Impact of domains on the orthorhombic-tetragonal transition of BaTiO$_3$: an \textit{ab initio} study

Anna Grünebohm$^1$ and Madhura Marathe$^{2,3}$

$^1$ICAMS, Ruhr-University Bochum, Bochum, Germany
$^2$Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193 Bellaterra, Spain.
$^3$Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.

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We investigate the multi-domain structures in the tetragonal and orthorhombic phases of BaTiO$_3$ and the impact of the presence of domain walls on the intermediary phase transition. We focus on the change in the transition temperatures resulting from various types of domain walls and their coupling with an external electric field. We employ molecular dynamics simulations of an \textit{ab initio} effective Hamiltonian in this study. After confirming that this model is applicable to multi-domain configurations, we show that the phase transition temperatures strongly depend on the presence of domains walls. Notably we show that elastic 90$^\circ$ walls can strongly reduce thermal hysteresis. Further analysis shows that the change in transition temperatures can be attributed to two main factors – long-range monoclinic distortions induced by walls within domains and domain wall widths. We also show that the coupling with the field further facilitates the reduction of thermal hysteresis for orthorhombic 90$^\circ$ walls making this configuration attractive for future applications.

I. INTRODUCTION

In the last decades the functional properties of ferroelectric (FE) perovskites came into focus for exciting applications\cite{1,2} in particular Pb-free BaTiO$_3$-based materials are promising for sustainable technologies with operating temperatures at and below room temperature. BaTiO$_3$ (BTO) crystallizes in the paraelectric (PE) cubic phase (R$3m$) at high temperatures and below 120°C, 5°C and -80°C the FE tetragonal (T), orthorhombic (O) and rhombohedral (R) phases with P4mm, Amm2 and R$3m$ symmetry occur\cite{3,4}. For applications close to ambient temperatures, in particular the T and O ferroelectric phases and the transition between them are relevant. There are only a few reports which have studied the T-O transition in detail.\cite{5,6} X-ray diffraction measurements have pointed to the existence of an intermediate phase with short-range monoclinic order at this transition\cite{6} and under an applied field the T-phase transforms to a monoclinic phase which remains stable after removing the field.\cite{7} Another measurement also confirmed the existence of monoclinic phases and reported a “thermotropic” phase boundary,\cite{8} which is the temperature-analog of concentration-dependent morphotropic phase boundaries. Such phase boundaries are related to flat energy landscapes, enhanced polarization rotation and in turn exceptional large functional responses\cite{9,10}.

The T–O transition is a first-order phase transition with phase coexistence and a broad thermal hysteresis between the transition temperatures for cooling ($T_C^-$) and heating ($T_C^+$).\cite{11} Furthermore, different nature of the phase transition with abrupt versus continuous changes in polarization while cooling and heating has been reported\cite{12,13}. The measured transition temperatures for the T–O transition have a large error bar of more than 10 K which is comparable to the magnitude of the hysteresis itself.\cite{14,15} Hysteresis potentially results in reduced reversible functional responses and a wide range of responses for different samples, making the material unsuitable for devices which require long operational lifetime.\cite{16,17,18} Therefore, it is important to understand the extrinsic and intrinsic factors which contribute to thermal hysteresis and the order of the transition. So far, the large error bars in $T_C$’s have been attributed to presence of domains.\cite{19,20} Domains and domain walls are also known as one of the major sources of extrinsic functional responses.\cite{21} Furthermore, recent developments in the field of sample preparation and measurement techniques with atomic resolution brings the idea of engineered domain walls (DW) within our reach and allows us to master hysteresis by microstructure design. Domain engineering designed for specific applications\cite{22,23} and optimization of functional responses\cite{24,25} have already been tested in experiments. Therefore, in the present study, we focus on domains and how the presence of multi-domain (MD) phases affects $T_C$, the nature of phase transition and its thermal hysteresis.

As dictated by underlying crystal symmetry, polarization $P$ along all $\langle 100 \rangle$ and $\langle 110 \rangle$ directions would lead to degenerate states for T and O phase, respectively. The single-domain (SD) system with polarization along any one of these directions would be the ground state for ideal materials under perfect screening. However, typically multi-domain phases are prevalent in which domains of different polarization directions coexist and are separated by a domain wall in which the polarization changes direction. These walls are characterized by the angle of the polarization rotation along the domain wall normal, e.g., 180$^\circ$ between domains with $\pm P$ along [010] or [011], respectively. Possible reasons for the stability of domain walls include local strain\cite{26}, presence of defects\cite{27} and depolarization fields\cite{28}. Furthermore domains may nucleate in the course of the heat treatment which are at least meta-stable afterwards\cite{29,30}.

So far the understanding of the coupling of domain...
FIG. 1. Local dipole configurations of the T and O phases of BaTiO$_3$ under study: (a)–(b) non-elastic 180° DWs, (c)–(d) elastic 90° DWs. Insets illustrate the polarization component parallel to the wall ($P_\parallel$) along [010], i.e. along $\pm b$ (a), [110]. (b), (c) and [110] (d) and the component perpendicular to elastic walls ($P_\perp$) along [001], i.e. along c (c) and [110] (d). For 180° walls, $P_\parallel$ is along [001].

structure and the T–O transition is only rudimentary. Piezoresponse force microscopy has been used to image domain patterns within the T and O phases as well as evolution of domains at the phase transition. In general, it is however challenging to visualize and interpret the complex domain structures especially near phase transitions and disentangle the impact of superposition of various DW and their interactions, defects and inhomogeneities in the real sample. Theoretical simulations provide an ideal tool to separate the different elements of the microstructure by considering an “idealised” system. However, previous theoretical studies have focused on the domain structure of the T or O phase either using density functional theory simulations at 0 K or phenomenological models, or phenomenological models defined for cubic perovskite ferroelectrics. Instead of treating all atomic positions as degrees of freedom, the collective atomic displacements are coarse-grained by local soft mode vectors $u_i$ and local acoustic displacement vectors $w_i$ of each unit cell $i$ in the simulation supercell. An internal optimization of $E(w_i)$ is used reducing the degree of freedoms per formula unit from 5 atoms times the three Cartesian directions (= 15) to the three components of the soft mode $u_i$ corresponding to the local polarization $P_i$, see Fig. 2. This method has been used extensively to study various properties such as phase diagrams, domain structures, or functional responses of ferroelectric materials.

The effective Hamiltonian is written as follows:

$$H_{\text{eff}} = \frac{M_{\text{dipole}}}{2} \sum_{i,\alpha} u_{\alpha, i}^2 + V_{\text{self}}(\{u\}) + V_{\text{dip}}(\{u\}) + V_{\text{short}}(\{u\}) + V_{\text{elas}, \text{homo}}(\eta_1, \ldots, \eta_6) + V_{\text{elas}, \text{inho}}(\{w\}) + V_{\text{coup}, \text{homo}}(\{u\}, \eta_1, \ldots, \eta_6) + V_{\text{coup}, \text{inho}}(\{u\}, \{w\}),$$

with $\eta_1, \ldots, \eta_6$ being the six components of homogeneous strain in Voigt notation. The first term represents the kinetic energies of the local soft modes while $M_{\text{dipole}}$ corresponds to the effective masses. Further, $V_{\text{self}}(\{u\})$ is the self-energy of the local mode, $V_{\text{dip}}(\{u\})$ is the long-range dipole-dipole interaction, $V_{\text{short}}(\{u\})$ is the short-range interaction between local soft modes,
between the soft modes and the inhomogeneous strains. $V_{\text{coup, homo}}(\{u\}, \eta_1, \ldots, \eta_6)$ is the coupling between the local soft modes and the homogeneous strain, and $V_{\text{coup, inho}}(\{u\}, \{w\})$ is the coupling between the soft modes and the inhomogeneous strains. The coupling with an external electric field $-Z^*E_iu_i$ is also included in the Hamiltonian, where $Z^*$ is the Born effective charge associated with the soft mode. The set of parameters for BaTiO$_3$ has been obtained using density functional theory simulation and is listed in Ref. [45].

Molecular dynamics simulations are performed by employing the ferm cod,$^{[22]}$ developed by Nishimatsu et al.$^{[17]}$ The Nosé-Poincaré thermostat,$^{[23]}$ is used to simulate annealing starting well apart from the transition temperatures of our model. At each $T$, after 120,000 fs thermalization, the local dipoles $P_i$ are averaged over 160,000 fs and the final configuration is used to restart the next $T$ step. We use temperature sweep rates of up to $2 \times 10^5$ K/s, and 5 K steps. At each $T$, the energy and the local polarization $P_i$ allow us to determine the phase. Although the symmetry of the sample may be reduced by domains, we speak of T and O phase if the system apart from domain walls has local polarization $P_{(100)}$ or $P_{(110)}$, respectively. We also use T and O to characterize phases with small field-induced monoclinic distortions, e.g. $0 < P_{[010]} << P_{[001]}$ is called T.

In experiments, nucleation of different domains is observed at phase boundaries which can also be found in our simulations. However recall that in simulations, the material is under “ideal” conditions, i.e., absence of inhomogeneities and depolarization effects as well as there are finite size effects, therefore the probability of nucleation of domain walls is much smaller than that in experiments. Further we want to understand the effects of different types of domain walls separately which would not be possible for randomly nucleated structures. Therefore, we initialize our system with a well-defined local dipole arrangement at a temperature well away from the phase boundaries. This allows us to study properties of a desired “geometry” i.e. orientation and size of domains for a multi-domain phase without any additional effects. For this purpose we use a supercell size of $96 \times 96 \times 96$ formula units being equivalent to a sample of about $38 \times 38 \times 38$ nm$^3$ with periodic boundary conditions. We initialize equally spaced domain walls with distances of $d = 19.1$ nm, 9.6 nm and 4.8 nm which correspond to presence of 2, 4 and 8 DW in the supercell, respectively. For 90$^\circ$ walls in the O phase, we furthermore considered $d = 23.9$ nm and $d = 12$ nm using 2 and 4 domains in combination with a 96 $\times$ 96 $\times$ 120 supercell. For 90$^\circ$ walls in the T phase, we restrict our study to the minimal number of 4 walls with $d = 13.5$ nm compatible with the periodic boundary conditions for these walls along [110]. The number of domain walls considered here for each structure is determined by the periodic boundary conditions and the size of the supercell.

### III. RESULTS AND DISCUSSION

As a starting point, we characterize multi-domain configurations in both tetragonal and orthorhombic phases separately using supercells with well-defined domain walls distances as described in Sec. [1]. We project the polarization on the two components (i) parallel ($P_{||}$) and (ii) perpendicular ($P_{\perp}$) to the wall; these directions are defined for each configuration in Fig. 1. We plot these two components for various MD configurations in Fig. 3. For the studied charge neutral walls, $P_{\perp}$ is constant across the domain walls as illustrated by dashed lines, with $P_{\perp} = P_{[001]}$ at the O90$^\circ$ wall, see (a), zero across non-elastic walls such as O180$^\circ$ as shown (b), and $P_{\perp} = P_{[110]}$ at the T90$^\circ$ wall, see (c). We do not find any significant change in $P_{\perp}$ for O90 and O180 walls, however for T90 walls, it increases as temperature is reduced towards the transition temperature. The parallel component $P_{||}$ reverses the sign across the DW for all the configurations. This is expected based on underlying symmetries for the MD phases. $P_{||}$ approximately follows a tanh-profile as previously discussed in literature$^{[22]}$ and decreases if the system approaches $T_C$ in the presence of elastic walls. We estimate the domain wall widths $2d_{DW}$ by fitting the polarization profile across a single wall with

$$P_{||}(z) = P_{0,||}(z_0) \cdot \tanh \left( \frac{z - z_0}{d_{DW}} \right), \tag{2}$$

as shown with solid lines in Fig. 3. Here $z - z_0$ corresponds to the distance from the center of the wall.

The calculated DW width is plotted in Fig. 4 for different types of walls. We find that T90 walls are thickest followed by O90 and O180 walls and the T180 walls are the narrowest among those under study. This trend compares well with those results obtained from the Ginzburg-Landau-Devonshire model$^{[22]}$ and density functional theory.$^{[22]}$ Note that no quantitative agreement may be expected due to the different approximations in the three simulation methods. We reproduce the findings in Ref.$^{[22]}$ that the walls occasionally shift via a transient state with broadened domain walls. Further, we observe the predicted increase of $d_{DW}$ with increasing temperature.$^{[22]}$ For 180$^\circ$ walls, the temperature dependence of $d_{DW}$ is
FIG. 3. Average polarization per layer $\langle P_{\parallel}\rangle_{\pm}(z-z_0)$ across O90 (a), O180 (b) and (c) T90 domain walls. Symbols correspond to simulated $P_{\parallel}$, solid lines to tanh-fit (Eq. (2)) and dashed lines to $P_{\perp}$. Here $z_0$ corresponds to the center of the DW. We note that $T_C$ for configuration (a), (b), and (c) correspond to 163 K and 179 K and 184 K respectively (discussed later in detail).

FIG. 4. Temperature dependence of $2d_{DW}$ for O90 (red), O180 (black), T180 (blue) and T90 (green) walls (a) approaching the T-O transition (b) in the whole T phase. Line types mark the wall distances $d$ and the data has been recorded in heating simulations. For three examples also results for cooling simulations have been added (symbols).

to paraelectric transition temperature due to large fluctuations associated with this transition. The observation of domain wall broadening close to $T_C$ goes beyond predictions by Ginzburg-Landau theory probably because the fluctuations of the order parameter are not fully included in that method.

The domain density does not affect the DW width even for minimal distances of 4.8 nm. It is further important to note that we obtain the same widths during the heating and cooling simulations as illustrated by symbols for some exemplary configurations in Fig. 4. Thus this property is a material property at any temperature and is not influenced by thermal history or changes of domain wall positions, etc. Along with this analysis of local polarization and DW widths, we also examined the energies of the MD configurations for different wall densities which qualitatively reproduces the ordering of total energies published earlier. Furthermore, the domain wall profiles and energies are converged with respect to the system size. From this analysis, we conclude that the MD configurations are well described within our model and simulation cell size.

We now turn to the main focus of our work: how do
FIG. 5. Schematic pictures of the observed changes of domain structure at the T-O transition: (a) SD O ⇌ SD T, e.g. between bc and c, (b) O90 ⇌ SD T, e.g., bc/-bc to c, (c) T90 ⇌ O SD, e.g. between b/c and bc, (d) T180° → O90°, e.g., from b/-b to bc/-bc, and (e) O180 → T180, e.g. ab/-a-b to b/-b. Note that in (e) dots and crosses mark polarization out of/in the plane, respectively. Arrows between two phases indicate transitions which are observed commonly (solid) and only occasionally due to nucleation (dotted).

The domains evolve near the transition and what is their impact on the transitions? In absence of domains and external field, we observe a sharp first-order transition with a jump of order parameter and energy at the transition temperature. Our calculated transition temperatures are $T^C_C = 138$ K for cooling and $T^H_C = 186$ K for heating, that is, we get a thermal hysteresis of about 50 K. The quantitative disagreement with experimental data is expected as the used model systematically underestimates transition temperatures and as the thermal hysteresis is considerably higher in ideal material.

In the presence of domains, we observe different types of transitions between SD and MD phases which are summarized in Fig. 5. In all cases, the walls do not disperse during the phase transition and the local polarization rotates by $45^\circ$ analogous to the SD case shown in Fig. 5(a). This results in two different scenarios – (1) for $90^\circ$ walls, the polarization in both domains rotates to the initial $P_\perp$ direction and transforms to the SD phase (panels b–c); and (2) for $180^\circ$ walls, no such rotation is possible and we observe T180 to O90 and O180 to T180 transitions (see panels d–e). We note that the first-order character of this phase transition persists in the presence of domains walls, and we observe an abrupt transition with a jump in energy and polarization for all the systems considered. Occasionally, multi-domain phases nucleate near the transition even for initial SD phases as illustrated by dashed arrows in Fig. 5. However, we do not discuss these transitions here as the probability of such nucleation is rather low in our simulations.

Transition temperatures in the presence of domain walls are plotted as a function of wall densities in Fig. 6. In all cases, the walls do not disperse during the phase transition and the local polarization rotates by $45^\circ$ analogous to the SD case shown in Fig. 5(a). This results in two different scenarios – (1) for $90^\circ$ walls, the polarization in both domains rotates to the initial $P_\perp$ direction and transforms to the SD phase (panels b–c); and (2) for $180^\circ$ walls, no such rotation is possible and we observe T180 to O90 and O180 to T180 transitions (see panels d–e). We note that for the densest DW considered within our study, the MD phases are not stable in the vicinity of the phase transition and the system transforms to the SD phase (that is, O-MD to O-SD and T-MD to T-SD phases) at a temperature $T^t$; indicated in blue in Fig. 6. The change in the transition temperatures is larger for $90^\circ$ walls than for $180^\circ$ walls. For example, heating from the O phase at $d = 9.6$ nm, we observe $T^C_C = 174$ K for decreasing DW density (equivalently increasing $d$) the volume fraction of dipoles near a DW as well as potential interactions between walls decrease. For $90^\circ$ walls, the change of $T_C$ with the wall distances is considerably smaller. Note that for the densest DW considered within our study, the MD phases are not stable in the vicinity of the phase transition and the system transforms to the SD phase (that is, O-MD to O-SD and T-MD to T-SD phases) at a temperature $T^t$; indicated in blue in Fig. 6.

The change in the transition temperatures is larger for $90^\circ$ walls than for $180^\circ$ walls. For example, heating from the O phase at $d = 9.6$ nm, we observe $T^C_C = 174$ K for
O180 and 151 K for O90 walls, respectively. While cooling down from the T-MD phases, the increase of $T_C$ by T180 walls is small (green crosses), whereas we observe a reduction of the thermal hysteresis to only 2 K in the presence of T90 walls with $d = 13.5$ nm.

To analyze the impact of domains on $T_C$, one may distinguish between rotation of polarization and strain variation observed in the domains (“volume effect”) and the properties of domain walls themselves (“interface effect”). To examine the volume effect, we look at the changes in polarization at the center of the domains where the effects arising from the interfaces themselves, i.e. the domain walls, should be minimal. For this purpose, we calculate the polarization in the center of the domain $P_{\parallel,0}$ using Eqn. [2]. The resulting polarization in the domain centers is plotted in Fig. 7 as a function of temperature. In case of 180° walls, the $P_{\parallel}$ component matches exactly to the magnitude of the overall polarization of the SD phases and $P_{\perp}$ is equal to zero. The impact of temperature on the polarization direction in both domains is negligible. Thus, 180° DW have no impact on the local polarization in the adjacent domains. In case of 90° walls, $P_{\perp}$ and $P_{\parallel}$ both correspond to $\langle 100 \rangle$ directions. Thus, if domain walls had no impact on the local polarization in the domain center, one would expect $P_{\parallel} = P_{\parallel}$ as $P = P_{\parallel} + P_{\perp}$ would point along the $\langle 110 \rangle$ direction of a particular orthorhombic variant. In contrast to that we observe a monoclinic distortion of the polarization with $P_{\parallel,0} > P_{\parallel,0}$, cf. red squares and red circles in Fig. 7. The monoclinic distortion is even larger in case of T90 wall for which the $P_{\parallel}$ and $P_{\perp}$ both correspond to $\langle 110 \rangle$ directions, cf. green stars and crosses.

Away from phase transitions, the monoclinic distortion increases with the domain wall density. The considerable monoclinic distortion even in the center of domains shows that the the elastic walls induce long-range modification in the system both in polarization and strain. This explains much slower convergence of $T_C$ with respect to $d$ for O90 walls compared to other configurations.

Approaching the transition temperatures, i.e., heating O90 or cooling T90 configurations, the monoclinic distortions increase for MD configurations. Enhanced monoclinic distortions close to ferroelectric-ferroelectric can be related to reduced anisotropy energy and energy penalty of reoriention of dipoles near the phase boundary and allow for monoclinic bridging phases which have been discussed earlier [55,56]. Such a monoclinic bridging state generally reduces the energy barrier between different phases promoting the phase transition. The changes in $T_C$ in our study are related to the size of the monoclinic distortion and indeed the largest change observed for T90 configuration corresponds to the largest distortion obtained in our study.

Secondly to examine the interface effects, we look at the properties of domains walls themselves. As discussed earlier (Fig. 4 and subsequent discussion), the 180° walls are extremely thin and their width doesn’t diverge even in the vicinity of the phase transition, whereas, the elastic walls are slightly wider and diverge as the system approaches transition. Furthermore, 180° walls are Ising-like, i.e., the polarization in the center of the wall does not point along the polarization direction of either domains but rather decreases in magnitude, only. However, for the O90 wall, the polarization in the center of the wall is pointing along $\langle 100 \rangle$ (i.e., along the spontaneous polarization of the T-phase), and for T90 wall, along $\langle 110 \rangle$ (i.e., along the spontaneous polarization of the O-phase) and may thus act as nucleation centers for the transition. Thus for 90° walls, both volume and interface effects come together to accelerate the phase transition, whereas for 180° walls, only interface effects contribute to the change in $T_C$.

Interestingly, the same trends also occur at the orthorhombic to rhombohedral transition where both O90 and O180 phases transform to R109 configurations with $[\pm 1 \pm 1]$ domains and with $P_{\perp} < P_{\parallel}$ similar to the O90 case. Similar to the discussion on the T-O transition, $T_C$ is enhanced by only 5–10 K and at the same time, there is no considerable monoclinic distortions in the initial O phase. This points to the general trend that the long-range monoclinic distortions induced by elastic walls are important to modify $T_C$. However, a detailed study of this transition is out of scope for this paper.

Next, to shed light on the DW-field coupling, we performed cooling and heating simulations in the presence of
an external field along (100). Recall that for MD phases, the relative orientation between the field and local polarization in each domain may be different, and the direction of the field relative to the DW also influences the field coupling. Unless specified otherwise, we applied the field parallel to the DW. The calculated transition temperatures are plotted in Fig. 8 as a function of applied field magnitude at several $d$. Note that for SD phases, both $T_{c1}$ and $T_{c2}$ reduce systematically with the increasing field magnitude. This can be understood because an external field along (001) favors the T-phase with the induced polarization along the applied field direction as has been reported by us in an earlier study as a reference the data is reproduced here, see black lines in Fig. 8. For MD phases, we observe three distinct trends: first, a comparable change in $T_c$ with $E$ to that found for SD phases for O90 walls (panel a) and O180 walls (region II in panel b); second, no or a very small change in $T_c$ with increasing field strength for O180 walls (region I in panel b) and for T180 walls (panel c green squares); and third, the reduction in the stability range of dense O90 walls and T180 walls with $E$ (blue symbols in panels a and c respectively), i.e. $T_{c1}(E)$ increases in cooling simulations and decreases in heating simulations. The shifts in $T_C$'s with respect to $d$ which already have been discussed in Fig. 5 are not affected by an application of the field.

Let us now look at the $T_C$ trends for MD configurations in more detail. In the first case, for O90 walls, all domains have the polarization component $P_{\perp}$ along the applied field direction which results in the partial rotation of dipoles towards the field direction throughout the system and finally the SD T phase parallel to the field. Recall that O90 walls promote the transition by DW broadening and an induced monoclinic symmetry throughout the domains. The applied field has a similar impact on the polarization direction and further enhances the monoclinic distortion with $P_a > P_b$ for the [100] field which is rather temperature independent at low temperatures and increases considerably close to $T_C$, see Fig. 9(a). The field also broadens the DW (not shown); these two effects add up and $T_c$ is reduced with increasing field. For the densest walls ($d = 4.8$ nm), the system is meta-stable near the phase transition even in the absence of an external field. The field-induced enhanced monoclinic distortions reduce $T_c$ systematically with field strength.

The case of O180 walls transforming to T180 is more complex and interesting because the field is neither fully aligned with initial or final polarization nor do all domains incline the same angle with $E$. For a field along [010], we observe two different scenarios: I. for small fields ($E \leq 30$ kV/cm), the polarization along \( \pm [110] \) transforms to the T180 phases with \( \pm [100] \), i.e. perpendicular to the field. In this case we neither observe a broadening of the domain wall nor a rotation of $P$ towards the field direction and $T_C$ shows a small dependence on applied field. II. for larger fields we observe a rotation of the dipoles in both domains to a state with monoclinic distortion and $|P_b| > |P_a|$ promoting the transition to the $\pm [010]$ phase collinear with the external field. Recall that without field O180 walls do not induce any monoclinic distortion. In the small field scenario I, we even observe...
a reduction of the polarization component antiparallel to the field, i.e. for a field along [010], the -b component in the -a-b domain is reduced. Mediated by the strain the perpendicular tetragonal direction is thus stabilized. In this case, the field neither considerably reduces the energy barrier for the phase transition nor does it stabilize the final state (as P in each domain is perpendicular to the field) and in turn \( T_C \) is not lowered by the field. The interesting consequence of this is that the transition temperatures fall outside of the coexistence region of the SD phase with the field. In contrast, higher fields (case II) overcome the energy barrier for a monoclinic distortion close to \( T_C \), see polarization component \( P_4 \) in Fig. 8b. Analogous to the SD case, the distortion promotes the phase transition and we obtain a similar slope of \( T_C(E) \) in this field range.

For T180 walls, the response for the field applied collinear to \( P_4 \) is similar to that observed for O180 walls with small fields and again can be understood by a reduced field coupling. The applied field would favor the parallel SD tetragonal phase. However, it is not strong enough to eliminate the walls. Instead the T180 domains with \( [0 \pm 10] \) transform to O90 domains with \( [0 \pm 11] \). In both phases the field is parallel to \( P_4 \) in one domain and would favor an increase of it, and by the strong strain-polarization coupling, also of the tetragonal strain. The effect of the field is opposite in the other domain reducing polarization and strain. Such a mismatch at the wall is unfavorable and thus the field-coupling is compensated in both phases and \( T_C \) is barely modified with field magnitude.

In this work, we focus on only one relative direction between field and domain wall for each type of walls. One would expect an anisotropic response to the applied field due to presence of DWs. The complete study of the anisotropy of the field is out of scope in this paper. As an example, we however applied \( E_{\perp} \) to T180 configuration and the corresponding results are shown in blue in Fig. 8c. Here, the applied field is perpendicular to polarization in both domains. In this case the energy barrier for rotating the dipoles uniformly towards the field direction is small and further decreases as the system approaches \( T_C \). Therefore, the walls easily disappear and the system transforms to the T-SD phase at \( T_t \) which increases with the field magnitude. To sum up, we show that the field coupling depends crucially on the relative direction of field and local polarization in the domains and in particular the combination of elastic walls and electric field along \( P_4 \) leads to a considerable reduction in thermal hysteresis and may thus allow for large reversible functional responses.

IV. SUMMARY AND OUTLOOK

We conducted a systematic study of the coupling of phase transition, domain walls and electrical field based on molecular dynamics simulations of an \textit{ab initio} effective Hamiltonian. Starting from the idealized bulk BaTiO\textsubscript{3} system, we introduced low-energy MD configurations in the orthorhombic and tetragonal phases which are commonly found as complex superstructures in experiments in order to separately discuss their impact on the phase transition.

Thereby we could show that these MD states once nucleated or initialized in the system remain meta-stable within a temperature range of interest, down to domain width of 4.8 nm. Our observations point to the fact that the monoclinic symmetry observed close to the O-T transition in experiments may be related to elastic domain walls present in the system. Another important consequence of our findings is that the large spread observed in the experimental transition temperatures can be partly related to different domain structures in the sample with no, or mainly 180\degree walls resulting in a broad hysteresis, while elastic walls may induce a monoclinic bridging phase.

Our most exciting finding is that elastic domain walls strongly modify the transition temperatures and reduce the thermal hysteresis by one order of magnitude. On the other hand, the impact of 180\degree walls is small. These trends are further amplified in the presence of an external field. The combination of external field and O90 walls allows to efficiently push \( T_C \) below the zero-field
coexistence range which is needed for a large reversible functional response. In contrast, 180° walls reduce the coupling between $T_c$ and the external field and as a result enhance the thermal hysteresis in the presence of an external field compared to the SD case. We have shown that these different trends can be attributed to I. volume effects, that is monoclinic distortions within domains, and II. interface effects, that is, large and diverging DW widths.

Our results are a significant finding for prospective applications using domain wall engineering to reduce thermal hysteresis of the ferroelectric to ferroelectric transition. Elastic domain walls may act as a bias to reduce the field strength needed to induce a complete transition in the system and thus yielding large functional responses. This reduction of thermal hysteresis combined with the enhanced piezoelectric response obtained for these systems[20] make domain-wall engineered materials especially attractive for applications such as solid-state cooling which require large response near room-temperature. With advanced and precise techniques available to control the growth of nano-ferroelectrics[23] we believe that our work would provide a practical guide for further development of functional devices.

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