Finite size effects on a core-shell model of barium titanate

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ABSTRACT

In this work we study the finite size effects on bulk properties of an atomistic model of ferroelectric barium titanate. The interaction potential is based on the core-shell model, which confers polarizability to ions, and a long range electrostatic potential. Results show that finite size effects are dependent on the property analyzed. Structural and static properties such as elastic constants and spontaneous polarization show minor deviation with chosen system size, while the transition temperatures and the coercive field are largely affected by it. The dielectric susceptibility, a static property commonly reported as being very sensitive to finite size effects, presents no deviations with system size in our study. The computation of the long range electrostatic energy contribution is not related to the finite size effects found in this model. We believe that the appearance of finite size effects for a subset of bulk properties is the strong dependence of the energy barriers in the potential energy landscape with the chosen system size.

1. Introduction

Ferroelectrics are materials that possess ferroelectricity, that is, the ability to retain electric polarization in the absence of an applied electric field. Moreover, a sufficiently strong electric field can change the polarization of a ferroelectric material. In oxides with a perovskite structure [1], a non-centrosymmetric unit cell is the building block for the emergence of an electric dipole. Ferroelectricity in perovskites arises from the competition between the long range electrostatic interaction, which favors the formation of polarized domains, and the short range elastic contribution, which favors a uniform strain field throughout the material [2]. Hence, the manybody manifestation of this competition is the appearance of a domain structure consisting of polarized regions with a given direction separated by domain walls.

One of the current challenges regarding ferroelectric perovskites is the relationship between structure and macroscopic properties. To address this problem, computer simulations become very important tools once it is possible to study a particular phenomenon systematically in a controlled manner. Among the different computer simulation techniques used to study ferroelectrics, molecular dynamics is particularly useful because it provides an atomic level description of the structure of a model material.

An accurate atomic level description of a ferroelectric material involves the calculation of long range electrostatic interactions.

When dealing with a model that reproduces the volumetric properties of a material in molecular dynamics, it is necessary to use an adequate system size that is both representative, in terms of the configuration space of the statistical ensemble, and computationally inexpensive. It turns out that the macroscopic properties calculated for a material model may have different sensitivities with respect to the system size employed, i.e. they possess finite-size effects arising from the numerical procedure. Figueirido et al. presented a systematic approach on how the truncation of the electrostatic interactions affect volume-dependent properties in aqueous solutions [3]. A molecular dynamics study of SPC/E water model showed that the dielectric constant had a strong dependence on system size while structural properties remained unchanged [4].

Finite-size effects studies in ionic liquids are in fact much more popular in the literature [5–8] when compared with ionic crystals. This work presents an assessment of the finite-size effects on computer simulations of an atomistic model for barium titanate monocrystal. We argue that the long range electrostatic energy computation may not be the main culprit for the appearance of size-dependent bulk properties. Based on the effective interatomic potential proposed by Tinte et al. [9], we show in this paper that the choice of the supercell size affect just a subset of macroscopic properties, namely those associated with an energy barrier against solid-solid phase transitions. In Section 2, the theoretical background and the employed methodology are described. In Section 3 the results are presented and discussed. In the final part of the manuscript, a summary of the main results and the conclusions are given.

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2. Theory and methodology

Molecular dynamics (MD) simulation was employed throughout this work [10]. We used the LAMMPS package [11] to run the simulations. The equations of motion were integrated using the standard velocity-Verlet algorithm. All simulation and calculation of thermodynamic properties were performed in the isothermal-isobaric ensemble [12] unless otherwise specified. The Nosé-Hoover barostat was employed to control the pressure, with a damping parameter equal to 0.3 ps. The Berendsen thermostat was employed with a damping parameter equal to 0.1 ps. It was observed that the choice of the damping parameters did not influence the results significantly. The interaction potential chosen to model barium titanate was developed by Tinte and co-workers [13]. It was shown that this model can reproduce the correct phase transition sequence and structural properties not only for $BaTiO_3$ but also for the barium-strontium titanate solid solution. Each ion is composed of a massive core (98% of the ion mass) and a light-weight shell connected by a restorative force. This kind of atomistic simulation is known as the adiabatic core-shell model. This method incorporates polarizability to the ions once it is possible to induce an electric dipole upon applied electric field.

All cores and shells possess fixed charges and, unless they belong to the same core-shell unit, they interact electrostatically. Long range electrostatic interactions are fully accounted via the particle-particle particle-mesh method [14] with a 1.2 nm real space cutoff and energy accuracy of 1×10^{-5}. The shells interact via the Buckingham potential. The complete description of the interaction potential can be found in Ref. [9]. An alternative long-range solver method, the Ewald sum, was also adopted for comparison and results were statistically identical. Another numerical method called the Wolf summation [15] often employed in previous studies also gives similar results if a 1.6 nm cutoff is used.

Finite-size effects of several properties were analyzed for bulk barium titanate. To this end, periodic boundary conditions were imposed in all dimensions. The use of periodic conditions effectively removes any surfaces regardless of the chosen system size. To ensure energy conservation, a time step of 0.4 fs was used. This somewhat small time step is required due to the high vibration frequency of the shells.

3. Results

The system was initially setup in the rhombohedral structure with a lattice constant equal to 4.008 Å and tilt angles equal to 89.67°. Fig. 1 shows the evolution of the lattice parameters during a heating procedure on systems with sizes $n \times n \times n$, where n is the number of unit cells along the sides of the simulation box. A constant heating rate of 2.5 K/ps from 10 to 460 K was applied. By analyzing the change of simulation box shape and size, it is possible to infer the phase transition that has taken place. In this case, the sequence is (during heating): rhombohedral → orthorhombic → tetragonal → cubic. One can observe that the phase transitions become sharper with increasing system size. In particular, it is very difficult to even identify the crystalline phases for the smallest system size due to the large fluctuation of the simulation box.

The phase transition temperatures dependence with the system size is shown in Fig. 2. The number of particles $N = 3430, 10,000, 17,280, 40,960$ correspond to system sizes with $n = 7, 10, 12, 16$, respectively. There is a strong finite-size effect for systems with $n = 7$ and 10. This effect is reduced for the two largest systems. Such a strong finite-size effect effectively sets a lower limit size of 10,000 particles in order to obtain reliable macroscopic bulk properties on specific crystal phases of this model.

The results for the transition temperatures using the largest system and the experimental values are summarized in Table 1. For comparison purposes, the experimental values and results from an MD study by Tinte et al. [13] using the same model with fewer particles are also shown. Our results show that the model is better than previously thought in reproducing the phase transition temperatures, specially the rhombohedral-to-orthorhombic and the tetragonal-to-cubic transitions. Moreover, discrepancies are found for all transition temperatures obtained by simulation. It is very likely that several factors including system size, core-shell mass ratio and heating procedure had an impact on the final results reported in Ref. [13]. Perhaps the most important factor is the correction of the pressure tensor, which is used by the barostat, when a core-shell simulation is performed. The true temperature of the system comes from the kinetic energy of the centers of mass of each core–shell unit. If we remove that correction, we obtain almost perfect agreement with the work of Chen et al. [16]. While that may not account for the discrepancies with Ref. [13], this analysis shows that our simulation reproduces results reported in the literature.

One possible explanation for the finite size effect found in the phase transition temperatures is the rate applied in the heating procedure. To check this possibility, a long simulation was performed for systems with $n = 10, 12$ and 16 at 300 K, with a starting configuration taken from the heating procedure discussed previously. According to Fig. 3(a) (and also Fig. 1), all systems are initially in the tetragonal phase. The lattice parameters a and c and the c/a ratio are the same within 0.1% precision for all system sizes. However, for $n = 10$ the c/a ratio drops to 1 after 100 ps of temporal evolution, i.e., the system passes to a cubic phase. In other words, the tetragonal phase for $n = 10$ is metastable at 300 K. The metastability at that temperature means that the transition temperature for $n = 10$ is very sensitive to the heating rate applied. A heating simulation using half the rate applied in Fig. 1 shows a decrease of 25 K on the tetragonal-to-cubic transition temperature. Meanwhile, a reduction of only 10 K was observed for the larger systems. The same trend was found for all the remaining transition temperatures.

We also checked if the phase transition temperatures and metastability found for $n = 10$ are associated with a larger instantaneous temperature fluctuations due to the thermostat. The temperature fluctuation for $n = 10$ is equal to 6 K, twice as large compared with $n = 16$. Temperature fluctuations are too small compared with the drop of the phase transition temperature. However, they may influence the degree of metastability if we consider that the solid-solid phase transitions in barium titanate are associated with finite energy barriers.

Although the tetragonal-to-cubic transition does not change the average potential energy per atom of -10.853 eV found in all three systems, there is a significant increase on the per-atom electrostatic energy (Fig. 3(b)). That means the short range potential decreases when the system passes to a cubic symmetry, that is, the non polarized phase is energetically more favorable due to the short range contribution. Additionally, the rise in electrostatic energy is three times higher in $n = 16$ than in $n = 10$. Assuming the system with $n = 7$ follows the same trend, the electrostatic energy rise becomes comparable with thermal fluctuations. That may contribute to the significantly smaller transition temperature found for $n = 7$.

Let us now turn the focus to the ferroelectric phase with the highest symmetry, the tetragonal crystal. Fig. 4 shows the size dependence of the elastic constants for tetragonal barium titanate at 300 K. Elastic constants were calculated using the stress-strain relations in the linear regime via uniform deformation of the simulation box. The box lengths were deformed by 0.0125% every 1000 time steps and stress averages were calculated using the last