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An electromechanical atomic-scale finite element method for simulating evolutions of ferroelectric nanodomains

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ABSTRACT

In this paper, a novel atomic-level computational method of perovskite ferroelectrics is established by combining the shell model and atomic-scale finite element method (AFEM). Its applicability is carefully testified for both bulk and nanoscale ferroelectrics, by comparing the calculated structural parameters and polarizations with the molecular dynamics (MD) simulations, first-principles calculations and experiment results. A comparison of the CPU time demonstrates that the developed method has a computational speed about 10 times over that of shell model MD method and its advantage becomes more evident as the computational scale becomes larger. Moreover, two effective calculation skills of long-range Coulomb force are introduced which can further enhance the computational efficiency by about 10 times. Using the developed atomic-level method, we investigate the various patterns of nanoscale domain structures in $BaTiO_3$ and their evolutions under electrical loadings. A domain structure with coexistence of vortex and streamline polarization patterns is revealed. Furthermore, the simulations of domain evolutions not only reproduce well the two-step 90° domain switching process observed in experiments on single domain under an anti-parallel electric field, but also provide a full evolution diagram among different domain patterns under various electric fields. A quantitative analysis indicates that the direction-dependent coercive field of multi-domain structure can be well described by that of single domain based on a simple analytical model. This study on domain patterns and evolutions may help us understand the behaviors of ferroelectrics from the atomic level.

1. Introduction

Ferroelectric materials, due to their excellent properties of electromechanical energy conversion and rapid response, have been widely used as smart devices in diverse sectors of industry (Damjanovic, 1998; Polla and Francis, 1998; Shieh et al., 2001; Bhattacharya and Ravichandran, 2003), ranging from aerospace, automotive, to medicine and microelectronics. Recently, with the rapid development of manufacturing technology, nanoscale ferroelectrics, such as ultra-thin film, nanowire, nanoparticle and nano-domain, have attracted intensive attentions because of their advantages in miniaturizing the functional devices and increasing the density of ferroelectric memories. This category of smart material has potential applications as nano-generator (Wang and Song, 2006), nanoactuator (Auciello et al., 1998), phased-array radars (Van Keuls et al., 2005), etc.

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In order to understand the unique properties of nanoscale ferroelectrics and the underlying mechanisms, many fundamental theoretical investigations have been carried on, mainly using the first-principles method (Padilla and Vanderbilt, 1997; Junquera and Ghosez, 2003; Naumov et al., 2004; Geneste et al., 2006; Pilania et al., 2009; Shimada et al., 2010), MD simulations (Tinte and Stachiotti, 2001; Sepliarsky et al., 2005b, 2006; Sang et al., 2008; Zhang et al., 2009, 2010a; Stachiotti and Sepliarsky, 2011), and phenomenological models based on Landau–Ginzburg–Devonshire (LGD) theory (Scott et al., 1988; Zhong et al., 1994b; Morozovska et al., 2006, 2007; Hong and Fang, 2008; Zheng et al., 2008). These studies revealed many interesting physical phenomenon of nano-ferroelectrics, such as the existence of critical size (Junquera and Ghosez, 2003; Geneste et al., 2006), the modulation of polarization via applied strain (Choi et al., 2004; Shimada et al., 2009; Zhang et al., 2010a). Note that most of these studies only considered the nano-ferroelectrics to be composed of single domains, and only limited literatures studied the complex multi-domain configuration and their evolutions. In these researches concerning polarization patterns, Naumov et al. (2004) and Pilania and Ramprasad (2010) utilized first-principles method in analyzing the stable polarization distribution of lead zirconium titanate (PZT) nanoparticle and $PbTiO_3$ nanowire, respectively, and both revealed the existence of vortex domain pattern; Hong et al. (2010) studied the polarization distribution of $BaTiO_3$ nanowire and obtained a novel streamline domain pattern; Shimada et al. (2010 and 2011) revealed a vortexlike closure domain in both $PbTiO_3$ nanofilm and bulk material; Stachiotti and Sepliarsky (2011) investigated the polarization distribution of $PbTiO_3$ nanoparticle by shell model MD simulations and found that size-induced topological transformations can lead to the stabilization of a ferroelectric bubble by the alignment of vortex cores along a closed path. Note that the nanoscale domain structure was also observed in experiments. For example, Schilling et al. (2006 and 2007) observed periodical 90° domain structure in $BaTiO_3$ nanowire by scanning transmission electron microscope, with the polarization direction lying parallel to the axis of the wire. They also revealed a "Forsbergh" domain pattern in free-standing $BaTiO_3$ nanodots (Schilling et al., 2009). By applying an external electric field, Ivry et al. (2010) observed a closure vortexlike structure of 90° ferroelastic domains in ferroelectric PZT ultra-thin films. In order to obtain a deep understanding on the formation and evolution of those nanodomain structures, theoretical investigations are still in urgent need, wherein a key issue is to develop an effective atomic-level computational method.

There are mainly two atomic-level computational methods of ferroelectric materials, the first-principles method, and the shell model MD method. The first-principles method is a computational method solving quantum mechanics equations that accurately accounts for the interactions of atoms and electrons around. It has been widely used in analyzing the atomic structure and electromechanical coupled behaviors in both bulk ferroelectrics (Cohen and Krakauer, 1990; Cohen, 1992; Kingsmith and Vanderbilt, 1993) and nano-ferroelectrics (Junquera and Ghosez, 2003; Naumov and Fu, 2005; Geneste et al., 2006; Pilania et al., 2009; Shimada et al., 2009, 2010; Stengel et al., 2009; Pilania and Ramprasad, 2010). But this method is not able to deal with large atomic systems due to the complexity of solving the quantum mechanics equations and limitation of computer capacity, and thus the reported simulation systems were usually within several hundreds of atoms. To overcome this limitation, the shell model MD method was introduced in the simulations of ferroelectric materials (Migoni et al., 1976; Khatib et al., 1989; Tinte et al., 1999; Sepliarsky et al., 2001, 2005a). This method models each atom as two charged particles, a massive core and a massless shell, and can effectively characterize the deformation of the electronic structure and spontaneous polarization of ferroelectric perovskites (Tinte et al., 1999). By treating the atomic interactions in the MD framework, the shell model can save much computation cost compared to the first-principles method. Thus this method has found many applications in modeling of nanoscale ferroelectrics, including the nanofilms (Tinte and Stachiotti, 2001; Sepliarsky et al., 2005b, 2006), nanowires (Zhang et al., 2009, 2010a) and nanoparticles (Stachiotti and Sepliarsky, 2011). Note that the shell model has also been incorporated in an anharmonic lattice statics method for analyzing 180° and 90° domain walls in tetragonal ferroelectric perovskites (Yavari et al., 2007a, 2007b; Angoshtari and Yavari, 2010, 2011). However, there are still two constraints that restrict the computational efficiency of shell model MD method. First, the shell mass of each atom is very small in the shell model, and thus the time step should be small enough to avoid the divergence of simulations. Second, with the increase of simulation system, the CPU time of the MD simulation usually increases much quicker than linear estimation. Thus the CPU time will increase rapidly when the dimension of simulation system increases to several nanometers. These two limitations can be overcome if the atomic-scale finite element method (AFEM) (Liu et al., 2004, 2005) is adopted to determine the atomic positions at the equilibrium state, instead of MD method. AFEM is a molecular statics method that solves the energy minimization problem in the finite element framework. Thus, the particle mass is not needed in the numerical calculation, and more importantly, the CPU time of this method increases almost linearly with the atom number (Liu et al., 2004, 2005).

On the other hand, the phase field method has been widely used in modeling the configurations and evolutions of domain structure in bulk ferroelectrics (Chen, 2002; Li et al., 2002; Wang et al., 2004; Xiao et al., 2005; Zhang and Bhattacharya, 2005a, 2005b; Su and Landis, 2007; Li et al., 2008, 2010; Shu et al., 2008; Kontsos and Landis, 2010; Zhang et al., 2010c; Li and Landis, 2011). Although the phase field method is based on a continuum description of polarization component, it can explain some size-dependent behaviors of nanoscale ferroelectrics (Wang and Zhang, 2006), through the introduction of an extrapolation length. However, the value of extrapolation length needs to be determined by atomic-scale simulations or experiments, and some physical phenomena related with atomic behaviors may not be studied by this method. For example, recent first principles calculations (Pilania et al., 2009; Hong et al., 2010) demonstrated that the polarizations distributions (both the cross-sectional and axial components) are completely different for $BaTiO_3$ nanowire with different surface terminations, which is mainly induced by the different atomic structures of BaO and TiO_2. Such surface effect may not be well understood by the phase field method. This difficulty can be overcome if an effective atomic-level computational method of ferroelectrics is complemented.

The motivation of this study is to develop an effective atomic-level computational method of ferroelectric perovskites by combining shell model and AFEM, and then investigate the electric field driven evolutions of various nanodomains. We