



Ferroelectricity in PbTiO_3 Thin Films: A First Principles Approach

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Abstract. The ground-state ferroelectric distortion of PbTiO_3 thin films is studied using a first-principles effective Hamiltonian to describe the structural energetics at a microscopic level. Under short-circuit electrical and zero-stress mechanical boundary conditions, (001) films as thin as one unit cell are found to support a stable perpendicular polarization. Size effects in the layer-by-layer ferroelectric distortion are discussed. The continuum limit of the first-principles effective Hamiltonian has the same form as the widely-used Landau-Ginzburg expression for the free energy near T_c , so that the present results can be directly related to those of previous phenomenological studies. In particular, a microscopic interpretation of the extrapolation length δ is proposed.

Keywords: ferroelectricity, thin films, perovskites, lattice instabilities, first principles

Ferroelectricity is a collective phenomenon involving the cooperation of polar distortions through both short-range chemical and long-range dipolar interactions. As such, it is expected that the ferroelectric transition in confined geometries, such as thin films, will be strongly affected, being usually (though not always) suppressed [1]. This behavior, of both fundamental and technological importance, has been the subject of extensive experimental investigation in a variety of ferroelectric materials [2]. In particular, in thin films of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), it has been generally thought that decreasing thickness suppresses ferroelectricity and eliminates it altogether at a critical thickness of about 10 nm [3].

However, as methods for the fabrication of ferroelectric thin films have continued to improve, ferroelectric instabilities have been observed to persist in films as thin as a few nm [4,5]. Indeed, very recently, a stable perpendicularly polarized state has been observed, under short circuit electrical boundary conditions, in PZT films well below the “critical thickness” [5]. The apparent inconsistency with earlier results may stem from a number of difficulties encountered in studying these thin film systems. It can be difficult to control and even to determine the electrical and mechanical boundary conditions in

thin-film and granular systems. In addition, it may be unclear how to separate intrinsic effects, characteristic of an ideal thin-film system, from extrinsic effects, such as defects and impurities, which are sensitive to sample preparation.

The theoretical investigation of thin-film systems through first-principles calculations represents a complementary approach, in which the boundary conditions and atomic arrangements can be directly controlled. Generally speaking, first-principles methods allow the computation of properties of the quantum-mechanical system of interacting nuclei and electrons which constitute the material of interest, without empirical input. Two key ingredients are the use of the Born-Oppenheimer approximation, which decouples electronic excitations from the motion of the nuclei, and density functional theory [6], which provides a mapping from the complex problem of interacting electrons in the external potential of the nuclei to a simpler problem of noninteracting electrons in an effective potential $V[\rho(\vec{r})]$ which depends on the electronic charge density. Though this mapping is in principle exact, approximations, such as the local density approximation (LDA), are necessary in practice. The noninteracting electron problem is solved using a bandstructure method, such as that of plane-wave pseudopotentials [7] used in the present work, and iterated to self consistency. The result is the

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total energy of the system as a function of nuclear positions $E_0[\{\vec{R}_i\}]$, from which forces on the ions and stresses on the unit cell can be obtained by taking appropriate derivatives.

First-principles methods provide detailed and useful information about the microscopic structural energetics of a compound of interest. The conditions at the atomic level are clean and controlled; in fact a perfect single crystal (with its periodic boundary conditions) is generally the easiest structural arrangement to study. This information, alone or combined with studies of individual defect structures, can be used to separate intrinsic and extrinsic effects in the system. The information about configurational energies, forces and stresses can also in principle be used for studies of dynamical properties (*ab initio* molecular dynamics) and finite-temperature behavior (*ab initio* Monte Carlo). In practice, however, for ferroelectric oxides such “computer experiments” are so computationally demanding as to be completely out of reach.

The physics of ferroelectric oxides suggests an alternative strategy for the first-principles investigation of dynamics, temperature effects, and confined geometries. In the example of PbTiO_3 , the ferroelectric transition is driven by the freezing-in of an unstable phonon of the cubic perovskite structure, where the positively charged metal ions move against the negatively charged oxygens, accompanied by a corresponding change in shape of the unit cell. This observation, in the framework of the soft mode theory of structural phase transitions [8], greatly simplifies the picture of the relevant structural energetics. The energy of the uniform distortion has a “double well” form, in which the crystal is unstable at the harmonic level and stabilized by anharmonic terms.

For dynamical, finite temperature, and confined geometry behavior, information is also needed about the corresponding non-uniform distortions. This can be most easily obtained from the full phonon dispersion relation of the cubic perovskite structure, computed using the first-principles density functional perturbation theory (DFPT) approach [9]. For PbTiO_3 , the dispersion relation [10] shows clearly that only a fraction of the phonon branches, and therefore of the total ionic degrees of freedom, are important in describing the ferroelectric instability. To describe the accompanying unit cell shape change, the six homogeneous strain degrees of freedom are also relevant.

With this in mind, we have developed an approach based on the construction of a first-principles “effective Hamiltonian” which acts only in the subspace of the relevant ionic degrees of freedom, through a projection or integrating out the complementary subspace [11]. For PbTiO_3 , the relevant subspace is defined by the unstable Γ phonon and the branches emanating from it. For the purposes of statistical mechanical modeling, it is more conventional to transform to a real space basis, which we have formulated as “lattice Wannier functions” [12]. For PbTiO_3 , this yields a model with a simple cubic lattice of vectors $\vec{\xi}_i$, centered at the Pb sites, which represent the local polar distortions, and the homogeneous strain degrees of freedom $\{e_{\alpha\beta}\}$, which represent uniform distortions of the lattice itself.

An explicit expression for the energy $E[\{\vec{\xi}_i, e_{\alpha\beta}\}]$ is obtained by a Taylor expansion around $\{\vec{\xi}_i = 0; e_{\alpha\beta} = 0\}$, with the coefficients in the expansion being determined by appropriate first-principles calculations. Full details are given in [13]. Using a classical Monte Carlo method on the resulting model, we have obtained the ferroelectric phase transition temperature, latent heat, strains, spontaneous polarization, and dielectric and piezoelectric responses for bulk PbTiO_3 in good agreement with experiment [13].

To extend this analysis to thin films, the minimal approach is directly to transfer the on-site and interaction parameters from the bulk to describe the energetics of local distortions and strains for the sites included in the thin film. The intersite interactions are of two types: (1) dipole-dipole interactions, where the local dipole moment is $\vec{p}_i = p_0 \vec{\xi}_i$; and (2) short range corrections to the dipole-dipole form, which primarily originate from higher order multipoles and from interactions associated with the partially-covalent character of the bonding. In addition, there is a linear-quadratic coupling between strain and the distortion vector on a given site.

The simplest case is that of an (001) oriented thin film with short-circuit electrical boundary conditions, corresponding to perfectly conducting plates on the top and bottom surfaces of the film, and free mechanical boundary conditions, corresponding to zero epitaxial stress. To evaluate the dipolar energy, we use the method of images. For an arbitrary configuration $\{\vec{\xi}_i\}$, this sum is evaluated using an Ewald summation method [14]. For a uniform configuration, the sum is much simpler. If the dipoles

are normal to the surfaces of the film, the corresponding array of image dipoles is a uniform simple cubic lattice, for which the energy is obtained using the familiar Lorentz technique [15]. Thus, the dipolar energy of the perpendicularly polarized film is rather favorable with short-circuit boundary conditions, far more so than in the energetically-costly open-circuit case. For parallel polarization, the image array is alternating slabs of oppositely oriented dipoles. This too is rather favorable in energy, and comparable to the perpendicularly polarized case.

For short-circuit boundary conditions, it is in the short-range part of the Hamiltonian where the energetic differences between perpendicular and parallel polarization emerge. The absence of material outside the film is treated as equivalent to setting $\xi_i = 0$ for sites i not within the film. For simplicity in the present discussion, we consider only the nearest neighbor short range interactions, noting that the full analysis for the short-range parameters of PbTiO₃ yields the same conclusion. Each surface vector then interacts with five nearest neighbors, rather than six. For perpendicular polarization, the missing neighbor has a longitudinal relationship to the surface vector, and $E_{surface} - E_{bulk} = -a_L \xi^2$, while for perpendicular polarization, the missing neighbor has a transverse relationship to the surface vector, and $E_{surface} - E_{bulk} = -a_T \xi^2$. Since in PbTiO₃, the nearest neighbor short-range longitudinal and transverse couplings a_L and a_T are positive and negative respectively, it can be seen that the presence of the surface energetically favors the perpendicular polarization.

In general, the ground state of the film will not have uniform values for the distortion vectors. It can be shown that for PbTiO₃, the distortion vectors in the lowest energy state are uniform within each layer, and symmetric across the center of the film. In Fig. 1, we show, relative to the bulk energy per unit cell, the energies of ground state configurations, including homogeneous strain relaxation, for films with perpendicular and parallel polarization and thicknesses $N = 1-10$ unit cells. It can be seen that parallel polarization is slightly unfavorable compared to the bulk for all thicknesses, while perpendicular polarization is favorable, with the surface enhancement becoming more and more dominant as the thickness of the film is reduced. In Fig. 2, we show the distortion profile of perpendicularly polarized films of thicknesses $N = 1-10$ unit cells. The value at the surface is enhanced over that of the interior layers in each case.

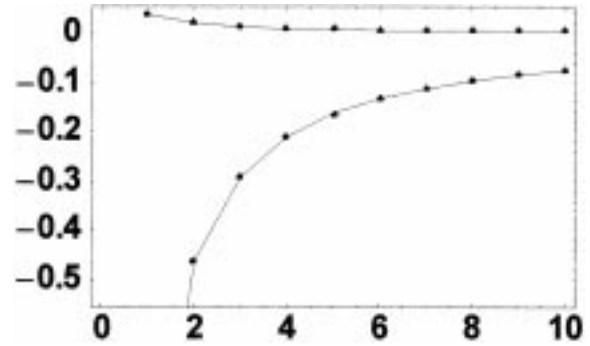


Fig. 1. Energy per unit cell, in eV, as a function of thickness ($N = 1-10$ unit cells) for perpendicularly polarized films (solid line) and for parallel polarization (dashed line). The zero of energy is taken as the bulk energy per unit cell.

As the thickness increases, the distortion in the interior layers decreases, but even for $N = 10$ is still well above the bulk value of 0.085. Thus, the overall effect in perpendicularly polarized films of PbTiO₃ is in fact the *enhancement* of the ferroelectric instability over the bulk.

The energetic contribution due to the truncation of short range interactions at the surface is completely analogous to the surface polarization term in phenomenological Landau-Ginzburg theories of ferroelectric thin films [16,17]. In these theories, an extra term $\frac{1}{2}C(P_-^2 + P_+^2)$ is added to the usual Landau-Ginzburg expression for the bulk ferroelectric. The parameter δ is called the “extrapolation length” with $\delta < 0$ corresponding to enhancement and $\delta > 0$ to suppression of the surface polarization, while C is a stiffness parameter which is always positive in these theories. The present analysis reveals the microscopic origin of this term. As a simple illustration, we write

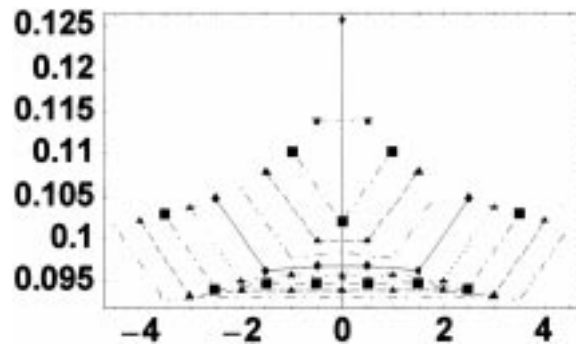


Fig. 2. Layer-by-layer profile of the local distortion ξ_z for films ranging in thickness from $N = 1$ to $N = 10$. The layers are numbered symmetrically around zero.

the energy of a single chain of vectors perpendicular to the surface, with the film terminating at site N . For the bulk, with uniform ξ at all sites i , the short range energy would be

$$\sum_i [(A + 2a)\xi_i^2 - a(\xi_i - \xi_{i-1})^2]$$

while if we set $\xi_i = 0$ for $i > N$, this would terminate the sum at $i = N$, with an extra term $-a\xi_N^2$. If the short range interaction is negative (i.e., ferroelectric), this corresponds to $\delta > 0$, or suppression of surface polarization, while if it is positive (antiferroelectric), this implies $\delta < 0$, or surface enhancement. If the short-range interaction a were the only intersite interaction in the ferroelectric model, it would necessarily have to be negative, and only suppression of surface polarization would be observed. However, since the overall ferroelectric instability is governed by the combination of the short-range and dipolar interactions, the short-range interaction can be either positive or negative, corresponding to either enhancement or suppression depending on the individual material.

The results described here are for the ground state of PbTiO_3 films using the minimal approach to modelling the effects of the film geometry. Further investigations in progress include behavior of the model at $T \neq 0$ through classical Monte Carlo simulations to examine shifts in T_c , modification of ferroelectric transition behavior in thin films, and comparison with other perovskites such as BaTiO_3 . In addition, we are exploring new approaches to deriving the thin-film effective Hamiltonian, including more sophisticated treatment of the local polarization and electric fields, and the incorporation of first-principles information about surface properties derived from slab calculations. Details will be described in an upcoming publication.

In summary, we have laid the foundation for the first-principles study of the intrinsic ferroelectric instability of PbTiO_3 thin films. For this purpose, both computational and conceptual advantages are offered by the use of an effective Hamiltonian, in which irrelevant ionic degrees of freedom are integrated out, and parameters are determined from first principles. For PbTiO_3 thin films, we have shown that for a simple model, parameters can be transferred from the previously constructed effective Hamiltonian for the bulk case. In short-circuit electrical and zero-stress mechanical boundary con-

ditions, the truncation of the short-range interactions at the surfaces of the film leads to an enhancement of surface polarization, analogous to that employed in phenomenological Landau-Ginzburg theories. This effect actually enhances the ferroelectric instability in perpendicularly polarized films of PbTiO_3 , in agreement with recent observations [5].

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