Atomic-level simulation of ferroelectricity in oxide materials

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Abstract

Recent work on using atomic-level simulation methods to study the ferroelectric properties of oxide materials is reviewed. In particular, it is illustrated how such methods can provide insights into the physical properties of a wide range of ferroelectric oxide materials inaccessible by other means. Approaches for further improvements in materials fidelity and increased range of applicability are discussed.

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1. Introduction

Ferroelectric oxides are critical for a wide range of applications including non-volatile memory devices, sensors, transducers, and high-k dielectrics for capacitors. The most widely applied of these materials is Pb(Zr,Ti)O3 (PZT). In the last 30 years, ferroelectric oxide solid solutions have also been developed with high electromechanical coupling. In particular, relaxor ferroelectrics, such as Pb(Zr1/3Nb2/3)O3-PbTiO3 (PZN–PT) and Pb(Mg1/3Nb2/3)O3–PbTiO3 (PMN–PT), have been shown to have superior electromechanical properties [1] and have great promise as the next generation of transducer devices.

Understanding the basic physics behind oxide ferroelectrics is both of fundamental interest and important in the design of application specific ferroelectric materials. Theoretical approaches have long provided important insights. Devonshire applied Ginzburg–Landau methods to describe the phase transition sequences in BaTiO3 by an expansion of the free energy in terms of polarization [2]. Recently, this approach was extended to explain the appearance of monoclinic phases in the new class of solid solution ferroelectrics [3]. Accurate ab initio methods, in particular density functional theory (DFT), have allowed for an electronic-structure level understanding of both classic ferroelectrics [4–7] and solid solution ferroelectric oxides [8,9]. While ab initio methods continue to be important in the study of ferroelectrics (see Refs. [10,11] for a review), because of the computational restriction to small system sizes, these methods are almost intractable for the direct simulation of many important features of ferroelectric materials such as phase transitions, domain wall motion, and disordered solid solutions. For example, there has been only one limited, but computationally expensive, study of the phase transitions in PbTiO3 via ab initio molecular dynamics (MD) simulations [12].

There have been two main approaches to bridging the length and time scales: the effective Hamiltonian method and atomic-level simulation based on interatomic potentials. We refer the reader to Refs. [10,13] for a more detailed discussion of the effective Hamiltonian approach. The focus of this review will be on the second approach—the direct atomic level simulation of ferroelectric oxides using atomic-level descriptions of the system, parameterized by interatomic potentials. An inherent advantage of the atomistic approach over effective Hamiltonians is that all degrees
of freedom are included. Therefore, one does not need to know a priori which dynamical modes are important in determining specific material properties. In Section 2 we will summarize recent interatomic potentials that have been developed for ferroelectric oxides while in Section 3 we will briefly review some of the recent applications. We will conclude with a discussion of future directions in this area in Section 4.

2. Interatomic potentials for ferroelectric oxides

Validated interatomic potentials are critical to accurate atomistic simulations. The particular form of the interatomic potential can vary considerably depending on the material and the particular properties of interest. Ferroelectric oxides are mainly ionic materials, but exhibit some degree of covalency. In fact, the hybridization between oxygen 2p and transition-metal d electrons is critical for the degree of covalency. In fact, the hybridization between oxygen 2p and transition-metal d electrons is critical for driving ferroelectric instabilities in ABO₃ perovskites [4,5]. As a consequence, a successful model for a ferroelectric compound must include both ionic and covalent interactions. The choice of a particular potential model is a compromise between accuracy and simplicity, and there is no unique best choice. However, the model must be both accurate enough to reproduce basic properties obtained from first-principles calculations, yet simple enough to allow simulations of large systems, at finite temperature, for a long simulated time (~1 ns), and under an applied electric field.

The shell model has been extensively used in atomistic simulations of oxides because it is a simple method to phenomenologically describe the deformation of the electronic structure of an ion (the ionic polarizability) due to the interactions with other atoms [14–16]. In the shell model, each atom is described as two charged and coupled particles: a massive core and a massless shell that are linked by a spring as illustrated in Fig. 1. There are electrostatic interactions among all cores and shells except between the core and shell of the same atom. Short-ranged interactions are normally restricted to act between shells only. Formally, short-range interactions represents any van der Waals attraction and the Pauli repulsion due to the overlap of the electron densities of two ions; in practice, however, the short-range part of the potential represents all the interactions not represented by the electrostatic interactions, regardless of their physical origin. For this reason the functional form for the short-range interaction varies in the literature, and includes Born-Mayer, Buckingham, Rydberg and Morse potentials. Covalency effects in the model are at least qualitatively accounted for through the ionic polarizability of the shell model, and the frequent adoption of non-formal charges for the total (core plus shell) charge of an ion. The core–shell interaction is traditionally described by an isotropic coupling with a harmonic spring term; however to describe the hybridization effects on the polarizability important for the ferroelectric behavior, it was found that anharmonic core–shell interactions are required.

There are several other potential models that have been used in the study of ferroelectric oxides. In the bond-valence model, the bond order (or bond strength) between ions is a function of the bond distance between ions and the bond-valence energy can be expressed in terms of bond distance (see Ref. [17] for the functional form of the bond-valence energy term). The bond-valence model has been used to study the phase diagram and domain walls of PbTiO₃ [18] and the compositional phase diagram of PZT [17]. Dipolar potential models, where the dipole–dipole interactions are included explicitly, have been used to simulate the phase diagram of PbTiO₃ [19]. An extended shell model that incorporates charge transfer has been applied to study the phase diagram of BaTiO₃ [20]. In this model, the charge of core and shell has a Gaussian spatial distribution, and charge transfer is allowed between shells of different atoms. Coulombic and short-range interactions similar to the shell model are added to each of the above potential models. All of these potential models have shown similar levels of accuracy as the shell model potentials. However, the charge transfer model contains a more flexible and realistic representation of the atomic interactions in ferroelectric oxides; we shall return to the charge transfer models in the final section.

For the classic ABO₃ ferroelectric oxides, the shell model has on the order of 15 disposable parameters. The relatively ease of generating data on energy, forces, stresses, and phonon properties for simple ordered configurations using density functional theory (DFT), an accurate first-principles method, allows us to generate an input database containing a broad range of observables. A large database is desirable in order to constrain the parameters and to reproduce as wide a range of the different materials properties as possible. In addition to reproducing the correct stable crystal structure and lattice parameter(s), the fitting data set should include data from lattice dynamics (phonon frequencies, eigenvectors, and effective charges), ferroelectric soft mode behavior and elastic properties. While the lattice dynamics is critical to the phase transi-

![Fig. 1. Schematic of the shell model composed of a positively charged core and a massless shell with a spherical charge distribution. If the center of the shell does not overlap the core then the atom is polarized (atom 1). The atomic interactions are dependent on the charges and positions of the core and shell centers. The interactions between core–shell and shell–shell are described in Section 2.](image)

tions, the fitting should include data away from the harmonic approximation. This information can be incorporated by examining higher energy structures and displacement patterns or by extracting snapshots from ab initio MD simulations at higher temperature. The stability of ferroelectric phases is sensitive to pressure; thus stress information should also be included explicitly in the fitting. For example, a large c/a strain stabilizes the tetragonal over the rhombohedral phase in the case of PbTiO$_3$ [4]. Obviously, inclusion of information such as the electromechanical constants would help further refine the model.

Once a satisfactory materials properties database has been generated, the parameters for the potential model can be obtained by a least squares fit using minimizing algorithms, such as the Levenberg–Marquardt method. Obtaining accurate potential parameters is not trivial due to the complex parameter space and correlated nature of the parameters. Global search methods, such as the Nelder–Mead simplex algorithm and simulated annealing [21], can help perform a more systematic search for suitable parameter sets. An important assumption, that must be carefully validated, is that the potentials are transferable beyond the environment of the input ab initio database. The issue of transferability is especially important in applying interatomic potentials to simulate solid solution ferroelectric oxides, surfaces, and interfaces.

In Table 1 we present the shell model potential parameters for several ABO$_3$ ferroelectrics from the literature. For the K(Nb,Ta)O$_3$ and (Ba,Sr)TiO$_3$ systems all interactions are described by a Buckingham potential, $V(r) = A \exp(-r/\rho) - C/r^6$. For PbTiO$_3$, the O–O interactions are described by the Buckingham potential, while all other short-range interatomic interactions are described by a Rydberg potential, $V(r) = (A + Cr)\exp(-r/\rho)$. For all of the potentials, the core–shell coupling potential term is given by $V(w) = c_2w^2/2 + c_4w^4/24$, where $w$ is the core–shell separation within an ion. We will discuss the applications of the shell model in Section 3.

### 3. Applications

The potentials in Table 1 have been used to simulate the finite temperature behavior of classical ferroelectrics, solid solutions, superlattices, and ferroelectric thin films. These applications will be reviewed briefly with emphasis on the work done in the last two years.

Early studies applied the shell model potential to examine the phase transitions of several ABO$_3$ ferroelectrics. These included studies of KNbO$_3$ [22–24], BaTiO$_3$ [25,26], PbTiO$_3$, and LiNbO$_3$ [29]. Excellent qualitative agreement with experimental results was achieved. For example, the phase transition sequence from rhombohedral to orthorhombic to tetragonal and finally to cubic phase for BaTiO$_3$ with increasing temperature was accurately reproduced by both an anisotropic shell model [25,26] and an isotropic, anharmonic shell mode [30]. The fitting of shell model parameters to a LDA database significantly underestimates the transition temperatures for ABO$_3$ perovskites (see Fig. 2) [28]. The main source of this error is not the shell model itself, but rather the well known underestimate of the experimental equilibrium volume of solids when using the LDA approximation for the exchange-correlation functional in DFT [4,7] which, in turn, lead to a significant underestimate in the polarization and the transition temperatures in the MD simulations. In the electronic-structure calculations, one can induce the ferroelectric state by applying an appropriate negative pressure to the system. The imposition of the corresponding negative pressure in the MD simulations, results in a significant upward shift in the transition temperatures, as shown for PbTiO$_3$ in Fig. 2. Obviously, such corrections are not possible for the study of novel materials where experimental data are

### Table 1

The parameters for shell model potentials of several ABO$_3$ ferroelectrics

<table>
<thead>
<tr>
<th>Atom</th>
<th>Core charge</th>
<th>Shell charge</th>
<th>$k_2$</th>
<th>$k_4$</th>
<th>Short-range</th>
<th>A</th>
<th>$\rho$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(Nb,Ta)O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.2394</td>
<td>–0.4189</td>
<td>225.0</td>
<td>0</td>
<td>K–O</td>
<td>124,872.44</td>
<td>0.1950</td>
<td>0.0</td>
</tr>
<tr>
<td>Nb</td>
<td>–2.9878</td>
<td>7.8265</td>
<td>250.67</td>
<td>400.0</td>
<td>Nb–O</td>
<td>1036.63</td>
<td>0.3900</td>
<td>0.0</td>
</tr>
<tr>
<td>Ta</td>
<td>–2.9878</td>
<td>7.8265</td>
<td>295.0</td>
<td>400.0</td>
<td>Ta–O</td>
<td>1046.63</td>
<td>0.3900</td>
<td>0.0</td>
</tr>
<tr>
<td>O</td>
<td>1.1236</td>
<td>–3.010</td>
<td>75.0</td>
<td>1500.0</td>
<td>O–O</td>
<td>3600.26</td>
<td>0.2834</td>
<td>200.0</td>
</tr>
<tr>
<td>(Ba,Sr)TiO$_3$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ba</td>
<td>5.62</td>
<td>–3.76</td>
<td>251.8</td>
<td>0</td>
<td>Ba–O</td>
<td>1061.30</td>
<td>0.3740</td>
<td>0.0</td>
</tr>
<tr>
<td>Sr</td>
<td>5.62</td>
<td>–3.76</td>
<td>623.3</td>
<td>0</td>
<td>Sr–O</td>
<td>167.32</td>
<td>0.4949</td>
<td>0.0</td>
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<tr>
<td>Ti</td>
<td>4.76</td>
<td>–1.58</td>
<td>322.0</td>
<td>500.0</td>
<td>Ti–O</td>
<td>3769.93</td>
<td>0.2589</td>
<td>0.0</td>
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<tr>
<td>O</td>
<td>0.91</td>
<td>–2.59</td>
<td>31.0</td>
<td>4000.0</td>
<td>O–O</td>
<td>4740.00</td>
<td>0.2686</td>
<td>160.0</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>4.958</td>
<td>–2.785</td>
<td>119.5</td>
<td>17968.0</td>
<td>Pb–Ti</td>
<td>0.09</td>
<td>2.4201</td>
<td>12.57</td>
</tr>
<tr>
<td>Ti</td>
<td>8.820</td>
<td>–5.138</td>
<td>1428.0</td>
<td>0.0</td>
<td>Pb–O</td>
<td>6766.27</td>
<td>0.2738</td>
<td>127.78</td>
</tr>
<tr>
<td>O</td>
<td>0.563</td>
<td>–2.508</td>
<td>23.3</td>
<td>4514.0</td>
<td>Ti–O</td>
<td>1130.01</td>
<td>0.3597</td>
<td>–160.84</td>
</tr>
</tbody>
</table>

See the text for description of the potential forms. For all parameters the units of energy, length, and charge are given in eV, Å and electrons respectively.
Recently, Wu and Cohen have proposed a modification to the GGA exchange functional that accurately predicts the ground state structure for solids [31]; this may resolve the problem of the lattice parameter in the DFT calculations and, as a consequence, the problem of low transition temperatures in the MD simulations. These limitations notwithstanding, it is important to recognize that overall the shell model reproduces the range of different phase transition sequences seen in the ferroelectric oxides in the correct order, and the transition temperatures at least semiquantitatively. Thus, as discussed below, even though shell model potentials are not the final word on interatomic descriptions of ferroelectrics, such potentials are an important first step, with the ability to address a number of materials issues not accessible to other approaches.

One of the unique capabilities of atomistic simulations is the ability to provide dynamical information. This capability has been exploited to evaluate the dynamics of the phase transition. In displacive dynamics, a phonon mode becomes soft (i.e. unstable) with a decrease in temperature, resulting in atomic displacements from the high symmetry structure to a lower symmetry ferroelectric structure [32,33]. In order–disorder dynamics [34], there are equivalent minima along the eight \( \langle 111 \rangle \) directions for the transition-metal displacement in the cubic structure and the particular phase corresponds to different occupation probabilities. For the cubic phase all eight sites are occupied with equal probability. There are four, two, and one sites occupied in the tetragonal, orthorhombic, and rhombohedral phases, respectively. Early studies of K\( \text{NbO}_3 \) [22–24] and Ba\( \text{TiO}_3 \) [25,26] confirmed that these materials undergo an order–disorder type transition. The dynamics of monodomain switching has also been elucidated [35]. Recently, the more complex phase transition behavior of Li\( \text{NbO}_3 \), a trigonal ferroelectric material, was examined [29] using a shell model proposed by Tomlinson et al. [36]. Li\( \text{NbO}_3 \) undergoes a phase transition from ferroelectric \( (\text{R}3\text{c}) \) to paraelectric \( (\text{R}3\text{c}) \) at 1483 K: the atomistic simulations predicted a \( T_c \) of 1400 K [29]. Closer examination of the behavior of the Li and Nb atoms during the phase transition showed that the ferroelectric to paraelectric phase transition is more complex than expected. In particular, the phase transition consists of a two-stage process. The Nb–O cages undergo a displacive transition from ferroelectric to paraelectric at 900 K, but the Li atoms maintain a net displacement from the O planes until the ferroelectric transition at 1400 K. The Li\( \text{NbO}_3 \) study illustrates the value of atomistic simulations in understanding the complex behavior of phase transitions in ferroelectric oxides.

A natural extension from the studies of the classic ABO\(_3\) ferroelectrics is the examination of solid solutions of mixtures of these materials. A solid solution requires the description of both compounds simultaneously; thus interactions present in both compounds (e.g. O–O interactions) have to be the same, so as to maintain a consistent description. This approach assumes transferability of the corresponding interactions in the two pure compounds to the solid solution. This approach was taken for K\( \text{NbO}_3 \) and K\( \text{TaO}_3 \), with the shell model successfully reproducing the phase diagram of K\( (\text{Nb}_{1/2}\text{Ta}_{1/2})\text{O}_3 \) (KNT) solid solution [37]. Recently, the Ba\( \text{TiO}_3 \) shell model potential was extended to (Ba,Sr)\( \text{TiO}_3 \) (BST) solid solutions by adding the Sr–O interactions [30]. Despite keeping the O–O and Ti–O interactions from the Ba\( \text{TiO}_3 \) shell model potential, the potential reproduced the general features of pure Sr\( \text{TiO}_3 \). The model predicted transition temperatures as a function of Sr\( \text{TiO}_3 \) composition that match well with experimental results (see Fig. 3). Recently, a shell model potential for the relaxor ferroelectric solid solution PMN–PT was derived from \textit{ab initio} data of both end members [38]. This work found a cubic phase for pure...
PMN at all temperatures, with PMN–PT becoming cubic at sufficiently high temperatures, independent of PT composition. At room temperature the transition from a rhombohedral phase to a tetragonal phase with increasing PT concentration occurs through an intermediate phase (see Fig. 4) at concentrations very close to the experimentally observed morphotropic boundary, albeit over a broader range of the concentration. A more precise evaluation of the symmetry of the intermediate phase requires MD simulations with larger cell sizes than were used in this first study. These limitations notwithstanding, these preliminary results indicate that the compositional phase diagram of PMN–PT can be reproduced, at least qualitatively using a shell model approach [38].

Ferroelectric superlattices can also be used to engineer materials with designed ferroelectric and dielectric properties. Since the length scale of the composition modulations of the multilayer systems is typically on the order of nm, they are ideal systems for characterization using atomistic simulations. Among the heterostructures, the KNbO$_3$/KTaO$_3$ symmetric superlattice is one of the experimentally best characterized [39–42]. From a microscopic point of view, the difference between a solid solution and a superlattice is the atomic arrangement, i.e. the atomic order. Simulations showed that the behavior of the superlattice in the modulation direction (i.e. the direction of stacking) can be understood in terms of both the intrinsic properties of ferroelectric KNbO$_3$ layers and the interaction between them [43,44]. While the polarization of individual layers becomes stronger when their thickness increases, the interaction between layers decreases as the thickness of the intervening paraelectric layers increase. In this case, the coupling between ferroelectric layers is mediated by the induced polarization of the intermediate paraelectric layer. As a consequence, we can identify three coupling regimes (see Fig. 5). For thin layers, the ferroelectric layers are strongly coupled and the system acts as a single material with a transition temperature from a ferroelectric to a paraelectric phase $T_c$ independent of the bilayer thickness ($A$). For $A > 12$, $T_c$ increases with the modulation length because the coupling increase within a single KNbO$_3$ layer dominates over the coupling decrease between KNbO$_3$ layers. Finally, for $A > 24$, the interaction between KNbO$_3$ layers is sufficiently weak that they respond essentially independently of each other.

With the rapid miniaturization of ferroelectric devices, attention is increasingly focusing on the role played by surfaces and interfaces in the overall performance of materials. The surface can modify the structural behavior of perovskites by modifying the strength of various instabilities. PbTiO$_3$ is a clear example, where the presence of the surface modifies the balance of ferroelectric and antiferrodistortive distortion (AFD). In this particular case, the shell model was able to describe surface properties in good agreement with ab initio and experimental results [45]. The model with parameters previously fitted to describe bulk properties of PT also reproduced the surface atomic structure. This surface structure consists of a single layer with an AFD reconstruction where oxygen cages are rotated around a [001] axis through the Ti ions. Moreover, a decrease in the tetragonality produced by the surface leads to the stabilization of a phase with non-vanishing in-plane polarization. The BaTiO$_3$ surface has also been examined, again using shell models derived from bulk input data [46]. The shell model was able to qualitatively reproduce the structural relaxations of both terminations of BaTiO$_3$. Such validations allowed the investigation of the critical thickness of ferroelectricity under open circuit electrical boundary conditions. SrTiO$_3$ and BaTiO$_3$ surfaces have also been studied with shell models fitted to experimental data [47,48].

![Fig. 4](image4.png) The lattice parameter of PMN–xPT as a function of PT concentration at 0 GPa and 300 K obtained from MD simulations. The region of the transition phase between the rhombohedral and tetragonal phase is marked by a box. Figure reproduced from Fig. 6a in Ref. [38].

![Fig. 5](image5.png) The transition temperature for KNbO$_3$/KTaO$_3$ superlattice as a function of modulation length obtained from MD simulations. Figure reproduced from Fig. 8 in Ref. [43].
4. Future directions

As shown by the examples in this brief review, atomistic simulations with interatomic potentials derived entirely from *ab initio* calculations have been successfully applied to a range of ferroelectric materials. While the shell model has been able to qualitatively capture the behavior of a range of ferroelectric oxide systems, it does have significant limitations in the transferability of interactions between compounds. Therefore, an important future direction will be the application of more sophisticated potential models to ferroelectric materials. Improved potentials are required to more accurately examine complex systems such as solid solutions, relaxors, superlattices, and ferroelectric materials in contact with electrodes or deposited on a semiconductor substrate. It is expected that accuracy can be increased by imparting more flexibility to the potential model. There are several models that may introduce this additional flexibility: one promising approach is to use models that incorporate charge transfer explicitly. Such models would allow the charges of the ions to depend on the local environment. This additional flexibility in the charge might be critical in modeling systems where the charge on a particular atom may vary greatly due to changes in local environment (i.e. surface, interface, disorder). There has been only one preliminary study of ferroelectric oxides incorporating charge transfer, the earlier mentioned study of BaTiO₃ [20] (see Section 2); it would be interesting to examine more complex ferroelectric materials with charge transfer potentials. The increase in computational power presents opportunities to apply more complex but realistic potential models to the study of ferroelectric oxide materials.

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