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Properties of ferroelectric ultrathin films from first principles

IGOR A. KORNEV*
Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA; Novgorod State University, Russia
E-mail: ikornev@uark.edu

HUAXIANG FU, LAURENT BELLAICHE
Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA

Advances in first-principles computational approaches have, over the past ten years, made possible the investigation of basic physical properties of simple ferroelectric systems. Recently, first-principles techniques also proved to be powerful methods for predicting finite-temperature properties of solid solutions in great details. Consequently, *bulk* perovskites are rather well understood nowadays. On the other hand, one task still remains to be accomplished by *ab-initio* methods, that is, an accurate description and a deep understanding of ferroelectric *nanostructures*. Despite the fact that nanometer scale ferroelectric materials have gained widespread interest both technologically and scientifically (partly because of novel effects arising in connection with the reduction of their spatial extension), first-principles-based calculations on ferroelectric nanostructures are rather scarce. For instance, the precise effects of the substrate, growth orientation, surface termination, boundary conditions and thickness on the finite-temperature ferroelectric properties of *ultrathin films* are not well established, since their full understandings require (i) microscopic insights on nanoscale behavior that are quite difficult to access and analyze via experimental probes, and (ii) the development of new computational schemes. One may also wonder how some striking features exhibited by some bulk materials evolve in the corresponding thin films. A typical example of such feature is the morphotropic phase boundary of various solid solutions, where unusual low-symmetry phases associated with a composition-induced rotation of the spontaneous polarization and an enhancement of dielectric and piezoelectric responses were recently discovered. In this paper, recent findings resulting from the development and use of numerical *first-principles-based* tools on ferroelectric ultrathin films are discussed.

1. Introduction

Ferroelectric materials are of unique importance for a variety of existing and potential device applications. Examples include piezoelectric transducers and actuators, nonvolatile ferroelectric memories, and dielectrics for microelectronics and wireless communication [1–3]. An important class of ferroelectric materials are the perovskites ABO_3. The perovskite crystal structure ABO_3 can be regarded as a three-dimensional network of corner sharing BO_6 octahedra, with the B ions in the center of the octahedra. In a cubic perovskite, the A site is twelvefold surrounded by oxygen ions. As the temperature is reduced, many of these compounds undergo a phase transition and develop a switchable spontaneous electric polarization, thus becoming ferroelectric. Most of the perovskite compounds that are of greater interests are not simple systems, but rather complex solid solutions with the general formula $A(B', B'')O_3$, i.e., with two kinds of B atoms

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[*] Author to whom all correspondence should be addressed.

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since their physical properties may be tailored by varying the concentration of B atoms. The $Pb(Zr,Ti)O_3$ (PZT) alloys, in particular, are sensitive to a change of the Ti concentration and are currently used, e.g., in the U.S. Navy transducers and actuators because of their large piezoelectricity [4]. Other examples include the $Pb(Mg,Nb)O_3$ and $Pb(Zn,Nb)O_3$ compounds which exhibit such extraordinarily high values of the piezoelectric constants when alloyed with $PbTiO_3$ [5] that they could result in a new generation of piezoelectric "wunderbar" devices [6]. A particularly relevant compositional region in solid solutions is the morphotropic phase boundary (MPB). This compositional region separates tetragonal and rhombohedral phases of various solid solutions and has been recently shown to possess unusual low-symmetry phases—that are associated with a composition-induced rotation of the spontaneous polarization and an enhancement of dielectric and piezoelectric responses [7–13].

Ferroelectric simple systems and solid solutions have been intensively studied both experimentally and theoretically in the past 5 years. Consequently, their properties are fairly well understood nowadays. On the other hand, understanding the physical properties in ferroelectric-based *nanostructures* has become one of the most intriguing and fundamental problems of modern physics. Advances in materials growth and characterization, which provide a driving force for ferroelectric-related theoretical study have, in the past decade, made possible the investigation of basic physical processes in new ferroelectric materials on a nanometer scale [14–20].

Physical properties at nanometer scales in low dimensional ferroelectric structures are attractive fundamentally, as well as technologically. As a matter of fact, there is a rapidly growing interest in ferroelectrics and ferroelectric/semiconductor integrated structures because of their potential applications in advanced microsystems (such as high-density nonvolatile ferroelectric memories), a new generation of gate dielectrics for faster and smaller computers, and tunable microwave devices (such as filters and phase shifters in smart communication and radar systems). Much of the recent activity in ferroelectrics has been motivated by the desire for developing miniaturized actuators for micro-electro-mechanical systems applications, which mostly involves nanostructures in *thin-film* forms. In search for multi-Gbit ferroelectric memories, the thickness of a ferroelectric film is also of a great concern. Auciello *et al*. [21] mention that thicknesses of less than 200 nm are necessary for future nonvolatile ferroelectric random-access memory, while Scott [22] discusses the possibility of thicknesses as low as 30 nm for some particular device applications.

The constantly decreasing size of such devices down to a nanoscale gives rise to many fundamental questions regarding the stability of different physical properties in these low-dimensional structures. One of the most important phenomena observed in ferroelectric films is indeed the size effect. As a matter of fact, Curie temperature, switching rate, coercivity as well as the field response all depend strongly on the *thickness* of ferroelectric films. Moreover, it was long thought that there is a critical size on the order of hundreds of angstroms below which ferroelectricity would disappear entirely [23].

The situation changed after experiments provided unambiguous evidence for ferroelectric ground states in 40 Å-thick perovskite oxide films [24] and in crystalline copolymer films as thin as 10 Å [25]. Similarly, and very recently, Fong *et al*.[26] provided the experimental evidence that ferroelectricity persists down to vanishingly small sizes. It thus appear that the answer to the crucial question of whether or not there is a critical thickness for ferroelectricity is still unsettled [24, 27–30]. Similarly, the precise effects of surface on the thermodynamic properties of ferroelectric nanostructures are open for discussion [29, 31–35]. This leads to a growing and general theoretical interest in the properties of nanoscale ferroelectric systems. Furthermore, considering the fact that phase transitions in a system are greatly affected when the object is confined to sizes that are comparable to the correlation length, one may thus wonder how some striking features—such as the existence of a MPB, exhibited by some bulk perovskite materials—evolve in the corresponding low-dimensional structures.

An intriguing problem in these films also concerns their polarization patterns. For instance, the various following patterns have recently been predicted or observed: out-of-plane *monodomains* [24, 27, 28, 36], 180° out-of-plane *stripe domains* [29, 36, 37], 90° multidomains that are oriented *parallel* to the film [38], and *microscopically-paraelectric* phases [28]. The fact that different patterns have been reported for similar *mechanical* boundary conditions supports a concept discussed in Refs. [28, 39, 40], namely that they arise from different *electrical* boundary conditions. A reactive atmosphere can indeed lead to a partial compensation of surface charges in films with nominal ideal open-circuit (OC) conditions [36], while metallic or semiconductor electrodes "sandwiching" films do not always provide *ideal* short-circuit conditions (SC)—resulting in a non-zero internal field [28]. The *degree* of surface charges' screening in thin films can thus vary from one experimental set-up to another, possibly generating *different* polarization patterns [28, 36].

Finally, multidomains and their formation mechanism in low-dimensional structures are still not well established. *Atomic-scale* details of multidomains are also scarce in ferroelectric thin films. One may also wonder if uncompensated depolarizing fields can yield ferroelectric phases that do *not* exist in the corresponding bulk material. Candidates for these latter anomalies are films made of alloys with a composition lying near their MPB, because of the easiness of rotating their polarization [8–10, 41].

One reason behind that lack of knowledge is that thin films are difficult to synthesize in a good quality form, and their characterization is by no means straightforward. Similarly, realistically simulating thin films is a challenge. Technically speaking, the main theoretical methods used/developed so far in the study of low-dimensional ferroelectrics fall into two categories, namely: (1) approaches based on the Landau-Ginzburg theory [42] versus (2) first-principles-based schemes.

In the Landau-Ginzburg approach, the free energy is expressed as a functional of the order parameter only, and all other degrees of freedom have been integrated out in the derivation of the theory starting from a microscopic Hamiltonian. In this approach, solids are often treated as continuum. Moreover, since the spatial inhomogeneity of the order parameter is important for low-dimensional structures, the analytical solution of corresponding Euler-Lagrange equations is barely possible [43]. Furthermore, some of the parameters needed in the expansion of the free-energy functional can only be estimated from the experimental data available.

Although continuum theories, like the Landau-Ginzburg theory, are expected to be valid only on length scales much larger than a lattice constant [42], it is noteworthy to realize that they are used in the analysis of the experimental results for the thinnest films and heterostructures down to the nanoscale. This is partly because the ferroelectric correlation length is about one lattice constant [31, 44]. The following argument is somewhat more intuitive than definite. If the size of a ferroelectric nanostructure is much larger than the correlation length of the order parameter fluctuations, results can be interpreted as bulk ferroelectricity affected by the presence of surface, which imply that a Landau-Ginzburg-type theory is valid.

Within this framework, many of the characteristics of nanoscale ferroelectrics can be faithfully reproduced (see, e.g., [29, 38, 43, 45], and references therein). However, microscopic foundations of phenomenological approaches are somewhat arbitrary and atomic-scale mechanisms are difficult to assess. A similar method makes use of the Ising model in a transverse field (IMTF) and the relationships between the IMTF and Landau-Ginzburg parameters have been established in Refs. [46, 47].

An alternative approach to continuum models are first-principles-based calculations that require no experimental input. Some phenomena in low-dimensional ferroelectrics can be understood by using *direct* first-principles methods. Although first-principles methods are rather accurate, their large computational cost currently prevents them from being used to study complex phenomena and/or systems. For instance, it is unlikely that direct first principles will capture the complexity of real disordered materials such as $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) solid solutions. Moreover, since these methods usually deal with the ground states of solids at zero temperature, the understanding of the sequence of phase transitions and their temperatures on a material-specific basis is hard to achieve. On the other hand, first-principles-*derived* computational approaches have proved to be powerful methods in recent years for understanding complex materials, as well as for predicting the finite-temperature physical properties of hypothetical (and "wunderbar") compounds that have not yet been synthesized [48]. In particular, effective Hamiltonian methods with parameters obtained by fitting direct first-principles computations [8, 9, 49, 50] provide insight into the role of atomic species in ferroelectrics, leading to the design of new materials [48, 51, 52].

The main purpose of the present review is to describe the understanding of physical properties of ferroelectric ultrathin films that has been recently gained using direct first-principles and first-principles-based approaches. More precisely, we selected some papers and summarize their results (we apologize for papers not included in this article and that we may have missed). A particular emphasis will be put to indicate the mechanical and electrical boundary conditions adopted in these studies since ferroelectrics should be very sensitive to such conditions. Among the other topics to be discussed here are the role of size and surface effects on properties of ultrathin films made of insulating perovskites.

2. Recent works on ultrathin films from first principles (in chronological order)

2.1. "Microscopic model of ferroelectricity in stress-free $PbTiO_3$ ultrathin films" by P. Ghosez and K.M. Rabe, *Appl. Phys. Lett.*76 (2000); 2767 "Ferroelectricity in $PbTiO_3$ Thin Films: A First Principles Approach" by K.M. Rabe and P. Ghosez, *J. Electroceram.* **4:2/3**, (2000) 379

In these two articles, first-principles-derived effective Hamiltonian calculations have indicated the possibility of retaining the ferroelectric ground state at very small thicknesses [27, 53]. More precisely, these authors applied the first-principles-based effective Hamiltonian approach to study the ferroelectric instability in ultrathin films, and predicted that *stress-free* (0 0 1) $PbTiO_3$ films under *short circuit* electrical boundary conditions (i.e., corresponding to the perfectly screened surface charges or equivalently to perfect electrodes) as thin as three unit cells [27] and one unit cell [53] remain to posses a stable polarization.

The effective Hamiltonian used for thin films was modified with respect to the one of the bulk by terminating the interatomic short-range force constants at the surface, changing the effective dipole-dipole interaction resulting from the perfect electrodes, and adding corrections to preserve global translational symmetry and charge neutrality. The authors also found that the perpendicular direction (i.e., along the [0 0 1]-z-axis) is more favorable than a direction lying in the (0 0 1) plane for the spontaneous polarization. Furthermore, while in the interior the polarization approaches the bulk value even for very thin films, it is significantly enhanced at the surface. The stability of the ferroelectric state relative to the paraelectric state was also predicted to increase with decreasing thickness. The results of Rabe and Ghosez are consistent with a related study on periodic slabs using direct first-principles simulations [31]. As a matter of fact, this latter study predicted ferroelectric ground states for various *stress-free* ultrathin ABO_3 slabs under the condition of vanishing internal electric field (i.e., under short-circuit boundary conditions).

To understand the ferroelectric instability and surface polarization enhancement in perpendicularly polarized films, a *simplified* model fitted to the effective Hamiltonian results has been considered [27]. It was obtained by (i) suppressing the periodic boundary conditions on the short-range terms, (ii) including the short-range surface corrections, (iii) changing in the effective dipole–dipole interaction to take into account the electrical boundary conditions. This "simple" model revealed that the combined effects of contributions (i) and (ii) were found to compete with the suppression of ferroelectricity by the dipolar contribution (iii).

It was also stressed that the first-principles-based results can be directly related to those of previous phenomenological studies. In particular, a microscopic interpretation of the so-called extrapolation length λ was proposed [53]. In the framework of the modified phenomenological Landau-Ginzburg theory [54] that is usually adopted to study the size effects in ferroelectric thin films, a surface energy term $\sim (P_+^2 + P_-^2)/\lambda$ is added to the usual expansion of the free energy, where λ is the "extrapolation length" which can be positive (corresponding to suppression) or negative (corresponding to enhancement of the polarization at the surface) and $P_\pm$ being the spontaneous polarization at the surfaces. Rabe and Ghosez [53] found that for short-circuit electrical and zero-stress mechanical boundary conditions, the truncation of the short range interactions at the surface leads to an enhancement of surface polarization, which results in a negative λ.

Note that, in principle, from layer-by-layer profiles of the polarization given in Refs. [27, 53] the value of λ and the correlation length can be easily estimated assuming that the deviation of the polarization from the bulk value decays with distance exponentially [54]. In the approaches used in Refs. [27, 31, 53], the epitaxial stress due to the lattice mismatch between a given substrate and the film, which can significantly change the ground state of the film was not studied. Moreover, the effects of a real metal-perovskite interface on both the atomic relaxation and polarization were also left out in these pioneering studies.

2.2. "Surface effects and ferroelectric phase transitions in $BaTiO_3$ ultrathin films" by Tinte and M.G. Stachiotti, *Phys. Rev. B* **64** (2001) 235403

Tinte and Stachiotti [29] used a first-principles-derived approach to study (0 0 1) $BaTiO_3$ thin films for different mechanical strains.They indicate that their electrical boundary conditions are not short-circuit (they are in fact close to be ideal open-circuit). Their starting point is an atomistic approach based on a shell model for $BaTiO_3$ bulk with parameters obtained from first-principles calculations.

It was first examined if the model describes properly the static surface properties of $BaTiO_3$. It is well known that a reduction of the system size enhances quite generally the relative importance of the surface boundaries. This is particularly true in the case of ferroelectric films. Existence of the vacuum surrounding films will cause surface-induced atomic relaxations and cell-shape changes near the film surfaces due to truncation of periodicity. Surfaces of ferroelectric materials have been studied using first principles methods [31–35]. Tinte and Stachiotti demonstrated that the model developed for the bulk material indeed is successful for describing surface properties, such as structural relaxations and surface energies for Ti-terminated surface. For the BaO surface, the description was less accurate. In agreement with direct first-principles results [31, 33, 34], they also show that ionic motions on surfaces could indeed dominate the bulk energetics for thin slabs.

Calculations for thin films were carried out in a periodic slab geometry; a vacuum region of 20 Å separating the periodic slabs was introduced to minimize the interaction between periodic images. It was found that the results are insensitive to the vacuum region size. (The reason is that the net *out-of-plane* polarization of the slab is zero). Technically, a (0 0 1) TiO_2 -terminated stress-free slab of 28 Å thick containing 8 TiO_2 layers and 7 BaO layers was chosen to perform some case studies indicated in the following.

Finite-temperature molecular dynamics simulations on stress-free films revealed a significant non-zero polarization parallel to the slab surface, while the polarization component perpendicular to the surface is zero at all temperatures, a direct result of huge internal polarizing fields along the growth axis and associated with open-circuit conditions. It was found that the polarization profile at the surface depends on the surface termination (i.e., TiO_2 vs BaO terminated), and in-plane ferroelectricity is strongly enhanced at the TiO_2-terminated surface and suppressed at the BaO-terminated surface, a fact that is in agreement with results [27, 31, 32, 53] from direct first-principles.

According to the obtained phase diagram of the (0 0 1) $BaTiO_3$ stress-free film, the transition temperatures for the paraelectric–$\langle 1\ 0\ 0 \rangle$ polarized and the$\langle 100 \rangle - \langle 1\ 1\ 0 \rangle$ polarized phases coincide with the cubic–tetragonal and tetragonal–orthorhombic transition temperatures of the bulk material.

The atomistic model was also used to investigate the strain effects on the ferroelectric properties of the film assuming that the internal elastic strain fields are homogeneous, so the 2D clamping holds throughout the ultrathin film. It was shown that at low temperature when the film is *compressively strained*, the polarization vector starts rotating towards the z-axis. In this case, a strain induced *multi-domain* ferroelectric state with an out-of-plane orientation of polarization can be stabilized. Another valuable microscopic information provided by this article is the fact that the 180° domain wall is centered on a Ba-O plane, i.e., the atomic displacements have odd symmetry across (and vanish on) the BaO plane, which indicates that the domain boundary is indeed very sharp, its width being of approximately one lattice constant, in agreement with Refs. [44, 55].

The authors have also done simulations on slabs of different widths using the same mechanical boundary condition (compressive strain of -1.5%; for this value of strain the in-plane polarization of the slab was zero) to determine the temperature at which the out-of-plane polarization of each domain vanishes. They predicted from these simulations that the strain effect produced by the presence of a hypothetical compressive substrate stabilizes stripe domains in a "not short-circuited" TiO_2-terminated $BaTiO_3$ film as thin as 20 Å.

2.3. "Critical thickness for ferroelectricity in perovskite ultrathin films" by J. Junquera and P. Ghosez, *Nature* **422** (2003) 506

Using the direct first-principles Siesta code [56], Junquera and Ghosez [28] have been able to simulate the structure of a realistic ferroelectric capacitor made of an (0 0 1) ultrathin film of $BaTiO_3$ between two metallic $SrRuO_3$ electrodes. This film was also mimicked to be under a specific compressive strain ($\sim -2\%$) by assuming that its in-plane lattice constant is the one of $SrTiO_3$. It was shown that as the film thickness decreases, the electrical boundary conditions move further away from the ideal short-circuit conditions. In other words, ultrathin films can have a depolarizing field, even when sandwiched between metallic electrodes, with this field increasing in magnitude when the size decreases. As a result of this depolarizing field, Junquera and Ghosez predicted a critical thickness for ferroelectricity to be about 6 unit cells ($\approx$ 24 Å). One has to remember, however, that the pioneering work of Junquera and Ghosez deals with paraelectric versus normally-polarized single domain ferroelectric thin films. In other words, the computational burden of direct first-principles techniques did not allow the authors to investigate the possibility of *multi-domain* formation as an alternative of their results.

2.4. "Ab initio study of the phase diagram of epitaxial $BaTiO_3$" by Oswaldo Diéguez, Silvia Tinte, A. Antons, Claudia Bungaro, J. B. Neaton, Karin M. Rabe and David Vanderbilt, *Phys. Rev. B* **69** (2004) 212101

One particular feature of films is the presence of large strain in the plane of the film due to the lattice mismatch between a substrate and the thin film. If such mismatch exists, the ferroelectric material inside the film will feel a compressive or tensile strain, which will have a drastic effect on the direction of the polarization. For instance, the polarization may lie in the layers or may have a component perpendicular to such layers.

Diéguez *et al.*'s paper [57] addresses this issue by reporting the temperature-misfit strain phase diagram for epitaxial (0 0 1) $BaTiO_3$, as predicted by direct first-principles and effective-Hamiltonian approaches [57]. The form of the strain tensor$\{\eta_\mu\}$ (in Voigt notation) is relevant to two cases of interest, namely stress-free versus epitaxially strained (0 0 1) films. In the former case, all the components of strain tensor fully relax. On the other hand, the second situation is associated with the freezing of three in-plane components of strain tensor due to the lattice mismatch δ between the film and the substrate, i.e. $\eta_6 = 0$ and $\eta_1 = \eta_2 = \delta$—while the other components relax during the simulations [38, 57, 58].

Direct first-principles calculations were carried out using the VASP software package [59, 60]. Systematic optimizations of the five-atom unit cell in the six possible phases considered in Ref. [58] have been performed. Namely, the following phases have been optimized by relaxing the atomic positions and the out-of-plane cell vector: p (P4/mmm) with zero polarization; c (P4mm) with polarization along the z direction; aa (Amm2) with xy-in-plane polarization, and $P_x = P_y$; a (Pmm2) with polarization along the x direction; ac (Pm) with xz-in-plane polarization, and $P_x \neq P_z$; r (Cm) with all non zero components of the polarization, and $P_x = P_y \neq P_z$, where P_x, P_y and P_z are the Cartesian components of the spontaneous polarization along the [1 0 0], [0 1 0] and [0 0 1] pseudo-cubic directions, respectively. The finite temperature studies of epitaxial $BaTiO_3$ were carried out using the effective Hamiltonian approach of Ref. [49, 50].

The result obtained in Ref. [57] is qualitatively different from that computed previously [58] using a Landau-Ginzburg-Devonshire theory with parameters fitted at temperatures in the vicinity of the bulk phase transitions. The *ab initio* calculations predicted that at $T = 0$ K epitaxial $BaTiO_3$ film undergos a sequence of c (P4mm)

— *r* (Cm) — *aa* (Amm2) phase transitions as strain grows. Finite-temperature simulations using effective-Hamiltonian predicted a temperature-strain phase diagram similar to Pertsev *et al.*'s [58] at high temperature, but without the *ac* phase at low temperature. Unlike Ref. [58], the resulting phase diagram is symmetric with respect to the zero misfit strain and shows that all phase transitions are of second-order. In this work, effects of *interfaces, thickness and surfaces* have not been considered since the simulated material is in fact a periodic bulk under mechanical constraints rather than a film with a finite thickness.

2.5. "Ultrathin films of Ferroelectric solid solutions under a residual depolarizing field" by I. Kornev, H. Fu and L. Bellaiche, *Phys. Rev. Lett.* **93**, (2004) 196104

In Ref. [61], Pb-O terminated (0 0 1) $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films "sandwiched" between non-polar systems (to simulate, e.g., air, vacuum, electrodes and/or non-ferroelectric substrates) were modeled. Such low-dimensional structures are mimicked by large periodic supercells that are elongated along the *z*-direction, and that contain a few number of PZT-layers. The non-polar region outside the film is much larger than the thickness of the film, to allow well-converged results for the film properties [29].

The authors of this article develop an effective Hamiltonian approach for which the total energy of thin film (under uncompensated depolarizing fields) is written as a sum of one term depending on bulk parameters and a second term that mimics the effects of an *internal* electric field—that arises from the *partial or full screening* of polarization-induced charges at the *surfaces*—on the films properties. This second term is directly proportional to a β parameter that characterizes the *strength* of the *total* electric field inside the film. Specifically, $\beta = 0$ corresponds to ideal OC conditions for which the depolarizing field has its maximum magnitude (when polarizations lie along the *z*-axis), while an increase in β lowers this magnitude. The value of β resulting in a vanishing total internal electric field is dependent on the supercell geometry, and in particular on the number of its non-polar layers [31]. This study thus allowed the investigation of electrical boundary conditions on properties of ultrathin films.

Extensive calculations were also made to clarify the effects of different mechanical boundary conditions on ferroelectric properties of (0 0 1) PZT ultrathin films. A rich variety of ferroelectric phases, including unusual triclinic and monoclinic states has been found, as well as, peculiar laminar nanodomains depending on the interplay between electrical and mechanical boundary conditions [61].

Specifically, the results obtained in Ref. [61] for *stress-free* ultrathin films, that are under *short-circuit* electrical boundary conditions, are remarkably similar to those of Ref. [27]. For instance, the polarization at the surfaces is significantly enhanced with respect to the bulk, and increases as the film thickness decreases. Under *stress-free* conditions, the film has a spontaneous polarization *aligned along the z*-axis for (large) values of β that correspond to a screening of at least 98% of the polarization-induced surface charges. On the other hand, when β becomes smaller, the internal field along the growth direction would be too strong to allow an out-of-plane component of the local mode [29]. As a result, the polarization aligns along an *in-plane*$\langle 0\ 1\ 0\rangle$ direction. The most striking result for stress-free PZT films is the polarization path when going from out-of-plane to in-plane. In this case, the polarization continuously rotates and passes through *low-symmetry* monoclinic and triclinic phases. It was also revealed that only in-plane components of the polarization appear in films under a *tensile* strain in the presence of depolarizing fields. Conversely, a large enough *compressive* strain annihilates the (in-plane) components of of the polarization for *any* β.

Another interesting result of this study [61] is the occurrence of *nanodomain* structures in ultrathin films under *compressive strain. Ab initio* simulation [28] has indicated that realistic electrode materials may not have sufficient carrier density to completely screen the depolarizing field for ultrathin single-domain ferroelectric films. In particular, spontaneous electric polarization can not be sustained in single-domain $BaTiO_3$ films of thickness smaller than 7 unit cells with $SrRuO_3$ electrodes. Another possibility to eliminate the depolarizing field and stabilize the ferroelectric phase is the appearance of a stripe domain structure in ultrathin films [26, 36]. Recently, investigation of the atomistic structure of the 180° — and 90° —domain boundaries in the ferroelectric perovskite compound $PbTiO_3$ have been performed using a first-principles ultrasoft-pseudopotential approach [55], establishing the geometry of the domain walls at the atomic level and calculating the creation energy of the domain walls. The domain wall was found to be very narrow, with a width in the order of the lattice constant. The quantitative support for the calculations has been provided by the experiment, that, in ultrathin films, 180° —stripe domains have a small equilibrium period and produce in the *X*-ray scattering pattern the characteristic features of ferroelectric phase [26, 36]. Similar calculations have been presented for the interactions between vacancies and ferroelectric domain walls, confirming the tendency of these defects to migrate to, and pin, the domain walls [62].

The morphology of nanodomains predicted in Ref. [61] contrasts with the two "simplest" pictures of *out-of-plane* 180° domains found in magnetic films, namely the flux-closure domain structures [42]—for which surfaces have solely *in-plane* magnetizations while the dipoles of the inside layers are either parallel or antiparallel *to the z*-axis—

and the open-stripe structures [42]—for which all the layers, including the ones at the surfaces, exhibit dipoles that are either parallel or antiparallel to the *z-axis*. The laminar nanodomains "only" exist for *compressive strain* and a *large-enough depolarizing field*, consistent with the experimental conditions of Ref. [36] and the theoretical findings of Refs. [29, 38]. The predicted period Λ of the laminar domains is $\simeq$ 8 in-plane lattice constants. This agrees well with the measurements of Ref. [36] yielding $\Lambda = 37$ Å for 20 Å-thick $PbTiO_3$ films. The stripe domain sizes observed in this study are intriguingly close to the ultimate limit of a single-molecule ferroelectric memory element. Interestingly, under compressive strain conditions and *partially* compensated depolarizing fields, "bubble" nanodomains were found to propagate throughout the entire thickness of the film. This situation is similar to that in which a bubble domain is formed in a ferromagnetic material with the easy-magnetization axis normal to the film surface by applying an external magnetic field. The phenomenon observed could provide a potential route toward ferroelectric bubble memory.

One criticism that can be raised regarding this study is the neglect of surface/interface effects that go beyond the surface charges (e.g., chemical bonding) in the modeling. Also, the misfit dislocations, which are a cause of stress relaxation and considerable strain reduction were not considered. A simple answer for that problem would be to use a temperature-dependent substrate effective lattice parameter allowing for the possible presence of misfit dislocations (or the thermal expansion difference between the substrate and the film) at the interface. Another point of the model presented in Ref. [61] is the fact that periodic boundary conditions was used in the *z*-direction of the supercell, which are not quite efficient due to the long-range nature of the dipole-dipole interaction which lead to artificial electrostatic interactions between the periodically repeated images of the film (to minimize the interaction between periodic images, a vacuum region of approximately 150Å separating the periodic images has been used).

2.6. "Ferroelectricity in $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films: critical thickness and 180° stripe domains" by Zhongqing Wu, Ningdong Huang, Zhirong Liu, Jian Wu, Wenhui Duan, Bing-Lin Gu, and Xiao-Wen Zhang, *Phys. Rev. B* **70** (2004) 104108

In Ref. [63], Monte Carlo simulations on the basis of a first-principles-derived Hamiltonian were made on the (0 0 1) $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films, under ideal open-circuit conditions and for different mechanical boundary conditions.

It is shown that the ferroelectricity in thin films depends critically on the strain constraint imposed by the substrate. For stress-free conditions, a nonzero polarization with an in-plane direction always exists in the system, i.e. it does not disappear even in the *monolayer* films. Under a compressive strain of -2% the out-of-plane polarization exhibits a strong dependence on the film thickness. Their calculations also reveal that the critical thickness appears only when the strain imposed by the substrate is strong enough to suppress the in-plane polarization. Above a critical thickness of about 3 unit cells (under the compressive strain of -2%), the out-of-plane polarization forms periodic 180°—stripe domains to screen the depolarizing field, and the domain period increases with the film thickness. Below the critical thickness, the stripe domain structure disappears, which suggests that the ferroelectricity can be suppressed even in the absence of the depolarizing electrostatic field. The competition between short-range and dipole–dipole interaction is revealed to be responsible for these phenomena.

2.7. "Properties of $Pb(Zr,Ti)O_3$ ultrathin films under stress-free and open-circuit electrical boundary conditions" by Emad Almahmoud, Yulia Navtsenya, Igor Kornev, Huaxiang Fu, and L. Bellaiche, *Phys. Rev. B* **70**, (2004) 220102(R)

Almahmoud *et al.*'s [64] investigated finite-temperature properties of (001) PZT stress-free ultrathin films under open-circuit electrical boundary conditions, that are PbO-terminated and have a Ti composition around 50%.

In Ref. [64] three additional terms (each with its own parameter) have been added to the effective Hamiltonian of bulk alloy to mimic explicit interactions between films and the vacuum. Two parameters quantify how the existence of the vacuum affects the *out-of-plane* components of the local modes and inhomogeneous strains near the surface. The third parameter characterizes the change, with respect to the bulk, of the short-range interaction between the *in-plane* components of the local modes near the surface. This approach was successfully tested, at low temperature, against direct first-principles calculations for ultrathin films. These simulations point out that the phase transition sequence can dramatically differ between bulks and thin films.

In particular, the authors found that (1) such films do not have any critical thickness under which ferroelectricity would disappear; (2) their polarization lies along directions perpendicular to the growth direction because of the huge depolarizing fields; (3) surface effects, and especially vacuum-induced changes of short-range interaction, significantly affect their local and macroscopic properties; (4) these ultrathin films exhibit a morphotropic phase boundary where the polarization continuously rotates, in a (0 0 1) plane between a $\langle 0\ 1\ 0\rangle$ and $\langle 1\ 1\ 0\rangle$ direction, as the Ti composition decreases at small temperature; (5) such rotation leads to large piezoelectric and dielectric coefficients; and (6) the nature of phase transitions can change when going from bulks to ultrathin films.

3. Concluding remarks

Recent works have shown that it is now possible to compute the physical properties of ferroelectric nanostructures from *direct* first-principles and first-principles-based techniques. An understanding (at a microscopic level) of ferroelectric-based nanostructures starts to emerge thanks to these approaches. In particular, it is now becoming clear how the surface, interface, thickness, electrical and mechanical boundary conditions affect the properties of ultrathin films.

It is reasonable to believe that while *ab initio* efforts will continue to focus on thin films, they may also be further extended to other ferroelectric nanostructures (e.g., dots, wires, etc...) [30, 65]. The anticipated insights may guide the synthesis of greatly improved materials and the realization of devices with new and/or improved capabilities.

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