Complex Electric-Field Induced Phenomena in Ferroelectric/Antiferroelectric Nanowires

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Complex Electric-Field Induced Phenomena in Ferroelectric/Antiferroelectric Nanowires

by

Ryan Christopher Herchig

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

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Dedication

My Parents for never giving up on me, without whom none of this would have been possible.

CIRCE administration For answering 1,000,001 questions of mine.
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I would like to acknowledge Dr. Inna Ponomareva for her guidance, instruction, and assistance in completing our research and my dissertation. I would also like to thank my committee members for their encouragement and constructive criticism. Lastly I would like to thank my colleagues Dr. Brajesh Mani, Dr. Kevin McCash, Dr. Chun-Min Chang, Dr. Qingteng Zhang, and Dr. Elena Glazkova for their help and support.

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Abstract

Perovskite ferroelectrics and antiferroelectrics have attracted a lot of attention owing to their potential for device applications including THz sensors, solid state cooling, ultra high density computer memory, and electromechanical actuators to name a few. The discovery of ferroelectricity at the nanoscale provides not only new and exciting possibilities for device miniaturization, but also a way to study the fundamental physics of nanoscale phenomena in these materials. Ferroelectric nanowires show a rich variety of physical characteristics which are advantageous to the design of nanoscale ferroelectric devices such as exotic dipole patterns, a strong dependence of the polarization and phonon frequencies on the electrical and mechanical boundary conditions, as well as a dependence of the transition temperatures on the diameter of the nanowire. Antiferroelectricity also exists at the nanoscale and, due to the proximity in energy of the ferroelectric and antiferroelectric phases, a phase transition from the ferroelectric to the antiferroelectric phase can be facilitated through the application of the appropriate mechanical and electrical boundary conditions. While much progress has been made over the past several decades to understand the nature of ferroelectricity/antiferroelectricity in nanowires, many questions remain unanswered. In particular, little is known about how the truncated dimensions affect the soft mode frequency dynamics or how various electrical and mechanical boundary conditions might change the nature of the phase transitions in these ferroelectric nanowires. Could nanowires offer a distinct advantage for solid state cooling applications? Few studies have been done to elucidate the fundamental physics of antiferroelectric nanowires. How the polarization in ferroelectric nanowires responds to a THz electric field remains relatively underexplored as well. In this work, the aim is to develop and use computational tools that allow first-principles-based
modeling of electric-field-induced phenomena in ferroelectric/antiferroelectric nanowires in order to address the aforementioned questions.

The effective Hamiltonian approach is a well validated model which reliably reproduces many static and dynamic properties of perovskite ferroelectric and antiferroelectrics. We begin by developing an effective Hamiltonian for the prototypical ferroelectric potassium niobate, a lead-free material which undergoes multiple structural phase transitions. Density functional theory calculations within the LDA and GGA are used to determine the effective Hamiltonian parameters for KNbO₃. By simulating an annealing within an NPT ensemble, we find that the KNbO₃ parameters found from first principles underestimate the experimental transition temperatures. We apply a universal scaling technique to all of the first-principles derived parameters and are thus able to more accurately reproduce the transition temperatures predicted by experiment as well as a number of other static and dynamic properties of potassium niobate.

Having determined the parameters of the effective Hamiltonian for KNbO₃, we use this as well as previously determined effective Hamiltonian parameters for PbTiO₃ and BaTiO₃ to study the electrocaloric effect in nanowires made of these materials. We determined that, in general, the electrocaloric effect in ferroelectric nanowires is diminished due to the reduced correlation length resulting from the finite lateral dimensions. However, certain temperature ranges were identified near ambient temperature where the electrocaloric response is enhanced with respect to bulk. The effective Hamiltonian model was also employed to study the response of the spontaneous polarization and temperature to tailored electric fields. We identified a novel means of reversing the polarization in ferroelectric nanowires which could potentially be used in the design of nanoscale THz sensors of ultra high density ferroelectric memory devices.

While the soft mode frequency dynamics of bulk ferroelectrics under various mechanical boundary conditions have been studied extensively, the effects of different mechanical boundary conditions on the soft mode dynamics in ferroelectric nanowires remains relatively
under-explored. We conduct a comprehensive study on PbTiO$_3$ nanowires which explores the effects of hydrostatic pressure, applied uniaxial stress, and biaxial strain on the structural properties, transition temperatures, and soft mode dynamics. We found that depending on the particular type of mechanical boundary condition, the nanowire can exhibit either monodomain or polydomain vortex phases, drastically different from what is found for PbTiO$_3$ bulk and originates from the critical role of the depolarizing field. We found a rich variety of dipole patterns, particularly for the polydomain states with the dipoles arranged in single and double polarization vortices depending on the type and strength of the mechanical boundary conditions. The soft mode frequency dynamics are also strongly affected by the mechanical boundary conditions. In particular we find that the frequency of the E mode in the P$_{4mm}$ phase is significantly larger than the A$_1$ mode which is in contrast with bulk PbTiO$_3$. This striking finding is attributed to the presence of the depolarizing field along the truncated directions which leads to mode hardening.

In the last chapter, we identify the emergence of a ferroelectric state in antiferroelectric PbZrO$_3$ nanowires and describe possible ways to stabilize the ferroelectric phase. Finally, we explore how our findings could potentially be used to improve existing technologies such as energy storage devices and electromechanical actuators as well as future technologies like solid state cooling devices.
1 Introduction

1.1 Historical Background

For centuries the pyroelectric effect, or, the ability of certain materials to generate a spontaneous dipole moment upon heating or cooling, was known of but not well understood. This was explained as the difference between the charge developed from uniform and non-uniform heating was due to the resulting thermal stress created in the material. Of all the early known pyroelectric materials, none were ferroelectric since none possessed a reversible electric dipole moment. The first known true ferroelectric material $NaKC_4H_4O_6 \cdot 4H_2O$, also known as Rochelle salt, has a relatively complex structure and was consequently not well understood at the time of its discovery. Additionally, given that it was the only known example of a ferroelectric material, ferroelectricity was believed to be somewhat of an anomaly in nature. It was not until the years of 1935 to 1938 that a group of ferroelectric materials was discovered which showed any kind of a structural pattern, the phosphates and the arsenates. Of the phosphates, the primary example is potassium dihydrogen phosphate with chemical formula $KH_2PO_4$, better known as KDP. Discovered also were the ammonium salts which did not develop a macroscopic polarization below their critical or Curie temperature. Though it was not known at the time, the reason for this is that $(NH_4)H_2PO_4$, abbreviated ADP, is actually an antiferroelectric so no net polarization should exist below the Curie temperature. During the World War II era, ADP replaced Rochelle Salt in sonar devices as it was not as sensitive to changes in temperature [2].

In the 1940’s barium titanate, a ceramic with a dimensionless dielectric constant of 1000 to 3000 at room temperature was discovered. It was later found that barium titanate (BaTiO$_3$) was ferroelectric at room temperature. The crystal structure of BaTiO$_3$ is much simpler than that of all previously discovered ferroelectrics making it much easier to study and understand.
Its discovery compelled scientists to search for other ferroelectrics with the same perovskite $\text{ABO}_3$ crystal structure. In the following years, other materials which were already known of were found to be ferroelectric. Some of these materials include $\text{KNbO}_3$, $\text{KTaO}_3$, $\text{LiNbO}_3$, $\text{LiTaO}_3$, and $\text{PbTiO}_3$. The relatively simple crystal structure of these perovskites allowed for the development of a microscopic theory of ferroelectric phase transitions. In 1950 John C. Slater proposed that the ferroelectric behavior in $\text{BaTiO}_3$ was due to the long-range dipolar forces which tend to destabilize the high-symmetry configuration which was favoured by the short-range forces. This assumption was correct and has since been verified by experiment and further theoretical development. In 1960 Anderson and Cochran proposed the soft mode theory of ferroelectrics. They proposed that only certain phonon modes are important to ferroelectric phase transitions and that the others can be safely neglected without loss of generality. [2]

The first application of thermodynamics to ferroelectric systems, Rochelle salt, was by Mueller in 1940. He wrote the free energy as an expansion in powers of polarization and strain. The expansion parameters were determined by associating them with measurable quantities. The theory was capable of explaining dielectric, piezoelectric, and elastic behavior at finite temperature using a free-energy polynomial containing a limited number of terms. This technique was further developed to describe polar and non-polar phases by Ginzburg and Devonshire with specific reference to $\text{BaTiO}_3$. It undergoes three phase transitions with each ferroelectric phase having a different polar axis. In 1951, Kittel further generalized the theory to include antiferroelectrics materials as well. [2]

Over the next several decades, a number of materials which had been previously studied were found to be ferroelectric. Many of the crystals for which dielectric anomalies had been reported were found to be ferroelectric or antiferroelectric. The list of materials known to be ferroelectric numbered in the hundreds. The problem had shifted from a preponderance of ferroelectric materials to that of a tendency to classify any antidistortive crystal as antiferroelectric and to categorize materials with merely a metastable polarization as ferroelectric [2].
A new theory, and rigorous definition of ferroelectricity, was needed to accurately characterize materials as ferroelectric.

Since the 1960’s, the theoretical emphasis has been on the lattice-dynamical or soft mode description of ferroelectricity. In the mid-nineties, the pioneering works of Zhong, Vanderbilt, Rabe et al. [3–5] has cast our theoretical understanding into the context of the effective Hamiltonian description of ferroelectric phase transitions. This interpretation capitalizes on the lattice-dynamics with the effective Hamiltonian written in terms of the soft modes and strain variables only. The effective Hamiltonian in general enough to describe essentially all types of ferroelectric instabilities yet simple enough to remain tractable such that the general aspects of ferroelectricity which are common to all systems can be identified. This is especially true of the perovskite ferroelectrics as their relatively basic crystal structure allows for theoretical progress to be made.

1.2 Theory of Ferroelectrics & Antiferroelectrics

Modern theories of ferroelectrics and antiferroelectrics can be divided into two main categories, macroscopic and microscopic approaches. The former typically use thermodynamic principles and symmetry arguments to describe ferroelectric phase transitions in a broad sense. These macroscopic theories are useful for comparison to experimental findings or for models which attempt to quantify results for application purposes, however they give no interpretation of the underlying mechanisms responsible for material properties and for complex phenomena such as structural phase transitions. Microscopic theories on the other hand have the capability of explaining why these phenomena occur by appealing to an atomistic description of the physical systems being studied, often times with nanometer spatial resolution and femtosecond temporal resolution. In the following sections, we will begin with an overview of ferroelectrics and antiferroelectrics, followed by a thermodynamic description of phase transitions, and a theoretical description of the electrocaloric effect. We will also discuss experimental techniques for synthesizing ferroelectric/antiferroelectric
nanowires, current and potential applications of ferroelectrics and antiferroelectrics, concluding with a discussion of how these applications can be improved through the incorporation of ferroelectric/antiferroelectric nanowires into their design.

1.2.1 Crystallography of Perovskites

Crystals are divided into 7 different crystal classes depending on their geometry. These different classes possess varying degrees of crystal symmetry with the triclinic system having the lowest symmetry and the cubic system being the most symmetric. Other phases include monoclinic, orthorhombic, tetragonal, rhombohedral, and hexagonal. These crystal systems are further divided into different crystal classes, of which there are 32 in total. Of these 32 classes, 11 possess a center of symmetry and therefore have no polar properties. If a uniform stress is applied to a centrosymmetric crystal, the resulting displacement of charge is distributed symmetrically throughout the crystal which causes full compensation of relative charge separations and no dipole moment. Though the application of an electric field does produce a strain, this strain is unchanged by the reversal of the electric field. This induced strain is known as electrostriction and is present in all materials, crystalline or amorphous.

Of the 21 remaining crystal classes, 20 of them are piezoelectric meaning they exhibit electric polarity when subjected to a stress. Of these 20 classes, 10 of them possess a unique polar axis. Crystals belonging to these classes are classified as polar since they have a polarization or a dipole moment per unit volume. If this polarization is discontinuous, for instance at the surface of a ferroelectric sample, it creates a depolarizing electric field which opposes the polarization. This depolarizing field can be compensated by the flow of free charge within the crystal and in the surrounding medium. The free charge can originate from a number of sources including free change carriers, molecular adsorbates, intrinsic surface states, and oxygen vacancies. The polarization is in most cases temperature dependent, a phenomenon known as pyroelectricity. The polarization can then be detected from the flow of charge to and from the surfaces as the temperature of the crystal is changed. These 10 remaining
crystal classes are thus referred to as the pyroelectric classes. [2,6,7]

A ferroelectric is a material which possesses a spontaneous polarization in the absence of an electric field which can be reversed by the application of an electric field. The ability of the orientational state to be reversed by the electric field is essential for classification of a material as a ferroelectric. These orientational states are identical in crystal structure, however they differ by the direction of the electric polarization vector at zero electric field. Additionally, these states should represent a completely stable configuration in the absence of an external electric field for the material to be classified as a true ferroelectric. In some materials, a metastable state can exist, often times induced by the external field, which can be switched upon reversal of the field. Technically, these materials are not classified as a true ferroelectric.

The term prototype phase is used to describe the highest symmetry phase that a ferroelectric crystal can exist in. It is with respect to this phase that the small displacements of the ions are described in reference to. The prototype phase exists as the highest temperature paraelectric phase, face-centered cubic, in PbTiO$_3$, Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$, and KNbO$_3$. A ferroelectric phase transition represents a change in crystal structure accompanied by the onset of a spontaneous polarization. Figures 1.1(a) and (b) show data from a simulated annealing of PbTiO$_3$ bulk. At the Curie temperature, about 605 K in computational temperature, the material undergoes a phase transition accompanied by the polarization spontaneously acquiring a non-zero component along one of the crystallographic directions. In most ferroelectrics, a diverging dielectric response or permittivity, $\varepsilon$, is typically associated with the phase transition from the paraelectric to the ferroelectric phase. This can be seen in Fig. 1.1(a) in which the inverse of the dielectric permittivity ($1/\varepsilon$) with respect to temperature nearly goes to zero at the Curie temperature. Figure 1.1(b) shows the spontaneous strain which is induced by the structural phase transition from cubic to tetragonal symmetry.

Figure 1.2(a) shows an example of a perovskite ABO$_3$ conventional cell in which the A (Pb) and B (Zr) ions are positively charged while the oxygen ions, 6 per conventional
Figure 1.1: Spontaneous polarization and inverse dielectric susceptibility (a) and spontaneous strain (b) as a function of temperature for PbTiO$_3$ bulk.

...cell forming an oxygen octahedron, are negatively charged. It is usually the case that a ferroelectric phase transition is associated with the condensation of a low-frequency mode (soft mode) of lattice vibration at the Brillouin zone center. Figure 1.2(b) shows the ionic displacement associated with the condensation of this phonon mode. When a structural phase transition is triggered by a zone-center soft mode it is called ferrodistortive. The definition of a ferroelectric can then be amended as a subgroup of the class of ferrodistortive transitions which involves the condensation of a polar or optically active mode which causes the appearance of a long-range polar order in the crystal. When mode condensation occurs at a place in the Brillouin zone other than the zone center, it is referred to as an antidistortive or antiferrodistortive structural phase transition. This most often occurs at the Brillouin zone boundary of the high-temperature phase and usually involves a doubling of the unit cell to account for both polarization directions. An example of this cell doubling can be seen in Fig. 1.2(c) in which the lead ions are displaced relative to one another in the Σ mode. Figure 1.2(d) depicts the oxygen octahedron rotations associated with the antiferrodistortive structural phase transition.

\footnote{Figure 1.2 has been previously published in A. K. Tagantsev et al., “The origin of antiferroelectricity in PbZrO$_3$”, Nature Communications, vol. 4, p. 2229, 2013, and has been reproduced with permission from Nature Publishing}
Though most ferroelectrics are ferrodistortive, it is not a necessary condition that a zone-center polar mode be the driving instability which leads to the structural phase transition. Due to a strong coupling between the soft mode and the long wavelength acoustic phonons, often referred to as strain variables, it is possible that a driving antidistortive mode can indirectly induce a spontaneous polarization. Such a transition is labelled intrinsically antidistortive but extrinsically ferroelectric. The primary order parameter is of antidistortive character making the spontaneous polarization the secondary order parameter of the phase transition. There always exists only one primary order parameter, however there can be a number of secondary or induced order parameters resulting from phonon couplings. [2,6]

Due to the piezoelectric interaction, resulting from the coupling of polar modes to acoustic modes, a spontaneous strain is virtually a universal characteristic of all ferroelectrics since they are all piezoelectric. If this strain can be reversed by the application of a stress, then
the material is said to be ferroelastic. Technically, the crystal is ferroelastic if it possesses two or more orientational states in the absence of both mechanical stress and an electric field and can be shifted from one to the other of these states by the application of a mechanical stress. These orientational states are identical in crystal structure and differ only in the mechanical strain tensor at zero mechanical stress and electric field.

1.2.2 Thermodynamics

The thermal, elastic, and dielectric behavior of a homogeneous dielectric is completely described by 6 different physical quantities, namely the temperature \( T \), the entropy \( S \), stress \( \sigma_i \), strain \( \eta_i \), electric field \( E \), and displacement electric field \( D \). There are 6 components of both stress and strain and 3 components of the electric and displacement fields giving a total of 20 thermodynamic coordinates necessary to fully specify the state of the system. A thermodynamic description of ferroelectrics typically begins with the first law of thermodynamics which states that the change in internal energy per unit volume is equal to the infinitesimal quantity of heat transferred to the unit volume plus the work done on the ferroelectric by electrical or mechanical forces and is given by

\[
dU = dQ + dW \tag{1.1}
\]
during the resulting quasi-static transformation. For quasi-static processes, the change in state of the system is reversible which further simplifies calculations such that the infinitesimal quantity of heat received by the unit volume is related to the absolute temperature and change in entropy of the system by the expression \( dQ = TdS \) where \( S \) is the entropy of the system. The work done by a uniform mechanical stress and uniform electric displacement field can be separated into their individual contributions giving

\[
dW = dW_M + dW_E = \int_V \left( \sigma_i d\eta_i + E_i dD_i \right) dV. \tag{1.2}
\]
Combining these two equations, the first law can be rewritten as

$$dU = TdS + \sigma_i d\eta_i + E_i dD_i$$  \hfill (1.3)

where both strain and electric displacement fields are assumed to be uniform. From equation (1.3), the exact differentials take their simplest form if $S$, or $\eta_i$, or $D$ are held constant. These are referred to as principal variables for the internal energy. It is then possible to calculate $T$, $\sigma_i$, and $E_i$ from Eq. 1.3

$$T = \left( \frac{\partial U}{\partial S} \right)_{\eta_i, D}, \quad \sigma_i = \left( \frac{\partial U}{\partial \eta_i} \right)_{S, D}, \quad E_i = \left( \frac{\partial U}{\partial D_i} \right)_{S, \eta_i}$$  \hfill (1.4)

where these three expressions describe the calorimetric, elastic, and dielectric equations of state respectively.

An example of a typical experimental situation under which static measurements are performed is with $T$, $\sigma_i$, and $E_i$ held constant. The thermodynamic potential in this case is the Gibbs free energy defined as

$$G = U - TS - \sigma_i \eta_i - E_i D_i$$  \hfill (1.5)

which can be used to derive the equation of state. The differential form is

$$dG = -SdT - \eta_i d\sigma_i - D_i dE_i$$  \hfill (1.6)

The differential form of the Gibbs free energy represented by equation 1.6 implies that the free energy is, in equilibrium, a stationary function with respect to changes in the principle variables. The second law of thermodynamics states that if a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically in successive instants of time, referred to as the law of increase of entropy. [8] Application of this law to the differential
of the thermodynamic potential in equation 1.6 with reference to non-equilibrium configurations reveals that these processes have the effect of bringing the system to a state of thermodynamic equilibrium. Consequently, as the system approaches equilibrium with the independent variables held constant, the free energy is minimized given that the variables being constrained are the principal ones. For the principle variables $T$, $\sigma_i$, and $E_i$, it is the Gibbs free energy which is minimized with respect to the constrained variables as the system reaches equilibrium. As a result, the values of the constrained variables then define the equilibrium values of the unconstrained variables in terms of $T$, $\sigma_i$, and $E_i$.

$$S = -\left( \frac{\partial G}{\partial T} \right)_\sigma E, \quad \eta_i = -\left( \frac{\partial G}{\partial \sigma_i} \right)_T E, \quad D_i = -\left( \frac{\partial G}{\partial E_i} \right)_T \sigma$$ (1.7)

Using these final relationships, the minimized free energy is thus expressed in terms of the principal values alone as

$$dG = \left( \frac{\partial G}{\partial T} \right)_\sigma E dT + \left( \frac{\partial G}{\partial \sigma_i} \right)_T E d\sigma_i + \left( \frac{\partial G}{\partial E_i} \right)_T \sigma dE_i$$ (1.8)

If two or more states are locally stable for the same set of constraints, the state with the smallest value of the free energy is called the absolutely stable state while the others are referred to as metastable state. In other words, the metastable states represent local minima in the free energy landscape, while the global minimum is the absolutely stable configuration. [2,9]

### 1.2.3 Landau-Devonshire Models & Phase Transitions

The Landau-Devonshire theory provides a description of ferroelectric behavior near phase transition for a system in equilibrium. The model is based solely on symmetry arguments and essentially relates measurable quantities to one another using a minimum set of input parameters which can be found either by experiment or from first-principles calculations. As previously mentioned, the thermodynamic state of a system is completely specified by the
values of certain variables. For bulk ferroelectrics these variables are the temperature (T),
the polarization (P), the electric field (E), the strain (η), and the stress (σ). Typically, an
electric field and elastic stresses are applied externally so the polarization and strain can be
regarded as being dependent variables. Landau-Devonshire theory utilizes two fundamental
postulates of thermodynamics applied to bulk ferroelectrics: The free energy $F$ of a system
can be expressed generally as a function of ten variables (three components of polarization,
six components of a stress tensor, and a temperature); and the values of the dependent
variables (polarization and strain) in thermal equilibrium are obtained at the free-energy
minimum when the free energy is optimized. [9]

A thermodynamic system cannot change smoothly between two phases of different sym-
metry. Additionally, since the thermodynamic states of two phases that are symmetrically
distinct are required to be the same at their shared transition line, the symmetry of one
phase must be higher than the symmetry of the other. The transition is characterized in
terms of the order parameter, a physical entity which is zero in the highest symmetry dis-
ordered phase and changes to a finite value as the symmetry is lowered. In the vicinity of
the phase transition, the free energy is expanded in powers of the dependent variables or
order parameters, the polarization and the strain, with the coefficients to be found from
experiment or from \textit{ab initio} calculations. Only symmetry compatible terms are retained in
the expansion. Due to cubic symmetry, in an expansion of the free energy in polarization,
only terms with even powers in the polarization would survive while terms with $P$, $P^3$, etc.
dependence are discarded. [7,9]

The Landau-Devonshire model is strictly a macroscopic theory and cannot describe any
microscopic physics associated with the phase transition such as atomic displacements, do-
main wall formation or motion, etc. In general, for Landau-Devonshire theory to be valid the
local fluctuations in the order parameter must be small compared to the value of the order
parameter itself. The characteristic length scale over which these fluctuations are considered
is given by the correlation length denoted by $\xi$. The correlation length corresponds to the
length scale over which the polarization exists above $T_0$, at $T = T_0$ the correlation length $\xi$ diverges, and for $T < T_0$ it describes the length scale over which $P$ varies from its equilibrium value. Landau theory works well when coordination number, or, the number of interacting neighbors for a given site, is high. This is achieved by large dimensionality or by long-range interactions. In ferroelectric systems, significant dipolar interactions contribute to these long-range interactions making Landau Theory a useful tool, however angular dependence of the dipolar force leads to non-Landau behaviour near phase transition. [2,9]

In the Landau-Devonshire phenomenological model of ferroelectricity, the free energy of a system can be written using the general expression

$$F_P = \frac{1}{2} a (T - T_0) P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 - EP$$

with $a$ and $c$ being positive coefficients for all known ferroelectric materials. From this equation, two distinct situations arise depending on the sign of $b$. For a 2nd order or continuous phase transition, $b > 0$ and the transition occurs at $T = T_0$. For a 2nd order transition, the free energy changes continuously and smoothly as shown in Fig. (1.3a). Above $T_0$, the only stable energy state exists at zero polarization. As the temperature is lowered below the transition temperature, the classic double-well energy landscape develops giving rise to the two stable polarization states. A 2nd order transition is termed continuous since as the temperature is decreased, the order parameter $P$ goes continuously to zero at the transition temperature as illustrated in Fig. (1.3b). In contrast, dielectric susceptibility diverges at $T_0$ as it is governed by the expression

$$\chi = \frac{\partial P}{\partial E} \bigg|_{P_0} = \frac{1}{2a} (T - T_0)^{-1}$$

where $a$ is the coefficient from Eq. 1.9 and $P_0$ is the equilibrium polarization. The divergence of the susceptibility predicted by Landau-Devonshire theory of course does not occur in nature. In practice, $\chi$ reaches finite albeit extremely large values in real ferroelectric materials.
which undergo 2nd order phase transitions [9].

![Figure 1.3: Second-order ferroelectric phase transition. (a) Free energy as a function of the polarization for $T > T_0$, $T = T_0$, and $T < T_0$; (b) Spontaneous polarization $P_0(T)$ as a function of temperature. (c) The susceptibility and its inverse, where $\chi = \partial P/\partial E|_{P_0}$ is evaluated at the equilibrium polarization $P_0(T)$.](image)

For negative values of $b$, the material will undergo a 1st order or discontinuous phase transition. Figure (1.4a) depicts this situation where, even for temperatures above the Curie point, the free energy landscape might have local minima with non-zero polarization vectors representing metastable states. As the temperature of the system is further reduced, equivalent to reducing $a$, these energy minima will further reduce until at temperatures $T_0 < T_C$, below the transition temperature, these states will drop below the energy of the zero polarization state and become the thermodynamically favored configuration. These energy minima represent the two stable ferroelectric states of the crystal, being equivalent in energy in the absence of an electric field with the unpolarized state being unstable. By applying an electric field, the system can be biased such that one energy state will be lower than the other. This will become the thermodynamically favored energy state; the dipole moments of each unit cell will tend to align themselves with the electric field leading to a preferred dipole configuration. A reversal of the electric field direction essentially amounts
to a reflection of the free energy vs. polarization curve about the energy axis with the dipoles reacting by reversing their directions \cite{2,9}.

An important feature characterizing the 1st order transition is that the order parameter $P$ jumps discontinuously to zero at the transition temperature, as illustrated by Fig. (1.4b). Consequently, the dielectric susceptibility also jumps discontinuously at the Curie temperature, $T_C$, as is shown in Fig. (1.4c). At $T = T_C$, all three states are energetically degenerate; the thermodynamic behavior of the system depends on whether the crystal is being heated from the lower temperature ferroelectric phase up to $T_C$ or being lowered to $T_C$ from the high temperature paraelectric phase. This is a phenomenon known as thermal hysteresis where the transition temperature depends on whether the sample is heated or cooled, depicted in Fig. (1.5). In Fig. 1.5, a simulated annealing and heating of a KNbO$_3$ bulk sample, the transition temperatures are lower for the cooling cycle than for heating by approximately 100 K.

Another type of hysteresis which is characteristic of ferroelectrics is that of electrical...
hysteresis as shown in Fig. 1.6. As the applied electric field is varied, the free energy minima change depth and switch their relative positions and the polarization in the material consequently reverses direction as the dipoles shift their spatial orientations. As there is an energy barrier between the two minima, a small electric field will not immediately reverse the polarization. [9]

Figure 1.6: Schematic diagram of hysteresis in an idealized ferroelectric. Accompanying the hysteresis curve are the corresponding free energy curves depicting the shape of the energy wells and the polarization orientation in the ferroelectric crystal.
The amount of polarization that remains when the electric field is zero is referred to as the remnant polarization represented by the point of intersection of the hysteresis curve and the polarization axis. The saturation polarization is the maximum amount of polarization achieved at the maximum electric field applied. This is the polarization that exists in the stable state at the minimum of energy (bottom of the lowest energy well). The coercive electric field is the electric field required to bring the polarization from one of the stable states to zero. This is the point where the hysteresis curve intersects with the electric field axis, where the polarization reversal occurs. [2]

It is important to recognize that in real physical systems, phase transitions are never completely 1st or 2nd order but instead represent some combination of these two idealized cases. Some phase transitions are predominately 1st or 2nd order, but these two extremes essentially represent limiting cases for the behavior of real crystal systems. They serve as tools for modelling ferroelectric materials and for predicting and explaining different features and properties of the system being studied.

1.3 The Electrocaloric Effect

The electrocaloric effect is defined as the adiabatic change in temperature or equivalently the isothermal change in entropy upon application of an external electric field. Due to their large dielectric susceptibility, ferroelectric materials display a strong electrocaloric response making them suitable candidates for studying the electrocaloric effect which could potentially be used in solid-state cooling applications. We will now provide a brief introduction to the physical concepts and mathematical expressions used to describe the electrocaloric effect.

1.3.1 Electrocaloric Cycles

The essential operating principles of an electrocaloric refrigeration cycle are analogous to those of a vapor compression cooling cycle. There must be some mechanism by which the electrocaloric material transfers heat to the surrounding environment as well as absorbs heat
from it. This is incorporated into a thermodynamic cycle as depicted in Fig. 1.7, a schematic representation of an electrocaloric refrigeration cycle. The cycle goes as follows:

1. Adiabatic polarization (A → B) - An isolated electrocaloric material is subjected to an electric field from $E_1$ to $E_2$ which results in ordering of the electric dipoles. The electric field polarizes the material causing the dipoles to align along the direction of the electric field. The refrigerant heat capacity and configurational entropy decreases ($S_1$ to $S_2$) and since the process is adiabatic (refrigerant isolated to heat exchange with environment) the temperature of the material increases as ($T_0 + \Delta T$).

2. Heat transfer (B → C) - The refrigerant is put into thermal contact with a hot reservoir ($T_h$), the electric field is held constant to ensure the process is isothermal (constant refrigerant temperature). Heat is expelled from the refrigerant to the heat reservoir according to $Q_h = T_h \Delta S_h$ where $\Delta S_h = S_3 - S_2$

![Figure 1.7: Schematic diagram of an electrocaloric refrigeration cycle.](image)

3. Adiabatic depolarizing (C → D) - The electrocaloric material is again isolated from the heat reservoir while the electric field is decreased ($E_3$ to $E_4$) allowing the dipoles to relax and depolarize, causing the configurational entropy to increase ($S_3$ to $S_4$). Since the
material is isolated from its surroundings (adiabatic conditions), no heat is exchanged and the refrigerant cools down ($T_0 - \Delta T$).

4. Entropy transfer (D $\rightarrow$ A) - The refrigerant is placed in thermal contact with the cold reservoir (or heat load). Heat migrates from the cold reservoir to the refrigerant causing the cold reservoir to cool down to $T_c$. The electrocaloric refrigerant absorbs heat from the cold reservoir as $Q_c = T_c\Delta S_c$ with $\Delta S_c = S_1 - S_4$ [10].

The Carnot cycle depicted in Fig. 1.7 is the most commonly studied and reported refrigeration cycle for electrocaloric refrigeration, other thermodynamic cycles have also been considered including the Brayton [11], Ericsson [10,12,13], Stirling cycles [10,14,15]. Another quantity of interest in electrocalorics research is the refrigerant capacity

$$RC = \int_{T_c}^{T_h} \Delta SdT \approx -\Delta S_m \times FWHM$$

where the integral is the area under the $\delta S (T)$ curve and $FWHM$ is the full width at half maximum of the $\Delta S (T)$ curve. A similar quantity is the relative cooling power defined as

$$RCP = \Delta T_{max} \times \delta T_{FWHM}$$

where $\Delta T_{max}$ is the maximum electrocaloric change in temperature and $\delta T_{FWHM}$ is the full width at half maximum of the $\Delta T (T)$ curve. These quantities are used to benchmark caloric materials in a reversible cycle to serve as a basis of comparison. It is a way to quantitatively measure which materials would perform best in caloric cooling devices. The coefficient of performance of the ideal Carnot cycle shown above is given as

$$COP_{CR} = \frac{T_c}{T_h - T_c}$$

while the efficiency of a refrigerator relative to the ideal Carnot cycle is

$$\eta = \frac{1}{1 + \frac{T_h S_{gen}}{\Delta S_c (T_h - T_c)}}$$

where $S_{gen} = \Delta S_h - \Delta S_c$ is the entropy from irreversible processes. Equation 1.12 predicts that in the limit that $S_{gen} \rightarrow 0$ or the product $\Delta S_c (T_h - T_c) \rightarrow \infty$, the efficiency of the real refrigeration cycle equals that of the ideal Carnot cycle. This means that efficiency can be achieved by minimizing the entropy due to irreversible processes and maximizing the change
in temperature times the change in configurational entropy.

1.3.2 Indirect Method for Estimating $\Delta T_{ECE}$

Given that the electrocaloric effect originates from an isothermal entropy change in the material, by appealing to equations from classical thermodynamics and electrodynamics, an equation which characterizes the electrocaloric effect in dielectric materials can be found. Beginning with the Gibbs free energy and by incorporating the Maxwell relations, an expression can be derived for the change in temperature as a function of the change in the polarization [10, 16].

In most experimental environments, the temperature, stress, and electric field are the independent variables making the Gibbs free energy the quantity of interest. The Gibbs free energy is written as follows

$$G = U - X_{ij}x_{ij} - E_iD_i - TS$$

(1.13)

where $X_{ij}$ are the components of the stress tensor, $x_{ij}$ is the corresponding strain components, $E_i$ the electric field components, and $D_i$ are the components of the electric displacement field. The subscripts $i$ and $j$ denote the fact that $E_i$ and $d_i$ are vectors while $X_{ij}$ and $x_{ij}$ are 2nd rank tensors. In differential form we have

$$dG = -x_{ij}dX_{ij} - D_iDE_i - SdT$$

(1.14)

for infinitesimal changes in $X_{ij}$, $E_i$, and $T$. If we consider the solid to be isolated from its environment, the derivative of the Gibbs free energy yields

$$(\frac{\partial G}{\partial X_{ij}})_{E,T} = -x_{ij}, \quad (\frac{\partial G}{\partial E_i})_{X,T} = -D_i, \quad (\frac{\partial G}{\partial T})_{E,X} = -S$$

(1.15)

The equations represent the principal effects, elasticity, dielectric permittivity, and heat capacity respectively [10]. The Maxwell relations are obtained by taking further derivatives.
of the principle effects equations giving mixed partial derivatives:

\[-\left(\frac{\partial^2 G}{\partial X_{ij}\partial E_k}\right)_{T} = \left(\frac{\partial x_{ij}}{\partial E_k}\right)_{X,T} = \left(\frac{\partial D_k}{\partial X_{ij}}\right)_{E,T} = d_{ijk} \quad (1.16)\]

\[-\left(\frac{\partial^2 G}{\partial X_{ij}\partial T}\right)_{E} = \left(\frac{\partial x_{ij}}{\partial T}\right)_{X,E} = \left(\frac{\partial S}{\partial X_{ij}}\right)_{E,T} = \alpha_{ij} \quad (1.17)\]

\[-\left(\frac{\partial^2 G}{\partial E_i\partial T}\right)_{X} = \left(\frac{\partial D_i}{\partial T}\right)_{X,E} = \left(\frac{\partial S}{\partial E_i}\right)_{X,T} = p_i \quad (1.18)\]

Equation 1.18 states that

\[\left(\frac{\partial D_i}{\partial T}\right)_{\sigma,E} = \left(\frac{\partial S}{\partial E_i}\right)_{\sigma,T} \quad (1.19)\]

thus

\[\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial D_i}{\partial T}\right)_{X,E} dE_j \quad (1.20)\]

where \(E_0\) and \(E_0 + \Delta E\) are the initial and final electric fields. Equation 1.20 is the adiabatic change in entropy under an applied electric field. To derive the adiabatic change in temperature, we begin with the full differential of the entropy as a function of temperature and electric field

\[dS = \left(\frac{\partial S}{\partial T}\right)_E dT + \left(\frac{\partial S}{\partial E}\right)_T dE. \quad (1.21)\]

Under adiabatic conditions the change in entropy is zero \((dS = 0)\), thus Eq. 1.21 becomes

\[-\left(\frac{\partial S}{\partial T}\right)_E dT = \left(\frac{\partial S}{\partial E}\right)_T dE. \quad (1.22)\]

The definition of heat capacity at constant electric field is
\[ C_E = T \left( \frac{\partial S}{\partial T} \right)_E \]  

which substituted into Eq. 1.22 for \( \left( \frac{\partial S}{\partial T} \right)_E \) gives

\[ -\frac{C_E}{T} dT = \left( \frac{\partial S}{\partial E} \right)_T dE \]  

for the adiabatic change in temperature where the negative sign indicates that for a positive change in \( E \), the temperature change resulting from the negative slope of \( \left( \frac{\partial D_i}{\partial T} \right)_{X,E} \) is positive. Finally, we substitute Eq. 1.19 into Eq. 1.24 to arrive at

\[ \frac{dT}{dE_i} = -\frac{T}{C_E} \left( \frac{\partial D_i}{\partial T} \right)_{X,E} \]  

Equation 1.25 is a first order differential equation with a solution \( T(E) \) satisfying the initial condition \( T(E_0) = T_0 \) [16]. The heat capacity is, in principle slightly dependent on the electric field and strongly dependent on the temperature. Equation 1.25 cannot be solved analytically, though a convenient way to approximate the electrocaloric change in temperature is through the expression

\[ \Delta T = -\int_{E_0}^{E_0 + \Delta E} \frac{T}{C_E} \left( \frac{\partial D_i}{\partial T} \right)_{X,E} dE \]  

where the temperature dependence of the heat capacity is ignored since it is approximately constant over the small temperature changes considered. Strictly speaking, this is not mathematically correct since it treats the temperature variable \( T \) as a constant over the interval \( E_0 \rightarrow E_0 + \Delta E \) while calculating the change in temperature. Further simplifications can be introduced by using equations from classical electrostatics relating the displacement field to the electric field and the electric susceptibility. Recognizing that for ferroelectric materials the susceptibility, \( \chi_e \), is much greater than 1, we can approximate the displacement field as
\[ D = \epsilon_0 E + P_0 + \epsilon_0 \chi_e E = P_0 + \epsilon_0 (1 + \chi_e) E \quad \chi_e \gg 1 \Rightarrow D \approx P_0 + \epsilon_0 \chi E = P \] (1.27)

in the linear approximation where \( P_0 \) is the spontaneous polarization. Equation (1.26) can then be written as follows

\[
\Delta T = -\frac{T}{C_E} \int_{E_0}^{E_0+\Delta E} \left( \frac{\partial P_i}{\partial T} \right)_{X,E} dE_i
\] (1.28)

where we have removed \( T \) from the integral under the assumption that the change in temperature is small.

This equation is in practice easier to use since the polarization as a function of \( T \) is typically available from either experimental or computational data. Equation 1.28 can be integrated numerically using data for \( P(T) \) where the numerical integration should be done using a dense grid of points to ensure the highest degree of possible accuracy. The \( P(T) \) curves calculated at different \( E \) are fitted with a polynomial of arbitrary order.

1.3.3 Direct Method for Obtaining \( \Delta T_{ECE} \)

The most common experimental technique for directly measuring the adiabatic change in temperature in a material is differential scanning calorimetry, or DSC [10]. This method is relatively sensitive for detecting enthalpy changes on the order of 0.01 J/g and is able to operate on relatively small samples \( \sim 10 \) mg. The method works by imposing a constant heat flow \( \frac{dH_r}{dt} \) on the reference sample resulting in a linear temperature ramp. A feedback loop forces the sample temperature to follow the reference temperature which changes the sample power input \( \frac{dH_s}{dt} \). The differential power, the measured quantity, \( \frac{dH}{dt} = \frac{dH_s}{dt} - \frac{dH_r}{dt} \) is integrated as \( \int \frac{dH}{dt} dt \), providing the enthalpy related to the thermal process taking place in the sample. From the measured heat flow, the electrocaloric entropy or electrocaloric temperature change can be calculated [10].

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Greater accuracy and precision can be achieved using the modified high-resolution calorimetry technique which provides very precise control of the thermal shield, resulting in near adiabatic conditions, and high-resolution measurements of the sample temperature [10]. This method instead of attempting to control the heat flow applies an electric field at constant temperature (an applied electric field under adiabatic conditions consistent with the definition of the electrocaloric effect). The electrocaloric heat can then be obtained by integrating the equation \( Q = \int_0^E \left( \frac{dQ}{dE'} \right) dE' \). The entropy change can then be determined by \( \Delta S = \frac{Q}{T} \). To obtain \( Q(T) \), multiple measurements can be performed at different measurement temperatures from heating to cooling. The electrocaloric change in temperature is related to the changes in entropy as \( \Delta T = T \frac{\Delta S}{C(0)} \) where \( C(0) \) is a constant zero-field and temperature independent heat capacity [17].

1.3.4 Applications of Bulk Ferroelectrics/Antiferroelectrics

The number of publications concerning ferroelectrics and related materials has risen drastically over the last 50 years, mostly owing to the diversity of technological applications for which ferroelectrics are essential. Studies of antiferroelectrics is gaining attention given that antiferroelectrics possess many properties which are attractive for the design of technological devices. The device applications which ferroelectrics and antiferroelectrics are currently or could potentially be used for include piezoelectric actuators and sensors, pyroelectric infrared imaging devices, and energy converters, solid-state refrigerators, ferroelectric random access memory (FRAM), nanoscale terahertz sensors and image resolution, and high permittivity dielectric capacitors. The following is a brief introduction to the theoretical concepts and design behind some of these technologies.

Antiferroelectrics have a small to non-existent remnant polarization and large saturation polarization meaning that the energy storage capability is large in these materials with relatively small dielectric losses coming from their characteristic double hysteresis loops. The energy storage densities seen in antiferroelectric materials are around 50 - 60 J/cm\(^3\)
compared to values for materials like Pt-buffered silicon of 7 - 8 J/cm$^3$ [18]. It is the electric field induced transition from the antiferroelectric to ferroelectric state which makes antiferroelectric materials excellent prospects for energy storage applications such as charge capacitors. Could the use of antiferroelectric nanowires further enhance the energy storage capabilities for use in capacitors or possibly increase the tunability of such devices allowing them to operate in a wider range of temperatures?

Ferroelectrics can also be utilized for energy conversion applications including the conversion of thermal energy to electrical energy via the pyroelectric effect [19,20] and also the conversion of solar energy to electricity in ferroelectric based solar cells [21]. In a recent article published by Science Daily [22] based on a Nature Photonics article by Jonathan E. Spanier of Drexel University [23], the depolarizing field present in ferroelectric nanostructures promotes impact ionization and carrier multiplication, increasing the efficiency of the solar cells. This application of ferroelectric materials to inorganic solar cell research could help create more efficient energy conversion mechanisms allowing for cheaper clean energy in the future. Currently, one of the major drawbacks of solar power is its lack of efficiency; a problem that nanoscaling of photoelectronic devices could potentially remedy especially since the depolarizing field is largely enhanced and highly tunable in ferroelectric nanostructures.

The characteristic frequency of the soft mode for ferroelectric materials is typically $\sim \text{1 - 6~terahertz (THz)}$ which falls between microwaves and infrared light on the electromagnetic spectrum. This makes ferroelectric materials perfect for the design of THz sensing and imaging applications as they are highly responsive to light of this frequency, though other materials are also used for these purposes. These applications are useful for a number of tasks including: THz ray spectroscopy, tomography, image rendering, bioaffinity sensing, as well as detecting “hidden objects” such as explosive devices and illegal drugs through layers of plastic and cloth [24–27]. Terahertz imaging devices essentially work the same way optical imaging devices work except that the THz rays propagate through many materials while being strongly absorbed by others. A THz source produces the rays which end up
at the THz detector with the object to be imaged between the two. The THz detector then reproduces a false color visible light image of the object. In other situations the THz detector is used as a spectrograph with different chemical compounds being identified by their unique cross-section vs. frequency signature. The use of ferroelectric nanostructures such as nanowires and nanotubes could revolutionize the field of THz frequency sensing and imaging by allowing devices to become smaller, even down to the micro and nanoscales.

Ferroelectric materials are currently being used in the design of computer memory called FRAM standing for ferroelectric random access memory and products are commercially available [28, 29] as shown in Fig. 1.8. Ferroelectric RAM works by using an electric field to polarize a sample of ferroelectric material, typically PZT, to store a bit of information depending on the direction of polarization. The information can later be read out by measuring the current output associated with the reorientation of the dipoles, a destructive process requiring the data to be re-written after reading. Figure 1.8 also shows a schematic diagram of the structure of a FRAM memory cell. The advantages of FRAM over conventional RAM are its low power usage, faster write performance, exceedingly long data retention times \( \sim 10 \) years at 85\(^\circ\)C, and greater read/write endurance \( \sim 10^{10} - 10^{14} \) cycles [30, 31]. Much of the current focus in the area of ferroelectric RAM is in developing ways of miniaturizing memory chips to improve the memory density while maintaining all of the advantages over conventional RAM previously mentioned [32–35].

The pyroelectric effect is the coupling of temperature to the polarization in a material. This means it will generate an electrical signal as the temperature of the material is changed [38]. There are two types of pyroelectric devices which are characterized by whether or not the operating temperature coincides with the Curie temperature. Conventional pyroelectrics are poled materials and operate in a temperature range below the Curie temperature away from the phase transition. The other type are called the phase-switching pyroelectrics which

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2Figure 1.8(a). 1T FeRAM cell structure. Cyferz at English Wikipedia, 2007, via en.wikipedia. Used under Creative Commons Attribution-Share Alike 3.0 Unported license.

3Figure 1.8(b) has been reproduced with permission from Cypress Semiconductor.
operate near the transition temperature using a bias field to stabilize the pyroelectric effect [39]. The electrical response in a pyroelectric is proportional to the rate of change of the polarization with respect to the temperature and pyroelectric devices can detect radiation from soft x-ray to far infrared though the detectable frequency can be controlled with an optical filter [40]. The pyroelectric effect can be used in fire alarms, gas analyzers, intrusion detectors, differential detectors, microwave and x-ray detectors, biomedical imaging, and thermal imaging devices [40]. Figure 1.9 shows an example of a false color rendering taken using an infrared imaging device. The figure also shows a schematic diagram of an infrared sensor built using a pyroelectric chip to detect changes in current produced by the materials change in polarization due to variations in temperature.

For roughly a century vapor compression techniques have been the dominant means of refrigeration and engineering air conditioning systems. Though these methods are reliable and inexpensive, they are extremely inefficient and harmful to the environment and possibly to individuals. Devices which utilize the electrocaloric effect offer a very promising and economical alternative to vapor compression cooling. Other cooling methods have been proposed and developed, namely those relying on thermoelectric and magnetocaloric effects.

\footnote{Figure 1.9(a). Cold nose, warm touch - Thermography of Cat. yellowcloud from Germany, 2011, (flicker). This file is licensed under the Creative Commons Attribution 2.0 Generic license.}

\footnote{Figure 1.9(b). Pyroelectric detectors from InfraTec. InfraTec GmbH (www.infratec.de), 2011. This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license.}

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However these methods have a number of drawbacks. Thermoelectric devices are very inefficient requiring large amounts of input energy for little cooling power. Magnetocaloric coolers require large magnetic fields to operate and consequently, large and bulky magnets [10]. This makes the prospect of miniaturization much more difficult to realize. Electocaloric coolers display high efficiency similar to that found in magnetocaloric coolers, but offer additional benefits as solid-state-cooling devices, such as, compact size, less weight, and easy device integration [10]. The electocaloric effect was, for a long time, thought to be too small to be of any practical importance. However, due to the discovery of the giant electocaloric effect of $\sim 12 \text{ K}$ in PbZr$_{0.95}$Ti$_{0.05}$O$_3$ thin films close to the antiferroelectric-paraelectric phase transition at $225\degree\text{C}$, the field has received a renewed interest and electocaloric materials are now seen as the key to future solid-state-cooling devices [43]. A Physics Today Online article stated that “Such materials (ferroelectrics) thus hold promise for compact, small-scale, solid-state refrigeration” [44].

Though ECE solid-state refrigeration has not yet reached the production stage, the concept of a solid-state refrigerator which utilizes the electocaloric effect has been tested in the laboratory environment providing proof of principle [11]. One such experiment was done by designing a working electocaloric solid-state refrigerator which implemented and characterized the electocaloric Brayton cycle using doped BaTiO$_3$ ferroelectric layers in a multilayer...
capacitor as the cooling element [11]. The capacitor is mechanically actuated allowing it to move between a heat source and a heat sink making thermal contact with each sequentially. The application of a bias electric field is synchronized with the mechanical motions creating a complete and controlled thermodynamic cycle. A schematic representation of this device is shown in Fig. 1.10 along with the temperature as a function of time profile for a cycle using a 300 kV/cm electric field. The total change in temperature is moderate, roughly 0.8°C from peak to trough and the period of the temperature change is about 150 seconds. This experiment proves that the electrocaloric effect can indeed be used in the design of solid-state refrigerators which will help eliminate the need for inefficient and hazardous vapor-compression refrigerators in the future.

![Figure 1.10](image)

Figure 1.10: (a) Experimental setup used to demonstrate the electrocaloric Brayton cooling cycle in doped BaTiO₃ ferroelectric layers in a multilayer capacitor. (b) Temporal temperature profile upon application and removal of a bias field of magnitude 300 kV/cm [11].

1.4 Nanowire Fabrication & Characterization Techniques

Various experimental techniques have been developed to synthesize 1-D nanostructures with different compositions, morphologies, and device applications. This section provides a brief summary of the methods used to create perovskite nanowires and nanotubes as well as

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6Figure 1.10 has been previously published in Y. Jia and Y. Sungtaek Ju, “A solid-state refrigerator based on the electrocaloric effect,” *Applied Physics Letters*, vol. 100, p. 242901, 2012., and has been reproduced with permission from *Applied Physics Letters*
One of the more commonly employed ways to synthesize 1-D nanocrystals in a laboratory is hydrothermal synthesis. This involves the crystallization of various chemical substances, chemical precursors, by annealing from high temperature an aqueous solution at relatively high vapor pressures. As the mixture is slowly cooled, the water evaporates and the chemicals react to form the desired crystal structure. This method has been used extensively to synthesize perovskite 1-D nanostructures [45,46]. The hydrothermal method was also recently used to synthesize individual PbTiO$_3$ nanowires with diameters in the range 40 - 500 nm and lengths of $\sim 400 \mu$m [47]. These nanowires were found to exhibit a tetragonal structure with cell parameters $a = b = 3.905$ Å and $c = 4.156$ Å giving a $c/a$ ratio of 1.064. Another commonly synthesized ferroelectric nanowire is Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) with different compositions of Zirconium and Titanium. This was done recently by Wang et. al. using the hydrothermal growth mechanism producing nanowires with a stoichiometry of roughly Pb(Zr$_{0.17}$ Ti$_{0.83}$)O$_3$ with a monocrystalline tetragonal structure having their [001] direction along the axial direction of the nanowires. The polarization vector was along the axial direction of the nanowires as indicated from TEM-SAED analysis and the nanowires had average diameters of $\sim 50$ to several hundred nanometers [45].

Another technique often used to grow nanocrystals and nanowires, especially using titanium oxide, is the sol-gel method. In this process, inorganic molecules particularly monomers, are mixed in a colloidal suspension (sol) which is subsequently evolved into a continuous liquid phase through the process of gelation (gel). This method was used to synthesize PbTiO$_3$, Pb(Zr$_{1-x}$Ti$_x$)O$_3$, and BaTiO$_3$ nanowires [48, 49]. Nanowires can also be grown parallel to a substrate surface as rows of nanowires. This was done using the sol-gel method using a microwave oven to anneal the BaTiO$_3$ nanowires for 2.5 - 5.0 minutes [49]. The lengths of the nanowires depends on how long they are annealed and ranged from 100 nm to 900 nm. Such nanowire arrays could be used for high density computer memory applications where sections of the nanowires could store bits of information.

The sol-gel and hydrothermal methods can also be combined as was done recently to
create K$_x$Na$_{1-x}$NbO$_3$ (KNN) nanowires with average diameter and length of 150 nm and 4 $\mu$m respectively [50]. These nanowires have various concentrations of potassium and niobium at the A site; the average concentration was determined from XRF results to be K$_{0.52}$Na$_{0.48}$NbO$_3$. While KNbO$_3$ is a ferroelectric, NaNbO$_3$ is an antiferroelectric material so the nanowires are expected to have interesting properties. The chemical precursor used in the sol-gel/hydrothermal method was K$_{1-x}$Na$_x$NbO$_3$ which was heated to 190$^\circ$C for 12 hours. Figure 1.11(a) shows an SEM image of the free-standing KNbO$_3$ nanowires. Raman spectroscopy done at room temperature confirms the nanowires to be in the KNbO$_3$ orthorhombic phase. Figure 1.11(b) shows the dielectric constant as a function of temperature for the K$_{0.52}$Na$_{0.48}$NbO$_3$ nanowires heated to 220$^\circ$C for 12 hours. The dielectric response peaks at 555$^\circ$C to a value of about 825 in dimensionless units.

![Figure 1.11: (a) SEM image of KNbO$_3$ nanowires in the orthorhombic phase grown through the sol-gel/hydrothermal method. (b) Dielectric constant of KNbO$_3$ nanowire powder vs. temperature where the frequencies of the applied electric fields are 1 kHz (solid line) and 10 kHz (dashed line) [50].](image)

Ferroelectric nanowires have also been created not as free standing nanowires but as nanowire arrays grown on a substrate [51–54]. In one such study, PbTiO$_3$ nanowire arrays were synthesized combining a liquid phase deposition method with alumina templates [52]. The liquid phase deposition method causes metal oxides to form through hydrolysis on a

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7Figure 1.11 has been previously published in C. Fu, W. Cai, L. Zhou, H. Chen, and Z. Liu, “Synthesis of self-assembly BaTiO$_3$ nanowire by sol-gel and microwave method,” Applied Surface Science, vol. 255, p. 9444, 2009, and has been reproduced with permission from Elsevier Publishing
substrate which is immersed in an aqueous solution of the reactants. The result is an array of highly crystalline and highly ordered nanowires which are homogeneous in diameter and length. The template is used to order the nanowires and arrange them as an array but is later removed chemically. These nanowires were characterized using X-ray diffraction (XRD), and selected area electron diffraction (SAED) via transmission electron microscopy (TEM).

Another process used to form ferroelectric/antiferroelectric nanostructures is pulsed laser deposition, or PLD. This method was employed to create PbZrO$_3$ nanotubes using an aluminium oxide template to force the deposited atoms to conform to the correct morphology. A disk shaped target made of an alloy of ZrO$_2$ and PbO was created by sintering at 1200°C for 8 hours. In an environment of free oxygen atoms, a high powered laser beam was used to evaporate the material from the target creating a plume of atoms which were then deposited onto the surface of the template. The resulting PbZrO$_3$ nanotubes had an orthorhombic crystal structure with average diameters of around 185 - 235 nm [55].

Ferroelectric nanowires are commercially available through companies which produce relatively large quantities of highly pure samples through the methods previously described. Figure 1.12 (a) and (b) show examples of PbTiO$_3$ and Pb(Ti$_x$Zr$_{1-x}$)O$_3$ nanowires sold by the gram to anyone wanting to use them for experiment or industrial purposes. The technological applications of ferroelectric and antiferroelectric nanowires will be discussed in section 1.5.

![Figure 1.12](image_url) (a) Scanning Electron Microscopy images of commercially available PbTiO$_3$ [56] and (b) Pb(Ti$_x$Zr$_{1-x}$)O$_3$ nanowires [57].
1.5 Current/Future Applications of Ferroelectric & Antiferroelectric Nanowires

Very recently, owing to advancements in experimental growth and characterization techniques [50,55,58–60] as well as in computing power and computational algorithms [61], and pursuit of device miniaturization [15,33,62–64], ferroelectric/antiferroelectric nanostructures are receiving increased attention [55, 65–69]. These ferroelectric nanostructures have properties not seen in their bulk counterparts. Particularly, ferroelectric nanowires develop a spontaneous polarization at the nanoscale [63,70–73] mainly due to the influence of electrical boundary conditions [71] which do not affect bulk materials with a large bulk to surface ratio. The polarization can be manipulated through coupling to temperature (pyroelectricity) [19,74], external stress inducing a strain (piezoelectricity) [58,73,75] as well as through the application of an external electric field [13,39,76]. Nanowires also allow for device miniaturization [63,67,70–72,74,77–79] and exhibit exotic dipole patterns [67,70,71,78] not found in bulk. Ferroelectric and antiferroelectric nanowires could be used in the technological devices listed in section 1.3.4 and could possibly improve the functionality, efficiency, or operating range (temperature, frequency, ect.) of these devices. Additionally, some potential nanoscale applications rely on the smaller size and/or unique characteristics of ferroelectric/antiferroelectric nanowires in order to operate. Examples of these include nanoscale electrical power generators and energy converters, ultra-high density computer memory, and logical computing elements to replace silicon-based microprocessors.

Figure 1.13 depicts the temperature as a function of the change in entropy for both 1st order and 2nd order phase transitions. This illustrates the essential difference between 1st

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8Figure 1.12(a) has been previously published in Tomoaki Yamada, Jin Wang, Osami Sakata, Cosmin S. Sandu, Zhanbing He, Takafumi Kamo, Shintaro Yasui, Nava Setter, Hiroshi Funakubo, “Synchrotron X-ray diffraction study on a single nanowire of PX-phase lead titanate,” Journal of the European Ceramic Society, vol. 30, p. 3259, 2010, and has been reproduced with permission from Elsevier Publishing.

9Figure 1.12(b) has been previously published in Alexander Kvasov, Leo J. McGilly, Jin Wang, Zhiyong Shi, Cosmin S. Sandu, Tomas Sluka, Alexander K. Tagantsev, Nava Setter, “Piezoelectric enhancement under negative pressure,” Nature Communications, vol. 7, p. 12136, 2016, and has been reproduced with permission from Nature Publishing.
and 2nd order phase transitions as they relate to solid-state refrigeration design. The abrupt structural change associated with the 1st order phase transition (right-hand plot) causes a large change in the entropy at the Curie temperature resulting in a large electrocaloric change in temperature. In a 2nd order phase transition (left-hand plot) the change in entropy is smaller resulting in a weaker electrocaloric response, however the change in entropy is not abrupt but smooth and continuous. So for a 2nd order phase transition while the total entropy change is smaller, the effect takes place over a larger range of temperatures as evidenced by the larger distance between $T_C - \Delta T$ and $T_C + \Delta T$ as compared to the 1st order transition where the range is smaller. There is essentially a trade-off between the operational temperature range and the maximum electrocaloric response depending on whether the phase transition is more 1st order or more 2nd order. For bulk ferroelectrics, the transition is typically 1st order and little can be done to change this behavior. For ferroelectric nanowires, the order of the phase transition depends on the diameter of the nanowire with $T_C$ being decreased for thinner nanowires [63]. This allows for increased tuning capabilities in solid-state refrigeration devices where the operational temperature range can be different depending on the desired application. Nanowires of different diameters could also be combined into a single device to provide both a wide operational temperature range as well as a strong electrocaloric response.

Figure 1.13: Schematic presentation of $T (\Delta S)$ diagram for the electrocaloric material with the second order ferroelectric $\rightarrow$ paraelectric phase transition (left) and first order ferroelectric $\rightarrow$ paraelectric phase transition (right) [80].
Another potential technological application for which ferroelectric nanowires could prove useful is for nanoscale sensing and energy harvesting. Figure 1.14 gives an example of one such device designed using a dense array of BaTiO$_3$ nanowires. The figure shows a schematic diagram depicting the design of the device as well as the basic operating principle behind its function. After fabricating the accelerometer device, the nanowires were poled using a dc field of $\sim 75$ kV/cm across the two electrodes for 12 hours. This aligns the dipoles in the material along the direction of the electric field, the axial direction of the nanowires. The acceleration is then determined by mounting the sensor to a vibrating surface and measuring the induced piezoelectric potential resulting from the dynamic stress created by the inertia of the solder on the nanowires top surface. The applied stress must be dynamic in order for the device to maintain a piezoelectric voltage; if the stress is constant or zero then the voltage will vanish. The piezoelectric voltage also depends on the direction, amplitude, and frequency of the stress yielding the dynamic characteristics of the system. This coupled with the small size of the apparatus makes piezoelectric sensors of this sort ideal for use in nano-electromechanical systems as nanosensors and power harvesting devices [51].

![Figure 1.14: Scanning Electron Microscopy cross-sectional image of BaTiO$_3$ nanowires (a). Schematic diagram of sensor device using BaTiO$_3$ nanowire arrays (b). Schematic of piezoelectric voltage generation from nanowires (c). Polarization direction (P) represents the alignment direction of the dipoles. Application of dynamic stress ($\sigma(t)$) on nanowire arrays produces voltage ($V(t)$) generation. [51].](image)

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Figure 1.15 shows a schematic diagram of the experimental setup used to study the polarization reversal of a single BaTiO$_3$ nanowire synthesized through solution-phase decomposition of barium titanium isopropoxide [77]. The study reveals a possible avenue for utilizing individual ferroelectric nanowires for memory storage applications which could greatly improve the storage density. In the experiment, an SEM tip is used to manipulate the polarization domains in the $\sim$ 12 nm diameter nanowire by applying a voltage perpendicular to the axial direction. The length of the segment over which a given domain occupies is $\sim$ 30 nm and the polarization was still present after 5 days in a high vacuum environment illustrating that the bit of information are non-volatile in nature. Images of the polarization manipulation can also be seen in Fig. 1.15 showing how the polarization direction is switched using the SEM tip. Ferroelectric nanowires have the potential to be used in integrated circuits for performing calculations [81, 82] including a patent filed in 2000 [83].

![Schematic diagram](image)

Figure 1.15: (A) Schematic diagram showing how an SEM tip is used to apply a voltage and control the polarization in a BaTiO$_3$ nanowire. (a) Three-dimensional topographic image of a 12 nm diameter BaTiO$_3$ nanowire. (b)-(f) Successive three-dimensional EFM images showing that four distinct polarization domains can be independently manipulated by an external electric field. In these EFM images, the bright and dark colors correspond to a resonance frequency shift of +10 Hz and -10 Hz, respectively, and the white arrows indicate the polarization directions. The upward and downward polarization spots were written with $V_{\text{tip}}$ -10 V and $V_{\text{tip}}$ +10 V, respectively. The distance between the tip and the top surface of the nanowire was 10 nm during the writing procedure and 35 nm during the reading procedure [63].

11 Figure 1.14 has been previously published in A. Koka and H. A. Sodano, “High-sensitivity accelerometer composed of ultra-long vertically aligned barium titanate nanowire arrays,” *Nature Communications*, vol. 4, p. 2682, 2013., and has been reproduced with permission from Nature Publishing.

12 Figure 1.15 has been previously published in J. E. Spanier, A. M. Kolpak, J. J. Urban, I. Grinberg, L. Ouyang, W. S. Yun, A. M. Rappe, and H. Park, “Ferroelectric phase transition in individual single-crystalline
As the applications scale down, the question arises whether or not we can take these applications to the nanoscale, potentially even finding new applications at the nanoscale! The most efficient way to address the question is to begin with an understanding of fundamental properties at the nanoscale. Ferroelectric nanostructures have been successfully synthesized [47,52,84–87] and are commercially available [88,89]. Among the different ferroelectric and antiferroelectric nanostructures, nanowires appear as promising candidates since they can be synthesized in a variety of ways [50,55,90], could be grown in the form of arrays [52,91], and could potentially be used to improve existing technological devices or allow for the creation of technology which requires the unique properties of nanowires in order to function [32,46,62,92]. However, while very promising from a technological point of view, achieving a fundamental understanding of such nanowires is a rather challenging task given the limitation of experimental tools. Therefore, the goal of this study is to develop and use accurate computational methods in order to advance our fundamental understanding of ferroelectric and antiferroelectric nanowires and predict novel potential applications. Specifically we aim:

Objective 1: To develop and use computational tools that allow first-principles-based modeling of electric-field-induced phenomena in ferroelectric/antiferroelectric nanowires.

Objective 2: To explore the fundamental and applied aspects of ultra fast dynamics in ferroelectric/antiferroelectric nanowires induced by tailored electric fields.

Objective 3: To establish an understanding of the intrinsic features of the electrocaloric effect in ferroelectric/antiferroelectric nanowires and possible ways to enhance this effect.
2 Methodology

Computational methods can be broken up into two main categories: classical and quantum mechanical approaches; the essential difference being whether the algorithm uses classical or quantum mechanical laws. Another way of looking at the difference is that classical methods do not explicitly take into account the electronic contribution to the energy, they ignore the internal structure of the particles involved in the interactions, while quantum mechanical methods treat the system as a collection of interacting electrons and nuclei. Density functional theory is a quantum mechanical approach as it attempts to solve an approximation of the time independent Schrödinger equation for many-body systems. The effective Hamiltonian Monte Carlo and Molecular Dynamics methods used in the present work are classical approaches as they are derived from classical theories of Newtonian and statistical mechanics.

2.1 Density Functional Theory

First principle calculations have, in recent years, become a valuable tool for determining the ground state (0 Kelvin) properties of ferroelectric materials. These methods find approximate solutions to the Schrödinger equation, requiring no empirical input. Plane wave density functional theory (DFT) is a particular first-principles method capable of describing the properties of a well-defined collection of atoms in their ground state using a plane wave basis set. Using DFT, one can answer the question of how the energy of a material changes as the positions of the atoms are altered. We use plane wave density functional theory to perform 0 Kelvin ground state structure calculations.
2.1.1 Basics of DFT Methods

Density functional theory attempts a numerical solution to an approximation of the time-independent Schrödinger equation by solving what are known as the Kohn-Sham equations. For a typical collection of atoms or molecules, the electrons are much lighter than the nuclei to which they are bound and respond much faster to an external stimulus than do the nuclei. This allows for the use of the Oppenheimer Approximation; interactions involving the electrons and interactions involving the nuclei can be considered separate mathematically. For materials in which many particles (electrons and nuclei) interact with each other, the time-independent Schrödinger equation is written as a summation over all particles considered to become

\[
\psi \approx \sqrt{\sum_{i=1}^{N} \psi_i (r_i )} \psi \psi_1 (r) \psi_2 (r) \cdots \psi_N (r) \tag{2.2}
\]

where \( m \) is the mass of the electron and \( \psi \) is the electronic wave function that is a function of the spatial coordinates of the \( N \) electrons, \( \psi = \psi (r_1, \cdots, r_N) \). The three terms in brackets which make up the Hamiltonian operator are in order, the kinetic energy of each electron, the interaction energy between each electron and the collection of atomic nuclei, and the interaction energy between the different electrons. [93,94]

The motivation for this approximation is that the total number of electrons \( N \) is much larger than the number of nuclei \( M \) since each atom contains many electrons for every nucleus. For systems of practical interest, \( \sim 5 \) to several hundred atoms, the full wave functions would have 3 times the number of atoms dimensions which would render the problem intractable.
The third term in brackets in equation 2.1, the electron-electron interaction term, prevents an exact analytical solution. [93, 94]

The solution proposed by Hohenberg and Kohn was to consider the ground state electron density \( n(\mathbf{r}) \) rather than the probability \( \psi^*(\mathbf{r}_1, \cdots, \mathbf{r}_N) \psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) \) of measuring the \( N \) electrons with the set of coordinates \( \mathbf{r}_1, \cdots, \mathbf{r}_N \). Their first theorem specifically states: The ground-state energy from Schrödinger’s equation is a unique functional of the electron density given by

\[
n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})
\]  

(2.3)

where the summation is over all the discrete electron wave functions which are occupied by electrons. Their second theorem states: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. The exact form is not known; progress is made by using approximate forms in conjunction with the variational principle to numerically solve the Schrödinger equation. [93]

In DFT, the energy \( \mathcal{E}[\{\psi_i\}] \) is the minimum of a functional of the charge density \( n(\mathbf{r}) \) where we impose the constraint that \( \int n(\mathbf{r}) \, d\mathbf{r} = N \). The energy functional can be written as follows

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

(2.4)

where the terms (from left to right) include the electron kinetic energies, the Coulomb interactions between the electrons and the atomic nuclei, the Coulomb interactions between pairs of electrons, the Coulomb interactions between pairs of nuclei, and the exchange-correlation functional. This final term is defined to include all interactions which are not accounted for in the four previous terms. This is still however a many-body problem. Kohn
and Sham showed that to find the correct electron density, one can consider solving a single set of equations which involve only single electrons. These are referred to as the Kohn-Sham equations and take the form

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

(2.5)

The terms include, the kinetic energy of the electron, the interaction between the electron and the nuclei, the Hartree potential, and the exchange-correlation energy. The Hartree potential describes the Coulomb repulsion experienced by the electron in one of the Kohn-Sham equations due to the total electron density from all of the electrons. The solutions to the Kohn-Sham equations are single-electron wave functions which depend on three spatial variables.

2.1.2 Density Functional Theory Algorithm

The general algorithm, illustrated by Fig. (2.1), used to solve the Kohn-Sham equations to find the ground state electron density is as follows:

1. Define some initial trial electron density \( n(r) \)

2. The Kohn-Sham equations are solved using the trial electron density giving the single-particle wave functions.

3. The electron density is then calculated using these Kohn-Sham single-particle wave functions from the previous step with the expression \( n_{KS}(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \).

4. The two electron densities, \( n(r) \) and \( n_{KS}(r) \) are compared. If their difference is within some small, predetermined value, the convergence criterion is satisfied and \( n_{KS}(r) \) is the ground state electron density. Otherwise the electron density is updated and the process is repeated beginning at step 2.

As can be seen from Fig. (2.1), this is an iterative process in which the electron density is used to calculate the effective potential, which is then used to solve the Kohn-Sham equations from which we get the new electron density. This solving of the Kohn-Sham
Figure 2.1: Schematic diagram depicting the density functional theory algorithm.

Solving the Kohn-Sham equations requires the specification of an exchange-correlation functional $E_{XC} [\{\psi_i\}]$. Though the Hohenberg-Kohn theorem guarantees its existence, the exact form of this functional is unknown necessitating the use of approximations when defining the exchange-correlation functional. There is one case in particular for which the Kohn-Sham equations can be solved for exactly, the uniform electron gas. The exchange-correlation functional is set as the known exchange-correlation potential for a uniform electron gas at the
electron density found at that position. This approximation is referred to as the local density approximation (LDA) since it uses only the electron density in the vicinity of the points considered [95]. While \( V_{XC} (\mathbf{r}) \) is by definition the exact exchange-correlation functional for the homogeneous electron gas, it works well to describe highly homogeneous systems and serves as a good starting point for more complex systems. This is one of the functionals used in our research, along with another well known class of functionals called the generalized gradient approximation or GGA. The GGA uses information about the local electron density coupled with the local gradient in the electron density to solve the Kohn-Sham equations.

The Hellmann-Feynman theorem, in its most general form, relates the derivative of the total energy of the system \( \mathcal{E} \) with respect to a parameter \( \lambda \) to the expectation value of the derivative of the Hamiltonian \( \hat{H} \) with respect to the same parameter. The equivalent statement in equation form is

\[
\frac{dE_\lambda}{d\lambda} = \int \psi_\lambda^* \frac{d\hat{H}_\lambda}{d\lambda} \psi_\lambda d^3r. \tag{2.6}
\]

If the parameter is taken to be the ionic displacement \( \mathbf{R} \) and the spatial distribution of the electrons is known, the interatomic forces can be calculated using electrostatics [96]. These are referred to as the Hellmann-Feynman forces and are one of the most important quantities which are calculated in DFT.

Another useful technique to calculate ground state properties is density functional perturbation theory (DFPT) in which the interatomic force constant matrix is calculated explicitly through knowledge of the ground-state charge density, \( n (\mathbf{r}) \), as well as of its linear response to a distortion of the nuclear geometry, \( \frac{\partial n (\mathbf{r})}{\partial \mathbf{R}} \) [97]. This method works to calculate such properties as the Born effective charge (\( Z^* \)), the optical dielectric constant (\( \epsilon_\infty \)), or the elastic constants (\( B_{11}, B_{12}, B_{44} \)) where a perturbation, electric field or strain, is applied to the system and the relationship between the desired properties and the perturbation are known. To achieve accurate results, the perturbation must be small.

Calculation of phonon modes is also done using DFPT. The key approximation used in
this theory is the harmonic approximation. This states that if the perturbations applied to a system are small such that the system remains close to equilibrium, the energy can be accurately represented by the lowest order terms in a Taylor series about the equilibrium position. This allows the derivation of a secular determinant of the form

\[
\left| D_{\alpha\beta,ij}(k) - \delta_{\alpha\beta}\delta_{ij} \omega^2(k) \right| = 0 \quad (2.7)
\]

where \(D_{\alpha\beta,ij}(k)\) is the dynamical matrix, related to the interatomic force constants matrix by a factor of the atomic masses, \(\alpha\) and \(\beta\) denote atomic coordinates, \(i\) and \(j\) are atomic indices, and \(\omega(k)\) are the phonon frequencies. The solution to this equation yields the normal modes of the lattice. The perovskite ABO\(_3\) unit cell is modeled using a 5 atom unit cell. This means that the IFC matrix will have dimensions of 15x15 resulting in 15 eigenvalues (phonon modes) in total. Due to degeneracy, there are only 5 distinct eigenvalues and 5 corresponding eigenvectors. For ferroelectrics, we are only concerned with 2 of these phonon modes, the lowest energy transverse optical mode and the long-wavelength acoustic mode. These correspond to the soft mode and the strain acoustic modes respectively. How these modes are identified in practice will be discussed in the chapter concerning the parametrization of KNbO\(_3\).

### 2.2 Effective Hamiltonian Method

Around 1994, a macroscopic computational approach that derived its origin in the soft mode theory of ferroelectrics was developed and applied to study prototypical ferroelectrics like BaTiO\(_3\) and PbTiO\(_3\) [3, 5, 98, 99]. This method is now known as the effective Hamiltonian. It has since been extended to include quantitative descriptions of solid solutions like Pb(Ti\(_x\)Zr\(_{1-x}\))O\(_3\) [100,101] as well as to include antiferrodistortive [61,102] and magnetic [103] degrees of freedom useful for describing materials like PbZrO\(_3\) and BiFeO\(_3\) respectively.

In computational physics, it is advantageous to deduce the simplest Hamiltonian possible
which still encapsulates all relevant features and characteristics of the system being studied. In this way, the intrinsic properties of the system can be probed and its statistical behavior studied. From this understanding, experimental deviations from this fundamental behavior can be interpreted as being due to small deviations of a real-system Hamiltonian. In the effective Hamiltonian method we first identify the most important degrees of freedom in a ferroelectric material, and then, based on symmetry arguments, we construct the internal energy of the system as a function of these degrees of freedom and their interactions. [104]

### 2.2.1 General Concept & Approximations

For a system in thermodynamic equilibrium, the partition function which can be found from the total potential energy function, can be used to determine the statistical properties of the system at finite temperature. From statistical mechanics the partition function is

$$Z = \frac{1}{N! h^{3N}} \int \cdots \int e^{-\beta \hat{H}(\mathbf{r}, \mathbf{q})} d\mathbf{r} d\mathbf{q} \quad (2.8)$$

where $\hat{H}$ is the Hamiltonian of the $N$-body system, $h$ is Planck’s constant [105]. The contribution to the partition function, Eq. 2.8, decreases exponentially with increasing energy. This makes it possible to obtain an accurate partition function while only including in the summation terms resulting from low energy contributions. For ferroelectric perovskites, these low energy configurations are due to small ionic displacements from strain deformations of the crystal structure as compared to the prototypical cubic structure. That is, all ionic configurations with significant contributions to the partition function will be close to the cubic structure [3]. This assumption allows for the energy surface to be approximated by a low-order Taylor series expansion in displacements from the cubic structure.

An exact analytical description of ferroelectricity would require 3 acoustic mode and 12 optical normal-mode coordinates per k-point in reciprocal space. However, experimentally measured and first-principles calculated phonon dispersion curves suggest that only the lowest energy transverse optical (TO) modes (soft modes) and long wavelength acoustic
phonons (strain variables) make an appreciable contribution to the phonon density of states at low energies. The softening, or shifting to lower frequencies, is known to occur during a ferroelectric phase transition along with the appearance of a strain in the crystal. Our second approximation is to assume that the ferroelectric phase transition can be well described by considering only the soft mode and strain variables in our calculations and the effective Hamiltonian depends on these variables only. This reduces the degrees of freedom per unit cell from 15 to 6. [3,99]

In this methodology, the zone center ($k=0$) soft mode is described over the entire Brillouin Zone as a collective motion of local modes. The eigenvector of the soft mode is given by

$$
\Xi_{\text{soft}} = \begin{pmatrix}
\xi_A \\
\xi_B \\
\xi_{O\parallel} \\
\xi_{O\perp}
\end{pmatrix}
$$

(2.9)

where $\xi_A$, $\xi_B$, $\xi_{O\parallel}$, and $\xi_{O\perp}$ are the normalized displacements for the A and B ions as well as the oxygen atoms, located at the cube faces, distinguished in terms of their position relative to the cube face with $O\parallel$ being parallel to the cube face and $O\perp$ perpendicular. For perovskite ABO$_3$ ferroelectrics, the local mode is either centered on the A or the B ion. This is determined by comparing the normalized displacements associated with the A and B ions in the soft mode. For an A-centered material like PbTiO$_3$, $\xi_A$ will be larger than $\xi_B$ and visa versa for B-centered materials [5]. In the case of an B-centered system, the local mode is then described as a motion of the central B atom by an amount $\xi_B$, the eight neighboring A atoms by amounts $\frac{\xi_A}{8}$, and the six neighboring O atoms by amounts $\frac{\xi_{O\parallel}}{2}$ or $\frac{\xi_{O\perp}}{2}$ along the $j$th Cartesian direction. An arbitrary zone-center soft mode is then described as a linear superposition of these local modes having identical amplitudes in every cell. The local dipole moment of a given unit cell is proportional to the local mode of that cell and the macroscopic polarization is proportional to the sum of all the individual local modes in the supercell. This
is shown in Fig. 2.2 for the case a B-centered local mode, examples of materials having this local mode centering include barium titanate and lead zirconate titanate. [3,98,99]

Figure 2.2: The relationship between the macroscopic soft mode and the microscopic local mode in perovskite ABO$_3$ ferroelectrics [106]. Note that the local mode is centered at the B ion.

### 2.2.2 Total Energy Landscape of a Prototypical Ferroelectric

In the framework of the effective Hamiltonian the total energy of a ferroelectric material is given by [3]

$$E_{tot} = E_{self} \{u\} + E_{dpl} \{u\} + E_{short} \{u\} + E_{elas} \{\eta\} + E_{int} \{u, \eta\}$$

where respectively $u$ and $\eta$ are the local soft modes and the local strain variables, $E_{self}$ is the energy of an isolated local mode, $E_{dpl}$ is the dipole-dipole interaction between local modes of different unit cells, $E_{short}$ is the short-range interaction between local modes, $E_{elas}$ is the elastic energy, the coupling energy between the local strain and the local mode is given by $E_{int}$. [3,99]. I will now describe each term of the effective Hamiltonian in detail.

The first term in Eq. (2.10) describes the sum of the self energies of single isolated local modes at unit cell $R_i$ with amplitude $u_i$ relative to the perfect cubic structure and is given

\footnote{Figure 2.2 has been previously published in Q. Zhang, Properties of Ferroelectric Perovskite Structures under Non-equilibrium Conditions Graduate School Theses and Dissertations, January 2011., and has been reproduced with permission from Dr. Qingteng Zhang}
by

$$\mathcal{E}^{\text{self}} (\{\mathbf{u}\}) = \sum_{i} \mathcal{E} (\mathbf{u}_i)$$  \hspace{1cm} (2.11)

and is a function of the local mode only. Given that the reference structure is cubic, only even-order terms are included in the summation which is terminated at 4th order yielding the expression

$$\mathcal{E} (\mathbf{u}_i) = \kappa_2 u_i^2 + \alpha u_i^4 + \gamma (u_{ix}^2 u_{iy}^2 + u_{iy}^2 u_{iz}^2 + u_{ix}^2 u_{iz}^2).$$  \hspace{1cm} (2.12)

where \(u_i = |\mathbf{u}_i|\) and \(\kappa_2, \alpha, \) and \(\gamma\) are expansion parameters which are determined from first-principles calculations.

The term \(\mathcal{E} (\mathbf{u}_i)\) contains both harmonic and anharmonic contributions; the anharmonic terms being necessary since ferroelectricity is intrinsically anharmonic phenomenon. (see fig 1.4 and 1.3 for explanation)

The second term in the total energy expression describes the long-range dipole-dipole interaction between local modes. Only dipole-dipole interactions are considered since higher order terms tend to be of short-range and their effect will be quantified in the short-range interaction term. For a unit cell \(i\), the associated dipole moment of that cell is \(d_i = Z^* \mathbf{u}_i\), where \(Z^*\) is the Born effective charge for the soft mode and is given by

$$Z^* = \xi_A Z_A^* + \xi_B Z_B^* + \xi_{O||} Z_{O||}^* + 2 \xi_{O\perp} Z_{O\perp}^*$$  \hspace{1cm} (2.13)

where \(Z_A^*, Z_B^*, Z_{O||}^*, Z_{O\perp}^*\) are the Born effective charges for the individual ions.

From classical electrostatics, the dipole interaction energy

$$\mathcal{E}^{\text{dip}} (\{\mathbf{u}\}) = \frac{Z^2}{\epsilon_\infty} \sum_{i<j} \frac{\mathbf{u}_i \cdot \mathbf{u}_j - 3 \left( \mathbf{\hat{R}}_{ij} \cdot \mathbf{u}_i \right) \left( \mathbf{\hat{R}}_{ij} \cdot \mathbf{u}_j \right)}{R_{ij}^3}$$  \hspace{1cm} (2.14)

where \(\epsilon_\infty\) is the optical dielectric constant of the material, \(R_{ij} = |\mathbf{R}_{ij}|, \mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j\), and
\( \hat{R}_{ij} = R_{ij}/R_{ij} \). For systems with periodic boundary conditions, equation 2.14 is not useful for calculation of the dipole-dipole interaction; we instead use an equation which utilizes an Ewald construction in its derivation. An Ewald-Kornfeld summation explicitly accounts for the periodic boundary conditions necessary for simulating ferroelectric bulk in which the supercell is replicated along all three Cartesian directions. Formulating the dipole-dipole interaction in this way takes into consideration the wrap-around effect; a dipole existing at the boundary of the supercell interacts with neighboring dipoles that exist in the replicated supercells along all directions for which periodic boundary conditions are applied. The expression used to calculate the dipole-dipole interaction is

\[
E_{\text{dpl}} = \frac{2Z^2}{\epsilon_\infty} \sum_{\beta \neq 0} \frac{1}{|G|^2} \exp \left( -\frac{|G|^2}{4\lambda^2} \right) \sum_{ij} (G \cdot u_i) (G \cdot u_j) \cos(G \cdot \hat{R}_{ij}) \sum_i \lambda^3 u_i^2 \pi \sum_{ij} \left[ Q_{ij,\alpha,\beta} u_i u_j \right] \tag{2.15}
\]

where \( \Omega_c \) is the volume of the supercell and \( G \) is the reciprocal lattice vector. The sum in equation 2.15 is terminated such that zone-center \( (k = 0) \) modes of the supercell will represent physical \( \text{TO}(\Gamma) \) modes. Also, the decay constant \( \lambda \) is chosen to be small enough such that the real-space summation can be entirely neglected. The calculation of \( E_{\text{dpl}} \) is the most time consuming part of the calculations in the effective Hamiltonian model. To reduce the computational load, a well justified approximation is implemented. The \( R_{ij} \) term in the denominator of equation 2.14 is in principle strain dependent. However, this dependence can be ignored since the equations representing the inter-site interactions between local modes are expanded only up to harmonic order and strain-induced changes of the dipole-dipole interaction are of greater than 2nd order [3]. To achieve this, all the reciprocal lattice vectors \( G \) and all the atomic position vectors \( R_i \) remain fixed throughout the simulation. The dipole energy terms thus becomes

\[
E_{\text{dpl}} = \sum_{ij,\alpha,\beta} Q_{ij,\alpha,\beta} u_i u_j \tag{2.16}
\]
with

\[
Q_{ij,\alpha\beta} = \frac{2Z^2}{\epsilon_\infty} \left[ \frac{\pi}{\Omega_c} \sum_{G \neq 0} \frac{1}{|G|^2} \exp \left( -\frac{|G|^2}{4\lambda^2} \right) \cos (G \cdot R_{ij}) G_\alpha G_\beta - \frac{\lambda^3}{30\pi} \delta_{\alpha\beta} \delta_{ij} \right] 
\]  

(2.17)

where \(\alpha\) and \(\beta\) denote Cartesian coordinates. The matrix \(Q\) is a constant and is calculated initially and stored for later use for calculation of the dipole-dipole interaction. [3]

The short-range interaction term accounts for the short-range interactions between local modes. This energy term comes from differences of the short-range repulsion and electronic hybridization between two adjacent local modes and two isolated local modes. Combined with the dipole-dipole interaction, this determines the soft mode energy away from the zone center \((k = 0)\). The equation quantifying the short-range interaction is

\[
E^{\text{short}}(\{u\}) = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} J_{ij,\alpha\beta} u_{i\alpha} u_{j\beta} 
\]  

(2.18)

where the coupling matrix \(J_{ij,\alpha\beta}\) is a function of \(R_{ij}\) and decays quickly with increasing \(|R_{ij}|\). We consider up to 3rd nearest neighbor since interactions between further neighbors makes a much smaller contribution to the total energy than does the dipole-dipole energy and can thus be neglected. The interaction matrix \(J_{ij,\alpha\beta}\) is greatly simplified due to cubic symmetry with the interaction parameters calculated from the following expressions

first NN : \(J_{ij,\alpha\beta} = \left[ j_1 + (j_2 - j_1) |\hat{R}_{ij,\alpha}| \right] \delta_{\alpha\beta} \),  

(2.19a)

second NN : \(J_{ij,\alpha\beta} = \left[ j_4 + \sqrt{2} (j_3 - j_4) |\hat{R}_{ij,\alpha}| \right] \delta_{\alpha\beta} + 2 j_5 \hat{R}_{ij,\alpha} \hat{R}_{ij,\beta} (1 - \delta_{\alpha\beta}) \),  

(2.19b)

third NN : \(J_{ij,\alpha\beta} = j_6 \delta_{\alpha\beta} + 3 j_7 \hat{R}_{ij,\alpha} \hat{R}_{ij,\beta} (1 - \delta_{\alpha\beta}) \)  

(2.19c)

where \(\hat{R}_{ij,\alpha}\) is the \(\alpha\) component of \(R_{ij}/R_{ij}\). The physical meaning of the coefficients
$j_1, j_2, \ldots, j_7$ is illustrated in Fig. 2.3 which depicts the positions of the neighbors and the directions of the "π"-like interactions between them.

Figure 2.3: Illustration of inter-site dipole interactions between 1st, 2nd, and 3rd nearest neighbors. [3].

To describe the state of elastic deformations of the ferroelectric crystal, we use local strain variables $\eta_l (R_i)$ where the Voigt notation is used ($l = 1, \ldots, 6$) and $R_i$ labels the cell center (B site). The term $\mathcal{E}^{\text{elas}}$, the elastic energy, is separated into two contributions, the homogeneous and inhomogeneous strain.

$$\mathcal{E}^{\text{elas}} \{\eta_l\} = \mathcal{E}^{\text{elas}} \{\eta_{1,l}\} + \mathcal{E}^{\text{elas}} \{\eta_{H,l}\}$$

(2.20)

The total elastic energy is expanded to quadratic order where the homogeneous strain energy is given by

$$\mathcal{E}^{\text{elas}} \{\eta_{H,l}\} = \frac{N}{2} B_{11} (\eta_{H,1}^2 + \eta_{H,2}^2 + \eta_{H,3}^2) + N B_{12} (\eta_{H,1} \eta_{H,2} + \eta_{H,2} \eta_{H,3} + \eta_{H,3} \eta_{H,1}) + \frac{N}{2} B_{44} (\eta_{H,4}^2 + \eta_{H,6}^2 + \eta_{H,6}^2).$$

(2.21)

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14Figure 2.3 has been previously published in W. Zhong, D. Vanderbilt, and K. Rabe, “First-principles theory of ferroelectric phase transitions for perovskites: The case of BaTiO$_3$,” Physical Review B, vol. 52, p. 6301, 1995., and has been reproduced with permission from the American Physical Society.
The homogeneous strain is calculated by introducing six homogeneous strain components \( \eta_{H,l} \) which allow the entire simulation cell to vary in shape and size. The constants \( B_{11}, B_{12}, \) and \( B_{44} \) are the elastic constants of the material expressed in energy units \( (B_{11} = a^3 C_{11}) \) and \( N \) is the number of primitive cells in the supercell. For the inhomogeneous strain deformations, the six variables per unit cell \( \{ \eta_l(R_i) \} \) are not independent, they are found from three independent displacement variables (local strain variables related to the acoustic phonons) per unit cell. These are the dimensionless displacements \( \mathbf{v}(R_i) \) which are in units of the lattice constant \( a \) defined at the cell corner (A sites) as \( R_i + (a/2, a/2, a/2) \). To satisfy the requirement of invariance under translations and rotations of the crystal as a whole, the energy is expanded in scalar products of differences between the \( \mathbf{v}(R_i) \). Additionally, the cubic crystal symmetry greatly reduces the number of independent parameters in the expansion. The inhomogeneous strain energy is then defined in terms of these dimensionless displacement variables as

\[
\mathcal{E}_I^{\text{elas}} = \sum_i \left\{ \gamma_{11} [v_x(R_i) - v_y(R_i \pm x)]^2 + \gamma_{12} [v_x(R_i) - v_x(R_i \pm x)][v_y(R_i) - v_y(R_i \pm y)] \\
\quad + \gamma_{44}[v_x(R_i) - v_x(R_i \pm y) + v_y(R_i) - v_y(R_i \pm x)]^2 \right\} + \text{cyclic permutations},
\]

(2.22)

which corresponds to bond stretching, bond correlation, and bond bending, respectively. Here, \( x \equiv a\hat{x}, y \equiv a\hat{y}, z \equiv a\hat{z} \) and \( \pm \) indicates multiple terms to be summed. The \( \gamma \) coefficients are related to the elastic constants by \( \gamma_{11} = B_{11}/4, \gamma_{12} = B_{12}/8, \) and \( \gamma_{44} = B_{44}/8 \). Defining the inhomogeneous contribution to the elastic deformations in terms of the variables \( \mathbf{v}(R_i) \) keeps the acoustic phonon frequencies well behaved throughout the entire Brillouin zone.

The \( \mathcal{E}^{\text{int}}(\{u\}; \{\eta\}) \) term describes the coupling between the local mode and the strain and includes contributions from both homogeneous and inhomogeneous strain variables \( \eta_l(R_i) = \eta_{H,l}(R_i) + \eta_{I,l}(R_i) \). As all ferroelectrics and antiferroelectrics are piezoelectrics, the soft phonon mode is coupled to the long-wavelength acoustic phonon mode meaning
that a ferroelectric or antiferrodistortive phase transition is accompanied by the onset of a strain. Conversely, the presence of a strain can induce a ferroelectric or antiferrodistortive phase transition or increase the magnitude of polar and non-polar distortions. Physically, the $\mathcal{E}^{\text{int}} \left( \{u\}, \{\eta\} \right)$ interaction quantifies the coupling between the soft mode and the acoustic mode allowing the Hamiltonian to capture this piezoelectric behavior. The equation which describes the on-site coupling between the elastic deformation and the local modes is given by

$$\mathcal{E}^{\text{int}} \left( \{u\}, \{\eta\} \right) = \frac{1}{2} \sum_i \sum_{l,\alpha,\beta} B_{l\alpha\beta} \eta_l \left( \mathbf{R}_i \right) u_\alpha \left( \mathbf{R}_i \right) u_\beta \left( \mathbf{R}_i \right) \quad (2.23)$$

where $B_{l\alpha\beta}$ is the coupling constant, $\alpha$ and $\beta$ represent Cartesian coordinates. As a result of cubic symmetry, there are only three independent coupling constants $B_{l\alpha\beta}$, specifically:

\begin{align*}
B_{1xx} &= B_{2yy} = B_{3zz}, \quad (2.24a) \\
B_{1yy} &= B_{1zz} = B_{2xx} = B_{2zz} = B_{3xx} = B_{3yy}, \quad (2.24b) \\
B_{4yz} &= B_{4zy} = B_{5xz} = B_{5zx} = B_{6xy} = B_{6yx}. \quad (2.24c)
\end{align*}

The strain tensor contains both homogeneous and inhomogeneous parts

$$\eta_l \left( \mathbf{R}_i \right) = \eta_{H,l} \left( \mathbf{R}_i \right) + \eta_{I,l} \left( \mathbf{R}_i \right). \quad (2.25)$$

The inhomogeneous strain variables, $\eta_{I,l} \left( \mathbf{R}_i \right)$, are expressed in terms of the local displacement vectors $\mathbf{v}$ as follows. Six average differential displacements are defined which are associated with the $\mathbf{R}_i$ as

$$\Delta v_{xx} = \sum_{d=0,y,z,y+z} \left[ v_x \left( \mathbf{R}_i - \mathbf{d} - \mathbf{y} \right) - v_x \left( \mathbf{R}_i - \mathbf{d} \right) \right], \quad (2.26)$$
\[ \Delta v_{xy} = \sum_{d=0,y,z,y+z} \left[ v_y (R_i - d - y) - v_y (R_i - d) \right], \quad (2.27) \]

and their cyclic permutations where \( v(R_i) \) is associated with position \( R_i + (a/2, a/2, a/2) \) [107]. This implies that \( \eta_{I,1}(R_i) = \Delta v_{xx}/4, \eta_{I,4}(R_i) = (\Delta v_{yz} + \Delta v_{zy})/4 \), etc.

The existence of dipoles in infinite bulk ferroelectrics creates alternating positive and negative charges which, when averaged over space, cancel out resulting in a zero net charge inside the material. In ferroelectric nanostructures, the dimensions of the sample are finite in 1 or more directions, creating a surface. Experimentally, this surface is present in a bulk sample though the ratio of surface to bulk is negligibly small and the sample can be modelled as infinite. The presence of a surface in a nanostructure creates an abrupt termination of the dipole pattern resulting in a build-up of positive and negative charge on either end of the sample. This point is illustrated in Fig. 2.4 with a net positive (negative) charge at the top (bottom) surface. The difference in potential created by the surface charge gives rise to a depolarizing electric field in the interior of the sample. The direction of this field is opposite to that of the polarization; the field attempts to destroy it. A common method for modelling the depolarizing field in dielectrics is to approximate the geometry of the sample as an ellipsoid where the components of the polarization \( P = P_x \hat{x} + P_y \hat{y} + P_z \hat{z} \) are referred to the principal axes of the ellipsoid. The components of the depolarizing field are then given by the following equations

\[ E_x^{(dep)} = -\frac{N_x P_x}{\varepsilon_0}; \quad E_y^{(dep)} = -\frac{N_y P_y}{\varepsilon_0}; \quad E_z^{(dep)} = -\frac{N_z P_z}{\varepsilon_0} \quad (2.28) \]

where \( N_x, N_y, N_z \) are called the depolarization factors which are all positive and satisfy \( N_x + N_y + N_z = 1 \) [6]. This formulation allows for straightforward calculations of the depolarization factors for the limiting cases of 2-D, 1-D, and 0-D nanostructures. Approximating the nanowire as a long circular cylinder oriented along the z axis, the depolarization factors are \( N_x = N_y = 1/2 \) and \( N_z = 0 \). This means the depolarizing field will have non-zero
components in the transverse directions and no component along the axial or longitudinal direction, of the nanowire.

The values for these depolarization factors represent theoretical limits. In our effective Hamiltonian simulations of nanowires, we apply some amount of surface charge compensation which decreases the strength of the depolarizing field, reducing effective $N_x$ and $N_y$.

To calculate the depolarizing energy in low-dimensional ferroelectrics, in our case ferroelectric nanowires, we recognize the fact that a system under perfect open-circuit (OC) electrical boundary conditions exhibits a maximum depolarizing field (if the polarization lies along a non-periodic direction), while ideal short-circuit (SC) electrical boundary conditions leads to a complete screening of charges at the ferroelectric nanostructures surfaces which fully annihilates any depolarizing field. Technically, this means that the depolarizing energy and field experienced by the ferroelectric nanostructure should involve a difference between the dipole-dipole interactions associated with these two extreme electrical boundary conditions. Within the effective Hamiltonian approach, the energy of the dipole-dipole interaction in any ferroelectric system can be written in the form [71]

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Figure 2.4 has been previously published in Q. Zhang, Properties of Ferroelectric Perovskite Structures under Non-equilibrium Conditions Graduate School Theses and Dissertations, January 2011., and has been reproduced with permission from Dr. Qingteng Zhang.
\[ \mathcal{E}_{\text{dep}}^{(D)} = \frac{Z^2}{2V} \sum_{\alpha\beta,ij} Q_{\alpha\beta,ij}^{(S,D)} u_{\alpha}(r_i) u_{\beta}(r_j), \] (2.29)

where \( D=3,2,1 \) represents a system periodic in 3, 2, and 1 directions, respectively; \( D=0 \) corresponds to non-periodic systems, and \( V \) is the volume. For bulk systems periodic in three directions, the \( Q_{\alpha\beta,ij}^{(S,3)} \) matrix is given by Eq. 2.17. For ferroelectric nanowires the \( Q_{\alpha\beta,ij}^{(S,1)} \) matrix is \[71\]

\[ Q_{\alpha\beta,ij}^{(S,1)} = 2 \sum_G G^2 \cos(G \cdot z_{ij}) \left\{ K_0(G \rho_{ij}) \delta_{\alpha z} \delta_{\beta z} + \frac{1}{\rho_{ij}} K_1(G \rho_{ij}) - \frac{1}{\rho_{ij}^2} K_2(G \rho_{ij}) \rho_{\alpha,ij} \rho_{\beta,ij} \right\} - 2 \sum_G G \sin(G \cdot z_{ij}) K_1(G \rho_{ij}) \rho_{ij}^{-1} G_{\alpha,ij} \rho_{\beta,ij} + \frac{1}{a^3} \] (2.30)

for nanowires which are periodic along only one direction (\( z \) in our case) where \( \lambda \) is referred to as the Ewald parameter. The Kronecker delta symbol is denoted by \( \delta_{ij} \), \( \rho_{ij} \) and \( z_{ij} \) are the projections of \( r_{ij} \) (the vector connecting the atomic sites \( i \) and \( j \)) on the \( \{x, y\} \) plane and the \( z \) axis respectively (i.e. \( r_{ij} = \rho_{ij} + z_{ij} \)), \( \rho_{ij} = |\rho_{ij}| \), and \( z_{ij} \) is the component of the \( z_{ij} \) vector which lies along the \( z \) axis. The supercell length in the \( z \) direction is given by \( a \) and \( K_n \) are the modified Bessel’s functions. We exclude contributions from \( \rho_{ij}=0 \) in \( Q_{\alpha\beta,ij}^{(S,1)} \) and the prime on the right-hand side of \( Q_{\alpha\beta,ij}^{(S,1)} \) indicates that the term \( n=0 \) has to be excluded when \( i=j \). \[68\]

Combining equation 2.29 with the \( Q \) matrix defined by equation 2.30 describe dipolar interactions in nanowires under ideal OC conditions. The dipole-dipole energy corresponding to ideal SC boundary conditions is that described by the \( D=3 \) \( Q \) matrix of Eq. 2.17. The maximum depolarizing energy per unit volume \( \mathcal{E}_{\text{dep}}^{(D)} \) in a ferroelectric nanowire is thus

55
calculated as the difference in dipole-dipole energies between perfect OC and SC electrical boundary conditions via the equation

$$
\varepsilon^{(1)}_{\text{dep}} = \varepsilon^{(1)}_{\text{dip}} - \varepsilon^{(3)}_{\text{dip}} = \frac{1}{2V} \sum_{\alpha\beta,ij} \left[ Q^{(S,1)}_{\alpha\beta,ij} - Q^{(S,3)}_{\alpha\beta,ij} \right] p_{\alpha}(r_i) p_{\beta}(r_j)
$$

(2.31)

where \( Q^{(S,1)}_{\alpha\beta,ij} \) and \( Q^{(S,3)}_{\alpha\beta,ij} \) are given by equations 2.17 and 2.30 respectively.

Specifically the surface charge screening is achieved by mimicking a screening of the maximum depolarizing field, with the magnitude of this screening being controlled by the coefficient \( \beta \) as

$$
\mathcal{E}^{\text{screen}} = Z^* \beta \sum_i \langle \mathbf{E}_{\text{dep}} \rangle \cdot \mathbf{u}(r_i)
$$

(2.32)

where \( \mathbf{E}_{\text{dep}} \) is the average depolarizing electric field given by [71]

$$
\langle \mathbf{E}_{\text{dep}} \rangle = \frac{-1}{Ng \varepsilon_\infty Z^*} \sum_j \frac{\partial \varepsilon^{(1)}_{\text{dep}}}{\partial \mathbf{u}(r_j)}.
$$

(2.33)

This gives us the capability of simulating both open and short circuit boundary conditions where \( \beta=1 \) and \( \beta=0 \) corresponding to ideal SC and OC electrical boundary conditions respectively. To simulate more realistic electrical boundary conditions, a value of \( \beta \) in-between these two extremes can be used. For instance, in our simulations of PbTiO₃ and Pb(Ti₀.₆Zr₀.₄)O₃ nanowires, we use a value \( \beta=0.1 \) to simulate realistic OC boundary conditions in which a small amount of the surface charge is screened. This is what would be expected for free-standing ferroelectric nanowires surrounded by air. The term \( \mathcal{E}^{\text{screen}} \) included in Eq. 2.10 essentially models a screening of the surface charge by free carriers [71]. The free carriers could be supplied by metal electrodes applied to the nanowire. This difference in potential will result in an electric field which will oppose the depolarizing field such that the total field inside the nanowire will depend on the polarization as well as the applied voltage [108]. The parameter \( \beta \) can be related to the finite screening length of the electrodes,
\( \lambda_{eff} \), and the nanowire’s lateral size, \( d \), as follows \( \beta = (1 + 2 \frac{\lambda_{eff}}{d})^{-1} \) [109]. The surface charge compensation does not necessarily require electrodes. Examples include surface charge compensation due to molecular adsorbates, charge carriers, intrinsic surface states, oxygen or other ionic vacancies, and others [110–114]. In these cases the screening parameter could be related to the concentration of free carriers, \( n \), as \( \beta = \frac{qnd}{2P_{bulk}} \), where \( q \) is the free carrier charge and \( P_{bulk} \) is the spontaneous polarization in the bulk [109].

In order to study the interaction of ferroelectrics and antiferroelectrics with an electric field, the Hamiltonian of Eq. 2.10 is further extended to include a term which describes the interaction of the local mode with an external electric field. The energy term used to characterize this interaction is given by

\[
\mathcal{E}_{field} = Z^* \sum_i E \cdot u_i
\]

where \( E \) is the applied electric field. From electrostatics, the potential energy of an electric dipole in an electric field is given by \( \mathcal{E}_{dip} = -p \cdot E \) [115]. Through this term we are able to apply static as well as time dependent electric fields.

### 2.2.3 Energy Terms Resulting from Antiferrodistortive Degrees of Freedom

The Hamiltonian of Eq. 2.10 was extended to study antiferroelectrics in Ref. [61]. The ground state structure of bulk PbZrO\(_3\) is an antiferroelectric (AFE) orthorhombic distorted perovskite structure. The dominant lattice distortions are from the \( \Sigma_2 \) and \( R_4^+ \) phonon modes with wavevectors \( q = \frac{2\pi}{a} (1/4,1/4,0) \) and \( q = \frac{2\pi}{a} (1/2,1/2,1/2) \) respectively. While distortion associated with the \( \Sigma_2 \) mode is responsible for the antipolar arrangements of the lead ions along the [110] direction, the \( R_4^+ \) distortion arises due to the oxygen octahedra rotation around the [110] direction [116].

Figure 2.5 gives the amplitude of the structural distortions for different symmetries of

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\(^{16}\)Figure 2.5 has been previously published in B. K. Mani, S. Lisenkov, and I. Ponomareva, “Finite-temperature properties of antiferroelectric PbZrO\(_3\) from atomistic simulations,” Phys. Rev. B, vol. 91, p. 134112, 2015., and has been reproduced with permission from the American Physical Society
Figure 2.5: Amplitude of structural distortions of different symmetry in the ground state of PbZrO$_3$ (shown by rectangles) and the cumulative energy gain (shown by circles) due to addition of each distortion. The energy of undistorted cubic structure is taken as the reference point. [61]

the ground state of PbZrO$_3$ as well as the cumulative energy gain due to each additional distortion. In other words, the bar graph shows the relative contributions from the different phonon modes to the total energy of the ground state structure, providing insight into which modes are predominantly responsible for the ground state orthorhombic structure of antiferroelectric PbZrO$_3$. Note that the energy of the undistorted cubic structure is chosen as the zero energy reference point. The phonon modes $\Sigma_2$ and $R_4^+$ are structurally and energetically the most influential distortions. Indeed these two distortions together with the elastic deformations provide more than 92% of the energy gain associated with the distortion of the ideal cubic perovskite structure. Based on this analysis the model was built to include $\Sigma_2$ and $R_4^+$ modes and strain deformations, $\eta_i$. $\Sigma_2$ and $R_4^+$ modes are localized on the A and B sites of the $ABO_3$ unit cell, respectively, following the approach of Ref. [117]. Furthermore, the local $\Sigma_2$ mode (or just the local mode) $u$ is defined from the atomic displacements in the $\Sigma_2$ mode, while the local $R_4^+$ mode (or antiferrodistortive local mode) $\omega$ is defined from $\Delta r = \frac{a_0}{2} \hat{R}_{ij} \times (\omega_i - \omega_j)$ [117], where $\Delta r$ is the oxygen displacement in a mode and $a_0$ is the cubic lattice constant. The three-dimensional vector $\omega$ is non-polar and describes antiferrodistortive oxygen octahedron tilts about the pseudocubic axes. The corresponding
order parameters are computed by averaging the local modes in the associated point of the Brillouin zone.

The additional degrees of freedom for the antiferrodristortive (AFD) extension of the Hamiltonian are the oxygen octahedron tilts about pseudocubic axes, $\omega_i$, that describe oxygen octahedron rotation. An additional term is added to the Hamiltonian of Eq. 2.10, $E^{\text{AFD}}$, which gives the energy due to the antiferrodristortive oxygen octahedra rotation mode that is similar to $E^{\text{AFE}}$ but excludes the dipole-dipole interactions as the antiferrodristortive local modes are nonpolar. The short-range antiferrodristortive interaction is implemented in exactly the same way as the short-range ferroelectric interactions described in Eq. 2.18 of section 2.2.2.

The terms $E^{\text{AFE-elas}}$, $E^{\text{AFD-elas}}$, and $E^{\text{AFE-AFD}}$ are the energy contributions due to the interactions between the antiferroelectric local modes and the strain, the antiferrodristortive local modes and the strain, and the antiferroelectric and antiferrodristortive local modes, respectively [3,117] and we consider only on-site couplings. The coupling between the acoustic phonons and the antiferrodristortive modes is written as [117]

$$E^{\text{AFD-elas}} = \frac{1}{2} \sum_{i\alpha\beta} B_{i\alpha\beta\gamma} \eta_{l} (\mathbf{R}_i) \left[ \bar{\omega}_{i,\alpha} (\mathbf{x}) \bar{\omega}_{i,\alpha} (\mathbf{x}) + \bar{\omega}_{i,\alpha} (-\mathbf{x}) \bar{\omega}_{i,\alpha} (-\mathbf{x}) \right]$$

+ cyclic permutations

(2.35)

where $\bar{\omega}_{i,\alpha} (\mathbf{d}) \equiv \omega_{\alpha} (\mathbf{R}_i + \mathbf{d}) - \omega_{\alpha} (\mathbf{R}_i)$ and $\mathbf{d}$ is defined in Eq. 2.26 of section 2.2.2. Cubic symmetry dictates that of the 162 possible matrix elements in $B_{i\alpha\beta\gamma}$, only 4 are independent coupling constants denoted $B_{1yyx}$, $B_{2yxx}$, $B_{3yyx}$, and $B_{4yzx}$.

The coupling between the ferroelectric soft mode and the antiferrodristortive mode contains terms which are linear in both $\mathbf{u}_i$ and $\omega_i$ as well as terms quadratic in these variables, denoted with the subscripts 1 and 2 respectively. The ferroelectric-antiferrodristortive coupling energy is then written as

59
\[ \mathcal{E}_{\text{ferro,AFD}} = \mathcal{E}_{\text{ferro,AFD}}^1 + \mathcal{E}_{\text{ferro,AFD}}^2. \]  

(2.36)

The lowest order (linear) coupling between the ferroelectric and antiferrodistortive degrees of freedom are expressed as [117]

\[ \mathcal{E}_{\text{ferro,AFD}}^1 = \sum_i G_{xy} u_x (R_i) \left[ \omega_y (R_i + z) - \omega_y (R_i - z) \right] + \text{cyclic permutations} \]  

(2.37)

though for the case of PbZrO\(_3\), the coupling term \( G_{xy} \) was found from first-principles calculations to be negligibly small and is approximated in the effective Hamiltonian as 0. The quadratic coupling is written as [117]

\[ \mathcal{E}_{\text{ferro,AFD}}^2 = \sum_i \left[ G_{xxxx} w_{i,x}^2 + G_{xxyy} w_{i,x}^2 \left( w_{i,y}^2 + w_{i,z}^2 \right) \right] + \text{cyclic permutations} \]  

(2.38)

where the \( w_{i,x} \) in Eq. 2.38 are defined as

\[ w_{i,x} = \frac{1}{8} \sum_{d=\pm y,\pm z} \left[ \omega_x (R_i + d) - \omega_x (R_i) \right] \]  

(2.39)

and similarly for \( w_{i,y} \) and \( w_{i,z} \).

In our effective Hamiltonian, the degrees of freedom associated with the antipolar \( \Sigma_2 \) mode are the local modes. Therefore, the \( \mathcal{E}^{\text{FE-elas}} \) coupling terms described in Eq. 2.23 also account for the \( \mathcal{E}^{\text{AFE-elas}} \) coupling. Similarly, the \( \mathcal{E}^{\text{FE-AFD}} \) terms given in eqs. 2.36, 2.37, and 2.38 account for the \( \mathcal{E}^{\text{AFE-AFD}} \) coupling.
2.2.4 Alloy Specific Energy Terms: Case of Lead Zirconate Titanate

Some perovskite ferroelectrics, referred to as alloys or solid solutions, have the A, B, or both lattice sites occupied by different species of atoms. Two of the most technologically important ferroelectric alloys are Lead Zirconate Titanate, Pb(Ti$_x$Zr$_{1-x}$)O$_3$, and Barium Strontium Titanate, (Ba$_x$Sr$_{1-x}$)TiO$_3$. In a disordered alloy, the lattice sites at which mixing occurs, A site for Barium Strontium Titanate and B site for Lead Zirconate Titanate, could contain either species of atom. The atomic species are randomly distributed throughout the sample; a realistic approach given that growing crystals with exact atomistic precision is not yet feasible. The different possible compositions can greatly vary the properties of the material. For instance, Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ is a ferroelectric material which undergoes one phase transition from cubic to tetragonal symmetry. However pure PbTiO$_3$ is a ferroelectric material while pure PbZrO$_3$ is antiferroelectric. The transition temperature and crystal symmetry of the alloy can be altered by changing the relative compositions of the different ions. Figure 2.6 depicts the phase diagram for Pb(Ti$_x$Zr$_{1-x}$)O$_3$ as a function of Zr concentration and temperature. For higher concentrations of Ti, the ferroelectric phase is tetragonal while for lower concentrations of Ti it is rhombohedral. For very small Ti concentrations, less than 7%, Pb(Ti$_x$Zr$_{1-x}$)O$_3$ becomes antiferroelectric orthorhombic below the Curie temperature.

The effective Hamiltonian which yields a total energy surface given by 2.10 requires extension in order to account for alloy effects in the crystal; in addition to the local mode and strain degrees of freedom compositional degrees of freedom are included. The total energy becomes

$$E_{tot} = E_{VCA} (\{u_i\}, \{v_i\}, \{\eta_H\}) + E_{loc} (\{u_i\}, \{v_i\}, \{\sigma_j\})$$

(2.40)

where $\sigma_j$ characterizes the atomic configuration where $\sigma_j$=+1 or -1 corresponding to the presence of a Zr or Ti atom respectively at the B position of lattice site $j$ [100]. The energy term $E_{VCA}$ represents all the contributions to the total energy involving the soft mode,
strain, and their mutual couplings, the same Hamiltonian defined in Eq. 2.10, while the $\{\sigma_j\}$ parameters are incorporated into the second energy term $\mathcal{E}_{\text{loc}}$.

The parameters used in the $\mathcal{E}_{\text{VCA}}$ energy term are found using first-principles calculations through the application of the virtual crystal approximation (VCA), i.e. replacing $A \left( B'_{1-x}, B''_x \right) O_3$ by a uniform but composition-dependent “virtual” $\text{ABO}_3$ system. The mixing of the two elemental species is done at the pseudopotential level with periodic boundary conditions applied to the system. The resulting parameters consequently reflect the properties of a true alloy at the specified concentration. The $\mathcal{E}_{\text{loc}}$ term can be thought of as a perturbative term stemming from the fact that $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ systems possess real Zr and Ti atoms on the B-sites rather than a virtual compositionally dependent $\langle A \rangle$ atom. It includes the onsite effect of alloying on the self-energy up to 4th order in $u_i$ and intersite interactions which are linear in $u_i$ and $v_i$ given by

Figure 2.6: Pb(Ti$_x$Zr$_{1-x}$)O$_3$ phase diagram depicting various phases as a function of Ti concentration and temperature.
\[ \mathcal{E}_{\text{loc}} \left( \{ \mathbf{u}_i \}, \{ \mathbf{v}_i \}, \{ \sigma_j \} \right) = \sum_i \left[ \Delta \alpha (\sigma_i) u_i^4 + \Delta \gamma (\sigma_i) \left( u_{ix}^2 u_{iy}^2 + u_{iy}^2 u_{iz}^2 + u_{iz}^2 u_{ix}^2 \right) \right] + \sum_{ij} \left[ Q_{j,i} (\sigma_j) \mathbf{e}_{ji} \cdot \mathbf{u}_i + R_{j,i} (\sigma_j) \mathbf{f}_{ji} \cdot \mathbf{v}_i \right] \]  

(2.41)

where \( j \) runs over the mixed sublattice sites [100]. The onsite contribution of alloying is denoted using \( \Delta \alpha (\sigma_i) \) and \( \Delta \gamma (\sigma_i) \); the change in the anharmonic coefficients relative to the VCA ABO\(_3\) onsite energy term. The matrices \( Q_{j,i} (\sigma_j) \) and \( R_{j,i} (\sigma_j) \) are related to alloy-induced intersite interactions, \( \mathbf{e}_{ji} \) is a unit vector joining site \( j \) to the center of the soft mode vector \( \mathbf{u}_i \), and \( \mathbf{f}_{ji} \) is a unit vector joining site \( j \) to the origin of the displacement vector \( \mathbf{v}_i \). Though terms with higher powers of \( \mathbf{u}_i \) and \( \mathbf{v}_i \) could be included in the energy expression to possibly improve the accuracy, numerous studies [100, 101, 104] have found that this level of expansion produces results which are in good agreement with experiment. Additionally, \( Q_{j,i} (\sigma_j) \) and \( R_{j,i} (\sigma_j) \) decrease rapidly as the distance between \( i \) and \( j \) increases meaning that contributions up to 3rd nearest neighbors for \( Q_{j,i} (\sigma_j) \) and over 1st nearest neighbor shell for \( R_{j,i} (\sigma_j) \) are sufficient.

### 2.3 Molecular Dynamics

Molecular Dynamics (MD) is a computational method used to calculate the time evolution of classical many-body systems. It uses numerical integration and Newton’s laws to solve N coupled equations of motion where N is the number of particles which make up the supercell. The motion of the constituent particles obey classical mechanics and MD provides a means of essentially simulating an experiment [118]. Molecular Dynamics is a deterministic algorithm meaning that the initial conditions determine the state of the system at any subsequent time. This implies that the state of the system at any step depends on the state of the system at all previous steps; in other words the initial conditions determine completely the time evolution of the system. In order to compare the ensemble averages multiple calculations...
with randomized velocities are required.

### 2.3.1 Numerical Integration Technique: Predictor-Corrector Algorithm

Our effective Hamiltonian Molecular Dynamics simulations use a predictor-corrector algorithm to numerically integrate the equation of motion

\[ M_u \frac{d^2 u}{dt^2} = F(u, t) \quad (2.42) \]

for the local mode variable \( u \) and time \( t \). The integration is a two-step process, the predictor step which solves Eq. 2.42 and the corrector step which makes any necessary corrections to the previously calculated integration. The predictor step for the \( \gamma = (x, y, z) \) coordinate of the local mode is defined by the following two expressions [119]

\[ u_\gamma (t + \Delta t) = u_\gamma (t) + \Delta t \dot{u}_\gamma (t) + (\Delta t)^2 \sum_{i=1}^{k-1} \alpha_i f (u_\gamma, t + [1 - i] \Delta t) \quad (2.43) \]

\[ \Delta t \dot{u}_\gamma (t + \Delta t) = u_\gamma (t + \Delta t) - u_\gamma (t) + (\Delta t)^2 \sum_{i=1}^{k-1} \alpha'_i f (u_\gamma, t + [1 - i] \Delta t) \quad (2.44) \]

where \( \Delta t \) is the chosen time step for the integration which is specified as an input parameter. The predictor extrapolates the value of \( u_\gamma (t + \Delta t) \) using the values of the position \( u_\gamma \), the velocity \( \dot{u}_\gamma \), and the acceleration \( \ddot{u}_\gamma \) at previous times \( t = t, \ t = t - \Delta t, \) etc. The corrector step is then used to recalculate values for \( x \) and \( \dot{x} \) which were estimated in the predictor step. The corrector is defined by the equations

\[ u_\gamma (t + \Delta t) = u_\gamma (t) + \Delta t \ddot{u}_\gamma (t) + (\Delta t)^2 \sum_{i=1}^{k-1} \beta_i f (u_\gamma, t + [2 - i] \Delta t) \quad (2.45) \]
\[
\Delta t \hat{u}_\gamma (t + \Delta t) = u_\gamma (t + \Delta t) - u_\gamma (t) + (\Delta t)^2 \sum_{i=1}^{k-1} \beta'_i f \left( u_\gamma, t + [2 - i] \Delta t \right)
\]  

(2.46)

where \( \alpha, \alpha', \beta, \) and \( \beta' \) are predetermined coefficients. These coefficients, as well as the predictor-corrector equations 2.43 - 2.46 themselves, are from the Adams-Boshford method of Ref. [119]. The value of \( k \), which determines the order of expansion and therefore the degree of accuracy of the integration, is set to the value 4. This order provides reasonable efficiency without loss of precision and accuracy.

### 2.3.2 Statistical & Thermodynamic Ensembles

In any Molecular Dynamics calculation, the collection of particles is simulated within a specified statistical ensemble in which different thermodynamical variables are held constant. This allows for simulation of various thermodynamical potentials (Gibbs, Helmholtz, etc.) and mimics the controlled environment of an experiment. A statistical ensemble is a collection of all possible systems which have different microscopic states but have an identical macroscopic or thermodynamic state. In other words, it is a large number of virtual copies of a system (probability distribution for the states of the system), each of which represents a possible state that the real system might be in. A closely related idea is that of a thermodynamic ensemble: a specific type of statistical ensemble that, in thermal equilibrium, is used to derive the macroscopic properties of the thermodynamic system (i.e. temperature, polarization, energy, etc.) [120]. A number of thermodynamic ensembles are used in Molecular Dynamics simulations, each one distinguished by the variables which are held constant throughout the calculation which determines the thermodynamic environment the system experiences during the simulation.

True classical Newtonian mechanics corresponds to an NVE (microcanonical) ensemble with a constant number of particles (N), volume (V), and total energy (E). In an NVE
ensemble, the total energy of the system is naturally conserved as long as the potential is a function of only the coordinates of the particles. Other ensembles include the canonical (NVT) ensemble where $T$ is the temperature and the isothermal-isobaric (NPT) ensemble with $P$ representing the pressure of the system. The characteristic state function for the NVT ensemble is the Helmholtz free energy $A(V,T) = U - TS$ while the NPT ensemble uses the Gibbs free energy defined as $G(P,T) = U + PV - TS$ for a constant number of particles. In experiments, the Gibbs free energy is of practical interest since the number of particles, the pressure and the temperature are relatively easy to control. For this reason, we commonly use the NPT ensemble in our simulations. The canonical and isothermal-isobaric ensembles both simulate a system in thermal contact with a heat bath; practically this is achieved in Molecular Dynamics simulations through the use of a thermostat. The thermostat used in our Molecular Dynamics simulations is the Evans-Hoover thermostat \[119\] in which the temperature is controlled through introducing a friction force into the equation of motion.

We simulate constant pressure by including a $PV$ term in the effective Hamiltonian \[121\]. This term ensures constant pressure by varying the homogeneous strain tensor (describes supercell deformations) throughout the simulation to compensate for fluctuations in pressure.

The Ergodic hypothesis states that a phase point for any isolated system passes in succession through every point compatible with the energy of the system before finally returning to its original position in the phase space \[122\]. If $\bar{x}$ is the time average of $x$ and $\langle \rangle$ denotes the ensemble average then a consequence of the Ergodic hypothesis is that

$$\langle x \rangle = \bar{x} \tag{2.47}$$

for a stochastic process whose joint probability distribution does not vary over time \[105\]. In Molecular Dynamics simulations, it is preferred that every possible state that the system can exist in be accessible in the simulation. In other words, every accessible point in configurational space can be reached by a finite number of Molecular Dynamics steps starting at any point in the space. In a Molecular Dynamics simulation, all possible states at a single
point in time cannot be determined. However if the system is ergodic and is allowed to visit all of the energetically relevant states by allowing for a sufficiently long simulation time, then through the ergodic hypothesis we are able to calculate meaningful values for statistical average of various quantities of interest.

2.3.3 Calculating Soft Mode Frequency at Finite Temperatures from $\varepsilon(\omega)$

First-principles techniques are useful for calculating phonon frequencies at 0 K. However, we are also interested in studying the soft mode frequency dynamics at finite temperatures. The characteristic soft mode frequency of a typical ferroelectric material falls within the range of 2 to 6 THz. Under a frequency dependent electric-field (0 to 15 THz in our calculations), a ferroelectric material will be most responsive to the electric field at the characteristic frequency. The frequency response will also depend on the temperature with the soft mode decreasing in frequency near the transition temperatures. This responsiveness of the material to an electric field is characterized by the frequency dependent dielectric response. Therefore, to study the frequency dynamics of ferroelectrics we first calculate the complex dielectric response following the approach of Refs. [121,123]

$$
\varepsilon(\nu) - 1 = \frac{1}{3\varepsilon_0 V k_B T} \left[ \langle M^2 \rangle + 2\pi i \nu \int_0^\infty e^{2\pi i\nu t} \langle M(t) \cdot M(0) \rangle dt \right] \tag{2.48}
$$

where “$\langle \rangle$” denotes the thermal average, $V$ is the volume of the supercell, and $t$ and $\nu$ are the time and frequency, respectively. The $\langle M^2 \rangle$ is the time-averaged square of the total dipole moment of the supercell while $\langle M(t) \cdot M(0) \rangle$ is the average autocorrelation function (ACF) for the dipole moment. The simulation begins with 20,000 MD steps within an NPT ensemble to equilibrate the structure for the chosen temperature. This was done in the presence of the bias field. This was followed by 5,000 steps within an NVE ensemble for which the thermostat and barostat are turned off and the homogeneous strain variable are held fixed. This ensemble allows to obtain dynamical properties and was subsequently used for the remainder of the simulation for 2,975,000 additional MD steps yielding 10,000
individual $M(t) \cdot M(0)$ functions. The $M(t) \cdot M(0)$ functions are calculated for the time interval $[0:8.2]$ ps and utilize the overlap approach of Ref. [119]. These $M(t) \cdot M(0)$ functions are next averaged to obtain the autocorrelation functions. The $M^2$ is averaged over the final 2,975,000 NVE steps of the simulation to obtain $\langle M^2 \rangle$. This average is used, along with the Fourier transform of the ACF, to determine $\varepsilon(\nu)$ from Eq. 2.48.

The dielectric function generated in our calculations is fit with the classical damped harmonic oscillator Lorentzian function

$$\varepsilon(\nu) = \varepsilon_\infty + \frac{S_0}{\nu_0^2 - \nu^2 + i\nu\gamma_0}$$

where $\nu_0$, $\gamma_0$, and $S_0$ are the characteristic frequency, damping constant, and oscillator strength respectively. The high-frequency permittivity $\varepsilon_\infty$ is not considered in the simulated response of our calculations since our model only accounts for a single ionic polar displacement per unit cell. We found that for the nanowires, computed $\varepsilon(\nu)$ can be fitted well with a single Lorentzian oscillator function. For PbTiO$_3$ bulk, the single mode splits below the transition temperature into the individual A1(TO1) and E(TO1) modes. This requires the use of two separate Lorentzian oscillator functions to properly fit the data. The results of the fit yield the mode characteristic frequency $\nu_0$ as a function of temperature ($T$) and the bias electric field ($E_{dc}$) as well as $S_0(T, E_{dc})$ and $\gamma_0(T, E_{dc})$.

### 2.4 Monte Carlo Methods

Another computational method that allows us to model various thermodynamical ensembles and is used in our research is Monte Carlo, so named for the fact that it incorporates probability into the calculations. As opposed to Molecular Dynamics, Monte Carlo (MC) methods do not calculate the time evolution of the system. They are used to find equilibrium properties of the system. Contrary to the deterministic Molecular Dynamics algorithm described in the previous section, Monte Carlo methods fall under the category of stochastic
methods. A stochastic process is a time sequence representing the evolution of some system represented by a variable whose change is subject to a random variation [124].

The central problem of Metropolis Monte Carlo is to calculate the thermal average of a quantity $Q$ which is given by the classical expression

$$
\langle Q \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N Q(\mathbf{p}^N, \mathbf{r}^N) e^{-\beta H(\mathbf{p}^N, \mathbf{r}^N)}}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-\beta H(\mathbf{p}^N, \mathbf{r}^N)}}
$$

(2.50)

where $Q$ is the observable to be averaged, $\beta = \frac{1}{k_B T}$, $H$ is the Hamiltonian of the system, $N$ is the number of sites or particles, and $\mathbf{p}$ and $\mathbf{r}$ are the momentum and position vectors respectively. The integration over the momenta can be done analytically leaving only the integration over the coordinates for $Q(\mathbf{r}^N)$ to be done numerically.

For a given integration mesh, the majority of points would yield an integrand for Eq. 2.50 which is nearly zero which can be safely neglected. This point is the motivation behind a method known as importance sampling; sampling mostly those points in phase space for which the Boltzmann factor has a non-zero value and ignoring points for which it is vanishingly small. Importance sampling is a way of reducing the amount of phase space which the algorithm needs to explore in order to converge on the lowest energy state. The basic idea is that some of the input variables which are varied in order to calculate the energy difference (the local mode $\mathbf{u}$ and the local strain $\eta$ in effective Hamiltonian Monte Carlo) have more impact on the potential energy function. That is, some local mode and strain variable configurations affect the energy landscape more significantly than other configurations and some configurations yield extremely high energies which lie far from the equilibrium value.

The Metropolis Monte Carlo algorithm we use to calculate equilibrium properties of ferroelectrics/antiferroelectrics is summarized in Fig. 2.7. The simulation is initialized using randomized local mode and local strain variables. We then attempt to update one of the variables (local mode of local strain) by replacing the $x$, $y$, and $z$ components of the variable with a randomly generated set of components and the change in energy resulting from the
variable update is calculated. If the system energy is lower as a result of the update, the trial move is accepted. If the variable update results in an increase in energy, the trial move is accepted with a probability proportional to the Boltzmann factor. To determine if a trial move will be accepted or rejected, a random number is generated from a uniform distribution within the interval [0,1] and compared with the probability of acceptance. The trial move is accepted if the random number is less than the probability of acceptance and rejected otherwise. This process is repeated over all sites for a predetermined number of Monte Carlo steps.

![Flow chart depicting the basic Metropolis Monte Carlo algorithm.](image)

Figure 2.7: Flow chart depicting the basic Metropolis Monte Carlo algorithm.

### 2.4.1 Adiabatic Monte Carlo

While the Metropolis Monte Carlo method explained previously simulates a canonical (NVT) ensemble, we are also interested in using Monte Carlo simulations to study ferroelectric/antiferroelectric materials during an adiabatic process in which the temperature is allowed to vary but there is no heat exchange with the surroundings. We use this approach in order to directly compute the electrocaloric effect. To derive such an approach, we begin with the enthalpic form...
of the first law of thermodynamics

\[ d\mathcal{H} = dQ - x_i dX_i - D_i dE_i \]  

(2.51)

where \( \mathcal{H} = U - X_i x_i - E_i D_i \) is the enthalpy, \( dQ \) is an infinitesimal quantity of heat, \( U \) is the internal energy, and \( X_i \) and \( x_i \) are the stress and strain respectively. Since we are using this method to study the electrocaloric effect, an adiabatic process by definition, \( dQ = 0 \). In order to achieve adiabatic simulations, we follow the spirit of Creutz microcanonical Monte Carlo algorithm [125, 126] and introduce additional degrees of freedom, referred to as "demons", which absorb, carry, or redistribute energy throughout the sample. In our simulations, the enthalpy is defined as follows:

\[ \mathcal{H} = \frac{1}{V} \left( U_{pot} + \sum_{i=1}^{N_{dem}} E_{i}^{dem} - V X_i x_i - Z^* E \sum_{j=1}^{N_{sites}} u_j \right) = H + \sum_{i=1}^{N_{dem}} E_{i}^{dem} \]  

(2.52)

where \( U_{pot} \) is the potential energy given by the effective Hamiltonian, \( E_{i}^{dem} \) is the energy carried by the \( i \)th demon, \( Z^* \) is the Born effective charge, \( u_j \) is the local mode at site \( j \) [16]. \( H \) is the enthalpy less the energy of all the demons. We determine the appropriate number of demons required to reproduce the computational value for \( C_{E=0} \) through the equation

\[ N_{dem} = \text{integer} \left[ \frac{1}{k_B} \left( C_{E=0} - \frac{\partial U_{pot}}{\partial T} \right) \right] = \text{integer} \left[ \frac{\partial U_{pot}}{\partial T} \left( \frac{1}{k_B V} - 1 \right) + \frac{15}{2} \frac{1}{V} \right] = 8 \]  

(2.53)

At each Monte Carlo step, an update for a degree of freedom is attempted and compared with the energy of a randomly chosen (or sequentially picked) demon \( E_{i}^{dem} \). If \( E_{i}^{dem} - \Delta H > 0 \) the move is accepted and the enthalpy and demon energy are updated as \( H \rightarrow H + \Delta H \) and \( E_{i}^{dem} \rightarrow E_{i}^{dem} - \Delta H \). If instead \( E_{i}^{dem} - \Delta H < 0 \), the trial move is rejected and the selected demon energy remains the same. One Monte Carlo sweep attempts to update
all the degrees of freedom sequentially. The temperature is calculated after each sweep as \( T = \sum_{i=1}^{N_{dem}} E_i^{dem} / k_B N_{dem} \) and is averaged over an appropriate number of Monte Carlo steps [16].
3 Parameterization of Potassium Niobate

Recently there has been concern regarding materials containing lead such as PbTiO$_3$ and Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ which is known to be toxic to both humans and the environment. As a result, there is a push for lead-free alternatives for materials which could potentially be used for technological application. For the perovskite ABO$_3$ class of materials, this can be achieved by using materials with less toxic elements such as Barium, Bismuth, or Potassium. The lead compounds Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ and PbTiO$_3$ have excellent caloric and ferroelectric properties; our goal is to identify whether lead-free materials can be used for potential applications which rely on these properties. We decided to focus on KNbO$_3$ since it remains relatively under-explored. KNbO$_3$ undergoes the same sequence of phase transitions as BaTiO$_3$ except at elevated transition temperatures. This means KNbO$_3$ could potentially be used for applications requiring a higher operating temperature range. The goal of this project is to derive a set of parameters for the effective Hamiltonian which will be used to study static and dynamic properties in KNbO$_3$ bulk and nanowires.

We used the Vienna Ab-Initio Simulation Package (VASP) to perform plane-wave density functional theory computations. [127–130] The functionals used were Projector augmented wave (PAW) [131,132] within the LDA [133] as well as the Perdew-Burke-Ernzerhof generalized gradient approximation PBE-GGA [134,135] functional. To represent points in k-space we used a Monkhorst-Pack [136] k-point mesh. For calculations involving a single perovskite unit cell, a mesh of 11x11x11 was used; for calculations involving multiple unit cells, we decrease the k-point mesh to 5x5x5 to take into account the size of the supercell in real space. The plane wave basis was truncated at 600 eV for all calculations and we used the default kinetic energy cutoff defined in the pseudopotential files for the respective chemical.
elements. We shall now describe the various parametrization steps in detail.

### 3.1 Lattice Constant

The parametrization begins with computation of the lattice constant, $a_{lat}$, corresponding to the perfect cubic perovskite structure. Since an effective Hamiltonian is a Taylor series expansion in small distortions from the cubic structure [3], the value of the lattice can have a large impact on the predictions of the model.

In order to determine the cubic lattice constant, we ran a series of total energy calculations on a single unit cell of KNbO$_3$ where the total energy, $E_{lat}$, is computed as a function of $a_{lat}$. The computational data are fitted with a third order polynomial

$$E_{lat} = E_0 + C_1 a_{lat} + C_2 a_{lat}^2 + C_3 a_{lat}^3 \tag{3.1}$$

where $C_1$, $C_2$, and $C_3$ are the fitting parameters. Equation 3.1 is subsequently minimized analytically to find the value of $a_{lat}$. Figure 3.1 shows the points for which calculations were carried out as well as the polynomial used to fit the data. The optimal lattice constant was different for the two functionals used. The lattice constant is 7.55 a.u. for LDA and 7.68 a.u. for GGA. These compare very well with the experimentally measured values of 7.63 a.u reported by Ref. [5] and 7.50 Å reported by Ref. [137].

A second method we used to find the cubic lattice constant was to allow the VASP code to relax the volume of a cubic unit cell. The code calculates the total energy of the unit cell with respect to volume using a conjugate gradient algorithm until the forces acting on the ions are zero and there are no stresses on the unit cell. The values of the lattice constants found by the relaxation method are 7.56 a.u. for LDA and 7.67 a.u. for GGA, in agreement with the first method.
Figure 3.1: The total energy of the KNbO$_3$ cubic unit cell as a function of the lattice constant using the LDA. The points represent the data calculated at each lattice constant value while the dashed line indicates the best fit.

### 3.2 Eigenvector of the Soft Mode

In the soft mode theory of ferroelectrics, the local dipole moment which gives rise to the macroscopic polarization is due to the relative displacement of the ions in the perovskite unit cell. These displacements are proportional to the dimensionless eigenvector, $\xi_i$, of the unstable zone-center phonon mode in the cubic phase. Therefore, the next step in the parametrization is the calculation of the normal phonon modes for the optimized cubic unit cell. In our first principle phonon calculations, we determine the eigenvalues and associated eigenvectors of the normal modes by diagonalization of the interatomic force constant (IFC) matrix whose elements are the second derivatives of the energy with respect to atomic displacement. The method we use to calculate the IFC matrix is referred to as the linear response method. It uses density functional perturbation theory (DFPT) in the linear response region in order to calculate the forces on the individual atoms [138]. We use numerical methods to diagonalize the 15x15 IFC matrix, also known as the Hessian matrix, obtained from the DFPT implementation VASP. Technically, the ions are displaced and the forces between them are calculated yielding the Hessian matrix. The eigenvalue associated with the soft mode is both negative and triply degenerate and the eigenvector corresponding to this eigenvalue is the soft mode eigenvector. This eigenvector points in the direction of the...
energy decrease.

Table 3.1: Components of the normalized eigenvectors for GGA and LDA describing the local mode in KNbO$_3$. Other values for the eigenvector determined using Vanderbilt ultrasoft pseudopotentials within LDA (Ref. [5]) as well as values derived from experimentally measured displacements. (Ref. [137]).

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref. [5]</th>
<th>Exp. Ref. [137]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_A$</td>
<td>-0.092</td>
<td>-0.173</td>
<td>0.18</td>
<td>0.32</td>
</tr>
<tr>
<td>$\xi_B$</td>
<td>-0.815</td>
<td>-0.808</td>
<td>0.80</td>
<td>0.73</td>
</tr>
<tr>
<td>$\xi_\parallel$</td>
<td>0.207</td>
<td>0.320</td>
<td>-0.31</td>
<td>-0.33</td>
</tr>
<tr>
<td>$\xi_\perp$</td>
<td>0.492</td>
<td>0.335</td>
<td>-0.37</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

Table 3.1 shows our computed eigenvectors and those reported in Ref. [5] as well as the ones calculated from experimentally measured displacements in Ref. [137]. The largest ionic displacement is seen, for both LDA and GGA, for the B-site while for the A-site there is almost no displacement. This suggests that KNbO$_3$ is a B-centered perovskite and that the dipole moment which develops in the ferroelectric phase of KNbO$_3$ is a result of the relative displacement of the B ion with respect to the oxygen octahedron. We will compare our parameters to those found from the first-principles calculations of Ref. [5] as well as experimental values given in Ref. [137] whenever possible. The first-principles parameter set provided by Ref. [5] is limited and does not contain all of the necessary parameters to run effective Hamiltonian simulations. The Hamiltonian used in this reference accounts for all dipole interactions through a single parameter $\kappa$ which is proportional to the square of the local mode. The Hamiltonian used in the total energy expression (Eq. 2.10) separates the dipole energy into a dipole self interaction, short-range dipole interactions, and long-range dipole interactions. To our knowledge, a full set of effective Hamiltonian parameters did not exist for KNbO$_3$ prior to our parametrization.

### 3.3 Anharmonic Coefficients $\alpha$ and $\gamma$

The energy of an isolated local mode is given by equation 2.12 where $u_i$ is the magnitude of the local mode for a single cell ($i=1$). The local mode self interaction contains a harmonic
term as well as two anharmonic terms for which the coefficients are $\alpha$ and $\gamma$. These anharmonic coefficients were found by calculating the total energy of the unit cell while varying the amplitude of the local mode $u$. This was done by applying a local mode along the [001], [110], and [111] directions. The displacements from the ideal cubic structure, $v_i$, are found in accordance with the equation $v_i = u \xi_i$ where $\xi_i$ is the dimensionless displacement for atom $i$ in the soft mode and $u$ is the magnitude of the local mode. Computational data for the total energy of the unit cell as a function of local mode are given in Fig. 3.2. The red, green, and blue curves correspond to ionic displacements along the [001], [110], and [111] crystallographic directions, respectively. Only positive values of the local mode are considered due to the symmetry of cubic structure. Figure 3.2 predicts a rhombohedral ground state with the polarization vector along the [111] direction, in the absence of coupling with the strain. This finding is in qualitative agreement with experiment [137].

![Figure 3.2: The total energy of the unit cell as a function of local mode for the three directions of the local mode for LDA (a) and GGA (b).](image)
The computational data of Fig. 3.2 was fitted using Eq. 2.12 as follows

\begin{align}
E ([001]) &= \kappa u^2 + \alpha u^4, \quad (3.2a) \\
E ([110]) &= \kappa u^2 + \alpha u^4 + \frac{\gamma'}{4} u^4, \quad (3.2b) \\
E ([111]) &= \kappa u^2 + \alpha u^4 + \frac{\gamma''}{3} u^4. \quad (3.2c)
\end{align}

During fitting, the value for \( \kappa \) is set to half the value of the soft mode eigenvalue. To find the value of \( \alpha \), we fit Eq. 3.2 a while \( \gamma \) is found by using the results of fitting eqs. 3.2 b and 3.2 c in conjunction with

\[ \gamma = \frac{\gamma' + \gamma''}{2}. \]  

(3.3)

Table 3.2 summarizes the values obtained from our first principle calculations for \( \alpha \) and \( \gamma \) showing good agreement with Ref. [5] which used the LDA.

Table 3.2: The anharmonic coefficients \( \alpha \) and \( \gamma \) for the LDA and GGA from our calculations and those of Ref. ( [5]) for comparison.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>LDA from ref. [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.4453</td>
<td>0.1213</td>
<td>0.378</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-0.7438</td>
<td>-0.5943</td>
<td>-0.613</td>
</tr>
</tbody>
</table>

3.4 Harmonic Coefficient & Short-Range Interaction Parameters

The harmonic coefficient \( \kappa_2 \) and the short-range interaction parameters \( j_1 - j_7 \) are determined through the approach proposed in Ref. [3]. A series of energy and force calculations which utilize the conjugate-gradient method to minimize the forces between the atoms, nine in total, are performed for different configurations of local modes which are shown in Fig. 3.3. For each configuration the energies and forces are calculated through the frozen phonon
method using the VASP. They represent different arrangements of local mode configurations which are characterized by different wave vectors \( (k) \) and polarization vectors \( (P) \). Figure 3.3 \( a \) represents the zone-center \( \Gamma \)-point distortion, Figs. 3.3 \( b \) and \( c \) correspond to the zone-boundary \( k \)-point \( X = (\pi/a, 0, 0) \) with the local mode vector in the \( \hat{z} \) and \( \hat{x} \) directions respectively. Figures 3.3 \( d \) and 3.3 \( e \) represent the \( M = (\pi/a, \pi/a, 0) \) point in the Brillouin zone with local mode vector in the \( \hat{z} \) and \( \hat{x} \) directions respectively while Fig. 3.3 \( f \) represents \( R = (\pi/a, \pi/a, \pi/a) \) with local mode vector in the \( z \) direction. The remaining two figures correspond to four-cell calculations in which the local mode vector has more than one non-zero component. The red point and vector signifies the corner of the supercell at which the origin is positioned. For the configurations in Figs. 3.3 \( a - f \) the calculations were done using a cubic supercell of 2x2x2 unit cells in size, while calculations for figures 3.3 \( g \) and 3.3 \( h \) required a larger supercell with \( n_x = n_z = 4 \) and \( n_y = 2 \). For each local mode configuration, we performed self-consistent energy calculations for various local mode amplitudes \( |u| = u \). The local mode amplitude was systematically increased for each calculation, from 0 to 0.1 in units of the equilibrium lattice constant. The maximum local mode displacement was limited to 0.1 since ferroelectricity in crystals is a result of small displacements from the ideal cubic structure.

For the calculations using figures 3.3 \( a - f \), the data for the energy is fitted with the equations

\[
E_{fig}(u) = \kappa_{fig} u^2 + \alpha u^4 \tag{3.4}
\]

while for the 160 atom supercell calculations in the direction \( u [101] \), we fit with the expressions

\[
E_{fig}(u) = \kappa_{fig} u^2 + \alpha u^4 + \frac{\gamma}{4} u^4 \tag{3.5}
\]

\[\text{Figure 3.3 has been used with the permission of Dr. Brajesh Kumar Mani}\]
where $\kappa_{fig}$, $\alpha$, and $\gamma$ are the fitting parameters. Note we obtain different $\kappa_{fig}$ values for each local mode configuration depicted in Fig. 3.3. By fitting the energy of each local mode configuration we can determine the harmonic coefficients corresponding to each configuration. The $\kappa_{fig}$ parameter represents contributions from three different interactions, namely the local mode self energy, the long-range dipole-dipole interaction, and the short-range inter-site interaction the strength of which is given by the parameters $j_1 \cdots j_7$. The $\kappa_{fig}$ associated with different local mode configurations given by figures 3.3 a - h are expressed.
using the following set of linear equations

$$\kappa (\text{Fig.}2a) = -2.094C + \kappa_2 + 2j_1 + j_2 + 4j_3 + 2j_4 + 4j_6, \quad (3.6a)$$

$$\kappa (\text{Fig.}2b) = 4.844C + \kappa_2 + 2j_1 - j_2 - 4j_3 + 2j_4 - 4j_6, \quad (3.6b)$$

$$\kappa (\text{Fig.}2c) = -2.422C + \kappa_2 + j_2 - 2j_4 - 4j_6, \quad (3.6c)$$

$$\kappa (\text{Fig.}2d) = -2.677C + \kappa_2 - 2j_1 + j_2 - 4j_3 + 2j_4 + 4j_6, \quad (3.6d)$$

$$\kappa (\text{Fig.}2e) = 1.338C + \kappa_2 - j_2 - 2j_4 + 4j_6, \quad (3.6e)$$

$$\kappa (\text{Fig.}2f) = 0C + \kappa_2 - 2j_1 - j_2 + 4j_3 + 2j_4 - 4j_6, \quad (3.6f)$$

$$\kappa (\text{Fig.}2g) = 2.932C + \kappa_2 + j_1 - 2j_5 - 4j_7, \quad (3.6g)$$

$$\kappa (\text{Fig.}2h) = 0.416C + \frac{\kappa_2}{2} - 2j_7. \quad (3.6h)$$

where the first term gives the contribution from the dipole-dipole interaction and the constant $C = \frac{Z^* e^2}{\epsilon_{\infty} a_{1s}^2}$ [140]. This set of linear equations is solved using a Gaussian elimination with back substitution algorithm to find the values of $\kappa_2$ and $j_1 - j_7$. The computational values are given in table 3.3.

Table 3.3: Short-range interaction parameters, $j_1 - j_7$, and 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>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_2$</td>
<td>0.1101</td>
<td>0.1213</td>
</tr>
<tr>
<td>$j_1$</td>
<td>-0.0165</td>
<td>-0.0212</td>
</tr>
<tr>
<td>$j_2$</td>
<td>-0.0738</td>
<td>-0.0488</td>
</tr>
<tr>
<td>$j_3$</td>
<td>0.0045</td>
<td>0.0058</td>
</tr>
<tr>
<td>$j_4$</td>
<td>-0.0032</td>
<td>-0.0040</td>
</tr>
<tr>
<td>$j_5$</td>
<td>-0.0185</td>
<td>-0.0161</td>
</tr>
<tr>
<td>$j_6$</td>
<td>0.0014</td>
<td>0.0018</td>
</tr>
<tr>
<td>$j_7$</td>
<td>0.0047</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

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3.5 Born effective Charge, Optical Dielectric Constant & Mass of Local Mode

The next three parameters which were calculated were the Born effective charge, $Z^*$, the mass of the local mode, $M_u^*$, and the optical dielectric constant, $\epsilon_\infty$. The Born effective charge for each ionic species and the optical dielectric constant are calculated internally using DFPT in VASP. Specifically, the Born effective charge tensor is calculated as

$$Z^*_{ij} = \frac{\Omega}{e} \frac{\partial P_i}{\partial u_j} \quad i, j = x, y, z$$

(3.7)

where $\Omega$ is the volume of the unit cell, $u_i$ is the lattice displacement, and $P_i$ is the polarization. The ion-clamped optical dielectric constant is calculated using the expression

$$\epsilon^\infty_{ij} = \delta_{ij} + 4\pi \frac{\partial P_i}{\partial E_j}, \quad i, j = x, y, z.$$  

(3.8)

During this calculation, the coordinates of the ions are held fixed to ensure that the resultant polarization is electronic. The Born effective charge of the local mode is calculated as

$$Z^* = \xi_K Z_K^* + \xi_{Nb} Z_{Nb}^* + \xi_O Z_O^* + 2\xi_O Z_O^\perp$$

(3.9)

where the subscript denotes the atomic species. Note that for a 5 atom unit cell there are 2 oxygen atoms perpendicular to the direction of polarization and 1 parallel. Due to the symmetry of the Born effective charge tensor, $x$ and $y$ components yield similar values for the Born effective charge of the local mode. The local mode mass is defined as

$$M_u^* = \sum_i \left(\xi_z^i\right)^2 M_i$$

(3.10)

with $M_i$ being the mass of the $i$th atom found in any periodic table of the elements. These parameters are listed in table 3.4 for both functionals.

The final entry in table 3.4 gives the value for the inhomogeneous strain mass. This was
Table 3.4: Values of the Born effective charge, $Z^*$, optical dielectric constant, $\varepsilon_\infty$, the local mode effective mass, $M^*_u$ and the inhomogeneous strain mass $M^*_\eta_n$. 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>9.924</td>
<td>9.892</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>6.712</td>
<td>6.836</td>
</tr>
<tr>
<td>$M^*_u$</td>
<td>66.895</td>
<td>67.234</td>
</tr>
<tr>
<td>$M^*_\eta_n$</td>
<td>180.001</td>
<td>180.001</td>
</tr>
</tbody>
</table>

calculated by adding up the contributions from each atomic species to the total mass of the 5-atom unit cell as

$$M^*_\eta_n = M_K + M_{Nb} + 3M_O$$ (3.11)

### 3.6 Phonon Dispersion Curve

At this point we have all the parameters necessary to compute phonon dispersion curves in the cubic phase. The phonon dispersion curves are obtained by computing the IFC matrix in different points of the Brillouin zone and diagonalizing the matrix to obtain the eigenvalues. Only parameters $\varepsilon_\infty$, $Z^*$, $\kappa_2$, $j_1$ - $j_7$, and $a_{lat}$ contribute to these calculations. The computed curves are given in Fig. 3.4. The data predicts two instabilities, one between the $M$ and $\Gamma$ points and another between the $\Gamma$ and $R$ points in the Brillouin zone which are inconsistent with ferroelectricity.

The local mode configurations given in Figs. 3.3 b, e, and f are A-site dominated meaning the largest ionic displacements are on the A-sites while the local mode for KNbO$_3$ is B-centered. This means that phonon modes corresponding to these higher energy configurations are not reproduced well using the frozen phonon method leading to errors in the calculation of the phonon dispersion curves. To correct for these phonons which are not well-behaved, we again use the 40 atom supercells corresponding to Figs. 3.3 b, e, and f to perform density functional perturbation theory calculations (see sections 3.1.4 & 3.1.5) after
relaxing the atomic positions of the structure while holding the lattice vectors fixed in the ideal cubic positions. We then extract the $\kappa_{fig}$ values described in the previous section by diagonalizing the interatomic force constant (IFC) matrix generated by the VASP code during the calculation. We use these new $\kappa_{fig}$ values to re-calculate $\kappa_2$ and the $j_i$ parameters using the same method explained in section (3.4). Once we have the new values for $j_i$, we replace those found from the Figs. 3.3 b, e, and f frozen phonon calculations with those calculated using DFPT. For both the LDA and GGA, the energies predicted by DFPT at points b, e, and f are increased with respect to the energies calculated using the frozen phonon method, most significantly for point f. This has the effect of altering the energy landscape in the vicinity of the Γ point, lowering this energy with respect to the surrounding energy in the surrounding reciprocal space. This provides us with a better set of parameters which more accurately predicts phonon dispersion for KNbO$_3$. The Γ points for both LDA and GGA in Fig. 3.5 represent the global minimum of energy indicating that the ferroelectric phase is stable after incorporating the new $j_i$ parameters.

Figure 3.5 shows the phonon dispersion curves for KNbO$_3$ generated using the updated
parameters for both LDA (a) and GGA (b). We see that the instabilities now lie at the Γ point for both exchange-correlation functionals predicting a ferroelectric ground state for both.

### 3.7 Elastic Stiffness Constants

The elastic stiffness constants for the perovskite crystal $C_{ij}$ are denoted by $B_{11}$, $B_{12}$, and $B_{44}$. Due to cubic symmetry, these are the only three independent elastic constants. They are expressed in atomic units of energy (Hartree) [3]. We calculate these constants using density functional perturbation theory (DFPT) in the linear response. The code applies six finite distortions to the lattice and the elastic constants are derived from the associated stress-strain relationship [141] as described in ref. [142]. The values for the elastic stiffness constants are summarized in table 3.5. The values given by the VASP code are multiplied by the volume of the cell to give the constants which are reported. Our parameters agree well with those found from first-principles calculations [5]. The $B_{11}$ and $B_{44}$ coupling constants shown in table 3.5 agree well with those reported from experimental Ref. [143] at 300 K,
Table 3.5: Values of the elastic stiffness constants obtained from DFT. We compare to elastic constants calculated by Ref. [5] using the ultrasoft pseudopotential method in the LDA as well as to experimental values reported in Ref. [143]. Units of the stiffness constants are Ha.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref. [5]</th>
<th>Ref. [143]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{11}$</td>
<td>5.71</td>
<td>6.40</td>
<td>6.54</td>
<td>3.48</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>1.11</td>
<td>1.12</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>$B_{44}$</td>
<td>1.38</td>
<td>1.34</td>
<td>1.37</td>
<td>1.15</td>
</tr>
</tbody>
</table>

especially after taking into account the temperature dependence of the elastic constants. As temperature decreases, the the lattice stiffens and the elastic constants get larger reaching a maximum at 0 K [6].

One effect which can occur during first-principle calculations that can lead to an error in the values of the elastic stiffness constants is called Pulay stress. The error originates from the fact that the plane wave basis set is not complete with respect to the changes in the volume of the cell. As a result, the diagonal elements of the stress tensor are all offset by a constant amount. The Pulay stress, being isotropic, has the effect of decreasing the real fully relaxed volume of the crystal as a whole. The way we remove the Pulay stress is by setting the plane wave energy cutoff to a slightly larger value than the default, specifically 30% larger in order to ensure that we achieve full convergence of the stress tensor. [141,144] We adopted this approach in our calculations by using an energy cut-off of 800 eV for this set of calculations.

3.8 Strain-Local Mode Coupling Constants

The coupling between the local mode and the strain is described using the on-site interaction by Eq. 2.23 where $B_{l\alpha\beta}$ are the coupling coefficients, $l$ is the strain component and runs from 1 to 6, and $\alpha$ and $\beta$ represent Cartesian coordinates. The three independent $B_{l\alpha\beta}$ are $B_{1xx}$, $B_{1yy}$, and $B_{4yz}$. We performed first-principles energy and force calculations for different $u$ in the range 0.00 - 0.06 in units of cubic lattice constant and for different amounts of applied strain in the range -0.02 to 0.02. Specifically, we choose the $\Gamma$ point local mode.
configuration (Fig. 2a) and apply strain along the $z$ direction for computing $B_{3zz}$, the $y$ direction for computing $B_{2zz}$, and the $x$-$z$ direction (shear strain) for computing $B_{5xz}$. These coupling coefficients are equivalent to $B_{1xx}$, $B_{1yy}$ and $B_{4yz}$, respectively, as a result of cubic symmetry and we report the coupling constants using the latter notation to conform to that of Ref. [5]. By fitting the energy as a function of local mode using a 6th order polynomial, we can extract the harmonic coefficient ($\kappa_\eta$) for each value of strain. We then fit the data for $\kappa_\eta$ as a function of relative strain using the following expression

$$\kappa_\eta(\eta) = \kappa_0 + B_{l\alpha\beta} \eta_l$$

Equation 2.23 reduces to Eq. 3.12 for the case when the local mode $u$ is constant. It is found by taking the second order derivative of the total energy (Eq. 2.10) with respect to the local mode ($u$) in the harmonic approximation. In this case, the anharmonic terms of Eq. 2.12 are neglected, the derivative of the elastic energy with respect to local mode is zero, and the second derivative of all terms harmonic in local mode are constant. The surviving term which in linear in strain comes from the strain-local mode coupling energy (Eq. 2.23). The slope of the line of best fit is therefore equal to the coupling coefficient $B_{l\alpha\beta}$. Figure 3.6 shows the data for $\kappa$ versus relative strain for the three sets of calculations along with the linear regression.

A second method by which we determined the coupling coefficients was through a series of DFPT calculations with various amounts of compressive, tensile, and shear strain applied to the 5 atom unit cells. These calculations generate an IFC matrix which was diagonalized using the standard LAPACK libraries yielding the respective eigenvalues for each value of strain. The first set of calculations was done to find $B_{1xx}$ and $B_{1yy}$, such that $\eta_1 \neq 0$. From the 15 different eigenvalues, two of the negative eigenvalues which are degenerate correspond to the case where the strained crystallographic direction and the direction of the ionic displacement are perpendicular to one another; this corresponds to $B_{1yy}$. Another non-degenerate but negative eigenvalue corresponds to the configuration where the ionic
displacements are along the same direction as the applied strain; this gives access to $B_{1xx}$. A second set of DFPT calculations was done for $\eta_4 \neq 0$, the case of shear strain on the unit cell where the ionic displacements are along the [011] crystallographic direction in the y-z plane. This set of calculations will produce the coefficient $B_{4yz}$. For each case, the value of $\kappa_\eta$ is taken to be half of the eigenvalue and we again fit the data for $\kappa_\eta$ as a function of relative strain via Eq. 3.12 yielding $B_{1xx}$, $B_{1yy}$, and $B_{4yz}$. Figure 3.7 shows the results of these LDA DFPT calculations depicting $\kappa_\eta$ versus $\eta$ for the three different coupling constants. The slope of each line gives the corresponding coupling constant.

Table 3.6 summarizes the final sets of strain-local mode parameters for the GGA and LDA. Additionally, we include the coupling constants found from the 5 atom frozen phonon calculations and also those found from the LDA calculations of Ref. [5].

Of the two methods we have followed to calculate the coupling coefficients, each has its advantages. The frozen phonon method allows one to place the atoms at the exact locations necessary to produce the desired local mode distortion. However this method requires data fitting at two points in the process which could introduce additional error into the final parameters. In the DFPT method, the eigenvector may be slightly different from the one
Figure 3.7: Results of 5-atom calculations showing \( \kappa \) vs. \( \eta \) used to extract strain-local mode coupling coefficients.

Table 3.6: \( B_{\alpha \beta} \) parameters for KNbO\(_3\) using the GGA and the LDA. Other theoretically calculated values are provided for comparison. The units of strain-local mode coupling constants is Ha/a\(^2\).

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>LDA DFPT</th>
<th>Ref. [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_{1xx} )</td>
<td>-3.19</td>
<td>-2.93</td>
<td>-2.86</td>
<td>-3.01</td>
</tr>
<tr>
<td>( B_{1yy} )</td>
<td>0.043</td>
<td>0.39</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>( B_{4yz} )</td>
<td>0.002</td>
<td>0.05</td>
<td>-0.003</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

used to define \( \mathbf{u} \) and the perturbations introduced by the code may not exactly represent the desired local mode displacements. For \( B_{1xx} \) and \( B_{1yy} \), the magnitude of the DFPT values are smaller than those found using the frozen phonon method for both the LDA and the GGA meaning that DFPT predicts a weaker coupling between the two phonon modes.

3.9 Parameter Assessment

The phonon dispersion curve calculations of section 3.6 provided a qualitative test of the effective Hamiltonian parameters by confirming that the lowest energy configuration of dipoles is associated with ferroelectricity. We test both parameter sets to determine how well they reproduce various static and dynamic properties of KNbO\(_3\) (such as the spontaneous polarization, phase transition sequence, unit cell volume, transition temperatures, and phonon
Table 3.7: Complete list of effective Hamiltonian parameters for KNbO$_3$ for LDA and GGA.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref [5]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a$_{lat}$</td>
<td></td>
<td></td>
<td>Lattice Constant</td>
</tr>
<tr>
<td>ξ$_A$</td>
<td>-0.0920</td>
<td>-0.1730</td>
<td>0.18</td>
<td>Components</td>
</tr>
<tr>
<td>ξ$_B$</td>
<td>-0.8150</td>
<td>-0.8080</td>
<td>0.80</td>
<td>of Soft Mode</td>
</tr>
<tr>
<td>ξ∥</td>
<td>0.2067</td>
<td>0.3202</td>
<td>-0.31</td>
<td>Eigenvector</td>
</tr>
<tr>
<td>ξ⊥</td>
<td>0.4924</td>
<td>0.3351</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>0.4453</td>
<td>0.3475</td>
<td>0.378</td>
<td>Anharmonic</td>
</tr>
<tr>
<td>γ</td>
<td>-0.7438</td>
<td>-0.5943</td>
<td>-0.613</td>
<td>Coefficients</td>
</tr>
<tr>
<td>B$_{1xx}$</td>
<td>-3.193700</td>
<td>-2.931760</td>
<td>-3.01</td>
<td>Coupling</td>
</tr>
<tr>
<td>B$_{1yy}$</td>
<td>0.04280100</td>
<td>0.392880</td>
<td>0.33</td>
<td>Coefficients</td>
</tr>
<tr>
<td>B$_{1yz}$</td>
<td>0.00153284</td>
<td>-0.0501142</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>B$_{11}$</td>
<td>5.7092387</td>
<td>6.40499696</td>
<td>6.54</td>
<td>Elastic</td>
</tr>
<tr>
<td>B$_{12}$</td>
<td>1.11327531</td>
<td>1.11818552</td>
<td>0.96</td>
<td>Constants</td>
</tr>
<tr>
<td>B$_{44}$</td>
<td>1.376800153</td>
<td>1.33974462</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>κ$_2$</td>
<td>0.11013649</td>
<td>0.12139664</td>
<td>-</td>
<td>Harmonic</td>
</tr>
<tr>
<td>j$_1$</td>
<td>-0.01648479</td>
<td>-0.02117859</td>
<td>-</td>
<td>On-site</td>
</tr>
<tr>
<td>j$_2$</td>
<td>-0.07377966</td>
<td>-0.04880503</td>
<td>-</td>
<td>and Short-Range</td>
</tr>
<tr>
<td>j$_3$</td>
<td>0.00453245</td>
<td>0.00576144</td>
<td>-</td>
<td>Interaction</td>
</tr>
<tr>
<td>j$_4$</td>
<td>-0.00315302</td>
<td>-0.00397203</td>
<td>-</td>
<td>Parameters</td>
</tr>
<tr>
<td>j$_5$</td>
<td>-0.01851650</td>
<td>-0.01608666</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>j$_6$</td>
<td>0.00143965</td>
<td>0.00179957</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>j$_7$</td>
<td>0.00468119</td>
<td>0.00117830</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ε$_{\infty}$</td>
<td>6.712</td>
<td>6.836</td>
<td>-</td>
<td>Optical Dielectric Constant</td>
</tr>
<tr>
<td>M$_{lu}^*$</td>
<td>67.23432</td>
<td>66.89473</td>
<td>65.992</td>
<td>Local Mode Eff. Mass</td>
</tr>
<tr>
<td>M$_{\eta\eta}^*$</td>
<td>180.0010</td>
<td>180.0010</td>
<td>-</td>
<td>Inhom. Strain Eff. Mass</td>
</tr>
</tbody>
</table>

frequencies ) at finite temperatures. The following sections will describe the results of this testing. Table 3.7 provides a complete list of parameters obtained using both the GGA and LDA as well as a comparison to Ref. [5] when available.

We first calculate the spontaneous polarization as a function of temperature using a simulated annealing approach which allows us to determine the sequence of phase transitions and associated transition temperatures. For this we use our effective Hamiltonian Molecular Dynamics within an NPT ensemble. A bulk sample is simulated with supercell 16x16x16
unit cells with periodic boundary conditions applied in all directions. A simulated annealing starts at 400 K for LDA and 800 K for GGA and proceeds in 5 K decrements, using 40,000 MD steps per temperature, until a temperature of 5 K is reached. The parameters listed in table 3.7 are used. Figure 3.8 depicts the polarization components as a function of temperature for the LDA (a) and GGA (b) parameters. In the high temperature phase, all three components of the polarization are zero which is indicative of the cubic phase. As the temperature is lowered, the polarization develops a single non-zero component indicating a transition from the cubic to the tetragonal phase below $T_C$. Further reduction of the temperature results in additional non-zero components of the polarization as the material undergoes additional phase transitions into first the orthorhombic followed by the rhombohedral phases. The temperatures at which these transitions occur correspond to the structural phase transitions in KNbO$_3$. Both sets of parameters yield the correct sequence of phase transitions from cubic to tetragonal, tetragonal to orthorhombic, and finally orthorhombic to rhombohedral. However, the LDA set of parameters severely underestimate the transition temperatures. The GGA set underestimates transition temperatures from $T_{C\rightarrow T}$ and $T_{T\rightarrow O}$ while $T_{O\rightarrow R}$ is overestimated as seen in Fig. 3.8.

![Figure 3.8: Dependence of the polarization components on temperature for bulk KNbO$_3$ using the LDA parameters (a) and GGA parameters (b). The vertical lines are the experimental transition temperatures.](image-url)
The possible origin for the overestimation/underestimation of the transition temperatures is found by examining the energy as a function of local mode for the 5-atom unit cell. The depth of the well for the energy as a function of local mode plot shown in Fig. 3.9 can be used to estimate the transition temperature by converting the energy from Hartree to degrees Kelvin. A shallower energy well corresponds to a lower transition temperature. By renormalizing the anharmonic coefficients in Eq. 3.2 to incorporate the effects of strain, we can better estimate the transition temperatures. In Fig. 3.9, the solid lines represent data in the absence of strain corrections while the dashed lines represent the strain-renormalized energy curves. We notice that the inclusion of strain has the effect of lowering the energy as a function of local mode. This lowering of the energy results from allowing for possible additional relaxations of the system through the coupling of the soft mode to the acoustic phonons [5]. For both the LDA and the GGA, the renormalized energy curves predict a rhombohedral ground state consistent with experimental findings [137]. Comparing the depths of the renormalized energy wells found using the LDA and GGA parameters, we find that the change in energy relative to the energy of the ideal cubic is smallest for LDA. These shallow energy wells result in the LDA parameters severely underestimating the transition temperatures. The local mode values considered in the calculation of $E(u)$ were within the range of -0.06 to 0.06 in units of the ideal cubic lattice constant. The local mode displacements corresponding to the energy minima for the GGA are larger than those for the LDA. Recalling that the dipole moment of the unit cell is proportional to the local mode displacement explains the larger spontaneous polarization seen for GGA than for LDA in Fig. 3.8.

Table 3.8 summarizes the data presented in Fig. 3.9 by including numerical values for the energy minima and their corresponding local mode displacements as well as the changes in energy and local mode resulting from the change in crystal symmetry. The change in energy between the tetragonal-orthorhombic and orthorhombic-rhombohedral symmetries can be used to qualitatively explain the temperature over which KNbO$_3$ exists in a given
Figure 3.9: Change in first-principles energy as a function of local mode for LDA (a) and GGA (b). Solid (dashed) lines are in the absence (presence) of strain.

phase in Fig. 3.8. Comparing the magnitudes of the change in energy in the presence of strain for LDA ($\Delta E_{T\rightarrow O}$ compared to $\Delta E_{O\rightarrow R}$) we see a larger change in going from the tetragonal to orthorhombic symmetry which predicts that KNbO$_3$ will be in the tetragonal phase over a wider range temperature range. We see a similar trend when comparing the changes in energy predicted by the GGA. In Fig. 3.8 we see a larger change in spontaneous polarization in going from the tetragonal to the orthorhombic phase then from orthorhombic to rhombohedral. We can again appeal to table 3.8 for an explanation. For both GGA and LDA we see the largest change in the local mode displacement between the tetragonal and orthorhombic symmetries. This larger displacement leads to a larger change in the average dipole moment per unit volume.

Table 3.9 summarizes different static properties calculated through our effective Hamiltonian using the LDA and GGA parameters. Wherever possible, we have compared to experimental values found in Ref. [137] and Ref. [145].

Figure 3.8 also allows for the analysis of the spontaneous polarization and comparison to experimental values from Ref. [137] for the tetragonal and orthorhombic phases. Table 3.9 lists the maximum spontaneous polarization for each phase; the maximum typically corresponding to the polarization just before a phase transition. The spontaneous polar-
Table 3.8: Energy minima, corresponding local mode, energy minima differences, and change in local mode corresponding to energy minima differences for LDA, GGA, as well as LDA and GGA incorporating the effects of strain. Energies are reported in eV and local modes in units of the ideal cubic lattice constant.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>GGA with $\eta$</th>
<th>LDA with $\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{min}}^T$</td>
<td>-0.0206818</td>
<td>-0.00276264</td>
<td>-0.0449962</td>
<td>-0.00634823</td>
</tr>
<tr>
<td>$u_{\text{min}}^T$</td>
<td>0.0264432</td>
<td>0.0173187</td>
<td>0.0390495</td>
<td>0.0262631</td>
</tr>
<tr>
<td>$E_{\text{min}}^O$</td>
<td>-0.0355096</td>
<td>-0.00482561</td>
<td>-0.0574466</td>
<td>-0.00721979</td>
</tr>
<tr>
<td>$u_{\text{min}}^O$</td>
<td>0.0346673</td>
<td>0.0229015</td>
<td>0.044092</td>
<td>0.028004</td>
</tr>
<tr>
<td>$E_{\text{min}}^R$</td>
<td>-0.0466606</td>
<td>-0.00642485</td>
<td>-0.0632833</td>
<td>-0.00756604</td>
</tr>
<tr>
<td>$u_{\text{min}}^R$</td>
<td>0.0397699</td>
<td>0.0263832</td>
<td>0.0462531</td>
<td>0.0286643</td>
</tr>
<tr>
<td>$\Delta E_{T\rightarrow O}$</td>
<td>-0.0148278</td>
<td>-0.00206297</td>
<td>-0.0124504</td>
<td>-0.00087156</td>
</tr>
<tr>
<td>$\Delta u_{T\rightarrow O}$</td>
<td>0.0082241</td>
<td>0.0055828</td>
<td>0.0050425</td>
<td>0.0017409</td>
</tr>
<tr>
<td>$\Delta E_{O\rightarrow R}$</td>
<td>-0.0111510</td>
<td>-0.00159924</td>
<td>-0.0058367</td>
<td>-0.00034625</td>
</tr>
<tr>
<td>$\Delta u_{O\rightarrow R}$</td>
<td>0.0051026</td>
<td>0.0034817</td>
<td>0.0021611</td>
<td>0.0006603</td>
</tr>
</tbody>
</table>

Table 3.9: Some static properties of KNbO$_3$ compiled from LDA, GGA, and from two experimental references.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref [137]</th>
<th>Ref [145]</th>
<th>Unit cell</th>
<th>Volume</th>
<th>Ferroelectric</th>
<th>Transition</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_s$ (T)</td>
<td>41.31</td>
<td>31.58</td>
<td>30 ± 2</td>
<td>-</td>
<td>Spontaneous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$P_s$ (O)</td>
<td>36.33</td>
<td>25.11</td>
<td>32 ± 3</td>
<td>-</td>
<td>Polarization</td>
<td>$\mu$C/cm$^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$P_s$ (R)</td>
<td>35.62</td>
<td>23.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$V$ (T)</td>
<td>68.729</td>
<td>64.202</td>
<td>64.911</td>
<td>-</td>
<td>Unit cell</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$V$ (O)</td>
<td>68.925</td>
<td>64.246</td>
<td>-</td>
<td>63.6</td>
<td>Volume</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$V$ (R)</td>
<td>69.271</td>
<td>64.319</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C-T</td>
<td>620 K</td>
<td>235 K</td>
<td>708 K</td>
<td>-</td>
<td>Ferroelectric</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T-O</td>
<td>435 K</td>
<td>115 K</td>
<td>498 K</td>
<td>-</td>
<td>Transition</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O-R</td>
<td>345 K</td>
<td>80 K</td>
<td>263 K</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
ization shows the correct trend with the values increasing with decreasing symmetry. The spontaneous polarization for the tetragonal phase calculated using the LDA parameters, $P_s(T) = 31.58 \mu C/cm^2$, compares particularly well with the experimental value of $P_T^{exp} = 30\pm 2 \mu C/cm^2$ [137]. The measured spontaneous polarization of $P_O^{exp} = 32\pm 3 \mu C/cm^2$ [137] lies between that calculated for LDA and GGA, $P_s^{GGA}(O) = 36.33$ and $P_s^{LDA}(O) = 25.11 \mu C/cm^2$ respectively.

Figure 3.10 shows the volume of the unit cell as a function of temperature calculated for both sets of parameters. At the highest temperature, the material is in the cubic paraelectric phase. In the cubic phase we see a different $V(T)$ response for LDA and GGA. For the case of LDA, a decrease in temperature leads to a decrease in the volume of the unit cell while for GGA we notice increase in volume with decreasing temperature. Once the Curie temperature is reached, the volume changes abruptly as a result of the structural phase transition. As the temperature is further reduced, the volume changes abruptly at the tetragonal to orthorhombic and orthorhombic to rhombohedral transitions before approaching the ground state value at 5 K. Table 3.9 lists for LDA and GGA the volumes calculated at the temperature corresponding to the maximum value of polarization in each phase. The unit cell volume for LDA, $V(T) = 64.2 \text{Å}^3$, agrees well with the experimentally measured value of $V_T^{exp} = 64.9 \text{Å}^3$ from Ref. [137] taken for KNbO$_3$ in the tetragonal phase. The volume of the unit cell in the orthorhombic phase calculated using the LDA parameters, $V(O) = 64.2 \text{Å}^3$, closely matches the experimentally measured volume from Ref. [145] of $V_O^{exp} = 63.6 \text{Å}^3$ for the same phase. In conclusion, we find better agreement with experimental measurements for the unit cell volume using our LDA parameters, though the GGA parameters provide a better prediction of the transition temperatures.

### 3.10 Tuning $T_C$ through Scaling of $H_{eff}$ Parameters

At this point, we have calculated effective Hamiltonian parameters with the LDA and GGA and assessed the accuracy of these parameters by using them to calculate a number of static
properties. The results from the simulations using the two parameters sets, while in qualitative agreement, predict significantly different transition temperatures. The inaccuracy in the transition temperature calculations is too large to allow ECE modeling. Given the variance in the transition temperatures predicted by the two exchange-correlation energy approximations, we must look beyond first-principles calculations in order to achieve parameters which more accurately describe the phase transitions in KNbO$_3$ and it is unlikely that further DFT calculations would correct this issue. The remedy is to tune the first-principles parameters we have calculated from LDA and GGA to better reproduce the correct transition temperatures. To do this, we follow a two step process. Firstly, we rescale all the parameters in such a way that the different energy terms in the effective Hamiltonian are scaled with the same factor $k$. Specifically, we rescale the parameters so as to increase the contribution from the long-range dipole-dipole interactions which favor the ferroelectric phase and decrease the contribution form the short-range interactions which favor the cubic paraelectric phase. This leads to the onset of ferroelectricity at higher temperatures where the thermal fluctuations would destroy the polarization for the unscaled interactions. A factor of $k > 1$ is expected to deepen the double wells of the energy profile (see Fig. 3.2 for example) and therefore in-
crease the transition temperatures. This changes both the transition temperatures and the spontaneous polarization since the former is related to the depth of the well while the latter is proportional to the amplitude of the local mode. We run additional annealing calculations using a range of scaling factors [1.42 - 1.48] to determine the one which provides the most improvement. The best improvement was found for a factor of 1.44 for LDA and 1.050 for GGA. The associated annealing data are presented in Fig. 3.11 where the vertical lines are used to label the experimental transition temperatures [137]. The transition temperatures for the LDA show a substantial improvement over those predicted by the unscaled first principles parameters; the new transition temperatures being \( T_{C\rightarrow T} = 715 \text{ K} \), \( T_{T\rightarrow O} = 340 \text{ K} \), and \( T_{O\rightarrow R} = 255 \text{ K} \). The scaled GGA parameters produce transition temperatures which are closer to the experimental values of \( T_{C\rightarrow T} = 708 \text{ K} \) and \( T_{T\rightarrow O} = 498 \text{ K} \) [137], the new transition temperatures being \( T_{C\rightarrow T} = 705 \text{ K} \), \( T_{T\rightarrow O} = 505 \text{ K} \). However given that the method we used to scale the effective Hamiltonian parameters moves all the transition temperatures in the same direction and the unscaled GGA parameters overestimated the orthorhombic to rhombohedral transition temperature, this transition temperature \( T_{O\rightarrow R} = 390 \text{ K} \) is now even further from the experimental value of \( T_{O\rightarrow R} = 263 \text{ K} \) [137].

\[
\begin{align*}
T_{C\rightarrow T} &= 715 \text{ K} \\
T_{T\rightarrow O} &= 340 \text{ K} \\
T_{O\rightarrow R} &= 255 \text{ K} \\
T_{C\rightarrow T} &= 705 \text{ K} \\
T_{T\rightarrow O} &= 505 \text{ K} \\
T_{O\rightarrow R} &= 390 \text{ K}
\end{align*}
\]

Figure 3.11: Dependence of the polarization components on temperature for bulk KNbO\(_3\) using the scaled LDA parameters (a) and GGA parameters (b). The vertical lines are the experimental transition temperatures.
Table 3.10: Complete list of universally scaled effective Hamiltonian parameters for KNbO$_3$ for LDA and GGA.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref [5]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{lat}$</td>
<td>7.681</td>
<td>7.550</td>
<td>7.472</td>
<td>Lattice Constant</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.424135</td>
<td>0.241335</td>
<td>0.378</td>
<td>Anharmonic Coefficients</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-0.708426</td>
<td>-0.412689</td>
<td>-0.613</td>
<td></td>
</tr>
<tr>
<td>$B_{1xx}$</td>
<td>-3.041619</td>
<td>-2.035944</td>
<td>-3.01</td>
<td>Coupling Coefficients</td>
</tr>
<tr>
<td>$B_{1yy}$</td>
<td>0.040762</td>
<td>0.272833</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>$B_{4y_2}$</td>
<td>0.001459</td>
<td>-0.034801</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>$B_{11}$</td>
<td>5.437370</td>
<td>4.447914</td>
<td>6.54</td>
<td>Elastic Constants</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>1.060262</td>
<td>0.776518</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>$B_{44}$</td>
<td>1.311238</td>
<td>0.930377</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>$\kappa_2$</td>
<td>0.11564331</td>
<td>0.1748111</td>
<td>-</td>
<td>Harmonic</td>
</tr>
<tr>
<td>$j_1$</td>
<td>-0.0086545</td>
<td>-0.0152485</td>
<td>-</td>
<td>On-site and Short-Range Interaction Parameters</td>
</tr>
<tr>
<td>$j_2$</td>
<td>-0.0387343</td>
<td>-0.0351396</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$j_3$</td>
<td>0.0023795</td>
<td>0.0041482</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$j_4$</td>
<td>-0.00165533</td>
<td>-0.0028598</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$j_5$</td>
<td>-0.00972116</td>
<td>-0.01158239</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$j_6$</td>
<td>0.00075582</td>
<td>0.00129568</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$j_7$</td>
<td>0.0024576</td>
<td>0.00084837</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$Z^*$</td>
<td>10.1690227</td>
<td>11.870676</td>
<td>-</td>
<td>Born Eff. Charge</td>
</tr>
<tr>
<td>$\varepsilon_{\infty}$</td>
<td>6.712</td>
<td>6.836</td>
<td>-</td>
<td>Optical Dielectric Constant</td>
</tr>
<tr>
<td>$M_u^*$</td>
<td>67.23432</td>
<td>66.89473</td>
<td>65.992</td>
<td>Local Mode Eff. Mass</td>
</tr>
</tbody>
</table>
Another static property we calculated to serve as a basis for comparison to experiment is the bulk modulus, defined as $B(T) = -V_0 \frac{\partial P}{\partial V}$ where $P$ and $V$ in the derivative are temperature dependent. We find that $V(P)$ is linear so that the derivative is a constant; also since $V$ depends weakly on the temperature we use the 0 pressure volume $V_0$ to calculate $B$. In our effective Hamiltonian simulations $P$ is the independent variable so we calculate the volume of the unit cell for hydrostatic pressure, in the range 0.0 - 2.0 GPa, and take the inverse of the derivative. Figure 3.12 shows the bulk modulus as a function of temperature for both sets of parameters. The three minima in the data occur at temperatures in the vicinities of the phase transitions and are due to the fact that the maximum change in unit cell volume occurs when the structural changes are the greatest. As the temperature is decreased, the point where $B(T)$ begins to decrease abruptly corresponds to the transition temperature. This is where a change in the hydrostatic pressure will produce the largest change in the volume of the unit cell. The temperature dependence of the bulk modulus agrees qualitatively with experimental data for bulk BaTiO$_3$ given in Ref. [146] where the minimum is centered at approximately 130°C, close to the experimental transition temperature of 120°C [147]. Our results for LDA ($B_{\text{LDA}}(O) = 111.22$ GPa) and GGA ($B_{\text{GGA}}(O) = 104.76$ GPa) underestimate by 50% the experimental value of 190.4 GPa reported for KNbO$_3$ in Ref. [145]. These measurements were taken at ambient temperature where the bulk sample has the orthorhombic crystal structure. The bulk moduli associated with the minima in Fig. 3.12 for both functionals are given in table 3.11. The rate of change in $B(T)$ with respect to temperature near the phase transitions is larger for the calculations using the GGA parameters than for LDA, particularly for the tetragonal to orthorhombic and orthorhombic to rhombohedral phase transitions owing to the more abrupt change in $V(T)$ seen in GGA as opposed to LDA at the transition temperatures.

Next the data given in Fig. 3.12 are used to determine the thermal expansion coefficient as a function of temperature, shown in Fig. 3.13. The thermal expansion coefficient, up to a first order approximation, is defined as $\alpha_{\text{exp}}(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$. We again see the maximum re-
Figure 3.12: Dependence of the bulk modulus on temperature for bulk KNbO$_3$ using the scaled LDA parameters (a) and GGA parameters (b). The vertical lines are the computational transition temperatures.

Figure 3.14 shows the heat capacity as a function of temperature for the LDA (a) and the GGA (b). The heat capacity at constant pressure is defined as $C_P = C_{E=0} = \frac{1}{V} \left( \frac{\partial U^{\text{pot}}}{\partial T} + \frac{15}{2} k_B \right)$ where $V$ is the unit cell volume, $U^{\text{pot}}_E$ is the potential energy defined in Eq. 2.10, and $k_B$ is Boltzmann’s constant. The factor of $\frac{15}{2}$ reflects the fact that there are 5 atoms per unit cell which each contribute $\frac{1}{2} k_B$ per degree of freedom to the kinetic
energy. Within each phase, the $U_E^{pot} (T)$ data are fit with a linear function, the slope being equal to $\frac{\partial U_E^{pot}}{\partial T}$. The heat capacity for both LDA and GGA are proportional to temperature in the ferroelectric phases. As the temperature of KNbO$_3$ is raised, more energy must be added to the material to bring about an equivalent change in temperature. At the transition temperatures where the structural phase transitions occur, the $C_P (T)$ data are divergent resulting from discontinuities in the $U_E^{pot} (T)$ curves where the change in potential energy with respect to temperature becomes large. Note that divergent points have been removed to preserve scale. For the LDA calculations, the heat capacity becomes inversely proportional

Table 3.11: Values for bulk modulus, thermal expansion coefficient, and heat capacity at constant pressure of KNbO$_3$ for LDA and GGA.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>Ref. [148]</th>
<th>Ref. [145]</th>
<th>Ref. [149]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (T)</td>
<td>97.06</td>
<td>102.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B (O)</td>
<td>104.76</td>
<td>111.22</td>
<td>-</td>
<td>190.4</td>
<td>-</td>
</tr>
<tr>
<td>B (R)</td>
<td>108.64</td>
<td>113.89</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha_{exp}$ (T)</td>
<td>11.6905</td>
<td>6.3060</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha_{exp}$ (O)</td>
<td>1.1903</td>
<td>3.5891</td>
<td>0.322</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{exp}$ (R)</td>
<td>1.0998</td>
<td>2.2477</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$C_P$ (T)</td>
<td>15.077</td>
<td>16.082</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$C_P$ (O)</td>
<td>15.023</td>
<td>16.016</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$C_P$ (R)</td>
<td>14.975</td>
<td>15.991</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.13: Dependence of the thermal expansion coefficient on temperature for bulk KNbO$_3$ using the scaled LDA parameters (a) and GGA parameters (b). The vertical lines are the computational transition temperatures.
to the temperature in the cubic phase while for the GGA data it approaches a maximum value of approximately 15.12 MJ/K m$^3$. Table 3.11 lists the calculated heat capacities at the transition temperatures.

![Figure 3.14: Dependence of the heat capacity on temperature for bulk KNbO$_3$ using the scaled LDA parameters (a) and GGA parameters (b). The vertical lines are the computational transition temperatures.](image)

### 3.11 Further Tuning Through Scaling $B_{l\alpha\beta}$

The next step in improving the predicted transition temperatures is to scale the strain-local mode coupling coefficients, in particular $B_{1xx}$ and $B_{1yy}$ since they make the largest contribution to the strength of the coupling. We chose to rescale the $B_{l\alpha\beta}$ for several reasons: (I) We need parameters which are involved in renormalizing the energy surface in the presence of strain which limits us to either the strain-local mode coupling coefficients or the elastic constants (II) The elastic constants are found using a DFPT algorithm internal in the VASP, the results of which are generally more reliable than the energy calculations outlined in section 3.8 used to determine the $B_{l\alpha\beta}$ coefficients (III) The stability of the ferroelectric phase is more sensitive to the values of the elastic constants than to the $B_{l\alpha\beta}$ parameters and even a slight modification of the elastic constants could render the ferroelectric phases unstable (IV) the elastic constants reported in table 3.10 agree well with the experimental values given in
table 3.5 while experimental coupling coefficients are not readily available. The coefficients were varied in the ranges of -1.758 to -4.102 and 0.234 to 0.546 for $B_{1xx}$ and $B_{1yy}$ respectively corresponding to $\pm 40\%$ of their first-principles values. This has the effect of shifting the transition temperatures with respect to one another, a relative shift rather than shifting all transition temperatures by the same amount and in the same direction as before. We then performed an extensive set of simulated annealing calculations, varying one parameter by $1\%$ while holding the other fixed, to determine which set produces the greatest improvement. Figure 3.15 shows the spontaneous polarization as a function of temperature for the data set yielded by the best combination of parameters, bringing the Curie temperature to within a few Kelvin of the experimental value and improving the tetragonal to orthorhombic transition temperature at the cost of decreasing the accuracy of the lowest transition temperature. The final set of transition temperatures is $T_{C\rightarrow T} = 705$ K, $T_{T\rightarrow O} = 420$ K, and $T_{O\rightarrow R} = 330$ K. Given that the improvement to the $T_{C\rightarrow T}$ and $T_{T\rightarrow O}$ transition temperatures for the GGA parameters came at the cost of worsening the $T_{O\rightarrow R}$ transition temperature, we decided not to pursue any further rescaling of the $B_{1\alpha\beta}$ parameters.

![Figure 3.15: Dependence of the polarization on temperature for bulk KNbO$_3$ using scaled LDA parameters. The temperatures above the graph are the experimental transition temperatures.](image)

The coupling coefficients are summarized in table 3.12 listing the final scaled LDA and
Table 3.12: Scaled strain-local mode coupling constants of the effective Hamiltonian.

<table>
<thead>
<tr>
<th></th>
<th>scaled LDA</th>
<th>original LDA</th>
<th>% Change</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1xx}$</td>
<td>-2.067</td>
<td>-2.93</td>
<td>29.5 %</td>
<td>Ha/$a_0^2$</td>
</tr>
<tr>
<td>$B_{1yy}$</td>
<td>0.239</td>
<td>0.39</td>
<td>-38.7 %</td>
<td>Ha/$a_0^2$</td>
</tr>
</tbody>
</table>

Table 3.13: Complete list of transition temperatures for KNbO$_3$ using unscaled LDA and GGA parameters and at various stages of the scaling procedure. The last column are the experimental transition temperatures.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>LDA</th>
<th>GGA-Scaled $\hat{H}_{eff}$</th>
<th>LDA-Scaled $\hat{H}_{eff}$</th>
<th>LDA-Scaled $B_{l\alpha\beta}$</th>
<th>Ref [137]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-T</td>
<td>620 K</td>
<td>235 K</td>
<td>705 K</td>
<td>715 K</td>
<td>705 K</td>
<td>708 K</td>
</tr>
<tr>
<td>T-O</td>
<td>435 K</td>
<td>115 K</td>
<td>505 K</td>
<td>340 K</td>
<td>420 K</td>
<td>498 K</td>
</tr>
<tr>
<td>O-R</td>
<td>345 K</td>
<td>80 K</td>
<td>390 K</td>
<td>255 K</td>
<td>330 K</td>
<td>263 K</td>
</tr>
</tbody>
</table>

original LDA values as well as the percentage change from that predicted by first-principles. The percent changes between the unscaled and scaled are relatively large, especially for the $B_{1yy}$ coefficient though this does less than $B_{1xx}$ to scale the interaction energy term defined in Eq. 2.23.

Table 3.13 codifies the transition temperatures associated with all sets of parameters both scaled and unscaled. The transition temperatures for the final set of LDA parameters represents a compromise with the error in the 2 low temperature phase transitions equally distributed while maintaining the accuracy of the Curie temperature. The scaled GGA parameters reproduce well the Curie point as well as the temperature for tetragonal to orthorhombic transition. The LDA parameters in which no further scaling was done to the $B_{l\alpha\beta}$ coefficients however predict the correct orthorhombic crystal symmetry at room temperature, important for studies concerning possible ferroelectric device applications.

### 3.12 Dynamical Properties

Thus far the properties we have reported, i.e. spontaneous polarization, transition temperatures, bulk modulus, thermal expansion coefficient, etc., have all been static in nature. However, we are also interested in studying dynamic properties of KNbO$_3$ such as the soft phonon mode dynamics. In order to test how well our parameters reproduce the dynamic...
characteristics of KNbO$_3$ we calculate the soft phonon mode frequency using several different methods and compare our results to the experimental data of Ref [67] and previous theoretical work [5]. The first method we use is to calculate the frequencies analytically using expressions derived from the effective Hamiltonian. To derive these expressions, we solve the equations of motion for the local mode given by

$$M_u \frac{\partial^2 u}{\partial t^2} = -\nabla_u H_{eff}$$  \hspace{1cm} (3.13)

where

$$H_{eff} = \kappa u^2 + \alpha' u^4 + \gamma' \left( u_x^2 u_y^2 + u_y^2 u_z^2 + u_z^2 u_x^2 \right)$$  \hspace{1cm} (3.14)

where $u^4 = (u_x^2 + u_y^2 + u_z^2)^2$ and the variable $\dot{u}$ is the first time derivative of the local soft mode. The potential energy of Eq. 3.14 is that of Eq. 2.12 with a substitution made for the anharmonic coefficients, $\alpha \to \alpha'$ and $\gamma \to \gamma'$. These parameters $\alpha'$ and $\gamma'$ incorporate the effects of strain, renormalizing the original anharmonic coefficients ($\alpha$ and $\gamma$) by adding terms proportional and inversely proportional to the elastic constants and the strain-local mode coupling constants [5]. These are defined in terms of the effective Hamiltonian parameters as

$$\alpha' = \alpha - \frac{1}{24} \left[ \frac{(B_{1xx} + 2B_{1yy})^2}{B_{11} + 2B_{12}} + 2 \frac{(B_{1xx} - B_{1yy})^2}{(B_{11} - B_{12})} \right]$$  \hspace{1cm} (3.15)

and

$$\gamma' = \gamma + \frac{1}{2} \left[ \frac{(B_{1xx} - B_{1yy})^2}{2(B_{11} - B_{12})} - \frac{B_{4yz}^2}{B_{14}} \right].$$  \hspace{1cm} (3.16)

The energy in Eq. 3.14 is expanded in a Taylor series about the ground state value of the local mode $u_{0,\alpha}$ with the substitution $\tau_\alpha = u_\alpha - u_{0,\alpha}$. These ground state local mode is given by [5]
and
\[ u_x = u_y = u_z = \sqrt{-\frac{\kappa}{6\alpha' + 2\gamma'}} \]  
\[ (3.17) \]
for the rhombohedral ground state. The corresponding energies for the tetragonal and rhombohedral ground states are
\[ E_T = -\frac{\kappa^2}{4\alpha'} \]  
\[ (3.18) \]
and
\[ E_R = -\frac{\kappa^2}{4(\alpha' + \gamma'/3)} \]  
\[ (3.19) \]
The frequency of the \( A_1 \) mode is given by
\[ \omega_{A_1} = \sqrt{-\frac{4\kappa}{M_u^*}} \]  
\[ (3.20) \]
and the \( E \) mode is given by
\[ \omega_E = \sqrt{\frac{2\kappa\gamma'}{M_u^* (3\alpha' + \gamma')}} \]  
\[ (3.21) \]
for the rhombohedral ground state. The \( A_1 \) mode describes the case where the local mode vibrates along the direction of the polarization while \( \omega_E \) corresponds to the vibrations of the local mode perpendicular to the direction of polarization. We calculate the frequencies analytically using Eq. 3.21 by first computing the dynamical mass of the local mode using Eq. 3.20 solved for \( M_u^* \) using the first-principles DFPT values for \( \omega_{A_1} \). The first 2 columns of table 3.14 are the phonon frequencies calculated for the unscaled LDA and GGA parameters, the next 2 columns for the case in which all \( H_{\text{eff}} \) parameters have been scaled by the same factor, and the 5th column the frequencies incorporating the additional scaling of the \( B_{i\alpha\beta} \) parameters. Equation 3.21 predicts \( \nu_E \) soft mode frequencies which are lower than those found through DFPT and from Raman spectroscopy measurements reported in Ref. [67].
The universal scaling has no effect on the frequency of the $E$ mode since the parameters used to calculate $\nu_E$ are all scaled by the same amount and the differences cancel out. The additional scaling of the $B_{\alpha\beta}$ parameters shifts the frequency of $\nu_E$ up slightly from 1.69 THz to 1.94 THz. We find the best agreement for the $\nu_E$ mode with experiment using the GGA parameters though the calculated frequencies are still about half what is found using DFPT.

We also calculated the 0 K phonon modes using DFPT as implemented in the VASP (for details of the calculation see section 3.2) with the unit cell having rhombohedral symmetry. Using the knowledge that $\omega_E$ and $\omega_{A_1}$ are the soft mode frequencies which are the lowest energy transverse optical modes, we select the lowest frequency optical phonon modes. Of these 3 phonon frequencies, 2 are degenerate corresponding to $\omega_E$ since 2 directions are perpendicular to the polarization; the remaining phonon frequency describing the $\omega_{A_1}$ mode. The DFPT results agree well with experiment.

The two methods for calculating $\omega_{A_1}$ and $\omega_E$ are limited to 0 K as they are, in the first case calculated analytically using the ground state of the effective Hamiltonian, or in the latter case calculated directly from first-principles. Next we test how well our parameters reproduce the soft mode frequencies in KNbO$_3$ at finite temperatures. To determine this we calculate the dielectric response of the material using effective Hamiltonian Molecular Dynamics (for details of the calculation see 4.1.4) as proposed in Ref. [121]. This is done using the parameter sets in which the scaling has been applied to all of the effective Hamiltonian parameters with no additional scaling to the $B_{\alpha\beta}$ coefficients. The values reported in table 3.14 were calculated at 5 K. We find that the frequencies calculated using Hamiltonian Molecular Dynamics agree well with those calculated analytically using Eqs. 3.20 and 3.21. The frequency of the $A_1$ mode for LDA and GGA agree well with the $A_1$ frequencies calculated

Table 3.14: Phonon frequencies of KNbO$_3$ for LDA and GGA. Reference [67] reports soft mode phonon frequencies at 300 K found through Raman spectroscopy.

<table>
<thead>
<tr>
<th></th>
<th>GGA $H_{\omega}$</th>
<th>LDA $H_{\omega}$</th>
<th>GGA $H_{\omega}$ Scaled</th>
<th>LDA $H_{\omega}$ Scaled</th>
<th>LDA $B_{\omega\beta}$</th>
<th>GGA DFPT</th>
<th>LDA DFPT</th>
<th>GGA MD</th>
<th>LDA MD</th>
<th>Ref [5]</th>
<th>Ref [67]</th>
<th>Phonon Freqs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{A_1}$</td>
<td>5.25</td>
<td>5.47</td>
<td>5.25</td>
<td>5.47</td>
<td>5.47</td>
<td>5.25</td>
<td>5.25</td>
<td>5.93</td>
<td>5.07</td>
<td>29.59</td>
<td>6.15</td>
<td>5.25 THz</td>
</tr>
<tr>
<td>$\omega_E$</td>
<td>2.33</td>
<td>1.69</td>
<td>2.33</td>
<td>1.69</td>
<td>1.94</td>
<td>5.20</td>
<td>4.55</td>
<td>2.60</td>
<td>1.56</td>
<td>10.49</td>
<td>5.25</td>
<td>107</td>
</tr>
</tbody>
</table>
from DFPT.
4 Ferroelectric Nanowires

In section 1.4 we discussed the experimental fabrication and characterization techniques used in the study of ferroelectric nanowires while section 1.5 was devoted to explaining current and possible applications. In this chapter, we explore both fundamental properties and nanoscale device applications of ferroelectric nanowires using our effective Hamiltonian. These theoretical findings provide insight into the static and dynamic properties of nanowires which could aid in the design of development of devices and help guide future research, both theoretical and experimental, into ferroelectric nanowires.

4.1 Fundamental Properties

In the following sections we discuss various fundamental properties of ferroelectric nanowires including size dependence of the transition temperature, smearing of the phase transition and dielectric response, emergence of polydomain vortex states, as well as the soft mode phonon frequency dynamics under different mechanical boundary conditions and in the presence of an electric field.

4.1.1 Electric Properties of Ferroelectric Nanowires

We begin our investigation of fundamental properties by examining the equilibrium properties of nanowires. It has been learned in the recent decades that ferroelectricity, which was once thought to vanish at a small scale due to the decreased long-range ordering of dipoles, is actually stable in nanostructures down to a few cells [69]. Experimental measurements show that bulk BaTiO$_3$ undergoes a sequence of phase transitions starting from paraelectric
cubic to a ferroelectric tetragonal phase transition at 393 K, followed by a transition to a ferroelectric orthorhombic phase at 273 K, and a transition to a ferroelectric rhombohedral phase at 183 K [147]. However, ferroelectricity has been found to exist in ultra-thin BaTiO$_3$ nanowires down to diameters $\sim 1.2$ nm [151]. In BaTiO$_3$ nanowires with polarization perpendicular to the nanowires axis, atomic force microscopy has been used to determine that the Curie temperature is depressed as the nanowire diameter $d_{nw}$ decreases [63]. This $1/d_{nw}$ scaling is illustrated in Fig. 4.1 (a) where for smaller diameters the transition temperature is strongly dependent on the diameter, this effect reaching saturation in the bulk limit.

To calculate the size dependence of the Curie temperature, we simulate nanowires made of BaTiO$_3$ ferroelectric perovskites modeled with a NxN unit cells square lateral cross-section and grown along the [001] pseudocubic direction where N ranges from 5 to 100 unit cells (1.98 to 39.54 nm). Nanowires made of BaTiO$_3$ have been synthesized experimentally [49]. Infinitely long nanowires are simulated using periodic boundary conditions applied along the nanowire’s axial direction ($z$-direction in our case). The use of periodic boundary conditions models a nanowire with an aspect ratio $D/L \ll 1$, where $D$ and $L$ are the nanowire’s diameter and length respectively. We used a first-principles based effective Hamiltonian method in the framework of classical Molecular Dynamics as described in chapter 2. We simulate nanowires with realistic open-circuit electrical boundary conditions by screening 10% of the surface charge [68]. This percentage of surface charge screening models a situation where nanowires are surrounded by a non-conducting medium such as air. A small concentration of molecular adsorbates and ionic vacancies would account for a small amount of partial surface charge screening. We begin our simulated annealing at 525 K and decrease the temperature in steps of 10 K (300,000 MD steps per temperature) until the temperature reaches 10 K. Figure 4.1 (b) shows computational data for the Curie temperature as a function of temperature for BaTiO$_3$ nanowires of different diameters.

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18 Figure 4.1 (a) has been previously published in J. E. Spanier, A. M. Kolpak, J. J. Urban, I. Grinberg, L. Ouyang, W. S. Yun, A. M. Rappe, and H. Park, “Ferroelectric phase transition in individual single-crystalline BaTiO$_3$ nanowires.” Nano Letters, vol. 6, p. 735, 2006., and has been reproduced with permission from the American Chemical Society.
Figure 4.1: (a) Curie temperature as a function of diameter in BaTiO$_3$ nanowires [63]. The solid circles are the experimentally determined $T_C$, the error bars are the uncertainties, and the solid line is the result of the fit using the $1/d_{nw}$ scaling relation. (b) Computational Curie temperature as a function of diameter for BaTiO$_3$ nanowires under realistic open-circuit boundary conditions, 10% screening.

This $1/d_{nw}$ scaling in ferroelectric nanowires can be attributed to a reduced correlation length in the nanowires. A variational method was used to solve for the Euler-Lagrange equation for the polarization by varying the polarization of the free energy functional $\Delta G = \Delta G_V + \Delta G_S$ where $\Delta G_V$ represents the bulk part and $\Delta G_S$ the surface part of the free energy variation [152]. It was found that in ferroelectric nanowires the short-range forces are strengthened in the lateral direction (resulting from bond contraction) while the long-range forces are enhanced along the axial direction (resulting from the elongation of bonds in the longitudinal direction). This causes the long-range correlations to become more pronounced in the axial direction (polar direction for the case of open-circuit boundary conditions) in comparison to the short-range forces. Since the long-range interactions favor the ferroelectric phase while the short-range forces favor the cubic phase, the ferroelectric phase is stabilized at lower temperatures as the diameter of the nanowire decreases. They also found that when considering transition temperature as a function of the radial and longitudinal dimensions of the nanowire, separate terms arise describing the shift in $T_C$ due to correlation effects as well as the depolarization field. Since these terms are always negative, they can only decrease...
the transition temperature with respect to $T_C$ in a bulk ferroelectric sample. The $T_C(h, R)$ dependence in the limit that the nanowire length is much greater than the radius ($h \gg R$) also suggests that as the nanowire radius increases the shift in the transition temperature is smaller approaching 0 in the bulk limit. This agrees well with the experimental data shown in Fig. 4.1 (a).

4.1.2 Smearing of the Phase Transition and the Dielectric Response

We simulate three nanowires of fixed diameter made of PbTiO$_3$, BaTiO$_3$, and KNbO$_3$ ferroelectric perovskites with a square lateral cross-section of 12x12 unit cells. We follow a similar approach from the previous section using periodic boundary conditions and realistic open-circuit boundary conditions within Molecular Dynamics simulations. Nanowires made of KNbO$_3$ [50] and PbTiO$_3$ [47] have been synthesized experimentally. We cross-checked our results using a 12x12x24 supercell and found no dependence on the size of the supercell along the periodic direction. To elucidate the effect of reduced dimensions, we compare our nanowire data to that of bulk. The three materials we simulate are chosen as representatives of ferroelectrics with single (PbTiO$_3$) and multiple (BaTiO$_3$ and KNbO$_3$) phase transitions. Experimentally, bulk PbTiO$_3$ undergoes a single transition from a paraelectric cubic to a ferroelectric tetragonal phase at 763 K [153]. Bulk KNbO$_3$ exhibits the same sequence of phase transitions as BaTiO$_3$, but at elevated temperatures of 708 K (the Curie point), 498 K, and 263 K [137].

We first investigate the sequence of phase transitions in nanowires using the simulated annealing approach. In such an approach the simulations begin at a temperature well above the Curie point and proceeds in steps of 5 K decrements until the simulated temperature reaches 5 K. For each temperature $3 \times 10^5$ MD steps are used. The temperature evolution of the polarization obtained from the annealing simulations is given in Fig.4.2. For comparison

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19Sections 4.1.2 and 4.1.3 have been adapted from work which was previously published in R. Herchig, C.-M. Chang, B. K. Mani, and I. Ponomareva, “Electrocaloric effect in ferroelectric nanowires from atomistic simulations,” Scientific Reports, vol. 5, p. 17294, 2015., and has been reproduced with permission from the Nature Publishing Group
we also include data for bulk. Note that the bulk material is simulated by applying periodic boundary conditions along all three Cartesian directions. Figure 4.2(a) shows the data for PbTiO$_3$ nanowire and the bulk. It demonstrates that the reduction in dimensionality leads to a decrease in transition temperature and a smearing of the phase transition [154]. The term smearing refers to the shift towards a more 2nd order type of phase transition behavior in the $P(T)$ curves. The decrease in transition temperature is in a qualitative agreement with the predictions from the semi-phenomenological theory [152,155,156]. For the BaTiO$_3$ nanowire (see Fig.4.2(b)) we find very little change in the ferroelectric transition temperature as compared to the bulk. However, the phase transition sequence is drastically different from the one in the bulk. We do not find any polarization along the nanowire’s truncated dimensions due to a prohibitively large depolarizing field associated with the chosen electrical boundary conditions. The ferroelectric transition in the nanowire has a slightly smeared character as compared to bulk. KNbO$_3$ nanowire data are given in Fig.4.2(c) and exhibit trends similar to the BaTiO$_3$ nanowire. In particular, the ferroelectric phase transition appears to be smeared, while no polarization is developed along the nanowire’s truncated dimensions.

To gain further insight into the ferroelectric phases and phase transitions character we computed dielectric constant $\varepsilon_{33}$ for all nanowires and their bulk counterparts using a direct simulation approach. In such an approach the electric field is applied along the $z-$ Cartesian direction in increments of 36 kV/cm, while the polarization is computed for each value of the electric field. For each electric field increment $5\times10^5$ MD steps are used. The zero field slope in the polarization versus electric field data is used to calculate the dielectric constant. The data are given in Figs.4.2(d)-(f). For the PbTiO$_3$ nanowire we observe a smearing of the dielectric constant; a broadening and shortening of the peak in the $\varepsilon(T)$. A sharper peak corresponds to a more 1st order transition while a broader peak indicates a more 2nd order transition. Similar trends were also observed for the ferroelectric thin films [157]. For the BaTiO$_3$ nanowire the smearing of the dielectric constant is less pronounced. The
Figure 4.2: Dependence of the polarization components on the temperature in bulk and nanowires (a)-(c). Dependence of the dielectric constant on the temperature in bulk and nanowire (d)-(f).

dielectric constant of KNbO$_3$ nanowire is also smeared, though not as strongly as PbTiO$_3$. For comparison, in nanowires composed of K$_{0.52}$Na$_{0.48}$NbO$_3$ the dielectric response exhibits a peak at 555°C with a value of about 825 in dimensionless units [50] which agrees qualitatively with our data where we see a peak at around 515°C.

4.1.3 Emergence of Toriodal Moment of Polarization

In the case of BaTiO$_3$, we notice a small peak in the dielectric constant around 120 K. To trace the origin of the peak we turn to the dipole pattern evolution which reveals that at 135 K the nanowire undergoes a transition into a polydomain phase that is best described by a combination of two order parameters - the polarization and the toroidal moment of polarization [70], $G$. The toroidal moment of polarization is defined as $G = \frac{e^2}{2N} \sum_i r_i \times u_i$, where $N$ is the number of unit cells and $r_i$ is the location of the local mode $i$ [70]. In this case both order parameters align along the nanowire’s axial direction. The temperature evol-
olution of the toroidal moment of polarization is given in Fig. 4.3(c)-(d). A similar transition occurs in KNbO$_3$ nanowire at a higher temperature of 420 K. Previous studies involving Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanodots [68] and nanodisks and nanorods [70] have found similar dipole patterns having a toroidal moment of polarization of 27 and $\sim 25 \, e\text{Å}^2$ respectively. These values compare well with our values of $28 \, e\text{Å}^2$ for BaTiO$_3$ nanowires and $36 \, e\text{Å}^2$ for KNbO$_3$ nanowires. A similar polydomain state has been found experimentally in Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanodot arrays which agree with our results for BaTiO$_3$ and KNbO$_3$ nanowires qualitatively showing a similar dipole pattern [53].

Figure 4.3: Dipole patterns for BaTiO$_3$ at (a) 5.0 K and (b) 200.0 K. Toroidal moment of polarization for BaTiO$_3$ (c) and KNbO$_3$ (d).

Our computational data predict that ferroelectric nanowires with a poorly compensated surface charge develop ferroelectric phases with a polarization along the axial direction. Nanowires, made of materials which undergo multiple phase transitions in bulk, may develop polydomain phases with multiple order parameters. The common features are the
smearing of the phase transition and the dielectric constant, strongest in PbTiO$_3$. They can be attributed to the decrease in the correlation length due to the reduced dimensionality. Previously, the correlation effects were found to decrease the transition temperature in nanorods [152]. Smaller correlation lengths are usually associated with diffuse phase transitions [2]. Interestingly, ferroics with smeared phase transitions are quite desirable for caloric applications as they usually demonstrate a broadened caloric response [158].

4.1.4 Soft Mode Dynamics in Electrically Biased Ferroelectric Nanowires

As previously mentioned, the width of the imaginary part of the dielectric response function determines the frequency range for which ferroelectric materials are sensitive to THz radiation. This frequency range is an important characteristic in the design of THz radiation sensors [104,159] and piezoelectric sensors [160–162]. Ferroelectric materials could also be used in the design of THz radiation waveguides which offer unique advantages for biochemical sensing, non-invasive imaging, and spectroscopy applications [163]. Ferroelectric nanowires offer the additional advantages of allowing for the design of nanoscale versions of these devices as well as increased tunability of the frequency response and phase transition temperatures.

Experimental studies on SrTiO$_3$ single crystals have found that the dielectric permittivity can be tuned through the application of an external electric field [164]. This change in dielectric permittivity is inversely proportional to the soft mode frequency and proportional to the oscillator strength $\Delta \varepsilon = \frac{S_0}{\nu_0^2}$. Upon cooling a ferroelectric, the frequency of the soft mode decreases leading to an increase in the dielectric response. However in order to stay within a specified temperature range, other methods must be used to tune the dielectric response. The application of an electric field to ferroelectric nanowires offers an energy efficient means of controlling the dielectric response which could in turn be used to create solid state variable capacitors “varactors” or improve the design of already existing technologies such as THz radiation sensors and piezoelectric sensors.
To determine the tunability of the frequency dependent dielectric response in the PbTiO$_3$ nanowires, it is necessary to study the soft mode dynamics, $\omega (E)$ since this determines the bandwidth over which these devices operate. We have completed calculations for PbTiO$_3$ bulk and nanowires both in the presence and absence of an electric field at 300 K. The $dc$ field used in our simulations varies in strength from 50 - 150 % of the polarization reversal field for the PbTiO$_3$ nanowire at ambient temperature. The aim of this study is to determine what is the effect of an electric field on the soft mode dynamics in both bulk and nanowires.

We performed classical Molecular Dynamics calculations using the first-principles based approach of Ref. [121, 123] using the effective Hamiltonian [3] outlined in section 2.2.2. We simulated nanowires made of PbTiO$_3$ with square cross-sections of 21.8 nm$^2$ and bulk crystals with supercells 21.8 nm$^3$. Bulk PbTiO$_3$ crystal is simulated by applying periodic boundary conditions along all three crystallographic directions, while for nanowires periodic boundary conditions were applied only along the axial direction, [001] in our case. We first perform simulated annealings using an NPT ensemble, constant number of particles, pressure, and temperature. The simulated annealings were run from 1250 K down to 5 K in steps of 5 K. For each temperature we used 40,000 MD steps with a time step of 1.0 fs. The Curie temperature was found to be 605 K for bulk and 540 K for the nanowire. The experimental transition temperatures for PbTiO$_3$ are 763 K for bulk [153] and 747 K for nanowires [165]. The results from the simulated annealing provide the equilibrated dipole configurations for all temperatures in the range considered to be used for further calculation of the frequency dependent dielectric response. Specifically, we follow the method of [121] outlined in section 2.3.3 to calculate the autocorrelation functions which are Fourier transformed to produce $\varepsilon (\omega)$. This data is fit with the single Lorentzian oscillator function defined in Eq. 2.49 to find the characteristic frequency $\nu_0$, damping constant $\gamma_0$, and oscillator strength $S_0$.

These calculations were performed for PbTiO$_3$ in both bulk and nanowire geometry in the temperature range of 1250 - 5 K and under a biased field with strengths from 194.22 kV/cm - 496.34 kV/cm. We simulated electric fields applied parallel to the direction of the initial
polarization vector first and then the field direction was changed to being anti-parallel to \( P \). As a basis of comparison we also ran calculations in the absence of an external electric field. In our previous study [166] we found that for a ferroelectric nanowire polarized along the axial direction, the strength of the bias field required to reverse the direction of the polarization decreases linearly with temperature. This field is referred to as the polarization reversal field, or PRF. This dependence is the same as that found in experimental results for ultrathin ferroelectric polymers [167]. For such films, the intrinsic coercive field was found to decrease linearly as the temperature is increased to the Curie point. The bias fields used in this study were chosen to represent different percentages of the electric field required to completely reverse the polarization in the PbTiO\(_3\) nanowire, specifically from 45 to 115 \% of this threshold field at 300 K. At 300 K 100 \% of this threshold field is sufficient to reverse the polarization; for lower temperatures where the system has less thermal energy the corresponding PRF is higher since the dipoles are more stable in their current configuration. For higher temperatures, the increased thermal energy in the system allows for the polarization to be reversed with a lower dc field than the PRF at 300 K.

Figures 4.4 and 4.5 show the characteristic frequency as a function of temperature for several representative electric fields for bulk and nanowires respectively. The zero field \( \nu_0 (T) \) curves are also included for comparative purposes. Comparison of the figures for bulk and nanowires confirms that the change in geometry affects the Curie temperature, shifting it to lower temperatures for the nanowire. We found a shift in the Curie temperature of 65 K in going from bulk to nanowire. The degree of softening of the optical phonon mode also changes from bulk to nanowires with the mode reaching a lower minimum frequency for the former.

The presence of the bias field also strongly influences the soft mode frequency for both systems. In general, the effect of the bias field is to shift the \( \nu_0 (T) \) curves with respect to their zero electric field positions. For the electric field and polarization anti-parallel (parallel), the curves are shifted to the left (right). The discontinuity in the curves for the
Anti-parallel polarization and electric field vectors is due to the reversal of the polarization in the nanowire. Technically, the nanowire undergoes a transition from a metastable state with the polarization and electric field vectors being anti-parallel to a state with the vectors aligned in parallel. The temperature at which this transition occurs is determined by the PRF at the given temperature. Since the PRF decreases as the temperature of the nanowire increases, for larger bias fields the discontinuity occurs at lower temperatures. After the polarization reverses, the dynamics are essentially the same as for the case of the electric field parallel to the polarization.

We found that for both the nanowire and bulk, the mode softening at the Curie temperature lessens with increasing bias field strength. In other words, the $\nu_0 (T)$ branches are shifted to higher frequencies with respect to the zero field curves for temperatures in the vicinity of the transition temperature (see Figs. 4.4 and 4.5). Though the minimum characteristic frequency at the transition temperature for each curve increases with the electric field, it does so less as the field strength gets larger. Quantitatively, for the nanowire the mode frequency increases by approximately 0.1 THz for every 100 kV/cm that the bias field is increased. Similarly, the transition temperature is also shifted to higher values as a result of the electric field. For instance, the transition temperature for the nanowire is 55 K higher.
Figure 4.5: Characteristic frequency of the soft mode as a function of temperature for PbTiO$_3$ nanowire with electric parallel (a) and anti-parallel (b) to the polarization.

for the 302 kV/cm curve than for the 194 kV/cm branch in Fig. 4.5. In a study which used a Green’s functions method to examine the electric field dependence of the Curie temperature in displacive ferroelectrics, it was determined that the shift in the Curie temperature under an applied field was a result of anharmonic effects of the lattice [168]. In their model, the relative magnitudes of the anharmonic coefficients govern the change in Curie temperature in the presence of an electric field.

4.1.5 Effect of Mechanical Boundary Conditions on the Soft Mode Dynamics of PbTiO$_3$ Nanowires

In a typical ferroelectric, the soft mode phonon which is responsible for ferroelectricity is strongly coupled to the acoustic phonons. As explained in section 1.2.1, this produces a coupled ferroelectric phase transition in which the dynamics of the soft mode phonon will exhibit a strong dependence on the mechanical boundary conditions such as hydrostatic pressure, stress, and strain [169]. Various studies concerning the effects of mechanical stresses, strains, and pressures on the frequency dynamics in ferroelectric bulk crystals have found that these dynamics are strongly influenced by the mechanical boundary conditions. Raman spectroscopy has shown that the soft mode frequency in bulk ferroelectrics is proportional
to positive uniaxial stress [170] and compressive hydrostatic pressure [171]. Bulk polycrystalline BaTiO$_3$ samples showed a shift in frequency of the lower $\nu_{A_1}(TO)$ branch of about 30 cm$^{-1}$ over a change in pressure of 9 GPa. First-principles DFT calculations on PbTiO$_3$ at 0 K revealed a colossal enhancement of piezoelectricity resulting from hydrostatic pressure [172]. Raman spectroscopy has also been used to determine the effect of stress [173] and epitaxial strain [174] on PbTiO$_3$ thin films. Reference [173] found that a biaxial stress of $\approx$ 1 GPa resulted in a shift in the soft mode frequency of about 6.3 cm$^{-1}$. In the epitaxially strained PbTiO$_3$ thin films, the range of strains considered was between -1% to 1% over which the soft mode frequency change was about 20 cm$^{-1}$. While studies on ferroelectrics with bulk and thin film geometries are relatively numerous [170, 171, 173, 174], studies concerning the effects of mechanical boundary conditions on ferroelectric nanowires are more limited [57, 175, 176]. Given the strong depolarizing field present in ferroelectric nanowires under open-circuit boundary conditions resulting in a reduced correlation length for the polarization, the soft mode dynamics are likely to be significantly distinct from those in bulk and thin film geometries.

Recent studies on PbTiO$_3$ nanowires have revealed that negative hydrostatic pressure, once thought to be unachievable in experiment, can be created through the structural transition from a lower density $PX$ phase to a higher density perovskite phase in PbTiO$_3$ nanowires [175]. The phase transition begins at the surface of the nanowire and continues inward causing the difference in densities between the two phases to induce a negative pressure while the transition occurs. This study found a large enhancement in the tetragonality (c/a ratio) which is attributed to the large induced negative pressure, however, the exact origin of the increased tetragonality remains unclear. The work also revealed a dependence of the soft mode frequency on the pressure, though the proposed analysis was unable to decouple the size effects from those resulting from the induced negative pressure. It was hypothesized that this method of producing hydrostatic negative pressure could be further extended to other ferroelectric materials [176]. This was confirmed by subsequent
experiments on PbTiO$_3$, Pb(Ti$_x$Zr$_{1-x}$)O$_3$, and BaTiO$_3$ in which an enhancement in the c/a ratio, spontaneous polarization, and the piezoelectric constants was found for nanowires made of these materials [57]. Phenomenological studies have been carried out on ferroelectric nanowires, in the context of Ginzburg-Landau theory, which have determined that biaxial compressive stress enhances the coercive electric field and remnant strain, while biaxial tensile stress has contrary effect [177]. If hydrostatic pressure is applied, increase in surface tension due to a decrease in the size of the nanowire, both the coercive field and remnant strain decrease. While these studies provide valuable insight into the effects of mechanical boundary conditions on the properties of ferroelectric nanowires, the effect of pressure, stress, and strain on the soft-mode dynamics remains unexplored. A comprehensive, atomistic study addressing the exact nature of the effect of mechanical boundary conditions on the soft-mode frequency dynamics in ferroelectric nanowires is necessary. The goals of this study are to: (i) to determine the equilibrium phases in PbTiO$_3$ nanowires subjected to different mechanical boundary conditions (ii) compare these dynamics with the limiting case of bulk PbTiO$_3$.

We simulate PbTiO$_3$ nanowires under different mechanical boundary conditions using the first-principles-based effective Hamiltonian for PbTiO$_3$ [178] extended to nanostructures in Ref. [179] and outlined in section 2.2.2 with classical Molecular Dynamics (MD) [119,121]. We apply realistic open-circuit electrical boundary conditions (10% surface charge screening) under which the nanowires develop a spontaneous polarization along the axial direction in the absence of a hydrostatic pressure, mechanical stress, or strain. The dimensions of a nanowire is 20x20x12 (square lateral cross-section of 60.6 nm$^2$) with periodic boundary conditions applied along the axial (z) direction. In addition to the energy terms described in section 2.2.2, the Hamiltonian used in this work contains a $+\sigma_j \eta_{j}^{\text{hom}}$ term which gives the interaction of the homogeneous strain variables, $\eta_{j}^{\text{hom}}$, with the external stress given by the stress tensor $\sigma_j$. In order to allow for comparison with previous work [169] concerning the effects of pressure on bulk PbTiO$_3$, we assign a positive sign to compressive stress and a neg-
ative sign to tensile stress. The $PV$ term explained in section 2.3.2 characterizes the energy contribution due to the external hydrostatic pressure $P$ and the volume of the supercell $V$. The Hamiltonian for PbTiO$_3$ correctly predicts different structural, thermodynamical, and dynamical properties of PbTiO$_3$ bulk including the polarization, Curie point, tetragonality, and the soft mode frequencies [178]. It has also been used previously to study dynamical properties in PbTiO$_3$ nanowires [166] as well as static properties such as spontaneous polarization and static dielectric response [180].

The effective Hamiltonian is used to calculate the force-field for the PbTiO$_3$ nanowires using a local mode mass taken from [178] since it reproduces soft mode frequencies which agree well with both first-principles calculations and experiment. We first use MD to obtain the equilibrium dipole configurations within a given thermodynamical ensemble. Depending on the specified mechanical boundary conditions, we simulate an $NPT$ (constant number of particles, pressure, and temperature), $N\sigma T$ (constant number of particles, stress, and temperature), or an $N\eta T$ (constant number of particles, strain, and temperature) ensemble. Within the $NPT$ ensemble, we apply an Evans-Hoover thermostat [119] and a barostat [121] which is mimicked by the $PV$ term in Eq. 2.10 to simulate the effect of hydrostatic pressure on the soft mode dynamics. The $N\sigma T$ is simulated by applying a thermostat while introducing a non-zero stress to the supercell defined in the $\sigma_j\eta^{hom}_j$ term of the effective Hamiltonian. The $N\eta T$ ensemble is simulated through application of a thermostat while simultaneously fixing some components of the homogeneous strain tensor; this simulates an epitaxial strain. The nanowire is slowly annealed from 1200 K down to 10 K in steps of 10 K using 100,000 MD steps (50 ps with a time step of 0.5 fs) per temperature, sufficient to reach equilibrium.

These equilibrium configurations are then used to initialize the subsequent 2.1 ns MD calculations in which the dipole moment of the supercell is used to calculate the autocorrelation functions in accordance with the method outlined in [121] and section 2.3.3. One crucial difference between our calculations and that of Ref. [121] is our use of the various thermodynamical ensembles to maintain the specified mechanical boundary conditions. The
autocorrelation functions are then Fourier transformed in order to obtain the complex dielectric response $\varepsilon(\nu_0)$ as explained in section 2.3.3. We fit the complex dielectric response data with a damped harmonic oscillator function defined in the same section in order to determine the characteristic soft mode frequency at each temperature.

The pressure and stresses we apply are within the range accessible in experiments. For example, in a recent study involving PbTiO$_3$ nanowires, a hydrostatic pressure of 4.5 GPa was achieved [175]. Ab-initio studies done on BaTiO$_3$, PbTiO$_3$, and Pb(Ti$_x$Zr$_{1-x}$)O$_3$ found that the perovskite unit cell was structurally stable under hydrostatic pressures of up to -5 GPa [57]. We apply external pressure and stresses in the range of -2 GPa to 2 GPa which for ferroelectric perovskites is within the linear regime [175]. Negative values of pressure/stress correspond to expansion/tension while positive values correspond to contraction/compression. For uniaxial stress, we chose one component of the stress tensor to be non-zero. We simulate uniaxial stress along one of the lateral directions as well as the axial direction of the nanowire. The epitaxial strain is applied within the range of -2 % to 2 % relative to the computational zero Kelvin lattice constant of cubic PbTiO$_3$ with the sign convention that negative strain corresponds to compression and positive strain to tension. The strains are also chosen to model realistic experimental conditions [181,182].

In a recent paper, the soft mode dynamics of PbTiO$_3$ bulk was studied for uniaxial and biaxial stresses, uniaxial and biaxial strains, as well as hydrostatic pressure [169]. This study revealed a strong dependence of the soft mode frequency on the mechanical boundary conditions as well as the temperature. The present work systematically explores the effects of hydrostatic pressure, stress, and strain on the soft mode dynamics in PbTiO$_3$ nanowires.

### 4.1.5.1 Hydrostatic Pressure

We begin our study with the case of positive and negative hydrostatic pressure. In order to understand the frequency dynamics in the PbTiO$_3$ nanowire under hydrostatic pressure, we first examine how the pressure affects the structural properties of the nanowire. Due
to the strong coupling between the soft mode and the acoustic phonons, the structural distortions of the unit cell influence the behaviour of the soft mode phonon frequencies. Figure 4.6 (a) shows the c/a ratio as a function of temperature for representative values of hydrostatic pressure. The tetragonality is increased for negative pressure compared to the case of zero pressure while compressive hydrostatic pressure, by contrast, decreases the tetragonality. Our results for the tetragonality as a function of temperature agree qualitatively with the experimental results of Ref. [175] for PbTiO$_3$ nanowires under tensile pressure. Figure 4.6 (b) shows the spontaneous polarization as a function of temperature for the same values of pressure referenced in Fig 4.6 (a). The increased tetragonality resulting from a larger displacement of charge leads to a larger spontaneous polarization compared to P = 0 GPa. On the other hand the polarization is diminished for positive pressure resulting from a smaller relative displacement of the oppositely charged ions.

Figure 4.6: The c/a ratio (a) and spontaneous polarization (b) for PbTiO$_3$ nanowire as a function of temperature for different hydrostatic pressures.

For all pressures within the range of -2 GPa to 2 GPa we observe a single phase transition from a paraelectric cubic P$_{m \bar{3} m}$ to a ferroelectric tetragonal P$_{4mm}$ phase. The Curie temperature as a function of hydrostatic pressure is given in Fig 4.7. We find that $T_C$ depends linearly on the applied pressure, with an increase in pressure resulting in a decrease in the Curie temperature. These results agree with the phenomenological model of Ref. [2] as well as those found through effective Hamiltonian Molecular Dynamics calculations for PbTiO$_3$ bulk [169]. Positive pressure favors the short-range interactions while negative pres-
sure favors the long-range interactions. It is this increased contribution from the short-range interactions which leads to a decrease in the Curie temperature while the enhanced role of the long-range dipole-dipole interactions give rise to the increase in $T_C$ [2].

Figure 4.7: Transition temperature as a function of hydrostatic pressure for PbTiO$_3$ nanowire.

Having established how the structural properties of the unit cell depend on the applied pressure, we now turn to examining its effect on the soft mode dynamics. Figure 4.8 (a) depicts the square of the soft mode frequency as a function of the hydrostatic pressure for both tensile (negative) and compressive (positive) pressure. Throughout the project, we only report the frequency of the lowest frequency transverse optical modes which are usually labeled (1TO); for convenience we have omitted this label. The lower frequency mode ($\nu_{A_1}$) is the frequency of ionic vibrations parallel to the direction of polarization while the higher frequency mode ($\nu_E$) represents the frequency of ionic vibrations perpendicular to the direction of polarization. Surprisingly, we see that the frequency of the E mode is much higher than that of the A$_1$ mode, contrary to what is known for bulk ferroelectrics [169, 171, 174]. This effect is exactly the same as TO-LO mode splitting for small wave vectors. More precisely, the larger depolarizing field along the truncated directions leads to a significant hardening of the E mode. Figure 4.8 (a) shows that as the hydrostatic pressure increases from -2.0 GPa to 2.0 Gpa, the $\nu_{A_1}$ mode softens or decreases in frequency. This can be understood by considering the c/a ratio and the spontaneous polarization for the
PbTiO$_3$ nanowires as a function of hydrostatic pressure shown in Figs. 4.6 (a) and (b) respectively. As the pressure increases, the polarization in the nanowire decreases. The increase in hydrostatic pressure favors the short-range forces which leads to mode hardening and a decrease in the polarization. Negative hydrostatic pressure, by contrast, favors long-range forces conducive to mode softening and an increased polarization. This is consistent with the 0 K findings of Ref. [172] where it was shown that a large hydrostatic pressure leads to a decreased polarization in PbTiO$_3$. Our computational data for the dependence of the $A_1$ mode frequency on the hydrostatic pressure agrees well with the results for PbTiO$_3$ bulk under hydrostatic pressure within the same range [169]. The same linear behavior is seen for both systems with the soft mode frequency decreasing as the pressure increases, though the frequency of $\nu_{A_1}$ is slightly higher in the nanowires than in bulk. Surprisingly, the $\nu_{E}$ mode is unaffected by the change in hydrostatic pressure and the frequency remains constant throughout the entire range of pressures. This insensitivity of the E mode to the hydrostatic pressure is related to the finite size of the nanowire and the fact that the pressure is applied equally to all sides of the nanowire. Figure 4.8 (b) shows the spontaneous strain as a function of temperature for several representative values of hydrostatic pressure. We find a large value of the $\eta_3$ component for each pressure while the $\eta_1$ and $\eta_2$ components remain relatively unchanged upon the application of pressure. The nanowire is better able to accommodate the hydrostatic pressure along the truncated directions associated with $\eta_1$ and $\eta_2$ while the axial direction associated with $\eta_3$ is strongly affected by the pressure. It is this relatively small change in the unit cell dimensions along the lateral directions which leads to an insensitivity of the E mode to the pressure while the large change in the dimensions along the axial direction leads to a pressure dependence of the $A_1$ mode.
Figure 4.8: (a) Soft mode frequency squared as a function of hydrostatic pressure for representative temperatures; colors differentiate temperatures. (b) Spontaneous strain as a function of temperature for representative values of the hydrostatic pressure.

4.1.5.2 Uniaxial Stress : Lateral Directions

We next turn to examining the soft mode dynamics under uniaxial stress in the range of -2.0 GPa to 2.0 GPa acting on the planes perpendicular to the [100] crystallographic direction (x-axis in our simulations). Note that the convention used in this project which assigns positive (negative) values to compressive (tensile) stress is used to keep with the sign convention used to describe hydrostatic pressure. We adopt this sign convention throughout the entire project. Figure 4.9 shows data for the cell parameters $a_x$, $a_y$, and $a_z$ of the unit cell for uniaxial stresses 2.0, 0.2, -0.6, and -2.0 GPa. The horizontal line represents the value of the cubic lattice constant. In going from an applied stress of 2.0 GPa to -2.0 GPa, we see the deformation of the unit cell change from being expanded along the axial direction to being expanded along the lateral direction. The degree of unit cell distortion varies depending on the amount of applied stress and for the entire range of stresses considered, we find that $a_x \neq a_y \neq a_z$. The uniaxial stress has the effect of lowering the symmetry with respect to a free nanowire.
The uniaxial stress applied to the planes perpendicular to the [100] direction changes the nature of the phase transitions in the PbTiO$_3$ nanowire significantly. Figure 4.10 gives the Curie temperature as a function of the uniaxial stress. We find that for uniaxial stress greater than or equal to -0.2 GPa, the nanowire exists in a monodomain state. For this range of stresses we observe a similar linear dependence of the Curie temperature on the perturbation as we did for the case of hydrostatic pressure except that an increase in uniaxial stress leads to an increase in $T_C$. The application of compressive uniaxial stress causes an increase in the Curie temperature with a change of 80 K in going from -0.2 GPa to 2.0 GPa. However, when we apply tensile uniaxial stress, we see no transition into the tetragonal ferroelectric phase but rather to a polydomain vortex state with counter-clockwise rotation of polarization. The polarization vortex state points along the $-\hat{z}$ direction. This change in behavior of the system, transitioning from the ferroelectric tetragonal to the polydomain phase with a polarization vortex, occurs between -0.2 and -0.4 GPa of uniaxial stress.
The monodomain state in Fig. 4.10 found within the range $\sigma = -0.2$ GPa to 2.0 GPa is best characterized by the spontaneous polarization order parameter defined as $P = Z^* \sum_i u_i$ where $Z^*$ is the Born effective charge and $u_i$ is the $i$th local mode. Figure 4.11 (a) shows the spontaneous polarization as a function of temperature for uniaxial stress with the zero stress data is given as a reference. The nanowire undergoes a phase transition at 630 K from the paraelectric $P_{4/mmm}$ phase into the ferroelectric $P_{mm2}$ phase. At 100 K the spontaneous polarization is about 76.6 $\mu$C/cm$^2$. Comparing the spontaneous polarization to the case of zero stress, we see that the compressive stress increases the polarization due to the increased tetragonality. The polarization is effectively zero for tensile stress for all temperatures considered. The origin of this zero polarization can be understood by recognizing that the dipole configuration for the polarization vortex is characterized by another order parameter, the toroidal moment of polarization. It is defined as $G = \frac{Z^*}{2N} \sum_i r_i \times u_i$, where $N$ is the number of unit cells and $r_i$ is the location of the $i$th local mode [70]. The component of polarization along the axial direction for the vortex states found for uniaxial stress within the range -0.4 to -2.0 GPa averages to zero since roughly as many dipoles posses a positive z component as
do a negative one. Figure 4.11 (b) shows the toroidal moment of polarization as a function of temperature for uniaxial stress. For the case of \( \sigma = 0 \) GPa, the toroidal moment of polarization is zero. As the external stress on the supercell is decreased the toroidal moment takes on a non-zero value below the Curie temperature reaching a maximum of \( 1.76 \text{ eÅ}^2 \) at 0 K for the case of \( \sigma = -0.6 \) GPa. For \( \sigma = -2 \) GPa, the nanowire develops a double polarization vortex state in which one vortex run clockwise and the other counter-clockwise polarized in the \( \hat{z} \) and \(-\hat{z}\) directions. Due to the opposite chirality of these vortex states the toroidal moment of polarization is on average zero through the cancellation of \( G \) and \(-G\).

Figure 4.11: Spontaneous polarization (a) and toroidal moment of polarization (b) vs. temperature for nanowire under uniaxial stress acting on the planes perpendicular to the [100] direction.

We next turn to the effect of uniaxial stress applied to the planes perpendicular to the [100] direction on the soft mode dynamics of the nanowire. Figure 4.12 (a) shows the square of the soft mode frequency as a function of the applied uniaxial stress. Within the stress range of -0.2 to 2.0 GPa, the dependence of \( \nu_{A_1} \) on the uniaxial stress is similar to bulk PbTiO\(_3\), a linear dependence with the frequency increasing as the pressure increases [169]. As with the case of the E mode found under applied hydrostatic pressure, the \( B_{1} \) mode is insensitive to the applied stress. This could be due to the influence of the depolarizing field which lessens the effects of the mechanical stress on the soft mode frequency. Note that due to the lack of symmetry between the 3 cell parameters in Fig. 4.9 we expect to see a total of 3 modes present for \( \sigma \geq -0.2 \) GPa in the monodomain phase, 1 low frequency mode
and 2 high frequency modes. The small differences between the $a_x$ and $a_y$ cell parameters result from small changes in the strain between the 2 directions which would cause the peaks associated with oscillations along each direction to be very close to one another. Our method of determining the soft mode frequency by fitting the imaginary part of the complex dielectric response with a damped harmonic oscillator does not have sufficient resolution to discern separate peaks. The abrupt change in the soft mode frequency between -0.2 and -0.4 GPa is indicative of a structural phase transition. It is within this range of stresses that we see the change in the nanowire from transitioning from the ferroelectric tetragonal to the polarization vortex state. For $\sigma \leq -0.4$ GPa, the nanowire exists in the polydomain state characterized by the toroidal moment of polarization, $\mathbf{G}$. We find that the lower frequency mode is associated with the dipole vibrations parallel to $\mathbf{G}$. The higher frequency mode is associated with dipole vibrations along the lateral directions. Interestingly, the significant decrease in the mode frequency for the polydomain state may suggest a new way to identify such vortex states. The toroidal moment of polarization found in the vortex state is typically associated with an ultra low frequency soft mode, as we see in Fig. 4.12 for stresses less than -0.2 GPa. Below -0.2 GPa, the lack of symmetry resulting from the formation of the polydomain state does not allow us to identify the proper mode labels and we will refer to them simply as the high and low frequency modes. For negative stresses, the high frequency mode shows a temperature dependence and the mode hardens slightly with decreasing stress. The low frequency mode shows a small dependence on the stress, also increasing with decreasing stress.
Figure 4.12: Frequency squared as a function of uniaxial stress applied to the planes perpendicular to the [100] direction for representative temperatures. Note that in the polydomain phase ($\sigma < -0.2$ GPa) the frequencies could not be labeled.

4.1.5.3 Uniaxial Stress: Axial Direction

To further explore the effect of uniaxial stress on the PbTiO$_3$ nanowires, we next simulate tensile and compressive stress acting on the planes perpendicular to the [001] direction (axial direction of the nanowire). Figure 4.13 (a) shows the unit cell parameters as a function of temperature for 2.0 GPa of compressive axial stress. The stress compresses the unit cell along the $z$ direction while expanding the unit cell in the $x$ and $y$ directions. Note that for all axial stresses, the cell parameters in the $x$ and $y$ directions are approximately the same due to the equivalence of these directions by symmetry. The data for $\sigma_3 = 0.2$ GPa is shown in panel (b) of Fig. 4.13. Here we see the same distortion of the unit cell as for $\sigma_3 = 2.0$ GPa but the magnitude of the distortion is reduced. For panel (c), $\sigma_3 = -0.6$ GPa, the unit cell is expanded in the $z$ direction. Figure 4.13 (d) shows data for the case of -2.0 GPa axial stress for which the expansion in the axial direction is increased.
Figure 4.13: Unit cell parameters as a function of temperature for uniaxial stresses $\sigma = 2.0$ GPa (a), $\sigma = 0.2$ GPa (b), $\sigma = -0.6$ GPa (c), and $\sigma = -2.0$ GPa (d) acting on the planes perpendicular to the [001] direction. Horizontal dashed line represents the cubic lattice constant.

For the case of uniaxial stresses acting on the planes perpendicular to the [100] direction, we found that the nanowire transitions into a ferroelectric tetragonal state for stresses greater than 0.4 GPa. In contrast, when the uniaxial stress acts on the planes perpendicular to the [001] direction, it is for stresses below 0 GPa that we see a transition into the tetragonal ferroelectric state. This is illustrated by Fig. 4.14 where we have plotted the Curie temperature as a function of the axial stress. For positive axial stress, the nanowire transitions into the polydomain phase with a single polarization vortex with the axis of rotation oriented along the nanowire axial direction. For both positive and negative stress, we find a linear dependence of $T_C$ on the applied stress, however the change in $T_C$ is larger for tensile stress compared to compressive stress.
Figure 4.14: Transition temperature as a function of axial stress acting on the planes perpendicular to the [001] direction for representative temperatures for PbTiO$_3$ nanowire.

Figure 4.15 (a) shows the spontaneous polarization as a function of temperature for representative axial stresses of $\sigma = 2.0$, 0.0, and -2.0 GPa. For an applied stress of -2.0 GPa, the dipoles are in a monodomain state with the polarization vector in the $\hat{z}$ direction. Figure 4.15 shows an increased spontaneous polarization resulting from the large tensile stress as compared to the $\sigma = 0$ curve. When a stress of 2.0 GPa is applied, the dipoles are in a polarization vortex state which produces no net polarization. This can be seen from the $\sigma = 2.0$ GPa curve in Fig. 4.15 (a) in which the polarization remains at zero for all temperatures. In Fig. 4.15 (b) the toriodal moment of polarization data is shown for $\sigma = -2.0$ and 2.0 GPa. For the case of negative axial stress where the spontaneous polarization takes on a finite value, the toroidal moment of polarization is zero. By contrast, when we apply a compressive stress along the axial direction, a vortex of polarization is induced and the toroidal moment of polarization is non-zero.
Figure 4.15: Spontaneous polarization (a) and toroidal moment of polarization (b) vs. temperature for nanowire under uniaxial stress acting on the planes perpendicular to the [001] direction.

Next we turn to examining the soft mode dynamics of the PbTiO$_3$ nanowire under axial stress. Figure 4.16 reports the square of the soft mode frequency as a function of the axial stress for representative temperatures. Comparing the data from Figs. 4.12 and 4.16, we notice that due to the symmetry of the nanowire the transition into the monodomain state is now seen for negative stresses while lateral stress produced a monodomain state for $\sigma \geq -0.2 \text{ GPa}$. We see that for compressive axial stress, the polydomain vortex state significantly decreases the frequency of vibration parallel to the nanowire axis while the influence of the depolarizing field hardens the high frequency mode. For negative axial stress, we again see the linear dependence of the $B_{1u}$ mode on the applied stress as well as a softening of the mode with increasing temperature. This is the same behaviour found in PbTiO$_3$ bulk under tensile stress in the tetragonal ferroelectric phase [169]. Under compressive stress however, the PbTiO$_3$ bulk transitions into a ferroelectric tetragonal state below the Curie temperature and the polarization vortices are not found for negative uniaxial stress. Consequently, the mode softening in PbTiO$_3$ bulk is not as drastic as in the nanowires since it is this polydomain state which softens the frequency of the mode. The $B_{2u}$ mode also hardens slightly with increasing tensile axial stress. The temperature dependence of the $B_{2u}$ mode is less pronounced compared to that of the $B_{1u}$ mode.
Figure 4.16: Frequency squared as a function of uniaxial stress acting on the planes perpendicular to the [001] direction for representative temperatures.

4.1.5.4 Epitaxial Strain

Having analyzed the effects of hydrostatic pressure as well as uniaxial stress on the soft mode dynamics in a PbTiO$_3$ nanowire, we next turn to examining how the presence of a biaxial strain applied in the $x$-$z$ plane of the nanowire affects these dynamics. Specifically, we apply epitaxial strain by simulating a PbTiO$_3$ nanowire grown on the surface of a substrate along the [010] direction ($y$-axis in our case). Figure 4.17 shows a schematic diagram of a nanowire grown on a substrate which would produce an epitaxial strain in the X-Z plane of the nanowire. Ferroelectric 1-D nanostructures have been grown experimentally on the surface of a substrate, as arrays of BaTiO$_3$ nanowires [49] and PbTiO$_3$ nanotubes [183]. We apply strain within the range of -2% to 2% in steps of 0.02% where the negative (positive) values corresponds to compressive (tensile) strain.

Figure 4.17: Schematic diagram of a nanowire grown on a substrate producing an epitaxial strain in the X-Z plane of the nanowire.
To understand the soft mode dynamics under epitaxial strain, we begin with structural characterization of the nanowire. Figure 4.18 (a)-(d) shows the cell parameters as a function of temperature for representative strains of $\eta = 0.02$ (a), $\eta = 0.01$ (b), $\eta = -0.01$ (c), and $\eta = -0.02$ (d) applied epitaxially in the $x-z$ plane of the nanowire. For all applied strains, the $a_x$ and $a_z$ cell parameters are fixed to the lattice constant of the substrate to provide the desired strain. For 2.0% strain, the $a_x$ and $a_z$ parameters are increased with respect to the cubic lattice constant while the $a_y$ parameter is reduced. In this case we find the nanowire to be in the monodomain state with the polarization pointing along the axial direction. As the strain is reduced to 1.0%, the distortion of the unit cell is reduced and the cell parameters are closer to the cubic values as compared to 2.0% strain. Figure 4.18 (c) shows the cell parameters under -1.0% strain; here we see that the unit cell distortions are reversed for negative strain such that $a_y$ is larger than the cubic lattice constant while $a_x$ and $a_z$ are smaller. This reversal of the cell distortions results in the phase transition to the vortex states with no net polarization. As the strain is further decreased to -2.0%, we find that the unit cell is expanded in the $y$ direction and further contracted along $z$.

Figure 4.18: Unit cell parameters as a function of temperature for biaxial strain $\eta = 0.02$ (a), $\eta = 0.01$ (b), $\eta = -0.1$ (c), and $\eta = -0.02$ (d) applied in the $x-z$ plane of the nanowire. Horizontal dashed line represents the cubic lattice constant.

The Curie temperature as a function of epitaxial strain is plotted in Fig. 4.19 over the
range of -2% to 2% strain. For strains of 0.4% and smaller, the nanowire transitions into a polydomain phase; a polarization vortex. For strain larger than 0.4%, the nanowire is in the ferroelectric $P_{mm2}$ phase below the Curie temperature. Within the range of epitaxial strains of 0.6% to 2.0%, the Curie temperature shows a strong linear dependence on the strain increasing with increasing strain. Our data suggest the epitaxial strain has a larger effect on the static properties than the stress. The Curie temperature changes by 330 K over the range of strains of $\eta = 0.4\%$ to 2.0% compared to a change of 230 K seen for the application of axial stress over the range of $\sigma = 0$ to 2.0 GPa. PbTiO$_3$ bulk show a similar trend with the transition temperature increasing linearly with respect to positive biaxial strain [169].

![Graph showing transition temperature as a function of biaxial strain for PbTiO$_3$ nanowire.](image)

Figure 4.19: Transition temperature as a function of biaxial strain for PbTiO$_3$ nanowire.

Next we study the effects of the epitaxial strain on the soft mode frequency. The square of the soft mode frequency vs. the biaxial strain is shown in Fig. 4.20. For the case of biaxial strain, we observe sudden changes in the soft mode frequency resulting from abrupt structural changes associated with phase transitions. Due to the symmetry of the nanowire and the biaxial strain, we observe 3 distinct phonon modes as opposed to the case of uniaxial stress acting on planes perpendicular to the [001] direction in which we find only 2. For strains within the range of $\eta = -2.0\%$ to $\eta = 0\%$, we find 1 low frequency mode and 2
higher frequency modes. For strains greater than \( \eta = 0\% \), we find 2 low frequency modes with similar frequency and 1 high frequency mode. For \( \eta \geq 0.6\% \) where we find a non-zero value for \( P \), the separation in frequency of the low frequency modes is diminished as the temperature increases. This separation between the low frequency modes goes to 0 at \( T_C \). In the polydomain phase, we observe the extreme softening of the low frequency mode associated with the polarization vortex.

![Graph showing frequency squared as a function of biaxial strain applied along the x and z directions for representative temperatures.](image)

Figure 4.20: Frequency squared as a function of biaxial strain applied along the \( x \) and \( z \) directions for representative temperatures.

We have examined the effect of various mechanical boundary conditions on the structural parameters and soft mode dynamics in PbTiO\(_3\) nanowires. We found that depending on the particular type of mechanical boundary condition, the nanowire can exhibit either monodomain or polydomain vortex phases which is drastically different from the bulk sample and originates from the critical role of the depolarizing field. For monodomain phases the Curie temperature was found to depend linearly on the pressure, stress, or biaxial strain, in agreement with findings for bulk PbTiO\(_3\) [169]. We found a rich variety of dipole patterns, particularly for the polydomain states with the dipoles arranged in single and double polarization vortices depending on the type and strength of the mechanical boundary conditions. Small positive values of biaxial strain yield a dipole pattern with both a toroidal moment of
polarization as well as a spontaneous polarization. The soft mode frequency dynamics are also strongly affected by the mechanical boundary conditions. In particular we find that the frequency of the E mode in the $P_{4mm}$ phase is significantly larger than the $A_1$ mode which is in contrast with bulk PbTiO$_3$. This striking finding is attributed to the presence of the depolarizing field along the truncated directions which leads to mode hardening. Where the $A_1$ mode with atomic vibrations along the axial direction responds to mechanical deformations similar to bulk, the E mode with vibrations along the lateral directions is significantly less dependent on the mechanical deformations. Another remarkable finding is that in the polydomain phase, the mode associated with ionic vibrations perpendicular to $G$ has relatively low frequency which may open a way to a new identification technique for such phases.

### 4.2 Proposed Applications

The following sections explore possible applications of ferroelectric nanowires such as nanoscale THz radiation sensors and logical elements which could be used to create ultra-dense computer memory. These applications are specific to ferroelectric nanowires and exploit their unique properties which were discussed in sections 1.4 and 1.5.

#### 4.2.1 Ferroelectric Nanowires for Terahertz Sensors

From the perspective of nanoscale applications, ferroelectric nanowires are also attractive as functional elements for nanoscale sensors. Similar to bulk ferroelectrics, the sensing potential of ferroelectric nanowires derives its origin from the dependence of the spontaneous polarization on the stress, strain and temperature [162]. One attractive feature which distinguishes ferroelectric nanowires from their bulk counterparts is the dependence of the nanowires’ fer-

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20Content from section 4.2.1 has been adapted from work which was previously published in R. Herchig, K. Schultz, K. McCash, and I. Ponomareva, “Terahertz sensing using ferroelectric nanowires,” Nanotechnology, vol. 24, p. 045501, 2013., and has been reproduced with permission from IOP Science Publishing
roelectric properties on their size which offers opportunities for creating nanoscale devices with enhanced tunability [67, 74]. The purpose of this study was to investigate the temperature and polarization response in ferroelectric nanowires through the application of a THz electric field pulse. We develop a mathematical model to approximate the resulting change in temperature and corresponding change in polarization under adiabatic conditions. Finally, we examine the potential for using these nanowires for nanoscale THz sensing applications.

We explored the possibility of polarization control via THz pulses by doing a systematic study of the interaction of a Gaussian shaped electric field pulse with nanowires of 2 different diameters. We simulated nanowires made of Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ with square lateral cross-sections of 4.8 and 6.4 nm. The nanowires are grown along the [001] crystallographic direction with [100], [101], and [001] corresponding to the x, y, and z directions respectively. The surface charge is partially screened in order to realistically simulate open-circuit boundary conditions. Under these boundary conditions the nanowires are known to develop polarization along the axial or [001] direction [73]. Nanowires made of PbTiO$_3$ were found to have the same symmetry, exhibiting a tetragonal structure and polarized along the axial direction [47].

Prior to studying the dynamics, the Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanowires were equilibrated within an isothermal-isobaric ensemble. To achieve this we perform a simulated annealing in which the initial temperature of the nanowires was 2000 K. The nanowires were cooled down to 10 K in steps of 5 K using an Evans-Hoover thermostat [119, 184] and a barostat which was created using a PV term in the effective Hamiltonian was used to maintain constant pressure [121]. We used 40 000 MD steps for each temperature with each MD step being 1.0 femtosecond.

We developed a computational approach to study the intrinsic dynamics of the nanowires due to the applied electric field. The nanowires were subjected to a time-dependent Gaussian-shaped electric field pulse in the THz frequency range. The pulse was modeled using the equation
\[
E(t) = E_0 e^{-\left(\frac{t-t_0}{\tau}\right)^2} \cos(\omega t)
\] (4.1)

where \(E_0\) is the amplitude of the electric field, \(\omega = 2\pi \nu\) is its frequency, \(t_0\) is the time around which the Gaussian pulse is centered, and \(\tau\) is the full width at half maximum.

Figure 4.21: Time evolution of the polarization and temperature in 4.8 nm thick nanowire subject to pulses with \(\tau = 4\) ps and \(E_0 = 0.5\) MV/cm and frequencies \(\nu = 1\) THz (panels (a) and (b)) or \(\nu = 4\) THz (panels (c) and (d)).

Figure 4.21 shows the polarization and temperature as a function of time for the 4.8 nm thick Pb(Ti\(_{0.6}\)Zr\(_{0.4}\))O\(_3\) nanowire. Initially, the nanowires temperature is 300 K and the polarization is \(P_0 = -0.84\) C/m\(^2\). A THz Gaussian pulse with parameters \(E_0 = 0.5\) MV/cm, \(\tau = 4\) ps, and \(\nu = 1\) THz (panels (a) and (b)) and \(\nu = 4\) THz (panels (c) and (d)) is applied to the nanowire under adiabatic conditions. Figure 4.21 reveals that the nanowire responds differently to the electric field pulse of different frequency. For Pb(Ti\(_{0.6}\)Zr\(_{0.4}\))O\(_3\) the intrinsic frequency is between 3.5 and 4.0 THz. Interestingly, depending on how close the pulse frequency is to the characteristic frequency of the material, the nanowire reacts to the stimulus of the pulse in different ways. The 1.0 THz pulse is well outside this range which
causes the temperature and the polarization to oscillate in phase with the electric field. For the higher frequency pulse ($\nu = 4$ THz) the polarization and temperature oscillations lag behind the electric field. This implies a difference in the interaction mechanism between the two cases. For the lower-frequency pulse no energy is absorbed by the nanowire during the interaction since the dipoles are able to keep up with the oscillations of the electric field. For the higher frequency pulse the dipoles are not able to adjust to the oscillations of the electric field and energy is consequently absorbed by the electric field. As energy is absorbed from the electric field, the temperature of the nanowire increases from 300 K to 390 K. This in turn causes the polarization to increase from its original value to $P = -0.82$ C/m$^2$. This suggests that the presence of the 4.0 THz pulse has been “imprinted” in the nanowire. This change in polarization in ferroelectric nanowires in response to a THz pulse could find potential application in nanoscale THz radiation sensors.

In order to gain a quantitative understanding of how the THz pulse interacts with the nanowire, we begin with the first law of thermodynamics $dU = dQ + EdD$, where $dU$ is the internal energy of the nanowire, $dQ$ is the quantity of heat received, and $E$ and $D$ are the electric and electric displacement fields respectively. Under adiabatic conditions in which no heat is allowed to be exchanged, $dQ = 0$ indicating that the change in the internal energy of the nanowire is entirely due to the work done by the electric field, $dU = EdD$. To estimate the change in the nanowires internal energy during one period of the electric field $T = \frac{2\pi}{\omega}$, we first assume that the electric field given by Eq. (4.1) can be approximated by $E(t) = A(t) \cos(\omega t)$ where $A(t)$ is the average field amplitude during the time $t_i - \frac{T}{2}$ to $t_i + \frac{T}{2}$. This essentially amounts to assuming that $\frac{2\pi}{\omega} \ll \tau$, or that the period of oscillations of the electric field are much shorter than the duration of the entire pulse. The response of the nanowire to the periodic field becomes $D(t) = A\varepsilon_0(t) [\varepsilon_1 \cos(\omega t) + \varepsilon_2 \sin(\omega t)]$ where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the complex dielectric response function $\varepsilon(\omega, T)$. Under this approximation we have $\Delta U = \int_T EdD = A^2(t) \varepsilon_2 \varepsilon_0 \omega^2$ where $A(t) = E_0 e^{-\left(\frac{t - t_0}{\tau}\right)^2}$ is the Gaussian function. We can then calculate the total change in the internal energy of
the nanowire due to its interaction with the pulse as

\[
\Delta U = \int_{-\infty}^{\infty} u(t) \, dt = E_0^2 \varepsilon_2 \varepsilon_0 \frac{\omega}{2} e^{-\frac{2\pi^2}{\tau^2}} \int_{-\infty}^{\infty} e^{-\frac{2\pi^2}{\tau^2} e^{\frac{4\pi^2}{\tau^2} t}} \, dt = \sqrt{\frac{\pi}{8}} \varepsilon_2(\omega, T) \varepsilon_0 E_0^2 \tau \omega \tag{4.2}
\]

given that \( \frac{2\pi}{\omega} \ll \tau \). The change in the nanowire temperature can then be expressed in terms of the change in internal energy as \( \Delta T = \frac{\Delta U}{C_P} \) where \( C_P \) is the heat capacity at constant pressure. The associated change in the polarization can be computed as

\[
\Delta P = \int_{\Delta T} p(T) \, dT \approx p(T) \Delta T \text{ where } p(T) \text{ is the pyroelectric coefficient of the material.}
\]

Combining these equations with \( \Delta U \) from Eq. 4.2 gives

\[
\Delta T \approx \sqrt{\frac{\pi}{8}} \varepsilon_2(\omega, T) \varepsilon_0 E_0^2 \tau \omega \tag{4.3}
\]

\[
\Delta P \approx p(T) \Delta T = \sqrt{\frac{\pi}{8}} \varepsilon_2(\omega, T) \varepsilon_0 E_0^2 \tau \omega p(T) \tag{4.4}
\]

Note, that these equations were derived under the assumption of adiabatic conditions. In practice such conditions are maintained since the interaction of the nanowires with the THz pulse occurs on an ultrafast femtosecond time scale, which is much shorter than the time typically required for thermalization of the nanowire with its surroundings. In other words, nearly adiabatic conditions will be maintained as long as the thermalization with the environment occurs at a slower rate as compared to the rate at which the THz radiation modifies the polarization of the nanowire.

Equations 4.3 and (4.4) can be used to analyze our computational data given that the changes in temperature and polarization are relatively small since under these conditions, \( C_P \) and \( p(T) \) can be regarded as constants while the temperature dependence of \( \varepsilon_2(\omega, T) \) can be neglected. Figure 4.22(a) depicts the change in temperature of the nanowire as a function of the pulse width \( \tau \). According to Eq. (4.3), the change in temperature is expected to increase linearly with increasing pulse width which is indeed the behavior seen in Fig.
4.22(a). Figure 4.22(b) shows a quadratic dependence of $\Delta T$ on $E_0$, in accordance with Eq. (4.3). Equation (4.3) states that the dependence of $\Delta T$ on the frequency of the pulse is non-linear. Since it depends on the product of $\varepsilon_2(\omega)$ with $\omega$. Figure 4.22(c) shows the non-linear dependence of $\Delta T$ on the pulse linear frequency where $\nu = \frac{\omega}{2\pi}$. For ferroelectric materials, the imaginary part of the dielectric response peaks in the THz frequency range due to the soft mode phonon [121,185–187]. We have calculated the loss function $\varepsilon_2(\omega)$ for bulk Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ at 300 K using the computational approach of Ref. [121]. Figure 4.22(d) shows the product of this dielectric loss function and the frequency $\varepsilon_2(\omega)\omega$ as a function of linear frequency $\nu$. By comparing Fig. 4.22(c) and Fig. 4.22(d), we observe good agreement in the shapes of the curves with the peaks both centered around the intrinsic frequency of Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$. This further confirms the accuracy of Eq. (4.3), in particular its ability to predict the frequency dependence of the change in temperature of the nanowire for a given electric field pulse. The broadening of the curves in Fig. 4.22(c) as compared to Fig. 4.22(d) is likely due to the approximations made in neglecting the temperature dependence of $C_T$ and $\varepsilon_2(\omega,T)$ in deriving Eq. (4.3). Also, the data for Fig. 4.22(d) was calculated for bulk rather than for a nanowire which could cause further differences between the shapes of the curves. Neglecting the temperature dependence of $p(T)$ would introduce further small discrepancies in calculating the change in the nanowire’s polarization. In general, Figs. 4.22(a-d) confirm that the thermodynamics of the nanowire’s interaction with the Gaussian shaped THz pulse is indeed described by Eqs. (4.3) and (4.4).

In summary, our data suggest that under adiabatic conditions, $\Delta T$ and $\Delta P$ can be well approximated by modeling the electric field as a periodic function with an average amplitude. It also predicts that the nanowire responds to the THz pulse by a change in polarization and temperature, confirming their potential as nanoscale THz radiation sensors. The change in polarization $\Delta P$ can be converted into an external current with an average current density of $\langle j \rangle = \frac{\Delta P}{\Delta t}$ where $\Delta P$ is the change in polarization in the nanowire and $\Delta t$ is the time it takes for this $\Delta P$ to occur. For example, the average current density associated with the change
Figure 4.22: Simulation data for the 4.8 nm thick nanowire. (a) The dependence of $\Delta T$ on the pulse half-width $\tau$ obtained from simulations with $\nu=3$ THz and $E_0=0.1$ MV/cm (circles); $\nu=0.6$ THz and $E_0=2.0$ MV/cm (triangles); $\nu=4$ THz and $E_0=0.1$ MV/cm (squares). (b) The dependence of $\Delta T$ on the $E_0^2$ obtained from simulations with $\tau=32$ ps and $\nu=3$ THz (circles); $\tau=22$ ps and $\nu=4$ THz (triangles); $\tau=32$ ps and $\nu=4$ THz (squares). (c) The dependence of $\Delta T$ on the $\nu$ obtained from simulations with $E_0=0.1$ MV/cm and $\tau=32$ ps (circles); $E_0=0.2$ MV/cm and $\tau=22$ ps (triangles) $E_0=0.2$ MV/cm and $\tau=32$ ps (squares). (d) The dependence of the product $\varepsilon_2(\omega)\omega$ on the frequency $\nu$ using $\varepsilon_2(\omega)$ of bulk Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$.  

in polarization given in Fig. 4.22(c) is 1.6 kA mm$^{-2}$. The imaginary part of the dielectric response function $\varepsilon_2(\omega)$ determines the bandwidth of the sensor, the wider the curve the larger the frequency range of the response. For ferroelectric nanowires, it is expected that the loss function $\varepsilon_2$ will depend on the diameter of the nanowire giving increased tunability. Furthermore, the pyroelectric coefficient $p(T)$ of the nanowire should also be size dependent which opens up more possibilities for tuning of these nanoscale sensors [188].
4.2.2 Remote Polarization Switching Using an Applied Electric Field

One challenge which impedes technological progress is that of energy efficiency and for this reason, devices should use the lowest operational fields possible. Ferroelectric nanowires could potentially be used in the design of memory technology which would rely on the ability to efficiently reverse electric polarization. More precisely, the read-write operation is achieved via polarization reversal by the application of an electric field. To meet the ever increasing demand for energy efficiency, it is desirable to use a relatively low electric field. However for many ferroelectrics the coercive field or, the electric field required to depolarize a ferroelectric material that is polarized to saturation, can be quite large [189–191]. The previous section examined how the application of a Gaussian-shaped THz electric field pulse to Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanowires under open-circuit boundary conditions affects the temperature and polarization. The electric pulse adds energy to the system which, under adiabatic conditions, results in an increase in temperature and a change in the polarization. Though the application of an electric field resulted in a change in polarization, complete polarization reversal was not achieved since the electric field was applied along the lateral direction of the nanowire. In this study, we have proposed a way to effectively reduce the polarization reversal field (PRF) in ferroelectric nanowires. Our approach was based on the superposition of a relatively low dc electric field (the bias field) and a Gaussian shaped pulse of ac electric field with a THz frequency (THz pulse). The bias field could be as low as half of the PRF at a given temperature. Nevertheless, it will reverse the
polarization if superpositioned with a properly tailored THz pulse. Moreover, this strategy could be attractive for other potential applications, such as THz radiation sensing and remote polarization switching. Alternatively, the THz pulses may be used to remotely switch the polarization. To demonstrate the concept we carried out computational experiments in which the nanowires are subjected to a variety of superpositioned fields. Our results demonstrate that; (i) it is indeed possible to reverse the polarization in the nanowire by applying a superposition of a relatively small bias electric field and THz pulsed radiation under adiabatic conditions and, (ii) there exists a controllable route to such polarization reversal.

Polarization reversal in BaTiO$_3$ nanowires under short-circuit electrical boundary conditions has been achieved experimentally [192,193]. This was done by applying a dc field using an AFM tip to a nanowire grown on a gold substrate. Though polarization reversal was achieved in these nanowires, maintaining the final polarization state required the continued application of the dc field and the polarization reverted back to its original direction once the bias was removed. This is due to the fact that a locally switched segment with reversed polarization becomes energetically highly unfavorable and as a result it spontaneously switches back to the original orientation [193]. By applying a combination of a dc field and a Gaussian THz electric field pulse to a nanowire grown under open-circuit boundary conditions, polarization reversal could be achieved with minimal energy expenditure. Once polarization reversal has been achieved, the bias field could be removed with the polarization remaining stable. This characteristic is an important requirement for non-volatile memory applications in which a stable polarization state in the absence of an external power source is necessary. Several experimental studies have also been carried out in BaTiO$_3$ nanowires in which an axial polarization was reversed [73,194]. However, in these studies it was also found that the switched polarization was unstable and subsequently reverted back to its original orientation upon removal of the bias field.

A computational approach similar to that of section 4.2.1 was used in this study to model both PbTiO$_3$ and Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanowires with square cross sections of 21.8 nm$^2$. The
electric field used in these simulations consisted of a small bias field and a Gaussian shaped
THz pulse. Using the equilibrated configurations for temperatures ranging from 5 to 1000 K
in steps of 5 K we first identify how the polarization reversal field of the nanowires depends
on the temperature. To accomplish this the nanowires are subjected to a bias field ($E_{dc}$) for
5 - 20 ps. The longer times are used for electric fields which are closer to the PRF at a given
temperature. The $dc$ electric fields used in the calculations were in the range of 10 - 2560
kV/cm. The data is reported in Fig. 4.23(a). The field, $E_{PR}$, is found to decrease linearly
with increasing temperature, in agreement with experimental data from Ref. [167].

Figure 4.23: Panel (a) shows the dependence of the polarization reversal field in PbTiO$_3$
nanowire on the temperature. Panel (b) summarizes the data for the dependence of the
characteristic frequency on the temperature in bulk PbTiO$_3$, biased and unbiased PbTiO$_3$
nanowire. The bias field is 450 kV/cm.

Figure 4.23 suggests that if the temperature of the nanowire is increased, the PRF will be
effectively decreased. Equation 4.3 predicts that an electric pulse can be used to increase the
temperature of the nanowire. Therefore, a combination of a subswitching bias field (dc elec-
tric field which is insufficient to reverse the polarization) and an electric pulse could be used
reverse the direction of the polarization. The bias field provides a “preferential” direction
for the polarization by increasing the depth of the energy well creating an asymmetry in the
free energy vs. polarization while the electric pulse provides the additional energy needed to
overcome the energy barrier. To test this we applied, $E(t)$, under adiabatic conditions an external electric field

$$E(t) = E_b + E_0 e^{-(t-t_0)\tau} \cos (\omega t),$$

(4.5)

where $E_b$ is the bias field. The amplitudes of the electric field pulses are chosen to satisfy the inequality $E_0 + E_b < E_{PR}$. This ensures that the maximum electric field of the nanowire never exceeds the PRF associated with the initial temperature. The pulse width is varied from $18 - 78 \text{ ps}$ in order to tailor the THz pulse since the change in temperature increases linearly with $\tau$. The parameter $t_0$ is chosen to be large enough as to allow the nanowire sufficient time to equilibrate before the pulse has an appreciable effect on it.

In order for the pulse to effectively raise the temperature of the nanowire, the frequency, $\omega$, of the pulse must lie within the frequency range associated with the large imaginary part of the complex dielectric susceptibility, $\varepsilon_2$, of the nanowire. This is the frequency range corresponding to the characteristic frequency of the nanowire, the “lossy” region. To calculate the frequency range for different temperatures, we use the computational method outlined in Ref. [121]. From this we were able to calculate the real and imaginary parts of the susceptibility for the nanowire for a range of temperatures and identify the peak associated with the imaginary part of $\varepsilon_2(\omega,T)$ as described in section 4.1.4. In PbTiO$_3$ the soft mode is underdamped at room temperature which causes a sharp peak or equivalently a narrow frequency range for which the nanowire is most responsive to the electric field. In Fig. 4.23(b) we report the characteristic frequency of the $A_1$ mode, $\nu_0$, as a function of temperature for the 21.8 nm$^2$ PbTiO$_3$ nanowire and bulk PbTiO$_3$ for comparison. It is evident from the figure that the reduced dimensions associated with the nanowire have the effect of shifting the $\nu_0(T)$ branches towards the lower frequency. The bias field also has an effect on the complex dielectric response of the nanowire. To investigate the effect of the bias field on the soft mode dynamics, we computed the characteristic frequencies of the nanowire in the presence of a $dc$ field of strength 450 kV/cm depicted in Fig. 4.23(b). The
effect of the bias field is again to shift the $\nu_0(T)$ branches even further to lower frequency. For temperatures well below the Curie point, the characteristic frequencies are about 1.0 THz lower than without the bias field present. The discontinuity in the $\nu_0(T)$ is due to the transition from a metastable state with the polarization pointing opposite to the bias field (for temperatures below $308 \pm 5$ K) to a stable state with the polarization vector aligned with the bias field direction (for temperatures $305 \pm 5$ K). In the absence of the bias field, the soft mode frequency is expected to be around 2.5 THz at ambient temperature. However, the bias field shifts this value to around 1.5 THz at 300 K.

![Figure 4.24](image)

Figure 4.24: Time dependence of the temperature (panel (a)) and polarization (panel (b)) in PbTiO$_3$ nanowire. The curve contours the Gaussian envelope of THz pulse.

In Fig. 4.24(a) the instantaneous temperature as a function of time is shown for an electric field pulse with the parameters $E_b = 143$ kV/cm, $E_0 = 214$ kV/cm, $\nu = 1.5$ THz, and $\tau = 48$ ps. The switching field for the nanowire at 300 K is 450 kV/cm. The sum of $E_b$ and $E_0$ is 357 kV/cm and does no exceed $0.74E_{PR}$ of the switching field strength. Figure 4.24(b) shows the instantaneous polarization as a function of time for the same parameters. The lines represent the Gaussian envelope used in the calculations. The polarization switches direction as the nanowire reaches 336 K and continues to increase in magnitude as it interacts
with the pulse. The temperature reaches a final value of 350 K with the polarization being completely reversed having a magnitude nearly equal to the initial value of \( P_0 = -0.57 \, \text{C/m}^2 \) but with opposite sign. It is important to note that the switching of the polarization is in fact due to the sub-switching bias field. The purpose of applying the THz pulse is to raise the temperature in the nanowire. If the bias field is removed, no polarization reversal occurs while the temperature of the nanowire still increases.

With proof of principle being provided by the data in Fig. 4.24, we next turn attention to the possibility of controlled polarization reversal through the application of tailored THz electric pulses coupled with bias fields \( (E_b) \) of various strengths. As previously mentioned, the bias field is entirely responsible for the polarization reversal. However in order for the polarization reversal to occur, sufficient energy needs to be supplied by the pulse in order to elevate the nanowire’s temperature. The degree to which the temperature is elevated can be controlled by careful choice of the pulse parameters \( E_0, \nu, \) and \( \tau \). The temperature difference required to achieve polarization reversal can be estimated from

\[
\Delta T \approx \frac{dT}{dE_{PR}} [E_b + E_0 - E_{PR (T_{init})}], \tag{4.6}
\]

where \( \frac{dT}{dE_{PR}} \) indicates the slope of the \( T (E_{PR}) \) curve in Fig. 4.23. However, the change in temperature in the nanowire due entirely to the influence of the THz pulse was found earlier and is given by Eq. (4.3). Equating these two expressions gives

\[
\sqrt{\frac{\pi}{8}} \varepsilon_2(\omega, T, E_b) E_0^2 \tau \omega = C_P [E_b + E_0 - E_{PR (T_{init})}], \tag{4.7}
\]

which provides a relationship between the parameters of the electric field associated with polarization reversal. In other words, the set of parameters \( (E_b, E_0, \nu, \) and \( \tau \) which satisfies Eq. (4.7) is expected to reverse the polarization in the nanowire. The number of parameters can be further reduced by recognizing that when the frequency \( \omega \) is relatively large, the \( E_0 \) term on the right hand side of Eq. (4.7) can be neglected. This is because
the period of oscillations of the electric field is much shorter than the time associated with
the polarization reversal. For instance in Fig. 4.24, the time required for the polarization to
reverse is approximately 90.0 ps whereas the period of oscillations associated with the pulse
frequency of $\omega = 9.42$ THz is $T = 0.106$ ps, about 850 times shorter than the switching time.
This high degree of tunability is advantageous when designing THz radiation sensors or even
ferroelectric memory devices since the conditions for which the polarization will reverse can
be controlled via the parameters associated with the pulse and the bias field.

A series of further calculations were carried out to test the validity of Eq. (4.7). For
these calculations the parameters ($E_b$, $E_0$, $\nu$, and $\tau$) were varied with the restriction that
$E_0 + E_b < E_{PR}$. Figure 4.25(a) reports the inverse square of the pulse amplitude ($\frac{1}{E_0^2}$) as a
function of the field frequency for several different bias field strengths. Equation 4.7 suggest
that if $\tau$ is held constant, the curve in Fig. 4.25(a) should follow $\varepsilon_2(\omega, T, E_b) \omega$. This is
indeed the case. Furthermore, the inverse square of the field amplitude is seen to be linear
in $\tau$ as suggested by Eq. 4.7. The computational data presented in Fig. (4.25) confirms the
validity of Eq. (4.7) and demonstrates the possibility of controlling the polarization reversal
in nanowires by using a subswitching bias field coupled with a tailored THz electric field
pulse. This also opens up the possibility for the sensing of THz radiation using ferroelectric
nanowires especially given that Fig. 4.25(a) shows the nanowires to be sensitive to only a
narrow region of the THz frequency range which is desirable for THz sensing applications.

We would also like to comment on our data for the Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ nanowire for which
the same calculations were carried out. The effective Hamiltonian used here overestimates
the Curie temperature, meaning a computational temperature of 600 K should be used to
model an ambient temperature of 300 K. In general, the same trends were observed in the
Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$ data as were seen in the PbTiO$_3$ nanowire. The PRF depends linearly with
a PRF of 940 kV/cm at ambient temperature, 600 K in the case of Pb(Ti$_{0.6}$Zr$_{0.4}$)O$_3$. As for
the case of PbTiO$_3$ we found the the polarization can be reversed by simultaneous application
of a subswitching bias field and a THz pulse. A series of simulations for different parameters
Figure 4.25: Dependence of the inverse square of the pulse field amplitude on the field’s frequency (panel (a)) and on the Gaussian envelope full width at half maximum (panel (b)).

\((E_b, E_0, \nu, \text{and } \tau)\) confirmed the validity of Eq. 4.7 for the \(\text{Pb(Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3\) nanowire as well. Although the simulation temperature and PRF differed for the \(\text{Pb(Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3\) nanowire as opposed to the \(\text{PbTiO}_3\) nanowire, similar trends were found in the data. [166]

In summary, we have proposed a novel route to polarization reversal in ferroelectric nanowires which combines a sub-switching bias electric field and a Gaussian-shaped THz electric field pulse. We have explored the electric field parameter space and quantified the interaction between the polarization and the electric field under adiabatic conditions allowing for a predictable polarization reversal in nanowires under open-circuit electrical boundary conditions. Our approach allows for a substantial reduction in the polarization reversal field which could potentially lead to lower energy consumption in applications utilizing polarization reversal. This polarization reversal mechanism could potentially be used in the design of ferroelectric memory elements in which each individual nanowire stores a bit of information as a polarization state. Additionally, the proposed approach could find applications in THz radiation sensors and remote switches given that the polarization reversal is triggered by a THz pulse.
5 Electrocaloric Properties of Ferroelectric Nanowires

Over the past decade, ferroelectric materials have received considerable attention as possible candidates for solid state cooling devices due to their strong thermal response to an applied electric field, a well known example being the giant electrocaloric response discovered in 2006 in thin films made of PbZr$_{0.95}$Ti$_{0.05}$O$_3$ [43]. The electrocaloric effect (ECE), defined as an adiabatic change in temperature or equivalently an isothermal change in entropy due to an applied electric field, could be used to extract heat from a system during a solid state refrigeration cycle. Practically, ferroelectric nanostructures seem the most attractive as they allow the application of a much larger applied electric field, impose fewer design restrictions as compared to bulk, allow increased tunability with respect to the operable temperature range as well as peak temperature response, could potentially be used for cooling nanoscale devices. In fact, the majority of giant electrocaloric effects were reported for thin films and polymer ferroelectric samples [43, 66, 195, 196]. While these materials have received much attention in caloric effect studies, research on other low dimensional structures such as nanowires and nanodots is limited at best [197–199]. Electrocaloric changes in temperature of $\sim$ 12 K were found in PbTiO$_3$ nanotubes using a Landau-Devonshire model when an electric field is applied in combination with a compressive strain of $\varepsilon_{11} = \varepsilon_{22} = -0.39\%$ applied in the plane of the nanotube (azimuthal direction in cylindrical coordinates) [198]. A giant ECE of 15-20 K was found in EuTiO$_3$ nanowires at room temperature using a phenomenological thermodynamic model [200]. This study also revealed that the ECE can be

\footnote{Content from this chapter has been adapted from work which was previously published in R. Herchig, C.-M. Chang, B. K. Mani, and I. Ponomareva, “Electrocaloric effect in ferroelectric nanowires from atomistic simulations,” Scientific Reports, vol. 5, p. 17294, 2015., and has been reproduced with permission from the Nature Publishing Group}
enhanced by adjusting the nanowire diameter as well as the external tensile stress. However, these studies were carried out using the indirect approach for calculating $\Delta T_{ECE}$. In the absence of experimental measurements on nanowires, first-principles-based simulations are critical to establish the effect the reduced dimensionality will have on the electrocaloric properties of ferroelectrics. Therefore, our goal in this study is to: (i) predict the intrinsic features of the ECE in ferroelectric ultrathin nanowires; (ii) to elucidate the effect of reduced dimensionality and size on the electrocaloric properties of nanoscale ferroelectrics; (iii) to explore the potential of ferroelectric nanowires for nanoscale cooling applications.

5.1 Electrocaloric Effect in Nanowires

Having established the equilibrium phases and electric properties of nanowires in section 4.1, we turn to the modeling of the ECE and developing a quantitative model for estimating the adiabatic change in temperature in terms of the spontaneous polarization and dielectric susceptibility. We use the equilibrated dipole configurations which were calculated while studying the static properties of PbTiO$_3$, BaTiO$_3$, and KNbO$_3$ nanowires through simulated annealings of section 4.1.

5.1.1 Adiabatic Temperature Change Under Application of $\vec{E}$

To simulate the ECE we apply an electric field along the nanowire’s axial direction under adiabatic conditions using the computational approach described in Refs [16, 201]. In bulk the electric field is applied along the polarization direction. Technically, the electric field was first applied and then removed very slowly at a rate of 100 V/m per one MC sweep to ensure reversibility. A total of 2,000,000 MC sweeps were used for each simulation. Figure 5.1 shows the adiabatic change in temperature as a function of the applied electric field for nanowires of all three materials. The data points for both increasing and decreasing electric field strength are plotted demonstrating the reversibility of the process.

The electrocaloric temperature was computed as a function of the applied field for dif-
Figure 5.1: Adiabatic change in temperature as a function of applied electric field for PbTiO$_3$ (a), BaTiO$_3$ (b), and KNbO$_3$ (c).

Different initial temperatures. The electrocaloric change in temperature as a function of the initial temperature is given in Fig.5.2 for a few different values of the applied electric field. We have also included data for the linear electrocaloric response, $dT/dE$, at low fields which were computed by taking the zero field slope of temperature versus electric field data. It should be noted that our computational data for BaTiO$_3$ are in excellent agreement with the direct experimental measurements on BaTiO$_3$ multilayer thick film (see Fig.5.2(b)). For the PbTiO$_3$ nanowire, we find a reduction in the maximum electrocaloric response as compared to the bulk. Similarly, we observe a reduced maximum electrocaloric response in both BaTiO$_3$ and KNbO$_3$ nanowires as compared to their bulk counterparts. Both BaTiO$_3$ and KNbO$_3$ mostly lose their electrocaloric properties in polydomain phases.

These qualitative findings, the reduction in the maximum ECE response and the lack of response in the polydomain phase, can be elucidated with the help of Maxwell relation for the electrocaloric change in temperature (see section 1.3.2)

$$\frac{dT}{dE} = -\frac{T}{C_E} \left( \frac{\partial P}{\partial T} \right)_E$$

where $C_E$ is the volumetric heat capacity, $P$ is the polarization, $T$ and $E$ are the temperature and the electric field, respectively. For a ferroelectric material, the total polarization is given by
Figure 5.2: The electrocaloric change in temperature as a function of initial temperature for a few values of the electric field (a)-(c). In (b) the triangles give the experimental data from the direct measurements on thick films [202]. The linear ECE as a function of the initial temperature. Note, that for bulk the electric field is applied along the polarization direction (d)-(f).

\[ P = P_{spon} + \varepsilon_0 \varepsilon E \]  \hspace{1cm} (5.2)

in the linear approximation valid for low electric fields. Substituting this expression for \( P \) into Eq. 5.1, the change in temperature with respect to electric field can be approximated as

\[ \frac{dT}{dE} \approx -\frac{T}{C_E} \left[ \left( \frac{\partial P_{spon}}{\partial T} \right)_{E=0} + \varepsilon_0 \left( \frac{\partial \varepsilon}{\partial T} \right)_{E=0} E \right] \]  \hspace{1cm} (5.3)

where \( P_{spon} \) is the spontaneous polarization and \( \varepsilon \) is the dielectric constant. The latter expression suggests that the linear ECE is proportional to the pyroelectric coefficient \( \left( \frac{\partial P_{spon}}{\partial T} \right)_{E=0} \) and the derivative of the dielectric constant with respect to temperature. Both
the spontaneous polarization and the dielectric constant are reduced in the nanowire as evident from Fig. 4.2 due to the reduced correlation length. This explains the observed decrease in the maximum ECE in the nanowire as compared to bulk and also why the reduction in ECE response is greatest when transitioning from bulk to nanowires in PbTiO$_3$, then KNbO$_3$, and decreased only slightly in BaTiO$_3$. To elucidate the reason why BaTiO$_3$ and KNbO$_3$ lose their ECE response in the polydomain phase we first notice that below the ferroelectric transition temperature the ECE is dominated by the pyroelectric coefficient. Indeed in a ferroelectric phase the two terms in the Maxwell relation have the opposite sign (as could be seen from inspection of Fig. 5.3) and compete with each other. The overall sign of the ECE is determined by the largest of the two terms and is positive in this case (see Fig. 5.2). The positive sign of ECE implies that the pyroelectric coefficient \( \left( \frac{\partial P_{\text{spont}}}{\partial T} \right)_{E=0} \) makes a dominant contribution to the ECE. In the polydomain phase the spontaneous polarization depends on the temperature only weakly (see Fig. 4.2) resulting in very small values of the pyroelectric coefficient and the associated ECE. More intuitively, the reduction of ECE in a polydomain phase could be understood by recalling that inside each domain the polarization is at an angle with the applied electric field \( \vec{E} = E \hat{z} \), as shown in Fig. 4.3(a) where \( \vec{G} = G \hat{z} \). As a result the application of a relatively low electric field does not significantly affect the configurational disorder and the entropy associated with it. The lack of the entropy change results in a negligible ECE.

Figure 5.3(a)-(c) shows the linear pyroelectric coefficient as a function of temperature for PbTiO$_3$, BaTiO$_3$, and KNbO$_3$ nanowires respectively as well as the temperature derivative of the dielectric susceptibility versus temperature (d)-(f). The strongest response for both derivatives is found in the vicinity of the Curie temperature leading to the largest electrocaloric changes in temperature. The two features in Fig. 5.3(e) and 5.3(f) near the polydomain to monodomain phase transition can clearly be seen as well as the flattening out of the pyroelectric response for the polydomain states of BaTiO$_3$ and KNbO$_3$; this is especially pronounced in KNbO$_3$ with \( dP/dT \) being essentially flat in the range of 0 to 400 K.
Figure 5.3: Pyroelectric coefficient (a)-(c) and temperature derivative of the dielectric susceptibility (d)-(f) vs. temperature for PbTiO$_3$, BaTiO$_3$, and KNbO$_3$ nanowires. The vertical lines correspond to the temperature at which the nanowire transitions into the polydomain phase.

### 5.1.2 Relative Cooling Power

To investigate the potential of the nanowires for cooling applications we computed the relative cooling power \[ RCP = \Delta T_{\text{max}} \times \delta T_{\text{FWHM}}, \] where \( \Delta T_{\text{max}} \) is the maximum of the electrocaloric temperature change and, \( \delta T_{\text{FWHM}} \) is the full width at half maximum. The \( RCP \) values for different electric fields are given in Table 5.1. In all cases we find that the \( RCP \) is reduced in nanowires, on an average by 20%.

<table>
<thead>
<tr>
<th>Electric field (kV/cm)</th>
<th>PbTiO$_3$ nanowire</th>
<th>PbTiO$_3$ bulk</th>
<th>BaTiO$_3$ nanowire</th>
<th>BaTiO$_3$ bulk</th>
<th>KNbO$_3$ nanowire</th>
<th>KNbO$_3$ bulk</th>
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<td>560</td>
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<td>936</td>
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<td>5914</td>
<td>2593</td>
<td>3202</td>
<td>4040</td>
<td>4973</td>
</tr>
</tbody>
</table>

Interestingly, our computational data predict that, while the maximum electrocaloric \( \Delta T \) as well as \( RCP \) are reduced in nanowires, their room temperature response could be
significantly enhanced. Indeed all nanowires exhibit a decrease in the ferroelectric transition temperature and associated shift in both dielectric and electrocaloric response (see Fig.4.2(c)-(d) and Fig.5.2(c)-(d)). As a result the room temperature $\Delta T$ of BaTiO$_3$ nanowire remains comparable to $\Delta T$ in bulk, while PbTiO$_3$ nanowire exhibits a 30% enhancement in the room temperature $\Delta T$, which is very attractive for near room temperature refrigeration.

In summary, we studied the ECE in poorly compensated ferroelectric ultrathin nanowires and compared the findings to the ECE in bulk ferroelectrics. The computational data demonstrate a reduction in the ECE in nanowires as compared to bulk which is attributed to the reduced correlation length. In nanowires with polydomains the ECE is nearly negligible. The electrocaloric change in temperature exhibits a strong correlation with the dielectric susceptibility. Among the three ferroelectric perovskites studied in this work we find the largest ECE and $RCP$ in PbTiO$_3$ followed by KNbO$_3$ and BaTiO$_3$. This behavior is well correlated with the trends in the dielectric susceptibility and the spontaneous polarization data where we find the largest values in PbTiO$_3$, followed by KNbO$_3$ and BaTiO$_3$. While nanowires exhibit reduction in maximum ECE, they offer the opportunity to tune the electrocaloric temperature change through variation of the transition temperature. For example, in case of PbTiO$_3$ nanowires we find nearly 30% increase in the room temperature $\Delta T$, which makes such nanowires attractive for room temperature cooling applications.
6 Antiferroelectric Nanowires

Antiferroelectrics are antipolar materials that develop long-range order but no spontaneous polarization. A feature which characterizes these materials is the existence of a ferroelectric phase which is very close in energy to the antiferroelectric phase. Through the application of an electric field, the transition between the ferroelectric and antiferroelectric phase can be facilitated which gives rise to the double hysteresis loops indicative of antiferroelectrics. There exist alternative ways to induce the ferroelectric-antiferroelectric phase transition in antiferroelectrics, one being the application of epitaxial strain. This can be done either through heterostructuring layers of antiferroelectric material with substrate layers [204, 205] or by growing antiferroelectric nanostructures on a substrate layer [65, 206]. In both of these methods the driving force responsible for the stabilization of the ferroelectric phase is the epitaxial strain resulting from the lattice mismatch between the antiferroelectric material and the substrate. Experimental evidence for this effect has been found in epitaxially strained PbZrO$_3$ single crystal thin films grown on SrRuO$_3$/SrTiO$_3$ substrates [205]. The films ranged in thickness from 5 to 160 nm with films thicker than 22 nm exhibiting the characteristic double hysteresis loops, while those thinner than 22 nm showing a single ferroelectric-like hysteresis behaviour. At zero electric field, all the films were reported to have non-zero remnant polarization indicative of a mixed ferroelectric-antiferroelectric character. In another study

\[23\]Content from this chapter has been adapted from work which was previously published in B. K. Mani, R. Herchig, E. Glazkova, S. Lisenkov, and I. Ponomareva, “Emergence of ferroelectricity in antiferroelectric nanostructures,” Nanotechnology, vol. 27, p. 195705, 2016., and has been reproduced with permission from the Institute of Physics Science Publishing

\[24\]Content from this chapter has been adapted from work which was previously published in R. Herchig, B. Mani, S. Lisenkov, and I. Ponomareva, “Nanoscale properties of PbZrO$_3$ nanowires: Phase competition for enhanced energy conversion and storage.” Computational Materials Science, vol. 117, p. 468, 2016., and has been reproduced with permission from Elsevier publishing
done using PbZrO$_3$ thin layers in epitaxial PbZrO$_3$/Pb(Zr$_{0.8}$Ti$_{0.2}$)O$_3$ multilayers, the samples were found to either have mixed antiferroelectric-ferroelectric or only ferroelectric behaviour depending on the number of bilayers. These layers were arranged as (PZO$_t$/PZT$_t$)$_m$ bilayers where $t$ refers to the thickness of the single layer, $m$ is the number of layers, and $T$ is the total thickness of the sample. The thickness of the film was held constant, $T = 100$ nm, while the number of bilayers was varied as ($m=1,2,4,6,$ and $8$). These values of $m$ correspond to single layer thicknesses of ($t=50$, $25$, $12.5$, $\sim 9$, and $\sim 6$ nm). It was determined that in samples with $t \leq 9$ the ferroelectric phase is stable while thicker films yield the antiferroelectric-ferroelectric behaviour [204]. These results suggest that for the thinner films where the epitaxial strain would have a greater effect on the antiferroelectric material, the strain tends to stabilize the ferroelectric phase.

In epitaxial PbZrO$_3$ films at room temperature, the orientation of the films was found to determine whether it existed in a ferroelectric, antiferroelectric, or mixed phase [206]. Throughout the temperature range of 4.2 to 400 K, PbZrO$_3$ films were grown with either a (120)$_O$ or (001)$_O$ orientation. The films with the (120)$_O$ orientation show a mixed ferroelectric and antiferroelectric behaviour through the entire temperature range with the ferroelectric phase being more stable at low temperatures. The (001)$_O$ films show ferroelectric behaviour only up to 60 K, above which they exhibit the characteristic double-loop hysteresis signature of an antiferroelectric [206].

While studies on thin films [204–214] have begun to reveal the nature of phase transitions and electric properties of quasi-2D antiferroelectrics, very little is known about antiferroelectric nanowires. Antiferroelectric nanowires composed of NaNbO$_3$ were synthesized and characterized [58]. It was found that the nanowires are ferroelectric after annealing from 500$^\circ$C down to ambient temperature. This same study found however that NaNbO$_3$ microcubes are in an antiferroelectric phase. This raises the question of whether dimensionality determines the phase.

In a recent study [102], first-principles-based effective Hamiltonian calculations were
used to predict a surface effect which could be responsible for the size-driven ferroelectric-antiferroelectric transition in antiferroelectric nanostructures. This surface effect stabilizes the ferroelectric phase by removing energetically costly short-range interactions between “head-to-tail” dipoles. Compared to thin films, nanowires have smaller interfacial area with a substrate as well as a larger surface-to-volume ratio which could result in an enhanced surface effect. Could this mechanism lead to the emergence of ferroelectricity in antiferroelectric nanowires?

This study aims to fill the gap in our current understanding of the antiferroelectric nanostructures through the use of first-principles based Monte Carlo simulations. Specifically we aim to: (i) predict the size-driven onset of ferroelectricity in antiferroelectric nanowires; (ii) establish the role of electrical boundary conditions, or partial surface charge compensation, in the nanoscale phases of such nanowires; (iii) to gain a microscopic understanding of the size effects in antiferroelectric nanowires.

6.1 Computational Methodology

Recent developments in the effective Hamiltonian model for antiferroelectric PbZrO$_3$ have made possible realistic simulations of nanoscale antipolar materials [61]. We simulate stress-free PbZrO$_3$ nanowires with square cross sections using a super cell of dimensions $N \times N \times 20$ where $N$ ranges from 8 to 20 unit cells corresponding to lateral sizes, $d$, in the range 3.3 - 8.3 nm. Periodic boundary conditions are applied along the axial direction to simulate infinitely long nanowires grown along the [001] pseudocubic direction. The first-principles-based Hamiltonian used in this study is that of Ref. [61] and outlined in section 2.2.3. We simulate different electrical boundary conditions using the screening energy term explained in section 2.2.2. This surface charge screening simulates indirectly electrodes or compensation due to molecular adsorbates, charge carriers, intrinsic surface states, oxygen or other ionic vacancies, as well as other mechanisms [110–114,215,216]. The parameter $\beta$ which controls the amount of surface charge screening ranges in values from 0 to 1 with 0 representing perfect
open-circuit boundary conditions and 1 being perfect short-circuit boundary conditions. For our nanowires, we consider realistic short-circuit boundary conditions using $\beta$ values in the range of 0.80 to 0.95 corresponding to 80 - 95 % of the surface charge being compensated. Nanowires made of BaTiO$_3$ have been synthesized under short-circuit electrical boundary conditions (nanowire grown on conducting substrate) in which the polarization was found to point along the radial direction of the nanowire [90]. The electric hysteresis loops are simulated using the term that describes the interaction with the electric field in the effective Hamiltonian described in section 2.2.2. To obtain the electric hysteresis loops the electric field is applied in the $x$ direction, perpendicular to the axial direction of the nanowire as shown in Fig. 6.1. For each MC run, we simulate a different strength electric field; starting from $E = 0.0$ kV/cm until the maximum of $E = 4.0$ kV/cm which we consider to be an equilibration period. We use at least 40,000 Monte Carlo sweeps for a single run with a canonical ensemble with the energy given by the effective Hamiltonian.

![Figure 6.1: Schematic setup for a possible route to performing the electric measurements in PbZrO$_3$ nanostructures.](image)

It is well known that the equilibrium phases in polar nanostructures are extremely sensitive to the surface charge compensation [63, 67, 71, 113, 217]. Yet the exact amount of the compensating charge remains impossible to measure or control experimentally. In fact, often times it is the nature of the nanostructure’s equilibrium phase that suggests whether
the surface charge compensation is efficient. In particular, polar phases with polarization perpendicular to the nanostructure surface are usually associated with good surface charge compensation [63,67,113], while patterns with no net polarization are typically attributed to poor surface charge compensation [71,217]. On the other hand, the surface charge compensation due to extrinsic free carriers or molecular absorbates is likely to vary from nanowire to nanowire or even within the same nanowire. To accommodate for both the uncertainty and variation in the amount of compensating charge, we carry out simulations for the range of $\beta$ from 80 to 95% that is associated with relatively good surface charge compensation.

6.2 Emergence of Ferroelectricity in Antiferroelectric PbZrO$_3$ Nanowires

Since the appearance of a ferroelectric phase is likely to result in a large depolarizing field, the stabilization of the ferroelectric phase in antiferroelectric nanowires requires a relatively efficient mechanism for surface charge compensation. We presently consider nanowires with good surface charge compensation, specifically with 86% - 98% of the surface charge screened. Figure 6.2 shows the hysteresis loops obtained for nanowires of different diameters and different values of $\beta$. Figure 6.2(a) indicates that as the lateral cross section decreases the coercive field decreases, saturation polarization increases, and the loops transition from the antiferroelectric double loop structure to mixed antiferroelectric-ferroelectric loops. These loops, however, are not associated with the coexistence of antiferroelectric and ferroelectric phases. For the smallest diameter nanowires we observe a ferroelectric behaviour with relatively small coercive fields. In other words, the thinnest nanowires behave as soft ferroelectrics. Under the chosen electrical boundary conditions, PbZrO$_3$ nanowires exhibit an unusual “mixed” antiferroelectric-ferroelectric electric hysteresis similar to experimental findings for PbZrO$_3$ films [206]. These hysteresis loops are the result of a strong competition between the antiferroelectric and ferroelectric phases and could indicate the possibility of stabilizing either of these phases in a zero electric field.
Figure 6.2: Room temperature hysteresis loops for PbZrO$_3$ nanowires with different percentages of charge compensation.

Figure 6.2(b) gives computational data for the nanowires with very well compensated surface charge that allows for a ferroelectric phase formation. Indeed we notice that in this case all nanowires exhibit a ferroelectric phase. We observe that as the diameter of the nanowires is reduced, the coercive field and remnant polarization increase signifying a further stabilization of ferroelectricity by the surface effects. Our data predict that antiferroelectric nanowires exhibit pronounced size effects that include the emergence of ferroelectric phases below some critical lateral size, tunability of the electrical properties, and competition between the antiferroelectric and ferroelectric phases. As stated previously it was recently proposed that, the presence of a surface favors the formation and stabilization of ferroelectric phase in antiferroelectrics by eliminating energetically costly “head-to-tail” dipoles [102]. This stabilizing effect is expected to increase as the surface-to-bulk dipole ratio increases.

The dipole pattern in Fig. 6.3(b) reveals that the antiferroelectric phase in the nanowires with the largest $d$ are associated with the $\Sigma_2$ point in the Brillouin zone and closely resembles the dipole pattern for bulk PbZrO$_3$. The dipoles are arranged in a striped domain pattern with dipoles pointing in opposite directions with a periodicity of 4 unit cells and showing orthogonal symmetry. Evidence for the surface effect can also be seen in this dipole pattern with the arrangement deviating significantly from the one inside the nanowire as the surface dipoles exhibit a tendency to align perpendicular to the surface. Figure 6.3(c), on the other
hand, shows the dipole pattern for the nanowires with the smallest $d$. The dipoles are arranged in a monodomain state with the average dipole moment pointing along the lateral $x$ direction. For these figures, we used the dipole pattern found at 5 K to reduce the effect of thermal fluctuations. Our calculations predict that ultrathin PbZrO$_3$ nanowires with good surface charge compensation develop ferroelectric phases below a certain critical diameter.

![Dipole Pattern](image)

Figure 6.3: (a) Low temperature zero field dipole pattern in the thickest nanowires used in Fig. 6.2(a). (b) Low temperature zero field dipole pattern in the thinnest nanowires used in Fig. 6.2(a).

### 6.3 Role of Surface Charge Compensation in Stabilization of the Ferroelectric Phase

We next look at the effect of partial surface charge compensation on the equilibrium phases, electrical properties, and antiferroelectric-ferroelectric phase transitions in PbZrO$_3$ nanowires. Figure 6.4(a) shows hysteresis loops for a nanowire with $d = 5.8$ nm obtained using different percentages of surface charge compensation. For poorly compensated nanowires ($\beta = 0.20$), we observe only a linear response of polarization to the applied electric field and no field-induced transition into the ferroelectric or antiferroelectric phase. As a greater percentage of the surface charge is compensated for ($\beta = 0.91$), the characteristic double hysteresis loop emerges and the nanowires response to the electric field is similar to that of the bulk anti-
ferroelectric. Further improvement of the surface charge compensation ($\beta = 0.95$) results in ferroelectric behaviour in the nanowire.

Figure 6.4: (a) Room temperature hysteresis loops for PbZrO$_3$ nanowires with different percentages of partial charge compensation. (b) Room temperature polarizations as a function of surface charge compensation for nanowires with different lateral sizes.

Figure 6.4(b) shows the spontaneous polarization as a function of the surface charge compensation for a few representative nanowire lateral sizes. For all lateral sizes shown, poor surface charge compensation results in the formation of an antiferroelectric bulk-like phase with no spontaneous polarization and the double striped dipole pattern shown in Fig. 6.3(b). As the quality of the surface charge screening improves, the nanowires exhibit an onset of ferroelectricity as evident from the abrupt increase in the polarization. Our calculations predict that the quality of the surface charge compensation plays a critical role in the development of the ferroelectric phases in antiferroelectric nanowires. Specifically, only nanowires with very good surface charge compensation are able to develop a ferroelectric phase while poor surface charge compensation leads to a large residual depolarizing field which is incompatible with the ferroelectric phase. This behaviour can be seen in Fig. 6.4(b) where for the nanowire with $d = 4.1$ nm, the ferroelectric phase develops around $\beta = 0.88$ while the thicker nanowire ($d = 8.3$ nm) transitions into the ferroelectric phase at $\beta = 0.92$. That is, as the lateral size of the nanowires decreases, the $P(\beta)$ curves move to the left indicating that smaller nanowires require less compensation charge to form the ferroelectric phases. Additionally, for the thicker nanowires the total polarization is reduced.
as compared to thinner nanowires at the same $\beta$ value.

Interestingly, when we compare the data from Fig. 6.4(b) to data for similar calculations for PbZrO$_3$ nanodots and thin films [218], the evidence for the stabilizing effect resulting from the presence of surface which favors the formation and stabilization of ferroelectric phase in antiferroelectrics [102] is even more pronounced. The ferroelectric phase in PbZrO$_3$ thin films is most sensitive to the amount of surface charge compensation requiring an excellent surface charge screening to develop a ferroelectric phase. By contrast, PbZrO$_3$ nanodots are able to develop a ferroelectric phase with a much less efficient screening mechanism resulting in much poorer surface charge compensation. For thin films with thickness roughly the same as the lateral size of the nanowires in Fig. 6.4(b), almost complete screening of the surface charge is required in order for a ferroelectric phase to develop with $\beta \sim 95 - 98 \%$ efficient. However, nanodots with approximately the same lateral dimensions only require $\sim 82 - 86 \%$ surface charge screening. This can be explained by the surface effects which favor the ferroelectric phase and disfavor the antiferroelectric phase [102]. Since the nanodot has the largest surface-to-volume ratio, it exhibits the largest stabilizing effect by more efficiently eliminating energetically costly “head-to-tail” dipoles while the thin film with only one finite dimension exhibits the weakest effect.

We find that the PbZrO$_3$ nanowires do not develop vortex states commonly found in ferroelectric nanowires under poor surface charge compensation [71,180]. The antiferroelectric nanowires rather remain in the antiferroelectric bulk-like phase under these conditions. This is a consequence of the energetic proximity of the antiferroelectric phase to the ferroelectric phase in antiferroelectrics [102].

We next discuss how the equilibrium phases and electrical properties of the PbZrO$_3$ nanowires respond to a reduction in lateral cross section. Figure 6.5 shows the dependence of the spontaneous polarization on the lateral size, $d$, for a few selected $\beta$ associated with good surface charge compensation. The thickest nanowires exhibit no spontaneous polarization and remain in the antiferroelectric phase. As the lateral cross section of the nanowires
Figure 6.5: Room temperature polarization as a function of lateral size, \( d \), for nanowires with different percentages of surface charge compensation.

decreases, holding the degree of surface charge compensation constant, they undergo a phase transition into the ferroelectric phase at some critical thickness. Below this critical thickness a decrease in the lateral size leads to an increase in the polarization due to further stabilization of the ferroelectric phase by the surface effects. The critical thickness for the size driven antiferroelectric-ferroelectric phase transition depends strongly on the surface charge compensation but typically is below 10 nm. These results agree well with experimental findings for PbZrO\(_3\) thin layers in epitaxial PbZrO\(_3\)/Pb(Zr\(_{0.8}\)Ti\(_{0.2}\))O\(_3\) multilayers [204]

6.4 Proposed Applications

The ever increasing need for energy supply has propelled the quest for cleanly-generated and renewable energy. At present the electric energy demand is increasing twice as fast as overall energy use and expected to rise by more than two-thirds by 2035. For example, in 2012 42% of primary energy used was converted into electricity [219]. This in turn drives the demands for devices for efficient storing, absorbing, supplying, and converting electricity. These devices require high energy storage densities, high power density, high energy efficiency and conversion characteristics. The demand for functional materials is even more urgent for miniaturized and integratable electronics and electrical systems. Among bulk materials antiferroelectrics are receiving a lot of attention owing to their potential
for energy storage and conversion that stems from the large saturation polarization, small remnant polarization, and excellent electromechanical characteristics. For example, optimized \((\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.98}\text{Ti}_{0.02})\text{O}_3\) thick films can exhibit energy storage density of up to 60 J/cm\(^3\) and nearly 40\% efficiency [220]. This is to be compared with a typical dielectric capacitor that can only store up to 2 J/cm\(^3\) of energy [18]. Another unique and technologically desirable feature of antiferroelectrics is the large change in strain that accompanies the antiferroelectric-to-ferroelectric phase transition induced by an electric field. For example, in antiferroelectric bulk ceramics the difference in strain between the antiferroelectric and ferroelectric phases can reach up to 0.4\% making them excellent candidates for microactuators [221].

While antiferroelectrics have emerged as strong competitors in the area of materials for energy applications, their prospects for use as miniaturized devices remain largely unknown. The majority of studies to date have focused on the thin film geometry owing to the advances in the films’ growth techniques [18, 221]. Antiferroelectric films have been reported to have an energy storage density in the range of 7- 37 J/cm\(^3\) [18] which is lower than the values found for the bulk. Somewhat similar is the trend in the electromechanical response which seems to become weaker in thin films. For instance, the strain in antiferroelectric thin films can only reach up to 0.2\% [222,223]. Could this deterioration of properties be caused by the tendency of the antiferroelectric thin films to develop ferroelectric phases [204,205,207–209]? On the other hand, the properties of antiferroelectric nanostructures beyond the planar geometry is even less investigated and understood [58,224–227], which is especially true for antiferroelectric nanowires. Nanowires can be synthesized using a variety of experimental techniques [58,72,224] and are particularly valuable as both interconnects and functional units in the fabrication of electronic, optoelectronic, electrochemical, and electromechanical nanodevices [228]. At the same time the prospects of antiferroelectric nanowires for energy related applications remain virtually unknown. Can antiferroelectric nanowires outperform their bulk counterparts for energy storing and converting properties or will the onset
of ferroelectricity at the nanoscale indeed cause a deterioration in functionality? While a
definite experimental answer is pending, the atomic-scale first-principles-based simulations
can already provide some valuable guidelines. Here we use first-principles-based simulations
to calculate various static properties in PbZrO$_3$ nanowires and explore the ways in which
these antiferroelectric nanowires could potentially enhance the performance of technological
deVICES.

6.4.1 Energy Storage Applications

Figure 6.6 (a) shows that for nanowires with poorly compensated surface charge the double
hysteresis loops characteristic of antiferroelectrics is seen while for more efficient surface
charge compensation mechanisms, the loops depict ferroelectric behavior while intermediate
values lead to a mixed behaviour. As previously mentioned in section 6.1, uncertainty and
variation in the amount of compensating charge exist under experimental conditions. In
order to more realistically reproduce these conditions in our calculations, the data for a
given nanowire lateral size are averaged over the entire range of $\beta = 0.85 – 0.96$; this can
be understood as an averaging of the range of hysteresis behaviour depicted in Fig. 6.6(a).
Such an approach models closely experimental conditions where the compensating charge is
only known at a qualitative level.
Figure 6.6: Electrical hysteresis behavior for 5.0 nm nanowire for representative $\beta$ (a) Dependence of the polarization on the electric field for nanowires of different lateral sizes obtained by averaging over different $\beta$ (b).

Fig.6.6(b) shows the room temperature $P(E)$ loops obtained by averaging over different $\beta$ for nanowires with $d$ of 5.0 and 8.3 nm. Note that for the remainder of the chapter we report data averaged over the entire range of $\beta$. We notice that the thinner nanowire exhibits a ferroelectric behavior while the thicker nanowire responds to the electric field similar to a lossy dielectric. Interestingly, our computational data for the thicker nanowire resemble closely the loops obtained for 22-100 nm thick PbZrO$_3$ films [205, 208, 209] which suggests that our model of variable surface charge compensation captures well the polarization charge screening in nanoscale antiferroelectrics. One remarkable feature of the $P(E)$ loops is the relatively large $dP/dE$ slope as compared to a typical dielectric. The reason behind such a large response is the mixed antiferroelectric-ferroelectric character of the room temperature phase. Both ferroelectric and antiferroelectric phases share large saturation polarization, however, the antiferroelectric phase leads to a reduced value of remnant polarization. We computed the dielectric response of different nanowires by calculating $dP/dE$ and extrapolating the slope to zero electric field (zero-field $dP/dE$ slopes). Because our computational method underestimates the dielectric susceptibility, $\chi$, of bulk PbZrO$_3$, the values for the nanowires are reported in Fig.6.7(b) relative to the computational susceptibility of bulk PbZrO$_3$. Our
computations predict a dramatic (up to eight times) increase of $\chi$ in nanowires as compared to the bulk. The improvement in the dielectric response is attributed to the contribution from the ferroelectric phase.

Figure 6.7: The dielectric susceptibility reported relative to bulk as a function of $d$ (a); recoverable energy density (b) and efficiency (c) as a function of nanowire lateral size.

The combination of large polarization with slim hysteresis loops is favorable for energy storage. For an equivalent difference in potential, a material with high dielectric constant will possess a greater energy density. As evidenced from Fig. 6.7(b), PbZrO$_3$ nanowires possess significantly larger dielectric constants than their bulk counterparts. Therefore, comparable energy densities can be achieved in PbZrO$_3$ nanowires at lower electric fields. This will increase energy efficiency while reducing the risk of dielectric breakdown or electrical aging/fatigue in the material [229]. To estimate the performance of PbZrO$_3$ nanowires in energy storage applications we calculated the recoverable energy density, $W_r$, and efficiency, $\eta_{eff}$. These quantities are defined by the expressions

$$W_r = \int EdP \quad \eta_{eff} = \frac{2W_r}{2W_r + W_{loss}}$$  \hspace{1cm} (6.1)$$

where $E$ is the applied electric field, $dP$ is the infinitesimal change in the polarization, and $W_{loss}$ represents the energy density lost per cycle and is depicted in Fig. 6.8.

The $W_r$ and $\eta_{eff}$ for nanowires of different lateral sizes computed for the maximum
electric field of 4.0 MV/cm are given in Fig.6.7(b) and (c) respectively. The straight horizontal lines give the value for bulk PbZrO$_3$. We first note that the bulk value for $W_r$ of 53 J/cm$^2$ compares well with the experimental values of 37-53 J/cm$^2$ obtained for optimized (Pb$_{0.2}$La$_{0.02}$)(Zr$_{0.95}$La$_{0.05}$)O$_3$ thick films under comparable electric fields [230]. Secondly, our model predicts that PbZrO$_3$ nanowires could significantly outperform their bulk counterparts in terms of the recoverable energy density. Indeed $W_r$ for thicker nanowires is about 50% larger than the bulk value. The enhancement in $W_r$ is attributed to smaller electric hysteresis in the thicker nanowires [see Fig.6.7(a)]. Thinner nanowires develop a ferroelectric phase which increases the electric hysteresis leading to a reduction in $W_r$, while the efficiency is comparable to bulk. Based on our numerical data we conclude that PbZrO$_3$ nanowires are promising candidates for energy storage applications in miniaturized devices.

6.4.2 Electrocaloric Coolers

Next we turn to the temperature evolution of the remnant polarization, $P_r$, in the nanowires. The data were obtained by heating the poled nanowires from 5 to 1200 K. Fig.6.9(a) gives a representative dependence $P_r(T)$ for the $d = 5.0$ nm nanowire. We notice the gradual onset of remnant polarization which originates from the coexistence of the ferroelectric and
antiferroelectric phases that compete with each other. The antiferroelectric phase is favored at higher temperatures, while the ferroelectric phase is preferred at lower temperatures. This is in agreement with the experimental findings for ultra thin PbZrO$_3$ films [206]. Such broad $P_r(T)$ dependence is highly desirable for cooling applications that utilize the electrocaloric effect as it allows for a much larger operating temperature range. Fig.6.9(b) shows the dependence of the temperature associated with the onset of spontaneous polarization, $T_P$, on the nanowires’ lateral size. $T_P$ increases with the decrease in $d$ consistent with the stabilizing role of the surface in the formation of the ferroelectric phase in PbZrO$_3$ nanostructures. In other words, as the lateral size of the nanowires decreases, the ferroelectric phase is favored at increasingly higher temperatures.

![Figure 6.9](image)

Figure 6.9: (a) Temperature dependence of the remnant polarization. (b) Dependence of the temperature associated with the onset of spontaneous polarization on the nanowire size.

### 6.4.3 Electromechanical Applications

Next we discuss the electromechanical properties of PbZrO$_3$ nanowires. Fig.6.10(a) and (b) shows the dependence of the $\eta_1$ and $\eta_3$ components of the strain tensor on the electric field for one representative nanowire ($d = 8.3$ nm). The $\eta_1(E)$ loop for the nanowire is in excellent
qualitative agreement with the standard ferroelectric amplitude curve for NaNbO$_3$ nanowires [58]. One interesting feature of the $\eta(E)$ loops is the diffused character of the field induced antiferroelectric-ferroelectric phase transition. Similar features were previously reported for antiferroelectric PLZST films [221]. In both cases the effect originates from the modified competition between the antiferroelectric and ferroelectric phases. In films the perturbation was attributed to the thermal mismatch between the film and substrate, while in nanowires considered here the perturbation is due to the surface charge compensation. Such diffused character of the antiferroelectric-ferroelectric phase transition is very attractive for analog actuation applications that require a faster response and more precise micropositioning [221].

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig6.10}
\caption{Dependence of the different components of the strain tensor on the electric field in 8.3 nm nanowire (a) and (b); Dependence of the piezoelectric coefficients on the nanowire size (c); Temperature evolution of spontaneous strain in 5 nm nanowire (d).}
\end{figure}

We have used the $\eta_1(E)$ and $\eta_3(E)$ dependencies to compute the piezoelectric coefficients $d_{11}$ and $d_{13}$, respectively, using the defining equation $d_{i\nu} = \left( \frac{\partial \eta_\nu}{\partial E_i} \right)_\sigma = \left( \frac{\partial P_\nu}{\partial \sigma_i} \right)_E$ [231]. Here, $E_i$ and $P_\nu$ are the $i$th components of the macroscopic electric field and the corresponding component of the polarization vector, and $\nu = \{1, 2, 3, 4, 5, 6\}$ denotes the component of the strain tensor in Voigt notation. Due to the symmetry of the nanowire, we calculate only the piezoelectric coefficients for the strain along the axial and non-axial directions due
to an electric field along the x (non-axial) direction. The computational data are given in Fig.6.10(c). The coefficients are in the range of 20 to 30 pC/N which is comparable to the coefficients in PZT away from the morphotropic phase boundary. Both coefficients are more than an order of magnitude larger than the coefficients of 1.1 pC/N computed for bulk PbZrO$_3$. The enhancement of the piezoelectric coefficients is a consequence of the diffused character of the field induced antiferroelectric-ferroelectric phase transition in the nanowires. We also computed the temperature evolution of the spontaneous strain in the nanowires. A representative data for $d = 5.0$ nm nanowire are given in Fig.6.10(d). The data predict a large variation of spontaneous strain in a wide temperature range which is very desirable for piezocaloric applications. In such applications the temperature is controlled by the application of external stress [201]. Our computational data suggest that PbZrO$_3$ nanowires have promising electromechanical properties.

In summary, our simulations predict that PbZrO$_3$ nanowires with imperfect surface charge compensation exhibit a strong competition between antiferroelectric and ferroelectric phases that is strongly influenced by the surface effects. This competition leads to the onset of ferroelectricity in ultra thin nanowires, and strong enhancement of both dielectric susceptibility and energy storage characteristics. The electric-field-induced phase transition acquires a diffused character leading to the enhancement of the piezoelectric constants in comparison with bulk. In fact, the piezoelectric coefficients in PbZrO$_3$ nanowires are predicted to exceed the ones for a typical piezoelectric material, ZnO. Furthermore, the temperature dependencies of the spontaneous polarization and strain in PbZrO$_3$ nanowires have a rather monotonic character which is attractive for potential applications in solid-state coolers.
7 Summary and Concluding Remarks

In conclusion, we have used an effective Hamiltonian approach to provide insight into the static and dynamic properties of ferroelectric/antiferroelectric nanowires at an atomistic scale. We developed an effective Hamiltonian for KNbO$_3$ which accurately predicts the Curie temperature and correct sequence of phase transitions, important for the study of caloric properties. The effective Hamiltonian was subsequently tested through the calculation of numerous static and dynamic properties including the unit cell volume, spontaneous polarization, bulk modulus, thermal expansion coefficients, phonon dispersion and frequencies.

We studied the fundamental properties of ferroelectric nanowires, identifying the emergence of a toroidal moment of polarization in BaTiO$_3$ and KNbO$_3$ nanowires within a low temperature polydomain phase. We also shed light on the nature of the ferroelectric phase transition in nanowires which, due to a reduced correlation length associated with the truncated dimensions, exhibit a smearing of the phase transition and dielectric response not found in bulk ferroelectrics. We conducted an extensive computational study on PbTiO$_3$ nanowires which explored the effects of hydrostatic pressure, applied uniaxial stress, and biaxial strain on the structural properties, transition temperatures, and soft mode dynamics. We discovered that depending on which specific mechanical boundary conditions were applied, the nanowire can exhibit either monodomain or polydomain vortex phases. This behavior is not found in bulk PbTiO$_3$ and originates from the critical role of the depolarizing field. We found a rich variety of dipole patterns, particularly for the polydomain states with the dipoles arranged in single and double polarization vortices depending on the type and
strength of the mechanical boundary conditions. The soft mode frequency dynamics are also strongly affected by the mechanical boundary conditions. For monodomain phases the Curie temperature was found to have a linear dependence on the pressure, stress, or biaxial strain, in agreement with findings for bulk PbTiO$_3$. In particular, we found that the frequency of the E mode in the P$_{4mm}$ phase is significantly larger than the A$_1$ mode which is in contrast with bulk PbTiO$_3$. This striking finding is attributed to the presence of the depolarizing field along the truncated directions which leads to mode hardening.

We explored the possibility of using tailored electric field pulses to control the temperature and polarization in ferroelectric nanowires under open-circuit boundary conditions using effective Hamiltonian Molecular Dynamics simulations within an NVE ensemble. Our data suggest that under adiabatic conditions, $\Delta T$ and $\Delta P$ can be well approximated by modeling the electric field as a periodic function with an average amplitude. It also predicts that the nanowire responds to the THz pulse by a change in polarization and temperature, confirming their potential as nanoscale THz radiation sensors. The imaginary part of the dielectric response function $\varepsilon_2(\omega)$ determines the bandwidth of the sensor, the wider the curve the larger the frequency range of the response. For ferroelectric nanowires, it is expected that the loss function $\varepsilon_2$ will depend on the diameter of the nanowire giving increased tunability. Furthermore, the pyroelectric coefficient $p(T)$ of the nanowire should also be size dependent which opens up more possibilities for tuning of these nanoscale sensors. We have proposed a novel route to polarization reversal in ferroelectric nanowires which combines a sub-switching bias electric field and a Gaussian-shaped THz electric field pulse. We have explored the electric field parameter space and quantified the interaction between the polarization and the electric field under adiabatic conditions allowing for a predictable polarization reversal in nanowires. Our approach allows for a substantial reduction in the polarization reversal field which could potentially lead to lower energy consumption in applications utilizing polarization reversal. This polarization reversal mechanism could potentially be used in the design of ferroelectric memory elements in which each individual nanowire stores a bit of information
as a polarization state. Additionally, the proposed approach could find applications in THz radiation sensors and remote switches given that the polarization reversal is triggered by a THz pulse.

We used the effective Hamiltonian method to study the ECE in poorly compensated ferroelectric ultrathin nanowires and compared the findings to the ECE in bulk ferroelectrics. The computational data demonstrate a reduction in the ECE in nanowires as compared to bulk which is attributed to the reduced correlation length. In nanowires with polydomains the ECE is nearly negligible. The electrocaloric change in temperature exhibits a strong correlation with the dielectric susceptibility. Among the three ferroelectric perovskites studied in this work we find the largest ECE and $RCP$ in PbTiO$_3$ followed by KNbO$_3$ and BaTiO$_3$. This behavior is well correlated with the trends in the dielectric susceptibility and the spontaneous polarization data where we find the largest values in PbTiO$_3$, followed by KNbO$_3$ and BaTiO$_3$. While nanowires exhibit reduction in maximum ECE, they offer the opportunity to tune the electrocaloric temperature change through variation of the transition temperature. For example, in case of PbTiO$_3$ nanowires we find nearly 30% increase in the room temperature $\Delta T$, which makes such nanowires attractive for room temperature cooling applications.

Atomistic simulations were carried out to explore static properties of antiferroelectric PbZrO$_3$ nanowires under short-circuit boundary conditions. Our simulations predict that PbZrO$_3$ nanowires with imperfect surface charge compensation exhibit a strong competition between antiferroelectric and ferroelectric phases that is strongly influenced by the surface effects. This competition leads to the onset of ferroelectricity in ultra thin nanowires, and strong enhancement of both dielectric susceptibility and energy storage characteristics. The electric-field-induced phase transition acquires a diffused character leading to the enhancement of the piezoelectric constants in comparison with bulk. In fact, the piezoelectric coefficients in PbZrO$_3$ nanowires are predicted to exceed the ones for a typical piezoelectric material, ZnO. Furthermore, the temperature dependencies of the spontaneous polarization
and strain in PbZrO$_3$ nanowires have a rather monotonic character which is attractive for potential applications in solid-state coolers.
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Publication: Nano Letters

Publisher: American Chemical Society

Date: Apr 1, 2006

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Appendix B  Publications


R. Herchig, B. K. Mani, S. Lisenkov, I. Ponomareva, ”Nanoscale properties of PbZrO₃ nanowires: Phase competition for enhanced energy conversion and storage”, Computational Materials Science 117, 468 (2016)

B. K. Mani, R. Herchig, E. Glaskova, S. Lisenkov, I. Ponomareva, ”Emergence of ferroelectricity in antiferroelectric nanostructures”, Nanotechnology 27, 195705 (2016)


Appendix C  Conference Presentations


03/2013 - "Polarization Reversal in Ferroelectric Nanowires Using Terahertz Pulses", Ryan Herchig, Kevin McCash, I. Ponomareva, American Physical Society March Meeting, Baltimore, Maryland

02/2012 - "Terahertz Frequency Dynamics of Ferroelectric Nanowires", Ryan Herchig, K. Schultz, Kevin McCash, I. Ponomareva, American Physical Society March Meeting, Boston, Massachusetts


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04/2011 - "Nanodynamics of Ferroelectric Ultrathin Films", Ryan Herchig, Qinteng Zhang, I. Ponomareva, University of South Florida 9th Annual Undergraduate Research Symposium and Celebration, Tampa, Florida

03/2011 - "Nanodynamics of Ferroelectric Ultrathin Films", Ryan Herchig, Qinteng Zhang, I. Ponomareva, American Physical Society March Meeting, Dallas, Texas
About the Author

Ryan Herchig was born in Lakeland Florida in July of 1981 where he lived until he graduated from Lake Gibson High School in 2000. After working numerous proletarian jobs, he decided to pursue a bachelors in physics, which he was awarded in 2012 from the University of South Florida. Being accepted to the graduate physics program at the University of South Florida, he earned his Master of Science Degree in Physics in 2012 while continuing the research he began as an undergraduate. In May of 2017, he received his Ph.D. in Applied Physics from the University of South Florida with a concentration in computational condensed matter theory.