaned from the rescaled “dynamic” set of parameters.

The parameters we have obtained by “tuning” the frequency of the \( E \) mode, shown in Table 4.8, should be able to reproduce dynamic properties at low temperature. To test the parameter set’s ability to reproduce the dynamical properties we calculate the complex dielectric response in the temperature range of 380 K to 5 K to extract the frequencies of
Table 4.8: Values for $B_{\alpha\beta}$ used to tune the dynamical properties of BTO. These values have been altered from those found using the LDA. The units of strain-local mode coupling constants is Ha/$a_0^2$.

<table>
<thead>
<tr>
<th></th>
<th>Static</th>
<th>Dynamic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1xx}$</td>
<td>-2.223106</td>
<td>-2.26652</td>
</tr>
<tr>
<td>$B_{1yy}$</td>
<td>-0.164490</td>
<td>-0.369</td>
</tr>
<tr>
<td>$B_{4yz}$</td>
<td>-0.017530</td>
<td>-0.10673</td>
</tr>
</tbody>
</table>

Figure 4.11: Frequencies of the $A_1$ and $E$ modes of BTO from the dynamical parameter set. These frequencies are calculated from fitting the complex dielectric response data obtained from MD simulations.

vibration as shown in Fig. 4.11.

At the lowest temperature tested, 5 K, the frequencies should be very close to those obtained from 0 K first-principles calculations. Indeed we find from our calculations that the frequencies of the $A_1$ and $E$ modes are 183.4 cm$^{-1}$ (5.5 THz) and 162.2 cm$^{-1}$ (4.9 THz) which is in good agreement with the frequencies obtained from DFT using the LDA. This reveals that our dynamical set of parameters accurately models the dynamical properties of BTO in the rhombohedral phase.
4.11 Conclusions

In summary we proposed a new route to the parameterization of ferroelectric perovskites with multiple phase transitions. We attempted to use methods that were successful in simultaneously describing both static and dynamic properties for ferroelectrics with only one phase transition. This new parameterization method includes using DFPT to calculate parameters that were previously obtained using the frozen-phonon method. We also used phonon frequencies calculated from first-principles to derive the effective mass of the local mode instead of using the eigenvector of the soft mode and the atomic masses.

This new method of parameterization 1) provides accurate description of static ferroelectric properties like transition temperatures and spontaneous polarization, 2) shows that the present form of the effective Hamiltonian does not allow for simultaneous description both static and dynamical properties 3) is useful to calculate sets of parameters that independently model static and dynamical properties. All four sets of parameters described above are summarized in Table 4.9.
Table 4.9: Complete sets of effective Hamiltonian parameters for BTO. All parameters are shown in atomic units. Also shown are the spontaneous polarization, transition temperatures and 0 K soft mode frequencies from the effective Hamiltonian.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>&quot;hybrid&quot;</th>
<th>Dynamical</th>
<th>Lattice Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{lat} )</td>
<td>7.633</td>
<td>7.468</td>
<td>7.574</td>
<td>7.4687</td>
<td></td>
</tr>
<tr>
<td>( \xi_A )</td>
<td>-0.1248</td>
<td>-0.2571</td>
<td>-0.2571</td>
<td></td>
<td>Components</td>
</tr>
<tr>
<td>( \xi_B )</td>
<td>-0.7719</td>
<td>-0.7438</td>
<td>-0.7438</td>
<td></td>
<td>of Soft-Mode</td>
</tr>
<tr>
<td>( \xi_\parallel )</td>
<td>0.5829</td>
<td>0.5161</td>
<td>0.5161</td>
<td></td>
<td>Eigenvector</td>
</tr>
<tr>
<td>( \xi_\perp )</td>
<td>0.1562</td>
<td>0.2391</td>
<td>0.2391</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2750</td>
<td>0.3209</td>
<td>0.2912</td>
<td>0.2407</td>
<td>Anharmonic</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-0.4519</td>
<td>-0.4806</td>
<td>-0.4620</td>
<td>-0.4645</td>
<td>Coefficients</td>
</tr>
<tr>
<td>( B_{1xx} )</td>
<td>-2.0372</td>
<td>-2.2231</td>
<td>-2.1177</td>
<td>-2.2665</td>
<td>Electrostrictive</td>
</tr>
<tr>
<td>( B_{1yy} )</td>
<td>-0.2881</td>
<td>-0.1645</td>
<td>-0.2517</td>
<td>-0.3690</td>
<td>Coefficients</td>
</tr>
<tr>
<td>( B_{4yz} )</td>
<td>-0.07211</td>
<td>-0.01753</td>
<td>-0.06553</td>
<td>-0.10673</td>
<td></td>
</tr>
<tr>
<td>( B_{11} )</td>
<td>4.1792</td>
<td>4.9038</td>
<td>4.4335</td>
<td>4.9038</td>
<td>Elastic</td>
</tr>
<tr>
<td>( B_{12} )</td>
<td>1.5242</td>
<td>1.6885</td>
<td>1.5819</td>
<td>1.6885</td>
<td>Constants</td>
</tr>
<tr>
<td>( B_{44} )</td>
<td>1.8027</td>
<td>1.8803</td>
<td>1.8290</td>
<td>1.8803</td>
<td></td>
</tr>
<tr>
<td>( \kappa_2 )</td>
<td>0.08295</td>
<td>0.08727</td>
<td>0.08447</td>
<td>0.08727</td>
<td>Harmonic</td>
</tr>
<tr>
<td>( j_1 )</td>
<td>-0.01988</td>
<td>-0.02282</td>
<td>-0.02091</td>
<td>-0.02282</td>
<td>On-site</td>
</tr>
<tr>
<td>( j_2 )</td>
<td>-0.02881</td>
<td>-0.005802</td>
<td>-0.02073</td>
<td>-0.005802</td>
<td>and Short-Range</td>
</tr>
<tr>
<td>( j_3 )</td>
<td>0.006426</td>
<td>0.007364</td>
<td>0.006755</td>
<td>0.007364</td>
<td>Interaction</td>
</tr>
<tr>
<td>( j_4 )</td>
<td>-0.005943</td>
<td>-0.005036</td>
<td>-0.005625</td>
<td>-0.005036</td>
<td>Parameters</td>
</tr>
<tr>
<td>( j_5 )</td>
<td>-0.002899</td>
<td>-0.003940</td>
<td>-0.003265</td>
<td>-0.003940</td>
<td></td>
</tr>
<tr>
<td>( j_6 )</td>
<td>0.0002828</td>
<td>0.002194</td>
<td>0.002605</td>
<td>0.002194</td>
<td></td>
</tr>
<tr>
<td>( j_7 )</td>
<td>0.007132</td>
<td>0.003968</td>
<td>0.006021</td>
<td>0.003968</td>
<td></td>
</tr>
<tr>
<td>( Z^* )</td>
<td>10.201</td>
<td>10.27</td>
<td>10.2252</td>
<td>10.27</td>
<td>Born Eff. Charge</td>
</tr>
<tr>
<td>( \varepsilon_\infty )</td>
<td>6.890</td>
<td>6.883</td>
<td>6.88754</td>
<td>6.883</td>
<td>Dielectric Constant</td>
</tr>
<tr>
<td>( M^*_u )</td>
<td>36.879</td>
<td>41.648</td>
<td>38.5529</td>
<td>40.1699</td>
<td>Local Mode Eff. Mass</td>
</tr>
<tr>
<td>( P_s (T) )</td>
<td>0.305</td>
<td>0.146</td>
<td>0.265</td>
<td>-</td>
<td>Spon. Polarization C/m²</td>
</tr>
<tr>
<td>( P_s (O) )</td>
<td>0.400</td>
<td>0.211</td>
<td>0.347</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( P_s (R) )</td>
<td>0.477</td>
<td>0.294</td>
<td>0.405</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>C-T</td>
<td>540 K</td>
<td>140 K</td>
<td>365 K</td>
<td>-</td>
<td>Ferroelectric Transition Temperatures</td>
</tr>
<tr>
<td>T-O</td>
<td>480 K</td>
<td>115 K</td>
<td>310 K</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>O-R</td>
<td>445 K</td>
<td>100 K</td>
<td>275 K</td>
<td>280 K</td>
<td></td>
</tr>
<tr>
<td>( \omega_{A_1} )</td>
<td>9.031</td>
<td>5.460</td>
<td>5.675</td>
<td>5.507</td>
<td>( H_{eff} ) Freqs. THz</td>
</tr>
<tr>
<td>( \omega_E )</td>
<td>5.154</td>
<td>2.976</td>
<td>2.9243</td>
<td>4.908</td>
<td></td>
</tr>
</tbody>
</table>
5 The Soft Mode Dynamics of PbTiO$_3$ Under Different Mechanical Boundary Conditions

It is important not only from a fundamental perspective but also for device applications to have a complete understanding of the underlying dynamics of ferroelectric materials. For many ferroelectrics the root of the ferroelectric phase transition lies in the softening of certain transverse optical modes that allow for the polar distortion to occur. In addition, the transverse optical soft mode of most ferroelectrics is strongly coupled to the acoustic phonons which gives rise to a structural phase transition. As a result of the coupling between the transverse optical soft mode and acoustic phonons, the dynamics of ferroelectrics exhibit strong dependence on mechanical boundary conditions such as hydrostatic pressure, stress and strains. This is potentially very useful as it allows for the manipulation of the mode dynamics by the correct choice of boundary conditions or the converse where one can identify the conditions present by measuring the change in the mode frequencies. These mechanical boundary conditions play a significant role in ferroelectric device applications since pressures, stresses and strains are inherent to any nanoscale samples and the change in mode dynamics provides a nondestructive avenue to investigate the magnitude of the internal stresses. For example, the mode dynamics were used to estimate the internal and residual stresses in thin films and superlattices [70–73]. Whenever a film is grown on a substrate with a significant lattice constant mismatch the epitaxial conditions result in stresses. In films that do not have full epitaxy, thick films for example, residual stresses result from the thickness dependent relaxation of the grown material.
The work of Cochran [74, 75] and Cowley [76] in the 1960’s sparked interest in the field of structural phase transitions, especially for ferroelectrics [77]. Cochran used a shell model applied to a diatomic lattice and showed that a transverse optical soft mode can be responsible for ferroelectricity without any anomalies in the temperature dependences of short-range forces which the prevailing theory predicted [74, 75, 77]. Cowley showed from a more microscopic approach that the soft mode concept closely followed from a damped harmonic oscillator model rather than Debye relaxation [76, 77]. The first important work concerning the structural phase transitions of perovskites was done via infrared reflectivity measurements on BTO and SrTiO$_3$ [78, 79]. SrTiO$_3$ is known to remain paraelectric at all temperatures however, it also contains the same soft-modes as its ferroelectric isomorphs. The work on BTO and SrTiO$_3$ showed that the low-frequency dielectric response of the crystals was due to a low-frequency optical phonon that could be described as the soft mode of Cochran [77–79].

Another perovskite that attracted a lot of attention was lead titanate, PbTiO$_3$ or PTO. PTO has been used as a prototypical ferroelectric material for studying soft modes and their influence on phase transitions mainly because of its single tetragonal ferroelectric phase. PTO has also been hallmarked as a typical displacive ferroelectric making it a prime example for studying intrinsic dynamics [5]. For many decades the phonon behavior of PTO has been studied experimentally using techniques such as Raman spectroscopy [80–83], infrared reflectivity [84] and neutron scattering [85]. These studies have mainly dealt with single crystals [80,81,86], powder samples [87,88] or thin films [89,90] in order to map the phonons to their frequencies and to uncover the reasons for discrepancies between the group theory [91, 92] and the experimental results [93]. Some experimental work has been carried out to study the effect of strain and pressure on the soft modes as well [71,94–98]. The work of Cerderia et al. [94] and Sanjuro et al. [95] reported that the frequency of the soft modes of PTO depend linearly on pressure. Basu et al. found that the ferroelectric phase of Pb$_{1-x}$Ca$_x$TiO$_3$ reappears after a critical pressure is applied as a result of shifts in the soft modes [96]. Sun et al. grew PTO thin films on lattice matched substrates and found
an increase in the frequencies of the $A_1$ and $E(1TO)$ modes [97] attributed to the stress from non-epitaxial conditions. The residual stress in thin films of PTO was reported by Fu et al. to have a similar effect on the soft mode frequencies to that from pressure [71]. Theoretical studies of the phonons in PTO have also been carried out at 0 K using \textit{ab initio} simulations [42,99] providing valuable information about the ground state mode dynamics.

A common trend in these studies is the formulation of analytical expressions that predict the frequency of the soft mode as a function of applied boundary conditions. Both experimental [94,95,100–102] and theoretical [103,104] studies on the effect of compressive hydrostatic pressure show that the frequency, $\nu$, of the soft mode can be accurately predicted using a Curie-Weiss pressure law of the form

$$\nu^2 = A_P (P - P_0), \quad (5.1)$$

where $A_P$, $P$ and $P_0$ are the Curie-Weiss pressure constant, the hydrostatic pressure and the pressure where the mode frequency extrapolates to zero, respectively. In this context the value of $A_P$ describes the sensitivity of the mode frequency to the application of pressure. Despite the fact that the validity of Eq. (5.1) for negative or expansive pressures and other boundary conditions has not been verified the Curie-Weiss pressure law has been used to estimate both compressive and tensile residual stresses in ferroelectric thin films [70–73]. The use of Eq. (5.1) in this way uncovers a gap in the understanding of the effects of mechanical boundary conditions since no analytical relationship for stresses or strains has ever been developed. One possible reason for the lack of understanding is the experimental difficulties that underly such an investigation since the controlled application of stress and strain is often prohibitively challenging. As a result of these experimental difficulties very few studies on the role of uniaxial and biaxial stresses and strains on the soft mode dynamics have been conducted [71,97].

Another open question concerning the effects of mechanical boundary conditions is the temperature dependence of the Curie-Weiss constants and the applicability of the Curie-
Weiss law in the paraelectric phase at high temperature. The studies used to formulate Eq. (5.1) were conducted at room temperature and therefore may not be completely reliable at other temperatures [94, 95, 100–102]. An added difficulty lies above the transition temperature where the soft mode is not Raman active meaning the typical Raman spectroscopy technique for measuring frequencies cannot be utilized.

Classical MD becomes a valuable tool to study the mode dynamics of ferroelectrics because the technique does not have the difficulties that arise in an experimental setting. MD also allows for investigation of the effects of mechanical boundary conditions in a wide range of temperatures both above and below the transition temperature. The goals of this study are to 1) systematically investigate the dynamical properties of PTO in response to hydrostatic pressure, uniaxial stress, biaxial stress and biaxial strain in a wide range of temperatures, 2) determine the existence of Curie-Weiss stress and strain laws for the soft mode frequencies for all temperatures investigated, 3) to uncover the temperature dependence of any Curie-Weiss constants that do exist and 4) to probe the overall role of mechanical boundary conditions in the soft mode dynamics.

5.1 Methodology and Computational Setup

To simulate the effect of mechanical boundary conditions we use the effective Hamiltonian discussed earlier and run all of the simulations on bulk configurations. A bulk sample is simulated by applying periodic boundary conditions in all directions on a 20x20x20 simulation supercell. Such a setup isolates the effect of the mechanical boundary conditions on the soft mode by eliminating all other contributing factors including electrical boundary conditions, sample size, dimensionality, and the presence of quasimodes just to name a few. This type of setup is also useful as it directly models a large number of other practical situations such as ferroelectric nanostructures under short-circuit boundary conditions and accurately models the soft mode dynamics of nanostructures with ionic vibrations along extended directions where the depolarizing field is usually small and the material may exhibit bulk-like
behavior [105]. These include the axial direction of ferroelectric nanowires and the in-plane dimensions of ferroelectric thin films and superlattices [105].

We begin by equilibrating structures at different temperatures for each of the tested mechanical boundary conditions. This is done by simulated annealing starting from $T=1200$ K down to $T=25$ K in steps of $\Delta T=25$ K using 40,000 MD steps 0.2 fs at each temperature decrement. For each temperature, we simulate the $NPT$ (constant number of particles, pressure and temperature), $N\sigma T$ (constant number of particles, stress and temperature), or $N\eta T$ (constant number of particles, strain and temperature) ensemble (depending on the choice of boundary condition) using the Evans-Hoover thermostat to control temperature. In order to simulate these different ensembles we use a modified effective Hamiltonian of the form, (5.2).

$$
\mathcal{H} = \mathcal{H}^0 + PV - \sigma \eta,
$$

(5.2)

here $\mathcal{H}^0$ is the effective Hamiltonian of Eq. (3.5), $\sigma$ is the stress tensor and $\eta$ is the strain tensor. The $NPT$ ensemble is simulated using the $PV$ term of Eq. (5.2) which mimicks a barostat [51, 68]. The $N\sigma T$ (constant stress) ensemble is simulated via the $\sigma \eta$ term of Eq. (5.2). This ensemble is used to simulate the effect of both biaxial and uniaxial stress on the soft mode dynamics. Similarly the $N\eta T$ (constant strain) ensemble is simulated by freezing the $\eta_1$, $\eta_2$ and $\eta_6$ components of the strain tensor [106] which models the effect of biaxial epitaxial strain.

The parameters for the effective Hamiltonian were taken from Ref. [64]. Pressures and stresses were tested in the range of -2 GPa to 2 GPa mostly because this range is comparable to the residual stresses found in ferroelectric thin films [70–73, 107]. In order to remove any ambiguity negative values represent expansion/tension where positive values represent compression. Strain was tested in the range of -2% to 2% lattice deformation with respect to the zero Kelvin cubic lattice parameter for PTO. In the case of epitaxial strain negative values represent compressive strain whereas positive values represent tensile strains.

To calculate the soft mode frequencies we use the approach proposed in Ref. [68]. The
simulations begin with equilibrium structures obtained in simulated annealing. An additional
8 ps of equilibration is run for each temperature followed by 2.1 ns MD runs to collect the
total dipole moment of the supercell and the autocorrelation functions. It is important to
note that in contrast to Ref. [68] the applicable ensemble (NPT, NσT, or NηT) is simulated
throughout the entire run. Once the autocorrelation functions have been collected they are
Fourier transformed to compute the complex dielectric response in the frequency range of 0
to 15 THz using the expression
\[
\varepsilon(\nu) - 1 = \frac{1}{3\varepsilon_0 V k_b T} \left[ \langle M^2 \rangle + i 2\pi \nu \int_0^\infty dt e^{2\pi \nu t} \langle M(t) \cdot M(0) \rangle \right].
\] (5.3)
Here \( \langle \cdot \rangle \) correspond to thermal averages while \( M, V, t \) and \( \nu \) are the total dipole moment,
supercell volume, the time and the frequency respectively.

The computational data for the complex dielectric response \( \varepsilon(\nu) \) was then fit using the
model of a classical damped harmonic oscillator [108,109] such that
\[
\varepsilon(\nu) = \varepsilon_\infty + \frac{S}{\nu^2 - \nu_o^2 + i\nu\gamma},
\] (5.4)
where \( \nu_o, \gamma \) and \( S \) are the intrinsic frequency, damping constant and oscillator (mode)
strength, respectively. The high-frequency permittivity \( \varepsilon_\infty \) is omitted since our model ac-
counts for only a single ionic polar displacement per unit cell [68]. When more than one
oscillator (mode) are present additional non-interacting oscillators are included in Eq. (5.4).

By fitting computational data for the complex dielectric response with Eq. (5.4) we
obtain the soft mode parameters, \( \nu_o, \gamma \) and \( S \), in the infrared (IR) frequency range for a
wide range of temperatures as shown in Fig. 5.1a. In order to identify the modes’ symmetry
we use the ISOTROPY Software Suite [69]. In the paraelectric phase PTO belongs to the
P_{m-3m} space group which allows only one triply degenerate IR active T_{1u} mode. From our
calculations we find this T_{1u} to soften to 14 cm\textsuperscript{-1} at \( T_C \). This is in good agreement with
recent experimental work of Hlinka et al. [110] who found by Raman scattering techniques
that the single paraelectric mode frequency softens to 17 cm$^{-1}$.

As PTO undergoes the ferroelectric structural phase transition the space group changes from P$_{m-3m}$ to P$_{4mm}$ at T$_C$. The change in symmetry causes the T$_{1u}$ mode to split into two separate modes that increase in frequency as the temperature decreases. These two modes are the $A_1$ and the doubly degenerate $E$ transverse optical (TO) modes. It is important to note that our technique is only able to trace IR active transverse optical modes. Other modes may be allowed, both IR silent, longitudinal and with higher energy however, they are not detected and will not be discussed here. The other modes are not included in the effective Hamiltonian and as a result we have dropped the (1TO) label that is often necessary from all symmetry indicators.

5.2 Hydrostatic Pressure

We begin by discussing the soft mode dynamics in the presence of hydrostatic pressure. Figure 5.1 reports the computational data for PTO under +2.0 GPa, -2.0 GPa and 0.0 GPa of hydrostatic pressure. Across the entire range of pressures investigated we find the same transition from a cubic paraelectric phase to a tetragonal ferroelectric phase that is seen in bulk PTO under normal conditions. This is due to the fact that hydrostatic pressure preserves the structural symmetry in both the paraelectric and ferroelectric phase. The transition temperature is also found to depend linearly on the applied pressure in agreement with a previously determined phenomenological result [5]. The linear dependence of T$_C$ on applied pressure, as shown in Fig. 5.1(b), is a result of the balance between the short-range and dipole-dipole interactions due to positive and negative pressures respectively.

We also find that the frequency of the $T_{1u}$, $A_1$ and $E$ modes exhibit a linear dependence on the applied pressure. Figure 5.2 shows the dependence of the mode frequency squared, $\nu^2$, for a few temperatures in the ferroelectric and paraelectric phases. We find that the $A_1$ and $E$ mode frequencies decrease with increasing pressure and the $T_{1u}$ mode frequency increases with increasing pressure. These results agree well with previous experimental studies on the
Figure 5.1: a) soft mode frequencies as a function of temperature for +2.0 GPa (green), -2.0 GPa (red) and zero applied pressure (blue). Black dashed lines indicate $T_C$ under pressure, while the black solid line indicates the zero pressure $T_C$. b) Change in $T_C$ as a function of applied pressure. [105]

effect of hydrostatic pressure on the mode frequencies of PTO [80, 95, 101, 110]. Figure 5.2 shows that the soft mode frequencies follow the Curie-Weiss pressure law across the entire range of tested pressures [105]. Since $\nu^2$ is a continuous function of pressure the same set of Curie-Weiss parameters, $A_P$ and $P_0$, can be used to estimate the soft mode frequency at negative pressures. This is potentially important for understanding the properties of ferroelectric alloys where chemical pressure plays an important role. Chemical pressures arise in these materials as the A-site or B-site ions in the ferroelectric matrix are not necessarily uniformly distributed.

Another observation of our simulations is that $\nu^2$ may show a discontinuity in the vicinity of the pressure induced phase transition from the cubic to tetragonal phases. This is indicated by the shift from a negative Curie-Weiss pressure constant to a positive one in the paraelectric phase as indicated by the change of slope between panels (a) and (b) of Fig. 5.2. This is explained by the fact that positive pressures favor short-range forces which result in mode
hardening, or increases in frequency, whereas negative pressures disfavor such forces and therefore lead to mode softening, or decreases in frequency [5].

Most studies on the soft mode dynamics of PTO under pressure are carried out at room temperature [95, 101] and therefore there is no information about the temperature dependence of the associated Curie-Weiss pressure constants. This is critically important from a device application point of view since the operation temperature of ferroelectric devices are likely not close to room temperature.

An advantage of our technique is that we can trace the pressure dependence of each mode at every temperature step. Our computational data, shown in Fig. 5.3, indicates that 1) the conclusions drawn from Fig. 5.2 are valid for all modes at all temperatures, 2) that the Curie-Weiss pressure constants for the $A_1$ and $E$ modes are temperature dependent with the $A_1$ mode being the most sensitive, 3) the dependence is seen most noticeably as the
temperature approaches the zero-pressure Curie point in the ferroelectric phase and 4) the $T_{1u}$ mode associated with the paraelectric phase is nearly independent of temperature. In addition the Curie-Weiss pressure constant of the $A_1$ mode is nearly 4 times that of the $E$ mode which is in good agreement with experimental findings at room temperature [95].

5.3 Uniaxial Stress

Uniaxial stress, tension or compression in only one crystallographic direction, can develop in a number of ferroelectric device or nanostructure geometries. For example, a nanostructure sandwiched between two electrodes can develop uniaxial stress along the out of plane direction as a result of the growth [110]. Thermal stresses in ferroelectric nanostructures can also develop uniaxially as a result of the device architecture [110]. Despite the practical implications of uniaxial stresses the role it plays in the dynamic properties is important in order to
complete a systematic understanding of the effect of mechanical boundary conditions [105].

The study of uniaxial stress is conducted similar to that of hydrostatic pressure. We study compressive stresses from 0.0 to 2.0 GPa and tensile stresses from -2.0 to 0.0 GPa. Each simulation is carried out in the presence of uniaxial stress acting on the planes perpendicular to the [001] crystallographic direction. In contrast to hydrostatic pressure we find a different ferroelectric phase for compressive and tensile stress. This is a result of the change in crystal symmetry as each unit cell is stretched or compressed in only one direction. For compressive stresses we find a ferroelectric orthorhombic phase of space group P\textit{mm}\textsubscript{2} and under tensile stress we find a space group of P\textit{4mm} indicating a tetragonal ferroelectric phase. The symmetry breaking also affects PTO at high temperature resulting in a tetragonal P\textit{4/mmm} phase. The differences between the zero-stress and stressed case are most readily observed in Fig. 5.4 (a) and (b) which give the frequency of the resulting modes across the range of temperatures tested.

Under a tensile load we find that as the structure transitions from the paraelectric to ferroelectric phase the polarization develops along the stretched axis. The ionic vibrations along this direction are associated with the A\textsubscript{1} mode and the vibrations along the two unstretched directions are associated with the doubly degenerate E mode. Under a compressive load the result is markedly different. Here the spontaneous polarization can choose between two equally likely directions as the piezoelectric coupling “squeezes” the polarization away from the axis of compression [105]. Therefore compressive loads result in an orthorhombic symmetry with polarization pointing perpendicular to the axis of compression. The change in symmetry lifts the degeneracy of the E mode and splits it into the B\textsubscript{1} and B\textsubscript{2} modes. The B\textsubscript{1} mode is associated with ionic vibrations along the axis of compression whereas the B\textsubscript{2} mode is associated with the vibrations along the uncompressed and non-polar direction. The A\textsubscript{1} mode, like the previous cases, is associated with ionic vibrations along the direction of polarization.

The Curie point shows strong dependence on the applied uniaxial stress, as shown in
Figure 5.4: (a) soft mode frequencies as a function of temperature for -2.0 GPa (red) of normal stress and zero applied stress (blue). (b) soft mode frequencies as a function of temperature for +2.0 GPa (green) of normal stress and zero applied stress (blue). (c) Change in $T_C$ as a function of applied uniaxial stress. [105]

Fig. 5.4(c). In contrast to hydrostatic pressure we see here that both compressive and tensile loads increase $T_C$. This is due to the fact that while hydrostatic pressure changes the volume and affects the balance between the long and short range interactions, stress mainly preserves the volume and enhances the polarization. An increased contribution from the piezoelectric coupling helps to stabilize the dipole-dipole interaction, enhancing the polarization as well as increasing the Curie temperature. Interestingly the increase in $T_C$ is much more dramatic for the case of tensile stresses and can be as much as 250 K under -2.0 GPa. This is much larger than either compressive uniaxial stress or hydrostatic pressure [105].

The effect of uniaxial stress on the soft mode dynamics is quite different from that of hydrostatic pressure. It can be seen in Fig. 5.5 that $\nu^2$ is no longer a continuous function of stress but shows a discontinuity at $\sigma = 0$ due to the change from the $P_{4mm}$ space group to the $P_{mm2}$. Here we notice that the frequencies of all modes increase with increasing amounts of both tensile and compressive stresses, $|\sigma|$, which is in contrast with hydrostatic pressure where compression decreases the frequency of the $A_1$ and $E$ modes [105].

At the quantitative level Fig. 5.5 also indicates that the effect of uniaxial stress is significantly different than the effects of hydrostatic pressure. Firstly -2.0 GPa of tensile uniaxial stress results in a 20% increase of the $A_1$ mode frequency at 250 K as opposed to only a
Figure 5.5: The dependence of the soft mode frequencies squared on the uniaxial stress. Panels (a) and (b) show the data in ferroelectric and paraelectric phases, respectively. [105]

10% increase under -2.0 GPa of hydrostatic pressure [105]. Similarly the $E$ mode frequency increases by 37% under uniaxial tensile stress compared to a 6% increase under the same amount of hydrostatic pressure. Compressive uniaxial stress has less of an impact on the mode frequencies with only a 5.6% difference in the $A_1$ mode frequency compared to a 10% change for hydrostatic pressure at 2.0 GPa. The $B_1$ mode however is enhanced increasing 28% under 2.0 GPa compressive stress where the $E$-mode frequency only decreases by 6.7% under hydrostatic pressure.

In the paraelectric phase we notice that the change of symmetry due to the application of uniaxial stress splits the $T_{1u}$ mode into the $A_{2u}$ and $E_u$ modes. The $A_{2u}$ mode characterizes the ionic vibrations along the axis of stress and the $E_u$ mode the vibrations along the two perpendicular directions. We find that both of these modes are continuous functions of stress with the $A_{2u}$ mode increasing with applied stress and the $E_u$ mode decreasing with increased stress as shown in Fig. 5.5.

When we consider how the mode frequencies change with temperature we find that for
all temperatures and stresses tested the soft modes follow the Curie-Weiss stress law

\[ \nu^2 = A^{(u)}_\sigma (\sigma - \sigma_0^{(u)}), \]  

(5.5)

where \( A^{(u)}_\sigma \) is the Curie-Weiss stress constant, or the measure of how the frequency squared changes with uniaxial stress, \( d\nu^2/d\sigma \), and \( \sigma_0^{(u)} \) is the value of uniaxial stress at which the soft mode frequency extrapolates to zero. The origin of Eq. (5.5) could be traced to the Lyddane-Sachs-Teller (LST) formula [111] that relates the frequency of polar modes to the static permittivity and has been found to follow a Curie-Weiss type behavior under biaxial stresses and strains [112]. The Curie-Weiss stress constant as a function of temperature is given in Fig. 5.6 for both compressive and tensile uniaxial stress.

Figure 5.6 provides quite a bit of significant information about the response of the modes in PTO to the application of uniaxial stress. First, in the paraelectric phase we see that the values of \( A^{(u)}_\sigma \) for both the \( A_{2u} \) and \( E_u \) modes remain constant across all temperatures
and under both compressive and tensile stresses. In comparison with the $T_{1u}$ mode under hydrostatic pressure the $A_{2u}$ and $E_u$ modes are generally less sensitive to uniaxial stresses with the $A_{2u}$ mode being the more sensitive of the two. In the ferroelectric phase and under compressive stress we notice that all of the Curie-Weiss constants are positive which is consistent with the mode hardening discussed earlier. The $B_1$ mode is the most sensitive to stress which is expected since this particular mode is associated with ionic vibrations along the stressed axis. We also notice a nearly linear dependence of $A^{(u)}_s$ below room temperature for the $B_1$ and $B_2$ modes and across all temperatures for the $A_1$ mode. Under tensile uniaxial stress the dependence of $A^{(u)}_s$, given in Fig. 5.6(b), is similar to that of compressive stress. Specifically, the dependence for the $A_1$ mode is nearly linear for all temperatures whereas the $E$ mode only has a linear dependence below room temperature. The only significant difference between the two cases is that the value of $A^{(u)}_s$ is negative for tensile stresses which is indicative of the mode hardening in response to tensile stresses.

5.4 Biaxial Stress

Biaxial stress frequently results from epitaxial growth [70–73] and is often seen in planar nanostructures such as thin films. Biaxial stresses can develop in these structures because of grain boundaries, lattice mismatch or from differences in thermal expansion coefficients. Understanding the effect of biaxial stress on the soft modes of notable importance and required for a systematic study.

To study the effect of biaxial stresses we use the same procedure as for tensile stress. The same range of temperatures and stresses were tested with the only difference being that the stress is applied to two sets of crystal planes instead of one. These planes are those perpendicular to the [100] and [010] crystallographic directions. Again, negative values of stress correspond to tension and positive values to compression. As in the case of uniaxial stress we find the $P_{4/mmm}$ tetragonal paraelectric phase above $T_C$ as well as the $P_{mm2}$ and $P_{4mm}$ orthorhombic and tetragonal ferroelectric phases below $T_C$, shown in Fig. 5.7(a) and
Figure 5.7: (a) soft mode frequencies as a function of temperature for -2.0 GPa (red) of biaxial stress and zero applied stress (blue). (b) soft mode frequencies as a function of temperature for +2.0 GPa (green) of biaxial stress and zero applied stress (blue). (c) Change in $T_C$ as a function of applied biaxial stress. [105]

(b). However, because the applied stress is biaxial the two phases are switched so that compressive biaxial stress results in a $P_{4mm}$ phase while tensile stress results in a $P_{mm2}$ phase. The preferred polarization directions are the [001], or unstressed direction, for compression and the [100] and [010], or stressed directions, for tension. Similar to tensile stresses we find that the Curie point shows strong dependence on applied stress and increases for both tensile and compressive stresses as shown in Fig. 5.7(c). In contrast to uniaxial stress however, the increases are nearly symmetric which is in agreement with previous studies [113, 114]. The increase in $T_C$ can be attributed to the stabilizing effect of the piezoelectric coupling [105].

In terms of frequency the modes also have a similar response to biaxial stress as they do to uniaxial stress. This is not unexpected since the same ferroelectric and paraelectric phases are present under both types. Figure 5.8 gives the dependence of $\nu^2$ on the applied biaxial stress $\sigma$. A very interesting consequence of this behavior is that under compressive loads the modes harden which is in contrast to the softening that is seen with compressive hydrostatic pressure [105]. This would suggest that the common technique to estimate residual stresses in ferroelectric thin films by using Eq. (5.1) is likely invalid in the case of compressive biaxial stresses [105].
Figure 5.8: The dependence of the soft mode frequencies squared on the biaxial stress. Panels (a) and (b) show the data in ferroelectric and paraelectric phases, respectively. [105]

considered taking the form

$$\nu^2 = A^{(b)}_\sigma (\sigma - \sigma^{(b)}_0),$$

(5.6)

where $A^{(b)}_\sigma$ is the Curie-Weiss stress constant, while $\sigma^{(b)}_0$ is biaxial stress where the frequency extrapolates to zero. Figure 5.9 gives the values of $A^{(b)}_\sigma$ for all temperatures considered.

Under compressive loads the Curie-Weiss stress constant is nearly linear in temperature across all temperatures for the $A_1$ mode and nearly linear for the $E$ mode below room temperature. This is very similar to the behavior seen for tensile uniaxial stress except that the $E$ mode is more sensitive to biaxial stress in this case. For tensile biaxial stresses the behavior of the modes is similar to that of compressive uniaxial stress, with the exception of an obvious sign change, however the sensitivity of all modes are enhanced with the greatest increase for the $A_1$ mode. We find the $B_1$ mode is least sensitive to biaxial stress. In the next section we will explore why exactly this is the case. The Curie-Weiss constants for the $A_1$ and $B_2$ modes are nearly equal in contrast with uniaxial stress where the response of the three
Figure 5.9: The temperature dependence of the Curie-Weiss stress constant under compressive (a) and tensile (b) biaxial stress. The error bars indicate the linear fitting error with respect to Eq. (5.6). The dashed vertical line indicates the Curie point at zero stress. [105]
modes were distinctly separated. The paraelectric phase is also strikingly similar to uniaxial stresses however the $E_u$ mode is more sensitive in the presence of biaxial stress and also takes on a positive value as a result of the additional stretched/compressed crystallographic direction.

### 5.5 Non-equilibrium Stresses

We have already discussed how inherent stresses can result from the growth or composition of a ferroelectric nanostructure. However, external stress can be applied post growth. In this case under low temperatures metastable structures could develop. Here we study such metastable structures and their soft mode dynamics.

In order to better understand the influence of stress on the soft mode dynamics of PTO post growth we calculate the soft mode frequencies as before except that in this case the equilibrium structures that start our simulations were obtained in the absence of stress. This allows us to compare two distinct scenarios the first where stress is applied during the annealing process (Scenario 1) and the second where stress is applied after annealing has been completed (Scenario 2). We find that the direction of polarization can play an important part in determining the dynamics of PTO in the second scenario. In Scenario 2 the stress is applied on the planes perpendicular to the [001] direction while the polarization vector lies in the [100] direction. As a result there was no change in dynamics for the case of compressive stress but significant differences from Scenario 1 occur for the case of tensile stress.

The difference between the two scenarios occurs once the temperature had been reduced to below $T_C$. In Scenario 1 only two modes are present at all temperatures below $T_C$ but in Scenario 2 a third mode appears at temperatures well below the transition as shown in Fig. 5.10. This mode occurs because stress is applied at a sufficiently low temperature to not allow reorientation of the polarization vector along a preferred direction and instead falls into a metastable state with different symmetry.
Figure 5.10: Comparison of Scenario 1 (red) and Scenario 2 (green) for PTO under 2.0 GPa of tensile uniaxial stress. Dashed line indicates $T_C$ and black line indicates the temperature where the deviation between the two scenarios occurs. At this point the PTO does not have enough thermal energy to reorient the polarization vector.
The polarization vector lies in the [100] direction after equilibration and as tensile stress is applied normal to the {001} planes the local dipole is effectively squeezed. This unfavorable configuration of the local dipole disrupts the ionic dynamics and allows a metastable state to occur. The result is a change in symmetry from the $P_{4mm}$ phase that occurs from tensile uniaxial stress into the $P_{mm2}$ phase which results from the application of compressive uniaxial stress. The change in symmetry alters the dynamics abruptly as seen in Fig. 5.10.

This metastable state is the result of the free energy profile at the lack of thermal energy available to the lattice at temperatures below 475 K. In this configuration the energy barrier to allow PTO to reorient the polarization from the [100] direction to the preferential [001] direction is sufficiently large to force it to remain in the initial orientation. Mapping the total free energy surface is difficult and requires an extensive amount of calculations however it is possible to determine the amount of thermal energy necessary to overcome the barrier and reorient the polarization vector. We find from our calculations for the case of 2.0 GPa of tensile stress that this free energy barrier is on the order of 30 to 40 meV which requires heating to approximately 430 K in order to find the minima.

This is a very intriguing observation as it provides a unique avenue to device application. For instance one could envision the application of uniaxial stress that could instantly change the operating frequency of a nanoscale ferroelectric.

5.6 Biaxial Strain

Biaxial strain often results from epitaxial growth due to the lattice mismatch with a substrate. These types of strains occur most commonly in ferroelectric thin films and super-lattices and can reach rather large values ($\sim 7\%$) [115]. As mentioned before these strains result in residual stresses and can stabilize a number of different phases and dipole patterns [115,116]. Despite the importance of biaxial strain very few studies exist on its effect on the soft mode dynamics [97,117,118].

To model the effects of epitaxial strain that results from a lattice mismatch between the
Figure 5.11: (a) soft mode frequencies as a function of temperature for -2.5% (red) of biaxial strain and unstrained PTO (blue). (b) soft mode frequencies as a function of temperature for +1.5% (green) of biaxial strain and unstrained PTO (blue). The gaps in the curves are a result of the structural transition around $T_C$ where the autocorrelation functions do not decay and the Fourier transform provides no useful information. (c) Change in $T_C$ as a function of applied biaxial strain. The area denoted in grey is an additional monoclinic phase that cannot be completely characterized as it appears only at very low temperature. [105]

substrate and a thin film we freeze the $\eta_{1}^{loc}$, $\eta_{2}^{loc}$ and $\eta_{6}^{loc}$ components of the local strain tensor. We set $\eta_{1}^{loc} = \eta_{2}^{loc} = \eta_{mis}$ where the mismatch strain is defined as $\eta_{mis} = \frac{a_{sub}-a}{a}$. The variables $a$ and $a_{sub}$ are defined as the lattice constant of PTO and a cubic substrate, respectively, for a given temperature [105]. The mismatch strain ranges from -2.5% compressive strain to 1.5% tensile strain which covers most of the experimentally realizable conditions [115]. The symmetry changes under biaxial strain are very similar to those found under the application of stress. Namely we find the $P_{4/mmm}$ paraelectric tetragonal phase above $T_C$ and the $P_{4mm}$ tetragonal ferroelectric phase below $T_C$ for values of $\eta_{mis} < 1%$. For values above 1% however, the tetragonal paraelectric phase transitions into a ferroelectric orthorhombic $A_{mm2}$ phase as shown in Fig. 5.11(c). This phase is different from the other orthorhombic phases seen under the application of uniaxial and biaxial stresses because the polarization vector lies in the [110] direction instead of along one of the principle crystallographic directions. The $A_{mm2}$ phase persists except for a small region at low temperature near 1% mismatch strain where a monoclinic phase appears which is shown in grey in Fig. 5.11(c). These findings are in agreement, at least qualitatively, with phenomenologically determined results [119].
We notice from Fig. 5.11 that there are similar increases in the value of $T_C$ with increasing amounts mismatch strain as was seen for biaxial strain. This is not surprising as biaxial strain can be generalized to very large biaxial stresses through the stress-strain coupling of Eq. (5.2).

The data for the dependence of the soft mode on the internal strain are given for a few temperatures in Fig. 5.12. Internal strain is defined in this case as the strain that results from the deformation of the lattice due to the combined effect of epitaxy and the structural changes associated with ferroelectricity. For the $P_{4mm}$ and $P_{4/mmm}$ phases the internal strain $\eta = \eta_{mis}$. However, for the $A_{mm2}$ phase this relationship is invalid [105]. As the $A_{mm2}$ phase does not exist in the absence of mismatch strain $\eta$ cannot be calculated by any standard approach as the equilibrium lattice constant is undefined. The internal strain must therefore be estimated indirectly. One practical approach to estimate the internal strain is to use the fact that the $B_1$ and $B_2$ modes cross at the point where the strain caused by epitaxy is equal to the strain caused by the piezoelectric deformation or $\eta = 0$. To validate this approach however we can use another method based on identifying a hypothetical equilibrium lattice constant $c$ for the $A_{mm2}$ phase. Near the $P_{4mm}$ to $A_{mm2}$ transition we assume the strain...
associated with each phase are equal. We define $\eta_{A_{mm2}} = \frac{a_{sub} - c}{c}$ and calculate $\eta_{P_{4mm}} = \frac{a_{sub} - a}{a}$.

We assume that $\eta_{A_{mm2}}$ is negative (compressive strain) and $\eta_{P_{4mm}}$ is positive (tensile strain) at least in the vicinity of the $P_{4mm}$ to $A_{mm2}$ transition. This means that $\eta_{P_{4mm}} = -\eta_{A_{mm2}}$ at the critical value of $\eta_{mis}$ where the transition occurs and allows for the calculation of $c$ and therefore the value of $\eta$ associated with the $A_{mm2}$ phase [105]. The values of strain found by these two methods are nearly identical however the data is only reported for the first method.

One of the most interesting features of Fig. 5.12 is that in the $P_{4mm}$ phase both of the modes soften with increasing amounts of tensile strain indicating that a measured downshift in mode frequency found in epitaxial films is the result of tensile strains and stresses. This suggests that Eq. (5.1), which indicates a downshift results from compressive loads, fails to predict the soft mode dynamics in epitaxial films [105]. This is a striking issue since a downshift in mode frequency observed experimentally was attributed to compressive residual stresses [114]. However, another study reported a similar downshift in the soft mode frequencies in epitaxial films under tensile stress which agrees very well with our findings [107]. The authors of Ref. [107] found that a residual tensile stress of $1.02 \pm 0.15$ GPa downshifts the frequency of the $E$ mode by $11.4$ cm$^{-1}$ and in excellent agreement Eq. (5.6) predicts the same change at $1.1$ GPa of tensile stress. In the paraelectric phase we observe similar mode behavior to the application of stress.

Inspection of Fig. 5.12 suggests that like the other mechanical boundary conditions tested in this study the application of epitaxial strain affects the soft mode frequencies with a Curie-Weiss behavior. This elucidates a Curie-Weiss strain law that has a similar form to Eqs. (5.1),(5.5) and (5.6)

$$\nu^2 = A_\eta (\eta - \eta_0), \quad (5.7)$$

where the values of $A_\eta$ is the Curie-Weiss strain constant and $\eta_0$ is the strain at which the soft mode frequency extrapolates to zero. This equation could also be elucidated from Eq. (5.6)
Figure 5.13: The temperature dependence of the Curie-Weiss strain constant. The error bars indicate the linear fitting error with respect to Eq. (5.7). The dashed vertical line indicates the Curie point for unstrained PTO. [105]

We also investigated the temperature evolution of the Curie-Weiss strain constants which are given in Fig. 5.13. In the $P_{4mm}$ phase the value of $A_\eta$ is negative for both the $A_1$ and $E$ modes suggesting mode softening for all temperatures [105]. The Curie-Weiss constant for the $E$ mode is seen to be nearly temperature independent which is most likely a result of the local stretching/compression along the same directions as those vibrations. In the $A_{mm2}$ phase all of the Curie-Weiss strain constants are positive indicating mode hardening at all temperatures. The sensitivity of both the $B_1$ and $B_2$ modes are nearly temperature independent as well. From Fig. 5.13 it appears that the $B_1$ mode is least sensitive to strain which agrees with the findings for uniaxial and biaxial stresses. The modes in the paraelectric phase appear to be nearly temperature independent as well indicating that the trends discussed earlier are valid for all temperatures.
5.7 Soft Mode Dynamics Under Pressure and Stress from Analytical Model

To better understand the response of the soft mode to pressure and stress found from our computational model we develop an analytical model based on the effective Hamiltonian. This model provides a way to predict the soft mode frequencies as a function of hydrostatic pressure, uniaxial stress and biaxial stress at 0 K. We begin by writing the zone center effective Hamiltonian [50]

\[ E = \kappa u^2 + \alpha u^4 + \gamma (u_x^2 u_y^2 + u_y^2 u_z^2 + u_z^2 u_x^2) + \frac{1}{2} \sum_{k\alpha\beta} B_{k\alpha\beta} \eta_k u_{\alpha} u_{\beta} + \frac{1}{2} \sum_{kj} B_{kj} \eta_k \eta_j + \sum_k \sigma_k \eta_k. \] (5.8)

Here \( u_x, u_y \) and \( u_z \) are the Cartesian components of the local mode vector and the subscripts \( \alpha \) and \( \beta \) are the Cartesian coordinates of the local mode. The strain \( \eta \) and stress \( \sigma \) tensors are written in the Voigt notation. The last term, the coupling to external stress, has a positive sign as we have adopted the convention that positive values indicate a compressive load where negative values indicate tensile loads. For easy manipulation Eq. (5.8) can be rewritten in matrix form following the notation of [50]

\[ E = \Phi(u) + \frac{1}{2} \eta^T C \eta + \frac{1}{2} \eta^T B \eta + \eta^T \sigma = \Phi(u) + \frac{1}{2} \eta^T (C \eta + B \eta + 2 \sigma), \] (5.9)

where \( \Phi(u) \) is local mode self energy containing the first three terms of Eq. (5.8) that depend only on powers of \( u_i \). The vectors \( \eta \), \( \sigma \) in Eq. (5.9) have components \( (u_x^2, u_y^2, u_z^2, u_y u_x, u_z u_x, u_x u_y), (\eta_1, \eta_2, \eta_3, \eta_4, \eta_5, \eta_6) \) and \( (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6) \), respectively. \( C \) and \( B \) are both symmetric 6\times6 matrices of the form [50]
\[ M = \begin{pmatrix} p & q & q & 0 & 0 & 0 \\ q & p & q & 0 & 0 & 0 \\ q & q & p & 0 & 0 & 0 \\ 0 & 0 & 0 & r & 0 & 0 \\ 0 & 0 & 0 & 0 & r & 0 \\ 0 & 0 & 0 & 0 & 0 & r \end{pmatrix}. \] (5.10)

The \( B \) matrix corresponds to elastic stiffness so that \( p = B_{11}, q = B_{12}, \) and \( r = B_{44}, \) while \( C \) matrix corresponds to the strain-local mode coupling with \( p = B_{1xx}, q = B_{1yy}, \) and \( r = 2B_{yz}. \)

Following the procedure of Ref. [50] we find the strain vector \( \tilde{\eta} \) that minimizes \( E \) by differentiation of Eq. (5.9) with respect to \( \eta \) and solving the resulting matrix equation

\[
\frac{1}{2} C_y + B \tilde{\eta} + \sigma = 0.
\] (5.11)

The solution of Eq. (5.11) is

\[
\tilde{\eta} = -\frac{1}{2} B^{-1}(C_y + 2\sigma). \] (5.12)

The minimum energy, \( \tilde{E} \), can now be found by substituting \( \tilde{\eta} \) back into in Eq. (5.9) and simplifying

\[
\tilde{E} = \Phi(u) - \frac{1}{8}(C_y + 2\sigma)^T[B^{-1}]^T(C_y + 2\sigma). \] (5.13)

Since \( B \) is a symmetric matrix its inverse \([B^{-1}]\) is also symmetric. Taking advantage of this fact and distributing terms in Eq. (5.13) we obtain the expression for the renormalized energy

\[
\tilde{E} = \Phi(u) - \frac{1}{8}(C_y)^T[B^{-1}](C_y) - \frac{1}{2}\sigma^T[B^{-1}](C_y) - \frac{1}{2}\sigma^T[B^{-1}]\sigma. \] (5.14)

Inspection of the terms in Eq. (5.14) shows that the second term depends only on the local mode and was shown in Ref. [50] to renormalize the values of \( \alpha \) and \( \gamma \) in \( \Phi(u) \). These
renormalized coefficients are denoted as $\alpha'$ and $\gamma'$ and are defined using Eqs. (4.5) and (4.6). The third term in Eq. (5.14) is the coupling between the local mode and stress tensor and will further renormalize $\Phi(u)$. The final term in Eq. (5.14) is a constant and will only shift the energy.

Since the third term couples $\mathbf{B}$ and $\mathbf{\sigma}$ we will focus on it. Using the procedure laid out by King-Smith et al. in Ref. [50] the matrix in Eq. (5.10) can be written as

$$
\mathbf{M} = \mathbf{Z}\Lambda(\mathbf{M})\mathbf{Z}^\dagger, \tag{5.15}
$$

where $\Lambda(\mathbf{M})$ and $\mathbf{Z}$ are the matrices of eigenvalues and eigenvectors of $\mathbf{M}$, respectively. The eigenvalues of $\Lambda(\mathbf{M})$ are $p + 2q$ (1), $p - q$ (2), and $r$ (3), where the number in parenthesis indicates the degeneracy [50].

By using Eq. (5.15) to rewrite the third term of Eq. (5.14) you obtain

$$
-\frac{1}{2}\mathbf{\sigma}^T\mathbf{B}^{-1}(\mathbf{C}y) = -\frac{1}{2}\mathbf{\sigma}^T[\mathbf{Z}\Lambda^{-1}(\mathbf{B})\mathbf{Z}^\dagger\mathbf{Z}\Lambda(\mathbf{C})\mathbf{Z}^\dagger]y. \tag{5.16}
$$

Using the fact that for symmetric matrices $\mathbf{Z}^\dagger\mathbf{Z} = \mathbf{I}$ we obtain another matrix of the form in Eq. (5.10) within the brackets with a diagonal matrix of eigenvalues $\Lambda^{-1}(\mathbf{B})\Lambda(\mathbf{C})$ [105]. These eigenvalues are $\frac{B_{1xx} + 2B_{1yy}}{B_{11} + 2B_{12}}$ (1), $\frac{B_{1xx} - B_{1yy}}{B_{11} - B_{12}}$ (2), and $\frac{2B_{2yy}}{B_{44}}$ (3) or using the notation of King-Smith et al. [50] $\frac{C}{B}$ (1), $\frac{\nu}{\mu_t}$ (2), and $2\frac{\nu_r}{\mu_r}$ (3), respectively. In this notation $B$ is the bulk modulus, $\mu_t$ and $\mu_r$ are the shear moduli for tetragonal distortions and rhombohedral distortions, respectively [50]. The values of $C$, $\nu_t$ and $\nu_r$ are analogously defined quantities obtained from the strain-local mode coupling constants [50]. The values of these variables
are given by

\[ B = B_{11} + 2B_{12}, \]  \hspace{1cm} (5.17a)

\[ \mu_t = \frac{1}{2} (B_{11} - B_{12}), \]  \hspace{1cm} (5.17b)

\[ \mu_r = B_{44}, \]  \hspace{1cm} (5.17c)

\[ C = B_{1xx} + 2B_{1yy}, \]  \hspace{1cm} (5.17d)

\[ \nu_t = \frac{1}{2} (B_{1xx} - B_{1yy}), \]  \hspace{1cm} (5.17e)

\[ \nu_r = B_{4yz}. \]  \hspace{1cm} (5.17f)

Using these eigenvalues we obtain the \( p, q \) and \( r \) values of \( \Lambda^{-1}(B)\Lambda(C) \). They are

\[ p = \frac{1}{3} \left( \frac{C}{B} + \frac{2\nu_t}{\mu_t} \right), \]  \hspace{1cm} (5.18a)

\[ q = \frac{1}{3} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right), \]  \hspace{1cm} (5.18b)

\[ r = \frac{2\nu_r}{\mu_r}. \]  \hspace{1cm} (5.18c)

We now substitute Eq. (5.16) into Eq. (5.14) and multiply the matrices resulting in

\[ \tilde{E} = \kappa'_x u_x^2 + \kappa'_y u_y^2 + \kappa'_z u_z^2 + \kappa'_{yz} u_y u_z + \kappa'_{xz} u_x u_z + \kappa'_{xy} u_x u_y + \alpha' u^4 + \gamma' (u_x^2 u_y^2 + u_y^2 u_z^2 + u_z^2 u_x^2), \]  \hspace{1cm} (5.19)
where,

\[ \kappa'_x = \kappa - \frac{1}{6} \left[ \frac{C}{B} (\sigma_1 + \sigma_2 + \sigma_3) + \frac{\nu_t}{\mu_t} (2\sigma_1 - \sigma_2 - \sigma_3) \right], \tag{5.20a} \]

\[ \kappa'_y = \kappa - \frac{1}{6} \left[ \frac{C}{B} (\sigma_1 + \sigma_2 + \sigma_3) + \frac{\nu_t}{\mu_t} (2\sigma_2 - \sigma_1 - \sigma_3) \right], \tag{5.20b} \]

\[ \kappa'_z = \kappa - \frac{1}{6} \left[ \frac{C'}{B} (\sigma_1 + \sigma_2 + \sigma_3) + \frac{\nu_t}{\mu_t} (2\sigma_3 - \sigma_1 - \sigma_2) \right], \tag{5.20c} \]

\[ \kappa'_{yz} = 2\sigma_4 \frac{\nu_t}{\mu_t}, \tag{5.20d} \]

\[ \kappa'_{zx} = 2\sigma_5 \frac{\nu_t}{\mu_t}, \tag{5.20e} \]

\[ \kappa'_{xy} = 2\sigma_6 \frac{\nu_t}{\mu_t}, \tag{5.20f} \]

and \( \alpha' \) and \( \gamma' \) are defined by Eqs. (4.5) and (4.6).

To determine the effect of stress on the soft mode dynamics we use a Taylor series expansion of the energy in Eq. (5.19) about \( u_0 \) which is the local mode associated with the energy minimum. We start by finding \( u_0 \) for the case of a tetragonal phase. First we set \( u_x = u_y = 0 \) and minimize Eq. (5.19) with respect to \( u_z \) to obtain

\[ \frac{d\tilde{E}}{du_z} = \kappa'_z u_z^2 + \alpha' u_z^4 = 0. \tag{5.21} \]

Therefore,

\[ u_{z,0} = \pm \sqrt{-\frac{\kappa'_z}{2\alpha'}}, \tag{5.22} \]

where the subscript on \( \kappa' \) can be changed to reflect the direction of polarization if necessary. We now take the series expansion of Eq. (5.19) to harmonic order around the local mode.
\[ \tilde{E}^{\text{harm}} = \tilde{E}(u_0) \]
\[ + \frac{\partial}{\partial u_x} \tilde{E}(u_0)(u_x - u_{0x}) + \frac{\partial}{\partial u_y} \tilde{E}(u_0)(u_y - u_{0y}) + \frac{\partial}{\partial u_z} \tilde{E}(u_0)(u_z - u_{0z}) \]
\[ + \frac{1}{2} \left( \frac{\partial^2}{\partial u_x^2} \tilde{E}(u_0)(u_x - u_{0x})^2 + \frac{\partial^2}{\partial u_y^2} \tilde{E}(u_0)(u_y - u_{0y})^2 + \frac{\partial^2}{\partial u_z^2} \tilde{E}(u_0)(u_z - u_{0z})^2 \right) \]
\[ + \frac{\partial^2}{\partial u_x \partial u_y} \tilde{E}(u_0)(u_x - u_{0x})(u_y - u_{0y}) + \frac{\partial^2}{\partial u_y \partial u_z} \tilde{E}(u_0)(u_y - u_{0y})(u_z - u_{0z}) \]
\[ + \frac{\partial^2}{\partial u_z \partial u_x} \tilde{E}(u_0)(u_z - u_{0z})(u_x - u_{0x}) \].

Using the definition of \( u_0 \) from Eq. (5.22) and the harmonic order energy expansion in Eq. (5.23) we can now solve the dynamical equation for the zone center soft mode [105]

\[ m\ddot{v} = -\nabla \tilde{E}^{\text{harm}}, \] (5.24)

where \( v \) is the displacement of the local mode from its equilibrium position so that \( v = u - u_0 \) and \( m \) is the effective mass of the local mode. In this case \( \tilde{E}^{\text{harm}} \) is written in powers of \( v \). The solution of the differential equation in Eq. (5.24) is \( v = A_v e^{i\omega t} \) and by solving this equation we obtain the characteristic frequencies of the soft mode in the presence of stress.

### 5.7.1 The Case of Hydrostatic Pressure

Hydrostatic pressure is a specific case of applied stress where \( \sigma_1 = \sigma_2 = \sigma_3 = P \) and \( \sigma_4 = \sigma_5 = \sigma_6 = 0 \) in Eqs. (5.19)- (5.20f) and Eq. (5.24). Inputting these \( \sigma_i \) values into Eqs. (5.20a) - (5.20f) we obtain

\[ \kappa'_x = \kappa'_y = \kappa'_z = \kappa - \frac{1}{2} \frac{C}{B} P; \] (5.25a)
\[ \kappa'_{yz} = \kappa'_{zx} = \kappa'_{xy} = 0. \] (5.25b)
We can then simplify Eq. (5.23) to

\[ \tilde{E}^{\text{harm}} = \kappa' u_{0z}^2 + \alpha' u_{0z}^4 + (2\kappa' u_{0z} + 4\alpha' u_{0z}^3) v_z + (\kappa' + 6\alpha' u_{0z}^2) v_z^2 \]  

(5.26)

where \( u_{0z} \) is given by Eq. (5.22) and assuming the polarization vector lies in the [001] direction. From Eq. (5.26) we can extract the following eigenvalues for the dynamical matrix

\[ \omega_{A_1}^2 = -\frac{4}{m} \left( \kappa - \frac{1}{2} C P \right) \]  

(5.27a)

\[ \omega_{E}^2 = -\frac{4}{m} \frac{\gamma'}{\alpha} \left( \kappa - \frac{1}{2} C P \right) \]  

(5.27b)

for the eigenvectors \( \left( \begin{array}{c} 0 \\ 0 \\ 1 \end{array} \right) \), \( \left( \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right) \) and \( \left( \begin{array}{c} 0 \\ 1 \\ 0 \end{array} \right) \), respectively. It is convenient to write Eqs. (5.27a) and (5.27b) in terms of the 0 Kelvin mode frequencies under zero pressure so that

\[ \omega_{A_1}^2 = \omega_{A_1,0}^2 + \frac{2}{m B} C P \]  

(5.28a)

\[ \omega_{E}^2 = \omega_{E,0}^2 + \frac{2}{m \alpha B} \gamma' C P \]  

(5.28b)

where \( \omega_{A_1,0}^2 = -\frac{4}{m} \kappa \) and \( \omega_{E,0}^2 = -\frac{4}{m \alpha} \gamma' \kappa \) are the soft mode frequencies at \( P = 0 \). Equations (5.28a) and (5.28b) give the Curie-Weiss pressure law in Eq. (5.1) and indicate that it originates from the stress-strain coupling. Another consequence of Eqs. (5.28a) and (5.28b) is that the Curie-Weiss pressure constants at 0 K can be extracted directly from them giving \( A_{P,A_1} = \frac{2}{m B} C \) and \( A_{P,E} = \frac{2}{m \alpha B} \gamma' C \) for the \( A_1 \) and \( E \) modes, respectively. In addition Eqs. (5.28a) and (5.28b) suggest a unique relationship between the Curie-Weiss constants and \( P = 0 \) mode frequencies

\[ \frac{A_{P,A_1}}{A_{P,E}} = \left( \frac{\omega_{A_1,0}}{\omega_{E,0}} \right)^2. \]  

(5.29)
5.7.2 The Case of Uniaxial Stress

For uniaxial stress we use $\sigma_3 = \sigma$ and set all other components of the stress tensor equal to zero. Inputting these values of $\sigma$ into Eqs. (5.20a) - (5.20f) we obtain,

$$\kappa'_z = \kappa - \frac{1}{6} \left( \frac{C}{B} + 2 \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.30a)$$

$$\kappa'_x = \kappa'_y = \kappa - \frac{1}{6} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.30b)$$

$$\kappa'_{yz} = \kappa'_{zx} = \kappa'_{xy} = 0. \quad (5.30c)$$

Using these values for $\kappa'$ we calculate the harmonic energy $\tilde{E}^{harm}$ as

$$\tilde{E}^{harm} = \kappa'_z u^2_{0z} + \alpha' u^4_{0z} + \left( 2 \kappa'_z u_{0z} + 4 \alpha' u^2_{0z} \right) v_z + \left( \kappa'_z + 6 \alpha' u^2_{0z} \right) v^2_z, \quad (5.31)$$

for $\sigma_3 < 0$ and

$$\tilde{E}^{harm} = \kappa'_x u^2_{0x} + \alpha' u^4_{0x} + \left( 2 \kappa'_x u_{0x} + 4 \alpha' u^2_{0x} \right) v_x + \left( \kappa'_x + 6 \alpha' u^2_{0x} \right) v^2_x, \quad (5.32)$$

for $\sigma_3 > 0$ assuming the polarization vector lies in the [001] and [100] directions, respectively. Solving the dynamical equation for Eqs. (5.31) and (5.32) we find the following eigenvalues for the $P_{4mm}$ phase

$$\omega^2_{A_1} = \omega^2_{A_1,0} + \frac{2}{3m} \left( \frac{C}{B} + 2 \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.33a)$$

$$\omega^2_E = \omega^2_{E,0} + \frac{1}{m} \left( \frac{\gamma'}{6\alpha'} \left( \frac{C}{B} + 2 \frac{\nu_t}{\mu_t} \right) + \frac{\nu_t}{\mu_t} \right) \sigma \quad (5.33b)$$

86
for eigenvectors \( \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \), \( \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \), respectively. For the \( P_{mm2} \) phase the frequencies are

\[
\begin{align*}
\omega_{A_1}^2 &= \omega_{A_1,0}^2 + \frac{2}{3m} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) \sigma; \\
\omega_{B_1}^2 &= \omega_{E,0}^2 + \frac{1}{m} \left( \frac{\gamma'}{6\alpha'} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) - \frac{\nu_t}{\mu_t} \right) \sigma; \\
\omega_{B_2}^2 &= \omega_{E,0}^2 + \frac{1}{m} \frac{\gamma'}{6\alpha'} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) \sigma
\end{align*}
\]

(5.34a) (5.34b) (5.34c)

for eigenvectors \( \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \), \( \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \), respectively. Again we recover the Curie-Weiss law under uniaxial stress from Eqs. (5.33a) and (5.33b) and Eqs. (5.34a)- (5.34c) with the Curie-Weiss stress constants equal to the coefficients in front of stress. As in the case of pressure the Curie-Weiss stress law originates from stress-strain coupling and electrostriction. From Eqs. (5.34b) and (5.34c) a relationship between the frequencies of the \( B_1 \) and \( B_2 \) modes can determined which indicates which of the two frequencies will be higher,

\[\omega_{B_2}^2 - \omega_{B_1}^2 = \frac{\nu_t}{m\mu_t} \sigma. \]

(5.35)

The value of \( \frac{\nu_t}{m\mu_t} \) is negative for PTO and therefore the \( B_1 \) mode is always higher than the \( B_2 \) mode. Equation (5.35) also indicates that the splitting between the \( B_1 \) and \( B_2 \) modes has a linear relationship with the applied stress

\[A_{\sigma,B_2}^{(u)} - A_{\sigma,B_1}^{(u)} = \frac{\nu_t}{m\mu_t} \sigma. \]

(5.36)

In PTO we find that \( A_{\sigma,B_1}^{(u)} \) is always greater than \( A_{\sigma,B_2}^{(u)} \) which follows from the fact that \( \frac{\nu_t}{m\mu_t} \) is negative for this material.
5.7.3 The Case of Biaxial Stress

In the case of biaxial stress we set \( \sigma_2 = \sigma_3 = \sigma \) and all other components of the stress tensor equal to zero. From Eqs. (5.20a) - (5.20f) we obtain

\[
\kappa'_y = \kappa'_z = \kappa - \frac{1}{3} \left( \frac{C}{B} + \frac{1}{2} \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.37a)
\]
\[
\kappa'_x = \kappa - \frac{1}{3} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.37b)
\]
\[
\kappa'_{yz} = \kappa'_{zx} = \kappa'_{xy} = 0. \quad (5.37c)
\]

Inputting these \( \kappa' \) values into Eq. (5.23) find

\[
\tilde{E}^{harm} = \kappa'_z u_{0x}^2 + \alpha' u_{0x}^4 + (2\kappa'_x u_{0x} + 4\alpha' u_{0x}^3) v_x + (\kappa'_x + 6\alpha' u_{0x}^2) v_x^2, \quad (5.38)
\]

for \( \sigma < 0 \) and

\[
\tilde{E}^{harm} = \kappa'_z u_{0z}^2 + \alpha' u_{0z}^4 + (2\kappa'_z u_{0z} + 4\alpha' u_{0z}^3) v_z + (\kappa'_z + 6\alpha' u_{0z}^2) v_z^2 \quad (5.39)
\]

for \( \sigma > 0 \) assuming polarization vector lies in the [100] and [001] directions, respectively.

Solving Eq. (5.24) for Eqs. (5.38) and (5.39) we find the soft mode frequencies for the \( P_{4mm} \) phase to be

\[
\omega_{A_1}^2 = \omega_{A_1,0}^2 + \frac{1}{3m} \left( \frac{C}{B} - \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.40a)
\]
\[
\omega^2 = \omega_{E,0}^2 + \frac{1}{m} \left( \frac{\gamma'}{6\alpha'} \left( \frac{C}{B} - 2 \frac{\nu_t}{\mu_t} \right) - \frac{\nu_t}{\mu_t} \right) \sigma; \quad (5.40b)
\]
for eigenvectors \((\frac{1}{0}, \frac{0}{1})\) and \((\frac{0}{0}, \frac{1}{0})\), respectively. For the \(P_{mm2}\) phase the eigenvalues of the dynamical matrix are

\[
\begin{align*}
\omega^2_{A_1} &= \omega^2_{A_1,0} + \frac{2}{3m} \left( \frac{2C}{B} + \frac{\nu_t}{\mu_t} \right) \sigma; \\
\omega^2_{B_1} &= \omega^2_{E,0} + \frac{1}{m} \left( \frac{\gamma'}{6\alpha'} \left( \frac{2C}{B} + \frac{\nu_t}{\mu_t} \right) + \frac{\nu_t}{\mu_t} \right) \sigma; \\
\omega^2_{B_2} &= \omega^2_{E,0} + \frac{1}{m} \frac{\gamma'}{6\alpha'} \left( \frac{2C}{B} + \frac{\nu_t}{\mu_t} \right) \sigma;
\end{align*}
\]

for eigenvectors \((\frac{1}{0}, \frac{0}{1})\) and \((\frac{0}{0}, \frac{1}{0})\), respectively. The Curie-Weiss stress law under biaxial stress given by Eqs. (5.40a), (5.40b) and (5.41a) - (5.41c) are strikingly similar to that of uniaxial stress despite the fact that resulting effects are different. The coefficients in front of \(\sigma\) appear quite different however, the relationship between the \(B_1\) and \(B_2\) modes under biaxial stress can also be characterized by Eq. (5.35). We also find that the Curie-Weiss stress constants for the \(B_1\) and \(B_2\) modes exhibit the same relationship, Eq. (5.36), under uniaxial and biaxial stress and that \(A^{(b)}_{\sigma,B_2} - A^{(b)}_{\sigma,B_1}\) is constant regardless of the type of stress applied. This is found to be true for the entire temperature range tested indicating that the \(B_1\) mode is generally more sensitive to stress than the \(B_2\) mode.

A careful comparison of the Curie-Weiss laws for pressure and stress given above indicates that the response of the soft mode to the hydrostatic pressure is fundamentally different than the response to stresses and therefore will fail to give stress estimates in ferroelectric nanostructures. By comparing these laws other useful information may be gleaned and can provide a basis for deriving relations between the Curie-Weiss constants within them. For instance the mode in the \(P_{4mm}\) phase we find that \(A_{P,A_1} = 4A^{(b)}_{\sigma,A_1} + A^{(u)}_{\sigma,A_1}\).

Equations (5.28a), (5.28b), (5.33a) - (5.34c) and (5.40a) - (5.41c) allow us to establish the mechanism responsible for the Curie-Weiss pressure and stress laws [105]. Firstly, stresses and pressure result in an additional force on the soft mode instead of renormalizing the existing forces like those due to the long-range and short-range interactions. Secondly, we observe that the additional force can either stabilize or destabilize the soft mode depending
on the sign of the Curie-Weiss constant and the sign of the stress or pressure. Lastly, this additional force originates from electrostriction as it is proportional to the strain-local mode couplings $B_{\alpha\beta}$.

5.8 Conclusions

In summary we have systematically studied the effects of a wide range of mechanical boundary conditions on the soft mode dynamics of PTO using both computational and analytical approaches. Our findings suggest that 1) the response of PTO to hydrostatic pressure is very different from the response to stresses and strains 2) the commonly used Curie-Weiss pressure law fails to predict the effects of other mechanical boundary conditions and as such should not be used to do so, 3) Curie-Weiss laws have been shown to exist for uniaxial stress, biaxial stress and biaxial strain in the variety of phases that can be stabilized in PTO and 4) the Curie-Weiss constants associated with these laws show nontrivial temperature evolution.

Another critical conclusion of this study is that the response of the ferroelectric soft mode can be heavily dependent on temperature and mechanical boundary conditions. Therefore, the use of materials like PTO in practical applications must be done carefully. Pressures, stresses and strains are often unavoidable in ferroelectric nanostructures so careful consideration must be taken when a device is designed to minimize the detrimental effects of those mechanical forces can be minimized. The converse is also true insomuch that with carefully inducing pressure, stress and/or strain the dynamics of a nanoscale ferroelectric could be enhanced well beyond its normal behavior and even leaves an avenue for tuning the dynamical properties of perovskite ferroelectrics.
6 Mechanisms for Polarization Reversal in Ferroelectric Nanowires

The advances in nanoscale fabrication of perovskite materials in recent decades have opened the door to investigating a multitude of new ferroelectric structures [27]. When the dimensions of a ferroelectric are decreased there are marked changes to the electrical, optical and ferroelectric properties such as decreases in the electric permittivity and phase transition temperature [27]. One-dimensional (1D) ferroelectric nanostructures have garnered a lot of attention in the last few years due to the expectation of their use in miniaturized devices [27]. One such type of structure, nanowires, have been fabricated from a large number of ferroelectric perovskites including BTO [120], PTO [121,122] and PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) [123,124]. The size of these experimentally synthesized nanowires range in diameter from 30-100 nm [27,121,124].

One promising application of ferroelectric nanostructures is in high-density computer memories. Of significant interest is the use of arrays of ferroelectric nanowires [27] where each logical bit of information would be stored in the polarization state of an individual nanowire. The polarization in ferroelectric nanowires can be restricted to the axial direction [3,125–130]. making differentiating bits of information relatively straightforward. Interest in this type of device is predicated by knowledge of how polarization reversal (PR) occurs in such nanowires. Reading and writing information into a polarization state requires switching a given nanowire’s polarization with the application of an external electric field. Understanding the PR dynamics of ferroelectric nanowires is critical to reveal the fundamental limits in the
performance of a memory of this type and any other potential application that utilizes PR in some way.

The dynamics of PR in ferroelectrics has been studied since the 1950’s, however these studies mostly focused on bulk and thin films [23, 131–138]. A seminal work by Merz in 1954 showed that PR in BTO single crystals occurs in three steps. The reversal begins with nucleation of a domain at a defect site, impurity or surface and then grows toward another such nucleation site resulting in a needle-like domain structure. This needle then spreads laterally and merges with other needle-like domains until the whole sample has completely reversed its polarization [23, 139]. This three step process has been widely accepted as the mechanism for PR in both bulk and thin films. Merz also empirically derived a relationship between the switching time $t_{sw}$ and the applied electric field $E$ [23]

$$t_{sw} \approx \frac{\beta d}{E - E''},$$

(6.1)

where $\beta$ is a constant, $d$ is the material thickness and $E''$ is the activation field [23]. Equation (6.1) has been termed Merz’s Law and is often used to interpret experimental results [131, 134, 135, 139].

There is another mechanism for PR that involves complete and uniform reversal that has been shown to exist both theoretically and experimentally in thin film samples [134–137, 139]. This type of PR is termed homogeneous PR because no ferroelectric domains are formed in the process [139]. Homogeneous PR only occurs, however, when the magnitude of the applied electric field is very large compared to the required field to induce domain switching [139].

The PR dynamics in ferroelectric thin and ultra-thin films have seen a lot of interest in recent years, thanks to improvements in film growth techniques, increased accuracy of characterization methods and the ability to apply much larger electric fields. The practical applications of ferroelectric thin films as well as the relatively low occurrence of defects at the nanoscale have also fueled interest and uncovered new understanding of PR and domain
wall dynamics. For instance, a recent study on Pb(Zr_{0.2}Ti_{0.8})O_3 thin films reported that the motion of domain walls is a creep process controlled by disorder and that the energy necessary to initiate the creep increases significantly with film thickness [140]. Another report on PZT epitaxial films showed that domain wall velocity is a nonlinear function of the applied electric field and follows three different regimes corresponding to creep, pinning-depinning and flow mechanisms [133]. Using aberration-corrected transmission electron microscopy the authors of Ref. [138] were able to directly witness domain nucleation and pinning of domain walls at defect sites within an epitaxial bilayer of ferroelectric BiFeO_3.

Despite the recent interest in PR dynamics in thin films there has been very little work done in the area of ferroelectric nanowires. The polarization in ferroelectric nanowires can be confined to the axial direction [27]. The confinement of the polarization vector to one direction and small size of ferroelectric nanowires makes them prime candidates for applications in computer memory or nanosensors. The ability to design and utilize such devices does, however, rely heavily on understanding the intrinsic polarization dynamics in nanowires, or even more generally at the nanoscale.

6.1 Computational Method

In order to study the PR dynamics of ferroelectric nanowires we use classical MD simulations with the force field derived from the effective Hamiltonian [141–143] discussed earlier. Our calculations focused on nanowires made of Pb(Zr_{0.4}Ti_{0.6})O_3 ferroelectric alloy that were defect free and had average diameters of 3.2 to 8 nm. This size range was chosen for two reasons. First, this size range keeps the computational cost of simulations low. Second, nanowires of this size would be the ideal choice for use in ferroelectric memories as they would provide significantly large bit storage density. We choose the [100], [010], and [001] crystallographic directions as the x, y and z directions, respectively, as shown in the schematic diagram in Fig. 6.1. We simulated axial growth along the [001] direction and applied periodic boundary conditions along the same direction in order to simulate infinitely long wires. The
Figure 6.1: Schematic diagram of the PZT nanowires simulated in this study. The directions of the crystallographic directions are indicated and the separation of the lateral dimensions into shells is shown. The direction of polarization $\mathbf{P}$ is also shown.

The nanowires were subject to realistic screening of the surface charge by 10% to simulate open circuit boundary conditions according to the technique of Ref. [143].

To bring the nanowires into equilibrium we conduct simulated annealing from $T=2010$ K to $T=10$ K in steps of $\Delta T=10$ K. Each temperature step in this annealing treatment was performed in the NPT ensemble using the Evans-Hoover thermostat and a barostat mimicked via a $PV$ term in the effective Hamiltonian [51, 68]. This treatment allows the entire energy surface to be explored at high temperature and as the temperature is reduced allows the system to fall into its most energetically favorable state. The nanowires polarized homogeneously along the axial direction under open-circuit boundary conditions which is consistent with other theoretical [126, 144, 145] and experimental [146–148] investigations of nanowires at temperatures well below $T_C$.

In order to induce PR in the nanowires we apply a $dc$ electric field opposite the direction of polarization with strengths ranging from 0.5 to 8 MV/cm. These field strengths are comparable to those used in experimental studies on thin film samples [133, 134, 149].
6.2 Results and Discussion

We find that over the range of electric fields considered there are two different mechanisms for PR within ferroelectric nanowires. At lower fields the PR is dominated by the formation of a coaxial domain originating at the surface of the wire where the energy barrier for reversal is smaller [150] and moving inwards. At higher fields we find that while the PR begins at the surface almost every dipole switches its direction simultaneously.

To quantitatively describe the dynamics of the PR we divide the nanowire into fictitious shells that are a single unit cell thick as shown in Fig. 6.1. As the PR process progresses we count the number of dipoles in each shell that have reversed their polarization direction and as a result we are able to trace the motion of domains through the nanowire. Figure 6.2a) shows the normalized number of flipped dipoles in a 7.2 x 7.2 nm cross-section nanowire under an electric field of $E = 2.8$ MV/cm. At the beginning of the simulation all dipoles have the same initial direction but as time progresses the dipoles in each shell begin to reverse. The PR occurs in a shell by shell basis and suggests that PR at this lower field strength occurs though the formation of a cylindrical coaxial domain at the surface of the wire that propagates inward toward the center of the wire. Figure 6.3 shows snapshots of the plane averaged polarization as viewed along the axial direction. In this schematic the propagation of the coaxial domain wall is seen to move through the nanowire. At larger fields, as shown in Fig. 6.2b), the data for individual shells becomes very difficult to resolve other than for the outermost shell. This indicates that the shells are switching almost simultaneously which suggests that the applied field is sufficiently strong to induce homogeneous PR. The difference between Fig. 6.2a) and Fig. 6.2b) seems to suggest that depending on the strength of the applied electric field there are two competing PR mechanisms at work in the nanowire. Domain-driven PR occurs at lower electric fields and is associated with the formation and propagation of coaxial domains. Under higher electric fields polarization reverses its direction homogeneously and without the formation of domains.

To identify the ranges of electric fields that are associated with the two mechanisms for
Figure 6.2: The normalized number of dipoles in the “up” state, \( N_{up} \), for two different field strengths. Dashed lines indicate counts for individual shells and solid black lines indicate counts for the entire wire. Within the domain-driven region (panel a) individual shells switch independently indicating the progress of a domain wall. For larger field strengths within the homogeneous PR regime (panel b) all shells but the outermost switch at almost the same instant indicating that there is no domain propagation.

Figure 6.3: Plane averaged cross sections of 18x18 unit cell nanowire showing domain-driven PR from initially “down” polarized state (blue) to the “up” polarized state (red). The cylindrical domain wall nucleates at the corners of the wire and propagates inward nearly symmetrically so that each shell of dipoles switch independently.
Figure 6.4: Radial and axial switching speeds as a function of applied electric field. The dashed lines where separation of regions with different PR mechanisms: domain-driven (DD), homogeneous (H) and competition (C).

PR we calculated the radial switching speed, \( v_r \), and the axial switching speed, \( v_a \). The radial switching speed was computed using the relation \( v_r = r/t_r \) where \( r \) is the distance from the outermost to the innermost shell and \( t_r \) is the time taken for the domain wall to propagate between them. The axial switching speed is defined as \( v_a = L/t_a \) where \( L \) is the length of the simulation supercell in the axial direction and \( t_a \) is the average time for PR to occur along a shell. Figure 6.4 shows how the speed in each direction depends on the electric field. There are three regions within the range of electric field strengths. Below 3.1 MV/cm we find \( v_a > v_r \) which indicates a faster propagation along the wire axis then radially toward the center. This accounts for the radial domain driven PR mentioned earlier. For fields 3.9 MV/cm and larger \( v_a < v_r \) which indicates homogeneous PR. Interestingly, the electric fields between 3.1 MV/cm and 3.9 MV/cm the two speeds are equal indicating that the two PR mechanisms are competing with each other.

In order to understand the underlying physics of the two PR mechanisms we begin with
a discussion of homogeneous switching from the point of view of free energy. At 0 K and in the absence of an electric field the Gibbs free energy is characterized by two equally likely and symmetric minima. This profile, shown in Fig. 6.5, is obtained directly from the effective Hamiltonian. The density of polarization states $p$ is given by

$$\rho(p) = A e^{-\frac{\mathcal{E}(p)}{k_B T}}. \quad (6.2)$$

Here $A$ is a normalization factor, $\mathcal{E}(p)$ is the internal energy directly calculated from the effective Hamiltonian, $k_B$ and $T$ are the Boltzmann constant and the temperature, respectively. For a given temperature the energy value of the minima corresponding to a particular polarization state will become less favorable when an electric field is applied in the direction opposite that particular polarization state. For instance, in the case of the nanowires investigated here the initial polarization state is in the negative $z$ direction and the electric field
is applied in the positive z direction which will decrease the well depth for the negative z polarization state and increase the energy well depth for the positive z direction as shown in Fig. 6.5. The value of applied electric field that forces the well depth for a particular polarization state to zero is the coercive field, \( E_C \), for homogeneous PR. This is because there is no longer any energy barrier to overcome in order for the nanowire to reverse its polarization direction.

For any fields below \( E_C \) there exists an energy barrier between the polarization states of opposite polar direction. This energy barrier can be overcome if the dipole is supplied with sufficient kinetic energy. If a dipole’s kinetic energy, \( \mathcal{E}_{\text{kin}} \), is taken to be approximately \( \frac{k_B T}{2} \) per degree of freedom then it is possible to predict qualitatively the coercive field’s dependence on temperature. Fig. 6.6 shows, in agreement with experimental reports [133], that the coercive field is inversely related to the temperature and that lower fields are required to switch the polarization in a nanowire at high temperature.

By including a kinetic energy term in the total energy of a dipole that is reversing polarization it is possible to define the total wire’s switching rate in terms of the speed \( u \) of the charges moving within that dipole. In a system of transitioning dipoles the moment of a given dipole can be defined in terms of the transition time \( t \) and the speed \( u \) by straightforward multiplication, \( p = u t \). In this framework the speed \( u \) can be defined as the average speed of propagation of dipole states under the driving force of the electric field. It is convenient in this case to consider the transition of dipole states within phase space. By integrating over all available states for a given polarization orientation one can arrive at an identity for the transition rate \( n(t) \) in terms of the average propagation speed \( u \) as

\[
\int_0^\infty \rho(p)dp = \int_0^\infty u \rho(ut)dt = \int_0^\infty n(t)dt = 1. \tag{6.3}
\]

By inputting Eq. (6.2) into the above identity and collecting the normalization constant into one coefficient one arrives at the following expression for the transition rate \( n(t) \)
Figure 6.6: Temperature dependence of the coercive field for homogeneous PR assuming $E_{\text{kin}} = \frac{k_B T}{2}$ (solid line) and $E_{\text{kin}} = \frac{3k_B T}{2}$ (dashed line). The open symbols indicate the coercive field calculated from MD simulations.
Figure 6.7: Fractional transition rates, \( n(t) \), for 2.8 MV/cm (panel a) and 4.5 MV/cm (panel b). Only three shells are plotted in panel a) for convenience. Dashed line in b) indicates the fitting with Eq. (6.4). Deviation from the data is most likely due to the idealized free energy landscape used to calculate the fit.

\[
n(t) = A u e^{-\frac{E(u t)}{k_B T}}.
\]  

(6.4)

To validate the above expression we compare it with time derivatives of the switched dipole counting curves for homogeneous PR, shown in Fig. 6.7b). The switching rates follow Eq. (6.4) remarkably well despite the fact that there is only one adjustable parameter, \( u \), in this expression. The discrepancy between the curve and the data is most likely due to the actual free energy profile deviating from the idealized free energy landscape used in Eq. (6.4). The model proposed in Eq. (6.4) and the computational data shown in Fig. 6.7 closely resemble the experimental measurements of polarization switching rate of PZT films [151].

Our model that approximates homogeneous PR by the propagation of dipole states in phase space correctly captures the physics behind such phenomenon. The average speed of propagation \( u \) is therefore proportional to the inverse switching time of the nanowire, \( t_{sw}^{-1} \). In the presence of a driving or applied electric field, \( E \), the dipoles gain additional kinetic
energy, $\mathcal{E}_{\text{kin}} = \frac{mu^2}{2}$, which is a result of the applied field being larger than the local field, $E_l$, felt by the dipoles. The local field holds dipoles within the material in their respective polarization states and can be written as the negative derivative of internal energy with respect to the polarization state or $E_l = -d\mathcal{E}/dp$. The local field screens the applied field so that the total electric field felt by a dipole is $E_{\text{tot}} = E - E_l$. Using the relation $\frac{mu^2}{2} = E_{\text{tot}}p$ it is possible to predict the speed of propagation as a function of applied field. Since $t_{\text{sw}}^{-1}$ is proportional to $u$ we can write the applied field dependence as

$$t_{\text{sw}}^{-1}(E) = t_0^{-1}\sqrt{E - E_C}. \quad (6.5)$$

Here $t_0^{-1}$ is a constant and $E_l$ has been replaced with $E_C$ since the local field is the atomistic counterpart to the macroscopic coercive field.Experimental measurements of the the switching of ferroelectric nanostructures is usually done through measuring the peak width in current versus time plots [5, 23, 151]. In our case the current is proportional to $n(t)$ from Eq. (6.4). Due to the small time scales associated with homogeneous PR the width of the peak can be comparable to the time it takes for the PR to initiate. As a result we define the switching time for homogeneous PR as the elapsed time from the application of the electric field until 90% of the sites in the wire have reversed direction. Ideally the elapsed time from application of the field until 100% of the sites had flipped would be used but this proves difficult when dealing with an atomistic model as we do here. Thermal fluctuations within a homogeneously polarized nanowire can cause some small fraction of the dipoles to have opposite direction to the net polarization vector and as a result 100% switching may not be practical. Furthermore the amount of kinetic energy gained by a dipole in a driving field may be large enough that after that dipole has reversed direction the charges have sufficient potential energy to begin moving back towards their original positions causing some dipoles to flip “back” to their original direction for a short time. To overcome these difficulties the value of 90% was selected because it is sufficiently large to give reasonable quantitative results without compromising the qualitative predictions.
The square root dependence of $t_{sw}^{-1}$ similar to that of Eq. (6.5) has been reported experimentally [134, 136, 137] and within a phenomenological framework [133]. The inverse switching time as a function of applied field for two tested temperatures is given in Fig. 6.8. Figure 6.8 also shows a fitting curve using Eq. (6.5) where only $t_0^{-1}$ was allowed to vary. Other models for the field dependence of $t_{sw}^{-1}$ including Merz’s Law, a power law dependence as well as a linear dependence have all been previously observed in measurements of the PR of ferroelectrics. These models fail to capture the observed trends of our computational results. Merz’s Law most likely fails because it is expected to model PR in domain driven regimes [23].

Up to this point all the PR dynamics described here have been within the homogeneous PR mechanism. We find that the discussion of domain driven PR is actually best described as a special case of the homogeneous description. The difference between the two mechanisms is that only dipoles in the vicinity of the domain wall will have the opportunity to flip. This is a
result of the reduction in the free energy barrier necessary for a dipole to reverse its direction when surrounded by both parallel and anti-parallel dipoles. By extracting switching rates, like those described in Eq. (6.4), for individual shells in the domain driven regime we find that the behavior is the same as for the whole wire in the homogeneous PR regime. Figure 6.7 shows the switching rates for three coaxial shells within a nanowire at a field strength of 2.8 MV/cm. The immediate conclusion from this behavior is that the domain driven PR is actually homogeneous PR within an individual shell of the nanowire. By replacing \( u \) and \( E(ut) \) in Eq. (6.4) with \( u_{dom} \) and \( E_{dom}(u_{dom}t) \) to reflect the dependence upon the location of the domain wall the same expression can be used. The new speed \( u_{dom} \) is the average transition speed of dipoles in the immediate vicinity of the domain wall. The switching time for the domain-driven process can be estimated by the expression

\[
t_{su} = \frac{R_{NW} t_i}{a_{lat}}
\]

(6.6)

where \( R_{NW} \) is the radius of the nanowire, \( t_i \) is the average transition time for a given shell \( i \) and \( a_{lat} \) is the lattice constant of PZT. The fraction \( \frac{a_{lat}}{t_i} \) is expected to be proportional to \( u_{dom} \) and therefore the \( t_{su}^{-1} \) for this process should be proportional to \( \frac{u_{dom}}{R_{NW}} \). This indicates that the domain-driven PR should have square root dependence similar to homogeneous PR but also scale with the size of the nanowire. If this is the case then the coercive field for the domain-driven PR should be lower than that of the homogeneous PR allowing for lower fields to activate the process. For a given dipole configuration, however, there is specific field strength that will activate the process. To allow for systematic study of the nanowires at all electric field strengths the starting configuration of dipoles in each size nanowire was identical and as a result we are not able to provide any information about the activation field from our study. We did find, however, that the domain-driven PR at T=100K can be fit with a square root dependence but the lack of data in this range makes it impossible to draw a definite conclusion on the validity of the model.

We find that the claims we have drawn concerning the PR dynamics of PZT remain valid
for all nanowires tested. The inverse switching time, shown in Fig. 6.9, shows very little dependence on the lateral dimension. For the lower temperature, T=100 K, the coercive field for homogeneous PR decreases very slightly with nanowire size. This is a consequence of the fact that the axial polarization decreases with the cross-sectional area of the wire. At elevated temperature, T=600 K, the coercive field for homogeneous PR decreases as predicted by our microscopic model in Fig. 6.6. At this temperature the inverse switching time is nearly independent of the nanowire size.

6.3 Conclusions

In summary we found the PR of ferroelectric nanowires is determined by the existence of two competing PR mechanisms. The first, which is domain-driven, activates at lower
field strengths but only allows a few dipoles to participate in the switching which results in longer switching times. The second mechanism associated with homogeneous PR activates at higher field strengths and completely overpowers the slower domain-driven PR as all dipoles engage simultaneously. In a narrow region of field strengths, 3.1-3.9 MV/cm in the case of Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$, these two mechanisms coexist with domain-driven PR in the outer section of the wire and homogeneous PR in the central part. We have also uncovered a power law dependence of the inverse switching time on the applied electric field.
7 Concluding Remarks

In conclusion we have shown how atomistic computer simulations can provide insightful predictions about the dynamics of perovskite ferroelectrics at the nanoscale.

We showed that within the framework of the present form of the effective Hamiltonian it is impossible to simultaneously describe the static and dynamical properties of perovskites that undergo a sequence of phase transitions. This indicates that additional work is needed to overcome the issue.

We also shed light on the soft mode dynamics of PTO in the presence of mechanical boundary conditions. We found that hydrostatic pressure, stress and strain have markedly different effects on the dynamical properties and must, therefore, be treated differently. Of high importance is the finding that all modes in all phases and at all temperatures follow Curie-Weiss behavior under pressure, stress or strain. Such predictable behavior provides an avenue for tailoring the dynamical properties of ferroelectrics at the nanoscale which is attractive from an application point of view.

Lastly we discussed the mechanisms of polarization reversal in ferroelectric nanowires. We found that domain-driven polarization reversal and homogeneous polarization reversal both exist for nanowires depending upon the field strength. These two mechanisms also compete with each other for a specific range of electric fields that lie between the two regimes. The implications of such a discovery may go well beyond the realm of only pseudo one-dimensional ferroelectrics and may explain the polarization reversal dynamics of planar and bulk geometries as well.
References


[54] L. Walizer, S. Lisenkov, and L. Bellaiche, “Finite-temperature properties of
(Ba,Sr)TiO$_3$ systems from atomistic simulations,” Phys. Rev. B, vol. 73, p. 144105,
2006.

[55] G. Kresse and J. Furthmüller, “Efficient iterative schemes for $ab$ initio total-energy

[56] G. Kresse and J. Furthmler, “Efficiency of ab-initio total energy calculations for metals
and semiconductors using a plane-wave basis set,” Comput. Mat. Sci., vol. 6, p. 15,
1996.

1994.

[58] G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector

[59] J. P. Perdew and A. Zunger, “Self-interaction correction to density-functional approx-


[61] J. P. Perdew, K. Burke, and M. Ernzerhof, “Erratum: Generalized Gradient Approx-


113


the strain and stress effects on the dielectric response of ferroelectric thin films,” *Appl. 

thin films deposited on Pt/Si substrates,” *J. Phys.: Condens. Matter*, vol. 12, p. 399, 
2000.


“Strain Tuning of Ferroelectric Thin Films,” *Ann. Rev. of Mat. Research*, vol. 37, 


comparative Raman study of ferroelectric PbTiO$_3$ single crystal and thin film prepared 


Appendix A  Proof of Copyright Permissions

Reproducing AAAS Material in your Thesis or Dissertation

NOTE: If you are the original Author of the AAAS article being reproduced, please refer to your License to Publish for rules on reproducing your paper in a dissertation or thesis. AAAS permits the use of content published in its journals Science, Science Technical Medicine, and Science Signaling, but only provided the following criteria are met.

1. If you are using figure(s)/table(s), permission is granted for use in print and electronic versions of your dissertation or thesis.

2. A full text article may be used only in print versions of a dissertation or thesis. AAAS does not permit the reproduction of full text articles in electronic versions of theses or dissertations.

3. The following credit line must be printed along with the AAAS material: “From [Full Reference Citation]. Reprinted with permission from AAAS.”

4. All required credit lines and notices must be visible any time a user accesses any part of the AAAS material and must appear on any printed copies that an authorized user might make.

5. The AAAS material may not be modified or altered except that figures and tables may be modified with permission from the author. Author permission for any such changes must be secured prior to your use.

6. AAAS must publish the full paper prior to your use of any of its text or figures.

7. If the AAAS material covered by this permission was published in Science during the years 1974–1994, you must also obtain permission from the author, who may grant or withhold permission, and who may or may not charge a fee if permission is granted. See original article for authors address. This condition does not apply to news articles.

8. If you are an Original Author on the AAAS article being reproduced, please refer to your License to Publish for rules on reproducing your paper in a dissertation or thesis.

Permission covers the distribution of your dissertation or thesis on demand by a third party distributor (e.g. ProQuest / UMI), provided the AAAS material covered by this permission remains in situ and is not distributed by that third party outside of the context of your Thesis/Dissertation.

Permission does not apply to figures/photos/artwork or any other content or materials included in your work that are credited to non-AAAS sources. If the requested material is sourced to or references non-AAAS sources, you must obtain authorization from that source as well before using that material. You agree to hold harmless and indemnify AAAS against any claims arising from your use of any content in your work that is credited to non-AAAS sources.

By using the AAAS Material identified in your request, you agree to abide by all the terms and conditions herein.

AAAS makes no representations or warranties as to the accuracy of any information contained in the AAAS material covered by this permission, including any warranties of merchantability or fitness for a particular purpose.

Questions about these terms can be directed to the AAAS Permissions department at permissions@aaas.org.
Thank you for your permission request dated Feb. 7, 2014. We are pleased to grant you a non-exclusive, non-transferable permission, English rights, limited to print and electronic format, provided you meet the criteria outlined below. Permission is for a one-time use and does not include permission for future editions, updates, databases, translations, or any other matters. Permission must be sought for each additional use. This permission does not include the right to modify APS material.

Please print the required copyright credit line on the first page that the material appears: “Reprinted (abstract/excerpt/figure) with permission from [FULL REFERENCE CITATION] as follows: authors names, journal title, volume number, page number and year of publication. Copyright (YEAR) by the American Physical Society.

The following language must appear somewhere on the website: “Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or part, without prior written permission from the American Physical Society.”

Provide a hyperlink from the reprinted APS material (the hyperlink may be embedded in the copyright credit line). APS’s link manager technology makes it convenient and easy to provide links to individual articles in APS journals. For information, see: http://link.aps.org/

You must also obtain permission from at least one of the authors for each separate work, if you haven’t done so already. The author’s name and address can be found on the first page of the published Article.

Use of the APS material must not imply any endorsement by the American Physical Society.

Permission is granted for use of the following APS material only:
- Fig. 7, Phys. Rev. 76, 1187–1201 (1949)
- Fig. 1, Phys. Rev. Lett. 105, 197603 (2010)
- Fig. 38, Rev. Mod. Phys. 84, 119–156 (2012)
- Fig. 1, Phys. Rev. B 52, 6301–6312 (1995)
- Fig. 1, Phys. Rev. Lett. 73, 1861–1864 (1994)

Permission is limited to the single title specified of the publication as follows:
A thesis entitled “The Soft-Mode Driven Dynamics and Other Phenomenon in Ferroelectric Perovskites at the Nanoscale: an Atomistic Study” to be published by the University of South Florida.

If you have any questions, please refer to the Copyright FAQ at: http://publish.aps.org/copyrightFAQ.html or send an email to assocpub@aps.org.

Sincerely,

Jamie L. Casey
Circulation and Fulfillment Assistant
Appendix B  Publications


Kevin McCash, S. Lisenkov, I. Ponomareva, “Universal nature of electrocaloric effect using phase transitions in perovskite ferroelectrics”, In Preparation
Appendix C  Conference Presentations

“Effect of Epitaxial Strain on the Dynamical Properties of Ferroelectric Perovskites” – Oral presentation given at APS March Meeting, Denver, CO, 2014


“Domain Wall Nucleation and Propagation within Ferroelectric Nanowires in High Strength Electric Fields” – Oral presentation given at APS March Meeting, Boston, MA, 2012

“Polarization Reversal in Ferroelectric Nanowires Under High Electric Fields” – Poster presentation at Fundamental Physics of Ferroelectric and Related Materials, Argonne, IL, 2012
**About the Author**

Kevin McCash was born in Colorado Springs, CO in 1986 where he lived until he graduated from Air Academy High School in 2004. He then attended the Colorado School of Mines in Golden, CO where he received a Bachelor of Science degree in Engineering Physics in 2008. He moved to Tampa, FL in 2010 to attend the University of South Florida as a graduate student in the Physics department. He received a Master of Science degree in Physics with an emphasis in Materials Physics in 2012. He completed the requirements for a Doctoral degree in Applied physics in 2014. He currently resides on the Eastern Shore of Maryland with his wife Hattie and their son Callan.