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Molecular statics simulations of head to head and tail to tail nanodomains of rhombohedral barium titanate

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ABSTRACT

Studies of head to head and tail to tail domain configurations of different sizes are performed in order to discover size effects in rhombohedral barium titanate. To this end, a molecular statics (MS) algorithm is applied to simulate ferroelectric barium titanate in the rhombohedral phase at 0 K (which is the standard restriction of MS). As a result the size effects on polarization patterns as well as the influence on the systems total energies are highlighted.

1. Introduction

Ferroelectric functional materials are simulated on all length scales, whereby various modeling approaches and computational resources are necessary. On the macroscopic length scale continuum mechanical approaches, e.g. the phase field method, are widely used in order to phenomenologically simulate ferroelectric material behaviour [1,2]. Nevertheless, some ferroelectric structures like e.g. surfaces or interfaces are too small in size to be simulated accurately by most of the available continuum mechanics models. Therefore atomistic simulations are necessary to not only predict but also to understand crystalline material behavior in general [3]. Furthermore atomistic simulations are used to improve or inform continuum mechanics models. Material parameters are adopted by continuum constitutive models to increase the accuracy of e.g. phase field or fracture modeling [4,5]. On the smallest length scale ab initio methods such as the density-functional theory (DFT) are able to determine internuclear interactions [6–8]. Simulations at the quantum level are very detailed but suffer from their significant computational costs, and therefore are not capable of simulating domain structures. Molecular dynamics (MD) simulations are able to calculate larger systems but still the computational costs are very high. Thus we apply a molecular statics (MS) algorithm in order to simulate domain configurations on the atomistic scale efficiently [9]. Experiments have shown the existence of different domain configurations at the length scale of about 0.1 mm [10]. Nevertheless, also nanodomain patterns have been observed by experiments [11]. Domain walls are investigated by experiments and simulations whereas especially 180° domain walls have been examined [12–16]. However, experiments at very low temperatures are difficult to realise and there are no detailed domain wall studies available for rhombohedral barium titante.

In this work we use the presented molecular statics algorithm in order to study size effects of head to head and tail to tail nanodomain configurations of ferroelectric barium titanate in the rhombohedral phase. Therefore we analyse different domain sizes and compare the potential energies of the different systems. The paper is organized as follows: In Section 2 we briefly introduce the theory and computation of molecular statics. The applied core–shell model for the simulation of ferroelectric barium titanate is highlighted in Section 3. We address the theory of the computation of polarization in Section 4. In Section 5 we present the numerical results of head to head and tail to tail nanodomains. Thereby different domain sizes are compared considering the polarization behavior at the interface as well as the differences in the potential energies. Finally a discussion and conclusions are presented in Section 6.

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2. Molecular statics algorithm

A molecular statics algorithm for the simulation of a discrete particle system has been implemented. Thereby the system's total potential energy reads as

$$E^{tot} = \Phi^{int}(\mathbf{r}) + \Phi^{ext}(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\Phi^{int}(\mathbf{r}_{ij}) + \sum_{i=1}^{N}\mathbf{f}_i^{ext}\cdot\mathbf{r}_i. \tag{1}$$

The distance vector between two particles i and j is represented by $\mathbf{r}_{ij} := \mathbf{r}_j - \mathbf{r}_i$. Particles interact by energy potentials which are given by Φ^{int} while an external conservative field at the position i is represented by $\mathbf{f}_i^{ext}$. The equilibrium configuration of the discrete particle system is computed by the stationary condition

$$\frac{\partial E^{tot}}{\partial \mathbf{r}} = \mathbf{0}. \tag{2}$$

Interpreting the interactions between particles computationally as one-dimensional nonlinear truss elements, (2) can be solved similar to a nonlinear FE truss network. The residual equation satisfies

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}^{ext}(\mathbf{r}) - \mathbf{F}^{int}(\mathbf{r}) = \mathbf{0} \tag{3}$$

in the equilibrium configuration. Linearisation as involved in a Newton-step reads as

$$\mathbf{K}\cdot \mathrm{d}\mathbf{r} = \mathbf{F}^{ext} - \mathbf{F}^{int}, \tag{4}$$

where $\mathbf{K}$ denotes the global stiffness matrix and $\mathbf{F}^{int}$ are the internal forces exerted on the particles. Considering an electromechanical problem, an external force acting on a particle i caused by an electric field $\mathbf{e}_i$ at the position i is calculated by (no summation on i)

$$\mathbf{f}_i^{ext} = \mathbf{e}_i\, q_i. \tag{5}$$

The local internal force vectors and stiffness matrices are calculated by derivation of the interaction potentials with respect to the particles positions

$$\mathbf{f}^{int} := \frac{\partial \Phi_{ij}}{\partial \mathbf{r}_{ij}}, \quad \mathbf{k} := \frac{\partial^2 \Phi_{ij}}{\partial \mathbf{r}_{ij}^2}. \tag{6}$$

All local interaction forces $\mathbf{f}^{int}$ and local stiffness matrices $\mathbf{k}$ have to be assembled into the global internal force vector $\mathbf{F}^{int}$ and the global stiffness matrix $\mathbf{K}$. Thereby the assembling follows similar to the assembly of a one-dimensional nonlinear finite elements truss network.

3. Core–shell model for the simulation of barium titanate

Ferroelectric materials like e.g. barium titanate have been simulated on all length scales and a large variety of material models are available [1,17,18]. For molecular dynamics simulations of ferroelectric materials the core–shell model is widely used since it is able to consider ionic polarization as well as electronic polarization [19–22]. In the core–shell model every ion is modeled by two particles. The first particle is representing the positively charged atom core of an ion while the second particle represents the negatively charged center of the electron shell. Three different energy potentials are applied to model the particles' interactions. Firstly, all particles except the atom core and the electron shell of the same ion interact by long range Coulomb interactions. For the sake of numerical stability and to allow a small interaction-cut-off radius R_c, we instead apply the Wolf summation

$$\Phi_i^{Wolf} = \frac{1}{4\pi\epsilon_0}\sum_{\substack{j>i\\ |\mathbf{r}_{ij}|<R_c}}\left[\frac{q_i q_j \mathrm{erfc}(\alpha|\mathbf{r}_{ij}|)}{|\mathbf{r}_{ij}|} - \lim_{|\mathbf{r}_{ij}|\to R_c}\left\{\frac{q_i q_j \mathrm{erfc}(\alpha|\mathbf{r}_{ij}|)}{|\mathbf{r}_{ij}|}\right\}\right] - \frac{1}{2}\left[\frac{\mathrm{erfc}(\alpha R_c)}{2R_c} + \frac{\alpha}{\pi^{\frac{1}{2}}}\right]\sum_{i=1}^{N} q_i^2. \tag{7}$$

Thereby the complementary error function is represented by $\mathrm{erfc}(x) = 1 - \frac{2}{\pi^{\frac{1}{2}}}\int_0^x e^{-\tau^2}\mathrm{d}\tau$ and α is a potential damping factor [23]. In order to reduce the computational effort in the sequel, the cut-off radius for all interactions has been chosen with $R_c = 10$ Å. Furthermore the potential damping factor in (7) has been chosen with $\alpha = 0.25$.

Short range energy potentials are interpreting the bonding between different electron shells and are represented by a Buckingham potential

$$V_{\mathbf{r}_{ij}}^{Buck} = A\,\exp\left(-\frac{|\mathbf{r}_{ij}|}{\rho}\right) - \frac{c}{|\mathbf{r}_{ij}|^6}. \tag{8}$$

The interactions of atom cores and electron shells of the same ions are modeled by a nonlinear spring

$$V_{\mathbf{r}_{ij}}^{Spring} = \frac{1}{2}k_2|\mathbf{r}_{ij}|^2 + \frac{1}{24}k_4|\mathbf{r}_{ij}|^4. \tag{9}$$

The applied model parameters for the simulation of barium titanate were predicted by [17] and are depicted in Table 1.

4. Computation of polarization

To calculate the polarization of the unit cells Born effective charges have been considered. Theoretically, polarization can be calculated based on the charges and the positions of the ions within a unit cell for they generate an electric dipole moment. However, the ions' nominal charges cannot be used due to quantum mechanical effects. Thus, for the proper calculation of polarization Born effective charges have to be considered. Born effective charges can be determined by first principle calculations (e.g. DFT) or by experiments and are widely used in atomistic simulations [24,25]. Note that in our calculations the Born effective charges are only used in post-processing to calculate the polarization and therefore have no influence on the calculated particles' displacements.

The change of polarization $\mathbf{p}$ of a single unit cell is described by

$$\delta\mathbf{p} = \frac{e}{V}\sum_{m=1}\mathbf{Z}_m\cdot\delta\mathbf{r}_m. \tag{10}$$

Here $\delta\mathbf{r}_m$ is the change of the position vector of the m-th basis atom and $\mathbf{Z}_m$ is the corresponding Born effective charge tensor [24]. Since Born effective charges have no dimensional unit e represents the elementary charge while V is the volume of the m-th unit cell in

Table 1
Core–shell model parameters for the simulation of BaTiO $_3$. The symbol ‖ and ⊥ indicate directions of the Ti–O bond [17].

Atom	Core charge ($\|e\|$)	Shell charge ($\|e\|$)	k_2(eVÅ^{-2})	k_4(eVÅ^{-4})
Ba	5.62	−3.76	251.80	–
Ti	4.76	−1.58	322.0	–
O	0.91	−2.59	31.0 (‖)101.27(⊥)	3000(⊥)
Short-range	A (eV)	ρ (Å)	c (eV Å^6)	
Ba–O	864.536	0.38729	0.0	
Ti–O	4526.635	0.25239	0.0	
O–O	4102.743	0.29581	300.0	

Table 2
Born effective charges of BaTiO $_3$. Z_1(O) and Z_2(O) refer to O displacements 1 and 2 of Fig. 1 [24].

Z(Ba)	Z(Ti)	Z_1(O)	Z_2(O)
2.75	7.16	−5.69	−2.11