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Multiscale Modeling of Perovskite Ferroelectrics: From First Principles to Coarse-Grained Descriptions

Krishna Chaitanya Pitike

University of Connecticut - Storrs, krishna.pitike@uconn.edu

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Ferroelectrics are an important class of materials that exhibit rich functional behavior and are being actively investigated for a variety of technological applications. Multiscale modeling of ferroelectric materials is necessary for accelerating the design and discovery of the next generation of functional materials and nanostructures. In this dissertation, we study the properties of perovskite based ferroelectric systems with the help of first principles calculations, as well as use the results of these calculations to develop coarse-grained descriptions of ferroelectric behavior. In particular we elucidate the electronic underpinnings of functional behavior arising from polarization rotations in classical and layered perovskite oxides containing electron lone-pair active ions, such as Pb$^{2+}$ and Sn$^{2+}$. We then devise a general approach for fitting the Landau-Devonshire theory based thermodynamic potentials from first principles for these compounds. The parameterized Landau potential for PbTiO$_3$, that we use as a test case, has the ability to accurately predict dielectric, piezoelectric and thermal properties at finite temperature as compared with the results produced by a popular potentials of the same form fitted from the experimental data. The parametrized potential was also applied to map the phase diagram under simple elastic boundary conditions — giving comparable results with the previous results. In closing, we demonstrate how such coarse-grained thermodynamic energy descriptions can be used to study the properties of
ferroelectric nanostructures at mesoscale, e.g., to evaluate the influence of size, shape and morphology on their functional behavior.
Multiscale Modeling of Perovskite Ferroelectrics: From First Principles to Coarse-Grained Descriptions

Krishna Chaitanya Pitike

B.Tech., Jawaharlal Nehru Technological University, 2008

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Doctor of Philosophy Dissertation

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From First Principles to Coarse-Grained Descriptions

Presented by

Krishna Chaitanya Pitike

Major Advisor

Serge M. Nakhmanson

Associate Advisor

S. Pamir Alpay

Associate Advisor

George A. Rossetti Jr.

University of Connecticut
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Dedicated to my family, for their perpetual love and support.
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List of Abbreviations

BFO  Bismuth Ferrite
BZ   Brillouin Zone
CBM  Conduction-Band Minimum
CU   Cube
DFPT Density Functional Perturbation Theory
DFT  Density Functional Theory
FEM  Finite Element Method
FPP  First Principles Parametrization
FP   First Principles
GGA  Generalized Gradient Approximation
LDA  Local Density Approximation
LDTP Landau Devonshire Thermodynamic Potential
LD   Landau Devonshire
LGD  Landau Ginzburg Devonshire
MBE  Molecular Beam Epitaxy
MC   Monte Carlo
MD   Molecular Dynamics
MP   Monkhorst-Pack
NC   Near Cube
NO   Near Octahedron
OC   Octahedron
OLS  Ordinary Least Squares
PAW  Plane Augmented Wave
PJTE  Pseudo Jahn-Teller Effect
PSTO  Lead Strontium Titanate
PZT   Lead Zirconate Titanate
QE    Quantum Espresso
RR    Ridge Regression
RSM   Reciprocal Space Map
RT    Room temperature
SHG   Simple Harmonic Generation
SP    Sphere
VASP  Vienna *Ab Initio* Simulation Package
VBM   Valence-Band Minimum
XC    Exchange Correlation
XPS   X-ray photoelectron spectroscopy

**Nomenclature**

$\alpha_i$  Dielectric stiffness coefficients
$\alpha_{ij}, \alpha_{ijk}$  Higher order dielectric stiffness coefficients
$\epsilon_{ij}^\infty$  High-frequency dielectric constant tensor
$\sigma_l$  Symmetric stress tensor in Voigt notation
$P, P_i$  Polarization density vector
$\varepsilon_e$  Epitaxial or misfit strain
$\varepsilon_l$  Symmetric strain tensor in Voigt notation
$C$  Curie constant
$i, j, k$  Cartesian axis direction index — takes values 1, 2, 3
$l, m, n$  Symmetric second rank tensor index — takes values 1, 2, 3, 4, 5, 6
$Q_{lm}$  Electrostriction coefficient in Voigt notation
$s_{lm}$  Elastic coefficient in Voigt notation
$T$  Temperature
$T_0$  Curie-Weiss temperature for ferroelectric phase transition
$T_t$  Phase transition temperature for ferroelectric phase transition
$Z^{*}_{\xi,ij}$  Born effective-charge tensor
Chapter 1

Introduction

Ferroelectrics are an important class of materials that are being actively investigated for a variety of technological applications utilizing their rich functional behavior. Specifically, ABO$_3$ perovskite oxides are well known for the wide range of useful dielectric, electrical and magnetic properties, encompassing ferroelectricity, ferromagnetism, ionic and electronic conduction, and superconductivity [1]. Although a number of piezoelectric and ferroelectric (FE) perovskite-oxide compounds exist, it is remarkable that a single family of PbTiO$_3$ based systems, such as lead zirconate titanate PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) [2–5] and a variety of lead-based relaxor ferroelectrics [2, 6, 7], is prevalent in most application areas for such materials. Outstanding polar, piezoelectric and dielectric properties of all of these systems emanate from strong lattice distortions — specifically, large displacements of both Pb$^{2+}$ and Ti$^{4+}$ ions away from their centrosymmetric positions in the undistorted perovskite structure.

On the level of underlying electronic phenomena, the nature of these distortions for
both cations is attributed to cooperative pseudo Jahn-Teller effect (coop-PJTE) [8, 9]. In particular, a spontaneous displacement of Ti from the centroid of the O$_6$ octahedron in the TiO$_6$ cluster allows for the mixing between empty Ti(3$d$) states and filled O(2$p$) states, which induces polarization in both classical ferroelectric perovskites PbTiO$_3$ and BaTiO$_3$. However, the presence of Pb$^{2+}$ cations carrying nonbonded 6$s^2$ electrons (or the so-called electron lone pair) in the former system leads to substantially larger ionic distortions and, consequently, stronger polarization.

Although up to this day PbTiO$_3$ based materials, such as piezoelectric PZT ceramics, are the mainstay for a number of electromechanical applications, the toxicity of Pb remains a major environmental concern. The need to avoid the inclusion of Pb into the next-generation electroactive compounds stimulated a search for novel Pb-free materials possessing property responses of comparable (or greater) magnitudes [10–15]. However, developing suitable replacements turned out to be a great challenge, as, paraphrasing the authors of Ref. [13], when performance, cost, ease of preparation and precursors availability are taken into account, PZT still remains the almost perfect all-around piezoelectric material.

Naively, one can expect that tin (Sn), an isoelectronic “younger brother” of lead, would be its natural replacement. Unlike lead, tin is environmentally benign, having been widely used for tableware in the form of pewter alloys since the beginning of the Bronze Age [16]. Tin is readily available in its 4$^+$ oxidation state, e.g., in the form of Sn(IV) oxide, or SnO$_2$ (rutile, mineral cassiterite). In contrast, its 2$^+$ oxidation state — the one whose behavior is also governed by strong (5$s^2$) electron lone-pair activity [17–20] and is highly desirable
for technological applications — is much more elusive. For example, Sn(II) oxide, or SnO (litharge), containing electron lone-pair active Sn$^{2+}$, is metastable with respect to transformation into SnO$_2$ over a wide range of oxygen pressures. A number of recent computational studies have suggested that substituting A = Sn$^{2+}$ for Pb$^{2+}$ in a polar perovskite (e.g., tetragonal $P4mm$) ATiO$_3$ structure results in piezo- and ferroelectric properties similar to, or exceeding those of bulk PbTiO$_3$ [21–24].

In particular, a detailed polymorph analysis of SnTiO$_3$ by Parker and coworkers [24] demonstrated that (i) the polar perovskite ($P4mm$) phase is likely to be the ground state and (ii) octahedral corner-sharing polar phases in general are more stable than face- and edge-sharing non-polar phases. Nonetheless, despite the computationally predicted stability of the Sn$^{2+}$ containing polar perovskite phases, reliable growth approaches for making such materials still have to be fully developed. A conventional ceramic synthetic route requires high temperatures, which leads to facile Sn$^{2+}$ disproportionation into Sn$^{4+}$ and Sn metal [23, 25], and, so far, there have been no reports of bulk perovskite SnTiO$_3$ being produced.

On the other hand, Sn based perovskite oxides have been recently grown in thin film form on p-type Si substrate using atomic-laser-deposition (ALD) technique [26, 27] and as a solid solution with SrTiO$_3$ on SrTiO$_3$ substrate using hybrid molecular beam epitaxy (MBE) [28]. Although it still remains to be seen how successful these initial investigations are in yielding Sn(II) based ferroelectric materials, as of this writing it is highly encouraging to see that the experimental efforts aimed at synthesizing them are continuing.

The first part of this dissertation is focused on elucidating the electronic level underpin-
nings of the functional behavior of Sn-based ferroelectrics, as well as comparing and con-
trasting this behavior against that of the exhaustively studied case of perovskite PbTiO$_3$.

In the process of this investigation, we evaluate the influence of numerous adjustable “dials” — such as chemical composition, strain and nanoconfinement (accomplished in quasi-2D perovskite slabs or 0D particles) — on the resulting functional properties. Epitaxial, or mis-
fit strain — arising from the difference in lattice constants between a ferroelectric film and the underlying substrate — has already been widely reported as a powerful vehicle [29] for controlling and manipulating ferroelectricity, with strain induced ferroelectricity in SrTiO$_3$ serving as an excellent example of its effects [30, 31]. In general, compressive epitaxial strain in known to enhance the out-of-plane component of the ferroelectric film polarization [32, 33], while tensile strain does the same for the in-plane polarization components [34].

Despite the isoelectronic nature of Pb$^{2+}$ and Sn$^{2+}$ at A-site, the initial computational investigation of epitaxially strained perovskite SnTiO$_3$ perovskite, conducted by Parker and coworkers [24], revealed interesting differences in its transitional behavior, compared to that of PbTiO$_3$ [35, 36]. In what follows, we conduct a thorough first principles study of epitaxial SnTiO$_3$ and PbTiO$_3$, connecting these differences to the subtleties of electronic interactions and electron lone-pair charge clouds alignment in both materials. Such electronic level insights will be useful for the design of a new generation of more efficient electromechanical devices utilizing lone-pair active perovskite compounds.

In addition to applying epitaxial strain, radical changes in functional responses or even emergence of completely new and unexpected materials properties can also be obtained by
creating different layered structures utilizing the basic ABO$_3$ perovskite building blocks. While the already mentioned “classical” ABO$_3$ perovskite oxides are being widely employed in applications since WWII, layered-perovskite oxides have only recently emerged as an attractive class of functional materials with widely customizable properties. The remarkable versatility of this materials class stems primarily from vast structural diversity of its constituent families of compounds. For example, a number of such families — or, the so-called homologous series — are constructed from perovskite slabs with (001) surfaces and include Ruddlesden-Popper [37–39] (RP; structural formula $A_{n+1}B_nO_{3n+1}$), Aurivillius and Dion-Jacobson compounds [40, 41]. Although sometimes more fickle in growth [42], layered-perovskite structures can usually inherit all of the major functional traits of their ABO$_3$ counterparts. More importantly, they also provide a number of additional channels not only for property modification and fine-tuning, but also for the design of new advanced functionalities that classical perovskites do not possess.

An $n = 2$ RP structure, constructed by stacking $2\frac{1}{2}$-unit-cell-thick perovskite slabs in the [001] direction, is shown in Fig. 1.1(a). The adjacent slabs within this structure are related by a $(\frac{1}{7},\frac{1}{2})$ translation in (001) basal plane. Unlike the centrosymmetric cubic ($Pm\bar{3}m$) aristotype for the ABO$_3$ perovskites, the centrosymmetric parent phase for the RP family belongs to the tetragonal $I4/mmm$ space group. The most obvious difference between the 3D bulk ABO$_3$ perovskite materials and their derivative layered structures is in dramatic anisotropy of the latter, when viewed along the in-plane and out-of-plane directions. Furthermore, the functional response in the out-of-plane direction can be fine-tuned by gradually changing
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the thickness of the perovskite slab (i.e., the value of \(n\) in the stoichiometric formula of the layered compound), as well as by manipulating the nature of the interface between the adjacent slabs [43–45].

One example of an unusual functionality not present in ABO\(_3\) systems was predicted for a simple layered-oxide superlattice \(\text{PbSr}_2\text{Ti}_2\text{O}_7\) (PSTO) that is depicted in Fig. 1.1(b). Under certain epitaxial strain conditions, this structure was found to develop a Goldstone-like
excitation involving an *easy* rotation of the polarization vector within the (basal) \( xy \)-plane [44]. The resulting free-energy density landscape \( f(P_x, P_y) \) is shown in Fig. 1.1(c,d) and has a distinctive sombrero-hat shape characteristic of a presence of a Goldstone-like or *phason* excitation [46–50] in the system. The ease with which the direction of the dipolar field can be manipulated in PSTO makes it an interesting medium for inducing a variety of exotic states, including vortices [51, 52], skyrmions and other polarization-closure patterns [53], whose topology can be controlled, e.g., by means of elasticity [52, 54–56] or electrostatics [57–61]. While conducting research related to the main subject of this dissertation, we have recently discovered that materials with Goldstone-like excitations possess anomalous pyroelectric response, which makes them useful for electrothremal energy interconversion, with potential applications in the field of solid state cooling/heating [62].

It is also worth pointing out, that as facile in-plane polarization rotation occurs along a transition path connecting structurally distinct phases with different directions of the polar vector, some aspects of the PSTO behavior could be similar to that of a system possessing a morphotropic phase boundary (MPB) [63]. The strong piezoelectric properties of PZT are credited to the MPB emergence at a certain Zr-to-Ti concentrations ratio [4, 60, 63, 64]. Therefore, it would be highly beneficial to acquire a better understanding of physical phenomena underpinning an MPB appearance, as well as their connection to the existence of Goldstone-like excitations, in a simple, quasi-two-dimensional system like PSTO — that is, in comparison to a compositionally complex, three-dimensionally-connected material, such as PZT. In this dissertation, we attempt to develop such knowledge by investigating the
properties of layered-perovskite Sn- and Pb-based systems.

The functionality engineering approaches discussed until now are applied to periodic structures (bulk or layered) through modifying their unit cells, for example, by changing their lattice constants or composition. However, an especially promising approach for altering the properties of ferroelectric materials can be realized through changing the size, shape and morphology of their nanoparticles. Recent advances in nanoparticle synthesis have demonstrated abilities to control both shape and size [65], and can pave the way to a new generation of highly tunable electroactive composite materials. For example, BaTiO$_3$ nanoparticles dispersed in parylene exhibit superparaelectric behavior [66] that could be exploited for energy storage applications, while their ordered superlattices display radically different hysteretic switching patterns depending on the size and packing order [67]. Understanding and controlling the collective behavior of both ordered and disordered assemblies of such particles, embedded into a variety of dielectric environments [66–72], is paramount for engineering of advanced functional properties.

Another critical problem for potential applications of ferroelectrics that can be resolved by utilization of nanocomposites is high dielectric loss [73]. Mitigating its negative effects and thereby greatly improving the performance of a wide range of different devices — including non-volatile memories [74–77], pyroelectric IR detectors, electrocaloric waste heat recovery systems [78], piezoelectric sensors, actuators, resonators [79–81], and tunable telecommunication arrays [82, 83] — can be readily accomplished by embedding ferroelectric components in the low-loss dielectric media.
However, since such particles are usually too large to be studied using atomistic techniques, course grained energy descriptions based on phenomenological Landau-Devonshire (LD) theory [84–86] are used instead to characterize their behavior. Unlike atomistic or other computational approaches tied to the system unit cell size (e.g., effective Hamiltonian techniques [87–89]), LD-style theories operate with thermodynamic potentials that represent the free energy of the system, as dependent on the variation of the continuous polarization field and other parameters. Although such descriptions are available for a number of popular perovskite ferroelectrics, these free energy expressions have been usually developed and tested through tedious, time consuming and expensive experimental efforts, spanning decades since the discovery of the corresponding ferroelectric materials.

An antiferromagnetic ferroelectric multiferroic BiFeO$_3$ serves as a good example of how long it takes to design a suitable LDTP-style energy parameterization. Although not exactly ‘new’ ferroelectric material (identified as such in 1970 [90]), it became popular in thin film form around 2003 [91], with first LD-type energy expressions put forward only in 2017 [92, 93]. However, even for an exhaustively studied material such as PbTiO$_3$, because of difficulties with growth of high-quality bulk crystals for intrinsic property measurements, multiple versions of LDTPs were produced [64, 94–97] together with radically different sets of polarization gradient energy parameters [98–101].

Naturally, developing computational approaches for constructing coarse-grained energy descriptions for novel, or even not yet synthesized compounds, such as perovskite SnTiO$_3$, will be extremely useful for predictively evaluating their thermodynamic properties and
transitional behavior at mesoscale. In the second part of this dissertation we present a general methodology for fitting LD thermodynamic potentials (LDTPs) for displacive perovskite ferroelectrics directly from first principles based simulations, such as the ones that are utilized by us for the studies of electronic properties of SnTiO$_3$, PbTiO$_3$ and other related compounds. As a test case, we first parameterize a PbTiO$_3$ potential completely from density-functional theory (DFT) calculations, under the only assumption of the first-order character of the polar-to-non-polar phase transition, and evaluate its performance against that of well-known empirical parameterizations. On the second step, the developed methodology is used to generate a parameterization for perovskite SnTiO$_3$, enabling us to predictively evaluate an approximate ‘biaxial strain – temperature – spontaneous polarization’ phase diagram for its thin films.

In the last part of this dissertation, such LD-style coarse-grained energy descriptions (combined with suitable parameterizations for the polarization gradient energy) are applied to the studies of intrinsic properties of ferroelectric nanoparticles embedded in a dielectric medium. Building on the results of a previous investigation [102], we attempt to elucidate the details of topological phase transformations of the local polarization fields (called in what follows polarization textures) in PbTiO$_3$ nanoparticles depending on the particle size and shape. Specifically, we probe shapes belonging to the superellipsoidal family, including octahedral, cubic and intermediate geometries. Critical particle sizes corresponding to polarization texture instabilities are found to be strongly dependent on the particle shape and symmetry, which can open up new avenues for controlling ferroelectricity at the nanoscale.
in a variety of technological applications.

1. Introduction

1.1 Dissertation main goals and structure

In this dissertation, we conduct a comprehensive multiscale study of the ferroelectric properties of Sn and Pb-based perovskite materials in their classical, layered and nanoparticle forms. Our investigation begins at the atomistic level (and temperature of absolute zero), where these materials are treated with first principles calculations as implemented in popular DFT software packages. The obtained insights and computational first principles data are then “recycled” into LD-style thermodynamic potentials using our original approach — thus building a bridge between the atomistic and mesoscopic descriptions of both materials. Finally, we use an “in-house” developed software package for simulating the properties of ferroics at mesoscale (ferret) to explore the influence of shape and size on the polar properties and phase transitions in PbTiO₃ nanoparticles embedded in a dielectric matrix. Empirical potentials similar to those that we generated from the first principles are employed to represent the energetics of the nanostructures. SnTiO₃ based nanoparticles are yet to be evaluated, since a parameterization for the polarization gradient energy in SnTiO₃ still needs to be developed. The connections between the different parts of this dissertation are schematically represented in Fig. 1.2. The rest of this dissertation is organized as follows:

- Chapter 2: Ferroelectric materials basics, including brief history, considerations of crystalline symmetry, structure and functional behavior of technologically important
perovskite ferroelectrics. The importance of engineering Pb-free ferroelectrics and the role of theory and computations in achieving this is also discussed.

- Chapter 3: A brief review of computational methods used to study ferroelectric materials. Detailed descriptions of modeling approaches utilized in this investigation, i.e., first principles techniques and phenomenological LD models, is also provided.

- Chapter 4: First-principles-based studies of the electronic structure underpinnings of functional behavior of perovskite PbTiO₃ and SnTiO₃, including their epitaxial and layered forms. Information on some other relevant materials and experimental collaborations resulting from these studies is also provided.

- Chapter 5: Development of course grained potentials for perovskite PbTiO₃ and SnTiO₃ from the results of first principles simulations, such as the ones presented in Chapter 4. Potential parameterization techniques and testing procedures are discussed in detail.

- Chapter 6: Mesoscale level studies of functional behavior and phase transformations in ferroelectric PbTiO₃ nanoparticles of different shapes and sizes, embedded in dielectric matrix, utilizing phenomenological energy descriptions, similar to those generated in Chapter 5.

- Chapter 7: Conclusions and future outlook.
Appendix A: Results of a collaborative project (with the group of Prof. Paul Evans at the University of Wisconsin – Madison) on the studies of electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films are presented.
Figure 1.2: Multiscale modeling investigations being connected through the course-grained energy descriptions, which are parameterized from first principles.
Chapter 2

Ferroelectrics

2.1 Dielectrics

Dielectric materials are electrical insulators and therefore do not contain an appreciable amount of free electrical charges that can be moved long distances inside the material by an application of an electric field $E$. Instead, bound electrical charges within dielectrics can be ‘polarized,’ or moved short distance (i.e., on the order of a typical interatomic bond length) by an applied electric field. Shifts in positions of the bound charges can cause an emergence of (or a change in) electric dipole moments $d_n$ associated with the structural units comprising the material, which in turn results in an emergence of (or a change in) the dielectric polarization density $P$: 
\[ P = \frac{1}{V} \sum_n d_n, \]  

(2.1)

where \( V \) is the volume of the crystallographic unit cell representing the periodic structure of the material. As will be discussed in Chapter 3, this naive representation of the polarization density leads to problems in its calculations in infinite and periodic systems; these problems are resolved in ‘modern theory of polarization’ by utilization of the Berry phase approach.

In a linear dielectric that does not possess any spontaneous polarization \( P(E = 0) \neq 0 \), dielectric polarization has a simple dependence on the applied electric field, as shown in Fig. 2.1(a) for a 1D case:

\[ P = \chi_e E, \]  

(2.2)

where \( \chi_e \) is the electric susceptibility of the material — a tensorial property that is related to polarizability of its constituent structural units.

Another important property of the dielectric material is its permittivity \( \epsilon \) (commonly known as a dielectric constant), which is also a tensorial property that is a measure of material resistance to an applied electric field. The response of dielectric materials to applied electric field also depends on the driving field frequency \( \omega \). I.e., the polarization developed in the material does not change instantaneously in response to the applied electric field. As a result, there is phase difference between the applied and induced fields, which mathematically can be represented by a complex dielectric permittivity, expressed as a function of \( \omega \). The dielectric loss of a material at a given frequency is the ratio of the imaginary part to the real
part of dielectric permittivity. Usually, the best dielectrics have strong polarization and low
dielectric loss.

In Fig. 2.1(c), free energy of the linear dielectric $G$, is plotted as a function of the
induced polarization $P$. It is calculated by integrating over the area under the $P(E)$ curve
in Fig. 2.1(a) and shows a parabolic behavior.

Unlike a simple linear dielectric that is non-polar under no applied electric field, a ferroelectric material can have nonzero polarization at $E = 0$, marked as $P_r$, or remanent polarization in Fig. 2.1(b). As the $E$-field is increased, the value of $P$ saturates, marked by $P_{\text{sat}}$. Another characteristic feature of a ferroelectric material is that the direction of the polarization can be switched by changing the direction of the applied $E$-field. The value of applied E-field at which the direction of $P$ changes is represented by coercive electric field $E_c$. This switching behavior is also illustrated in Fig. 2.1(b). As a result of the nonlinear behavior and multiple equilibrium $P$ states, oriented in different directions, the energy landscape of a ferroelectric material can be complex, possessing multiple local minima. Fig. 2.1(d) shows a representative “double well” energy landscape for a typical ferroelectric in 1D.

### 2.1.1 The influence of crystal symmetry

Understanding the connection between ferroelectric behavior and crystal symmetry is important for establishing the origins and hierarchy of functional material properties related to dielectric polarization. By definition, in order to have a non-zero polarization within a
Figure 2.1: The variation of polarization $P$ with applied electric field $E$ for (a) linear dielectric and (b) ferroelectric materials. Saturated polarization $P_{\text{sat}}$, remanent polarization $P_r$ and coercive electric field $E_c$ are marked for the ferroelectric hysteresis loop. Representative free energy surfaces for (c) linear dielectric and (d) ferroelectric materials.
material, the positive and negative charge centers in its unit cell must be separated by some distance. Therefore, a polar material cannot possess a center of symmetry (also called a center of inversion), i.e., it cannot belong to a centrosymmetric point group.

Fig. 2.2 shows a chart with a classification of different dielectric materials according to their point group symmetry. A general case of a linear dielectric is shown at the top for all of the 32 point groups. 11 of these groups are centrosymmetric, i.e., possess a ‘center
of inversion’ symmetry element that is incompatible with any vectorial material property, such as spontaneous polarization. Therefore, these crystals cannot exhibit any intrinsic polar properties (e.g., piezo- or pyro-electricity) and are called nonpolar.

Out of the materials described by the remaining 21 non-centrosymmetric point groups, those belonging to 20 groups can display piezoelectricity. The excluded group is 432, where the piezoelectric charges developed along the [111] crystallographic direction cancel each other out [103]. For some of the 20 piezoelectric point groups, negative and positive charge centers in the unit cell can still coincide in location, producing no spontaneous polarization. But due to the lack of an inversion center, these charge centers respond differently to applied distortions, such as mechanical stress and electric fields, which results in the emergence of piezoelectric effects. On the other hand, in crystals described by 10 pyroelectric point groups, negative and positive charge centers no longer coincide, and therefore such materials exhibit spontaneous polarization. Furthermore, all pyroelectric crystals also display piezoelectric effects. Finally, ferroelectric crystals are defined as such pyroelectric crystals whose spontaneous polarization can be oriented along multiple, symmetrically equivalent directions within the unit cell (which is usually done with applied electric field). All ferroelectric crystals exhibit both pyroelectric and piezoelectric effects.

Formation of polar domains within a ferroelectric crystal is another major characteristic feature of such materials. I.e., due to the existence of multiple possible directions in the material unit cell along which the polarization can point, orientationally distinct ‘polar variants’ may develop in different regions of the crystal, e.g., as it is being cooled down below
the polar phase transition temperature. As these polar regions grow and meet, a network of polar-domain walls is established, which, depending on the crystal properties and geometry, can be quite complex [104]. Furthermore, the strongly non-linear hysteretic behavior of ferroelectric materials, shown in Fig. 2.1(b), is intimately connected to the presence of polar domains. For example, at the coercive point $E = E_c$, the ferroelectric crystal would typically still have multiple polar domains (rather than becoming paraelectric), but due to equal volume fractions of the oppositely oriented domains — as schematically represented by red up and black down arrows in Fig. 2.1(b) — its macroscopic polarization would be zero. At $E > E_c$, the volume fraction of the domains oriented parallel to the applied $E$-field increases at the expense of mis-oriented domains, which leads to non-zero macroscopic polarization.

In closing of this section, it is worthwhile to note that about 30% of all materials (out of about several millions known today) are non-centrosymmetric. However, piezoelectric properties persist in only a few thousands of them, with about several hundred displaying piezoelectric response strong enough for technological applications [103]. I.e., the absence of a center of inversion is a necessary, but not sufficient condition for a material to have useful piezoelectric properties. Thus, symmetry considerations may serve as a convenient guide for the determination of what type of dielectric behavior is possible for a particular material. However, they cannot guarantee that these symmetrically allowed responses will be strong and therefore this kind of information must be obtained by other means.
2.2 History of the phenomenon

Rochelle salt, NaKC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}·4H\textsubscript{2}O, is the first well-known material that exhibits piezoelectric and pyroelectric properties, which was demonstrated in the early 19\textsuperscript{th} century. It was synthesized around 1675 for medicinal purposes, i.e., more than a century before the discovery of its piezoelectric and pyroelectric behavior (circa 1820s) [105]. Numerical characterization of the piezoelectric and pyroelectric properties of rochelle salt was reported nearly a century later — in 1922 by Valasek [106], who also described its ferroelectric behavior.

Rochelle salt became the only known ferroelectric material for approximately a decade, during which ferroelectricity was believed to be one of nature’s serendipities. Complex structure of the rochelle salt posed a significant challenge for its reliable experimental determination. It was not until 1936, when a structurally more simple material, perovskite BaTiO\textsubscript{3}, was discovered to also display ferroelectric behavior. Due to the simplicity of the aristotype ABO\textsubscript{3} perovskite crystal structure [107], perovskites in general and BaTiO\textsubscript{3} in particular have become prototypical template models of functional dielectrics: both for theoretical studies and technological applications [1]. The very first phenomenological descriptions for the ferroelectric behavior in BaTiO\textsubscript{3}, based on the Landau theory of phase transitions [84], were introduced by Devonshire in 1950s [108, 109]. More elaborate discussion of the historical development of the field of ferroelectric materials and phenomena is given in Refs. [110–112].
2.3 Perovskite ferroelectrics

Since WWII, ferroelectric oxides, and specifically ABO$_3$ type perovskite oxides, have played an important role in applied solid state physics. These materials had been extensively investigated for their rich functional behavior, as well as exploited in wide range of technological applications. In addition to ferroelectricity, these materials exhibit piezoelectric, pyroelectric and non-linear optical responses, as well as ionic conductivity. Furthermore, structures including magnetic ions display interesting behavior involving magnetism, such as superconductivity, giant magneto-resistance and magnetoelectric multiferroic response. Further information about these materials can be found in a number of dedicated monographs [1, 75, 86, 113–115].

Examples of typical niche applications of perovskite ferroelectric materials include:

1. Energy storage — BaTiO$_3$ compounds exhibit large dielectric response at the transition temperature. However, a transition temperature close to RT and a broad peak in the dielectric permittivity thermal dependence are desired for strong dielectric response throughout a wide range of operational temperatures. This is usually achieved by adding small quantities (1–8 wt%) of other materials, such as SrTiO$_3$, CaZrO$_3$, MgZrO$_3$, CaTiO$_3$ and etc. to BaTiO$_3$ [110].

2. Energy conversion — since ferroelectric materials exhibit pyroelectricity and piezoelectricity, they find applications in transducers, i.e., devices that convert one type of energy into another. Specifically, PbTiO$_3$ based oxides, such as PZT, are widely used
in pyroelectric detectors, thermal imaging, sonar, atomic force microscopy (AFM), acoustic sensors, etc. [3, 110, 116–119]

3. Electronic data storage — multistability and switchability of the ferroelectric polarization orientation can be exploited for electronic memory technologies, specifically in non-volatile memory devices. Besides PZT and its derivatives, a layered perovskite SrBi$_2$Ta$_2$O$_7$ is the current material of choice, especially when considering its favorable switching fatigue performance [110, 120].

### 2.3.1 Crystallographic structure and phase transformations

A variety of different polar distortions could be realized in perovskite ferroelectrics, with exact nature and symmetry of the resulting phases dictated by quantum mechanical interactions among the constituent ions. However, all of such phases can be considered as inversion-symmetry breaking distortions of a parent centrosymmetric-cubic aristotype phase and therefore must be in a group-subgroup relationship with that parent phase. The cubic aristotype phase of perovskite ABO$_3$ is shown in Fig. 2.3 together with some of the typical distorted polar phases descended from it that have different directions of spontaneous polarization within the unit cell. In the case of PbTiO$_3$, only one distortion variant — cubic into $P4mm$ tetragonal — is realized during the paraelectric to ferroelectric phase transformation. On the other hand, BaTiO$_3$ experiences a succession of transformations from cubic to tetragonal, to orthorhombic, to rhombohedral, as its temperature is decreased [1].
Figure 2.3: Crystal structure of (a) cubic perovskite $\text{ATiO}_3$ aristotype, space group $Pm\overline{3}m$, and its polar distortions leading to non-centrosymmetric structures with the following symmetries: (b) $P4\text{mm}$, $P \sim (00c)$, (c) $Amm2$, $P \sim (aa0)$, and (d) $Cm$, $P \sim (aac)$. TiO$_6$ coordination cages are represented by semi- ($Pm\overline{3}m$) and completely (all other phases) translucent polyhedra while Sn atoms are shown in pink (dark gray). Arrows attached to the Ti ion indicate the direction of polarization in the non-centrosymmetric structures (b–d).

The structure of the high-temperature centrosymmetric phase of perovskite $\text{ABO}_3$ is shown in Fig. 2.3(a), where A, B and O species occupy the corner (0,0,0), body-centered ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and face-centered ($\frac{1}{2},\frac{1}{2},0$) positions, respectively. PbTiO$_3$ undergoes a spontaneous phase transition into the tetragonal $P4\text{mm}$ phase by off-centering the cations in the (00c) direction, as shown for the B-site ion in Fig. 2.3(b). When subjected to applied stress or strain, PbTiO$_3$ can also exist in other phases, such as orthorhombic $Amm2$ and monoclinic $Cm$ [121], that are depicted in Fig. 2.3(c-d). The arrow attached to the B-site ion shows the direction of the developed spontaneous polarization in each phase. Furthermore, due to the electrostrictive coupling [1] between polarization and strain, the unit cell typically elongates in the direction of the polarization and contracts in the perpendicular direction.

We should also point out that polar ionic distortions, i.e., the ones collected in Fig. 2.3 and Table 2.1, are not the only system of distortions that the perovskite structure can
Table 2.1: Connection between the direction of the order parameter $\mathbf{P} = (P_1, P_2, P_3)$ and the symmetry of the perovskite structure.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Lattice System</th>
<th>$\mathbf{P} = (P_1, P_2, P_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm3m</td>
<td>Cubic (000)</td>
<td>$P_1 = P_2 = P_3 = 0$</td>
</tr>
<tr>
<td>R3m</td>
<td>Trigonal (aaa)</td>
<td>$P_1 = P_2 = P_3 \neq 0$</td>
</tr>
<tr>
<td>P4mm</td>
<td>Tetragonal (00c)</td>
<td>$P_1 = P_2 = 0, P_3 \neq 0$</td>
</tr>
<tr>
<td>Amm2</td>
<td>Orthorhombic (aa0)</td>
<td>$P_1 = P_2 \neq 0, P_3 = 0$</td>
</tr>
<tr>
<td>Cm</td>
<td>Monoclinic (aac)</td>
<td>$P_1 = P_2 \neq 0, P_3 \neq 0$</td>
</tr>
<tr>
<td>P1</td>
<td>Arbitrary (abc)</td>
<td>$P_1 \neq P_2 \neq P_3 \neq 0$</td>
</tr>
</tbody>
</table>

Figure 2.4: An example of an octahedral tilt distortion in a perovskite structure.
support. Another such system that is quite prevalent in perovskite hettotypes [107] consists of the so-called antiferrodistortive (AFD) distortions that are represented by various kinds of rotations and tilts within the network of the corner sharing octahedral oxygen cages, as shown in an example in Fig. 2.4. Tilted octahedral arrangements are found in a number of well-known perovskite oxides, including CaTiO$_3$, NaNbO$_3$ and BiFeO$_3$. Remarkably, in the case of NaNbO$_3$ and BiFeO$_3$, octahedral rotations are present alongside the polar distortions. In general, octahedral tilts have a considerable effect on the lattice parameters, unit cell volume and observed symmetry of perovskite crystals, with 23 archetypical tilt systems classified by Glazer in 1970s [122]. While vibrational modes associated with polar distortions are typically present at the Brillouin Zone (BZ) center of the cubic aristotype unit cell, modes representing octahedral rotations appear at the BZ edges (more information on BZs and phonon modes can be found in Ref. [123]). In this dissertation, most of the ferroelectric crystal structures under consideration (with the exception of BiFeO$_3$) do not possess stable octahedral tilt distortions and therefore these will not be extensively discussed further.

Finally, as already hinted above, transitional behavior of ferroelectric crystals under changing temperature is characterized by the presence of a ferroelectric to paraelectric phase transformation. I.e., as the temperature is decreased, the high-$T$ nonpolar centrosymmetric cubic phase transforms into a polar non-centrosymmetric phase at the transition temperature $T_t$ that is specific for the particular material. Fig. 2.5 shows an example of such a transition between the $Pmar{3}m$ and $P4mm$ phases in PbTiO$_3$. Furthermore, multiple ferroelectric to
ferroelectric phase transitions are also possible in perovskites at $T < T_t$, with the system polarization spontaneously changing direction within the unit cell, as exemplified by the case of BaTiO$_3$. More information about the specifics of these phase transformations is presented in the following chapters.

### 2.4 The role of theory and modeling

Since the discovery of ferroelectricity in Rochelle salt [106], a number of scientists have endeavored to understand both microscopic origins and macroscopic manifestations of ferro-
electric behavior. Phenomenological theories developed by Ginzburg [124] and Devonshire [108, 109] employed models that did not assume any microscopic mechanisms, instead describing ferroelectric properties and the associated phase transformations on the empirical level. On the other hand, first principles based methods provided insights into underlying electronic interactions and mechanisms responsible for the polar phase stability. In this section we briefly introduce the hierarchy of theoretical methods that are currently being used to study ferroelectric materials and phenomena. Detailed descriptions of specific theoretical methods and computational approaches utilized in this dissertation are provided in Chapter 3.

First principles based methods rely on the quantum mechanical Schrödinger equation to describe the behavior of materials. Though this equation in its original form cannot be solved directly for realistic material systems, it can be made tractable by adopting a number of different approximations, as demonstrated by the Density Functional Theory (DFT) formulation [125, 126]. By virtue of the ‘first principles’ nature of DFT, practical calculations of materials properties require no empirical input; the only things that need to be known are (i) what kind of atomic species comprise the system and (ii) where all the atoms are located. This constitutes a significant advantage over any other methods that may have to depend on empirical data, as such ‘predictive capabilities’ of DFT allow it to characterize even virtual or fictitious, i.e., not yet synthesized, material systems.

Unsurprisingly, DFT has been the technique of choice for computational studies of ferroelectric materials at the atomic scale. Their bulk properties, including structural (lattice
constants), electronic (band structure and polarization) and vibrational, have been successfully evaluated with DFT at the crystallographic unit cell level under periodic boundary conditions. For example, soon after the discovery of ferroelectricity in BaTiO$_3$, Slater [127] expressed a hope that, owing to its simple structure, this material could be “fairly completely understood.” This goal remained elusive until DFT calculations were used in early 1990s to understand the electronic origins of the ferroelectricity in BaTiO$_3$. The polar instability in BaTiO$_3$ was identified, with its origin attributed to the electronic hybridization between Ti(3$d$) and O(2$p$) states [128]. Later, the differences in the ferroelectric behavior of BaTiO$_3$ and PbTiO$_3$ were studied by similar techniques [129] revealing that in addition to the Ti(3$d$)–O(2$p$) hybridization, in PbTiO$_3$ hybridization between Pb(6$s$) and O(2$P$) states is mostly responsible for its large polarization [130]. Over a period of time between 1990 and 2000, DFT-based electronic-structure calculations had provided a fundamental theoretical understanding of the nature of bonding in ferroelectric perovskites with ABO$_3$ stoichiometry [89, 128, 129, 131]. Furthermore, the energy landscapes were also mapped out as a function of the polar instability amplitude, demonstrating that at low temperatures the cubic phase becomes dynamically unstable with respect to polar lattice distortions, thus confirming the ‘displacive’ picture of the ferroelectric to paraelectric transition in perovskites.

Unfortunately, despite all of their benefits, the DFT calculations are also subject to a number of limitations: they can operate mostly only at absolute zero temperature and, due to very high computational costs, they can process only relatively small unit cells (i.e., no disordered structures) and small number of atoms (typically no more than a few hundred).
Due to these constraints, DFT calculations are severely limited in investigating any long length and time scale phenomena, e.g., those involving movement of ferroelectric domain walls, as well as finite temperature behavior. Instead, some of these ‘longer range’ investigations were attempted using atomic-scale simulation methods employing classical empirical potentials with either a shell model [132–135] or a bond-valence model [136, 137] to represent the effects of polarization. Being much less computationally costly, such classical potentials are usually used in molecular dynamics (MD) and Monte Carlo (MC) simulations that may include thousands (sometimes millions) of atoms and can operate at finite temperatures by rescaling of the atomic kinetic energy terms. For example, in the bond-valence model, the bond strength between ions in ABO$_3$ unit cell, is a function of the interatomic distance and the bond-valence energy is expressed in terms of the same bond length [137]. Insights into nucleation and evolution of 180° domain walls in PbTiO$_3$ were obtained using bond valence model [138], revealing a small square critical nuclei with a diffuse interface. Compositional phase diagram of PZT [139] and coherent control of ionic positions through shaped terahertz fields was also predicted in PbTiO$_3$ by using the bond-valence models in MD simulations [140]. On the other hand, classical atomistic models no longer have the ‘predictive power’ of the DFT-based methods and usually they cannot handle any drastic coordination changes within the studied system, such as, e.g., melting transitions.

Further coarse graining is achieved by replacing atoms and their distortions in the unit cell by polar displacement vectors, as demonstrated in the effective Hamiltonian theory [87–89]. In this theory, the free energy of the system is expressed as a function of discrete dipole
moments $\mathbf{d}_n$, similar to those employed in Eq. (2.1), that are associated with the polarization of each unit cell. Effective Hamiltonian theory can be used in combination with MC and MD simulations, to study large systems of up to a few 10s of nm in size.

Nonetheless, a typical ferroelectric nanostructures or device components could have sizes ranging from 100s of nm to 10s of $\mu$m (this size interval is called *mesoscale* in what follows), also typically operating at near RT. Computational analysis of systems at such large length scale is currently not practical with any of the aforementioned methods. In particular, when attempting to elucidate the influence of size, shape, and morphology on ferroelectric behavior, any descriptions tied to the perovskite unit cell length scale tend to become prohibitive in their computational costs. Instead, coarse-grained continuum-based approaches, such as phase-field methods [141], have been successfully used for exploring the behavior of ferroelectric materials and heterostructures at mesoscale. Thermodynamic energy descriptions of the ferroelectric systems compatible with the phase-field approaches are usually provided by Landau-Ginzburg-Devonshire (LGD) theory [108, 109], which will be discussed in detail in Sec. 3.2. The LGD free energy of the system is expressed as a symmetry-adapted polynomial function of continuous variables (also called ‘order parameters’ and/or ‘fields’) that include polarization and its spacial gradient, as well as (inhomogeneous) stresses and strains. Specific material parameters describing the energy of the system in the LGD theory are typically obtained from relevant experimental observations [85, 142].

The hierarchy of all the discussed theoretical and computational methods in the order of increasing coarse graining is presented in Fig. 2.6.
Figure 2.6: (a) Atomic scale structural model along with its electronic charge density represented by translucent yellow surfaces. This example includes a single perovskite unit cell that would usually be used in DFT calculations. (b) Structural model of a large supercell used in classical MD simulations. Here, computationally expensive electronic interactions are replaced by empirical interatomic potentials. (c) In the effective Hamiltonian based methods, atoms and bonds in each perovskite unit cell are replaced with polar displacement vectors (shown in blue arrows), whose magnitudes are proportional to the value of local polarization. Due to replacing the atoms by a single dipole moment, computational cost is further reduced, allowing for larger length scale simulations. (d) LGD theory treats polarization as a continuous variable, with the free energy of the system expressed as a function of polarization and its gradient. Local values of the polarization field are shown in color on the surface of the ferroelectric particle, while arrows indicate the polarization direction. Large length scale simulations subject to complex elastic and electrical boundary conditions can be processes within this framework at relatively low computational cost.
Chapter 3

Modeling Perovskite Ferroelectrics

This chapter provides detailed descriptions of all computational methods used in this dissertation to study perovskite ferroelectrics. A general framework and important equations with necessary references are presented for each method.

3.1 First-Principles Methods

All first-principles methods are based on a fundamental equation, known as Schrödinger equation [143]. The solution of this fundamental equation provides the most complete description that can be given of a quantum mechanical system. The electronic properties of a material at quantum mechanical level are obtained by solving the Schrödinger equation for the interacting electrons. Time-independent, nonrelativistic Schrödinger equation is of the
where $\Psi(R_I, r_i)$ is a many-electron wave function with $R_I$ and $r_i$ representing positions of all nuclei and all electrons, respectively. By operating on the $\Psi(R_I, r_i)$ with the Hamiltonian operator $\mathcal{H}$, the total energy of the system $E$ can be obtained.

The Hamiltonian operator describing the interacting electrons and nuclei is expressed as sum of kinetic and Coulomb energy operators:

$$\mathcal{H}(R_I, r_i) = T_e(r_i) + T_N(R_I) + V_{ee}(r_i, r_j) + V_{eN}(r_i, R_I) + V_{NN}(R_I, R_J),$$

where $T_e$ and $T_N$ are the kinetic energy operators for the electrons and nuclei, respectively, and $V_{ee}, V_{eN}$ and $V_{NN}$ are the electrostatic energy operators for the electron-electron, electron-nuclear and nuclear-nuclear interactions. Each operator is described below:

$$T_e = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2,$$

$$T_N = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2,$$

$$V_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|},$$

$$V_{eN} = -\sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|},$$

$$V_{NN} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|}.$$

Here, $Z_I$ and $M_I$ are the charge and mass of the nucleus $I$, and $m_e$ and $e$ are the mass and charge of an electron. Due to much larger mass of the nuclei (3 to 5 orders of magnitude
larger than $m_e$), it is reasonable to assume that electrons can adjust almost instantaneously to the change in positions of the nuclei. As a result, the kinetic energy term $T_N$ in Eq. (3.2) can be decoupled from the rest of the energy term in the same equation. The process of decoupling of the nuclei and electron degrees of freedom into separate mathematical problems is called the *Born-Oppenheimer* or *adiabatic* approximation. The lowest energy configuration or *ground state* of the electron system (with static nuclei) is then obtained by solving the Hamiltonian $\mathcal{H}_e$:

$$\mathcal{H}_e(R_I, r_i) = T_e(r_i) + V_{ee}(r_i, r_j) + V_{eN}(r_i, R_I) + V_{NN}(R_I, R_J)$$  \hspace{1cm} (3.8)

Unfortunately, even the adiabatic approximation $\mathcal{H}_e$ as described by Eq. (3.8) is still too complicated to be useful for treating practical material systems [144]. This difficulty was resolved by Hohenberg, Kohn and Sham [125, 126], as discussed in the following section.

### 3.1.1 Density Functional Theory

DFT was developed to avoid the use of overly complicated many-particle wave function formulations, instead expressing the necessary observables as functions of the electron charge density only. This philosophy is shown in Fig. 3.1. DFT formulation is based on two theorems proved by Hohenberg, Kohn and Sham in 1962 [125, 126].

1. *The ground-state solution of the Schrödinger equation is a unique function of the electron density.* In other words, there exists a one-to-one mapping between the ground-
Figure 3.1: The schematic representation of (a) Many electron system, where electron-electron interactions are treated explicitly. $\mathcal{H}$ and $\Psi$ are the many electron Hamiltonian and wave function. (b) DFT formalism, where explicit electron-electron interactions are collapsed into an effective electron potential, represented by the shaded background. Single-electron wave function of the $i^{th}$ electron, $\psi_i$ is determined in order to obtain the ground state Kohn-Sham energy $e_i$.

state wave function and electron charge density $\rho(r)$. Furthermore, the ground-state energy $E$ can be expressed as $E[\rho(r)]$.

An important consequence of this theorem is that the knowledge of $n(r)$ uniquely determines all of the system ground state properties, including the energy and wave function. This result is extremely important because, now the the Schrödinger equation can be solved by finding a function of three spatial variables, i.e., the electron charge density, instead of the many electron wave function, which is a function of many variables. For example, the problem of finding the ground state of a nanoparticle consisting of
100 Pd atoms is reduced from more than 23,000 dimensions to a problem with only 3 dimensions [144]. Nevertheless, the functional form of the $E[n(r)]$ dependence is still unknown, but some of its properties are described by the second theorem.

2. The electron charge density that minimizes the energy of the overall functional is the true electron charge density corresponding to the full solution of the Schrödinger equation. Therefore, if the functional form of $E[\rho(r)]$ is known, the ground state of the system can be obtained by minimizing this functional.

---

1. Initial guess
   - Initial value for charge density $\rho(r)$
2. Calculate $V_{eff}$
3. Solve Kohn-Sham equations
   - Approximate $E_{XC}$ using LDA, GGA, etc.
4. Re-evaluate $\rho(r)$ and calculate $E_{tot}$
   - Check for force tolerance
   - Check for stress tolerance
   - Check for energy convergence
5. Converged $\Rightarrow$ stop
6. Output total energy $E_{tot}$

---

**Figure 3.2:** A flowchart for solving the Kohn-Sham equations self-consistently.
The DFT approach replaces the more elaborate picture of a many-electron interacting system by a picture where a ‘mean field’ system with independent electrons is considered that nonetheless faithfully reproduces the effects of many-electron interactions. The Schrödinger equation is effectively replaced by the set of Kohn-Sham equations formulated for the single-electron wave functions $\psi_i(\mathbf{r})$:

$$E[\psi_i] = E_{\text{known}}[\psi_i] + E_{\text{XC}}[\psi_i],$$

$$E_{\text{known}}[\psi_i] = -\frac{\hbar^2}{2m_e} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(\mathbf{r})\rho(\mathbf{r})d^3r + E_{\text{ion}}$$

The “known” energy terms are (in order) electron kinetic energies, electron-nuclei Coulomb interactions, electron-electron Coulomb interactions and nucleus-nucleus Coulomb interactions. However, the remaining term in the total energy description, $E_{\text{XC}}[\psi_i]$, or the exchange–correlation energy term, includes all the other quantum mechanical effects in the system that are not precisely known. This last term has to be approximated in some way to allow the Kohn-Sham equations

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eN}(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = e_i \psi_i(\mathbf{r})$$

(3.11)

to be solved, e.g., iteratively as shown in Fig. 3.2.

3.1.1.1 Approximations

The derivations presented in the previous section are exact, meaning that no specific approximations have been introduced yet. However, in order to solve the Kohn-Sham equa-
tions for practical systems, several computational approximations including those specifying the form of the exchange-correlation potential are necessary to make numerical calculations tractable.

**Exchange-correlation energy:** DFT formulation allows us to obtain the ground-state energy of the Schrödinger equation, by minimizing the energy of an electron charge density functional. This can be achieved by finding a self-consistent solution to a set of single-electron wave function equations. In order for the DFT calculations to be useful for practical purposes, the form of the exchange-correlation potential should be approximated.

For example, one of the first approximations is the so-called *Local Density Approximation* (LDA) [145]. In fact, LDA is the exact exchange-correlation potential for the homogeneous electron gas — i.e., a system whose electron charge density is constant throughout the space, $\rho(r) = \text{constant}$ [144]. In general, the LDA functional is one of the most popular and widely used ones [146] for the DFT calculations. In this dissertation, most calculations (except those involving BiFeO$_3$ systems that require more elaborate treatment) are done using LDA. Within LDA, the exchange-correlation energy of the system is assumed to operate locally as would the uniform electron gas at same electron density, i.e.,

$$V_{\text{XC}}^{\text{LDA}} = V_{\text{XC}}^{\text{LDA}}[\rho(r)] \quad (3.12)$$

In real systems, the electron charge density is not homogeneous, and therefore the LDA exchange-correlation potential is considered to be a rather simple approximation (but a very useful one nonetheless). Besides LDA, there are several other standard and well known
exchange-correlation potentials. For example, \textit{generalized gradient approximation} (GGA) is expressed as a function of both electron density and its gradient [147–151].

\[ V_{\text{XC}}^{\text{GGA}} = V_{\text{XC}}^{\text{GGA}}[\rho(r), |\nabla \rho(r)|] \tag{3.13} \]

As of now, there are over 200 exchange-correlation functionals and a curious reader can consult articles such as Ref. [152] for a comprehensive review.

**System periodicity:** Applying DFT formalism to bulk systems involves yet another complication due to the explosion of the number of nuclei and electrons in the system. Crystallographic periodicity is exploited for the bulk materials, as they are typically modeled by atoms occupying equilibrium positions in a unit cell representative of the crystal symmetry that is repeated throughout space by periodic translations. Therefore, all the potential energy terms present in the Kohn-Sham equations must have the same periodicity as that of the crystal in question, i.e.,

\[ V(r + R) = V(r). \tag{3.14} \]

Here \( R \) is the real space lattice translation vector that in 3D can be represented as a linear combination of three lattice vectors, \( a, b \) and \( c \):

\[ R = n_1 a + n_2 b + n_3 c. \tag{3.15} \]

The solutions of the Schrödinger equation for such periodic systems should also satisfy the periodic boundary conditions and, according to Bloch’s theorem [123], the the appropriate
electronic wave functions can be expressed as

$$\psi_k(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(r), \quad (3.16)$$

where $u_k(r)$ is lattice periodic. The Schrödinger equation can then be solved independently at each value of $\mathbf{k}$, which is a vector of the reciprocal space of the system represented by its Brillouin Zone (BZ) [123].

**K-point sampling**: In practical DFT calculations, observable system properties are usually averaged over the BZ by evaluating the following integral:

$$\langle g \rangle = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d\mathbf{k} g(\mathbf{k}) \quad (3.17)$$

Numerically, the integration over the reciprocal space has to be discretized as a summation over the grid of $k$-points. Several standard approaches to sample $k$-points in the reciprocal space are available. For example, Monkhorst-Pack (MP) sampling [153] is a careful selection of $k$-points on a 3D grid to ensure the accuracy and efficiency of the calculations. Usually, the $k$-point grid density has to be carefully optimized for specific systems to provide the most accurate results in reasonable time, as tested by the convergence of total energy with respect to the grid density.

**Pseudopotentials**: Until now, in order to solve Kohn-Sham equations, as shown in Eq. (3.11), the electronic wave functions were assumed to be expressed in terms of, e.g., plane wave basis functions, and the solutions were obtained in reciprocal space. Since valence electrons dominate the chemical bonding and interatomic interactions in materials, it
is possible to avoid treating all the core electrons explicitly by using pseudopotentials [144]. Typically, pseudopotentials have to be developed separately for each atomic type. They also have to be thoroughly tested for transferability, i.e., their accuracy in different chemical environments, e.g., such as a drastic change of coordination.

3.1.1.2 Berry phases

The modern theory of polarization [154–156] was developed in early 1990s, addressing the problems experienced by the classical approach of computing polarization density $P$ in infinite periodic systems. The issue with the classical approach is its failure to produce a unique value for the polarization, as the unit cell dipole moment depends on the shape and position of the cell within the crystal, both of which can be changed arbitrarily. Instead, the modern theory considers the changes in polarization $\Delta P$ arising from the developing structural distortions away from the ‘naturally nonpolar’ system state.

In the modern theory of polarization, the macroscopic polarization is an intrinsically multivalued quantity defined as a *Berry phase* (which is, naturally, an angle belonging to the $[0, 2\pi]$ interval) of the electronic Bloch wave function. The total polarization of a material is divided into electronic and ionic parts,

$$P = P_{\text{ion}} + P_e, \quad (3.18)$$

$$P_{\text{ion}} = \frac{|e|}{V_{\text{cell}}} \sum_i Z_{i}^{\text{ion}} R_i, \quad (3.19)$$

$$P_e = -\frac{|e|}{(2\pi)^3} \sum_n \int \langle u_{nk}|\nabla_k|u_{nk}\rangle dk \quad (3.20)$$
The ionic contribution is calculated using a simple summation over point charges that represent ionic cores. $Z_{i}^{\text{ion}}$ and $\mathbf{R}_i$ are the charge and position vector of ion $i$, and $V_{\text{cell}}$ is the unit cell volume. On the other hand, the electronic contribution is more complicated and involves the summation over the Berry phase contributions $\langle u_{nk}|\nabla_{\mathbf{k}}|u_{nk}\rangle$ of all the occupied electronic states $n$. The inner integral is over $\mathbf{k}$-vectors parallel to the direction of $\mathbf{P}$ and the states $|u_{nk}\rangle$ are the cell-periodic parts of the Bloch functions, $\psi_{kn}(\mathbf{r}) = u_{nk}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$. Currently, Berry-phase approach based routines for computing polarization are implemented in most popular DFT codes.

### 3.1.2 Density Functional Perturbation Theory

Up to this point, we have discussed mathematical formulation of DFT, its general approximations and various approaches used to obtain material properties with reasonable accuracy. E.g., adiabatic approximation is one of the important ingredients, where the atomic motion is decoupled from the evolution of electronic wave functions. However, a wide range of physical properties, such as, specific heat, thermal expansion, heat conduction and etc. depend on the lattice vibrations of the solid [157].

Early attempts of describing the lattice dynamics have treated solids as linear elastic materials. Even without considering the electronic interactions, these treatments were fairly successful in computing vibrational frequencies and periodic patterns of atomic displacements, or phonons, in simple materials. Obviously, interatomic forces and hence the vibra-
Figure 3.3: Phonon band dispersion for perovskite PbTiO$_3$ in (a) non-polar cubic and (b) polar tetragonal phases, computed using DFPT.

Vibrational properties strongly depend on the electronic interactions between the atoms, especially in more complex materials, such as perovskites and other oxides. Rapid advances in DFT computational methods have also paved a way for developing techniques for evaluation of vibrational properties of complex materials from first principles. One such popular formulation is the *Density Functional Perturbation Theory* (DFPT) [158, 159]. This theory can be used to compute phonon band dispersions throughout the BZ, i.e., it can be applied at any \( k \)-point within the BZ and it can correctly account for the non-analytic behavior of the phonon bands near the \( \Gamma \) point in ionic (polarizable) materials.

Fig. 3.3 shows phonon band dispersions computed for the stress-free PbTiO$_3$ crystal in the (a) non-polar cubic and (b) polar tetragonal phases. The non-polar cubic phase shows
imaginary phonon frequencies (plotted as negative values), suggesting that its structure is dynamically unstable and some of the lattice distortions possible in this system have no restoring force. Lattice vibrations associated with such imaginary frequencies are usually called *unstable* or *soft* modes. On the other hand, in the polar tetragonal phase, there are no imaginary phonon frequencies, which proves that this phase is dynamically stable and every possible distortion in it has a non-zero restoring force.

### 3.1.3 Computational details

#### 3.1.3.1 SnTiO₃, PbTiO₃ and Sn-doped SrTiO₃

All DFT calculations presented in this study were performed using the Vienna Ab Initio Simulation Package (VASP) [160, 161] and QUANTUM ESPRESSO (QE) [162] within the local density approximation (LDA), parameterized by Perdew and Zunger [145]. Projector-augmented plane-wave (PAW) method [163, 164] with 900 eV energy cutoff was utilized in VASP, with the following electronic configurations for the involved elements: Pb (5d¹⁰6s²6p²), Sn (4d¹⁰5s²5p²), Ti (2p⁶3d²4s²) Sr (4s²4p⁶5s²) and O (1s²2s²2p⁴). In calculations done with QE, Vanderbilt ultrasoft [165] pseudopotentials were used, with electronic wave functions (density) expanded up to 30 Ry (300 Ry) kinetic energy cutoff. Zone-edge-shifted 8 × 8 × 8 Monkhorst-Pack (MP) [153] k-point meshes were employed for the BZ integration with both simulation packages. In all calculations, including lattice parameter and internal ionic position optimization, ionic forces were relaxed to less than 0.2×10⁻⁵ Ry bohr⁻¹ (∼0.5×10⁻⁴ eV
Å\(^{-1}\)) and the appropriate stress tensor components \(\sigma_{ij}\) (with indices \(i\) and \(j\) corresponding to \(x, y, z\)), including shear stresses for monoclinic and triclinic phases, were converged to values below 0.1 kbar.

The components of the ionic Born effective-charge (BEC) tensors \(Z^*_{\xi,ij}\), where \(\xi\) is the ion number, and high-frequency dielectric permittivity tensor \(\epsilon_{ij}^\infty\), as well as the system phonon bands, eigenvectors and eigenvalues across the BZ were calculated with the help of the DFPT approach implemented in QE [159], utilizing the 6\(\times\)6\(\times\)6 (unshifted) MP mesh. The same BEC tensor components were also computed in VASP within the PAW framework [158, 166], producing good agreement with the results obtained with QE. The values of \(P_i\) were evaluated by a linearized approximation [167] involving products of \(Z^*_{\xi,ij}\) and ionic displacements away from their centrosymmetric positions. For some of the high-symmetry system configurations (e.g., stable tetragonal and orthorhombic phases), spontaneous polarization was also calculated using the Berry phase approach [154, 156]. Good agreement (within 2%) was obtained between the values produced by both methods. Elastic boundary conditions representing biaxial strain from epitaxial clamping of thin films to the substrate were simulated by fixing the value of in-plane lattice constant \(a\) and relaxing the out-of-plane lattice constant \(c\) to a small value of the stress-tensor component \(\sigma_{zz}\).

### 3.1.3.2 BiFeO\(_3\)

For BiFeO\(_3\), the DFT calculations were performed with the Perdew-Burke-Ernzerhof (PBE) spin density approximation [151, 168] in the generalized gradient (\(\sigma\)GGA) scheme.
An on-site Coulomb parameter $U = 8$ eV was applied to account for the increased Coulomb repulsion between the Fe 3$d$ states [169]. The value of the $U$ parameter was chosen using a procedure described in detail below in order to match results of the GGA+$U$ approximation with a more computationally expensive Heyd-Scuseria-Ernzerhof (HSE) functional [170, 171].

Magnetic moments on Fe atoms in all calculations were arranged in a G-type antiferromagnetic configuration. The projector-augmented plane-wave method [163, 164], using GGA-PBE energies modeled the core-valence electron interactions with pseudovalences of $6s^25d^10p^3$ for Bi, $3p^64s^13d^7$ for Fe, and $2s^22p^4$ for O. A basis set wave-function cutoff of 1000 eV was used to converge the calculated energies of rhombohedral $R$, tetragonal $T$, $R$-like, and $T$-like and cubic perovskite $Pm\bar{3}m$ BiFeO$_3$ polymorphs to within 1 meV per formula unit. Γ-point centered $7\times7\times4$ Monkhorst-Pack (MP) $k$-point meshes for the $T$, $T$-like and $R$-like phases (a $7\times7\times3$ mesh for the $R$ phase) sampled the BZ, converging the energies within 10 meV per formula unit. Forces on individual ions were relaxed to less than 1 meVÅ$^{-1}$ and the stress tensor components $\sigma_{ij}$ on the simulation cell were relaxed to less than 0.1 kbar. The $R$ phase was simulated using a primitive cell containing 30 atoms (six formula units) while the $T$, $T$-like, and $R$-like phases were simulated using $\sqrt{2} \times \sqrt{2} \times \sqrt{2}$ supercells of the pseudocubic unit cell containing 20 atoms (four formula units). This large supercell containing four formula units of BiFeO$_3$ for the $T$, $T$-like, and $R$-like phases was required to accommodate the G-type antiferromagnetic configuration. Elastic boundary conditions arising from epitaxy were simulated by fixing the value of in-plane pseudo-cubic lattice constant $a$ and relaxing the out-of-plane lattice constant $c$. For the monoclinic phases, the values of
c and the monoclinic angle $\beta$ were relaxed simultaneously.

3.2 Phenomenological Models

This section provides a basic introduction to the Landau-Devonshire (LD) theory, which is a widely used phenomenological model for describing the thermodynamical behavior of ferroelectrics. Landau theory (not to be confused with LD theory) is a general mathematical formulation based group theoretical considerations involving system symmetry changes near the phase transition point [86]. In addition to ferroelectrics, it has been proven useful in studying phase transitions in magnetic materials [115]. Landau theory was first applied to a ferroelectric system by Devonshire [85, 108, 109] (hence the name, Landau-Devonshire theory) who described the ferroelectric phase transition by utilizing polarization as its primary order parameter.

3.2.1 Landau-Devonshire theory

3.2.1.1 Notation

In this section, as well as in Chapters 5 and 6, we utilize the notation following that of Ref. [121] for the first-, second-, third- and fourth-rank tensorial properties. The components of vectorial variables, such as spontaneous polarization $\mathbf{P}$ and phonon mode amplitude $\mathbf{A}$, as well as tensorial properties in explicit notation are enumerated by indices $i, j, k$ representing three Cartesian directions $x_1, x_2, x_3$. The components of second- and higher-rank tensorial
properties (excluding dielectric susceptibilities $\epsilon$), such as stresses $\sigma$, strains $\varepsilon$, elastic compliances $s$, piezoelectric constants $d$ and electrostrictive coefficients $Q$, are also expressed in abbreviated Voigt notation [172] with letter suffices $l, m, n$ ranging from 1 to 6.

### 3.2.1.2 General considerations

Landau theory stipulates that in the vicinity of a phase transition, the free energy of the system can be expressed as a series expansion of the order parameter. In the case of ferroelectric systems, the order parameter is polarization $\mathbf{P}$. Only the symmetry-compatible terms are retained in the free energy expansion, which is valid both above and below the transition point. As an example, Eq. (3.21) presents the Taylor expansion describing the Gibbs free energy of a 1D ferroelectric under stress free conditions:

$$G_{1D} = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6,$$

with the temperature dependent quadratic coefficient $\alpha_1 \equiv \alpha_1^0 (T - T_0)$, so that $\alpha_1 > 0$ for $T > T_0$ and $\alpha_1 < 0$ for $T < T_0$, where $T_0$ is the Curie–Weiss temperature of the ferroelectric to paraelectric phase transition. The order of phase transition is controlled by the sign of the quartic coefficient $\alpha_{11}$, with positive and negative values corresponding to the second and first order transitions, respectively. The variation of the energy as a function of polarization with temperature in the case of both first- and second-order phase transitions is discussed in Sec. 3.2.1.3. The coupling of polarization with the elastic stress will be discussed in Sec. 3.2.1.4.
In two and three dimensions, free energy polynomial expansions become more complex, especially when *spatially nonuniform* polarization distributions, i.e., the so-called Ginzburg energy terms proportional to $|\nabla \cdot \mathbf{P}(\mathbf{r})|^2$, and/or couplings to other order parameters, such as magnetization and octahedral tilts, are considered. LD expressions have been developed for a variety of different materials and are consolidated in Ref. [173].

### 3.2.1.3 Order of the phase transition

Fig. 3.4(a) and (b) shows the equilibrium polarization value $P_s$ plotted as a function of $T$ in the case of $\alpha_{11} < 0$ and $\alpha_{11} > 0$, respectively. $P_s$ is determined by finding the minima of $G_{1D}$ with respect to $P$,

$$\frac{\partial G_{1D}}{\partial P} = 0 \quad (3.22)$$

Gibbs free energy $G_{1D}$ is also plotted as a function of $P$ at various temperatures, in the case of $\alpha_{11} < 0$ and $\alpha_{11} > 0$ in Fig. 3.4(c) and (d), respectively. Clearly, polarization discontinuity is observed at transition temperature $T_t$ for $\alpha_{11} < 0$ (Fig. 3.4(a)) in the case of the first-order phase transition. A continuous decrease of $P_s$ to zero at $T_t$ is observed for $\alpha_{11} > 0$ (Fig. 3.4(b)) in the case of the second-order phase transition.

In the case of the first-order phase transition, it is worthwhile to note that the transition temperature $T_t$ is different from the Curie–Weiss temperature $T_0$, appearing in the temperature dependent quadratic coefficient $\alpha_1 \equiv \alpha_1^0(T - T_0)$. Observing the evolution of the free energy in Fig. 3.4(c) with changing temperature, the following information can be deduced for the first-order phase transition:
Figure 3.4: Representative equilibrium polarization $P_s$ profiles as a function of $T$ in the case of (a) first- and (b) second-order phase transitions, as obtained by minimizing the energy function $G_{1D}(P)$. Variation of the free energy, plotted as a function of polarization magnitude, $|P|$ for (c) first-order phase transition at $T < T_0$ (blue), $T = T_0$ (cyan), $T = T_t$ (green), $T = T^*$ (black), $T = T_1$ (red) and (d) second-order phase transition at $T < T_t$ (blue), $T = T_t$ (green), $T > T_t$ (red). For the first- and second-order phase transitions, $T_0 < T_t < T^*$ and $T_0 = T_t = T^*$, respectively [1, 95].
1. $T < T_0$ (blue curve) — polar phase is stable at $T < T_0$

2. $T = T_0$ (cyan curve) — polar phase is stable even at $T = T_0$

3. $T = T_t$ (green curve) — the free energy values of the polar and nonpolar phase are equal, as shown by the triple-well-like energy surface. Polar $\leftrightarrow$ non-polar phase transition occurs at $T_t$, where $T_t > T_0$.

4. $T = T^*$ (black curve) — polar phase is metastable up to the upper phase stability limit $T^*$, where $T^* > T_t$. All free energy surfaces between the green and black curves have a local minimum at $P \neq 0$ and a global minimum at $P = 0$.

5. In general, $T^* > T_t > T_0$

The terminology and variables used for the different temperature properties related to the phase transition [95] are consolidated in Table 3.1. In the case of the second-order phase transition $T^* = T_t = T_0$, which implies that the phase transition occurs exactly at the Curie–Weiss temperature. Most of the technologically important perovskite ferroelectrics — for example, PbTiO$_3$ and BaTiO$_3$ — exhibit the first-order phase transition.

### 3.2.1.4 Coupling polarization with elastic stress

An important characteristic of ferroelectric ceramics is their high sensitivity to elastic distortions. Consider a non-polar cubic crystal, for example PbTiO$_3$ at $T > T_t$, that undergoes a phase transition to the polar tetragonal phase with polarization developing in the
Table 3.1: Temperature properties, related to the ferroelectric phase transition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Fig. 3.4(c)</th>
<th>Fig. 3.4(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First-order</td>
<td>Cyan curve</td>
<td>Green curve</td>
</tr>
<tr>
<td></td>
<td>Second-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_0$</td>
<td>Curie–Weiss temperature</td>
<td>Cyan curve</td>
<td>Green curve</td>
</tr>
<tr>
<td>$T_t$</td>
<td>Transition temperature</td>
<td>Green curve</td>
<td>Green curve</td>
</tr>
<tr>
<td>$T^*$</td>
<td>Upper phase stability limit</td>
<td>Black curve</td>
<td>Green curve</td>
</tr>
</tbody>
</table>

$x_3$ direction. Following the $Pm\bar{3}m \rightarrow P4mm$ symmetry breaking due to the developing polarization, the unit cell lattice constants also change from cubic to tetragonal. The change in the lattice constants can be perceived as a spontaneous stress-free strain in the crystal due to the distortion away from the parent cubic phase. The polarization (vector) is coupled to strain (2-nd rank tensor) through the fourth-rank electrostrictive tensor $Q_{ijkl}$:

$$\varepsilon_{ij} = Q_{ijkl} P_k P_l$$  

(3.23)

Here, $i, j, k, l$ represent three Cartesian directions $x_1, x_2, x_3$.

### 3.2.2 Finite element analysis

#### 3.2.2.1 System energies

The standard expression from the thermodynamic LGD theory representing the total free energy $F$ of the ferroelectric system in the domain $V$:

$$F = \int_V f \, d^3r = \int_V [f_{\text{elastic}} + f_{\text{bulk}} + f_{\text{wall}} + f_{\text{elec}} + f_{\text{coupled}}] \, d^3r,$$  

(3.24)
where

\[
 f_{\text{elastic}} \equiv \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl}, \quad (3.25)
\]

\[
 f_{\text{bulk}} \equiv \alpha_{ij} P_i P_j + \beta_{ijk} P_i P_j P_k + \gamma_{ijkl} P_i P_j P_k P_l + \omega_{ijklm} P_i P_j P_k P_m P_l P_m P_n + \delta_{ijklmn} P_i P_j P_k P_m P_n P_l P_m P_n, \quad (3.26)
\]

\[
 f_{\text{wall}} \equiv G_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}, \quad (3.27)
\]

\[
 f_{\text{elec}} \equiv -P_k \frac{\partial \Phi}{\partial x_k}, \quad (3.28)
\]

and

\[
 f_{\text{coupled}} \equiv C_{ijmn} Q_{mnkl} \varepsilon_{ij} P_k P_l. \quad (3.29)
\]

Here, \( i, j, k, l, m, n \) represent three Cartesian directions \( x_1, x_2, x_3 \). \( \mathbf{P}(\mathbf{r}) \) is the polarization field, \( \varepsilon_{ij} = \frac{1}{2} (\partial u_i / \partial x_j + \partial u_j / \partial x_i) \) is the elastic strain tensor, \( \mathbf{u}(\mathbf{r}) \) is the displacement field and \( \Phi(\mathbf{r}) \) is the electrostatic potential. Einstein summation convention is assumed in what follows for the Cartesian indices. Linear elastic energy density \( f_{\text{elastic}} \) accounts for the elastic strain contributions to the total energy, with \( C_{ijkl} \) being the elastic stiffness tensor. \( f_{\text{bulk}} \) is bulk free energy, with expansion coefficients \( \alpha_{ij}, \beta_{ijk}, \gamma_{ijkl} \) and so on determining the preferred magnitude and direction of the ferroelectric distortion in the unit cell below \( T_0 \). \( G_{ijkl} \) are the gradient energy coefficients, and \( f_{\text{wall}} \) term expresses the energy contributions arising from the gradients in the polarization density. Electrostatic energy density \( f_{\text{elec}} \) represents
3. Modeling Perovskite Ferroelectrics

Interactions of the ferroelectric polarization with internal and external electric fields. \( f_{\text{coupled}} \) governs the coupling strength between the elastic strains and polarization, with \( Q_{ijkl} \) being the electrostrictive tensor. Note that some works [98, 99] combine \( f_{\text{elastic}} \) and \( f_{\text{coupled}} \) into one term. Here, we have chosen to separate them out due to the fact that the result of the variational differentiation (with respect to \( P \)) will only give nonzero results for terms that explicitly contain \( P \).

3.2.2.2 Materials parameters

Parameters \( \alpha_{ij}, \beta_{ijk}, \gamma_{ijkl}, \omega_{ijklm}, \delta_{ijklmn}, G_{ijkl}, C_{ijkl} \) and \( Q_{ijkl} \), are material dependent, obey symmetries of the crystal lattice, and in general can all be temperature dependent. Here, \( i, j, k, l, m, n \) represent three Cartesian directions \( x_1, x_2, x_3 \). Group-theoretical methods [174, 175] can be used to reduce the number of these parameters to a minimum by exploiting materials symmetries. For the perovskite ferroelectric PbTiO\(_3\), bulk and domain wall energy density expressions have the following forms:

\[
f_{\text{bulk}} = \alpha_1 \left( P_1^2 + P_2^2 + P_3^2 \right) + \alpha_{11} \left( P_1^4 + P_2^4 + P_3^4 \right) \\
+ \alpha_{12} \left( P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2 \right) + \alpha_{111} \left( P_1^6 + P_2^6 + P_3^6 \right) \\
+ \alpha_{112} \left[ P_1^4 \left( P_2^2 + P_3^2 \right) + P_2^4 \left( P_1^2 + P_3^2 \right) + P_3^4 \left( P_1^2 + P_2^2 \right) \right] \\
+ \alpha_{123} \left( P_1^2 P_2^2 P_3^2 \right),
\]
The bulk and gradient energy coefficients for PbTiO$_3$ are listed in Table 3.2. Note that PbTiO$_3$ displays low electrostriction but high spontaneous polarization at room temperature, $P_s \approx 0.75 \text{ C/m}^2$. In Chapter 6, SrTiO$_3$ is used as a matrix dielectric material enveloping ferroelectric PbTiO$_3$ inclusions. We assume that it is an isotropic and linear elastic-dielectric medium with the dielectric strength $\epsilon_m = 300$. Elastic, electrostrictive and dielectric material coefficients used in this work for SrTiO$_3$ and PbTiO$_3$ are listed in Table 3.3. The elastic coefficients of the SrTiO$_3$ matrix were averaged as $C_{11} = C_{33} = 2\mu + \lambda$, $C_{12} = C_{13} = \lambda = 99.7 \text{ GPa}$, and $C_{44} = C_{66} = \mu = 109.6 \text{ GPa}$ [177, 178], which is a reasonable experimentally relevant assumption, since $V_{\text{matrix}}$ is a much larger volume than that of the ferroelectric inclusion and likely not to be single crystal.
Table 3.2: Bulk [96, 98, 121] and gradient [101] energy parameters for PbTiO$_3$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>PbTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>752</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>J·m/[C²K]</td>
<td>$-7.1 \times 10^7(T - T_0)$</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>J·m$^5$/C$^4$</td>
<td>$-7.3 \times 10^7$</td>
</tr>
<tr>
<td>$\alpha_{12}$</td>
<td>J·m$^5$/C$^4$</td>
<td>$7.5 \times 10^8$</td>
</tr>
<tr>
<td>$\alpha_{111}$</td>
<td>J·m$^9$/C$^6$</td>
<td>$2.6 \times 10^8$</td>
</tr>
<tr>
<td>$\alpha_{112}$</td>
<td>J·m$^9$/C$^6$</td>
<td>$6.1 \times 10^8$</td>
</tr>
<tr>
<td>$\alpha_{123}$</td>
<td>J·m$^9$/C$^6$</td>
<td>$-3.7 \times 10^9$</td>
</tr>
<tr>
<td>$G_{110}$</td>
<td>J·m$^3$/C$^2$</td>
<td>$1.73 \times 10^{-10}$</td>
</tr>
<tr>
<td>$G_{11}/G_{110}$</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>$G_{12}/G_{110}$</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>$G_{44}/G_{110}$</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>$G'<em>{44}/G</em>{110}$</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3.3: Elastic stiffness tensor components in units of GPa for SrTiO$_3$ and PbTiO$_3$ were compiled from the Materials Project data [177, 178]. Also listed are the electrostrictive tensor coefficients [98] for PbTiO$_3$ in units of m$^4$C$^{-2}$ and the background dielectric constants of both materials in units of relative permittivity [179]. Both tensor components are given in Voight notation [172]. $\epsilon_\alpha$ is the background dielectric constant of the ferroelectric PbTiO$_3$ ($\alpha = b$) that originates from polarization of the core electrons, or the dielectric constant of the SrTiO$_3$ matrix ($\alpha = m$).

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$Q_{11}$</th>
<th>$Q_{12}$</th>
<th>$Q_{44}$</th>
<th>$\epsilon_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>319</td>
<td>100</td>
<td>110</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>281</td>
<td>116</td>
<td>97</td>
<td>0.089</td>
<td>-0.026</td>
<td>0.034</td>
<td>8</td>
</tr>
</tbody>
</table>
3.2.2.3 Finite element analysis code description

Ferret [180] is an open-source package developed within the multiphysics finite element framework MOOSE [181] for simulating thermodynamical properties of ferroelectric nanostructures. Unlike spectral methods [98, 99, 101, 182] that rely on regular parallelepiped meshes, the method utilized here implements a real-space approach based on irregular unstructured meshes, which allows it to process irregular geometries (using the LibMesh [183] library).

Evolution of the polarization distribution field $P(r)$ in the inclusion embedded in a linear dielectric elastic material is described by the time-dependent Landau-Ginzburg-Devonshire (TDLGD) equation,

$$-\gamma \frac{\partial P}{\partial t} = \frac{\delta}{\delta P} \int_V d^3r \ f(P),$$  \hspace{1cm} (3.32)

where $\gamma$ is a time-scaling parameter related to domain-wall mobility [184]. $\gamma$ is set to unity in this investigation and, therefore, the TDLGD equation is solved in an arbitrary scaled time. Since in real materials, elastic strain usually relaxes much faster than the polarization [185], we can assume that the local displacement field $u(r)$ instantaneously adjusts to the current state of the polarization field $P(r)$. This results in the following mechanical equilibrium condition for the system that has to be satisfied at every time step of the evolution of $P(r)$:

$$\frac{\partial}{\partial x_j} [C_{ijkl} (\varepsilon_{kl} - Q_{ijmn} P_m P_n)] = 0$$  \hspace{1cm} (3.33)

Here, $i, j, k, l$ represent three Cartesian directions $x_1, x_2, x_3$. Furthermore, the evolution of $P$ is also coupled with that of the local (internal) electrostatic potential $\Phi$ by the Poisson
equation:

$$\nabla \cdot (\epsilon_b \nabla \Phi) = \rho_b. \quad (3.34)$$

Here, $\rho_b$ is bound volume charge that is equal to $-\nabla \cdot \mathbf{P}$. Solving Eq. (3.34) accounts for the long-range Coulomb interactions within the system, including the potential emergence of the so-called depolarization field that originates from the presence of unscreened charges on the surface of the ferroelectric $\partial V$. Parameter $\epsilon_b$, sometimes called the background dielectric constant, represents contributions from core electrons to the dielectric response of the ferroelectric [159, 186] that can moderately screen the polarization field. In previous investigations, this parameter has been varied widely for PbTiO$_3$, as well as for BaTiO$_3$: $\epsilon_b \equiv (4 - 70) \epsilon_0$ [101, 182, 187]. We choose $\epsilon_b = 8$ for PbTiO$_3$, i.e., use a value that is close to that of the electronic contribution $\epsilon^\infty$ to the total dielectric permittivity [159] for this material. It should also be noted that varying this parameter does not seem to affect the results presented in this work.

The state of the dielectric matrix surrounding the ferroelectric volume is governed by a different set of equations. E.g., SrTiO$_3$ is assumed to be a linear dielectric with an isotropic dielectric permittivity $\epsilon_m$. The following equation has to be satisfied for the electrostatic potential within the matrix:

$$\nabla \cdot (\epsilon_m \nabla \Phi) = 0, \quad (3.35)$$
complemented by the stress divergence equation:

\[ \frac{\partial \sigma_{ij}}{\partial x_j} = 0. \]  

(3.36)

The system boundary conditions include vanishing elastic distortions far away from the ferroelectric volume, i.e., \((u \rightarrow 0)\) at \(\partial V_{\text{matrix}}\). Also, a short-circuited \([99]\) boundary condition on \(\Phi\) is chosen for the pair of opposite sides of the cube \(V_{\text{matrix}}\) with plane normals oriented along \([00 \pm 1]\). By adjusting the values of \(\Phi\) on these two sides, an external electric field can be applied. In the absence of the applied field, \(\Phi \rightarrow 0\) is enforced on the boundary planes of \(V_{\text{matrix}}\), which are assumed to be far away from the ferroelectric inclusion. Consistency checks were done to make sure that, as a function of the size of the ferroelectric volume, the internal (fringing) electrostatic potential and the strain fields originating from elastic distortions did in fact vanish at the boundaries of the computational domain. Larger medium domains were needed to ensure fringing fields from larger ferroelectric inclusions vanished.

Our approach implemented in Ferret \([180]\) allows for solving coupled Eqs. (3.32) through (3.36) self-consistently for the displacement vector field \(u(r)\), polarization vector field \(P(r, t)\), and electrostatic potential scalar field \(\Phi(r)\). These equations are first separated into their respective subdomains, and then cast into the weak-form suitable for Galerkin’s finite element method. A fully implicit time integration is implemented in a Newton-Raphson scheme. The iterative Generalized Minimal Residual \([188]\) algorithm is used to solve the block diagonal preconditioned linear system.

Since Eq. (3.32) is a partial differential equation that depends on time, an initial condition
for evolving the $\mathbf{P}$ field must be chosen. For this particular problem, we adopt an initial condition that resembles a paraelectric state of the material at some $T > T_t$, which forces $\mathbf{P}$ to be randomly distributed near zero. The rationale for choosing such random paraelectric initial condition (RPEIC) is to ensure that there is no “memory” bias in the domain structure that forms as the energy is dissipated out of the system by the gradient descent algorithm. Such condition is widely used in phase field modeling of ferroelectric materials [98, 99, 182]. The temperature is then immediately set below $T_t$ and the TDLGD Eq. (3.32) is evolved — together with solving Eqs. (3.34) and (3.33) at each time step — until a (local) energy minimum has been found. Simulation exit criterion is achieved when the difference in the magnitude of the total energy is below 0.1% during the two consecutive time steps.
Chapter 4

First principles investigation of polar properties of Sn- and Pb-based perovskite oxides

4.1 Classical ABO$_3$ perovskite structures

As already discussed in Chapter 1, the need to avoid the inclusion of a toxic element, such as lead, into next-generation electroactive compounds stimulated a search for novel Pb-free materials possessing comparable property responses [10–15]. However, the issues of identification, design and evaluation of suitable replacement materials remain challenging, as may be exemplified by the case of PZT, which currently remains the best technological piezoelectric material [13]. The exceptional piezoelectric properties of PZT, compared to
only moderate piezoelectricity of PbTiO$_3$, are attributed to the emergence of an MPB [4, 63, 189–191] near the Zr:Ti = 52:48 and high mobility of FE domain walls, indicating that the existence of large polar distortions is a necessary but not sufficient ingredient for attaining colossal property responses. At present, MPB engineering is achieved by precisely controlling the composition of solid-solution or relaxor ferroelectrics [190, 192], producing materials that are “usually complex, engineered, solid solutions, which complicates their manufacture as well as introducing complexity in the study of the microscopic origins of their properties” [193]. This statement also perfectly summarizes the problems that arise in predictive computational studies of such structures utilizing DFT methods, which are currently a tool of choice for the design of better, more efficient materials and nanostructures.

In this regard, exploring the effects of an isoelectronic substitution of tin in place of lead in ferroelectric perovskite oxides constitutes a logically straightforward and technically simple approach to the problem of lead-free electroactive materials design — at least on the level of atomistic theories, such as DFT. A number of computational studies have already explored this issue, reporting an improvement of polar properties (e.g., spontaneous polarization) in perovskite Sn(II)TiO$_3$ [21–23]. On the other hand, conventional solid-state synthesis of this or similar material retaining the Sn$^{2+}$ oxidation state (and the associated lone-par activity which leads to strong polar structural distortions) is difficult, as this route requires high temperatures that facilitate its disproportionation into Sn$^{4+}$ and Sn metal [23, 194].

We should point out though, that the aforementioned problems with high-temperature synthesis of ceramics have not discouraged other attempts to harness the attractive chemical
properties of the Sn\(^{2+}\) oxidation state. For example, doping (Ba,Ca)TiO\(_3\) FE ceramics and the incipient FE SrTiO\(_3\) with tin resulted in the enhancement [195–198] and emergence [28, 199] of polar properties in both cases, attributed to the presence of Sn\(^{2+}\) ions in the perovskite A-site positions. A divalent tin-containing compound Sn\(_2\)TiO\(_4\) (isostructural with the low temperature form of Pb\(_3\)O\(_4\)) [199–201] and a series of tungsten-based compounds SnWO\(_4\) [202, 203], Sn\(_2\)WO\(_5\) and Sn\(_3\)WO\(_6\) [204] have also been manufactured and characterized. Although, none of these structures exhibit spectacular electroactive properties, they still serve as (a) potential precursors for the chemically assisted growth of structures that could possess such properties and (b) important test beds for elucidating the behavior of the Sn\(^{2+}\) 5s\(^2\) electron lone pairs, especially in the ways it differs from the behavior of the Pb\(^{2+}\) 6s\(^2\) lone pairs.

Modern epitaxial engineering techniques offer an alternative approach to avoid the restrictions imposed by bulk thermodynamics in order to grow novel materials with enhanced properties as they can stabilize metastable structures through artificial elastic boundary conditions (misfit strain) and/or rate-limited kinetics [205]. However, a recent attempt to synthesize SnTiO\(_3\) films on sapphire and perovskite substrates from ceramic SnO\(_2\) and TiO\(_2\) targets utilizing pulsed laser deposition (PLD) produced nonpolar ilmenite-type structures with only traces of a second phase compatible with perovskite geometry [206]. An emergence of a centrosymmetric crystal structure indicates the loss of electron lone pair activity (along with the associated polar lattice distortions), suggesting that the Sn\(^{2+}\) oxidation state was not sufficiently achieved in the PLD-grown films.
In a previous computational study, Parker and coworkers have evaluated the structural stability of tin titanate polymorphs with SnTiO$_3$ stoichiometry, including the epitaxial thin-film phases [24]. One of the important conclusions of that study was that polymorphs possessing corner-sharing TiO$_6$ octahedra and polar cation displacements have lower energies, compared to centrosymmetric polymorphs, such as ilmenite-type structure. It was also demonstrated that, although the stress-free ground state of polar-perovskite SnTiO$_3$ is the same as that of PbTiO$_3$ [i.e., tetragonal, with space group $P4mm$ and spontaneous polarization $P \sim (00c)$], under biaxial tension, the former compound undergoes a transition into a monoclinic $Cm$ phase, $P \sim (aac)$, while the latter transitions to the $Amm2$ phase, $P \sim (aa0)$ [35, 36]. All of the aforementioned structures, together with the non-polar cubic $Pm\bar{3}m$ aristotype, are depicted in Fig.2.3. Space group, lattice system (notation used) and polarization character of typical polar phases in perovskites is given Table 2.1.

Probably the most interesting finding associated with the transitional behavior of both compounds under epitaxial tension is that the drastic reduction of symmetry caused by the $P4mm \rightarrow Cm$ phase transformation induces a large ($\sim 0.7 \rightarrow 1.4$ eV) change in the value of the SnTiO$_3$ electronic band gap $E_{\text{gap}}$ — at least, as predicted by standard DFT calculations [24]. This effect can then be utilized to tune the band gap elastically, by flexing the substrate, or electrically, by applying an electric field. Although the electronic-level underpinnings of such dramatic $E_{\text{gap}}$ variation in epitaxial perovskite SnTiO$_3$ were elucidated and attributed to a particular sensitivity of one of the energy levels to tensile distortions, it is still unclear why the transitional behavior of SnTiO$_3$ is different from that of PbTiO$_3$. Furthermore, with
the proposed $E_{\text{gap}}$ opening mechanism being quite generic, it may be useful to investigate how pronounced the same effect would be in epitaxial PbTiO$_3$ as it undergoes a transition into the more symmetric $Amm\bar{2}$ phase.

Here, we utilize first-principles DFT-based calculations to address both of these questions. We find that the $E_{\text{gap}}$ tuning effect in $P4mm \rightarrow Amm\bar{2}$ PbTiO$_3$ is much weaker than in $P4mm \rightarrow Cm$ SnTiO$_3$. We then trace the contrasting transitional behavior of PbTiO$_3$ and SnTiO$_3$ to differences in stereochemical lone-pair activity of Pb$^{2+}$ and Sn$^{2+}$ ions. Specifically, we demonstrate that optimization of repulsive Coulomb interactions between negatively charged oxygen ions — comprising the cuboctahedral cage around the A$^{2+}$ cation — and the electron lone-pair charge cloud leads to dissimilar spatial orientations of the latter in the tin- and lead-based compounds.

### 4.1.1 Epitaxial phase structure

Table 4.1, aggregates the relative energies, lattice parameters, and $E_{\text{gap}}$ values for the polar phases and non-polar cubic phase, of perovskite SnTiO$_3$ and PbTiO$_3$. All of these phases were relaxed to small normal stresses while keeping their symmetries intact under the condition that no shear distortions are allowed. For both compounds, polar tetragonal $P4mm$ structures are found as the lowest energy stress-free phases that occur under biaxial compression with respect to the optimized lattice constant of the cubic aristotype phase. Although experimental observations are not available for lattice constants of SnTiO$_3$,
Table 4.1: Energy differences ($\Delta E$) per formula unit (f.u.) with respect to the lowest energy phase for all the considered perovskite ATiO$_3$ ($A = \text{Pb, Sn}$) structures. Here and in what follows, the phases are arranged in the order of decreasing symmetry. For both tin- and lead-based compounds, the $P4mm$ phase has the lowest energy, which is taken as zero. Lattice parameters and band gap values $E_{\text{gap}}$ are also presented for all the structures. Values in parentheses (calculated using ultrasoft instead of PAW pseudopotentials) are shown to illustrate the comparability of results from the two methods on these systems.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$ (eV/f.u.)</th>
<th>$a$ (Å)</th>
<th>$c/a$</th>
<th>$E_{\text{gap}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnTiO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Pm\bar{3}m$</td>
<td>0.341 (0.325)</td>
<td>3.871 (3.861)</td>
<td>1.000</td>
<td>0.905 (0.927)</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>0.000</td>
<td>3.786 (3.784)</td>
<td>1.134</td>
<td>0.694 (0.732)</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>0.053 (0.049)</td>
<td>3.957 (3.945)</td>
<td>0.965</td>
<td>0.983 (1.034)</td>
</tr>
<tr>
<td>$Cm$</td>
<td>0.036 (0.033)</td>
<td>3.913 (3.901)</td>
<td>0.999</td>
<td>1.402 (1.448)</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Pm\bar{3}m$</td>
<td>0.059 (0.057)</td>
<td>3.890 (3.879)</td>
<td>1.000</td>
<td>1.471 (1.562)</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>0.000</td>
<td>3.865 (3.852)</td>
<td>1.044</td>
<td>1.489 (1.535)</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>0.013 (0.012)</td>
<td>3.930 (3.917)</td>
<td>0.984</td>
<td>1.778 (1.710)</td>
</tr>
<tr>
<td>$Cm$</td>
<td>0.015 (0.014)</td>
<td>3.907 (3.895)</td>
<td>1.000</td>
<td>1.895 (1.927)</td>
</tr>
</tbody>
</table>

Comparison between the computed and experimentally measured values of $a$ and $c$ for polar tetragonal PbTiO$_3$ shows that they underestimated by 0.94% and 2.9%, respectively, typical for DFT-LDA (see, e.g., Ref. [207]). Band gap of PbTiO$_3$ was severely ($\sim 54\%$) underestimated [208] when utilizing DFT-LDA, which is a well-known deficiency of this approach. However, this underestimation is not critical for the present investigation that is focused only on the variations of band gap with epitaxial strain $\varepsilon_e = \varepsilon_1 = \varepsilon_2$. Therefore, the trends in the change of relative valence-band maximum (VBM) and conduction-band minimum (CBM) positions as a function of epitaxial strain $\varepsilon_e$, and associated polarization rotations — discussed in more detail in Sec. 4.1.1.1 — should remain robust.
Table 4.2: Polar off-centerings (Å) of A and Ti ions in the considered perovskite ATiO$_3$ (A = Pb, Sn) structures. These displacements are computed with respect to the center of mass of the oxygen cage surrounding the appropriate cation: 12-atom cuboctahedral cage for Pb and Sn, and 6-atom octahedral cage for Ti.

<table>
<thead>
<tr>
<th></th>
<th>P4mm</th>
<th>Amm2</th>
<th>Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>SnTiO$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0.000</td>
<td>0.000</td>
<td>0.737</td>
</tr>
<tr>
<td>Ti</td>
<td>0.000</td>
<td>0.000</td>
<td>0.470</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.000</td>
<td>0.000</td>
<td>0.395</td>
</tr>
<tr>
<td>Ti</td>
<td>0.000</td>
<td>0.000</td>
<td>0.261</td>
</tr>
</tbody>
</table>

The magnitudes of polar cation distortions in all of the aforementioned ATiO$_3$ (A = Pb, Sn) hettotypes are assembled in Table 4.2. The polar cation displacements are calculated as the displacements of the ions from the geometric center of their respective surrounding oxygen nets — cuboctahedron and octahedron shaped nets for A-site and B-site ions respectively. Sn$^{2+}$ polar distortions are approximately twice as large as those of the Pb$^{2+}$ ion. Furthermore, Ti$^{4+}$ polar distortions in SnTiO$_3$, are also, 50–60% more pronounced than those in PbTiO$_3$. While the polar cation displacements are large in SnTiO$_3$ as compared with PbTiO$_3$, it is noteworthy that that the unit-cell volumes of both compounds are quite similar (mean absolute difference of 0.6 Å$^3$/f.u. between isomorphs). Increase in the polar cation distortions in SnTiO$_3$ results results in a larger polarization ($\sim$1.2 Cm$^{-2}$; see Ref. [24] for details) as compared to its lead-based counterpart.
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

4.1.1.1 Strain induced band-gap tuning

Under epitaxial compression, both PbTiO$_3$ and SnTiO$_3$ adopt the lowest-energy $P4mm$ phase. Under small epitaxial tension, both compounds transition from that phase into the monoclinic $Cm$ phase. However, the epitaxial strain stability range of $Cm$ phase is very narrow in PbTiO$_3$, and its polarization $P$ vector quickly rotates into the $xy$-plane as the value of $\varepsilon_e$ is further increased, resulting in a state with $Amm2$ symmetry. The $P4mm \rightarrow Amm2$ phase transition observed in PbTiO$_3$ is in agreement with previous computational results obtained with comparable DFT-based approaches [35, 36]. Whereas, in the case of SnTiO$_3$, the $Cm$ phase persists up to large tensile epitaxial strains with no traces of $Amm2$ phase observed even for relatively large biaxial tensions [24]. Also, it is important to emphasize that both of the representative (stress-free) polar epitaxial phases in PbTiO$_3$ have similar structural parameters and are close to each other in energy — the $Amm2$ state being only 2 meV lower than the $Cm$ one. On the other hand, in SnTiO$_3$ we see much stronger changes in the relative energies ($\sim$20 meV) and structural parameters of the involved relaxed polar epitaxial phases.

As shown in Table 4.1 for the representative polar phases and in Fig. 4.1 for the complete $\pm 2\%$ interval of epitaxial strains, the $E_{\text{gap}}$ tuning during the $P4mm \rightarrow Amm2$ phase transition in PbTiO$_3$ is limited to 0.2–0.3 eV (slightly more if the borderline $Cm$ phase could be stabilized). Therefore, although the generic trend for the band gap opening under lowering structural symmetry is indeed present in PbTiO$_3$, individual differences between the
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

Figure 4.1: VBM [circles] and CBM [squares] of epitaxially strained PbTiO$_3$ across the $P4mm \rightarrow Amm2$ phase transition as functions of biaxial strain. The same data for the $P4/mmm$ PbTiO$_3$ structure is shown in dotted lines. Open (red) square and circle at zero strain mark the VBM and CBM positions in the cubic $Pm\bar{3}m$ structure. VBM and CBM data for the $P4mm \rightarrow Cm$ phase transformation in SnTiO$_3$ [same as in Fig. 4 of Ref. [24]] is also presented here in dashed lines. The CBM/VBM curves for SnTiO$_3$ are shifted to match the CBM values of both compounds in the $P4mm$ phase.

DFT-based $E_{\text{gap}}$ values of various phases are small. This is in sharp contrast with the large effect ($\sim 0.7$ eV or 100\% change) observed for the $P4mm \rightarrow Cm$ phase transition in SnTiO$_3$, according to the Table 4.1 data for the representative phases and the $\pm 2\%$ epitaxial strain interval dependencies shown in Fig. 4 of Ref. [24] and repeated here in Fig. 4.1.

Furthermore, since it is well known that the DFT-LDA approach underestimates the value of the band gap, we computed more accurate band gap values for the perovskite SnTiO$_3$ using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional [170, 171]. Fig. 4.2
Figure 4.2: CBM (green) and VBM (black) values calculated using LDA (dotted lines) and HSE (solid lines). In the latter case, a band gap of 2.175 eV is obtained for compressive and zero strains ($P4mm$ phase), which increases to 2.655 eV in polar monoclinic $Cm$ phase stabilized by tensile misfit strain. The location of the CBM and VBM energy levels is referenced with respect to the low-lying O 2$s$ state, which is assumed to be undisturbed by any structural distortions.

presents both the HSE- and LDA-computed band gap values, published in collaboration with Agarwal et. al. [27]. As expected, the usage of the HSE approximation produces much larger band gaps in both $P4mm$ and $Cm$ epitaxial phases, while preserving the same general trends in the VBM and CBM position variation under applied strain, as already observed with DFT-LDA. In turn, this results in a much smaller tuning effect of strain on the band gap value: $\sim$35\% for HSE vs $\sim$100\% for LDA. Nonetheless, even a 35\% $E_{\text{gap}}$ change under a small ($\leq 0.5\%$) applied strain is still remarkable for an oxide material or nanostructure
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

[209].

4.1.1.2 Search for lone pairs in the electronic density of states

Electron localization functions (ELFs) are customarily used to visualize electron lone pairs: usually to highlight the pronounced differences between the electron cloud shapes of centrosymmetric non-polar and non-centrosymmetric polar phases or polymorphs of the same material.[203, 210–212] However, when comparing the ELF plots of the structurally similar \( P4mm \), \( Amm2 \) and \( Cm \) phases for the \( ATiO_3 \) perovskite structure — all non-centrosymmetric and polar, but with different directions of the unit-cell polarization vector — we did not observe any noticeable distinctions among them. Alternatively, following an approach of Watson and coworkers [17, 19, 20, 213, 214] that utilizes energy-resolved, or partial, electron charge density maps to visualize specific regions of the EDOS that are associated with the asymmetric nature of lone pairs allowed us to resolve the distinctions among these phases.

Fig. 4.3 presents total and partial (ion- and \( l \) quantum number-resolved) EDOS in (a) \( Pm\bar{3}m \) non-polar cubic and (b) \( P4mm \) polar tetragonal phases of perovskite \( SnTiO_3 \). For each phase, valence bands are divided into three regions that highlight specific interactions among the pseudoatomic wave functions centered on various ions [17, 19, 20, 213, 214]. The same information was also obtained for all other structures considered in this investigation (data not shown). Only minor differences were found in the shapes of the EDOS curves for all the polar variants of each \( ATiO_3 \) (\( A = Sn, Pb \)) compound.
Figure 4.3: Total and partial, i.e., ion and $l$ quantum number resolved, EDOS for (a) $Pm\bar{3}m$ non-polar cubic and (b) $P4mm$ polar tetragonal phases of perovskite SnTiO$_3$ showing three energy regions utilized for visualization of partial electron charge density maps. These regions are identified individually for each phase.
For each phase of SnTiO\textsubscript{3} and PbTiO\textsubscript{3}, the respective values of partial densities of the A\textsuperscript{2+} ion s and p states, as well as the oxygen 2p states, define the boundaries between the regions. Region I, lying approximately between -9 and -6 eV, encompasses the highly pronounced EDOS peak for the A(s) states and highlights bonding interactions between them and O(2p), with a small admixture of Ti(3d). The boundary between regions I and II is placed at the minimum that separates the A(s) EDOS states peak from the neighboring peak at higher energy. Region II, extending from that boundary to approximately -3, or -3.5 eV, is comprised mostly of EDOS parts that correspond to bonding interactions between Ti(3d) and O(2p) states with some contributions from A(p). The boundary between regions II and III is assigned to the energy where the A(s) states density again becomes denser than that of the A(p) states, as another A(s) EDOS peak is formed within region III. Region III, spanning from this boundary to the Fermi level, is formed by EDOS parts that include antibonding interactions of A(s) and O(2p) states, also with a small admixture of A(p). Region boundaries are determined individually for each particular material/phase combination. Small variations in their location do not appreciably change the results of our calculations. For example, boundary assignments for the non-polar $Pm\bar{3}m$ and $P4mm$ polar tetragonal phases of perovskite SnTiO\textsubscript{3} are shown in Fig. 4.3.

In Fig. 4.4, we present partial charge density maps corresponding to energy regions I, II and III using the $Amm2$ phase of SnTiO\textsubscript{3} as an example. The aforementioned specific interactions — bonding between Sn and O in region I, bonding between Ti and O in region II, and antibonding between Sn and O in region III — are visualized in panels (a), (b) and
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Figure 4.4: Partial charge density maps in energy regions (a) I, (b) II, and (c) III in the (110) plane of the Amm2 phase of SnTiO$_3$. Here, unlike the Ti-centered units of Fig. 2.3, cells are centered on the $\text{A}^{2+}$ cation with its cuboctahedral coordination cage explicitly outlined in red. Sn, Ti, and O ions are represented by gray, light blue (light gray), and red (dark gray) spheres, respectively. Contour levels shown are between 0 (blue) and 0.16 $e/\text{Å}^3$ (red).

Partial electron charge density maps presented here and in the next figure were created using the VESTA [215] software package.

(c), respectively. The classical picture of orbital hybridization, where an electron lone pair is formed as a result of intra-atomic mixing of $s$ and $p$ orbitals on the same cation [216, 217], places the associated charge density into region I. This hybrid orbital is chemically inert, but sterically active, and is projected to the side of the cation, distorting the lattice. That is clearly not the case for the partial charge density in region I, shown in Fig. 4.4(a) — the density is rather round in shape and thus does not have the required directionality that would promote steric activity [this same behavior in region I was obtained for all the other structures considered here]. Only relatively recent computational investigations for a variety of materials have proven that lone-pair electronic states are more subtle than the classical picture suggests: the interactions between the cation $s$ and $p$ orbitals are actually mediated through the $p$ orbitals of the neighboring anion [17–20, 211, 212]. This interaction
mechanism can be interpreted as a double PJTE where the anion $p$ states insert themselves in the middle of the energy gap between the cation states and then hybridize with the $s$ states below, and $p$ states above. Therefore, currently, the lone pair is identified as a complex cation(s,p)–anion(p) hybrid formed by combinations of electron bands that are positioned right below the Fermi level. These bands correspond to the partial charge density residing in energy region III. Our results for SnTiO$_3$ agree with the previous findings [17–20, 211, 212] showing the characteristic asymmetric charge density lobe within region III situated to the side of the cation and pointing away from the nearest oxygen, as depicted in Fig. 4.4(c).

### 4.1.1.3 Lone-pair activity and phase stability

In Fig. 4.5, we present ‘region III’ partial charge density maps for the polar $P4mm$, $Amm2$ and $Cm$ phases, as well as for the non-polar $Pm\bar{3}m$ phase in both SnTiO$_3$ and PbTiO$_3$. Just as described in the previous paragraph, in all polar phases, we observe asymmetric charge density distributions associated with stereochemical electron lone pair activity while, in non-polar $Pm\bar{3}m$ phases, such charge density distributions have spherical symmetry. Using the same arguments as in the investigation of tungsten-based AWO$_4$ ($A = $ Sn, Pb) compounds [203], we interpret these visualization results as the Sn$^{2+}$ lone pairs being “more compact” and the Pb$^{2+}$ ones “more diffuse.”

To evaluate the amount of electron charge $Q$ contained within the lone pair lobe (or sphere, in the case of non-polar geometries) in each structure, we numerically integrated the ‘region III’ partial charge density inside a volume $V$ around the A-site ion, including all
Region III partial charge density maps in the (110) plane, depicting the characteristic asymmetric charge-density lobes associated with stereochemically active electron lone pairs in ATiO$_3$ (A = Pb, Sn). Just as in Fig. 4.4, A$^{2+}$ cation-centered cells are used, with A$^{2+}$, Ti, and O ions represented by gray, light blue (light gray) and red (dark gray) spheres, respectively. SnTiO$_3$ structures are shown in the top row: (a) $P4mm$, (b) $Amm2$, (c) $Cm$, and (d) non-polar $Pm3m$. PbTiO$_3$ structures are assembled in the bottom row: (e) $P4mm$, (f) $Amm2$, (g) $Cm$ and (h) non-polar $Pm3m$. Contour levels shown are between 0 (blue) and 0.24 (red) for SnTiO$_3$, and 0 (blue) and 0.16 e/A$^3$ (red) for PbTiO$_3$.

the grid points with charge density that are greater than some small value $S$. The shape of the volume $V$, as well as the smallness of charge-density isosurface cutoff $S$, and the position of the boundary separating energy regions II and III, were varied to verify that the resulting lone-pair charges do not change appreciably. The values of $V$, $Q$, and $S$ are assembled in Table 4.3. Two major differences in the properties of Sn$^{2+}$ and Pb$^{2+}$ lone pairs stand out: first, although all the integrated charges are considerably smaller than the
formal charge of $2e$, for the structures of the same symmetry, charge found for the Sn$^{2+}$ lone pair is, on average, twice as large as that found for the Pb$^{2+}$ lone pair; and second, volumes surrounding the lone-pair charges in SnTiO$_3$ structures are also larger than those in their lead-based counterparts. Therefore, refining the argument presented in the previous paragraph, we can claim that, in perovskite ATiO$_3$ structures, A = Sn$^{2+}$ lone pairs carry slightly more charge per unit volume than those of A = Pb$^{2+}$. However, it would be incorrect to regard the former ones as “more compact” since they occupy more space. Furthermore, we can infer a yet more subtle observation connected to the transitional behavior of both compounds under epitaxial tension from the results of Table 4.3. For SnTiO$_3$, comparing the lone pair charges of the tensile polar phases, we see that $Q(Cm)$ is

Table 4.3:  Total charge $Q$ integrated around the A = Pb, Sn ion within the volume $V$ enclosed by the iso-surface with charge density $S$, calculated for all the considered perovskite ATiO$_3$ phases. Average lone-pair charge densities $Q/V$ are shown in the last column.

<table>
<thead>
<tr>
<th></th>
<th>SnTiO$_3$</th>
<th>PbTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pm3m$</td>
<td>0.0154</td>
<td>4.076</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>0.0090</td>
<td>5.348</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>0.0126</td>
<td>5.550</td>
</tr>
<tr>
<td>$Cm$</td>
<td>0.0090</td>
<td>5.292</td>
</tr>
<tr>
<td>$Pm3m$</td>
<td>0.0086</td>
<td>3.543</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>0.0106</td>
<td>3.697</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>0.0114</td>
<td>3.374</td>
</tr>
<tr>
<td>$Cm$</td>
<td>0.0114</td>
<td>2.591</td>
</tr>
</tbody>
</table>
substantially smaller (by $\sim 0.17e$) than $Q(Amm2)$. On the other hand, for PbTiO$_3$, $Q(Cm)$ is slightly larger (by $\sim 0.01e$) than $Q(Amm2)$. Thus, we can conclude that, in each case, the system prefers to transition into a phase that possesses a smaller lone-pair charge, specifically, the $Cm$ phase for SnTiO$_3$ and $Amm2$ phase for PbTiO$_3$. The same trend can also be seen for the polar structure lone-pair charge densities $Q/V$: they are, on average, 20% higher in the metastable phases ($Amm2$ for SnTiO$_3$ and $Cm$ for PbTiO$_3$), compared to those that actually occur during the phase transition. For each compound, the magnitude of the charge difference between the competing phases tracks the size of their energy difference $\Delta E$, shown in Table 4.1. So, the stronger energetic preference of SnTiO$_3$ to adopt the $Cm$ symmetry in tension is connected to a significant draining effect that this geometrical conformation has on the lone pair charge $Q$. Conversely, for PbTiO$_3$, the lone pair charges of both phases are very close, which results in a rather weak anisotropy of polar distortions. We have already shown before that, under certain conditions, Pb$^{2+}$ ions can exhibit similar behavior, which may lead to almost complete loss of directional anisotropy of their polar off-centerings [44].

Finally, we point out that, for both compounds, the stable $P4mm$ phase is exempt from the “minimal $Q$” rule, having a lone-pair charge that is 0.01–0.02e higher than that of the preferred tensile phase. This exemption may be explained when, in addition to the lone pair activity, we consider distortions inside the TiO$_6$ unit, where Ti displacements along the [001] direction, i.e., toward a corner of the octahedron, are always heavily favored [218] (note that Ti and Pb off-centerings happen in lockstep). Therefore, minimization of the repulsive Coulomb interactions between the A-site cation lone pair and the negatively charged oxygen
cage surrounding it becomes more important only when Ti is forced to off-center along a sub-optimal direction, such as toward an edge (Amm2) or a face (Cm) of the octahedral unit.

4.1.2 Discussion and insights

In this project, following the results of a previous DFT-based study of epitaxial phases of a fictitious perovskite ferroelectric SnTiO$_3$, we have investigated the same effect in epitaxial PbTiO$_3$, a well-known ferroelectric material that is isoelectronic to SnTiO$_3$. We found the band gap tuning in PbTiO$_3$ to be considerably weaker than in SnTiO$_3$. This relatively weaker tunability may be attributed to (i) higher symmetry of the preferred Amm2 tensile phase in the lead-based compound compared to Cm in SnTiO$_3$, and (ii) weaker interactions of Pb(6s) and O(2p) orbitals that do not exhibit a pronounced dependence on the direction of the polar distortion. This lack of dependence on polar distortion results in a flatness of the PbTiO$_3$ VBM level across the $P4mm \rightarrow Amm2$ phase transition.

We then investigated the stereochemical lone-pair activity of Pb$^{2+}$ and Sn$^{2+}$ ions in polar-perovskite ATiO$_3$ hettotypes possessing $P4mm$, Amm2, and Cm symmetries. Structural differences among these phases stem from distinct spatial orientations of the lone-pair charge cloud within the cuboctahedral oxygen cage around the A$^{2+}$ cation. The contrasting tendencies for PbTiO$_3$ and SnTiO$_3$ to form different phases under epitaxial tension were linked to the amount of charge concentrated within the lone pair lobes. Specifically, in the
energetically more stable tensile phase, as much charge as possible is transferred out of the lobe, which lowers the cost of Coulomb repulsion between the lone pair and the surrounding negatively charged oxygen cage. These insights into the electronic-level underpinnings of transitional behavior and functional property tuning in epitaxial ferroelectrics, such as PbTiO$_3$ and SnTiO$_3$, will be useful for the design of a new generation of more efficient electromechanical and electrooptical devices.

4.1.3 Experimental system: Sn-doped SrTiO$_3$

Although, as described in the beginning of this Chapter, synthesis of ‘pure’ perovskite compounds containing Sn$^{2+}$ on the A-site remains difficult, there have been attempts to infuse already grown perovskite materials with tin through doping [28, 195–199]. We have participated in an experimental collaboration that explored the effects of A- and B-site tin doping of epitaxial SrTiO$_3$ films on SrTiO$_3$ (001) substrates grown using a hybrid molecular beam epitaxy (MBE) approach [28]. In addition to addressing the outstanding challenge of incorporating Sn$^{2+}$ on the A-site of a perovskite structure, this investigation was focused on understanding growth kinetics of Sn-alloyed perovskite oxides and its influence on the incorporation of Sn within the crystal lattice. Epitaxial Sn-doped SrTiO$_3$ films were grown on the SrTiO$_3$ (001) substrates with MBE using hexamethylditin (HMDT) and titanium tetraisopropoxide (TTIP) as the metal-organic chemical precursors for Sn and Ti, respectively. More specific details on the thin film synthesis and characterization are provided in
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Figure 4.6: Representative $2 \times 2 \times 2$ supercells for (a) SrTiO$_3$, (b) 1Sn[A] model with one Sn substituting Sr at an A-site, (c) 1Sn[A] + 1Sn[B] model with two Sn replacing one Sr at an A-site and one Ti at a B-site, (d) a variant of a 1Sn[A] + 2Sn[B] model with three Sn replacing one Sr at an A-site and two Ti at B-sites. Sr, Sn, Ti and O atoms are represented by green, black, light blue and red spheres, respectively. Note the structural models represented in (a) through (d) correspond to $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratio value of 0, 0.0625, 0.125 and 0.1875 respectively.

Ref. [28].

Structural models for Sn-alloyed SrTiO$_3$ were created by taking a 40-atom supercell consisting of a $2 \times 2 \times 2$ perovskite unit-cell arrangement and then replacing some of the B-site Ti and/or A-site Sr with Sn. Examples of Sn arrangements on both A- and B-sites for some specific concentrations are shown in Fig. 4.6. DFT calculations were performed on these representative models to evaluate their lattice parameters and compare them with those obtained in experiments, making it possible to extract information about the relative fractions of Sn incorporation on A- and B-sites. Such highly-ordered models are available only for a small discrete set of stoichiometries and thus values of the $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratios, and cannot faithfully reflect the disordered nature of the alloyed compound. Nevertheless, they are easy to process with standard DFT techniques and can still provide useful information.
on the basic geometrical parameters of the substituted system.

Determination of all the possible arrangements of Sn is especially straightforward in the case of the exclusively B-site doped SrTi$_{1-x}$Sn$_x$O$_3$ system. Only eight different stoichiometrical variants are possible, with the $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratio values ranging from 0 to $\frac{1}{2}$ in increments of $\frac{1}{16}$, where the limiting cases represent pure SrTiO$_3$ and SrSnO$_3$, for $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratio of 0 and $\frac{1}{2}$ respectively. For these compositions, ones corresponding to the ratios of $\frac{2}{16}$ (12.50%) and $\frac{6}{16}$ (37.50%) have five possible symmetrically distinct ordering arrangements of Ti and Sn on the B-sites, while those corresponding to the ratios of $\frac{3}{16}$ (18.75%), $\frac{4}{16}$ (25.00%) and $\frac{5}{16}$ (31.25%) have six symmetrically distinct arrangements. The remaining compositions of $\frac{1}{16}$ (6.25%) and $\frac{6}{16}$ (43.75%) are represented by one model each. None of the examined B-site Sn arrangements result in non-centrosymmetric space groups and therefore none of the corresponding structural models include any polar distortions. For each of the Sn concentrations, the value of the out-of-plane lattice parameter $a_{op}$ in the disordered substituted system was approximated by averaging of the $a_{op}$ values of all the possible ordered structures.

Fig. 4.7 shows the $a_{op}$ of Sn-alloyed SrTiO$_3$ as a function of the $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ atomic % (at. %) ratio measured using XPS (blue squares) [28]. The experimental data presented in the plot shows an unusual behavior of the $a_{op}$ with an increasing value of $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratio, which initially increases and then decreases starting with the ratio of $\sim 0.1$. The off-axis reciprocal space map (RSM) data showed a completely coherent film for all Sn concentration samples, suggesting that the origin of a reduced $a_{op}$ is not associated with strain relaxation.
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Figure 4.7: The out-of-plane lattice parameter $a_{\text{op}}$ of the epitaxial SrTi$_{1-x}$Sn$_x$O$_3$ film as a function of $x/2$. Dotted lines show calculated $a_{\text{op}}$ as a function of $x/2$ assuming Sn on B-sites (red), and assuming Sn on both B- and A-sites (black) for completely strained films on SrTiO$_3$ (001).

Dashed lines in Fig. 4.7 depict the calculated $a_{\text{op}}$ of the Sn-alloyed SrTiO$_3$ films with B-site doping (red dashed-dotted line) and mixed A- and B-site doping (black dashed line) as a function of the $\frac{\text{Sn}}{(\text{Sr}+\text{Ti}+\text{Sn})}$ at. % ratio, assuming a completely strained film on the SrTiO$_3$ (001) substrate. The computed results for the B-site doped structures follow a straight line in compliance with the Vegards law. All of these values are shifted up by 0.043 Å, which constitutes the difference between the experimental (3.905 Å) and theoretical (3.862 Å) estimates of the lattice constant of cubic SrTiO$_3$, to compensate for the well-known “overbinding” behavior of the DFT-LDA techniques.

On the other hand, when Sn was allowed to occupy both B- and A-sites (black dashed line), for ratios above 0.18-0.20, the calculated $a_{\text{op}}$ behavior deviates strongly from the Veg-
ard’s law, remaining constant or even decreasing slightly with increasing Sn concentration. Although the DFT-based estimates for \( a_{op} \) do not coincide precisely with those obtained in experiments (potentially due to insufficient sampling of different Sn-dopant arrangements within the system), they do reproduce the same general trend, which suggests that the transfer of a certain number of Sn\(^{2+}\) ions onto the A-site, replacing Sr\(^{2+}\), results in a noticeable decrease of the \( a_{op} \). This result also indicates that the films with measured \( \frac{\text{Sn}}{(\text{Sr+Ti+Sn})} \) at. % ratio < 0.10 may also contain a small fraction of tin as Sn\(^{2+}\) and that the decrease in \( a_{op} \) is observed only when the fraction of Sn\(^{2+}\) at A-site increases. As a result of Sn ion occupying A-site as Sn\(^{2+}\), it will off-center due to the lone-pair activity, thus breaking the inversion symmetry of the system and making it polar. The polar character of the films was confirmed with the help of optical second harmonic generation (SHG) polarimetry measurements, thus providing strong experimental evidence for the presence of Sn\(^{2+}\) on the A-site of the doped SrTiO\(_3\) thin film structure [28].

4.2 Physical origins of Goldstone-like excitations in perovskite-oxide multilayers

Layered-perovskite oxides have recently emerged as an attractive class of functional materials with widely customizable properties. Although usually more difficult to grow [42], these structures usually inherit all of the major functional traits of their “classical” ABO\(_3\)
counterparts, including ferroelectricity, ferromagnetism, ionic and electronic conduction, and superconductivity. More importantly, they also provide a number of additional channels not only for property modification and fine-tuning, but also for the design of new advanced functionalities that classical perovskites do not possess. The remarkable versatility of this materials class stems primarily from vast structural diversity of its constituent families of compounds. As already mentioned, a number of different families of layered oxides exists, with the most well-known ones incorporating perovskite slabs with (001) surfaces, such as RP [37–39], Aurivillius and Dion-Jacobson [40, 41], while families based on other surface cuts, e.g., (110) and (111), have also been reported or proposed [40].

In a series of previous investigations [43, 44, 52], some properties of a simple layered-oxide superlattice PSTO that is based on an “$n = 2$” $A_3B_2O_7$ RP structural arrangement [see Fig. 1.1(a-b) for sketches] have been explored and characterized. The most unique feature of this system is that when unstrained or subjected to slight compressive biaxial strain in the basal plane it loses anisotropy with respect to the direction of the (planar) polar distortion [44]. In turn, this leads to an emergence of Goldstone-like excitations or phasons [46–50] that manifest themselves as easy — i.e., requiring almost no consumption of energy — rotations of the polar vector within the plane. Therefore, with the exception of ferroelectric liquid crystals [50], which have spontaneous polarizations much smaller than those of archetypical perovskite [1] and polymer (e.g., polyvinylidenene fluoride and copolymers [219, 220]) ferroelectrics, right now PSTO is the only proposed ferroelectric material that is analogous to a soft ferromagnet, such as permalloy.
The ease with which the direction of the dipolar field can be curved in PSTO makes it an interesting medium for inducing a variety of exotic states, including vortices [51, 52], skyrmions and other polarization-closure patterns [53], whose topology and transitional behavior can be controlled and manipulated by applied electric and elastic fields. Also, since some aspects of the Goldstone-like excitation behavior in PSTO are similar to that of a system possessing an MPB (specifically, very low energy energy barriers between phases with different orientation of the polarization vector), this so-far virtual material can serve as a convenient template for acquiring a better understanding of physical phenomena underpinning an MPB appearance. As the outstanding piezoelectric properties of PZT, which is a compositionally and structurally complex, three-dimensionally-connected material, are intimately connected with the presence of an MPB on its phase diagram, developing new routes towards identification and manufacturing compounds with engineered MPBs is critically important for advanced technological applications of electroactive materials.

In the previous work, simple explanation was provided for how the peculiar sombrero-hat shaped energy landscape [with respect to planar polar distortions, see Fig. 1.1(c-d)] can be formed in the PSTO system, leading to Goldstone-like behavior [44]. Specifically, analyzing the form of vibrational eigenvectors corresponding to these distortions revealed that, unlike in PbTiO$_3$ where polar vibrational modes involve cooperative displacements of both Ti$^{4+}$ and Pb$^{2+}$ sites, in PSTO the Ti ion remains pinned close to the geometrical center of the TiO$_6$ octahedron. Therefore, the polarization arises solely due to the Pb ion off-centering in a rather spacious, cuboctahedral cage, i.e., it can be considered a perfect A-site driven
ferroelectric. When just the right amount of biaxial strain is applied to the basal plane of the system, stabilization energy gains due to the Pb displacements along the [100] or the [110] crystallographic directions become close, with these two sets of four symmetrically equivalent energy minima coalescing into a circular groove in the energy landscape.

Although the outlined vibrational-eigenvector-based description provided some insight into the emergence mechanism — or the “how?” — of the Goldstone-like state, a number of important “why?” questions were not investigated in the original study [44]: (i) Is the observed polarization-direction anisotropy collapse purely accidental, or is there an underlying reason — manifested in electronic properties — for this symmetry increase? (ii) As it is reasonable to assume that the layered nature of PSTO is crucial for the emergence of Goldstone-like excitations, what is the role of each atomic monolayer within the structure in condensing these states? E.g., it was determined that the polarization develops within the PbO monolayer, while Ti ions in the TiO$_2$ monolayers do not off-center (why?). What, if any, is the role of the outlying SrO monolayer; is it needed just for completing the TiO$_6$ octahedral cages, or maybe it can be safely thrown out? (iii) Furthermore, going beyond a single perovskite slab, what is the influence of uniting the slabs into a three-dimensional RP, or potentially some other structure? (iv) Granted that it is better to replace Pb with a more environmentally friendly ion, is electron lone-pair activity still required for producing Goldstone-like states? Since we have previously shown that under certain conditions Sn may be a sensible replacement for Pb in a classical ATiO$_3$ perovskite oxide [24, 26–28, 221], would a tin-based variation of the ASr$_2$Ti$_2$O$_7$ layered structure be capable of supporting
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

Figure 4.8: (Color online) Schematics of the $\text{AA}'_2\text{Ti}_2\text{O}_7$, $A = \{\text{Pb, Sn}\}$, $A' = \text{Sr}$, structural models utilized in this investigation. $A$ and $A'$ atoms are shown as large violet (dark gray), and green (light gray) spheres, respectively. Oxygens are shown as small red (dark gray) spheres and TiO$_6$ cages are represented by semi-translucent octahedra. (a) Bulk aristo-type RP structure with $I4/mmm$ symmetry. Lattice parameters $a$ and $c$ for the $P4/mmm$ tetragonal unit cell comprised of two $\text{AA}'_2\text{Ti}_2\text{O}_7$ structural units (s.u.) connected by the body-centring translation are also shown. (b) A model for the (infinite) isolated perovskite slab, obtained by disjoining the RP structure shown in panel (a), with vacuum regions above and below. The outline shows a primitive unit cell with a 1×1 perovskite basal plane. (c) An $xy$-plane view of the perovskite slab, slicing through the central AO monolayer, with delineated crystallographic [100] and [110] directions.

Goldstone-like excitations?

4.2.1 Structural models and general approach to property evaluations

As outlined above, here we are operating under assumption that the properties of individual monolayers, comprising the SrO–TiO$_2$–AO–TiO$_2$–SrO slab, as well as the interactions between these monolayers, are critically important ingredients for the emergence of the
Goldstone-like excitations. Therefore, while considering the behavior of bulk \( \text{ASr}_2\text{Ti}_2\text{O}_7 \) RP compounds as reference, we concentrate on studying the properties of different slab systems from which such RP structures can be constructed. For example, a periodic five-layer slab model with a unit cell containing exactly one \( \text{ASr}_2\text{Ti}_2\text{O}_7 \) structural unit (s.u.) separated from the (symmetrically equivalent) neighboring units that would be surrounding it from above and below in the bulk RP geometry is depicted in Fig. 4.8 together with the sketch of the original RP structure. Furthermore, the \( z \)-direction discontinuity of the \( \text{TiO}_6 \) octahedral network in bulk RP systems effectively decouples the polar states in the neighboring perovskite slabs. Therefore, investigating the properties of an isolated \( \text{ASr}_2\text{Ti}_2\text{O}_7 \) perovskite slab, as shown in Fig. 4.8(b-c), may be sufficient to obtain clues pointing to the origins of the Goldstone-like excitations emergence.

![Flow chart describing the method of deconstructing](image)

Figure 4.9: Flow chart describing the method of deconstructing (a) the five layered \( \text{SrO—TiO}_2—\text{SnO—TiO}_2—\text{SrO} \) slab to (b) the isolated sheets of \( 2\times\text{SrO} \), \( 2\times\text{TiO}_2 \) and \( 1\times\text{SnO} \). From the individual sheets, (c) the three layered \( \text{TiO}_2—\text{SnO—TiO}_2 \) slab is constructed by adding \( 2\times\text{TiO}_2 \) sheets to the \( \text{SnO} \) sheet. Finally, \( 2\times\text{SrO} \) sheets are added to the three layer slab to reconstruct the initial (d) five layered \( \text{SrO—TiO}_2—\text{SnO—TiO}_2—\text{SrO} \) slab. During reconstruction, the mirror plane present in the \( \text{SnO} \) sheet is preserved in every step. \( \text{Sn}, \text{Sr}, \text{Ti} \) and \( \text{O} \) ions are represented by gray (medium gray), green (dark gray), sky blue (light gray) and red (dark gray) spheres respectively.
To study the electronic interactions within the ASr$_2$Ti$_2$O$_7$ slab, we have adopted the “bottom up” approach inspired by the work of R. Hoffmann [222], as it had been applied to the studies of bonding in a number of different materials, e.g., α and β polymorphs of lead monoxide [222]. Fig. 4.9 schematically summarizes the approach, where a complex structure is analyzed by breaking it into the smallest constituent pieces, that are then gradually put back together and evaluated, until the original structure is recovered. Following this approach, we decomposed the ASr$_2$Ti$_2$O$_7$ slab (which was held under an epitaxial strain condition compatible with the existence of Goldstone-like excitations) into its constituent oxide monolayers. The first step of the procedure, shown in Fig. 4.9(a-b), describes the breaking of the slab into its constituent monolayer sheets — 2×SrO, 2×TiO$_2$ and 1×AO — at fixed in-plane lattice parameter compatible with the Goldstone-like behavior. Electronic interactions within each isolated sheet are studied to identify those responsible for the preferred orientations of planar distortions. On the second step, shown in Fig. 4.9(c), an intermediate trilayer TiO$_2$—AO—TiO$_2$ (ATi$_2$O$_5$) structure is constructed by adding TiO$_2$ sheets to the AO sheet on top and bottom. The electronic interactions among sheets are evaluated and compared with those of the individual sheets. On the final step, described in Fig. 4.9(d), SrO sheets are added to the trilayer system on top and bottom, reconstructing the original SrO—TiO$_2$—AO—TiO$_2$—SrO (ASr$_2$Ti$_2$O$_7$) slab. The electronic properties of the complete slab are then compared with those of individual monolayers and the trilayer structure. This detailed analysis allows us to establish an insight into the workings of the cooperative PJTE [8, 9] within the slab: i.e., for a given unstable vibrational mode breaking
the system centrosymmetry, we can identify both specific electronic bands that are able to interact due to the symmetry reduction, as well as actual BZ \( k \)-points where they do so.

### 4.2.2 Goldstone-like excitations in \( \text{SnSr}_2\text{Ti}_2\text{O}_7 \)

In order to answer the first question — whether \( \text{Sn}^{2+} \) can replace \( \text{Pb}^{2+} \) and still have Goldstone-like polarization rotations, we have computed the phonon-bands dispersion for the isolated perovskite \( \text{SnSr}_2\text{Ti}_2\text{O}_7 \) slab, optimized under the \( P4/mmm \) symmetry restriction \((a = b = 3.814 \text{ Å}, \varepsilon = 0\%)\). Fig. 4.10(a) shows the phonon-bands dispersion for the optimized stress-free \( \text{SnSr}_2\text{Ti}_2\text{O}_7 \) slab. Visualizing the eigenvectors of the strongest instability (soft mode) at \( \Gamma \), we have found that the instability is doubly degenerate and ionic distortions are in symmetrically equivalent \([100]\) and \([010]\) directions. Because of this degeneracy, the structure could develop a structural distortion in any direction defined by the linear combination of the associated eigenvectors \((\hat{e}_x)\) and \((\hat{e}_y)\) with directions \([1,0,0]\) and \([0,1,0]\), respectively. To find the local energy minimum for the distorted structure, we have sampled the energy surface for the slab by freezing in the linear combinations of the eigenvectors \((Q = Q_x\hat{e}_x + Q_y\hat{e}_y)\) with the amplitudes, \(Q_x\) and \(Q_y\) varied on a grid from \((0,0)\) to \((18,18)\). For distortions along the high symmetry \([100]\) and \([110]\) directions, \( Pmm2 \) (local minimum) and \( Amm2 \) (saddle point) phases are obtained, respectively. We observe a reasonably circular depression in the energy surface at \( E = -120 \text{ meV} \) (blue dotted) contour in Fig. 4.10(d), suggesting that the energy minimum is not in a well defined direction, but
Figure 4.10: (a), (b) and (c) Phonon-band dispersions of the $P4/mmm$ SnSr$_2$Ti$_2$O$_7$ slab at 0%, 0.5% and 1.1% tensile epitaxial strains, respectively. (d), (e) and (f) Energy surfaces with frozen-in doubly degenerate ferroelectric distortions in the SnSr$_2$Ti$_2$O$_7$ slab at 0%, 0.5% and 1.1% tensile epitaxial strains, respectively.
rather a continuous nearly circular trench, in which the polarization can rotate with a small energy penalty ($P_{mm2} \rightarrow A_{mm2}$ transition is $\sim 5$ meV).

We have repeated the same procedure of computing the energy surface at different epitaxial strains of the SnSr$_2$Ti$_2$O$_7$ slab, in search of the strain state at which the energy surface inside the minimum trench is flat. Fig. 4.10(e) and (f) shows the energy contour maps for the slab at $\varepsilon = 0.5\%$ and $\varepsilon = 1.1\%$, respectively. The competing energy minima systems along the [100] and [110] directions have nearly the same depth near the optimal epitaxial strain value of 0.5%, as shown in Fig. 4.10(e). As discussed before, such behavior, manifested by the characteristic sombrero-hat form of the energy surface [48–50] is indicative of the presence of a Goldstone-like excitation within the slab. Therefore, further analysis of the properties of the Sn-based slab and related structures was done at this particular strain state.

### 4.2.3 Monolayers

Electronic and vibrational properties of 2D SnO, PbO, TiO$_2$ and SrO sheets were analyzed, starting from centrosymmetric $P4/mmm$ structure, by computing their phonon-band dispersions, shown in Fig. 4.11(a,c,e,g). All of these sheets have strong FE instabilities at $\Gamma$. The energy landscapes of SnO, PbO, TiO$_2$ and SrO sheets plotted in Fig. 4.11(b,d,f,h), respectively, were obtained by energy surface sampling technique as discussed previously. SnO and PbO sheets have strong distortions along the [100] direction. Whereas Ti$^{4+}$ and Sr$^{2+}$
ions in their respective sheets have weak distortions in the [110] and [100] directions, respectively. To analyze the electronic underpinnings for the preferred distortions in all the sheets, we have computed their electronic band structure, total EDOS and projected (l quantum-number-resolved) EDOS. We find that the EDOS profiles of both SnO and PbO sheets are similar and in what follows only present the EDOS the former sheet where electronic interactions are more pronounced. The detailed analysis given below and accompanying Fig. 4.12 is done for the SnO sheet, however, the same evaluation can be conducted for any of the involved sheets.

Fig. 4.12(a) shows the total EDOS (dashed lines) and projected density of states (PDOS) of the Sn(s) pseudo-atomic orbital (solid lines). The PDOS curves of the other valence pseudo-atomic orbitals present in the SnO sheet, Sn(p_x, p_y), Sn(p_z), O(p_x, p_y) and O(p_z) are plotted in Fig. 4.12(b), (c), (d) and (e), respectively. Three different types of electronic interactions between the Sn^{2+} and O^{2−} ions were identified as responsible for the energetic preference toward the polar Pmnm2 phase. (i) The sharp peak in the P4/mmm structure in the energy range of -7 to -6 eV shown in Fig. 4.12(a) is broadened into two smaller peaks near -8 and -6 eV for the Pmnm2 structure in the second panel. The broadening decreases as the polarization rotates from 0° in the second panel to 45° in the fifth panel, forming a peak for the Amm2 phase. Therefore, the P4/mmm \rightarrow Pmnm2 phase transition involves shifting of electron charge density to lower energies, decreasing the total energy of the system. (ii) The bonding interaction between Sn(p_x) and O(p_y), as shown in Fig. 4.12(b) and (d), also decreases the total energy of the SnO sheet upon the transition from the non-polar P4/mmm
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

Figure 4.11: Phonon-band dispersions for the centrosymmetric (space group $P4/mmm$) monolayers of (a) SnO, (c) PbO, (e) TiO$_2$ and (g) SrO. Imaginary frequencies associated with unstable phonon modes are plotted as negative numbers below the zero line. (b), (d), (f) and (h): the associated monolayer energy landscapes with respect to the magnitude of the strongest frozen-in Γ-point lattice instabilities. Here and below, $Q_x$ and $Q_y$ are the amplitudes of the (doubly degenerate) vibrational eigenvectors, corresponding to the lattice distortions, that are polarized along the $x$ and $y$ axes, respectively. For each system, the energy of the undistorted $P4/mmm$ configuration is taken as zero, while $a$ is the value of the in-plane lattice constant.
Figure 4.12: (a) Total EDOS and \( l \) quantum-number-resolved PDOS of Sn(\( s \)), plotted for an isolated SnO sheet. (b) and (c) PDOS of Sn(\( p_x/y \)) and Sn(\( p_z \)), respectively. (d) and (e) PDOS of O(\( p_x/y \)) and O(\( p_z \)), respectively. Each panel within the same plot contains the DOS of the structure with no polar distortion (first panel from bottom) and with polar distortions induced at the angles of \( 0^\circ \) (second panel), \( 15^\circ \) (third panel), \( 30^\circ \) (fourth panel) and \( 45^\circ \) (fifth panel) with the [100] direction. The color legends shown in (a) are valid for all plots and for easy visualization are color synced with the polarization direction schematic in the bottom left corner.
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to polar phases. In the second panel of Fig. 4.12(b) and (d), showing the O($p_y$) EDOS, formation of a sharp peak at -4 eV represents bonding interaction between Sn($p_x$) and O($p_y$), where the charge density is pushed to lower energy states after breaking of the $P4/mmm$ symmetry. As polarization rotates from the [100] to [110] direction, or from the $Pmm2$ to $Amm2$ phase, the peak moves up in energy, which results in the increase of the total energy of the system. (iii) Fig. 4.12(c, e) show that the interaction between Sn($p_z$) and O($p_z$) is weak and almost undisturbed by the polarization rotation. To summarize, the Sn$^{2+}$ lone pair within the SnO sheet prefers to orient itself in the [100] direction where it points away from the neighboring O($p_x$) and ($p_y$) wavefunctions.

4.2.4 Trilayer structure

Fig. 4.13(a,c) displays the phonon band dispersions for the SnO- and PbO-based trilayer slabs, constructed by adding two TiO$_2$ monolayers, as shown in Fig. 4.9(c). Strong doubly-degenerate structural instabilities, $\sim$-200i and $\sim$-150i for A = {Sn,Pb} respectively, are also found for both systems at $\Gamma$. Fig. 4.13(b,d) presents the corresponding energy landscapes with respect to the frozen-in $\Gamma$-point structural distortion in the SnO- and PbO-based trilayer slabs. Both of these landscapes are square in shape and similar to that of the TiO$_2$ sheet, cf. Fig. 4.11(f), which indicates no presence of Goldstone-like modes. Fig. 4.14 shows the total EDOS and some of the PDOS curves for the SnO based trilayer slab. Though changes in EDOS and PDOS distributions with polarization rotation are modest here, as compared
Figure 4.13: (a) and (c): Phonon-band dispersions of the SnO- and PbO-based trilayer epitaxial slabs (TiO$_2$—AO—TiO$_2$). (b) and (d): energy landscapes with respect to the magnitude of the strongest frozen-in Γ-point lattice instabilities for the same slabs.
Figure 4.14: (a) Total EDOS of the SnO-based trilayer epitaxial slab. (b) PDOS of Sn(s) and (c) PDOS of O(p_x) and O(p_y), respectively, in the same slab. Each panel within the same plot contains the DOS of the structure with no polar distortion (first panel from bottom) and with polar distortions induced at the angles of 0° (second panel), 15° (third panel), 30° (fourth panel) and 45° (fifth panel) with the [100] direction.

with the AO monolayer sheets, the differences in electronic level couplings along the [100] and [110] directions can still be recognized. In general, sandwiching the SnO sheet between the TiO_2 sheets completely changes the orientation of the preferred structural distortions in the system, that switch from being dominated by the Sn–O lone-pair induced interactions along [100] to the Ti–O dominated interactions along [110].

4.2.5 Five layers: back to the original slab

Fig. 4.15 shows the phonon-band dispersions and strongest structural instability energy landscapes for the five-layer SnO- and PbO-based systems constructed by adding the SrO sheets on top and bottom of the appropriate trilayer structures. Both energy landscapes look
Figure 4.15: (Color online) (a) and (c) Phonon-band dispersions for the $P4/mmm$ SnSr$_2$Ti$_2$O$_7$ and PbSr$_2$Ti$_2$O$_7$ epitaxial slabs, respectively. (b) and (d) Energy surfaces with respect to frozen-in doubly degenerate ferroelectric distortions in the same slabs.
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Figure 4.16: Total EDOS plotted for the SnSr$_2$Ti$_2$O$_7$ slab. Each panel contains the EDOS of the structure with no polar distortion (first panel from bottom) and with polar distortions induced at the angles of 0° (second panel), 15° (third panel), 30° (fourth panel) and 45° (fifth panel) with the [100] direction.

round in shape and similar to the one previously observed in the PSTO bulk RP system [see Fig. 1.1(c,d)], which is indicative of the presence of the Goldstone-like excitations of the polarization vector in these slabs. For the SnO based five-layer slab, the total EDOS plots are shown in Fig. 4.16 for the polar distortions oriented at 0°, 15°, 30° and 45° angles from the [100] direction. Unlike on the two previous steps involving monolayer and trilayer structures, here we observe no significant change in the total EDOS with respect to the direction of the
polar distortion.

### 4.2.6 Discussion and insights

At this point, it should be possible to answer all the questions about the possible origins of the Goldstone-like excitations in this system that were formulated in the beginning of this section:

(i) *Is the observed polarization-direction anisotropy collapse purely accidental, or is there an underlying reason — manifested in electronic properties — for this symmetry increase?* No symmetry related loss of anisotropy was observed in electronic interactions. Two different schemes for the electronic wavefunction hybridization are at work for the distortions along the [100] and [110] directions, but at some epitaxial strain both of these mechanisms generate energy minima of the same depth for the same value of $|P|$.

(ii) *What is the role of each atomic monolayer within the structure in condensing these states?* As seen from the comparison of the three- and five-layer slab behavior, the combination of AO, TiO$_2$ and SrO sheets in proper sequence is required to create the sombrero-hat shaped energy landscape of the system. In particular, the presence of the SrO sheets at the slab boundaries is critically important for inducing Goldstone-like behavior, as their effect amounts to bracing the Ti ions in the neighboring sheets, which results in polar distortions involving only the A$^{2+}$ ions inside their spacious cuboctahedral oxygen cages.

(iii) *What is the influence of uniting the slabs into a three-dimensional RP, or potentially*
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some other structure? Although bulk RP structure is not necessary — as we have shown the existence of appropriate energy landscapes in individual slabs — it actually helps with promoting the polar ground state of the system by ‘pushing up’ (stabilizing) the BZ-boundary structural instabilities that are present in the phonon-band dispersion plots and (although being weaker than the Γ-point instabilities) can still influence the ground state of the slab.

(iv) Is electron lone-pair activity still required for producing Goldstone-like states? Specifically, would it work with Sn\(^{2+}\)? As shown above, both Sn\(^{2+}\) and Pb\(^{2+}\) based ASrTi\(_2\)O\(_7\) slabs display this phenomenon. That strongly indicates that layered structures containing lone-pair active ions in large (e.g., cuboctahedral) anion cages may be generically susceptible to exhibiting Goldstone-like excitations if other competing distortion modes can be suppressed. On the other hand, the same effect was also predicted in a weakly polar BaZr\(_2\)O\(_4\) RP structure subjected to large epitaxial tension (≥ 3.5%) [45], i.e., cases where such behavior can be triggered by purely elastic interactions involving “spectator” (non lone-pair active) ions are also possible.

4.3 Landau-type free energy expression for a layered perovskite from first principles

The DFT-based evaluations of the energetics and directionality of in-plane polar distortions in layered RP-type oxides, e.g., presented in the previous section or done earlier for
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

the PSTO system [44], produced large amounts of data — usually in the form of the system energy landscapes $E(\varepsilon_e, Q_x, Q_y)$, such as the ones shown in Fig. 4.10 (d-f). Here, same as in the figures above, $\varepsilon_e \equiv \varepsilon_{11} = \varepsilon_{22}$ is the biaxial strain, while $Q_x$ and $Q_y$ are the (doubly degenerate) polar distortion amplitudes along the [100] $x$ and [010] $y$ axes, respectively, that can be easily converted into polarization magnitudes $P_i$ with the help of Born effective charge tensors (see Eq. 5.8 below as an example). It is, therefore, tempting to convert this data into a simple Landau-style coarse-grained thermodynamic potential. A first attempt at fitting this DFT procured data for PSTO to a polynomial expansion, symmetry-adapted for the RP $I4/mmm$ aristotype, was made by Lee and coworkers [52] in 2014, with a greatly improved parameterization put forward by Mangeri and coworkers [62] in 2016. The latter expansion is presented and discussed below.

4.3.1 Free energy parameterization for the PSTO system

Since it was already predicted that low-$n$ RP structures cannot support out-of-plane polarization [44, 223], the free energy polynomial expansion included a two component order parameter for the in-plane system polarization ($P_1, P_2$). The expansion also contained simple couplings to biaxial epitaxial strain $\varepsilon_e$ (other strain components were not considered) and in-plane applied electric field ($\varepsilon_1, \varepsilon_2$). The value of the Curie-Weiss temperature $T_0$ ($\sim 120$ K) was estimated from energy differences between the non-polar $I4/mmm$ and polarized $P \parallel [100]$, and $P \parallel [110]$ states of the system. Importantly, both linear and quadratic cou-
plings with \( \varepsilon_e \) had to be retained in the expansion to reproduce the evolution of the system energy landscape, including the slight asymmetry of its sombrero-hat shaped features, under changing strain.

With all of these considerations in mind, the symmetry-adapted quasi-2D free energy expression for PSTO is

\[
f = \alpha_1 (T - T_0) \left( P_{1}^2 + P_{2}^2 \right) + \alpha_2 \left( P_{1}^4 + P_{2}^4 \right) \\
+ \alpha_3 P_{1}^2 P_{2}^2 + \alpha_4 \left( P_{1}^6 + P_{2}^6 \right) + \alpha_5 \left( P_{1}^4 P_{2}^2 + P_{1}^2 P_{2}^4 \right) \\
+ \left( \chi_1 \left( P_{1}^2 + P_{2}^2 \right) + \chi_2 \left( P_{1}^4 + P_{2}^4 \right) + \chi_3 P_{1}^2 P_{2}^2 \right) \varepsilon_e \\
+ \left( \chi_4 \left( P_{1}^2 + P_{2}^2 \right) + \chi_5 \left( P_{1}^4 + P_{2}^4 \right) + \chi_6 P_{1}^2 P_{2}^2 \right) \varepsilon_e^2 - P_1 \delta_1 - P_2 \delta_2,
\]

Table 4.4 presents the parameterized values of the \( \{\alpha\} \) and \( \{\chi\} \) coefficient sets that were obtained using the Ordinary Least Squares fitting algorithm. This parameterization procedure was then adopted and modified to construct LD-type thermodynamic potentials in 3D for “classical” ABO₃ perovskites, including PbTiO₃ and SnTiO₃, directly from first principles, i.e., utilizing as much of the DFT-derived information as possible. That project is discussed in detail in the following chapter.

### 4.3.2 Specific heat evaluation

The developed free energy expression (4.1) was used by Mangeri and collaborators to predictively evaluate the thermodynamic behavior of the PSTO slab system, including its pyroelectric and electrocaloric responses [62]. An important ingredient necessary for this
Table 4.4: Coefficients of the Landau-style free energy expansion $f(\varepsilon, P_1, P_2)$ for PSTO with their determination errors.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>$1.27 \times 10^6$</td>
<td>$(\pm 1.0 \times 10^4)$</td>
<td>J/K m$^3$C$^2$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>$1.76 \times 10^9$</td>
<td>$(\pm 2.5 \times 10^7)$</td>
<td>J/ m$^3$C$^4$</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>$3.73 \times 10^9$</td>
<td>$(\pm 2.83 \times 10^7)$</td>
<td>J/ m$^3$C$^6$</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>$-5.91 \times 10^8$</td>
<td>$(\pm 1.45 \times 10^8)$</td>
<td>J/ m$^3$C$^6$</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>$-6.51 \times 10^8$</td>
<td>$(\pm 1.13 \times 10^8)$</td>
<td>J/ m$^3$C$^6$</td>
</tr>
<tr>
<td>$\chi_1$</td>
<td>$-4.18 \times 10^9$</td>
<td>$(\pm 7.16 \times 10^7)$</td>
<td>J/ m$^3$C$^2$</td>
</tr>
<tr>
<td>$\chi_2$</td>
<td>$-3.69 \times 10^{10}$</td>
<td>$(\pm 1.16 \times 10^9)$</td>
<td>J/ m$^3$C$^4$</td>
</tr>
<tr>
<td>$\chi_3$</td>
<td>$-2.51 \times 10^{11}$</td>
<td>$(\pm 1.48 \times 10^9)$</td>
<td>J/ m$^3$C$^4$</td>
</tr>
<tr>
<td>$\chi_4$</td>
<td>$1.21 \times 10^{11}$</td>
<td>$(\pm 3.44 \times 10^9)$</td>
<td>J/ m$^3$C$^2$</td>
</tr>
<tr>
<td>$\chi_5$</td>
<td>$2.41 \times 10^{12}$</td>
<td>$(\pm 4.77 \times 10^{10})$</td>
<td>J/ m$^3$C$^4$</td>
</tr>
<tr>
<td>$\chi_6$</td>
<td>$6.49 \times 10^{12}$</td>
<td>$(\pm 7.54 \times 10^{10})$</td>
<td>J/ m$^3$C$^4$</td>
</tr>
</tbody>
</table>

Analysis — specifically for the determination of the adiabatic change in the system temperature $\Delta T$ under the influence of varying applied electric field $\varepsilon_i$ — is the system total heat capacity $C(T)$ [224]. As PSTO still is a fictitious material, $C(T)$ also had to be computed from first principles. Here, we demonstrate how $C(T)$ can be obtained from the system vibrational density of states (VDOS) $g(x)$ [225, 226], which in turn can be computed using the DFPT approach implemented in QE, as discussed in Sec. 3.1.2:

$$C(T) = 3R \int_0^{x_{\text{max}}} \left(\frac{x}{k_BT}\right)^2 \frac{e^{x/k_BT}}{(e^{x/k_BT} - 1)^2} g(x) dx,$$

where $x = \hbar \omega$ and $g(x)$ is normalized to unity. In this notation, vibration frequency $\omega = x/\hbar$. The computed PSTO VDOS and $C(T)$ are shown, respectively, in panels (a) and (b) of Fig. 4.17 for values of applied biaxial strain $\varepsilon_e$ ranging from 2% compression to 2% tension.
4. First principles investigation of polar properties of Sn- and Pb-based perovskites

Figure 4.17: (a) Normalized VDOS computed for PSTO (non-polar configuration, space group $I4/mmm$) with the help of QE for $\varepsilon_e = 0, \pm 1, \pm 2\%$. (b) Heat capacity $C(T)$ evaluated for the same strains using VDOS presented in panel (a).
Chapter 5

Landau-Devonshire thermodynamic potentials for perovskite ferroelectrics from first principles

5.1 Introduction and motivations

With the continuing trend toward miniaturization of electronic, electromechanical and other devices, it is imperative to develop capabilities for rapid predictive evaluation and optimization of materials properties at the relevant time- and length-scales. In many cases, the properties of interest are controlled by phenomena occurring on the mesoscale, which spans from 10s of nm to 100s of \( \mu \text{m} \) [227–230]. However, in attempting to elucidate the influence of size, shape, and morphology on ferroelectric behavior, quantitative descriptions of the
phase transformations and properties of perovskite-structured materials tend to become prohibitive in their computational costs. Instead, coarse-grained continuum-based approaches, such as phase-field methods [141], have been successfully used for exploring the behavior of ferroelectric materials and heterostructures at the mesoscale.

At the continuum level, the thermodynamic behavior of ferroelectrics is described by the Landau-Devonshire (LD) theory [84–86], which provides a complete three-dimensional representation of the macroscopic material responses. As the dielectric displacement $D = \epsilon_0 E + P \approx P$ in ferroelectrics, it is usually convenient to take temperature $T$, polarization $P$, and stress $\sigma$ as independent variables. For this choice of variables, the Gibbs free energy thermodynamic potential of the system adopts the following form:

$$\Delta G = \alpha_{ij}(T)P_iP_j + \alpha_{ijkl}P_iP_jP_kP_l + \alpha_{ijklmn}P_iP_jP_kP_lP_mP_n + \ldots$$

$$- Q_{ijkl}P_kP_l - \frac{1}{2} s_{ijkl}P_{ij}P_{kl} + \zeta_{ijkl}(\nabla_i P_j \cdot \nabla_k P_l) - \varepsilon_i P_i,$$

(5.1)

wherein the $\alpha$ parameters are the dielectric stiffness coefficients, $Q$ are the electrostriction constants, $s$ are the elastic compliances, $\zeta$ are the coefficients accompanying the Ginzburg gradient term, and $E$ is the electric field. Here, $i, j, k, l, m, n$ represent three Cartesian directions $x_1, x_2, x_3$. The first three terms on the RHS of Eq. (5.1) comprise the Landau polynomial describing transitions among paraelectric and ferroelectric phases, and the remaining terms represent the electrostrictive coupling energy, elastic energy, gradient energy, and electrostatic energy, respectively. Other choices of independent variables are possible, such as, e.g., temperature, polarization and strain ($\varepsilon$) used in the Helmholtz free energy...
thermodynamic potential.

The non-zero components of the various tensor quantities present in Eq. (5.1) are restricted by the point group symmetry of the cubic ABO$_3$ ($m\overline{3}m$) structure [175] and the Landau polynomial can describe transitions from the paraelectric cubic phase into any of the symmetry-allowed proper ferroelectric phases [231]. The rhombohedral ($3m$) and tetragonal ($4mm$) phases are reproduced when the polynomial is truncated at order four; the orthorhombic ($mm2$) phase when truncated at order six; the three monoclinic ($m$) phases when truncated at order eight; and the triclinic (1) phase when truncated at order twelve [232]. Except when a description of the low-symmetry monoclinic or triclinic phases is needed, it is usually sufficient to consider the conventional truncated 2–4–6 Landau polynomial. Apart from providing for the stabilization of the orthorhombic phase, the inclusion of the sixth-rank terms permits both first- and second-order paraelectric to ferroelectric transitions. The paraelectric to ferroelectric transition is of first order when the quartic term in Eq. (5.1) is less than zero, and of second order when it is greater than zero. The analysis of the free energy becomes more complex, when spatially nonuniform polarization distributions associated with the Ginzburg energy terms are taken into account, or when coupling to other order parameters, such as magnetization and oxygen octahedra rotations, are considered. Nevertheless, LD thermodynamic potential (LDTP) expressions have been developed for a variety of different materials [173].

As a parameterized phenomenological theory, even when truncated at order six, suitable experimental data must be available to determine the Curie and Curie-Weiss temperatures,
the six dielectric stiffnesses, the three electrostriction constants and the three elastic compliance coefficients. All of these parameters can be measured, in principle, by a variety of appropriate experimental methods [85, 142]. However, the main difficulty in obtaining these parameters experimentally is the availability of good quality single crystals. Hence, the development of accurate LDTPs for already known ferroelectric perovskites is not always straightforward as the fidelity of differing parameterization schemes is dependent both on the quality of the samples investigated and the accuracy of the measurements used to characterize them.

These difficulties are exemplified in the case of BiFeO$_3$, an antiferromagnetic ferroelectric multiferroic that is currently being actively investigated. It was identified as a ferroelectric in 1970 [90] and stimulated widespread interest as a magnetoelectric compound in thin film form in 2003 [91]. However, adequate LD-type energy expressions for BiFeO$_3$ became available only in 2017 [92, 93]. Similarly, even for an exhaustively studied material like PbTiO$_3$, for which high-quality crystals are difficult to obtain, there exist multiple sets of LDTP [64, 94–97] and polarization gradient energy [98–101] parameters. In fact, the polarization interaction terms for PbTiO$_3$ have not been directly determined [64] but rather were obtained by fitting the morphotropic phase boundary between the tetragonal and rhombohedral phases of the PbTiO$_3$–PbZrO$_3$ (PZT) phase diagram [96]. Obviously, the development of LDTPs for ‘novel’ or yet to be synthesized compounds presents an even more formidable challenge.

Remarkably, there have so far been very few attempts to utilize first principles methods, e.g., based on density functional theory (DFT), for construction of LDTPs for perovskite
ferroelectrics, or evaluation of other useful parameters, such as the gradient energy coefficients. Very recently, Marton and coworkers introduced a first-principles-based LDTP for BiFeO$_3$ [92]. In earlier work by Hlinka and Marton, a parameterization for the gradient energy coefficients in BaTiO$_3$, based on fitting of soft phonon dispersion curves across the BZ was reported [186]. Also, as already discussed in the previous Chapter, a fully ab initio LD-style potential was constructed for the fictitious layered perovskite PSTO system [44] of the Ruddlesden-Popper type [37, 38], which was shown to possess unusual pyroelectric and electrocaloric properties [62]. In that instance, due to the tetragonal symmetry and quasi-two-dimensional geometry of PSTO, the associated LD-style energy expression is especially simple, involving a combination of a two-component polarization $\mathbf{P} = (P_1, P_2)$ with only one specific type of elastic distortion representing biaxial misfit strain.

In this investigation, we extend the previously reported procedure for fitting the LDTP parameters directly from first principles [62] to the case of a displacive ferroelectric material in three dimensions. We then apply this procedure to the well-studied ferroelectric compound PbTiO$_3$ in order to compare the predictions of the first-principles derived LDTP against those of other potentials constructed from experimental data [64, 94, 96, 97]. After validating the efficacy of the parameterization procedure, a LDTP is developed for the fictitious perovskite SnTiO$_3$, whose electronic and polar properties are throughly described in Sec. 4.1. In the course of this work, some basic questions concerning the development of such methodologies are also addressed: (i) Can all parameters of a typical LDTP be completely and adequately determined from DFT methods, or is there information that must be inferred from other
sources? (ii) When the fitting procedure is established, how quickly can a satisfactory LDTP description be obtained? (iii) How well can such an LDTP reproduce experimentally available data?

For the ferroelectric systems investigated here, only the coupling between dielectric and elastic responses of the system were explicitly considered. However, it is expected that similar parameterization schemes can be devised for coupling to additional order parameters, such as magnetization and octahedral rotations. Of course, the development of more advanced LDTP formulations requires proportionally increased planning and computational efforts, e.g., due to utilization of larger unit cells in the DFT calculations. For example, the LDTP of Marton and coworkers includes 50+ parameters, which necessitated extensive time and preparation to determine adequate fitting procedures for the complex energy landscape of BiFeO$_3$ [92]. Also, although the Ginzburg energy terms were not considered here, it is presumed that the Hlinka-Marton procedure [233] can be applied to evaluate the influence of the polarization gradients on material behavior.

5.2 LDTP parameterization

5.2.1 The free energy expression

A three-dimensional Gibbs LDTP for a ferroelectric system with a cubic parent phase can be written as a polynomial expansion involving three independent variables: temperature $T$, 
polarization $P_i$ and stress $\sigma_i$, i.e.,

$$G = G_0 + G_{\text{bulk}} + G_{\text{elastic}} + G_{\text{str}},$$  \hfill (5.2)

$$G_{\text{bulk}} = \alpha_1[P_1^2 + P_2^2 + P_3^2] + \alpha_{11}[P_1^4 + P_2^4 + P_3^4]$$

$$+ \alpha_{12}[P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2] + \alpha_{111}[P_1^6 + P_2^6 + P_3^6]$$

$$+ \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_3^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)]$$

$$+ \alpha_{123}[P_1^2P_2^2P_3^2];$$

$$G_{\text{elastic}} = -\frac{1}{2}s_{11}[\sigma_1^2 + \sigma_2^2 + \sigma_3^2]$$

$$- s_{12}[\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1] - \frac{1}{2}s_{44}[\sigma_4^2 + \sigma_5^2 + \sigma_6^2];$$

$$G_{\text{str}} = -Q_{11}[\sigma_1P_1^2 + \sigma_2P_2^2 + \sigma_3P_3^2]$$

$$- Q_{12}[\sigma_1(P_2^2 + P_3^2) + \sigma_2(P_3^2 + P_1^2) + \sigma_3(P_1^2 + P_2^2)]$$

$$- Q_{44}[P_2P_3\sigma_4 + P_1P_3\sigma_5 + P_1P_2\sigma_6].$$

Here, $G_0$ is the reference free energy of the parent (aristotype) cubic phase, which could be taken as zero, and $G_{\text{bulk}}, G_{\text{elastic}}$ and $G_{\text{str}}$ are, respectively, bulk, elastic and electrostrictive energy terms. The set of $\{\alpha\}$ parameters in the bulk energy term includes the dielectric stiffness and higher-order stiffness coefficients at constant stress ($\sigma_i = 0$). In general, all of these parameters can be temperature dependent, however, PbTiO$_3$ and similar materials often can be described sufficiently well by making only the quadratic coefficient $\alpha_1$ depend on temperature according to the Curie-Weiss law i.e., as $\alpha_1(T) = \alpha_0^0(T - T_0)$, where $T_0$ is
the Curie-Weiss temperature [173]. We should note that there is no specific reason why this need be the case. If the Landau polynomial is convergent, the temperature-dependent terms play a minor role near the phase transition where the polynomial becomes asymptotically accurate. At lower temperatures, however, these terms may become important, as in the case, for example, of BaTiO$_3$. For materials exhibiting a first-order phase transition, such as bulk PbTiO$_3$ or BaTiO$_3$, the transition temperature $T_t > T_0$ is defined as the temperature where the free energies of the paraelectric and ferroelectric phases are equal [94].

Utilizing PbTiO$_3$ as a test case, we had to determine all — or as many as possible — of the parameters in the expansion for $G$ in Eq. (5.2) directly from DFT simulations. In order to evaluate the accuracy of the developed first-principles-based potential, referred to as FPP1 for PbTiO$_3$ (and FPP2 for the case of SnTiO$_3$), we compared its performance in reproducing the target system properties and behavior to that of four well-known empirical potentials parameterized by:

1. A. Amin et al. (AAM), see Ref. [64]

2. M. J. Haun et al. (MJH), see Ref. [96]

3. G. A. Rossetti et al. (GAR), see Ref. [94]

4. A. A. Heitmann et al. (AAH), see Ref. [97]
Table 5.1: Relations between the direction of the spontaneous polarization $\mathbf{P} = (P_1, P_2, P_3)$ and the symmetry in each of the proper ferroelectric phases. Abbreviations for the symmetries of different polar phases are given in brackets in the middle column. Note that only one out of the three possible monoclinic phases is considered here.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Lattice System</th>
<th>$\mathbf{P} = (P_1, P_2, P_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pm\bar{3}m$</td>
<td>Cubic (000)</td>
<td>$P_1 = P_2 = P_3 = 0$</td>
</tr>
<tr>
<td>$R\bar{3}m$</td>
<td>Trigonal (aaa)</td>
<td>$P_1 = P_2 = P_3 \neq 0$</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>Tetragonal (00c)</td>
<td>$P_1 = P_2 = 0, P_3 \neq 0$</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>Orthorhombic (aa0)</td>
<td>$P_1 = P_2 \neq 0, P_3 = 0$</td>
</tr>
<tr>
<td>$Cm$</td>
<td>Monoclinic (aac)</td>
<td>$P_1 = P_2 \neq 0, P_3 \neq 0$</td>
</tr>
<tr>
<td>$P1$</td>
<td>Arbitrary (abc)</td>
<td>$P_1 \neq P_2 \neq P_3 \neq 0$</td>
</tr>
</tbody>
</table>

5.2.2 The nature of the polar distortion

The first step of the fitting procedure involves determination of the ionic distortion pattern in the (centrosymmetric) parent cubic unit cell that can be associated with the emergence of the spontaneous polarization within the system at $T < T_0$. In displacive ferroelectrics, this distortion pattern can be obtained as an eigenvector of an unstable IR-active phonon mode at the $\Gamma$ point (triply degenerate for $Pm\bar{3}m$ symmetry) that has a ‘polar’ character, which can be identified by the largeness of its plasma frequency [234–237]. Fig. 5.1(a) and (b) show phonon-band BZ dispersions for the centrosymmetric $Pm\bar{3}m$ phases of PbTiO$_3$ and SnTiO$_3$, respectively, both of which exhibit such a polar lattice instability that can be straightforwardly associated with the magnitude of $\mathbf{P}$.

The ground state of the polar system can then be found by distorting the symmetry of the centrosymmetric parent phase, referred as $R(000)$ in what follows (see Table 5.1 for
Figure 5.1: Phonon-band dispersion curves for (a) PbTiO$_3$, and (b) SnTiO$_3$ calculated using DFPT (see Sec. 3.1.2 and 3.1.3) with QE. Imaginary frequencies corresponding to lattice instabilities are represented by negative values. Both compounds have strong polar instabilities at $\Gamma$.

the symmetry abbreviations, which is similar to Table 2.1). This symmetry breaking is accomplished by altering the ionic positions within the parent phase by ‘freezing in’ one (tetragonal symmetry) or a linear combination of multiple (orthorhombic, rhombohedral and monoclinic symmetries) polar mode eigenvectors $\eta^{\Gamma}(\xi, i)$, i.e.,

$$R(abc) = R(000) + \sum_{i=1}^{3} A_i \eta^{\Gamma}(\xi, i). \quad (5.6)$$

Here $R(abc)$ represents an arbitrary polar distortion of the original centrosymmetric system state, $\xi$ is the ion number and $A_i$ are the amplitudes of these distortions — following the ionic displacement motifs set by polar eigenvectors $\eta^{\Gamma}(\xi, i)$ — along the Cartesian axes $x_1, x_2, x_3$. For a number of systems, where ionic displacements corresponding to the polar mode are relatively small (e.g., BaTiO$_3$), Eq. (5.6) with optimized amplitudes $A_i$ may already constitute a very good approximation for the equilibrium ionic positions in the polar phase. However, this is not the case for PbTiO$_3$ and SnTiO$_3$. Since the actual polar ionic
displacements in both of these compounds are very large [24, 221], their phonon eigenvector representations (that do not account for the presence of vibrational anharmonicitites) cannot accurately reproduce the equilibrium structure of the polar phases. In our analysis we found normalized relaxed ionic displacements, obtained by an optimization of the distorted ionic positions and lattice constants to their new equilibrium values under the appropriate symmetry constraints, preferable as representations of the system polar distortions, compared to the usage of the phonon eigenvectors. With this replacement, Eq. (5.6) can be recast as

\[ R(abc) = R(000) + \sum_{i=1}^{3} A_i \tilde{\eta}(\xi, i), \]  

where \( \tilde{\eta}(\xi, i) \) is the normalized vector of the relaxed ionic displacements along the direction \( x_i \).

### 5.2.3 Bulk energy term

Determination of the set of dielectric stiffness coefficients \( \{\alpha\} \) in the bulk energy term \( G_{\text{bulk}} \) is the most computationally intensive part of the LDTP parameterization process. The expression for \( G_{\text{bulk}} \), provided by Eq. (5.3), was fitted on a three-dimensional grid of the normalized relaxed ionic displacement vector amplitudes \( \mathbf{A} = (A_1, A_2, A_3) \) corresponding to the polar distortions of the system, described by Eq. (5.7). The maximum value of \( \mathbf{A} \) was chosen to ensure that the local energy minima for all of the polar phases of interest — i.e., tetragonal, orthorhombic, rhombohedral and monoclinic in the case of PbTiO\(_3\), as shown in Table 5.1 — are sampled. In most cases, (15,15,15) amplitude grids for the positive
octant $A_1, A_2, A_3 \geq 0$ were found to be sufficient for both PbTiO$_3$ and SnTiO$_3$. Grid points corresponding to large values of $|\mathbf{A}| \gg A_i$ were usually dropped from the fitting because of the approximation of Eq. (5.7) for the ionic positions becoming poor for such high-energy system configurations.

In addition to computing the total energy of the polar configuration the system polarization was evaluated as

$$
P_i = A_i \frac{e}{V} \sum_\xi Z^*_{\xi,ii} \hat{\eta}(\xi, i).$$

Here $V$ is the volume of the unit cell, which was obtained for each value of the amplitude $\mathbf{A}$ by relaxing the stress tensor components $\sigma_l$ to less than 0.1 kbar while keeping the ionic positions fixed to preserve the polarization orientation prescribed by Eq. (5.7). Tensor components $Z^*_{\xi,ij}$ are the ionic Born effective charges on ion $\xi$, computed within the DFPT formalism in QE.

Due to the high symmetry of the parent cubic structure, the number of DFT calculations needed to parameterize $G_{\text{bulk}}$ can be reduced from $N^3$ to $N(N+1)(N+2)/2$, where $N$ is the number of points in the amplitude grid along one direction. For the standard DFT codes such as VASP and QE, the average computation time required to conduct the stress tensor components relaxation for each grid point system configuration is approximately 1 hour on a 16-core Intel Xeon E5-2650 node. Therefore, for a modest HPC allocation allowing for 10 such jobs running at the same time, it should take around three days to collect all the data needed for the parameterization. Naturally, as the number and complexity of the coupled
parameters increases, so does the size of the system supercell, as well as, potentially, the distortion amplitude grid density, which should result in substantially longer calculations.

![Graph showing the variation of free energy vs. polarization](image)

**Figure 5.2:** The variation of the free energy of PbTiO$_3$ as a function of its polarization for the tetragonal (00$c$) structural distortion. Energy minima are located at $|P| \approx 0.88$ C/m$^2$. No particular fitting procedure was applied to this data and the line connecting the points is just a guide for the eye.

For example, Fig. 5.2 shows a slice of the collected DFT data, which is the change in the system free energy $G$ as a function of $P_3$ under the tetragonal (00$c$) distortion. Importantly, an unrestricted ordinary least squares (OLS) fitting procedure applied to this data produces a potential with $\alpha_{11} > 0$ that describes a second-order ferroelectric to paraelectric phase transition. Although competing views exist [238], PbTiO$_3$ is typically considered a system that undergoes a strongly first-order phase transition [94–96]. In order to reproduce this feature in the fitted expression for $G_{\text{bulk}}$, we parameterized it using ridge regression (RR)
Table 5.2: FPP1 (PbTiO$_3$) and FPP2 (SnTiO$_3$) Landau polynomial coefficient sets, parameterized from first-principles simulations along with their determination uncertainties. The uncertainties were estimated by iteratively removing one unique data point from the DFT dataset and refitting to collect statistics on the variation of the fit coefficients. Each of the fit coefficient distributions was found to be approximately normal. The presented values of the uncertainties are standard deviations of these distributions listed as percentages. Landau polynomial coefficients obtained with ordinary least squares (OLS) unrestricted fitting procedure are also given for comparison.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1^0$</td>
<td>$10^5 \times J \cdot m/[K \cdot C^2]$</td>
<td>3.751 (0.013%)</td>
<td>5.317</td>
<td>1.601 (0.016%)</td>
<td>2.638</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>$10^7 \times J \cdot m^5/C^4$</td>
<td>-10.65 (0.004%)</td>
<td>13.85</td>
<td>-15.86 (0.010%)</td>
<td>20.50</td>
</tr>
<tr>
<td>$\alpha_{12}$</td>
<td>$10^8 \times J \cdot m^5/C^4$</td>
<td>0.5028 (0.003%)</td>
<td>6.174</td>
<td>2.169 (0.014%)</td>
<td>1.518</td>
</tr>
<tr>
<td>$\alpha_{111}$</td>
<td>$10^8 \times J \cdot m^9/C^6$</td>
<td>2.331 (0.003%)</td>
<td>0.7593</td>
<td>1.320 (0.009%)</td>
<td>0.5171</td>
</tr>
<tr>
<td>$\alpha_{112}$</td>
<td>$10^8 \times J \cdot m^9/C^6$</td>
<td>9.561 (0.008%)</td>
<td>1.125</td>
<td>6.273 (0.020%)</td>
<td>8.530</td>
</tr>
<tr>
<td>$\alpha_{123}$</td>
<td>$10^8 \times J \cdot m^9/C^6$</td>
<td>13.51 (0.002%)</td>
<td>1.567</td>
<td>-2.858 (0.004%)</td>
<td>6.441</td>
</tr>
</tbody>
</table>
while enforcing $\alpha_{11} < 0$. During the fitting, the value of the RR “smoothing parameter” $\alpha$ (not to be confused with the dielectric stiffness coefficients) was optimized iteratively to ensure that the resulting set of the LDTP parameters accurately replicated both the first-order character of the phase transition and the equilibrium DFT energies of all the high symmetry system configurations in Table 5.1. The goodness-of-fit $R^2$ coefficient was close to 99% for the unrestricted OLS fitting, but decreased to $\sim$96% for the RR procedure. The parameters of PbTiO$_3$ and SnTiO$_3$ obtained from both RR and OLS along with individual coefficient determination uncertainties are given in Table 5.2.

### 5.2.4 Elastic energy term

Table 5.3: FPP1 (PbTiO$_3$) and FPP2 (SnTiO$_3$) elastic compliances parameterized from first-principles simulations. The elastic compliances from Ref. [240], determined from experimental measurements are also given from comparison.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Ref [240] (PbTiO$_3$)</th>
<th>FPP1 (PbTiO$_3$)</th>
<th>FPP2 (SnTiO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{11}$ $[10^{-12} \times \text{m}^3/\text{J}]$</td>
<td>8.0</td>
<td>3.485</td>
<td>3.452</td>
</tr>
<tr>
<td>$s_{12}$ $[10^{-12} \times \text{m}^3/\text{J}]$</td>
<td>-2.5</td>
<td>-0.9611</td>
<td>-0.9587</td>
</tr>
<tr>
<td>$s_{44}$ $[10^{-12} \times \text{m}^3/\text{J}]$</td>
<td>9.0</td>
<td>9.301</td>
<td>10.41</td>
</tr>
</tbody>
</table>

Elastic compliances $s_{lm}$ were parameterized following the method described in Ref. [241] by applying distortions to the cubic parent structure unit cell. DFT total energies obtained for the deformed unit cells were fitted as a function of the cell distortion magnitude $\delta$, as
the following strains were applied to them:

\[
\varepsilon_i^H = \delta \begin{pmatrix} 1 & 1 & 1 & 0 & 0 & 0 \end{pmatrix}, \quad \text{(5.9)}
\]

\[
\varepsilon_i^U = \delta \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad \text{(5.10)}
\]

\[
\varepsilon_i^S = \delta \begin{pmatrix} 0 & 0 & 0 & 1 & 1 & 1 \end{pmatrix}. \quad \text{(5.11)}
\]

The total energy expressions corresponding to these unit cell distortions are, respectively

\[
E^H(\delta) = \frac{3}{2}(s_{11} + 2s_{12})\delta^2 + (O_1)\delta^4, \quad \text{(5.12)}
\]

\[
E^U(\delta) = \frac{1}{2}(s_{11})\delta^2 + (O_2)\delta^4, \quad \text{(5.13)}
\]

\[
E^S(\delta) = \frac{3}{2}(s_{44})\delta^2 + (O_2)\delta^4, \quad \text{(5.14)}
\]

which constitutes a system of equations for the determination of all of the elastic compliance coefficients present in \(G_{\text{elastic}}\). (\(O_1\) and \(O_2\) are nonlinear elastic coefficients not used in LDTP parameterization.) Table 5.3 collects the elastic compliance constants fitted for PbTiO\(_3\) and SnTiO\(_3\) from the Eqs. (5.12), (5.13) and (5.14).

We have also computed the elastic stiffness tensor components \(c_{lm}\) using the finite lattice distortion method [242] implemented in VASP. The obtained \(c_{lm}\) values for PbTiO\(_3\) are in good agreement with those reported in other theoretical investigations utilizing the same computational approach [243, 244].
5.2.5 Electrostrictive energy term

Electrostrictive coefficients $Q_{lm}$ were also parameterized following the methodology of Ref. [241]. Strain tensor components $\varepsilon_l$ (obtained from the optimized lattice constants) and the corresponding values of spontaneous polarization $P_i$ were computed for the tetragonal (00c) and orthorhombic (aa0) distortions. In the tetragonal configuration, $\varepsilon_1 = \varepsilon_2 < 0$, $\varepsilon_3 > 0$ and $\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$, while in the orthorhombic configuration, $\varepsilon_1 = \varepsilon_2 > 0$, $\varepsilon_3 < 0$, $\varepsilon_6 > 0$ and $\varepsilon_4 = \varepsilon_5 = 0$. Electrostrictive coefficients $Q_{11}$, $Q_{12}$ and $Q_{44}$ were then fitted from the $\{P_i, \varepsilon_l\}$ data sets using the following equations:

$$\varepsilon_3 = Q_{11}(P_3^2)$$  \hspace{1cm} (5.15)

$$\varepsilon_3 = Q_{12}(P_1^2 + P_2^2)$$  \hspace{1cm} (5.16)

$$\varepsilon_6 = Q_{44}(P_1P_2)$$  \hspace{1cm} (5.17)

Table 5.4 summarizes the electrostrictive coefficients fitted for PbTiO$_3$ from the Eqs. (5.15), (5.16) and (5.17). The values presented in the third column are obtained using the spontaneous polarizations computed at $T = 0$ K, i.e., typical DFT setup. These values, however, are consistently smaller than the respective experimental coefficients that were measured at temperatures greater than 300 K. This underestimation can be partially corrected by rescaling the polarization values from 0 K to 300 K, e.g., by using the data as shown in Fig. 5.3(c) for an appropriate polar system distortion. Temperature corrected $Q_{lm}$ coefficients are presented in the final column of Table 5.4. However, to retain the purity of our computational experiments, for the testing of the produced LDTP parameterization we
utilize the uncorrected $Q_{lm}$ set obtained from the DFT calculations at $T = 0$ K.

Table 5.4: The values of electrostrictive coefficients $Q_{lm}$ for PbTiO$_3$ parameterized from Eqs. (5.15), (5.16) and (5.17). The same coefficients from the MJH set are provided for comparison in the second column. Two sets of the DFT fitted coefficients, computed at $T = 0$ K and rescaled for room temperature values for $P_i$, are shown in the third and fourth columns, respectively. Percentages in parentheses represent deviations of the coefficient values from those of the MJH set.

<table>
<thead>
<tr>
<th></th>
<th>MJH</th>
<th>$T = 0$ K</th>
<th>$T = 300$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{11}$ [m$^4$/C$^2$]</td>
<td>0.0890</td>
<td>0.0592 (33%)</td>
<td>0.0726 (18%)</td>
</tr>
<tr>
<td>$Q_{12}$ [m$^4$/C$^2$]</td>
<td>-0.0260</td>
<td>-0.0115 (56%)</td>
<td>-0.0152 (42%)</td>
</tr>
<tr>
<td>$Q_{44}$ [m$^4$/C$^2$]</td>
<td>0.0675</td>
<td>0.0443 (34%)</td>
<td>0.0585 (13%)</td>
</tr>
</tbody>
</table>

5.2.6 Temperature dependence of the dielectric stiffness

In this investigation, the value of the Curie-Weiss temperature $T_0$ is evaluated from the energy difference $\Delta E$ between the high temperature (000) non-polar parent phase and the stable (stress free) low temperature (00c) polar phase. Although this is indeed a very crude estimate, it is also most easily obtainable from standard DFT calculations for new and yet unsynthesized materials, for which no experimental $T_0$ measurements or advanced statistical data are presumed to be available. In the case of our reference PbTiO$_3$ system, this estimate works surprisingly well, producing the value of $T_0 = \Delta E/K_b = 697$ K, which is 18 to 61 K smaller than the experimentally determined values ranging between 715 and 758 K [94, 96, 245–252]. However, such a good agreement must be treated as a fortunate coincidence, with no expectation of the similar accuracy (e.g., ±10%) for other materials.
Table 5.5: FPP1 (PbTiO$_3$) and FPP2 (SnTiO$_3$) LDTP coefficient sets, parameterized from first-principles simulations. The AAM, MJH, GAR and AAH coefficient sets (for PbTiO$_3$) are also presented for comparison. Since the GAR coefficient set does not include the values of the off-diagonal dielectric stiffnesses $\alpha_{12}$, $\alpha_{112}$ and $\alpha_{123}$, it can only describe the cubic to tetragonal phase transition. For the AAH parameterization, $\alpha'_1(T) = 3.98 \times 10^{-3} (T - T_0)$.

Note that the 6-th order dielectric stiffness coefficients of the AAM potential differ dramatically from those of all other PbTiO$_3$ potentials, including FPP1.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Unit</th>
<th>AAM (PbTiO$_3$)</th>
<th>MJH (PbTiO$_3$)</th>
<th>GAR (PbTiO$_3$)</th>
<th>AAH (PbTiO$_3$)</th>
<th>FPP1 (PbTiO$_3$)</th>
<th>FPP2 (SnTiO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>749.1</td>
<td>751.8</td>
<td>751.5</td>
<td>748.0</td>
<td>697.1</td>
<td>3956.9</td>
</tr>
<tr>
<td>$\alpha'_1$</td>
<td>$10^5 \times J \cdot m/[K \cdot C^2]$</td>
<td>3.77</td>
<td>3.76</td>
<td>4.52</td>
<td>3.98</td>
<td>3.75</td>
<td>1.60</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>$10^7 \times J \cdot m^5/C^4$</td>
<td>-9.24</td>
<td>-7.25</td>
<td>-7.79</td>
<td>-7.20 +$\alpha'_1(T)$</td>
<td>-10.65</td>
<td>-15.86</td>
</tr>
<tr>
<td>$\alpha_{12}$</td>
<td>$10^8 \times J \cdot m^5/C^4$</td>
<td>11.08</td>
<td>7.50</td>
<td>—</td>
<td>3.39</td>
<td>0.50</td>
<td>2.17</td>
</tr>
<tr>
<td>$\alpha_{111}$</td>
<td>$10^8 \times J \cdot m^9/C^6$</td>
<td>3.47</td>
<td>2.61</td>
<td>2.64</td>
<td>2.57</td>
<td>2.33</td>
<td>1.32</td>
</tr>
<tr>
<td>$\alpha_{112}$</td>
<td>$10^9 \times J \cdot m^9/C^6$</td>
<td>60.21</td>
<td>6.10</td>
<td>—</td>
<td>6.95</td>
<td>9.56</td>
<td>6.27</td>
</tr>
<tr>
<td>$\alpha_{123}$</td>
<td>$10^9 \times J \cdot m^9/C^6$</td>
<td>-150.50</td>
<td>-37.00</td>
<td>—</td>
<td>13.13</td>
<td>13.51</td>
<td>-2.86</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>$10^{-2} \times m^4/C^2$</td>
<td>7.40</td>
<td>8.90</td>
<td>8.83</td>
<td>8.40</td>
<td>5.92</td>
<td>6.87</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>$10^{-2} \times m^4/C^2$</td>
<td>-3.60</td>
<td>-2.60</td>
<td>-2.52</td>
<td>-2.50</td>
<td>-1.15</td>
<td>-2.36</td>
</tr>
<tr>
<td>$Q_{44}$</td>
<td>$10^{-2} \times m^4/C^2$</td>
<td>—</td>
<td>6.75</td>
<td>—</td>
<td>3.50</td>
<td>4.43</td>
<td>4.84</td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

The FPP1 (PbTiO$_3$) and FPP2 (SnTiO$_3$) LDTP coefficient sets, parameterized following the procedures described in Sec. 5.2, are assembled in Table 5.5, with the AAM, MJH, GAR and AAH coefficient sets also included for comparison. Remarkably, even a cursory inspection of the FPP1 dielectric stiffness coefficients $\{\alpha\}$ suggests that the resulting form of the expression for the DFT-derived bulk energy term $G_{\text{bulk}}(\mathbf{P})$ must differ appreciably from those of its experimentally fitted counterparts. The only exception is the AAH set, whose coefficients, as well as ratios among them, match those of FPP1 fairly close, with the only large difference being the value of $\alpha_{12}$. In the following subsection, we evaluate the performance of the FPP1 potential in describing the paraelectric to ferroelectric transition and properties of PbTiO$_3$. We demonstrate that despite its superficial differences with the empirical sets this potential produces qualitatively similar results and can potentially be used as an alternative to the AAH and MJH parameterizations.

5.3.1 PbTiO$_3$

The following tests were chosen to evaluate the FPP1 LDTP in reproducing the thermophysical properties in comparison to the experimentally fitted parameterizations: (1) The $(00c) \rightarrow (000)$ phase transition characteristics are related to the diagonal dielectric stiffness components $\alpha_1$, $\alpha_{11}$ and $\alpha_{111}$. The fitting of these coefficients together with $Q_{11}$ and $Q_{12}$ was tested by computing the spontaneous polarization $P_s(T)$, elastic strain $\varepsilon_l(T)$, internal
Table 5.6: Thermophysical properties of PbTiO$_3$ and SnTiO$_3$ obtained from the FPP1 and FPP2 LDTP coefficient sets, respectively, and compared with the same properties derived from the GAR and AAH parameterizations.

<table>
<thead>
<tr>
<th>Property (Temperature)</th>
<th>Notation</th>
<th>Unit</th>
<th>GAR (PbTiO$_3$)</th>
<th>AAH (PbTiO$_3$)</th>
<th>FPP1 (PbTiO$_3$)</th>
<th>FPP2 (SnTiO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie-Weiss temperature</td>
<td>$T_0$</td>
<td>K</td>
<td>751.5</td>
<td>748.0</td>
<td>697.1</td>
<td>3956.9</td>
</tr>
<tr>
<td>Transition temperature</td>
<td>$T_t$</td>
<td>K</td>
<td>764.2</td>
<td>760.8</td>
<td>729.4</td>
<td>4254.6</td>
</tr>
<tr>
<td>Latent heat ($T_t$)</td>
<td>$E_t$</td>
<td>$10^6 \times$ J/m$^3$</td>
<td>51.4</td>
<td>43.3</td>
<td>60.2</td>
<td>409.6</td>
</tr>
<tr>
<td>Curie constant</td>
<td>$C$</td>
<td>$10^5 \times$ K</td>
<td>1.25</td>
<td>1.42</td>
<td>1.50</td>
<td>3.53</td>
</tr>
<tr>
<td>Spontaneous polarization (0 K)</td>
<td>$P_s^0$</td>
<td>C/m$^2$</td>
<td>0.87</td>
<td>0.83</td>
<td>0.89</td>
<td>1.31</td>
</tr>
<tr>
<td>Spontaneous polarization (300 K)</td>
<td>$P_s^{RT}$</td>
<td>C/m$^2$</td>
<td>0.78</td>
<td>0.75</td>
<td>0.80</td>
<td>1.30</td>
</tr>
<tr>
<td>Polarization discontinuity ($T_t$)</td>
<td>$P_t$</td>
<td>C/m$^2$</td>
<td>0.38</td>
<td>0.38</td>
<td>0.48</td>
<td>0.76</td>
</tr>
<tr>
<td>Hydrostatic electrostrictive constant</td>
<td>$Q_h$</td>
<td>$10^{-2} \times$ m$^4$/C$^2$</td>
<td>3.79</td>
<td>3.40</td>
<td>4.01</td>
<td>2.15</td>
</tr>
</tbody>
</table>
energy $E(T)$ and latent heat associated with the cubic to tetragonal phase change, and comparing with the same dependencies derived from the GAR and AAH parameterizations. Comparison with the GAR parameterization was emphasized because its parameters were obtained from the specific heat measurements of the energetics of the $(00c) \rightarrow (000)$ phase transition. Although the GAR parameters were obtained from a polycrystalline sample, a companion study [95] conducted on a single-crystal sample produced closely comparable results. (2) The anisotropies in dielectric susceptibilities $\epsilon_{ij}$ and piezoelectric constants $d_{lm}$ are related to the off-diagonal dielectric stiffness components $\alpha_{12}$, $\alpha_{112}$ and $\alpha_{123}$. The fitting of these coefficients was tested by computing the dielectric and piezoelectric properties of PbTiO$_3$, and comparing them with the results derived from the AAM, MJH and AAH parameterizations. The GAR parameterization was not used here as it does not include any off-diagonal coefficients. (3) Finally, as a trial application of the developed FPP1 LDTP, we generated a biaxial strain-temperature (or Pertsev [121]) phase diagram for the PbTiO$_3$ thin-film and compared its features with the those of the same diagrams produced by some of the experimentally fitted potentials.

5.3.1.1 Paraelectric to ferroelectric transition

Fig. 5.3(a) shows the $T = 0$ K free energy $G(P)$ dependence for bulk (stress free) PbTiO$_3$ produced by the FPP1 potential for the polar structural distortions along the three high-symmetry crystallographic directions: tetragonal $(00c)$, orthorhombic $(aa0)$ and rhombohedral $(aaa)$. The DFT energies and ordering of equilibrium phases are accurately repro-
5. Landau-Devonshire thermodynamic potentials for perovskite ferroelectrics

Figure 5.3: (a) Free energy curves $G(P)$ for the tetragonal (00c), orthorhombic (aa0) and rhombohedral (aaa) polar distortions at $T = 0$ K in bulk PbTiO$_3$ produced by the FPP1 potential. (b) The same $G(P)$ dependence for the tetragonal (00c) polar distortion in bulk PbTiO$_3$ at $T = 710$ K ($T < T_t$), $T = 730$ K ($T \approx T_t$) and $T = 740$ K ($T > T_t$), highlighting the strong first-order character of the transitional behavior exhibited by the FPP1 parameterization. Note that due to the large change in temperature, the energy and polarization scales are different in the (a) and (b) panels. (c) Spontaneous polarization $P_3$ as a function of temperature for the tetragonal (00c) polar distortion in bulk PbTiO$_3$ for the FPP1, AAH and GAR parameterizations, all of which display strong first-order transitional behavior and similar $P_3(T)$ profiles.

Produced by this parameterization, with $G(000) \equiv 0 > G(aaa) = -0.102 > G(aa0) = -0.107 > G(00c) = -0.158$ GJ·m$^{-3}$. In Fig. 5.3(b), a high-temperature FPP1 parameterized $G(P)$ dependence is presented for the tetragonal (00c) distortion in PbTiO$_3$, with energy curves corresponding to the temperature above, at and below $T_t$ highlighting the strongly first-order character of the phase transition. Local energy minima observed in the (aa0) and (aaa) distorted structures remain above those shown for the (00c) distortion as $T$ varies between 0 K and $T_t$. Fig. 5.4 shows the free energy curves produced by the AAM, MJH, GAR and AAH potentials, which are quantitatively similar to the ones displayed in Fig. 5.3(a).

Fig. 5.3(c) plots the spontaneous polarization $P_3$ of the tetragonally distorted PbTiO$_3$
Figure 5.4: Free energy curves $G(P)$ for the tetragonal (00c) polar distortions at $T = 0$ K in bulk PbTiO$_3$ produced by AAM, MJH, GAR, AAH and FPP1 parameterizations. The values of \{$P_s, G_s$\} corresponding to the global minimum range between \{0.785, -0.128\} for AAM and \{0.885, -0.158\} for GAR. Compared to the values obtained by the empirical potentials, FPP1 overestimates $P_s$ by 1.4% to 12.7% and $E_s$ within $\sim$20% error.

Figure 5.5:  (a) Internal energy $E$ of PbTiO$_3$, as computed by FPP1, AAH and GAR, plotted as a function of $T$. The values of the latent heat $E_l$ are given in Table 5.6. (b) The strain tensor components $\varepsilon_1$ are plotted as a function of $T$. As expected in (00c) phase, $\varepsilon_1 = \varepsilon_2 < 0$, $\varepsilon_3 > 0$ and all shear components are zero.
Figure 5.6: (a) Spontaneous polarization $P_3$ as a function of temperature for the tetragonal (00c) polar distortion in bulk PbTiO$_3$ computed by the FPP1, AAM and MJH parameterizations, all of which display strong first-order transitional behavior and similar $P_3(T)$ profiles. (b) Internal energy $E$ of PbTiO$_3$, as computed by the FPP1, AAM and MJH potentials, plotted as a function of $T$. (c) Strain tensor components $\varepsilon_l$ plotted as a function of $T$. As expected in the (00c) phase, $\varepsilon_1 = \varepsilon_2 < 0$, $\varepsilon_3 > 0$ and all shear components are zero.

as a function of $T$ for the FPP1, AAH and GAR coefficient sets. Similar plots for the AAM and MJH sets are shown in Fig. 5.6(a). All three dependencies exhibit equivalent behavior, with the polarization having a discontinuity at $T_t$, which is, again, characteristic of the first-order phase transition. The FPP1 potential produces overall a slightly higher value of the spontaneous polarization (unsurprising, since it is fitted to the properties of a perfect crystal), as well as the larger size of the polarization discontinuity $P_t$, which is approximately 25% bigger, compared with the estimates provided by the GAR and AAH potentials (see Table 5.6). The FPP1 potential also produces the value of $T_t = 729$ K that is only about 5% lower than the one extracted from the AAH and GAR parameterizations (again, see Table 5.6).

Since LDTPs are often used to assess thermophysical and thermodynamic properties of
ferroelectrics, it is instructive to evaluate the internal energy of the system $E$ as a function of $T$, as well as the latent heat of the transition $E_t$, which is the internal energy change at $T = T_t$. The internal energy can be computed from the $G(T)$ as

$$E = T \left( \frac{\partial G}{\partial T} \right)_P - G. \quad (5.18)$$

Fig. 5.5(a) shows the dependence of $E$ on $T$ obtained from the FPP1, AAH and GAR parameterizations. As expected for the first-order phase transition, a discontinuous jump in $E$ is observed for all three potentials in the vicinity of $T = T_t$, with the magnitude of the discontinuity being the latent heat $E_t$ of the transition. The values of $E_t$ computed for all of the potentials are shown in Table 5.6, with the value obtained from the FPP1 parameterization being 13 and 20% higher than the values produced by the GAR and AAH parameterizations, respectively. In comparison, experimentally measured values of $E_t$ for PbTiO$_3$ range from 47 ($\pm$ 5) MJ·m$^{-3}$ for a single crystal [95] to 58 MJ·m$^{-3}$ for a polycrystalline ceramics [94].

Fig. 5.5(b) shows the variation of normal components of $\varepsilon_l$ with $T$ obtained from the FPP1, AAH and GAR parameterizations. Strain component behavior obtained from the AAM and MJH sets is similar to the one presented here and the associated plots are shown in Fig. 5.6(c), together with the derived plot of the PbTiO$_3$ lattice parameter dependence on $T$. As expected for the tetragonal phase, $\varepsilon_1 = \varepsilon_2 < 0$, $\varepsilon_3 > 0$ and all shear components are zero for all of the potentials. The values of the developed strains predicted by the FPP1 potential are lower than those obtained by the AAH and GAR potentials, which can be traced back to the smallness of the $Q_{lm}$ coefficients computed from DFT. The usage of
the temperature corrected $Q_{lm}$ set should significantly improve the agreement between the results produced by the FPP1 and the experimentally fitted potentials.

In general, despite the apparent differences with the experimentally fitted LDTPs, the FPP1 potential correctly captures the main characteristics of the critical transition properties of PbTiO$_3$. In particular, transition temperature $T_t$, polarization discontinuity $P_t$ and the latent heat associated with polarization discontinuity $E_t$ are all quantitatively comparable with the values obtained from the GAR and AAH parameterizations. Furthermore, with the exception of the $\varepsilon(T)$ dependence, the other temperature dependent properties examined here, such as $P(T)$ and $E(T)$, also show good agreement with those produced by the empirical potentials.

5.3.1.2 Dielectric and piezoelectric anisotropy

Here we test the validity of the off-diagonal dielectric stiffness coefficients, $\alpha_{12}$, $\alpha_{112}$ and $\alpha_{123}$ by evaluating the anisotropies in dielectric susceptibility and piezoelectric properties obtained with different LDTPs. Since in the empirical potentials these off-diagonal coefficients were determined without directly measuring the dielectric and piezoelectric anisotropy, comparing these properties allows us to ascertain how well the first-principles derived parameterization reproduces the behavior predicted by the indirect empirical fitting methods previously employed.

Dielectric susceptibility tensor components can be derived from the expression for $G$
Figure 5.7: Non-zero components of the dielectric susceptibility $\epsilon_{ij}$ tensor plotted as a function of temperature for (a) FPP1, (b) AAH and (c) MJH potentials. The in-plane and out-of-plane normal components of $\epsilon_{ij}$ are the same for the high-temperature cubic (000) phase and different in the low-temperature tetragonal (00c) phase. Non-zero components of the piezoelectric charge coefficients $d_{lm}$ plotted as a function of temperature for (d) FPP1, (e) AAH and (f) MJH potentials.

using the relation:

$$\epsilon_{ij} = \left(\epsilon_0 \frac{\partial^2 G}{\partial P_i \partial P_j}\right)^{-1}, \quad (5.19)$$

where $\epsilon_0$ is the dielectric permittivity of free space. The piezoelectric coefficients, $b_{ijk}$ and piezoelectric charge coefficients, $d_{ijk}$ are determined as:

$$b_{ijk} = \frac{\partial^2 G}{\partial P_i \partial \sigma_{jk}}, \quad d_{ijk} = \epsilon_{ij} b_{ijk}. \quad (5.20)$$
Figure 5.8: Non-zero components of the (a) dielectric susceptibility tensor \( \epsilon_{ij} \) and (b) piezoelectric coefficient tensor \( d_{lm} \) plotted as a function of temperature using the AAM potential. The longitudinal and transverse components of \( \epsilon_{ij} \) are the same for the high-temperature cubic (000) phase and different in the low-temperature tetragonal (00c) phase.

The piezoelectric charge coefficients are hereafter referred to as \( d_{lm} \) in Voigt notation [172]. In the (00c) phase, there are only three non-zero components for both \( \epsilon_{ij} \) (\( \epsilon_{11}, \epsilon_{22} \) and \( \epsilon_{33} \)) and \( d_{lm} \) (\( d_{33}, d_{31} \) and \( d_{15} \)). The temperature dependencies for the \( \epsilon_{ii} \) and \( d_{lm} \) tensor components are plotted in Fig. 5.7, with the first, second and third columns of panels corresponding to the results obtained by the FPP1, AAH and MJH potentials, respectively. We observe a qualitative agreement in the behavior of both dielectric susceptibilities and piezoelectric charge coefficients evaluated by all three potentials, with all of the non-zero components diverging in the same fashion in the vicinity of \( T_t \).

As can be seen from the results presented in the second and third columns of Fig. 5.7, the AAH and MJH potentials exhibit close similarities in their piezoelectric responses, while their dielectric responses are quite different at \( T < T_t \). The \( \epsilon_{ii}(T) \) dependencies produced by the
FPP1 potential closely match those of the AAH parameterization. On the other hand, the FPP1 $d_{lm}(T)$ curves show sharper divergence at $T \sim T_t$ for $d_{33}$ and $d_{31}$, and greater variation of $d_{15}$ between 0 K and $T_t$, compared with the dependencies obtained from both empirical potentials. In this case, the usage of the temperature corrected $Q_{lm}$ set also produces better agreement between the FPP1 and empirical potential results, both increasing the values of piezoelectric coefficients and predicting a smoother $T \rightarrow T_t$ transition for the $d_{33}$ and $d_{31}$ dependencies. Finally, we note that the $\epsilon_{ii}(T)$ and $d_{lm}(T)$ curves computed with the AAM potential, shown in Fig. 5.8(a,b), are markedly different from the results produced by all three potentials shown in Fig. 5.7. This deviation may be a consequence of large differences in the values of the 6-th order dielectric stiffness coefficients of the AAM potential, compared to those of all other PbTiO$_3$ potentials, including FPP1 (see Table 5.5).

### 5.3.1.3 A trial application: strain-temperature phase diagram

LDTPs, usually in combination with the gradient energy term, are often used for evaluating the domain structure evolution and phase transitions in a variety of ferroelectric nanostructures subject to different mechanical and electrical boundary conditions [253]. In this section, we explore the FPP1 potential capabilities for predicting phase stability under simple mechanical boundary conditions. For this purpose, a so-called Pertsev phase diagrams [121] were computed for an epitaxial thin film of PbTiO$_3$ utilizing the FPP1 and MJH potentials to identify different phase stability regions and their polarization with respect to changing temperature and applied homogeneous equibiaxial strain $\varepsilon_e \equiv \varepsilon_1 = \varepsilon_2$. 
Figure 5.9: Misfit or equibiaxial epitaxial strain phase diagrams for PbTiO$_3$ thin films obtained from the (a) FPP1 and (b) MJH potentials, following the approach of Pertsev et al. [121]. The epitaxial strain $\varepsilon_e \equiv \varepsilon_1 = \varepsilon_2$ is plotted along the horizontal axis, with negative and positive values representing compressive and tensile strains, respectively, while temperature is plotted along the vertical axis. The magnitude of the polarization $|P|$ in both diagrams is represented by the color shading, with the color bar for the polarization values shown on the right.

Following the approach of Pertsev and coworkers, the thermodynamic potential describing an epitaxially clamped thin film can be obtained by the Legendre transformation of the ‘standard’ potential $G(T)$ as

$$\tilde{G} = G + \sum_{m=1}^{6} \varepsilon_m \sigma_m,$$

which is subject to the following boundary conditions: (i) Commensurate interface between the film and the substrate, $\varepsilon_1 = \varepsilon_2 = \varepsilon_e$, with no shear strain, $\varepsilon_6 = 0$; (ii) The film can relax to a stress-free state along its growth direction, $\sigma_3 = 0$; (iii) Shear deformations perpendicular to the film plane are also allowed, $\sigma_4 = \sigma_5 = 0$. Pertsev et al. showed that
Figure 5.10: Equibiaxial epitaxial strain vs. temperature phase diagram for PbTiO$_3$ thin film obtained from the AAH potential following the approach of Pertsev et al. [121]. The epitaxial strain $\varepsilon_e \equiv \varepsilon_1 = \varepsilon_2$ is plotted along the horizontal axis, with negative and positive values representing compressive and tensile strains, respectively, while temperature is plotted along the vertical axis. The magnitude of the polarization $|P|$ is represented by the color shading, with the color bar for the polarization values shown on the right.

such ‘2D-clamping’ mechanical boundary conditions result in renormalization of the second- and fourth-order dielectric stiffness coefficients $\{\alpha\}$ (see Ref. [121] for more details).

Fig. 5.9 shows the Pertsev phase diagrams computed from the FPP1 and MJH parameterizations, with the latter reproducing the original result of Ref. [121]. We can claim that the FPP1 potential closely replicates the main topological features of the original phase diagram. The perceived discrepancies are subtle and involve, e.g., different widths of the monoclinic ($aac$) regions at low temperatures, as well as slightly different shapes of the
tetragonal-monoclinic and monoclinic-orthorhombic phase boundaries. The Pertsev phase diagram obtained from the AAH potential is shown in Fig. 5.10 and also shows small variations in the location of the phase boundaries, as compared with both diagrams presented in Fig. 5.9.

In conclusion, the presented test results, encompassing not only the quantitative comparison of phase transition characteristics, such as $P_t$ and $E_t$, but also the qualitative comparison of the dielectric and piezoelectric responses, suggest that the developed DFT-based LDTP coefficient fitting procedure is robust for the case of a displacive ferroelectric material that is described by one primary (vectorial) order parameter. As a trial application of the DFT-based LDTP, we constructed a strain-temperature phase diagram for the epitaxially clamped PbTiO$_3$ thin film, whose topological features are in close agreement with the results of previous work [121], that are also reproduced here.

5.3.2 SnTiO$_3$

The FPP2 LDTP coefficient set for SnTiO$_3$, obtained by utilizing the same methodology as described in Sec. 5.2, is presented in the last column of Table 5.5, while some of the derived properties are shown in the last column of Table 5.6. As with PbTiO$_3$, a first-order paraelectric to ferroelectric phase transition was imposed for SnTiO$_3$ during the coefficient fitting procedure. Due to the much larger amplitude of the (00c) polar distortion and the associated value of stabilization energy $\Delta E$ in stress-free SnTiO$_3$, compared to those of
PbTiO$_3$, the former compound is perceived to be supertetragonal in its pure form [24, 221]. It is nonetheless possible to produce solid solutions incorporating perovskite SnTiO$_3$ phases that exhibit ferroelectric switching, as suggested in a recent experimental study involving both A- and B-site Sn-doped SrTiO$_3$ [28].

Since the value of $\Delta E$ for SnTiO$_3$ is $\sim$6 times greater than that of PbTiO$_3$, the simple estimate of its Curie temperature results in $T_0 = 3957$ K. This unphysically large temperature is most probably higher than the melting temperature $T_m$ of SnTiO$_3$, as for generic perovskite oxides such temperatures range from 1000 to 3000 K [254, 255]. For example, $T_m$ of BaTiO$_3$ is 1891 K [255], while $T_m$ of SrTiO$_3$ is 2313 K [254]. Therefore, in this regard, SnTiO$_3$ is similar to polyvinylidene fluoride (PVDF), which is a well-known polymer ferroelectric that melts before reaching its $T_0$ [256–258].

Fig. 5.11 presents the temperature dependence of the spontaneous polarization $P_3$ and internal energy $E$ for the tetragonal (00$c$) phase of SnTiO$_3$ obtained with the FPP2 parameterization, i.e., the same data as shown for PbTiO$_3$ in Figs. 5.3(c) and 5.5(a). Other information for SnTiO$_3$, such as the free energy $G(P)$ curves, thermal variation of the dielectric susceptibility and piezoelectric tensor components, are shown in Fig. 5.12.

Fig. 5.13(a) displays the (Pertsev) phase diagram of SnTiO$_3$ with respect to changing $\varepsilon_e$ and $T$. Apart from the already discussed much higher thermal stability of SnTiO$_3$, which makes the upper part of the diagram unphysical, its main topological features are quite similar to those exhibited by PbTiO$_3$, as shown in Fig. 5.9. The main difference in the transitional behavior of the two compounds is in the much wider region of stability of the
Figure 5.11: Temperature dependence of the spontaneous polarization $P_3$ (left vertical axis, solid line) and internal energy $E$ (right vertical axis, dashed line) for the tetragonal ($00c$) phase of SnTiO$_3$ obtained with the FPP2 parameterization. A strong first-order character of the phase transition is prominent at $T_t = 4255$ K.

Figure 5.12: (a) Free energy curves $G(P)$ for the tetragonal ($00c$), orthorhombic ($aa0$) and rhombohedral ($aaa$) polar distortions at $T = 0$ K in bulk SnTiO$_3$, as produced by the FPP2 potential. Non-zero components of the (b) dielectric susceptibility tensor $\epsilon_{ij}$ and (c) piezoelectric coefficient tensor $d_{lm}$ plotted as a function of temperature using the FPP2 potential. Longitudinal and transverse components of $\epsilon_{ij}$ are the same for the high-temperature cubic (000) phase and different in the low-temperature tetragonal ($00c$) phase.
Figure 5.13:  (a) Pertsev phase diagram for the SnTiO₃ thin film system obtained with the FPP2 parameterization. The data plotting conventions are the same as in Fig. 5.9. With the exception of the much higher thermal stability of SnTiO₃, compared to the PbTiO₃ system, the main topological distinction of this phase diagram is in the much wider region of stability of the monoclinic (aac) phase, which is dominating at low temperatures for all reasonable epitaxial tensile strains. (b) The variation of the azimuthal angle $\phi$ between the direction of the polarization vector $\mathbf{P}$ and the orthorhombic (aa0) direction in the $x_1x_2$ plane of the ABO₃ unit cell as a function of $\varepsilon_e$, computed with the FPP1 and FPP2 potentials. The unit cell schematic including Cartesian directions $x_1, x_2, x_3$ is shown in the insert. The $\phi(\varepsilon_e)$ dependence is obtained from the LDTP parameterizations developed in this work and illustrates the polarization rotation in both PbTiO₃ and SnTiO₃ from the tetragonal (00c) phase to the orthorhombic (aa0) phase through the intermediate monoclinic (aac) phase at the increasing tensile strain. DFT data for SnTiO₃, originating from Refs. [24] and [221], is also shown for comparison.
monoclinic \((aac)\) phase exhibited by SnTiO$_3$. For PbTiO$_3$, the \((aac)\) phase can be loosely regarded as a boundary region between the tetragonal \((00c)\) and orthorhombic \((aa0)\) phases. For SnTiO$_3$, the \((aac)\) phase dominates at low temperatures, completely displacing the \((aa0)\) phase for all reasonable epitaxial tensile strains. The origins of this behavior can be traced to distinct spatial orientations of the lone-pair charge cloud within the cuboctahedral oxygen cage around the \(A^{2+}\) cation in PbTiO$_3$ and SnTiO$_3$, as elucidated in detail in our previous investigation [221].

In Fig. 5.13(b) we plot the variation of the azimuthal angle \(\phi\) between the direction of \(\mathbf{P}\) and the orthorhombic \((aa0)\) direction in the \(x_1x_2\) plane of the ABO$_3$ unit cell as a function of \(\varepsilon_e\) for PbTiO$_3$ and SnTiO$_3$. For both compounds, an abrupt change in \(\phi\) is detected [see top left corner of the plot] for the \((00c) \rightarrow (aac)\) phase transition, pointing to its first-order character. Following that, the \(\mathbf{P}\) vector rotates gradually towards the \(x_1x_2\) plane at increasing tensile strains. For PbTiO$_3$, the next, second order \((aac) \rightarrow (aa0)\) phase transition is observed for \(\varepsilon_e \leq 2\%\). On the other hand, for SnTiO$_3$, the \((aac)\) phase persists, with \(\mathbf{P}\) showing no indication for ‘falling into the plane’ at \(\varepsilon_e \simeq 2\%\). DFT computed \(\phi(\varepsilon_e)\) dependence for SnTiO$_3$ (originating from our previous investigations that utilized a slightly different computational setup [24, 221]) is also shown in Fig. 5.13(b) and demonstrates a close resemblance with the curve produced by the FPP2 parameterization.
5.4 Conclusions

We have developed a DFT-based approach for fitting of LDTP expressions directly from first principles for displacive ferroelectric materials whose behavior can be described by one primary vectorial order parameter. This procedure emphasizes utility and minimization of the involved computational costs, by employing only standard calculations that can be done conveniently and quickly in most DFT-based setups. In turn, this allows one to roughly map out phase diagrams of new or even fictitious polar compounds, for which experimental data may be slim or even completely unavailable. The natural drawback of the described approach is the lack of accuracy in determination of the system transition temperatures and temperature-dependent properties, which are notoriously hard to evaluate with standard DFT techniques. However, this aspect of the LDTP construction can be consistently improved by using more advanced computational approaches [259–262] and by considering more elaborate dependencies of the LDTP coefficients on temperature, e.g., if they are warranted by the nature of phase transitions exhibited by the material.

In addition to the knowledge of transition temperatures — which may be more or less accurately evaluated computationally, or obtained from experiments — the only other important piece of \textit{a priori} information for the LDTP fitting is the nature, or order, of the paraelectric to ferroelectric phase transformation. An unrestricted sampling of different structural configurations results in thermodynamic potentials whose polarization is smoothly varying between the polar and non-polar phases, which is representative of a second-order
transitional behavior. In this investigation, the desired transformation order was imposed by utilization of ridge regression (i.e., a form of machine learning) with the iteratively determined regularization parameter $\alpha$, however, a different regression analysis method, such as, e.g., LASSO [263], may also be useful for the same purpose.

We evaluated the performance of the DFT-based LDTP created for the test case of PbTiO$_3$, revealing that it can reasonably reproduce not only the thermodynamic characteristics of the phase transition, but also the dielectric and piezoelectric responses, as well as strain-temperature phase diagrams, as compared with the results obtained with the experimentally parameterized polynomials [64, 94, 96, 97]. It must be pointed out that such close resemblance between the output of the ab initio fitted and empirical potentials may be a fortunate coincidence for PbTiO$_3$, since the crude estimate of its $T_0$, based on DFT energy differences, falls very close to the experimentally determined values. Finally, we generated a DFT-based LDTP for a fictitious lead-free polar perovskite SnTiO$_3$ to illustrate the utility of the developed technique for mapping out the properties and/or phase diagrams of yet to be synthesized materials.

Although both compounds considered here display only one phase transformation between paraelectric and ferroelectric states, described by a single (proper) order parameter, we believe that similar fitting schemes for more complex systems incorporating additional transitions and more elaborate couplings with extra order parameters can also be developed — naturally, at the expense of the appropriately increased computational cost.
Chapter 6

Metastable vortex-like polarization textures in ferroelectric nanoparticles

6.1 Introduction and motivations

Transformative advances in ferroelectric nanoparticle synthesis, with demonstrated ability to control both shape and size, can pave the way to a new generation of highly tunable electroactive composite materials. In the recent pioneering work of Caruntu and collaborators, spherical and cubic particles were grown, with the latter having either sharp or bevelled edges [65]. Understanding and controlling the collective behavior of both ordered and disordered assemblies of such particles, embedded into a variety of dielectric environments [66–72], is paramount for engineering of advanced functional properties, not present in the bulk or other nanoscopic phases (e.g., thin films) of the parent ferroelectric compounds.
For example, BaTiO$_3$ nanoparticles dispersed in parylene exhibit superparaelectric behavior [66] that could be exploited for energy storage applications, while their ordered superlattices display radically different hysteretic switching patterns depending on the size and packing order [67].

Another critical problem for potential applications of ferroelectrics that can be resolved by utilization of nanocomposites is high dielectric loss [73]. Mitigating its negative effects and thereby greatly improving the performance of a wide range of different devices — including non-volatile memories [74–77], pyroelectric IR detectors, electrocaloric waste heat recovery systems [78], piezoelectric sensors, actuators, resonators [79–81], and tunable telecommunication arrays [82, 83] — can be readily accomplished by embedding ferroelectric components in the low-loss dielectric media. For example, finite element analysis combined with Landau theory of phase transformations suggests that a relatively large dielectric response and a considerable dielectric tunability can be obtained in spherical ferroelectric particle reinforced linear-dielectric matrix composites for the ferroelectric component volume fraction as low as 27% [264, 265].

Even the properties of individual ferroelectric particles have been characterized experimentally with piezoforce microscopy [266] and Raman spectroscopy [65], uncovering the persistence of polar ordering down to a size of 5 nm. Other experimental techniques, including high resolution transmission electron microscopy (HR TEM) [266–268], atomic force microscopy [269] and Bragg coherent diffractive imaging [270] have also proven to be revealing for visualization of complex topological configurations of polarization fields that can
emerge in such particles. In particular, elucidating the applied electric field response and switching behavior of vortex-like polarization-closure patterns in ferroelectric nanostructures would be vital for their potential applications as memory elements for new paradigms in computer architecture design [271, 272]. Since these patterns are not true topological vortices, we use a ‘-like’ suffix to describe them. The significant interest in understanding the intrinsic properties of ferroelectric nanostructures embedded in a dielectric medium has produced a number of theoretical investigations aimed at unraveling the influence of size effects in these systems [102, 273–275]. For example, a recent study of Mangeri and coworkers focused on elucidating the details of size dependent topological phase transformations in spherical ferroelectric nanoparticles immersed in linear dielectric media [102]. The obtained results revealed that a high-permittivity matrix can accommodate the uncompensated electric charges on the surface of the particle, supporting the existence of a monodomain polar ordering within it down to the size of a few nm in diameter. At larger particle sizes, the polar ordering was found to evolve from the monodomain to a vortex-like and then to a polydomain texture, thus reducing the electrostatic and polarization-gradient contributions to the system energy. Such dramatic changes in equilibrium polarization topology with particle diameter produced radically different polarization vs electric field responses and highly tunable size-dependent dielectric properties that should be possible to observe experimentally.

Although the existence of vortex-like states in ferroelectric nanostructures, such as nanodots and nanowires, is well known [53], up until recently the shapes of these structures were limited to simple rectilinear, cylindrical, or spherical geometries. However, as pre-
presented below, utilization of more elaborate nanoparticle shapes involving changing curvature and sharp geometrical features can result in distinctive new modes of functional behavior that may be particularly easy to control with external means. In this work, utilizing finite element-based simulations combined with a three-dimensional time-dependent Landau-Ginzburg-Devonshire (LGD) approach, we investigate the dependence of the emerging polarization textures on both particle size and shape for the superellipsoidal (SE) family of shapes [276–278] that can be smoothly transformed from an octahedron to a sphere and then to a cube through a continuous variation of a single parameter. In addition to the two primary octahedral and cubic shapes, and the previously considered spherical shape [102], we introduce two intermediate shapes, called in what follows near-octahedron and near-cube, and use perovskite PbTiO$_3$ and SrTiO$_3$ as representative materials for the ferroelectric nanoparticle and surrounding dielectric medium, respectively.

We show that the general trend of transformations from monodomain, through vortex-like, to multidomain polarization texture holds for all of the particle shapes as the size increases. However, the critical sizes at which the polarization pattern instabilities develop are strongly shape dependent, with octahedral particles undergoing their sequence of transitions at much larger sizes, compared to the spherical and cubic particles. Unexpectedly, we also discovered that due to the greatly reduced symmetry (compared to that of a sphere) of all of the particle shapes considered here, it is possible to stabilize their vortex-like polarization textures in a variety of different configurations. Specifically, the cylindrical cores — which are either paraelectric, or have greatly diminished polarization [102] — of the vortex-like tex-
tures can be aligned with each of the rotational axes belonging to the point symmetry group describing the particle shape. If a convenient procedure for switching among the different vortex core orientations can be developed, such nanoparticles could be useful for a variety of advanced electronic and electromechanical applications, including memory elements, sensors and energy storage, and harvesting devices.

### 6.2 Computational methods

#### 6.2.1 Geometrical models

SE family shapes, including those considered in this study, are described by the following general equation:

$$\left| \frac{x}{R} \right|^t + \left| \frac{y}{R} \right|^t + \left| \frac{z}{R} \right|^t \leq 1,$$

where parameters $R$ and $t$, both positive real numbers, control the particle size (semi-diameter) and shape, respectively. Specific particle geometries utilized in this investigation are shown in Fig. 6.1, while their parameters and relevant abbreviations are aggregated in Table 6.1.

As shown in Table 6.1, the major separation in particle shapes happens at $t = 2$ (sphere). For smaller $t$, octahedral shapes are produced by Eq. (6.1), while for larger $t$, cubic shapes are obtained, with $t \to \infty$ being the limiting case of a perfect cube. The volume $V_{SE}$ of the
SE solids scales as $R^3$:

$$V_{SE} = \kappa R^3,$$

(6.2)

where the scaling factor $\kappa$ depends on the parameter $t$.

Figure 6.1: Superellipsoidal particle shapes considered in this investigation shown as solid (top row panels a-e) and meshed (bottom row panels f-j) block geometries. Orientations of the primary coordinate axes $x, y, z$, coincident with the directions of the four-fold rotational symmetry axes in each nonspherical particle shape, are also presented as an insert.

Table 6.1: Names, abbreviations, shape parameter $t$ and volume scaling factor $\kappa$ for all of the SE particle geometries used in this investigation. Both $t$ and $\kappa$ are unitless. References to the panels of Fig. 6.1 showing specific geometry sketches are assembled in the last column.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>$t$</th>
<th>$\kappa$</th>
<th>Fig. 6.1 panel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedron</td>
<td>OC</td>
<td>1</td>
<td>4/3</td>
<td>(a, f)</td>
</tr>
<tr>
<td>Near octahedron</td>
<td>NO</td>
<td>1.5</td>
<td>3.3347</td>
<td>(b, g)</td>
</tr>
<tr>
<td>Sphere</td>
<td>SP</td>
<td>2</td>
<td>4\pi/3</td>
<td>(c, h)</td>
</tr>
<tr>
<td>Near cube</td>
<td>NC</td>
<td>10</td>
<td>7.5245</td>
<td>(d, i)</td>
</tr>
<tr>
<td>Cube</td>
<td>CU</td>
<td>$\infty$</td>
<td>8</td>
<td>(e, j)</td>
</tr>
</tbody>
</table>
Simple geometries, such as OC, SP and CU, can be created directly and then meshed using typical computer-aided design (CAD) tools and standard mesh generation libraries. On the other hand, ‘intermediate’ NO and NC geometries shown in Fig. 6.1(b) and 6.1(d) require special attention, because their complex external surfaces include combinations of flat and curved faces. The initial models for these shapes were created in MATHEMATICA [279] in the stereolithography (STL) file format and processed with the Design Modeler tool in ANSYS [280], and exported in the STP file format. The STP files were meshed with TRELIS [281] package using an unstructured grid of tetrahedrons (TetMesh). The geometrical models for the simple shapes were made in TRELIS directly and meshed using the same procedure. The finite-element mesh spacing was chosen to ensure sufficient resolution and convergence of the elastic and polar fields within and at the surface of the structural block representing the particle geometry. The unstructured mesh size for the ferroelectric subdomain is chosen such that there are approximately $2 - 5$ elements across the domain wall length scale. Outside of the inclusion, such spatial resolution is not needed, and the mesh is allowed to coarsen with increasing distance from the inclusion surface to improve computational efficiency. The ratio of the coarse boundary mesh size to the inclusion mesh size is usually kept fixed throughout the calculations. Typical meshes obtained for various shapes are shown in Fig. 6.1(f-j).

The finite-element models utilized here consisted of the ferroelectric inclusion of the SE shape embedded in a dielectric-medium cube of the volume $V_M$ that was also meshed using an unstructured grid of tetrahedrons. The interface between the inclusion and the matrix was assumed to be coherent. The Cartesian reference system axes $X, Y, Z$ were associated with
Figure 6.2: Schematics of the alignment among the Cartesian reference system $X, Y, Z$ (associated with the dielectric medium cube $V_M$), the primary particle shape axes $x, y, z$ and the tetragonal $P4mm$ PbTiO$_3$ crystallographic directions $a, b, c$. Orientations of the primary axes $x, y, z$ are aligned with the directions of the four-fold rotational symmetry axes of the particle shape. Sketches for the (top left) OC and (top right) CU shapes are shown, as well as (bottom) an expanded view of the PbTiO$_3$ crystal at atomic scale, consisting of periodically repeated 5-atom unit cells.
the edges of the dielectric-medium cube $V_M$. The primary axes $x, y, z$ for each ferroelectric particle shape, as shown in the insert to Fig. 6.1, were aligned with the $X, Y, Z$ coordinate system. Fig. 6.2 schematically shows this alignment for octahedral and cube shaped particles. In turn, the crystallographic directions $a, b, c$ of the tetragonal perovskite PbTiO$_3$ phase were chosen to be collinear with the $x, y, z$ axes (again, see Fig. 6.2). In general, other orientations of the crystallographic axes ($a', b', c'$) with respect to the ferroelectric inclusion geometrical features may be possible, but these were not probed in this investigation.

Below we briefly summarize the thermodynamic considerations and computational approach utilized for simulating the properties of the superellipsoidal ferroelectric inclusions embedded in the linear dielectric-elastic medium. More specific details of the involved methodology are covered in Sec. 3.2.2. Computational domain of the problem is split into two volumes: volume $V_{SE}$ of the inclusion at the center of a cube volume $V_M$ representing the surrounding dielectric matrix. The outer bounding surfaces of the $V_M$ volume are denoted $\partial V_M$, while the surface of the inclusion volume $V_{SE}$ is denoted $\partial V_{SE}$. We assume a coherent interface between the inclusion and outside medium. Sketches of ferroelectric inclusion $V_{SE}$ orientation with the dielectric matrix volume $V_M$ are shown in Fig. 6.2 for the OC and CU particle shapes.
6.2.2 System energy

The free energy $F$ of the ferroelectric inclusion $V_{SE}$ surrounded by the dielectric matrix $V_M$ in three dimensions (3D) can be described by an LGD thermodynamic potential depending on the position-dependent polarization density, electrostatic potential and elastic displacement fields $P$, $\Phi$ and $u$ (boldface font marks vector fields):

$$F = \int_{V_{SE}} [f_{\text{bulk}} + f_{\text{wall}} + f_{\text{elastic}} + f_{\text{elec}} + f_{\text{coupled}}] d^3r.$$  \hspace{1cm} (6.3)

Here, $f_{\text{bulk}}$ is the bulk ferroelectric energy density, $f_{\text{wall}}$ is the energy density that arises from local gradients in $P$, $f_{\text{elastic}}$ is the linear elastic energy density, $f_{\text{coupled}}$ is the energy density of electrostrictive coupling between the ferroelectric polarization density and the strain, and $f_{\text{elec}}$ is the electrostatic energy density. Detailed expressions for all of the free-energy densities are provided in Sec. 3.2.2.

Perovskite PbTiO$_3$, exhibiting high spontaneous polarization at room temperature, $P_s \simeq 0.75 \text{ C/m}^2$, was chosen as the ferroelectric material in the SE inclusion. Isotropic and linear elastic SrTiO$_3$ was used as a matrix material of high dielectric strength ($\epsilon_m = 300$) enveloping the inclusion. The values of all of the materials parameters for PbTiO$_3$ and SrTiO$_3$ used in this investigation are listed in Tables 3.2 and 3.3. The parameters of PbTiO$_3$ used in this study are from MJH LDTP (see Sec. 5.2).
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6.2.3 Energy minimization

The minimization of the ferroelectric-dielectric system free energy can be accomplished with the help of the gradient-flow approach that propagates the set of system variables \( \{P_i, u_i, \Phi\} \) in time towards an equilibrium state by dissipating the energy out of the system until it reaches a local minimum. The evolution of the polarization density field \( \mathbf{P}(\mathbf{r}) \) is governed by the time-dependent LGD equation (TDLGD)

\[
- \gamma \frac{\partial \mathbf{P}}{\partial t} = \frac{\delta}{\delta \mathbf{P}} F(\mathbf{P}),
\]

where \( \delta/\delta \mathbf{P} \) denotes the variational derivative with respect to polarization. The time constant \( \gamma \) is related to domain-wall mobility [184, 282], and was set to unity in this investigation, as we were interested not in the temporal evolution of the system, but rather in its final (local) equilibrium state. As an initial condition on the \( \mathbf{P}(\mathbf{r}) \) field, a random distribution \( \langle \mathbf{P} \rangle \approx 0 \) was adopted for all of the SE particle shapes and sizes. The utilization of this condition ensures no initial bias or accidental symmetry that may constrain the time evolution path of the system [98, 99]. Outside the ferroelectric inclusion, \( \mathbf{P} \equiv 0 \), and the behavior of the matrix is governed by the equations for the linear elastic-dielectric medium.

On each step in the system time evolution following Eq. (6.4), coupled auxiliary mechanical (stress-divergence) equation

\[
\frac{\partial}{\partial x_j} C_{ijkl} (\varepsilon_{kl} - Q_{klmn} P_m P_n) = 0,
\]
and electrostatic (Poisson) equation

\[
\frac{\partial}{\partial x_k} \left( \epsilon_\alpha \frac{\partial \Phi}{\partial x_k} \right) = \frac{\partial P_i}{\partial x_i}, \tag{6.6}
\]

have to be solved for both the ferroelectric inclusion and the dielectric matrix computational domains, which is equivalent to an assumption that characteristic relaxation times for the \(\Phi\) and \(u\) fields are much shorter than that of the \(P\) field. Here, \(i, j, k, l, m, n\) represent three Cartesian directions \(x_1, x_2, x_3\). \(C_{ijkl}\) and \(Q_{ijkl}\) are the elastic stiffness and electrostrictive tensor components, respectively, while \(\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)\) is the elastic strain tensor. \(\epsilon_\alpha\) is either the background permittivity [186] of PbTiO\(_3\) (\(\alpha = b\)) in the ferroelectric inclusion, or the dielectric permittivity of the SrTiO\(_3\) matrix (\(\alpha = m\)).

The coupled system of Eqs. (6.4), (6.5) and (6.6) can be solved in 3D utilizing a general real-space finite-element approach, which is particularly well-suited for the studies of complex systems at mesoscale, i.e., for characteristic lengths that range from few nm to few microns, i.e., for system sizes that cannot be evaluated with atomistic techniques. All the numerical simulations presented here were done with the Ferret package [180], which is based on the Multiphysics Object-Oriented Simulation Environment (MOOSE) framework [181]. All of the governing Eqs. (6.4–6.6) were first separated into their respective material domains and then cast into their weak-form representations suitable for the application of Galerkin’s finite element method. System (Dirichlet) boundary conditions were chosen such that both the elastic displacement field \(u\) and the electrostatic potential \(\Phi\) vanish sufficiently far away from the inclusion.
All calculations presented here were done at room temperature (RT). Further details of the computational methods are presented in the Sec. 3.2.2. For all inclusion shapes and sizes, the total free energy of the system, including both ferroelectric and dielectric components, was considered to be converged when its relative change between consecutive time steps during the evolution of Eq. (6.4) was below 0.1% and the relative residual norm was less than $10^{-7}$. We should also note that contributions from fringing strain fields within the dielectric at the inclusion-matrix interface were found to be small relative to the energy terms in Eq. (6.3) regardless of the particle size, shape, or the topology of its polarization texture.

### 6.3 Size-dependent transitions for different shapes

In this section, we discuss the evolution of the polarization texture $\mathbf{P}(\mathbf{r})$ as a function of size, or semi-diameter $R$, in nanoparticles of different shapes. Fig. 6.3 aggregates representative results of these studies, showing variation of $\mathbf{P}(\mathbf{r})$ in each of the four SE shapes (one row per shape) with increasing $R$. From the top to bottom row, OC, NO, NC and CU particle shapes are presented. Specific values of $R$ are marked out for each nanoparticle / figure panel, as $R$ increases from left to right. As predicted in the previous investigation [102] for spherical PbTiO$_3$ nanoparticles in the SrTiO$_3$ matrix, for each of the shapes considered here the same sequence of the polarization texture transformations is observed: monodomain to vortex-like to multidomain. At small $R$, the nanoparticle cannot support the existence of
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any domain walls and thus a monodomain polar state is found. As shown in Fig. 6.3(a),
(d), (g) and (j), the polarization magnitude in such configurations is diminished roughly by
50%, compared to the RT $P_s$ of bulk PbTiO$_3$, but no paraelectric states are obtained for
any of the shapes. However, paraelectric states are likely to develop for weaker dielectric
media [102] because of minimization of the polarization and polarizability mismatch across
the particle-matrix interface.

At the increased value of $R$, the polarization texture transforms from the monodomain
to a vortex-like state that is illustrated in Fig. 6.3(b), (e), (h) and (k) for the different
shapes. The most prominent topological feature of the polarization field arrangement in all
of these sketches is the presence of a cylindrically shaped ‘core’ area, completely penetrating
the particle, where the polarization is either completely absent or strongly suppressed. This
behavior is completely different from that of ferromagnetic vortices, where, at temperatures
below $T_C$, magnetization density at the core is constant [52, 283]. The spontaneous polar-
ization magnitude in the near particle surface areas of the vortex-like textures is closer to
its RT value in bulk PbTiO$_3$, which is especially prominent in the NC and CU shapes, as
shown in Fig. 6.3(h) and (k). The formation of the vortex-like state with polarization vectors
pointing tangentially to the particle surface, leads to a minimization of the amount of the
uncompensated surface charge and a decrease in the system electrostatic energy.

Finally, at even larger $R$, the polarization texture adopts the multidomain state that is
shown in Fig. 6.3(c), (f), (i) and (l). This state is characterized by the disappearance of the
paraelectric core in favor of relatively large areas of correlated $P$ divided by domain walls
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Figure 6.3: Volume $P(r)$ field distribution for particles of different SE shapes and sizes, the latter characterized by the value of $R$ in nm: (a-c) OC, (d-f) NO, (g-i) NC and (j-l) CU. Polarization field magnitude $|P|$ is represented by a color map, with a scale shown on the right, while its direction is designated by the arrows. The left column assembles small particles that exhibit monodomain polarization textures. The middle column shows medium size particles that display vortex-like polarization configurations, while the right column aggregates large particles with multidomain configurations.
that, although closely resembling their 90° and 180° bulk variants, may still contain some localized vorticity. Individual domains also tend to orient their polarization tangentially to the inclusion surface in order to minimize the electrostatic energy.

The critical values of $R$ (or $V_{SE}$) around which the actual phase transitions take place for each specific particle shape can be traced by following the variation of its normalized gradient energy

$$F_{wall} = \frac{1}{V_{SE}} \int_{V_{SE}} f_{wall} \, d^3r,$$  \hspace{1cm} (6.7)

that constitutes a direct measure of the energy penalty associated with the presence of domain walls in the ferroelectric system. Figs. 6.4(a) and (b) display the dependence of $F_{wall}$ on $R$ and $V_{SE}$, respectively, computed for every SE particle shape considered here, as well as

Figure 6.4: Normalized gradient energy $F_{wall}$ as a function of particle (a) semi-diameter $R$ and (b) volume $V_{SE}$. For most sizes, multiple minimizations of $F$ were conducted starting from different random initial conditions $\langle P \rangle \approx 0$, with the error bars shown on the plot representing variations of the converged $F_{wall}$. Data points for the spherical (SP) particles from our previous investigation [102] are also included for comparison.
for the spherical particles evaluated in the prior investigation [102].

The variation of $F_{\text{wall}}$ with respect to changing particle size, as depicted in Fig. 6.4(a-b), can be separated into three different regions. At small sizes corresponding to monodomain polar states, $F_{\text{wall}} \approx 0$, since for such configurations no polarization gradients are present in the system. At the increased particle sizes, when the transition into the polar vortex-like state takes place, $F_{\text{wall}}$ grows sharply and then goes through a maximum. This behavior can be understood by envisioning the vortex-like state as consisting of a large number of domain walls separating small regions with sub-optimal mutual polarization arrangements (as opposed to optimal orientations of $90^\circ$ and $180^\circ$, in the case of PbTiO$_3$). Finally, for even larger particle sizes characteristic of multidomain polar configurations, $F_{\text{wall}}$ gradually diminishes and then saturates at a constant value that is greater than zero, indicating the presence of some domain walls in the system in combination with some remaining vorticity of $\mathbf{P}(\mathbf{r})$.

Turning to the analysis of the polarization texture transitions dependence on the particle shape, we observe a considerable variation of the critical sizes for the transition onset for different particle geometries. In particular, both cubic shapes exhibit a transition to the vortex-like state at very small $R \approx 1$ nm, with a sharp peak in the $F_{\text{wall}}(R)$ dependence followed by a rapid decrease and saturation at $R \approx 4$ nm. On the other hand, the same transition sequence occurs much later for the octahedral particles, i.e., at $R \approx 2$ and $4$ nm for the NO shape, and $5$ and $10$ nm for the OC shape. Furthermore, a clear tendency for an expansion of a size interval where vortex-like states are supported is observed as $t$ is
decreased, indicating a more sharp change of polar textures for the cubic shapes and a more diffuse one for the octahedral shapes. Results obtained for the spherical particles in our previous investigation [102] are also shown in Fig. 6.4(a-b) and point to similarities in the transitional behavior of the SP and OC shapes.

It should be noted that in the previous investigation [102] it was found that the behavior of the $F_{\text{wall}}(R)$ curve, and especially the critical particle size for the multidomain phase transition, is sensitively dependent on the choice of the $G_{ijkl}$ coefficients parameterization. For PbTiO$_3$, at least three different parameterizations exist, attributed to Li et al., [98, 99], Wang et al. [100] and Hong et al. [101] In this work, the latter set of coefficients is utilized; however, except for the changing size for the multidomain transition onset, the general nature of the phase transitions and the behavior of the polarization textures in between transitions is expected to be the same for all three parameterizations.

6.4 Vortex core alignment and its dependence on shape

Although the emergence and topology of the vortex-like polar textures observed in the SP shapes have been thoroughly discussed in the previous investigation of Mangeri and coworkers [102], the equilibrium orientations of the cylindrical vortex cores within these shapes were purely random due to their high symmetry. That is, however, not the case for the less
symmetric particle shapes considered here. In general, for any non-SP SE particle of the size that supports the vortex-like polar state (e.g., as shown in Fig. 6.4), we observe only few well defined, symmetrically inequivalent orientations that the vortex core can adopt with respect to the particle geometrical features. Examples of such orientations are presented in Fig. 6.5 for the OC and NC shapes, and are further discussed below. From the examination of these sketches we can conclude that — for the chosen mutual orientation of the particle $x, y, z$ and crystallographic $a, b, c$ axes — the vortex cores align only with certain high-symmetry directions associated with the particle shape, such as the lines connecting its face centers (panels a and d), edge centers (panels b and e) and corners (panels c and f). The same lines serve as two-, three- and four-fold rotational axes belonging to the particle point symmetry group.

Table 6.2: Basic symmetry properties of the different sites on the surfaces of octahedral and cubic particle shapes. References to the appropriate panels of Fig. 6.5, illustrating the corresponding polar vortex core arrangements, are also included.

<table>
<thead>
<tr>
<th>Vortex Pinning</th>
<th>Property</th>
<th>OC (NO)</th>
<th>NC (CU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face Center</td>
<td>Site Symmetry</td>
<td>$3m$</td>
<td>$4mm$</td>
</tr>
<tr>
<td></td>
<td>Multiplicity</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Fig. 6.5</td>
<td>(a)</td>
<td>(d)</td>
</tr>
<tr>
<td>Edge Center</td>
<td>Site Symmetry</td>
<td>$mm2$</td>
<td>$mm2$</td>
</tr>
<tr>
<td></td>
<td>Multiplicity</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Fig. 6.5</td>
<td>(b)</td>
<td>(e)</td>
</tr>
<tr>
<td>Corner</td>
<td>Site Symmetry</td>
<td>$4mm$</td>
<td>$3m$</td>
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<tr>
<td></td>
<td>Multiplicity</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Fig. 6.5</td>
<td>(c)</td>
<td>(f)</td>
</tr>
</tbody>
</table>
Figure 6.5: Sketches of different polar vortex core alignments with respect to the high-symmetry lines of the particle shapes. Examples for the OC ($R = 6.9$ nm) and NC ($R = 1.9$ nm) shapes are shown in the top and bottom rows, respectively, for the following orientations: (a) and (d) face center, (b) and (e) edge center, and (c) and (f) corner.

Table 6.2 lists the point group symmetries and multiplicities $M$ for all of the special sites on the particle surface that are associated with the observed vortex core orientations, while Fig. 6.6 presents the normalized free energies of all the possible core orientations for each of the particle shapes. The data in Fig. 6.6 was collected by conducting multiple minimizations of the particle free energy $F$, as given by Eq. (6.3), with different random initial conditions $\langle \mathbf{P} \rangle \approx 0$, and checking the topology and orientation of the polarization texture obtained in the system state that is converged to the local energy minimum. On average, close to 100
energy minimizations were done for each shape, which included evaluation of the particles of different sizes (although all corresponding to the vortex-like polarization state). The free energies of the particles were normalized by volume in order to be placed on the same plot.

![Figure 6.6](image)

Figure 6.6: Volume-normalized total free energy $F$ dependence on the particle shape and polar-vortex core orientation. Numbers shown on each bar represent multiplicities $M$ of the symmetry elements aligned with particular core orientations. Error bars on the energy values were obtained as standard deviations resulting from multiple simulations with different random initial conditions $\langle P \rangle \approx 0$.

The most striking result presented in Fig. 6.6 is common for all of the considered particle shapes. Within the calculation error, the energetically stable vortex core orientation in any shape always aligns with the direction of the four-fold rotational axis ($M = 6$), which is the highest symmetry axis present in all of the particle geometries. Furthermore, for all of the shapes the next most energetically favorable vortex core orientation is associated with the two-fold rotational axis ($M = 12$), while the least energetically favorable core orientation is
aligned with the three-fold rotational axis \( M = 8 \). For the NC and CU shapes the energy differences between the two metastable states are relatively small, while for the NO and in particular the OC shape these differences are more pronounced.

### 6.5 Discussion and Conclusions

We have investigated the influence of size and shape on the topology and transitional behavior of polarization texture of a ferroelectric nanoparticle embedded in a dielectric medium. A variety of shapes belonging to the SE class was considered for PbTiO\(_3\), a generic ferroelectric inclusion, in a SrTiO\(_3\) dielectric matrix. For all of the shapes, the sequence of the polarization texture transformations with increasing particle size was found to be from monodomain to vortex-like to multidomain state, i.e., the same as previously observed for the spherical particles [102]. However, the calculated critical particle size for the onset of transformation was found to be strongly dependent on shape; cubic \( t > 2 \) particles exhibited sharp transitions at smaller sizes and octahedral \( t < 2 \) particles exhibited more diffuse transitions at larger sizes.

For nanoparticles of intermediate size, which supports the vortex-like polarization texture, we have also investigated the connection between particle shape and minimum-energy orientation of the paraelectric vortex core within the particle volume. Compared to spherical nanoparticles, the shapes considered here have greatly reduced (finite) symmetry, which leads to pinning of the vortex core orientation along special directions associated with the
particle point symmetry group. We determined that all the possible local energy minima for the vortex-like polarization textures correspond to a vortex core alignment with one of the rotational symmetry axes of the particle shape. For all of the considered shapes, the most energetically stable core pinning location was found to be along the four-fold rotational axis (4mm, $M = 6$). The locations of the energetically metastable pinning sites were determined to be the same for all of the shapes, with the free energy of the two-fold rotational axis aligned orientation (mm2, $M = 12$) always being lower than that of the three-fold rotational axis aligned orientation ($3m$, $M = 8$).

We expect that it should be possible to fabricate PbTiO$_3$ nanoparticles of the particular shapes and within the size range as described here. In addition to the already mentioned work of Caruntu and collaborators involving BaTiO$_3$ [65], a variety of other synthetic techniques have been recently used to make cubic and octahedrally shaped nanoparticles of both binary [284–286] and ternary [287–290] oxides. Although polarization charges on nanoparticle surfaces can be compensated by different ionic and molecular species upon ambient exposure, there exist well established experimental techniques for preserving these surfaces in their pristine state during the ferroelectric-dielectric nanocomposite sintering process [291, 292].

Vortex-like and other polarization textures predicted in this computational study can be detected and characterized by a number of different experimental approaches. For larger particle sizes of above 50–60 nm, Bragg coherent diffraction imaging can be utilized [270], while for smaller particles down to 5–10 nm in size it should be possible to elucidate the
topology and sense of rotation of the polarization field with aberration corrected HR TEM [266, 293]. Furthermore, it may be fruitful to probe larger size ferroelectric nanoparticles with second harmonic generation (SHG) microscopy, as the shape of their SHG spectra should also be dependent on the topology and orientation of the polarization textures within them [294–296].

The insights obtained in our investigation can provide a better understanding of the topology and transitional behavior of polarization textures in ferroelectric nanoparticles, including functional nanocomposites containing these particles as the dispersed phase. The predicted metastability of the vortex-like polar states can also be utilized in a number of future device applications, especially if a procedure for switching among the different core orientations can be developed. At present, we speculate that vortex core orientation switching can be accomplished by an application of elastic or electric field, or potentially a combination of both, although other viable approaches may also exist [297]. For example, the system can be polarized into a monodomain state in the desired direction by a large electric field, but will have to adopt a vortex-like state of a compatible orientation to avoid having uncompensated surface charges after the release of the field. Computational work to test such switching scenarios is currently underway.
Chapter 7

Conclusions and future outlook

7.1 Conclusions

In this dissertation, we have conducted a theoretical and computational investigation of PbTiO$_3$ and also environmentally benign isoelectronic material, SnTiO$_3$ which can potentially replace it. On the first step, *ab initio* methods (specifically, DFT calculations) were used to study the electronic level underpinnings of transitional behavior in Pb- and Sn-based perovskite oxides under epitaxial strain. The differences in that behavior between PbTiO$_3$ and SnTiO$_3$ were found to be related to the charge and spatial orientation of electron lone pairs on the A-site ion, i.e., Pb$^{2+}$ or Sn$^{2+}$. Layered versions of both Pb- and Sn-based perovskite oxides were also studied with the same methodology, uncovering a number of interesting physical effects. On the second step, an original technique was introduced for recycling the data generated from DFT calculations, such as the ones conducted on the
first step, into mesoscale level coarse-grained thermodynamic potentials. PbTiO$_3$, as an already thoroughly studied ferroelectric material, was chosen as a test case for the technique development, while yet to be synthesized SnTiO$_3$ was utilized to demonstrate the predictive capabilities of the technique. On the final step, mesoscopic energy descriptions, such as the ones constructed on the second step, were utilized in conjunction with finite element based numerical simulations to evaluate the polar properties of ferroelectric-dielectric nanocomposite materials — by studying the influence of size and shape of the (dispersed phase) PbTiO$_3$ nanoparticles on the topology and transitional behavior of their polarization textures. Specific accomplishments achieved on each step are assembled below. The [P... ] quotes accompanying each item refer to the list of publications produced in the course of this dissertation research.

1. The contrasting tendencies for PbTiO$_3$ and SnTiO$_3$ to form different phases under epitaxial tension were linked to the amount of charge concentrated within the the A-site ion electron lone-pair lobes. In particular, it was observed that in the energetically more stable phase, as much charge as possible is transferred out of the lobe, which lowers the cost of Coulomb repulsion between the lone pair and the surrounding negatively charged oxygen cage [P1].

2. The electronic origins of Goldstone-like excitations in layered-perovskite Sn- and Pb-based oxides were elucidated by adopting the “bottom-up” approach, in the spirit of Hoffman [222]. The minimum energy “groove” in the system energy landscape, respon-
sible for easy polarization rotation, was determined to be the result of a competition of different electronic interactions activated in different directions of the material basal plane and fine-tuned by biaxial epitaxial strain. The role of each monoatomic layer within the ASr$_2$Ti$_2$O$_7$ perovskite slab in nucleating the Goldstone-like excitation was clarified and it was also uncovered that arranging the perovskite slabs into the RP structure is not specifically required for inducing Goldstone-like behavior [P9].

3. The DFT data produced in the course of the investigation of the properties of layered-perovskite oxides was used to parameterize a quasi-2D Landau-Devonshire-style thermodynamic potential for the fictitious PbSr$_2$Ti$_2$O$_7$ RP structure, known to exhibit Goldstone-like excitations at certain values of epitaxial strain. This potential was then utilized to evaluate the pyroelectric and electrocaloric responses of the PbSr$_2$Ti$_2$O$_7$ structure, predicting that it should possess anomalous pyroelectric properties and that both electrocaloric heating and cooling regimes are possible in that system, depending on the applied mechanical conditions [P3].

4. As an extension of the work on quasi-2D layered-perovskite oxides, a general machine-learning approach was developed for the fitting of Landau-Devonshire-style energy expressions directly from first principles for displacive ferroelectric materials in 3D, specifically for perovskites whose behavior can be described by one primary vectorial order parameter. The parameterized energy description for the test case of PbTiO$_3$ accurately predicted its phase transition behavior and dielectric and piezoelectric prop-
erties, as compared with the results produced by several well known phenomenological potentials. The predictive capabilities of this approach were demonstrated by developing a similar energy description for the case of fictitious perovskite SnTiO$_3$ and evaluating the ‘strain – temperature – polarization’ phase diagram for its epitaxial thin film [P7].

5. The influence of size and shape of ferroelectric PbTiO$_3$ nanoparticles, embedded in a dielectric medium, on the topology and transitional behavior of polarization textures within them was investigated with a coarse-grained finite-element-based computational approach utilizing Landau-Devonshire-style thermodynamic potentials (combined with polarization gradient energy terms) as the system energy descriptions. For all of the studied shapes, belonging to the superellipsoidal class of solids including octahedral, spherical, cubic and intermediate geometries, the polarization texture transformations with increasing particle size were mapped out as a sequence of transitions from monodomian to vortex-like to multidomain state. In addition, it was determined that the finite symmetry (compared to a sphere) of the superellipsoidal class shapes enforces preferential directions of the polarization vortex cores within the ferroelectric particles, which are parallel to those of the highest possible (four-fold) rotational symmetry axes. Other polarization vortex-core alignments, parallel to the three- and two-fold rotational axes, were also found to be possible, but energetically metastable with respect to the alignment with the four-fold rotational axes [P8].
6. In a number of collaborative projects with other experimental and computational groups, the properties and transitional behavior of PbTiO$_3$, SnTiO$_3$, Sn-doped SrTiO$_3$ and BiFeO$_3$ were also studied. DFT calculations were utilized as the backbone for all of these studies, providing valuable insights into the nature of these lone-pair active material systems [P2, P4, P5, P6].

7.2 Future outlook

This work has elucidated the electronic underpinnings of the transitional behavior in perovskite oxides and demonstrated a procedure to bridge first principles techniques with mesoscopic theories. Moving forward, several possible extension of these research efforts are presented.

1. The developed techniques and understanding for the treatment of lone-pair active systems can be applied to other materials whose transitional behavior is currently not yet fully understood. For example, the properties of the Na$_{1/2}$Bi$_{1/2}$TiO$_3$ system can be evaluated with the same approach as the one presented in [P1].

2. In the case of systems that include more complicated property couplings, compared to displacive ferroelectrics, such as oxygen octahedral cage rotations, magnetism and etc., first-principles-based LDTP generation routines presented in [P7] can be expanded to include additional interactions. At the same time, even in the simple case of displacive
ferroelectrics, many other materials that are less well studied as PbTiO$_3$ can be quickly characterized on the mesoscale level, as well as in a variety of nanostructured forms, including thin films, pillars and particles.

3. In addition to bulk, elastic and electrostrictive energy terms of LDTPs, the *polarization gradient energy parameters* are also required to quantitatively describe the energy contributions of the domain boundaries. These parameters can be extracted from phonon dispersion curves associated with the polar soft mode [298]. Since phonon dispersion curves of materials can be predictively evaluated with DFT-based approaches, the gradient energy parameters can also be predicted for most classical or layered perovskite oxides, thus greatly improving our capabilities for generating coarse-grained energy descriptions of these functional systems.

4. In Chapter 5, the value of the Curie-Weiss temperature was crudely evaluated from the energy difference between the high temperature non-polar parent phase and the low temperature polar ground-state phase. However, more advanced computational approaches, such as *Wang-Landau* [259–262] Monte Carlo methods could be used to obtain insights into phase transition behavior and evaluate the associated critical temperatures.

5. In ferroelectric-dielectric composite materials, switching behavior between metastable polar vortex-like states in the particles, as well as their $P$–$E$ loops can be studied for different particle shapes and sizes, and for different crystallographic orientations of
the material with respect to the particle geometrical features. Furthermore, studies of interactions between two or more particles within the dielectric, under the influence of applied mechanical and electrical boundary conditions, should provide useful insights and guidance for the development of more efficient and highly tunable dielectric and electromechanical devices.
7.3 Publications related to this dissertation


Appendix A

Electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films

As an example of property engineering through strain, in this section we briefly discuss phase transition properties of another lone-pair active perovskite oxide, BiFeO$_3$ (BFO), under epitaxial compression. In previous experimental work it was reported that thin BFO films, grown at specific values of built-in epitaxial strain, can transform between rhombohedral-like ($R$-like) and tetragonal-like ($T$-like) symmetries by an application of an electric field. This transformation is accompanied by a very large lattice expansion along the thin-film sample out-of-plane direction, with the effective piezoelectric expansion reaching several
A. Electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films

percent [299]. Furthermore, large portions of an epitaxially compressed BFO thin film can be transformed by an application of short electrical pulses in less than 100 ns [300]. Steady-state measurements following the electric field pulse show that some fraction of the BFO volume is stable in the transformed state, while another fraction returns to the original configuration.

Although the X-ray diffraction experiments can reveal the symmetries of the phases participating in such electric field induced transformations, understanding the transformation details and energetics requires atomistic simulations of the electronic structure (e.g., using DFT) of the involved phases subjected to realistic strain conditions. We modeled the $R$-like, $T$-like and the true tetragonal ($T$) phases of BFO using monoclinic $Cc$, $Cm$ and tetragonal $P4mm$ space groups, respectively. The $R$-like phase has both in-plane and out-of-plane polarization components, whereas, in the $T$ phase, the in-plane polarization is zero. Key differences between the structures of the $R$-like and $T$-like phases are the ratio of lattice parameters along the in-plane and out-of-plane directions, labeled $a$ and $c$ in Fig. A.1, and the rotation of the oxygen octahedra. Table A.1 reports the properties of the three distinct BFO phases, obtained with the DFT approach utilizing three different approximations for the exchange-correlation functional.

The DFT calculations were first used to estimate the ranges of energetic stability for each of the competing phases under various epitaxial strains. The $c/a$ ratio of the $R$-like phase is always less than that of the $T$-like phase at an equal value of $a$. The lower $c/a$ ratio in the former may result from stress relaxation achieved through oxygen cage rotations. All of
A. Electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films

Table A.1: DFT parameters for the three high-symmetry structures of BFO. (*) indicates that the strain free $R$-like phase is identical to the bulk $R$ phase in this structural model.

<table>
<thead>
<tr>
<th></th>
<th>$R3c$ (Pure $R^*$)</th>
<th>$P4mm$ (Pure $T$)</th>
<th>$Cm$ (T-like)</th>
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<tr>
<td></td>
<td>GGA</td>
<td>GGA+U</td>
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<td>F.u. per unit cell</td>
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<td>6</td>
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<tr>
<td>$a$ [Å]</td>
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<td>5.63</td>
<td>5.5</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>5.63</td>
<td>5.63</td>
<td>5.5</td>
</tr>
<tr>
<td>$\gamma$ [°]</td>
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<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Unit cell volume [Å$^3$]</td>
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<td>385.56</td>
<td>346.81</td>
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<td>Magnetic moment [$\mu B$]</td>
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<td>4.46</td>
<td>4.11</td>
</tr>
<tr>
<td>Band gap [eV]</td>
<td>1.06</td>
<td>2.78</td>
<td>3.16</td>
</tr>
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</table>

these phases are stable under compressive strain $\varepsilon_e$, which is calculated with respect to the pseudo-cubic lattice parameter of the $R$ phase. Fig. A.1(a) plots changes in total energy $E$ per f.u. (with the energy of the $R$ structure taken as zero) with respect to varying pseudo-cubic in-plane lattice constant $a$. Under all experimentally achievable values of epitaxial strain, the $T$-like phase is energetically more favorable than the $T$ phase, in agreement with previous calculations [301].

The $R$-like phase is energetically preferable over the $T$-like phase at compressive strains $\varepsilon_e$ less than 3%. The $R$-like phase with $\varepsilon_e = 0$ has $c/a = 1$ and is therefore equivalent to the $R$ phase. Increasing $\varepsilon_e$ to 3% results in crossing of the energies of the $R$-like and $T$-like phases. At this strain, the $T$-like phase has a $c/a$ ratio of 1.28. A fourth order polynomial fit to each structure’s energies over varying in-plane lattice parameter allows identification of the value
Figure A.1: Structures of the (a) $R$-like ($C_c$ symmetry) rhombohedral-like phase and (b) $T$-like ($Cm$ symmetry) tetragonal-like phase studied here with DFT calculations. Spheres in violet, gold and red colors represent Bi, Fe and O ions, respectively. Green arrows indicate spin directions on Fe ions.

of $a$ where the $R$-like and $T$-like phases have equal energies. The two fits representing the $R$-like and $T$-like phases intersect at $a_{R-T} = 3.881$ Å.

The elastic influence of an out-of-plane electric field was approximated by elongating or compressing the pseudo-cubic unit cell in this direction and allowing all the ionic forces to relax to small values. We have not included the electric field explicitly in the calculations because the static $U$ parameter used in tandem with the GGA-PBE approximation needed to open the DFT band gap of BFO would be unable to describe the changes in electron
A. Electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films

Figure A.2: Total energies per formula unit of BFO phases relative to the relaxed bulk $R$ structure as a function of the lattice parameter under elastic conditions corresponding to (a) epitaxial growth and (b) subsequent elastic deformation via the converse piezoelectric effect. (a) Energies of the $R$-like (modeled as $Cc$ symmetry), $T$-like ($Cm$), and $T$ ($P4mm$) phases as a function of the in-plane lattice parameter $a$, where the out-of-plane $c$ lattice parameter and monoclinic angle $\beta$ are fully relaxed at each value of $a$. (b) Energies of the $R$-like and $T$-like phases as a function of the pseudocubic out-of-plane lattice parameter $c$, at fixed $a = 3.881$ Å. Model structures of the $T$, $T$-like, and $R$-like phases are inset in (a) and (b). Green arrows indicate spin directions on Fe ions.

interactions that an applied field would effect. Instead, we rely on the more well-defined ground state inside the $\sigma$GGA+$U$ approximation at varying cell compressions or elongations. Fig. A.1(b) shows the variation of the total energy with respect to the value of $c$ for the competing monoclinic phases. The minimum of each curve lies at the optimized value of $c$ for that phase under the common epitaxial condition $a = 3.881$ Å.

Combining the presented above DFT-based information with the results of the experimental study of the field induced BFO film switching between the $R$-like and $T$-like phases
A. Electric field induced phase transitions in epitaxially strained BiFeO$_3$ thin films

[300], it was possible to evaluate the possible phase transformation mechanisms and dynamics, as well as to determine the approximate BFO volume fractions that either remain stable in the new phase after the transformation, or return to the original phase.
References


[60] X. Fu, I. I. Naumov, and H. Fu, Collective Dipole Behavior and Unusual Morphotropic Phase Boundary in Ferroelectric Pb(Zr\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} Nanowires, Nano Lett. \textbf{13}, 491 (2013).


[180] The Ferret code-repository is developed within the open-source MOOSE environment [181] and is available at bitbucket.org/mesoscience/ferret.


REFERENCES

[230] See also BESAC report “From Quanta to the Continuum: Opportunities for Mesoscale Science” available from http://science.energy.gov/ as well as the complete volume 40 of the MRS Bulletin from November 2015.


[281] TRELIS is a nongovernment version of the CUBIT software package developed by Sandia National Laboratories and is available at www.csimsoft.com/trelis.


