#### AN ABSTRACT OF THE DISSERTATION OF

<u>Dennis L. Jackson</u> for the degree of <u>Doctor of Philosophy</u> in <u>Physics</u> presented on <u>December 1, 2011</u>. Title: <u>An Ising-like Model to Predict Dielectric Properties of the</u> Relaxor Ferroelectric Solid Solution  $BaTiO_3 - Bi(Zn_{1/2}Ti_{1/2})O_3$ 

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#### David J. Roundy

We developed a model to investigate the dielectric properties of the  $BaTiO_3 - Bi(Zn_{1/2}Ti_{1/2})O_3$  (BT-BZT) solid solution, which is a relaxor ferroelectric and exhibits long range disorder. The model uses *ab initio* methods to determine all polarization states for every atomic configuration of  $2 \times 2 \times 2$ supercells of BT-BZT. Each supercell is placed on a lattice with an Ising-like interaction between neighboring cell polarizations. This method allows us to consider long range disorder, which is not possible with *ab initio* methods alone, and is required to properly understand relaxor ferroelectric materials. We analyze the Monte Carlo data for a single lattice configuration using the multiple histogram method, and develop a modified histogram technique to combine data from multiple lattice configurations. Our calculated values of dielectric constant, specific heat, and polarization agree reasonably well with experiment. <sup>©</sup>Copyright by Dennis L. Jackson December 1, 2011 All Rights Reserved

# An Ising-like Model to Predict Dielectric Properties of the Relaxor Ferroelectric Solid Solution $BaTiO_3 - Bi(Zn_{1/2}Ti_{1/2})O_3$

by

Dennis L. Jackson

# A DISSERTATION

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Dennis L. Jackson, Author

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#### <u>Academic</u>

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# AN ISING-LIKE MODEL TO PREDICT DIELECTRIC PROPERTIES OF THE RELAXOR FERROELECTRIC SOLID SOLUTION

 $BaTiO_3 - Bi(Zn_{1/2}Ti_{1/2})O_3$ 

## 1 INTRODUCTION

### 1.1 Perovskites

Perovskites are a fascinating family of materials. The term comes from the mineral  $CaTiO_3$ , commonly known as perovskite, which was discovered in 1839 by Gustav Rose and is named after the Russian mineralogist, L. A. Perovski (1792 - 1856). More generally, a perovskite is any solid of the form  $ABO_3$  where A and B are cations, with A located at the corners of the unit cell, B at the center of the cell, and oxygen at the center of each face of the cell, as shown in Figure 1.1. Other common examples of perovskites include  $PbTiO_3$  (PT),  $BaTiO_3$  (BT), and  $SrTiO_3$ . Perovskites have many interesting properties including superconductivity, piezoelectricity, pyroelectricity, paraelectricity and ferroelectricity.



FIGURE 1.1: The smallest unit cell of a perovskite structure. Perovskites have the form  $ABO_3$ , with the A sites located on the corners, the B sites located at the center, and the oxygen atoms located on the center of each face.

### **1.2** Paraelectricity

All materials, perovskites included, are polarizable to some extent when placed in an external electric field. This phenomenon is known as paraelectricity. The key feature of paraelectric materials is that once the electric field is removed, the induced polarization in the material is also removed. For small electric fields, there is a linear relationship between polarization and electric field,

$$\vec{P} = \chi \vec{E} , \qquad (1.1)$$

but in the presence of large electric fields the relationship becomes non-linear and eventually breaks down.

### **1.3** Ferroelectricity

Another class of materials that is similar to paraelectrics is known as ferroelectrics, with the primary difference being that ferroelectrics remain polarized in the absence of an applied field. This spontaneous polarization may be changed in the presence of an applied field to align with the field. This behavior results in a hysteresis of polarization versus applied electric field. Ferroelectrics are used in many electronic devices from electric RAM to PTC thermistors [1].

As the temperature of a ferroelectric material is increased, there is a phase transition into a paraelectric phase. This transition temperature is known as the Curie temperature, which is a term borrowed from ferromagnetism. At high temperatures the electric susceptibility obeys the Curie-Weiss law,

$$\chi = \frac{C}{T - T_c} , \qquad (1.2)$$

where C is a material specific constant and  $T_c$  is the critical Curie temperature. At temperatures below  $T_c$  the material is in its ferroelectric phase and has a spontaneous polarization.

### 1.4 Piezoelectricity

All ferroelectrics are at least somewhat piezoelectric as well. A piezoelectric is a material that develops a strain in the presence of an applied electric field. Conversely, if a stress is applied to a piezoelectric it will induce a polarization in the material.

Depending on the application, the amount of piezoelectricity may be more or less desirable. For devices such as capacitors and RAM the amount of piezoelectricity should be as small as possible. If the piezoelectric response is large, the resulting deformation may over time lead to fatigue, and may compromise the electrical properties as well.

### 1.5 High-Permittivity Linear Dielectrics

Linear dielectrics are well studied in undergraduate physics courses. Their properties are easily understood and nearly all materials have linear dielectric behavior for some range of electric fields. High-permittivity dielectrics require a much lower applied electric field to achieve the same polarization as a normal dielectric material, which makes them desirable for applications such as energy storage in capacitors rather than RAM.

### **1.6** Relaxor Ferroelectrics

There is a family of materials related to ferroelectrics and paraelectrics, which is called relaxor ferroelectrics, also known as relaxors. Relaxors may be used in many of the same applications as regular ferroelectrics and highpermittivity dielectrics, since they exhibit many of the same properties. However, relaxors do not have a true ferroelectric phase, and are more similar to high-permittivity dielectrics in many cases. Thus, relaxors are better suited for energy storage applications than RAM applications. Some common perovskite relaxors are  $Pb(Sc_{1/2}Nb_{1/2})O_3$ ,  $Pb(Mg_{1/3}Nb_{2/3})O_3$ , and  $Pb(Mg_{1/3}Ta_{2/3})O_3$  [2–4]. There is a simple 1:1 or 1:2 ratio of B-site cations for perovskite ferroelectrics of this form. Since not all B-sites are not identical, microscopic disorder can and does occur because there is no restriction on layering or homogeneity. This microscopic disorder gives relaxors their unique behavior, which is discussed below, and distinguishes them from normal ferroelectrics [2].

#### 1.6.1 Diffuse phase Transition

One obvious difference between relaxors and normal ferroelectrics is the behavior at the critical Curie temperature. As was previously explained, normal ferroelectrics have a sharp transition from ferroelectric state to a paraelectric state at the Curie temperature. Relaxors do not have a critical temperature and are said to have a diffuse phase transition. This terminology is misleading in that relaxors do not actually have a ferroelectric phase [2]. Instead there is a more gradual transition from low to high permittivity as the temperature changes. As the Curie-Weiss law (Eq. 1.2) suggests, there is a singularity in the susceptibility at the Curie temperature for normal ferroelectrics. Relaxors do not obey this same law, and in fact the susceptibility deviates strongly from it [5, 6]. This is due to the lack of a critical temperature and different low temperature phase, which is similar to the spin glass phase [6, 7].

#### 1.6.2 Polar Nano-Regions

Rather than a ferroelectric phase with a spontaneous long-range polarization, relaxors spontaneously develop small polar nano-regions (PNR) with differing polarizations [8–11]. Typically, PNRs are on the order of a few to a few dozen nanometers in diameter. In normal ferroelectrics, the entire material polarizes uniformly. In relaxors, while there is spontaneous polarization, there is no long-range order, and thus restricts the entire material from obtaining a uniform polarization. Figure 1.2 shows a cartoon example of how PNRs prohibit the entire material from polarizing uniformly.



FIGURE 1.2: A cartoon example of polar nano-regions. This cartoon shows some PNRs that are uniformly polarized, but each region may have a different polarization.

The PNRs in relaxors are generally formed around a *pinning center*, which is a region of the material that has a preferred polarization, commonly caused by structural ordering in a small region. The polarization of the region surrounding the pinning center is likely to align with the polarization of the ordered region to lower the energy of the system. Since there are likely to be many pinning centers in a given sample, multiple PNRs form with differing polarization directions to create a situation like that illustrated in Figure 1.2.

The Burns temperature is the point below which PNRs form [12]. In normal ferroelectrics, this point is well above the Curie temperature. The Burns temperature is well defined and provides a good metric for comparison with other relaxors, whereas the Curie temperature is not well defined since there is no critical behavior. Experimentalists use the index of refraction to determine that the structure of a material has changed, and thus measure the Burns temperature [13].

#### 1.7 Lead-Free Perovskites

Due to increasingly strict environmental and health regulations, there is an increased demand for lead-free ferroelectric and relaxor materials. Until the push to eliminate the use of lead, many ferroelectric and high-permittivity dielectric devices used lead in some form, and many still do. PbTiO<sub>3</sub> (PT), Pb( $Zr_xTi_{1-x}$ )O<sub>3</sub>, and Pb( $Mg_{1/3}Nb_{2/3}$ ) are prime examples of well-known and commonly used materials [2, 14]. As a result of the need to reduce the use of toxic materials, many researchers are studying  $BaTiO_3$  (BT) based solid solutions instead of those based on PT [15–21]. BT is the canonical example of a lead-free ferroelectric perovskite. It has been well studied, and the mechanical, thermal, and dielectric properties are very well understood both theoretically and experimentally. The unit cell of BT is identical to the form in Figure 1.1, and shown explicitly in Figure 1.3. Some key physical properties of BT are shown in Table 1.1.



FIGURE 1.3: BaTiO<sub>3</sub> cubic unit cell. The Ba atoms are located at the A-sites, and the Ti atoms are located on the B-sites.

### **1.8 BT-BZT**

By combining BT with other perovskite materials it is possible to create a ceramic that is a relaxor ferroelectric [15–20]. The combination we chose to study is  $xBaTiO_3 + (1-x)Bi(Zn_{1/2}Ti_{1/2})O_3$  (BT-BZT), with x = 1 corresponding to pure BT. This material behaves like a relaxor for certain values

Curie Temp.	393 K
Paraelectric Phase	Cubic
Ferroelectric Phase	Tetragonal
Cubie Lattice Const	$4.015 \text{ Å}(\exp)$
Cubic Lattice Collst.	3.989  Å(theory)

TABLE 1.1: Important properties of  $BaTiO_3$ . The theoretical lattice constant was determined using methods described in Section 2.3, and well known experimental data is shown [22, 23].

of the composition x, but it has not been studied as extensively as other compounds [15, 16, 20]. One of the goals of this study is to observe BT-BZT from a theoretical/computational standpoint.

#### **1.8.1** Structural Phase depends on Composition

When combining BT and BZT, the resulting perovskite is tetragonal for compositions consisting mostly of BT ( $x \gtrsim 0.9$ ) and rhombohedral for lower compositions [15]. The material  $Bi(Zn_{1/2}Ti_{1/2})O_3$  (BZT) by itself is highly tetragonal, and depending on the atomic ordering in the unit cell the c/aratio can be as large as 1.286 [24]. The c/a ratio for BT-BZT is at most that of pure BT, which is about 1.013.

#### 1.8.2 Relaxor Behavior

Experiments show that as the composition of BT-BZT contains less BT, the sharp ferroelectric phase transition is lost, and the solid solution begins to resemble a relaxor [15, 20, 23]. The peak in dielectric constant that is present at the transition temperature of pure BT broadens and eventually disappears altogether as the composition decreases, as shown in Figure 1.4. Also, the Burns temperature and the magnitude of the polarization at low temperatures both decrease with decreasing composition.



FIGURE 1.4: Experimental dielectric constant for various compositions. As the composition of BT-BZT decreases, the peak in dielectric constant broadens and vanishes, indicating the transition to a relaxor phase. The experimental data shown here is courtesy of Huang and Cann [15].

As shown by Huang and Cann [15] the strain of BT-BZT is greatly decreased as the composition shifts from high to low BT content. This is directly related to the piezoelectric response. Thus, a lower strain corresponds to a lower piezoelectric effect. The maximum strain reported was 0.13% for pure BT in a field of 70 KV/cm.

#### **1.9** Computational Models

Relaxors are not easy to model effectively, although there have been many attempts with varying levels of success. These methods include molecular dynamics (MD) simulations [4,25–27], density functional theory (DFT) calculations [2,24,28], spherical random-bond-random-field model [29], random field-Ising-models [30,31], other Monte Carlo (MC) simulations [32]. For a good summary of many of these methods applied to relaxors, see Burton et. al. [2]. The model we created combines both DFT and a MC Ising-like method to try and capture the accuracy of DFT, while utilizing the longrange scaling of Ising models.

#### 1.9.1 Density Functional Theory

Density functional theory (DFT) is based on the idea that the density of electrons in a system is all that is needed to determine the ground state energy. DFT is derived from the variational principle,

$$E_{ground} = \min_{\psi} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} , \qquad (1.3)$$

where H is the Hamiltonian and the optimal  $\psi$  is the many-body wave function that minimizes the energy of the system. Minimizing Equation 1.3 is challenging because the many-body wave function of the system  $\psi$  grows exponentially with the number of electrons in the system. Hohenburg and Kohn introduced a theorem in 1964 that allows for minimizing over the density of the electrons, instead of the actual wave function:

$$E_{ground} = \min_{n(\vec{r})} \left[ F[n(\vec{r})] + \int n(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \right], \qquad (1.4)$$

where  $n(\vec{r})$  is the electron density,  $V_{ext}(\vec{r})$  is the external potential included in the Hamiltonian, and  $F[n(\vec{r})]$  is a universal functional of the density. This functional is not known exactly, but can be reasonably approximated. The Kohn-Sham Equations are the usual approach to construct such an approximate functional:

$$F[n(\vec{r})] = T[n(\vec{r})] + V_{Hartree}[n(\vec{r})] + E_{xc}[n(\vec{r})] , \qquad (1.5)$$

where  $T[n(\vec{r})]$  is the kinetic energy of a non-interacting set of electrons,  $V_{Hartree}[n(\vec{r})]$  is an approximate Coulomb electron-electron interaction term (known as the Hartree term), and  $E_{xc}[n(\vec{r})]$  is the exchange-correlation energy, which is a small correction to the functional that in principle gives the correct answer. The kinetic energy term is given by

$$T[n(\vec{r})] = \min_{\{\phi_i\}} \left[ \sum_i \int \phi_i^* \left( \frac{-\hbar^2 \nabla^2}{2m} \right) \phi_i d\vec{r} \right], \qquad (1.6)$$

where  $\phi_i$  are the single electron orbitals of each electron and are restricted by orthonormality and produce the electron density by  $n(\vec{r}) = \sum_i |\phi_i|^2$ . The Hartree term is the electron-electron Coulomb interaction potential

$$V_{Hartree}[n(\vec{r})] = \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} d\vec{r'} .$$
(1.7)

By combining Equations 1.4 - 1.7 we obtain the total ground state energy

$$E_{ground} = \min_{n(\vec{r})} \left[ \min_{\{\phi_i\}} \left\{ \sum_i \int \phi_i^* \left( \frac{-\hbar^2 \nabla^2}{2m} \right) \phi_i d\vec{r} \right\} + \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \int n(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + E_{xc}[n(\vec{r})] \right].$$
(1.8)

The exchange-correlation term is not known exactly, and there are a variety of approximations used to describe it. The two most common approximations are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). The LDA is purely local in that it explicitly depends only on the local density of the electrons, while GGA is non-local because it depends on the density as well as the gradient of the density. The LDA method has the advantage of being uniquely defined, but it is rarely used because GGA usually gives better results. The problem with GGA is that there are many types, such as PBE, PW91, and BLYP, and each type is better in certain cases and worse at others. GGA methods are also somewhat more computationally intensive than LDA, so the benefits of GGA must outweigh the computational cost.

One approximation that is commonly used with DFT is the pseudopotential approximation, which allows us to treat explicitly only a subset of the electrons in a given atom. The core electrons of an atom are bound tightly to the nucleus and only the valence electrons are able to move freely. Because of this we can make an approximation that includes only the valence electrons. For elements with so-called "semi-core" states that are not so tightly bound, these may also be treated explicitly within the pseudopotential approximation.

DFT is widely used to calculate a wide range of material properties, such as interaction energies, lattice parameters, phonon frequencies, and band structures, as well as electronic and optical properties. One particular application that will be particularly useful for studying ferroelectrics is the linear response method for calculating the polarization of a system.

#### **1.9.2** Modern Theory of Polarization

When studying ferroelectrics, it helps to be able to calculate the polarization of a unit cell in a solid. At first glance this would seem trivial, given the nuclear positions and electron density. For finite sized systems this is the case, and we are able to determine the electron contribution to the polarization in the straight forward way

$$\vec{P}^{\text{elec}} = -\frac{e}{\Omega} \int n(\vec{r}) \vec{r} d\vec{r} , \qquad (1.9)$$

where  $\Omega$  is the volume of the cell in question, and  $n(\vec{r})$  is the electron density. However, for systems with periodic boundary conditions, as we use with DFT, the position vector  $\vec{r}$  is not uniquely defined. Therefore, the total polarization—which is the sum of electronic and ionic contributions—in a bulk system is not well defined. Thus, it is a non-trivial task to compute the electronic polarization and it cannot be done by a simple dipole calculation using the electron density as one would hope. Figure 1.5 illustrates how the electron density changes the polarization for a finite cell and a periodic cell. While the true polarization may be better represented by Figure 1.5(a), the calculated polarization is determined by Figure 1.5(b).



FIGURE 1.5: Polarization ambiguity of periodic cells. The dotted line represents the electron cloud surrounding the black atom, and the arrow shows the direction of the polarization for each cell. The polarization for a finite cell is shown on the left, and the polarization of a periodic cell is shown on the right. The actual bulk polarization is not well defined in the classical sense, and is only valid modulo  $e\vec{R}/\Omega$ , as discussed in the text.

The Modern Theory of Polarization (MTP) method proposed by King-Smith and Vanderbilt [33, 34], and reviewed by Resta and Vanderbilt [35], allows us to compute the electronic contribution to the polarization by

$$\vec{P}^{\text{elec}} = -\frac{e}{8\pi^3} \sum_n \int_{BZ} d\vec{k} \langle u_{n,\vec{k}} | \nabla_{\vec{k}} | u_{n,\vec{k}} \rangle , \qquad (1.10)$$

where the sum is over all occupied states, the integral is over the entire Brillouin zone, and  $|u_{n,\vec{k}}\rangle$  are the Bloch functions of the Hamiltonian taken in an appropriate gauge.

Because the electronic polarization makes use of the Bloch functions  $|u_{n,\vec{k}}\rangle$ , there is an ambiguity in the polarization. Since the Bloch functions are periodic, the polarization can only be calculated to within some modulus of the actual value, which is determined by  $e\vec{R}/\Omega$ , where  $\vec{R}$  is a lattice vector. This modulus value corresponds to translating one electron by a lattice vector. If spin degeneracy is included in the polarization calculations, both the electronic polarization and the modulus will have an extra factor of two.

The total polarization is a sum of the electronic term  $\vec{P}^{\rm elec}$  and the ionic term

$$\vec{P}_{total} = \vec{P}^{\text{elec}} + \vec{P}^{\text{ion}} , \qquad (1.11)$$

with

$$\vec{P}^{\rm ion} = \frac{e}{\Omega} \sum_{i} Z_i^{\rm ion} \vec{r}_i , \qquad (1.12)$$

where  $Z_i^{(ion)}$  is the nuclear charge of the  $i^{th}$  atom located at position  $\vec{r_i}$ , and  $\Omega$  is the volume of the cell.

DFT together with MTP provides a powerful tool for predicting the dielectric properties of materials, and there have been many studies of perovskites, ferroelectrics, and relaxors using these methods. Simple perovskite studies include BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, CaTiO<sub>3</sub>, KNbO<sub>3</sub>, NaNbO<sub>3</sub>, PbTiO<sub>3</sub>,

PbZrO<sub>3</sub>, and BaZrO<sub>3</sub> [14,36], which are focused on cell shapes and volumes, c/a ratios, elastic constants, phonon frequencies, band structures, piezoelectricity, and spontaneous polarizations. Studies of ferroelectric perovskites with B-site disorder include Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> [37], Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> [38], and  $Bi(Zn_{1/2}Ti_{1/2})O_3$  [24]. The calculations of the properties of these materials are similar to that of the simple perovskites, but the B-site disorder introduces a level of structural complexity that is also of interest. Solid solution relaxors similar to BT-BZT, including

 $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ ,  $Pb(Zn_{1/3}Nb_{2/3})O_3 - PbTiO_3$  [28,39], and Bi $(Zn_{1/2}Ti_{1/2})O_3 - PbTiO_3$  [40], are also studied for structural and electronic properties. Of those materials discussed above, the largest supercell for a DFT calculation contains only 60 atoms in a  $3 \times 2 \times 2$  perovskite supercell.

There are drawbacks to restricting studies to only DFT and MTP calculations. Specifically, these methods are computationally expensive and are therefore feasible only for moderately sized systems with tens to hundreds of atoms. To incorporate the long-range disorder needed to effectively model relaxors, another method is needed. One type of model that would allow for the necessary long-range disorder is a lattice model similar to the Ising model of magnetic spins.

#### 1.9.3 Classical Ising Model

Ferromagnetic materials have been modeled for years using the Ising model, which is a simple model based on the interaction between neighboring spin-up and spin-down particles placed on a lattice. The Ising Hamiltonian is given by

$$H = -\frac{J}{2} \sum_{i}^{cells} \sum_{j}^{NN} \sigma_i \sigma_j - \sum_{i} \sigma_i M , \qquad (1.13)$$

where  $\sigma_i$  is the spin of the *i*<sup>th</sup> particle, *J* is a positive coupling constant, *M* is the external applied magnetic field, and the factor of two in the interaction term is to avoid double counting. If the spins on the lattice are all aligned the energy of the system will be minimum, and if the spins are randomly aligned the energy will be high. In the presence of an external field, if the spins point in the direction of the field the system is in a lower energy state. This model is a valuable tool used in thermal physics courses for understanding phase transitions. The one dimensional case was solved exactly by Ising in his PhD thesis in 1924 and later as a journal publication [41], and the two dimensional case was solved analytically in the absence of a magnetic field by Lars Onsager in 1944 [42]. Generally, the two- and three-dimensional models are solved using Monte Carlo simulations, and the phase transition may be approximately described using mean field theory for higher dimensional cases [43].

#### 1.9.4 Potts Model

The Ising model is based on a two state system. This simple case has been expanded to a more complicated system with more than two available spins. The q-state Potts model concerns a system where each particle has qavailable magnetization states distributed evenly around a circle [44]. The angles corresponding to each state are given by

$$\theta_n = \frac{2\pi n}{q} , \qquad (1.14)$$

where n = 1, 2, ..., q. The Hamiltonian is given by

$$H = -\frac{J}{2} \sum_{i}^{cells} \sum_{j}^{NN} \cos\left(\theta_{n_i} - \theta_{m_j}\right) - M \sum_{i} \cos(\theta_{n_i}) , \qquad (1.15)$$

where J is again the coupling constant and M is the external field. While this model is more general than the classical Ising model, it is still very restricted in that the magnetization states must lie in a single plane and can have only certain values.

A 3D Potts model also exists with the interaction Hamiltonian of

$$H = -2\sum_{i}^{cells} \sum_{j}^{NN} \delta\left(q_i, q_j\right) , \qquad (1.16)$$

where  $q_i$  is the magnetization state of the  $i^{th}$  cell [45,46]. Note that the delta function gives zero interaction energy if the spins are not aligned.

#### 1.9.5 Heisenberg Model

As a further expansion of the Ising model, the Heisenberg model allows for a lattice of magnetization states that may be oriented in any direction. This fully vectored equation is described by the Hamiltonian

$$H = -\frac{J}{2} \sum_{i,j} \vec{s}_i \cdot \vec{s}_j - \vec{M} \cdot \left(\sum_i \vec{s}_i\right) , \qquad (1.17)$$

with the only restriction being that each vector  $\vec{s_i}$  is of unit length. An important difference between the 3D Potts and Heisenberg models is that the Heisenberg interaction energy is not zero if the magnetization states are not exactly aligned.

#### 1.10 A New Hope

We will introduce a new model, which combines methods such as DFT and MTP, that can predict effects of short-range disorder, with a model such as the Ising or Potts model that is capable of examining phenomena involving long-range disorder. DFT and MTP are unable to address the long range disorder because the number of atoms required to capture the longrange effects would be much too large for a reasonable DFT calculation. By performing DFT calculations on a small number of atoms, and using an Isinglike model to scale up the system to a macroscopic level, the computational resource requirements are much lower than a pure DFT calculation.

Since there is still much to understand about relaxors, this model may give insight into the underlying physics at both microscopic and macroscopic levels. Areas of particular interest are the physics of relaxors near the Burns temperature and the dielectric properties as a function of temperature and applied electric field.

### 2 AB INITIO CALCULATIONS

## 2.1 Supercells, Atomic Configurations, and Symmetries

Barium titanate (BT) is cubic above the Curie temperature of 393K [23], but is slightly tetragonal below the Curie temperature. The solid solution  $\rm BaTiO_3$  -  $\rm Bi(Zn_{1/2}Ti_{1/2})O_3~(BT\text{-}BZT)$  is also slightly tetragonal at both high and low temperatures [15]. The c/a ratio for BT-BZT was shown to be very near unity in Section 1.8. As an approximation, BT-BZT is assumed to be cubic for the purposes of this model. For the solid solution BT-BZT we choose the smallest possible stoichiometric cubic cell. This supercell has a lattice constant that is twice that of the unit cell of cubic BT, and a volume that is eight times larger. If we restrict ourselves to supercells of this  $2 \times 2 \times 2$  size, only compositions of x = 0, 0.25, 0.5, 0.75, 1 are allowed given the solid solution formula  $Ba_x Bi_{(1-x)} Zn_{(1-x)/2} Ti_{(1+x)/2} O_3$ . Figure 2.1 shows one atomic configuration of a  $2 \times 2 \times 2$  supercell with a composition of x = 0.75. A composition of x = 1 corresponds to a  $2 \times 2 \times 2$  supercell of BT that contains 40 atoms. We could use larger supercells, or other geometries, which would allow cells to have additional compositions not available in the  $2 \times 2 \times 2$  configuration. Larger supercells, however, are computationally expensive because of the large number of atoms, and other geometries do not preserve the cubic symmetry that is desired for the latter part of the model.

Thus, both larger supercells and non-cubic geometries are not studied here.

Depending on the composition, the  $2 \times 2 \times 2$  supercell may have many possible atomic configurations. The number of unique configurations for each composition are shown in Table 2.1. Unique configurations are determined by first finding all possible atomic configurations and then applying symmetry operations such as rotations, reflections and translations to each configuration. If two configurations are identical with the application of a symmetry operation, then the configuration is degenerate and only one instance of the configuration need be computed. See Figure 2.2(a) for a cartoon example of atomic configurations that are related by a symmetry operation, and Figure 2.2(b) for an example of unique atomic configurations. Once all unique atomic configurations are known for each composition, we are able to use *ab initio* methods to begin to predict some of the properties of BT-BZT.

Number of Zn atoms	Composition $x$	Distinct atomic configurations
0	1.0	1
1	0.75	3
2	0.50	26
3	0.25	13
4	0.0	6

TABLE 2.1: The number of unique atomic configurations for each composition of a  $2 \times 2 \times 2$  supercell.


FIGURE 2.1: BT-BZT cubic  $2 \times 2 \times 2$  supercell example with x = 0.75. The lattice constant of the supercell is twice that of the smallest cubic BT unit cell.



(a) Degenerate configurations related by a 90 degree rotation.



(b) Two unique configurations not related by any symmetry operation.

FIGURE 2.2: A cartoon example distinguishing between degenerate and unique atomic configurations.

### 2.2 Density Functional Theory Calculations

DFT is a widely-used tool for determining various properties of solids and molecules, as explained in Section 1.9.1. Here, we use DFT to find the selfconsistent ground state energy of each  $2 \times 2 \times 2$  supercell configuration, using the Quantum Espresso package [47] with a PBE-GGA exchange-correlation functional, ultrasoft pseudopotentials, a cutoff energy of 80 Rydberg, and a  $2 \times 2 \times 2$  Monkhorst-Pack k-point grid.

The energy of each atomic configuration is calculated in two cases. The symmetric case consists of all atoms being positioned directly on the coordinate axes and evenly spaced, and the relaxed case begins with the atoms randomly displaced slightly away from the symmetric positions. By minimizing the forces on each atom, which also minimizes the energy, the final relaxed positions are determined self-consistently. See Figure 2.3 for an example of a symmetric atomic positions versus final relaxed atomic positions. We repeat this relaxation procedure several times and with different random atom displacements in order to check for cases with multiple local minima. However, for each  $2 \times 2 \times 2$  atomic configuration, we were only able to find one relaxed state.



FIGURE 2.3: Symmetric and relaxed atomic positions for one atomic configuration with x = 0.75. There are four supercells shown together for clarity.

### 2.3 Lattice Constant and Bulk Modulus

One important parameter, which can serve as either input or output of any DFT calculation is the lattice constant of the unit cell. In a perfect world the theoretical lattice parameter which minimizes the energy would match exactly to the experimental value at zero temperature. However, because we are using an approximate exchange-correlation functional this is simply not true.

In order to find the theoretical lattice constant for cubic BT, we first use the experimental parameter as a starting guess. If an experimental value is not known, a reasonable estimate is all that is needed. Then DFT calculations are done for several lattice parameters near the initial guess. The lattice constant that has the lowest energy is closest to the correct theoretical lattice parameter. We can fit the energy vs lattice parameter data to a quadratic function in order to determine the minimum value more precisely. This method for a single cubic cell of BT gives a lattice parameter of a = 3.989Å using the same energy cutoff, pseudopotentials, k-point grid, and PBE-GGA exchange correlation functional as described above. The calculated lattice constant agrees well with the experimental lattice constant of a = 4.015Å [22] as shown in Table 1.1.

The bulk modulus, defined by

$$B = V \frac{\partial^2 E}{\partial V^2} , \qquad (2.1)$$

where V is the volume of the cell and E is the energy of the system, can also be computed with this same procedure. By varying the volume slightly near the value that gives the minimum energy, and fitting a quadratic function as we did to find the lattice constant, we can find the curvature near the minimum and obtain the bulk modulus. We calculated the bulk modulus for pure cubic BT to be 164 GPa, which is slightly below the experimentally measured values in the range of 179 GPa to 191 GPa [48].

## 2.4 Polarization of Relaxed States

Once the minimized energies and relaxed atomic positions of each  $2 \times 2 \times 2$ supercell have been found, we apply the Modern Theory of Polarization (MTP) method from Section 1.9.2 to find the polarization of each supercell using the Quantum Espresso package. Unfortunately, MTP only calculates the polarization to within some modulus of the true value due to the periodic boundary conditions of the DFT calculations. We can, however, find the polarization of the relaxed configurations relative to the symmetric configurations by making a few extra calculations.

The first step is to determine the polarization of the supercell with atoms in the symmetric positions, which will serve as our reference state. The next step is to adiabatically displace the atoms from the symmetric positions toward the fully relaxed positions and calculate the polarization for each displacement step. Each time the atoms are displaced toward the fully relaxed positions, a new set of DFT/MTP calculations is needed. To avoid unnecessary calculations, we can perform only a few displacement steps and use the slope of the polarization vs displacement curve to find the correct polarization for the fully relaxed state relative to the symmetric state. We are able to use the slope because the fully relaxed displacements are small and the polarization difference is approximated as a linear dipole moment. The final polarization of the fully relaxed case is found by adding or subtracting the known modulus value to the relaxed polarization until it lies on the line determined by the adiabatic displacement method. If it does not lie exactly on the line, the value closest to the line is chosen. Figure 2.4 shows one example of adding the modulus to the final polarization value until it lies on the line determined by the adiabatic displacements.



FIGURE 2.4: Polarizations of adiabatically displaced atoms. By displacing the atoms from the symmetric positions to the relaxed positions adiabatically, the relative polarization can be determined using the known modulus and the slope of the adiabatic displacement curve. In this case the modulus is subtracted from the original polarization twice to obtain the polarization relative to the value of the symmetric configuration.

Depending on the atomic configuration and structural symmetry of the supercell there are often several degenerate ground states with different polarizations. The simple cubic unit cell for BT, for instance, has eight degenerate polarization states, one in each of the (111) directions. The adiabatic displacement method gives a polarization value in a single (111) direction. By applying all symmetry operations to the cubic supercell of BT, we find a polarization in all (111) directions.

For some of the more structurally interesting atomic configurations there may be between 2 and 48 degenerate polarization states for a single  $2 \times 2 \times 2$ supercell of BT-BZT. Figure 2.5 is a cartoon example of a configuration with only two unique polarization states, and Figure 2.6 shows two actual examples of available polarization states after applying all symmetry operations. Table 2.2 shows the number of available polarization states for every atomic configuration.



FIGURE 2.5: A cartoon example of two possible polarization states of the same atomic configuration of a less symmetric structure. The arrow represents the individual dipole moment of each individual cell. The adiabatic displacement method is used to find a single polarization, and the remaining available polarizations are found using symmetry operations.



FIGURE 2.6: Two examples of polarization states projected onto the x-y plane from two different atomic configurations of the same composition. Clearly, not every atomic configuration has the same available polarization states.

TABLE 2.2: The number of available polarization states for each atomic configuration. The maximum number of polarization states is 48, since there are 48 symmetry operations of a cube. The configuration number is arbitrary and is used only to identify unique configurations.

x	Config #	Polarization States	Х	Config #	Polarization States
1	1	8	0.5	22	8
0.75	1	2	(com.)	$\frac{23}{24}$	16
	2	4		25	8
	3	6		26	48
0.5	1	4	0.25	1	2
	2	8		2	4
	3	16		3	4
	4	8		4	2
	5	16		5	4
	6	4		6	4
	7	4		7	2
	8	12		8	2
	9	2		9	4
				10	4
	11			11	4
	12	4		12	4 19
	14	2		10	12
	15	4	0.0	1	2
	16	4	0.0	$\overline{2}$	4
	17	$\overline{2}$		$\overline{3}$	4
	18	4		4	2
	19	8		5	4
	20	8		6	2
	21	8			

# 3 A NEW ISING-LIKE MODEL

Using the energies from density functional theory (DFT) and the polarization states from the adiabatically relaxed modern theory of polarization (MTP) data for each type of cell, we arrange many cells on a 3D lattice using a stochastic process directed by Boltzmann statistics in the grand canonical ensemble. The polarization of each cell interacts with its nearest neighbors with the Ising-like Hamiltonian:

$$H = -J \sum_{i}^{cells} \sum_{j}^{NN} \vec{p}_i \cdot \vec{p}_j - \sum_{i}^{cells} \vec{p}_i \cdot \vec{E} , \qquad (3.1)$$

where  $\vec{p_i}$  is the polarization of a single cell,  $\vec{E}$  is the external electric field and J is a coupling constant, which we tune to match the experimental Curie temperature of pure barium titanate (BT). The notation of the Hamiltonian may be simplified as

$$H = E - \vec{p} \cdot \vec{E} , \qquad (3.2)$$

where E is the total interaction energy and  $\vec{p}$  is the total polarization of the entire system. This simple notation will be referred to throughout this dissertation.

This model is similar to a traditional Ising, Potts, or Heisenberg model, but differs in that each cell has a discrete number of possible states (similar to Potts), and not every cell has the same available states or even the same magnitude. For example, one type of cell may have eight polarization states in each of the (111) directions as is the case for pure BT, while another type of cell may have six states that point in each of the (100) directions. This enables us to introduce and model disordered solid solutions. The actual polarization states available in this model are much more complex, with cells having up to 48 available polarization states as shown in Table 2.2.

# 3.1 The Monte Carlo Simulation

The Monte Carlo method is a technique based on random sampling of data. The general method is used in many scientific areas as well as the financial sector [49,50]. The random sampling we are concerned with is that of the polarizations on a lattice. Each cell on the lattice has a polarization that is pseudo-randomly flipped from one available state to the next, as we describe later in Section 3.1.2. After a certain number of cell flips, the polarization and energy of the entire lattice are sampled. Thus, our MC data is a random sampling of polarizations and energies.

To begin an individual Monte Carlo simulation there are some important matters to address. The first is the lattice size. Nearly all calculations reported here were performed with a lattice size of  $16 \times 16 \times 16$  cells, where each cell represents a  $2 \times 2 \times 2$  perovskite supercell. Thus, our simulation represents 163840 atoms (with 40 atoms per supercell) which would be challenging to handle even with classical Molecular Dynamics simulations and prohibitive with DFT. We performed additional calculations with larger cells to ensure the results are consistent. The  $16 \times 16 \times 16$  size was chosen to allow for some long range disordering, while keeping the computational time reasonably low.

#### 3.1.1 Populating the lattice

We begin each MC simulation by determining the atomic configuration for each of the cells on the lattice. For a simulation of pure BT this is not an issue since every cell of BT is identical and has the same polarization states available in any possible rotation or reflection. Treating a solid solution requires additional effort.

To populate the lattice, we determine the proper number of each configuration of BT-BZT to match the desired composition. We do this using a grand canonical ensemble where the chemical potential is determined by the DFT ground state energy difference between BT-BZT cells of differing composition. This means that configurations with a lower ground state energy will be used more often to populate the lattice than supercells with higher energy, with the appropriate Boltzmann ratio.

Once the proper number of each type of cell has been found, each cell is randomly placed on the lattice with a random orientation. This is especially important for cells that do not have cubicly symmetric polarization states. One problem that may occur due to this random placement and random rotation and/or reflection of each cell on the lattice, is that in certain cases the mean polarization may never be zero. For pure BT, where each cell has the same available cubicly symmetric polarization states, the mean polarization will always approach zero for a very long simulation. Since the BT-BZT mixtures may not have the same symmetry, the mean polarization will rarely approach zero for a long simulation, given a finite lattice size. To avoid this inconvenience, we mirror the lattice for all BT-BZT mixtures and double its size. This extends a  $16 \times 16 \times 16$  lattice to a  $16 \times 16 \times 32$  lattice. Each cell on the original lattice has its mirror image also placed on the lattice. The result is that the mean polarization is guaranteed to be zero in the limit of an infinitely long simulation.

#### 3.1.2 Equilibration and Data Gathering

As was explained in the previous section, the cells on the lattice start with a random polarization state, which corresponds to a high energy, high temperature state. We allow the system to equilibrate at a given temperature using the Metropolis algorithm, which was designed for constructing a canonical ensemble.

First, we determine the energy of the entire system based on the Hamiltonian. Next, a random change is proposed. In our case we change the polarization at a single site. The change in energy of the system is then calculated, and if the energy decreased after the change, then the change is allowed to remain. If the energy increased after the change, then the change is allowed to remain with a probability determined by the Boltzmann factor

$$F = \exp\left(-\frac{\Delta E}{k_B T}\right) \ . \tag{3.3}$$

If the change in energy is comparable to  $k_BT$ , then there is a reasonable

probability that the change may occur naturally. A temperature that is low relative to the energy difference indicates a low probability and high temperatures indicate a high probability. In a ferroelectric, this leads to a uniformly polarized lattice at low temperatures and a randomly polarized lattice for high temperatures as will be shown in the next chapter. This algorithm is applied many millions of times to reach equilibrium. Once equilibrium is reached, we can calculate properties such as the Curie temperature.

The system undergoes at least  $10^6$  changes per site, and the total polarization and energy are recorded after every 10 changes per site. Equilibrium is considered to be reached and the system is said to be "warmed up" when the system has run for several energy correlation times. Once the system has reached equilibrium, we can calculate the mean value of any function of the energy and polarization simply by

$$\langle f(E, \vec{p}) \rangle = \frac{1}{N} \sum_{i=1}^{N} f(E_i, \vec{p_i}) ,$$
 (3.4)

where the subscript i is the index of a particular data sample, and N is the total number of samples. We can then calculate properties such as the dielectric constant and specific heat using the variance of the polarization and energy respectively.

A cluster algorithm such as the Wolff method would be better suited for convergence at low temperatures using an Ising model, but such methods are challenging to apply to our heterogeneous system. Not all cells have the same available polarization states, making it hard to classify if two neighboring cells belong to the same cluster.

# 3.2 Boltzmann Probability

The probability of finding a system in in a given microstate in thermal equilibrium at a given temperature can be found by examining the appropriate Boltzmann factor,

$$P_i = \frac{1}{Z} \exp(-\beta E_i) , \qquad (3.5)$$

and its associated partition function,

$$Z = \sum_{i=1}^{N} \exp(-\beta E_i) , \qquad (3.6)$$

where  $\beta = 1/(k_B T)$ ,  $E_i$  is the energy of the  $i^{th}$  microstate, and N is the total number of microstates. The mean value of any function  $f(E_i)$  can now be determined by

$$\langle f(E) \rangle = \sum_{i=1}^{N} f(E_i) P_i , \qquad (3.7)$$

Expanding this formula to include the polarization microstates and the electric field term in the Hamiltonian in Equation 3.2 gives

$$\langle f(E, \vec{p}) \rangle = \frac{\sum_{i=1}^{N} f(E_i, \vec{p}_i) \exp(-\beta (E_i - \vec{p}_i \cdot \vec{E}))}{\sum_{i=1}^{N} \exp(-\beta (E_i - \vec{p}_i \cdot \vec{E}))} .$$
(3.8)

## 3.3 Susceptibility

The dielectric constant is an important property in ferroelectric and relaxor materials. In order to create an effective model of these materials it is important that the dielectric constant will be predicted accurately. Starting with the electric field in a medium, we can find the dielectric constant and the susceptibility of the medium:

$$\vec{D} = \vec{E} + 4\pi \vec{P} \tag{3.9}$$

$$\epsilon \vec{E} = \vec{E} + 4\pi \vec{P} \tag{3.10}$$

$$\vec{P} = \frac{1}{4\pi} (\epsilon - 1) \vec{E} = \chi \vec{E}$$
 (3.11)

In relation to the Monte Carlo data it is the mean of the polarization that is of interest:

$$\langle \vec{P} \rangle = \chi \vec{E} \tag{3.12}$$

The susceptibility is a tensor response function, valid for small changes in electric field, and each component is defined separately by

$$\chi_{xx} = \frac{\partial \langle P_x \rangle}{\partial E_x} \,. \tag{3.13}$$

By taking the derivative of Equation 3.7, we can express the susceptibility as the variance of the polarization:

$$\chi_{xx} = \beta \left( \langle P_x^2 \rangle - \langle P_x \rangle^2 \right) \tag{3.14}$$

By simply calculating  $\langle P_i \rangle$  and  $\langle P_i^2 \rangle$  (where *i* is either *x*, *y*, or *z* in this case) of a given simulation, we can compute the susceptibility in any particular

direction of the material.

Once the susceptibility is known, it is then a simple matter to determine the dielectric constant using

$$\epsilon = 1 + 4\pi\chi . \tag{3.15}$$

It is important to note that this is the zero frequency value of the dielectric constant. It is not possible to determine the frequency dependence without including dynamics, which are not included in a Metropolis Monte Carlo simulation.

# 3.4 Specific Heat

Another property of any solid, which is particularly interesting in phase transitions, is the specific heat. Thermodynamically, the intensive dimensionless specific heat at constant volume is defined as

$$c_v = \frac{1}{Nk_B} \left(\frac{\partial U}{\partial T}\right)_v , \qquad (3.16)$$

where  $k_B$  is the Boltzmann constant, N is the number of cells on the lattice, U is the internal energy of the system, and T is the temperature. By substituting  $\beta = 1/(k_B T)$  and  $U = \langle E \rangle$  into Equation 3.16, the specific heat becomes

$$c = -\frac{\beta^2}{N} \frac{\partial \langle E \rangle}{\partial \beta} , \qquad (3.17)$$

where we have dropped the constant volume subscript, since our model does not include volume effects. Taking the derivative of Equation 3.7 the specific heat can be expressed as the variance of the energy:

$$c = \frac{\beta^2}{N} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) . \tag{3.18}$$

Similar to the susceptibility, the specific heat of the material can be determined by calculating only  $\langle E \rangle$  and  $\langle E^2 \rangle$  for a given simulation.

### 3.5 Finite-size scaling

Because the correlation length diverges at phase transitions, it is particularly important to examine finite-size scaling in systems with a critical temperature [51, 52]. This divergence makes it difficult to obtain good results at or near the critical temperature. However, since the solid solution BT-BZT behaves as a relaxor, there is no phase transition and thus no critical temperature. For this reason, we ignore most finite-size scaling issues. However, in order to accurately find the Curie temperature of BT, we use the Binder cumulant method, since finite-size issues are important for critical systems.

### 3.5.1 Binder cumulant

We use the Binder cumulant method [53] to determine the coupling constant J which reproduces the experimental Curie temperature of BT. The fourth order cumulant is independent of the number of cells in the lattice at the critical temperature, and is given by:

$$U_L = 1 - \frac{\langle \vec{p}^4 \rangle}{3 \langle \vec{p}^2 \rangle^2} , \qquad (3.19)$$

where the mean values  $\langle \vec{p}^{\,4} \rangle$  and  $\langle \vec{p}^{\,2} \rangle$  are calculated using Equation 3.8.

Considering pure BT where the system does indeed have a critical temperature, we ran Monte Carlo simulations for various lattice sizes and temperatures near the Curie temperature. By plotting the cumulant as a function of temperature for different lattice sizes L, the intersection point is at the critical temperature as shown in Figure 3.1. The coupling constant J is then tuned such that the correct critical temperature for pure BT at 393K is obtained for the model. Since BT-BZT does not have a Curie temperature, we must approximate the coupling constant for compositions other than x = 1. We do so by using the same coupling constant for interactions between neighboring cells of all compositions and configurations as we do for interactions between neighboring BT cells.



FIGURE 3.1: The fourth-order Binder cumulant as a function of temperature for a range of cell sizes. The intersection point reveals the critical temperature, since this cumulant becomes independent of the lattice size at the critical value. The coupling constant J is found by tuning this cumulant intersection to the critical temperature of BaTiO<sub>3</sub>.

### 3.6 Strain

Since BT and BT-BZT are both at least somewhat piezoelectric, it is important to discuss the effect of strain on the system. Experimentally, the maximum strain for BT due to a large applied electric field is less than 0.13%, and lower still for solid solutions of BT-BZT [15].

The strain we are concerned with is that which is due to placing many supercells on a lattice, and whether or not using cubic supercells is a good approximation, as well as how the polarization from neighboring cells will affect a given cell. Relaxors with PNRs may undergo a great deal of deformation due to stresses caused by the large regions of uniform polarization [54], and if this is true for BT-BZT our simplistic approach may not be sufficient.

To determine an upper bound on the energy difference due to strain between two neighboring cells, we relax the system into a natural rhombohedral state (stretched in the direction of the polarization for pure BT), and then force it into an unnatural rhombohedral state (in a (111) direction that is not in the direction of the polarization), and compute the difference in the energy of those two states using DFT. For a cubic unit cell of BT, as shown in Figure 1.3, the difference in energies of the two rhombohedral systems comes out to be  $3.2 \times 10^{-5}$  Hartree.

We compare this energy difference with the interaction energy of the Isinglike Hamiltonian,  $E_{int} = -J\vec{p}_i \cdot \left(\sum_j \vec{p}_j\right)$ . Considering only a cubic lattice where each cell has six nearest neighbors, and avoiding double counting of neighbors, the energy equation expands slightly to  $E = -\frac{6}{2}J\vec{p}_i \cdot \left(\sum_j \vec{p}_j\right)$ . Given the polarization value,  $\vec{p} \approx (1, 1, 1) \times 0.0039 e/a_0^2$ , for BT, and the coupling constant  $J \approx 19$  we obtain a value for the interaction energy of  $E = 8.29 \times 10^{-4}$  Hartree. Comparing the strain energy to the interaction energy we get  $E_{diff}/(3Jp^2) = 4\%$ . Since the calculated strain energy is small compared to the model interaction energy, and the experimental strain is low, we expect that our cubic-only model will give qualitatively correct predictions.

### 3.7 Thermal Expansion

Another aspect of stress-related effects is the variation of cell size and shape with temperature. The temperature values we are interested in range from 250-500 K. Over this range of temperatures, pure BT (x = 1) undergoes multiple phase changes from cubic to tetragonal to orthorhombic, and has a maximum thermal expansion of  $1.9 \times 10^{-5} K^{-1}$  at room temperature [23]. The value of common materials ranges from  $0.1 - 9.0 \times 10^{-5} K^{-1}$ . The value for BT-BZT is expected to be lower than that of pure BT, simply because it does not undergo such a drastic phase change, and it's c/a ratio is very nearly one.

If a hydrostatic pressure is applied to pure BT, the Curie temperature decreases linearly. For a pressure of 3000 atm, the Curie temperature drops by about 20 K [23]. This pressure corresponds to a strain of  $\epsilon = 1.5 \times 10^{-3}$ . At

atmospheric pressure BT-BZT has an experimental volume strain of  $7 \times 10^{-3}$  [15] over the entire range of compositions we are interested in, which is larger than the effect of thermal expansion of BT. This compositional strain effect corresponds to a change in the Curie temperature of approximately 100 K. Thus, the thermal effects of strain are not as important as the compositional effects.

Since the coupling constant J is determined using the Curie temperature as a fitting parameter, an uncertainty is introduced as the critical temperature varies with a change in the lattice parameter. Any value of J that gives a Curie temperature of BT within the 100 K range described above does not affect the qualitative results we are interested in. The magnitude of the polarization, dielectric constant and specific heat would all have the same behavior as we see in the next chapter, but the critical behavior would shift to a lower temperature.

To keep our model from having too much complexity, we would like to ignore the effects due to variations in the lattice constant. Compared to other approximations that we make, this variation is much less important in qualitatively determining the properties we are interested in, such as the overall shape of the dielectric constant or specific heat. We use the same coupling parameter J for interactions between cells of all compositions as that of BT cells, and by doing so we are unable to account for any compositional effects on J. We expect that the largest errors in our model are due to the approximation of the coupling constant J in this way, and the fact that the interaction energy is a dot product of relative cell polarizations.

# 3.8 Application to Other Relaxors

As it stands, the new Ising-like model could be applied to any solid solution that has a ferroelectric composition with a known experimental Curie temperature. We are choosing to focus on  $BaTiO_3 - Bi(Zn_{1/2}Ti_{1/2})O_3$ , but this model may be applied to PbTiO<sub>3</sub> based solid solutions including Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> - PbTiO<sub>3</sub>, Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> - PbTiO<sub>3</sub> [28,39], or Bi(Zn<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub> - PbTiO<sub>3</sub> [40], as well as other BaTiO<sub>3</sub> based materials like (La<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub> - BaTiO<sub>3</sub> [55], just as easily. For the PbTiO<sub>3</sub> based materials, the experimental Curie temperature of PbTiO<sub>3</sub> would be used to find the coupling parameter. The things that would be different for each type of solid solution are the number of configurations and resulting polarization states of the supercells to be placed on the lattice.

This model uses a coupling constant determined by fitting to the Curie temperature for a ferroelectric phase of a given composition of the solid solution. By estimating a coupling constant instead of fitting to a ferroelectric Curie temperature, this model can be applied to relaxors that do not have composition with a known Curie temperature. This would at least give qualitatively reasonable results, as the coupling constant only shifts the temperature of critical behavior.

# 4 DIRECT MONTE CARLO RESULTS

### 4.1 Pure BT

Lets begin the analysis by examining pure barium titanate (BT) simulations with various lattice sizes. Simulations were run at every 5 Kelvin from 250 K to 500 K, for a minimum of  $10^6$  iterations per site, while sampling the polarization and energy every 10 iterations per site. The initial polarizations on the lattice are randomized, and each temperature simulation starts in the same lattice configuration for a given lattice size. The magnitude of the polarization, the dielectric constant, and the specific heat are all calculated using the mean values shown in Equation 3.4. Figures 4.1 - 4.3 respectively show the polarization magnitude, dielectric constant, and specific heat as functions of temperature lattice sizes of  $16 \times 16 \times 16$ ,  $24 \times 24 \times 24$ , and  $32 \times 32 \times 32$ . These lattice sizes correspond to a total of 163840, 552960, and 1310720 atoms respectively, where each cell contains 40 atoms.

The nonzero magnitude of the polarization which is apparent below the Curie temperature of 393K in Figure 4.1 indicates ferroelectric behavior. Above the Curie temperature, BT is in a paraelectric phase and should have zero polarization for very large lattice sizes. The slight difference in polarization, and the fact the value is not exactly zero, above the Curie temperature is a finite lattice size effect.

There is a distinct peak in both the specific heat and dielectric constant



FIGURE 4.1: The magnitude of the polarization density as a function of temperature for various cell sizes of pure BT (x=1).



FIGURE 4.2: The specific heat as a function of temperature for various cell sizes of pure BT (x=1).

shown in Figures 4.2 and 4.3 respectively. These peaks are expected since they occur at the phase transition temperature, and the singularity of the dielectric constant is consistent with the Curie-Weiss law shown in Equation 1.2. Fluctuations are apparent in the dielectric constant (Figure 4.3) at low temperatures which are due to the random nature of Monte Carlo simulations. For well converged simulations, the fluctuations should subside. However, using the Metropolis algorithm it would take a very long time to obtain well converged results. As was previously discussed, cluster algorithms would help to hasten the convergence, but clusters are challenging to describe when compositional disorder is present in the solid solution.



FIGURE 4.3: The dielectric constant as a function of temperature for various cell sizes of pure BT (x=1).

Independent of the algorithm used, well converged simulations would give

dramatically different dielectric constant at low temperatures. In the simulations shown here, only a single polarization state is reached and the entire system is not likely to flip to another polarization state in a reasonable amount of time. In a well converged system, the entire polarization will change directions sporadically. If the system is allowed to change polarization states freely, the dielectric constant will be large. However, if the system is restricted to a single polarization state, the dielectric constant will be small as we see in Figure 4.3.

# 4.2 BT-BZT Solid Solution

Lets now turn our attention to the BaTiO<sub>3</sub> - Bi $(Zn_{1/2}Ti_{1/2})O_3$  (BT-BZT) solid solution, focusing on the composition of x = 0.95. Again we plot the polarization, specific heat, and dielectric constant as a function of temperature in Figures 4.4 - 4.6.

The polarization as a function of temperature for BT-BZT (Figure 4.4) is clearly different from that of pure BT. As the cell size increases, the polarization magnitude approaches zero for the entire temperature range. This is consistent with the finite lattice size effect that is seen in Figure 4.1. The specific heat shown in Figure 4.6 does not show any large peak, which indicates that there is no phase transition.

In order to capture the long range disorder behavior, it is best to use a large lattice size. However, larger lattice sizes take much more computational



FIGURE 4.4: The magnitude of the polarization density as a function of temperature for various cell sizes of BT-BZT (x=0.95). The polarization of x = 1 for N = 32 of Figure 4.1 is also plotted in black to show the vast difference in polarization magnitudes at low temperatures. The inset shows how the polarization magnitude decreases with increased lattice size.



FIGURE 4.5: The specific heat as a function of temperature for various cell sizes of BT-BZT (x=0.95). The specific heat of x = 1 for N = 32 of Figure 4.2 is also plotted in black. The absence of a peak for x = 0.95 indicates that there is no phase transition.



FIGURE 4.6: The dielectric constant as a function of temperature for various cell sizes of BT-BZT (x=0.95). There is a large discrepancy at low temperatures, but as we will show, this is not a finite cell size effect.

effort than smaller lattice sizes, so if the larger size does not have different physics than that of a smaller cell, then there is a benefit to using the smaller lattice size. Figures 4.1 - 4.5 have a negligible difference between the various cell sizes. Therefore, the smaller lattice size shown should be acceptable. Figure 4.6, however, does have a noticeable difference in the dielectric constant between the different cell sizes at low temperatures. As we will demonstrate in the next section, there is a reason for the difference other than cell size.

## 4.3 Lattice Configurations

In general, the outcome of any two Monte Carlo simulations may be slightly different depending on the random number generators or random number seeds used. If the simulation is run for a large number of iterations, the results for different random number seeds will approach the same value. This is the nature of Monte Carlo methods.

There is a difference in the outcome of a simulation depending on the random number seed used populate the lattice. Each lattice configuration may not approach the same equilibrium value. Figures 4.7 - 4.9 show the polarization magnitude, specific heat, and dielectric constant for single lattice size of  $16 \times 16 \times 16$  (32) and a composition of x = 0.95 for five different initial starting conditions. At high temperatures where the system is almost completely disordered, the different lattice configurations do not have a large effect. At low temperature where the system is mostly ordered the different

lattice configurations play a huge role. This make sense as the low temperature simulations may freeze into a particular polarization state, and the frozen polarizations will differ greatly depending on the lattice configuration. We will need to average over many lattice configurations in order to get the correct answer. Another way to get this type of spatial averaging would be to use larger lattice sizes. The multiple histogram method discussed in Chapter 5 is the technique we chose to do this type of averaging.



FIGURE 4.7: The magnitude of the polarization density as a function of temperature for different lattice configurations of BT-BZT (x=0.95).



FIGURE 4.8: The specific heat as a function of temperature for different lattice configurations of BT-BZT (x=0.95).



FIGURE 4.9: The dielectric constant as a function of temperature for different lattice configurations of BT-BZT (x=0.95).

### 4.4 Correlation Time

The MC simulation output is a list of energy and polarization values. One important feature of the output data is how correlated the data samples are. Ideally, each sample would be completely independent, and sequential iterations would be uncorrelated. To determine the correlation between samples in a given simulation, we use the normalized autocorrelation coefficient as a function of lag k:

$$f_{AC}(k) = \frac{\sum_{i=1}^{N-k} E_i E_{i+k} - \langle E \rangle^2}{\sum_{i=1}^{N} E_i^2 - \langle E \rangle^2} , \qquad (4.1)$$

where  $0 \le k < N$  has a maximum value of one at k = 0. The autocorrelation coefficient is a measure of the correlation in the energy, which is one of the quantities of great interest for this model.

To determine the correlation time  $\tau$ , which is a measure of randomness of the samples in the simulation,  $f_{AC}(k)$  is fit to a decaying exponential exponential  $\exp(-k/\tau)$ . A set of completely random samples will have a correlation time of zero. The term 'correlation time' may be slightly misleading in that it is the Monte Carlo samples that we are interested in, which are not a function of any real time.

For each simulation used in this model, the data was sampled at every 10 iterations per site in order to reduce the correlation time to less than one in most temperatures away from the Curie temperature. Near the Curie temperature, the correlation time is greatly increased as is to be expected for
any material with critical behavior. If the data is sampled too often, much of it will be redundant.

# 4.5 Correlation Length

A related quantity of interest is the spatial correlation function. The same technique is applied as was used to find the correlation time. The same type of correlation coefficient is found,

$$f_{AC}(k_x) = \frac{\sum_{i=1}^{L_x - k_x} \vec{p}_i \cdot \vec{p}_{i+k_x} - \langle \vec{p} \rangle \cdot \langle \vec{p} \rangle}{\sum_{i=1}^{L_x} \vec{p}_i \cdot \vec{p}_i - \langle \vec{p} \rangle \cdot \langle \vec{p} \rangle} , \qquad (4.2)$$

where  $\vec{p_i}$  is the polarization of the individual cell at site *i*,  $k_x$  is the lag in the *x*-direction,  $L_x$  is the lattice size in the *x*-direction, and the randomness is a measure of the polarization instead of energy. The correlation length  $\lambda_x$  is found by again fitting the correlation coefficient function to an exponential  $\exp(-k_x/\lambda_x)$ . As is clear by the notation, this only determines the correlation length in the *x*-direction of the lattice. The correlation lengths are found in the *y* and *z* directions as well. The total correlation length used here is the average of the three components,

$$\lambda = \frac{\lambda_x + \lambda_y + \lambda_z}{3} . \tag{4.3}$$

By observing an individual sample of the polarizations of each cell on the lattice, the correlation length may also be observed visually. The maximum correlation length possible is only L/2 given the finite cell size used, so any

value greater than L/2 means the system is totally correlated. A correlation length of 0 is completely uncorrelated. The correlation length roughly corresponds to the size of the uniformly polarized regions.

Figures 4.10 - 4.18 show snapshots of the ordering of equilibrated systems at various compositions and temperatures. Each figure shows the relative magnitude and direction of the polarization of each cell projected onto the yz-plane for a single x-coordinate value, and the color represents the interaction energy of each cell with its nearest neighbors  $E_{int} = -J\vec{p}_i \cdot \left(\sum_j \vec{p}_j\right)$ . Blue regions correspond to low energy where neighboring cells are aligned, red regions correspond to high energy states where neighboring cells are oppositely aligned, and white regions correspond to uncorrelated polarizations.

The energy-vector diagrams of pure BT are shown in Figures 4.10 - 4.12. For the low temperature simulation at 250 K in Figure 4.10, nearly all cells are uniformly polarized which is clear by the near solid blue energy surface, as well as observing the individual cell polarization projections. Figure 4.11 has almost no blue or red regions, which means the system is uncorrelated and the cells are randomly polarized. This behavior is expected for a simulation at a temperature of 500K, which is well above the Curie temperature. Figure 4.12 is simulated at a temperature of 385 K, which is slightly below the Curie temperature, and the energy surface shows some small regions of correlation and some regions of randomness. The correlation lengths for each simulation are shown in Table 4.1, and should roughly correspond to the size of the blue correlated regions of each energy-vector diagram. The energy-vector diagrams for x = 0.95 and x = 0.9 are shown in Figures 4.13 - 4.18 for the same simulation temperatures of 250 K, 385 K, and 500 K. Many features are similar to that of pure BT, with large correlated regions at low temperatures and small correlated regions at high temperatures. The correlated regions are areas of uniform polarization, which is also known as a polar nano-region (PNR). Using a lattice size of 8Å for each  $2 \times 2 \times 2$  supercell and the correlation length of each simulation, we obtain approximate diameters for the PNRs which are also shown in Table 4.1, with a minimum diameter of the size of a single supercell.

Color alone is not enough to determine PNR size or existence in the energy-vector diagrams. We must also look at the polarization projections of each cell. Compositions of both x = 0.95 and x = 0.9 have large low energy (blue) regions, but the polarization arrows are not all aligned in the same direction as they are for pure BT. This is a clear indication that there are PNRs for compositions less than one, even at low temperatures.

TABLE 4.1: Correlation lengths and PNR size for various compositions and temperatures. A correlation length of zero corresponds to a completely uncorrelated system, and a correlation length of greater than half of the lattice size is completely correlated. The PNR diameter is calculated by multiplying the correlation length by the supercell lattice constant of 8Å. The minimum PNR size must be at least the size of a supercell, and if the correlation length is larger than half of the lattice size (16 in this case), then the PNR diameter is infinite.

Composition	Temperature (K)	Correlation length	Approx. PNR
		(#  cells)	size (Å)
x = 1	250	9.0	$\infty$
	385	1.7	14
	500	0.6	8
x = 0.95	250	3.2	26
	385	1.0	8
	500	0.7	8
x = 0.9	250	1.4	11
	385	1.0	8
	500	0.8	8



(x=1) at 250K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. The correlation length of this system is 9.0, which is greater than half of the cell size. FIGURE 4.10: The interaction energy of each cell with its neighbors for one equilibrium state for pure BT



FIGURE 4.11: The interaction energy of each cell with its neighbors for one equilibrium state for pure BT (x=1) at 500K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. The correlation length of this system is 0.6.



FIGURE 4.12: The interaction energy of each cell with its neighbors for one equilibrium state for pure BT (x=1) at 385K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. The correlation length of this system is 1.7.



at 250K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 3.2. FIGURE 4.13: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.95



at 500K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 0.7. FIGURE 4.14: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.95



at 385K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 1.0. FIGURE 4.15: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.95



FIGURE 4.16: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.9 at 250K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 1.4.



FIGURE 4.17: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.9 at 500K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 0.8.



FIGURE 4.18: The interaction energy of each cell with its neighbors for one equilibrium state for x=0.9 at 385K. Low interaction energy is represented in blue and high energy in red. The arrows show the polarization projection of each on the yz-plane. Arrow color represents the number of zinc atoms in each cell, with black=0, red=1, orange=2, yellow=3, white=4. The correlation length of this system is 1.0.

# 5 THE MONTE CARLO HISTOGRAM METHOD

### 5.1 Single Histogram Method

Using Equation 3.4, we can find the mean value of any function of energy and polarization. Unfortunately, this method only gives results at the temperature used to create the sampled data, which means we need to perform a computationally expensive Monte Carlo simulation for each temperature we wish to study. Using the single histogram method, we can use data from a simulation at one temperature to predict properties at another similar temperature [56].

The histogram method was created to extract as much information as possible from a Monte Carlo simulation, while using as little data as is necessary. This technique relies on the fact that if the probability of finding the system in each microstate at a given temperature is precisely known, then in principle we can predict the probability of finding the system in any of those microstates at any other temperature. In practice, we can only approximate these probabilities, and our predictions are limited to similar temperatures.

The single histogram method allows us to calculate the probability at a particular temperature, given that we know the histogram of microstates. The histogram  $H(E, \vec{p})$  is determined by a Monte Carlo simulation, where each data sample fills a bin of the histogram, and is a record of how likely a given microstate happens to be. The probability of finding the system in a

particular microstate at a similar temperature is given by

$$P_{\beta}(E,\vec{p}) = \frac{1}{Z_{\beta}} H(E,\vec{p}) \exp(-(\beta - \beta_0)(E - \vec{p} \cdot \vec{E})) , \qquad (5.1)$$

where  $\beta_0 = 1/(k_B T_0)$  with  $T_0$  being the simulation temperature,  $\beta = 1/(k_B T)$ with T being the desired temperature, and  $Z_\beta$  is a new partition function

$$Z_{\beta} = \sum_{E,\vec{p}} H(E,\vec{p}) \exp(-(\beta - \beta_0)(E - \vec{p} \cdot \vec{E})) .$$
 (5.2)

The mean value of a quantity at the desired temperature is then found in the usual way,

$$\langle f(E,\vec{p})\rangle_{\beta} = \sum_{E,\vec{p}} f(E,\vec{p}) P_{\beta}(E,\vec{p}) .$$
(5.3)

This technique is only accurate if T is near  $T_0$ . The sums in Equations 5.2 and 5.3 are over all of the energy and polarization bins of the histogram  $H(E, \vec{p})$ .

To fill a histogram as a function of energies and magnetizations of a simple Ising model is easy. The energy and magnetization of every conceivable microstate are known *a priori*, for a given lattice size. Thus, the number of samples with each energy and each magnetization are clear. For an Ising model, the histogram bin sizes are known exactly and correspond to the difference in energy and magnetization for a single cell flip.

For our relaxor model, instead of calculating every possible microstate of energy and polarization, a standard bin size is used because different lattice configurations may have different sets of energy and polarization states. As will be shown later, this enables us to readily combine data from multiple simulations. The bin size that is used here was determined by calculating the energy and polarization differences for a single flip of the cells with the smallest polarization. The histogram is then filled with the simulation data according to the smallest bin sizes. Bin size effects are discussed in more detail in Section 5.3.

## 5.2 Multiple Histogram Method

The single histogram method allows us to perform calculations near the temperature used for an individual simulation. For temperatures far from the simulation temperature the technique is not effective, because the simulation will fail to sample microstates that may be populated at the new temperature. One solution to this problem is to combine data for multiple simulations over a range of temperatures. This will allow us to essentially interpolate as if we ran simulations at any given temperature near any of the simulated temperatures. Fewer simulations are needed to obtain results for a large range of temperatures than running a simulation for each temperature. This also allows us to get more precise results, even at the simulation temperatures, and also leads to much faster computation time.

In order to combine multiple simulations into a single probability, a new method must be applied. The multiple histogram equations proposed by Ferrenberg and Swendsen [57], are given by

$$\tilde{P}_{\beta}(E,\vec{p}) = \frac{\sum_{n=1}^{N} H_n(E,\vec{p}) g_n^{-1} \exp\left(-\beta E\right)}{\sum_{m=1}^{N} n_m g_m^{-1} \exp\left(-\beta_m E - f_m\right)},$$
(5.4)

where  $\beta_m = 1/k_B T_m$ , N is the number of simulations,  $H_n(E, \vec{p})$  is the histogram of the  $n^{th}$  simulation,  $n_m$  is the total number of samples included in the  $m^{th}$  histogram,  $g_n = 1 + 2\tau_n$  and  $\tau_n$  is the correlation time calculated using the method described in Section 4.4, and  $f_m$  is an estimate of the dimensionless free energy of the  $m^{th}$  simulation. The correlation time is incorporated as a weighting factor to account for the differing correlation times of the samples for different simulations. Simulations with longer correlation times will not contribute as much to the probability as simulations with short correlation times, since that would effectively count the same data more than once. The free energies serve as a correction factor due to combining data from multiple temperatures, and are calculated self consistently using

$$\exp\left(f_m\right) = \dot{P}_{\beta_m}(E, \vec{p}) . \tag{5.5}$$

Note that Equation 5.4 does not give the actual probability, but a probability distribution function that is unnormalized. To normalize the distribution function and obtain an actual probability, it is just a matter of dividing by yet another partition function

$$P_{\beta}(E, \vec{p}) = \frac{P_{\beta}(E, \vec{p})}{\sum_{E, \vec{p}} \tilde{P}_{\beta}(E, \vec{p})} .$$
(5.6)

Once the probabilities are determined, we are able to calculate the mean value of a quantity using Equation 3.7 as before. Figure 5.1 compares the

dielectric constant and specific heat for single simulations at every 10 K and the multiple histogram method using the data from the same input simulations.



(a) Dielectric constant with and without histogram method



(b) Specific heat with and without histogram method

FIGURE 5.1: Dielectric constant and Specific Heat of BT (x = 1) on a  $16 \times 16 \times 16$  lattice using raw data and the multiple histogram method. The simulations used for the old method are also the inputs in this multiple histogram method. The multiple histogram method is sampled every 1K, while the input simulations were performed every 10K.

## 5.3 Histogram Bin Size

As was previously discussed, the bin size that determines the allowable microstates for energy and polarization is not as easily defined as for the simple Ising model. The bigger the bin size, the smaller the computational cost, since the mean value of any function of E and  $\vec{p}$  is a sum over the available microstates. More bins equal more microstates, and more microstates equal more computational time. However, there is a limit to the maximum size a bin may be before the technique loses accuracy.



FIGURE 5.2: The dielectric constant dependence on polarization histogram bin size. A bin size of one corresponds to the minimum possible polarization difference of a single flipped cell.

Figures 5.2 and 5.3 are a direct analysis of the dependence of the dielectric constant and specific heat on the bin size. The dielectric constant is the



FIGURE 5.3: The specific heat dependence on energy histogram bin size. A bin size of one corresponds to the minimum possible energy difference of a single flipped cell.

variance of the polarization, and thus depends only on the bin size of the polarizations. Similarly, the specific heat only depends on the bin size of the energy because it is the variance of the energy. The figures show the results using a range of bin sizes, with the smallest bin being calculated based on the energy and polarization differences due to the flipping of a single cell. The maximum accurate bin size for both energy and polarization seems to be about four times the minimum bin size.

### 5.4 Combining Histograms of Different Configurations

Due to the large variation of the results of specific heat and dielectric constant for different lattice configurations as discussed in Section 4.3, it is necessary to find a way to combine the data into a single result. Simply taking an average of each value is not correct in this situation, because each lattice configuration does not necessarily have the same available energy and polarization states. The usual multiple histogram method does not allow for combination of systems with different available microstates.

Consider the case of two systems with the same composition and lattice size, but different lattice configurations. The two systems may be combined into one large system with twice the volume and number of cells of each original system. To get accurate results for this larger system we must calculate the probabilities for the new larger system prior to obtaining the averaged values from Equation 3.7. Instead of running the full Monte Carlo simulation of the larger cell, the probability of finding each microstate may be approximated using the probability distributions of the smaller subsystems.

In general, the probability of finding multiple configurations each with a particular energy is the product of the individual probabilities

$$P_{tot}(E_1, E_2, \dots, E_n) = P_1(E_1)P_2(E_2) \times \dots \times P_N(E_n) , \qquad (5.7)$$

where  $P_i(E_{j_i})$  is the probability of finding system *i* with energy  $E_i$ . The caveat is that each system is considered non-interacting and independent.

To describe a system that combines multiple systems together into a larger volume, the resulting probability should be a function of the total energy, rather than the energy of each subsystem as in Equation 5.7. This is accomplished by integrating over all energy microstates with an appropriate delta function constraining the total energy

$$P_{tot}(E_{tot}) = \int dE_1 \int dE_2 \dots \int dE_n P_1(E_{j_1}) P_2(E_{j_2}) \times \dots$$

$$\times P_N(E_{j_n}) \delta(E - (E_1 + E_2 + \dots + E_n)) .$$
(5.8)

Considering only discrete states and including the polarization dimension as well, the combined probability becomes

$$P_{\beta,tot}(E,\vec{p}) = \sum_{E_1,\vec{p}_1} \sum_{E_2,\vec{p}_2} \dots \sum_{E_n,\vec{p}_n} P_{\beta,1}(E_1,\vec{p}_1) P_{\beta,2}(E_2,\vec{p}_2) \times \dots \times P_{\beta,N}(E_N,\vec{p}_N) \times \delta_{E,(E_1+E_2+\dots+E_N)} \times \delta_{\vec{p},(\vec{p}_1+\vec{p}_2+\dots+\vec{p}_N)},$$
(5.9)

where the subscript  $\beta$  indicates the dependence of probability on temperature.

One problem that arises when calculating the total probability this way is that it is very computationally expensive. If each sum is order  $\mathcal{O}(M)$ , where M is the number of energy and polarization microstates for an individual lattice configuration, and the total probability is a combination of N lattice configurations, the resulting probability calculation is order  $\mathcal{O}(M^N)$ . Obviously, this can be a real problem for combining more than just a few lattice configurations. A solution is needed to speed up the computational process. A convolution of two functions f(t) and g(t) is defined as

$$(f \circ g)(t) \equiv \int_{-\infty}^{\infty} f(\tau)g(t-\tau)d\tau . \qquad (5.10)$$

To quickly calculate convolutions we employ the convolution theorem, which states that the Fourier transform of a convolution is proportional to the product of the Fourier transforms of its parts

$$\mathcal{F}[f \circ g] = A \cdot \mathcal{F}[f] \cdot \mathcal{F}[g] , \qquad (5.11)$$

where A is determined by the Fourier transform normalization convention.

Recognizing the similarity between the new total probability and a series of convolutions allows us to take advantage of discrete Fourier transforms to calculate the final probability:

$$P_{\beta,tot}\left(E,\vec{p}\right) = A\mathcal{F}^{-1} \Big[ \mathcal{F}[P_{\beta,1}\left(E_{1},\vec{p_{1}}\right)] \cdot \mathcal{F}[P_{\beta,2}\left(E_{2},\vec{p_{2}}\right)] \cdot \dots \\ \cdot \mathcal{F}[P_{\beta,N}\left(E_{N},\vec{p_{N}}\right)] \Big] , \qquad (5.12)$$

where A is a normalization constant. The value of A is unimportant, since  $P_{\beta,tot}(E, \vec{p})$  must be divided by the new total partition function

$$Z_{\beta,tot} = \sum_{E,\vec{p}} P_{\beta,tot}(E,\vec{p}) . \qquad (5.13)$$

In order to use the Fourier transform technique, each individual probability must have the same number of microstates as the total probability. As was previously stated, the number of microstates of the final probability is of order  $\mathcal{O}(M^N)$ . This number can be dramatically reduced by making the bins of each individual histogram, and subsequently each polarization, conform to the same microstate grid. If each histogram has the same bin size and is centered on the same values, the number of microstates of the final polarization can be reduced to

$$M_{E_{total}} = \left[ M_{E_1} + M_{E_2} + \dots + M_{E_N} - (N-1) \right], \qquad (5.14)$$

$$M_{\vec{p}_{total}} = \left[ M_{\vec{p}_1} + M_{\vec{p}_2} + \dots + M_{\vec{p}_N} - (N-1) \right], \qquad (5.15)$$

$$M = M_{E_{total}} \times M_{\vec{p}_{total}} , \qquad (5.16)$$

where  $M_{E_i}$ ,  $M_{\vec{p}_i}$  are the number of energy and polarization microstates of the  $i^{th}$  lattice configuration respectively, and N is the number of lattice configurations being combined. To calculate the total probability of Equation 5.9, there are N convolutions required and 3N FFTs per convolution. Each FFT is of order  $\mathcal{O}(M \log M)$ , so the total probability calculation is of order  $\mathcal{O}(N \times M \log M)$ . When combining many simulations, or even a few simulations with many bins, this can be computationally challenging.

Once the probabilities are determined for any given microstate, the dielectric constant and specific heat can be determined by use of the Boltzmann mean in Equation 3.7. For a given lattice configuration, the polarization and dielectric constant are calculated in each cartesian coordinate. Since the lattice configuration is not invariant under rotations, this is essentially the same as calculating a single component of the polarization and dielectric constant for three separate lattice configurations. Thus, the three components of polarization and associated dielectric constant values must be combined into a single result using this new convolution method. Pure BT has only one lattice configuration, so combining different lattice configurations of BT with this new method is moot. Other compositions are interesting when combined this way, and we analyze x = 0.95 and x = 0.9here. Figures 5.4 and 5.5 show the dielectric constant for each cartesian coordinate of the polarization, as well as the result of the combination of each probability using the convolution method. The specific heat is not analyzed in this way since it depends only on the energy, and the energy microstates are independent of rotation.



FIGURE 5.4: The dielectric constant of each cartesian coordinate of the polarization for a single lattice configuration of x = 0.9 compared with the combined histogram method. Each of the three values are combined using the convolution method and the result is plotted in black.



FIGURE 5.5: The dielectric constant of each cartesian coordinate of the polarization for a single lattice configuration of x = 0.95 compared with the combined histogram method. Each of the three values are combined using the convolution method and the result is plotted in black.

Another interesting case is the combination of different lattice configurations. Figures 5.7 and 5.6 show the dielectric constant and specific heat for five different lattice configurations and a single component of the polarization, as well as the convolved combination of each configuration. In this case, the specific heat convolution is interesting since each lattice configuration has different energy microstates available.



FIGURE 5.6: The dielectric constant of a single component of the polarization for each of five different lattice configurations and the combined result for x = 0.95.

The convolved result looks very much like a weighted average of each other result for both the specific heat and the dielectric constant. At high



FIGURE 5.7: The specific heat of five different lattice configurations and the combined result for x = 0.95.

temperatures, where the results from each lattice configuration are very similar, the convolved results are quite smooth. At low temperatures, there is quite a difference in the results for each lattice configuration. The convolved results begin to smooth out compared to the results for an individual simulation, but there is still a high degree of uncertainty, and it seems that additional lattice configurations would reduce the uncertainties.

#### 5.5 Uncertainties

The amount of confidence we have in any computed quantity is always of great importance, and the multiple histogram method is no exception. In general, Monte Carlo methods have the advantage of begin able to produce strong statistical error bars. The statistical uncertainty of the multiple histogram probability is given by

$$\delta P_{\beta}\left(E,\vec{p}\right) = \left(\sum_{n=1}^{N} \frac{H_n\left(E,\vec{p}\right)}{g_n}\right)^{-1/2} P_{\beta}\left(E,\vec{p}\right) , \qquad (5.17)$$

where the sum is over all simulations,  $H_n(E, \vec{p})$  is the histogram of a single simulation, and  $g_n = 1 + 2\tau_n$  is the correlation time factor [57].

The form of Equation 5.17 is similar to that of any counting experiment, with a relative uncertainty proportional to  $1/\sqrt{N}$ . Just as more counts reduce the uncertainty in any normal counting experiment, more counts per bin of each histogram will reduce the statistical error in the probabilities here. If the relative uncertainty is high, we must obtain more Monte Carlo data to fill in the gaps for those microstates. The relative uncertainty should be low for the entire range of occupied microstates in order to produce reliable results at a given temperature. Figure 5.8 shows the relative uncertainty of Equation 5.17 using both two and three simulation temperatures. The relative uncertainty with only two simulations has a region of high uncertainty, while adding a third simulation reduces the uncertainty for a larger temperature range. The uncertainty at the end points diverges as there are no occupied microstates far from the simulated temperatures.



FIGURE 5.8: The relative uncertainty for two different multiple histograms. One with simulations at T=450,500K, and the other with simulations at T=450,475,500K. The relative uncertainty with only two simulations has a region of higher uncertainty. Adding a third simulation to the histogram data lowers the uncertainty in the center region so the relative uncertainty of the probability for the entire valid region is less than 2%. The end points diverge since there is no data outside of this small energy range.

Another source of error in histogram re-weighting is due to using a finite

number of samples in the histogram. For a great source of discussion on all errors associated with the histogram method, see Newman and Palmer [58], in which they discuss the finite sampling error. As long as the histograms of every simulation temperature have sufficient overlap, the finite sample error will be small for the entire temperature range. Figure 5.9 shows the overlap of three histograms at different simulation temperatures. If the amount of overlap is sufficient, the finite sample error will be small because the value of the histogram is large. At the end points of the histogram the finite sample error becomes large because the histogram is not filled in that region. This becomes extremely important if the histogram contains empty bins. According to Equation 5.17, the relative statistical uncertainty is infinite for microstates with empty bins. To avoid this problem, we ensure that we use only data that has a reasonably high number of samples. Thus, the statistical error will dominate over finite sampling errors and remain finite. This may require more simulations or longer runs.

Equation 5.17 gives the statistical error for the normal multiple histogram method. When combining multiple lattice configurations, the uncertainty equation must be modified in a way that is consistent with the combined probability of Equation 5.9. To make this clear, a shorthand for the probability in Equation 5.9 is introduced as

$$P_{tot} = \sum_{1} \sum_{2} \dots \sum_{N} P_1 P_2 \dots P_N , \qquad (5.18)$$

where the summation is over the microstates of the probabilities of the same



FIGURE 5.9: Single and multiple energy histograms of BT. Each of the three histograms have considerable overlap and combine to form one continuous multiple histogram. Sufficient overlap of histograms reduces the finite sample error.

subscript, and the delta functions are simply implied. The uncertainty in the total probability is then given by

$$\delta P_{tot}^2 = \sum_{1} \left( \frac{\partial P}{\partial P_1} \delta P_1 \right)^2 + \sum_{2} \left( \frac{\partial P}{\partial P_2} \delta P_2 \right)^2 + \dots + \sum_{N} \left( \frac{\partial P}{\partial P_N} \delta P_N \right)^2 , \qquad (5.19)$$

where the uncertainty for each lattice configuration  $\delta P_i$  is calculated using Equation 5.17. This method is valid if each probability is independent and random. Different lattice configuration simulations are independent and random, but different polarization directions of a single lattice configuration are not independent. While both types of data are combined with this combined histogram method, the uncertainty is not exact when we include multiple polarizations from each lattice configuration.

The derivative of Equation 5.9 with respect to a single lattice configuration probability is

$$\frac{\partial P}{\partial P_i} = \sum_1 \dots \sum_{i-1} \sum_{i+1} \dots \sum_N P_1 \dots P_{i-1} P_{i+1} \dots P_N .$$
(5.20)

The error in the total probability is then given by

$$\delta P_{tot}^{2} = \sum_{1} \left[ (\delta P_{1})^{2} \left( \sum_{2} \sum_{3} \dots \sum_{N} P_{2} P_{3} \dots P_{N} \right)^{2} \right] + \sum_{2} \left[ (\delta P_{2})^{2} \left( \sum_{1} \sum_{3} \dots \sum_{N} P_{1} P_{3} \dots P_{N} \right)^{2} \right] + \dots$$
(5.21)
$$+ \sum_{N} \left[ (\delta P_{N})^{2} \left( \sum_{1} \sum_{2} \dots \sum_{N-1} P_{1} P_{2} \dots P_{N-1} \right)^{2} \right].$$

While this method is accurate considering the assumption that each probability is random and independent, it is computationally challenging, even when we take advantage of FFTs to do the convolutions. Since convolutions are essentially three discrete Fourier transforms, each convolution scales as that of an FFT, which is of order  $\mathcal{O}(M \log M)$ , with M being the number of microstates and histogram bins. The uncertainty of the combined probability requires  $N^2$  convolutions, thus the computational time is order  $\mathcal{O}(N^2 \times M \log M)$ . As we saw when computing the polarization, many simulations or many bins creates a challenge for computing the uncertainties as well.

Once the total uncertainty  $\delta P$  is found, we are able to determine the uncertainties in the polarization magnitude, specific heat, and dielectric constant. First, consider the polarization magnitude. The uncertainty in the mean magnitude of polarization is given by

$$\delta \langle |\vec{p}| \rangle^2 = \sum_{E,\vec{p}} \left( \frac{\partial \langle |\vec{p}| \rangle}{\partial P_{\beta}(E,\vec{p})} \delta P_{\beta}(E,\vec{p}) \right)^2 \,. \tag{5.22}$$

Taking the derivative of Equation 3.8 we obtain

$$\delta \langle |\vec{p}| \rangle^2 = \sum_{E,\vec{p}} (|\vec{p}| - \langle |\vec{p}| \rangle)^2 \left(\frac{\delta P}{Z}\right)^2 .$$
(5.23)

The uncertainties of the susceptibility can be determined in the same manner as Equation 5.22,

$$\delta\chi^{2} = \sum_{E,\vec{p}} \left( \frac{\partial\chi\left(\vec{p}\right)}{\partial P_{\beta}\left(E,\vec{p}\right)} \delta P_{\beta}\left(E,\vec{p}\right) \right)^{2}.$$
(5.24)

By carrying out the derivative of Equation 3.13, and using the average values in the form of Equation 3.8, we get

$$\delta\chi^{2} = \frac{\beta^{2}}{Z_{\beta}^{2}} \sum_{E,\vec{p}} \left[ \left[ \vec{p}^{2} - \langle \vec{p}^{2} \rangle + 2\langle \vec{p} \rangle^{2} - 2\langle \vec{p} \rangle \vec{p} \right]^{2} \left( \delta P_{\beta} \left( E, \vec{p} \right) \right)^{2} \right], \quad (5.25)$$

and similarly for the specific heat,

$$\delta c^{2} = \frac{\beta^{4}}{M^{2} Z_{\beta}^{2}} \sum_{E,\vec{p}} \left[ \left[ E^{2} - \langle E^{2} \rangle + 2 \langle E \rangle^{2} - 2 \langle E \rangle E \right]^{2} \left( \delta P_{\beta} \left( E, \vec{p} \right) \right)^{2} \right], \quad (5.26)$$

where M is the number of cells on the lattice.

## 6 RESULTS AND DISCUSSION

In this chapter, we present results of the model introduced in Chapter 3 and compare these results with the experiments of Huang and Cann [15]. All of the results produced by the model presented here are found using the combined histogram method discussed in Section 5.4. Each combined data set is found using simulations performed on a  $16 \times 16 \times 16$  (32) lattice at every 5 Kelvin, each with at least  $10^6$  Monte Carlo flips per cell.

## 6.1 Dielectric Constant

Figures 6.1 - 6.5 show the dielectric constant for the model and experiment for various compositions. Each of the experimental results of the dielectric constant are shown for a range of frequencies. In general, at high temperatures there is little to no frequency dependence of the experimental dielectric constant, while at low temperature there is some frequency dependence that grows larger as the composition decreases. The predicted dielectric constant at low temperatures does not match experiment for any composition, due to the frequency dependence and the fact that our model only predicts the zero-frequency limit.

Figure 6.1 shows the dielectric constant for pure barium titanate (BT) (x = 1). The experimental results show a clear transition near the Curie
temperature and almost no difference between the various frequencies. The model prediction shows very a precise curve, as the error bars are smaller than the thickness of the line. However, the value of the curve is not as accurate as one could hope. The predicted dielectric constant is well above the experimental value for all temperatures. For temperatures slightly above the critical point, the dielectric constant is almost an order of magnitude too high, and at high temperatures the difference is around a factor of two.



FIGURE 6.1: The dielectric constant of pure BT (x = 1) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15].

Below the critical point, the predicted value diverges, while the experi-

mental value drops down significantly. This divergence can be understood by considering that the model computes the zero frequency limit (DC) in thermal equilibrium [32]. The direct analysis of the MC data shows a drop in the dielectric constant below the critical temperature, as seen in Figure 4.3.

The direct analysis method fails to sample all accessible polarization states at low temperatures, while the multiple histogram method combines multiple simulations, which leads to better sampling of all available polarization states. As more states are included in the analysis through the combined histogram method, the calculated dielectric constant will approach the true value in the DC limit. This is roughly equivalent to the results that would be predicted by a well-converged straight-forward MC simulation.

Physically, the direct analysis is more representative of an actual ferroelectric at non-zero frequencies. At low temperatures, a ferroelectric is not likely to change polarizations over short time scales. Thus, only a single polarization state is all that is needed to determine the dielectric properties. The combined histogram method includes many polarization states for each temperature, and thus gives a non-physical result below the critical temperature. One possible solution would be to break the symmetry of the system by calculating the probabilities used to determine the dielectric constant in the presence of a small applied electric field. This would force the system to have only those polar states that are aligned with the electric field. In practice, the symmetry breaking leads to instabilities in both the dielectric constant and specific heat, which is likely due to poor convergence in our low temperature simulations.

Figures 6.2 and 6.3 show the experimental and model data for  $BaTiO_3$  -Bi $(Zn_{1/2}Ti_{1/2})O_3$  (BT-BZT) with compositions of x = 0.95 and x = 0.9respectively. For each of these figures, the model data was found using the combined histogram method with the  $\hat{x}$ ,  $\hat{y}$ , and  $\hat{z}$  components of the polarization for five different lattice configurations. This is roughly equivalent to using a single component of the polarization for 15 separate lattice configurations. Since there are multiple configurations being considered, there is a visibly larger uncertainty in the dielectric constant for both x = 0.95 and x = 0.9.



FIGURE 6.2: The dielectric constant of BT-BZT (x=0.95) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15].

The experimental data for x = 0.95 still shows some critical behavior at a slightly lower temperature than pure BT. For x = 0.9, the experimental data does not show any criticallity. Figure 6.3 clearly shows the dielectric constant has a low temperature frequency dependence.



FIGURE 6.3: The dielectric constant of BT-BZT (x=0.9) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15].

The model predicts the dielectric constant reasonably well for both x = 0.95 and x = 0.9 at high temperatures. The difference between the model data and experimental data is now much less than a factor of two, even as the temperature decreases. For lower temperatures the model predictions still diverge for these compositions. The temperature at which this divergence occurs, however, is much lower than that of pure BT.

Figures 6.4 and 6.5 show the model and experimental dielectric constant for x = 0.8 and x = 0.7. These model results were found using the three polarization components of only two and three atomic configurations respectively. For these lower compositions, the model dielectric constant is no longer higher, but lower than experiment. At medium and high temperatures, both theoretical values are still within a factor of two of the experiment. At low temperatures, both the x = 0.8 and x = 0.7 curves have an upward trend similar to that of the higher compositions and the DC limit.



FIGURE 6.4: The dielectric constant of BT-BZT (x=0.8) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15].



FIGURE 6.5: The dielectric constant of BT-BZT (x=0.7) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15].

### 6.2 Curie-Weiss Law at High Temperature

As was previously discussed, the Curie temperature is the critical temperature below which ferroelectric materials are spontaneously polarized. The Curie-Weiss law (Equation 1.2) indicates an inverse relationship between temperature and the susceptibility. Figures 6.6 - 6.8 show the inverse susceptibility as a function of temperature for various compositions. At high temperatures, if the Curie-Weiss law is obeyed, the curve will be linear with the x-intercept of the linear portion corresponding to the Curie temperature.

Figure 6.6 shows the inverse susceptibility for pure BT (x=1), which displays clear linear behavior at high temperature in the experimental data. The theoretical curve is also linear at high temperatures, but with a much smaller slope. Since the theoretical model was fit to the Curie temperature of BT using the Binder cumulant method, the linear portion of the model data might be expected to intercept the x-axis at the correct Curie temperature. Unfortunately, due to finite size effects, this is not the case. The dashed lines show a linear approximation to the high temperature portion of each curve. The x-intercept of the experimental curve is at approximately 397K, while the theoretical value is approximately 408K. Both values of the x-intercept are above the experimental Curie temperature of 393K.

Figure 6.7 shows the inverse susceptibility for x = 0.95. The experimental curves are essentially linear above the critical temperature. The theoretical curve is slightly nonlinear, even at high temperatures. The slopes of the



FIGURE 6.6: The inverse susceptibility of pure BT (x=1) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15]. The dashed lines show an approximate linear trend of the high temperature data, which is comparable to the Curie-Weiss law.



FIGURE 6.7: The inverse susceptibility of BT-BZT (x=0.95) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15]. The dashed lines show an approximate linear trend of the high temperature data, which is comparable to the Curie-Weiss law.

approximately linear region at high temperature for experiment and theory are approximately the same, but the x-intercept differs by about 20K.

For a composition of x = 0.9, the inverse susceptibility curve has no linear region as shown in Figure 6.8. This deviation from the linear Curie-Weiss law is expected for relaxor ferroelectrics, as was discussed in Section 1.6.1. Thus, it can said that this composition does behave as a relaxor. Compositions below x = 0.9 are qualitatively similar to this.



FIGURE 6.8: The inverse susceptibility of BT-BZT (x=0.9) compared with experiment. The predicted result is compared with multiple frequencies of experimental results of Huang and Cann [15]. There does not appear to be a linear trend at high temperatures, and thus a deviation from the linear Curie-Weiss law.

# 6.3 Polarization Magnitude

The simplest indicator of ferroelectric behavior is the magnitude of the polarization as a function of temperature. Above the Curie temperature for a true ferroelectric the net polarization should be zero, and below the critical point there should be a spontaneous polarization. This can be seen in Figure 6.9, where the magnitude of the polarization density is shown for various compositions. Due to finite-size effects, we do not expect the mean polarization ever to vanish, but instead to approach some small value.



FIGURE 6.9: The magnitude of the polarization density for various compositions as a function of temperature. For x = 1, there is a clear transition at the Curie temperature. For x < 1, there is no ferroelectric state as indicated by the absence of a spontaneous polarization.

By observing the magnitude of the polarization of the solid solutions, it is clear that true ferroelectric behavior is not present for  $x \leq 0.95$ . Referring back to Section 4.5, the solid solutions appear to have polar nano-regions in random orientations, and disorder that keeps the entire system from uniformly polarizing.

#### 6.4 Specific heat

Figure 6.10 shows the predicted specific heat for various compositions, but there are no experimental results currently available for the specific heat of the solid solution BT-BZT. There have, however, been studies of the specific heat of pure BT near its critical point. Experimentally, there is a discontinuity directly at the critical temperature, with a nearly constant specific heat both above and below the critical point, where each phase has a different value of specific heat [59]. The predicted specific heat has a peak near the Curie temperature which is consistent with experiment, and above the critical point the specific heat is nearly constant. Below the critical value the predicted specific heat decays as temperature decreases, which does not agree with experiment. The disagreement is due to finite size effects, and in the limit of infinite lattice size the model result should approach a delta function peak at the critical point.



FIGURE 6.10: The specific heat as a function of temperature for multiple compositions. There is a clear phase transition as indicated by the sharp peak for the x = 1 case. There are no peaks for x < 1, and thus no apparent phase transitions.

### 6.5 Non-Zero External Electric Field

So far our discussion and analysis has only included effects from the nearest neighbor interaction term in the Hamiltonian in Equation 3.1. For ferroelectric materials it helps to understand the behavior of the material in the presence of an external electric field. To include the second term in the Hamiltonian in our analysis, we only need to modify our probability (Eq. 5.4) to include this new term in the energy:

$$P_{\beta,\vec{E}}(E,\vec{p}) = \frac{\sum_{n=1}^{N} H_n(E,\vec{p}) g_n^{-1} \exp\left(-\beta \left(E - \vec{p} \cdot \vec{E}\right)\right)}{\sum_{m=1}^{N} n_m g_m^{-1} \exp\left(-\beta_m E - f_m\right)} .$$
(6.1)

Note that the energy in the denominator does not include the electric field term, because all simulations were done with zero electric field applied. The beauty of the histogram method is that as long as the polarization and energy microstates exist in the histogram, then the probability of finding the system with that microstate can be found. The energy in the denominator of Equation 6.1 corresponds to the Hamiltonian used in each simulation. This is made clear since it is this energy that is multiplied by  $\beta_m$ , which corresponds to the simulation temperatures. Since the value of  $\beta$  in the numerator corresponds to the desired temperature, the desired electric field term also makes an appearance. Thus, using the histogram method it is possible to use data simulated at zero applied E-field to get a probability at a non-zero E-field.

Figure 6.11 shows the polarization density in the direction of the field as

a function of electric field for both the model and experimental data of pure BT at room temperature. The obvious difference between the model and experiment is that the model is completely polarized in the direction of the applied field, even for small fields. Since pure BT is ferroelectric at room temperature, the large polarization is expected, even in the absence of an applied electric field.



FIGURE 6.11: Polarization vs electric field for pure BT (x = 1) compared with experiment at room temperature. The model data is fully saturated in the presence of very small fields, since BT is only in the ferroelectric state and fully polarized at room temperature. Experimental data provided by Huang and Cann [15].

The magnitude differs from the experimental values at low fields because

the Monte Carlo model predicts a DC value, which corresponds to the infinite time limit of an applied DC field. This leads to the drawback that we are unable to predict the hysteretic behavior shown by experiment. The slope of the polarization versus electric field curve is the susceptibility in the limit of small electric fields. The discontinuity of the predicted curve shows an infinite slope for small fields. This corresponds with the divergence of the dielectric constant below the Curie temperature of BT in Figure 6.1. In the limit of high field, the experiment and model agree quite nicely. This is due to the fact that high field strengths force the system into a single bulk polarization state that is equivalent to the equilibrium state for the model.

Figures 6.12 - 6.15 show the polarization density vs electric field with compositions of 0.95, 0.9, 0.8, and 0.7, for both experiment and model data. As was previously stated, and may be more obvious here, the model fails to predict hysteresis, since there can only be one true equilibrium state in the presence of an electric field.

One feature that occurs for all x < 1, is that the maximum polarization of the model is much lower than the maximum for the experiment. This is most likely due to the lack of available microstates with high polarizations in the model. Since the input simulations are all performed with zero applied electric field, the high polarization states most likely have not been sampled. This is clear by observing the low polarization value of the solid solutions in Figure 6.9. If the solid solutions had high polarization states available as input to the histogram method, the maximum polarization of the  $\vec{P}$  vs  $\vec{E}$ 



FIGURE 6.12: Polarization vs electric field for BT-BZT (x = 0.95) compared with experiment at room temperature. The polarization of the model is saturated at a much lower value than the experimental data of Huang and Cann [15]. This effect is due to the fact that large polarization states have not been sampled for this composition, which is apparent in Figure 6.9.



FIGURE 6.13: Polarization vs electric field for BT-BZT (x = 0.90) compared with experiment (x = 0.92) at room temperature. The polarization of the model is saturated at a much lower value than the experimental data of Huang and Cann [15]. This effect is due to the fact that large polarization states have not been sampled for this composition, which is apparent in Figure 6.9. In the range of small electric field, the slope is in a very good agreement with experimental data.

graphs would better match the experimental values, which suggests that we would benefit from performing additional MC simulations with an applied finite electric field. Even so, the combined multiple histogram method helps us by reducing the number of such simulations required. For BT this issue did not arise because the high polarizations were sampled, since the low temperature states with zero field are identical to states with a large electric field applied.

For all of the solid solution polarization versus electric field graphs there is a finite slope at small applied field, while the slope of the x = 1 graph is infinite. The linear behavior of this slope at small applied fields indicates that the materials with lower composition are linear dielectrics, and the value of the slope and the dielectric constant show that they are in fact high permittivity linear dielectrics.



FIGURE 6.14: Polarization vs electric field for BT-BZT (x = 0.8) compared with experiment at room temperature. The polarization of the model is saturated at a much lower value than the experimental data of Huang and Cann [15]. This effect is due to the fact that large polarization states have not been sampled for this composition, which is apparent in Figure 6.9. In the range of small electric field, the slope is in a very good agreement with experimental data.



FIGURE 6.15: Polarization vs electric field for BT-BZT (x = 0.7) compared with experiment at room temperature. The polarization of the model is saturated at a much lower value than the experimental data of Huang and Cann [15]. This effect is due to the fact that large polarization states have not been sampled for this composition, which is apparent in Figure 6.9. In the range of small electric field, the slope is in a very good agreement with experimental data.

### 7 CONCLUSIONS

Using only *ab initio* methods and the experimental Curie temperature of BaTiO<sub>3</sub> (BT), we developed a model to predict the dielectric properties of BaTiO<sub>3</sub> - Bi(Zn<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub> (BT-BZT) in solid solution. This material behaves as a relaxor ferroelectric for some compositions as shown experimentally [15] and through our own predictions.

We first use Density Functional Theory (DFT) to calculate the ground state energies of small  $2 \times 2 \times 2$  cubic supercells of the BT-BZT solid solution. This is a slight challenge, since there are many atomic configurations of the solid solution supercells. We then use the Modern Theory of Polarization (MTP) to determine the available polarization states of each supercell. DFT and MTP alone are unable to effectively model relaxors due to the importance of long range disorder.

In order to model the long-range disorder effects of relaxors we introduce a Monte Carlo lattice Ising-like model, where the cells on the lattice are the supercells used in the DFT calculations with polarization states determined by MTP. Our model differs from Ising, Potts, and Heisenberg models in that each cell has a finite number of polarization states that are of differing magnitude and orientation, and not every cell on the lattice has the same available states. The interaction energy coupling constant needed for this Ising-like model was determined by fitting to the experimental Curie temperature of BT.

To analyze the Monte Carlo data we use the multiple histogram method to combine data from simulations of a single lattice configuration at multiple temperatures. However, to combine simulations of multiple lattice configurations we had to develop a modified version of the multiple histogram method. Using this new analysis tool, we combine Monte Carlo data from multiple simulations and temperatures to obtain the most statistically accurate data possible.

The new model and analysis method allow us to predict a dielectric constant that has reasonable agreement with experiment, especially at high temperatures. The manner in which the predicted dielectric constant as a function of temperature changes with respect to the composition is consistent with that of experiment. We also predict the behavior of the polarization of BT-BZT in the presence of an applied external electric field, with reasonable agreement in the range of small electric fields.

Future work could incorporate long-range effects of strain, by including non-cubic cells. This may give better results at lower temperatures. It would also be interesting to run simulations of lower compositions with applied electric fields to try and sample high-polarization states. The resulting polarization versus electric field plots should be more accurate in the presence of high electric fields. Finally, this type of model should be used to study other relaxor materials. BT-BZT has not been studied experimentally as extensively as many lead based solid solutions, and this model may give more insights when applied to other relaxors.

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