Domain wall acceleration by ultrafast field ramping and non-equilibrium dipoles dynamics: an ab initio based molecular dynamics study

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Although being crucial for GHz and THz applications, the ferroelectric response to ultrafast field stimuli is so far not well understood. We utilize ab initio based molecular dynamics simulations to analyze the ultrafast response of 180° domain walls in the prototypical ferroelectric material BaTiO3. We reveal an initial acceleration of the domain wall up to 200% by non-equilibrium dipole switching and the equilibration to the steady-state by transient negative capacitance. Our detailed analysis reveals that the latter is a result of excess charge formation by switched local dipoles with low correlation. In addition, we suggest a relation between average bound charge and spacial dipoles distribution which can be used for statistical analyses of ferroelectric materials.

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I. INTRODUCTION

Switchable polarization makes ferroelectrics indispensable in contemporary electronics [1] ranging from ferroelectric data storage [2, 3] to ferroelectric tunnel junctions [4] and other nanoelectronics [5–7]. In particular high frequency operation and ultrafast field pulses become increasingly important, for instance for ultrafast ferroelectric memories [8]. Several studies of ultrafast field applications show significant role of field ramping in formation of transient effects [9, 10], including an unexpected non-linear velocity of a domain wall (DW) was recently observed in a ferroelectric capacitor [11].

BaTiO3 is not only a promising environmentally friendly material, with a wide range of applications [12], but also a prototypical ferroelectric perovskite which allows studying properties of ferroelectrics without a loss of generality. In this work, we focus on BaTiO3 in a tetragonal phase. Below Curie, temperature ferroelectrics consist of regions with homogeneous polarization, called domains separated by DWs. This work focuses on the inelastic and charge-neutral walls separating domains with antiparallel polarization directions. Known as 180° DW, they are the most common and well studied types of inelastic and charge free [13–16].

While both domains intrinsically have the same energy, an electrical field favors the domains with parallel polarization (positive domains) over those with anti-parallel (negative domains) orientation. It is now commonly accepted that field-driven polarization process goes through nucleation and growth of positive domains [17–19]. Under relatively high fields, the formation of new domains is possible, otherwise field-driven polarization is due to the expansion of the existing domains [20]. An expansion of a favorable domain at the expense of the negative domain takes place by the propagation of a DW. It is now commonly accepted that DW propagation evolves by reverse nuclei formation with its further expansion. Reverse nuclei formation unavoidably arises bound charge with associated energy expanses [21, 22]. This energy cost has to be overcome by an applied field to form a stable nucleus. When a critical nucleus size is reached [23] bound charge further facilitate stripe-like nucleus propagation [24–26], which is then followed by sidewise expansion.

Beside the influence of bound charge on polarization kinetics [27–30], it has been shown by means of density functional theory that local charges may modify the ferroelectric instability [31–33]. Important to note that bound charge is always present in a materials due to thermal fluctuations of dipoles and it modifies the free energy of ferroelectrics [34].

Although it is thus established that bound charge plays a crucial role in the ferroelectric stability and DW propagation, so far it is little known about the evolution of bound charge during field-driven polarization switching and its feedback on dipoles dynamics.

This lack of knowledge becomes increasingly important in the case of ultra-fast field applications which drive the system out of equilibrium [9] and may induce new functional properties. For example, a giant electrocaloric response [35] and a negative coupling between field and polarization [10] including transient negative capacitance (NC) [36, 37] have already been reported.

In its original definition, NC is the decrease of voltage for an increased charge on a capacitor. As suggested by Landauer more than 40 years ago NC may happen during polarization switching [38]. Although being counter-intuitive at the first glance NC could be related to the switching of dipoles against the applied field and has been related to antiparallel local depolarization fields which may overcompensate the applied electric field [9, 39]. Indeed NC has already been reported during the nucleation of reversed domains [40] or DW propagation [11, 37, 41, 42]. In spite of the progress in this field, the microscopic picture of NC as well as its impact on DW propagation is not yet well investigated.

To close these gaps in knowledge, we study the coupling between the dynamics of local charges, local polarization, and motion of 180° DWs in BaTiO3 driven out
of equilibrium by ultrafast field application. We opt for coarse-grained \textit{ab initio} based molecular dynamic (MD) simulation which allows us to efficiently gather statics while including dynamics and thermal fluctuations of the local polarization. We find how an ultrafast field application can accelerate DW and then induce NC as an internal property of a material. We find a transient NC during 180° DW propagation and discuss its impact on the DW velocity.

II. \textbf{METH\textit{OD}}

A. \textbf{Computational details}

We perform MD simulations using \textit{feram} code [43]. The code is based on the effective Hamiltonian approach proposed by Zhong et al. [44] with parametrization for BaTiO\textsubscript{3} [45]. This Hamiltonian has proven its validity by modelling functional properties and domain structures of BaTiO\textsubscript{3} [46–49]. The code is very efficient, as the collective atomic displacements are coarse-grained to the most relevant degrees of freedom which are the local soft mode, \(\vec{u}\), related to the local dipole moment \(\vec{p}\), while the local acoustic displacement vectors \(\vec{w}\) related to the local strain. Using an internal optimization of \(\vec{w}\), only one vector per unit cell is treated explicitly in the MD simulations rather than at least 5 \times 3 atomic degrees of freedom used in case of atomistic potentials. The Hamiltonian is given as

\[
H_{\text{eff}} = \frac{M_{\text{dipole}}^*}{2} \sum_{i,\alpha} \dot{\vec{u}}^2_{\alpha, i} + V_{\text{self}}(\{\vec{u}\}) + V_{\text{dip}}(\{\vec{u}\}) + V_{\text{short}}(\{\vec{u}\}) + V_{\text{elas, homo}}(\{\eta_1, \ldots, \eta_6\}) + V_{\text{elas, inho}}(\{\vec{w}\}) + V_{\text{coup, homo}}(\{\vec{u}\}, \{\eta_1, \ldots, \eta_6\}) + V_{\text{coup, inho}}(\{\vec{u}\}, \{\vec{w}\}) - \sum_i E_i \cdot \vec{p}_i,
\]

where the first term represents the kinetic energy of the local soft modes with effective mass \(M_{\text{dipole}}^*\), \(V_{\text{self}}(\{\vec{u}\})\) is the self-energy of the local mode, \(V_{\text{dip}}(\{\vec{u}\})\) is the long-range dipole-dipole interaction, and \(V_{\text{short}}(\{\vec{u}\})\) is the short-range interaction between local soft modes. The elastic energy depends on homogeneous strain \(V_{\text{elas, homo}}(\{\eta_1, \ldots, \eta_6\})\) and inhomogeneous strain \(V_{\text{elas, inho}}(\{\vec{w}\})\), with \(\eta_i\) the strain tensor in Voigt notation, and \(V_{\text{coup, homo}}(\{\vec{u}\}, \{\eta_1, \ldots, \eta_6\})\) and \(V_{\text{coup, inho}}(\{\vec{u}\}, \{\vec{w}\})\) include the couplings between local soft mode and homogeneous and inhomogeneous strain, respectively.

We use a time step of 1 fs and the Nosé-Poincaré thermostat [50] to equilibrate the system well in the tetragonal phase (at 260 K which is 40 K below the cubic to a tetragonal transition temperature and 125 K above the tetragonal to orthorhombic transition temperature in the frame of the model).

In order to study the field response of a multi-domain material, we subdivide the system into two domains with opposite polarization directions \(\pm \vec{p}_z\), as illustrated in Fig. 1. Due to periodic boundary conditions two DWs are present in the system which however do not interact due to a minimal system size of 48 \times 48 \times 48 u.c. This bi-domain structure is initialized by local fields of \(\pm 1\) kV/mm in positive and negative domains, respectively, which are step-wise reduced to 0.7 kV/mm, 0.4 kV/mm, 0.1 kV/mm, and 0.0 kV/mm followed by 30 ps of equilibration for each field strength. After this initialization, we apply a homogeneous electric fields along the \(z\) direction (\(E_{\text{ext}}\)), see red arrow in Fig. 1, sampling the field interval from 15 to 40 kV/mm in steps of 5 kV/mm. We model the impact of ultrafast field application by ramping the field from 0 kV/mm to its final value: (a) the instantaneous onset (0 ps ramping time) of the field and (b) the linear increase of \(E_{\text{ext}}\) in a short time interval (0.1–1 ps ramping time). Afterwards we keep the field constant for further 200 ps. To track the time evolution of the total polarization (\(p_z^{\text{total}}\)) we analyze snapshots of dipoles every 0.05 ps (time frame: 0–5 ps), every 1.2 ps (time frame: 5–60 ps), and every 20 ps (time frame: 60–200 ps). In order to investigate the propagation of the walls, we monitor the evolution of the average polarization of separate layers (\(\langle p_z \rangle\)) in \(yz\) (\(x_n\)) planes, i.e. parallel to the walls.

FIG. 1. (color online) Visualization of the initial bi-domain structure structure by ovito [51]. Each unit of BaTiO\textsubscript{3} is illustrated by a dot and colors mark the sign of the local polarization along \(z\) axis. Domains with \(\pm \vec{p}_z\) are separated by an 180° DW with normal vector \(x\) (gray plane). Initially, the wall is at \(x_n = 1\). After the field \(E_{\text{ext}}\) is applied along \(c\) (red arrow), the wall moves to the right with velocity \(v_{\text{DW}}\).
for we derived the relation 2.

Given as \( \sigma \) large (transitional) depolarization fields \([52]\) and in turn taken into account. These local bound charges induces be fully understood if local (bound) charges dynamics are without defects, the field-driven dipole dynamics can only

\[
\begin{align*}
\text{For the mean value} & \quad \langle \rho \rangle = \frac{1}{2} \sqrt{\langle \sigma^2 \rangle} \\
\text{and positive charges respectively} & \quad \text{electric fields: (left) defect-free charge neutral systems may anyway host local charges which induce an overall electric field (black arrow), (center) although a large standard deviation (SD(\rho)) of the local dipoles is a necessary condition for the formation of local bound charge it is not a sufficient condition as \( \langle \sigma_i \rangle \) is zero for full correlation along \( z \) (R\text{ }_z = 1), \text{in contrast to (right) where R}\_z < 1 and bound charge is present because of non zero polarization gradient.}
\end{align*}
\]

\[\text{FIG. 2. (Color online) Relation between local dipole ordering and the formation of local charges (red and blue stand for negative and positive charges respectively) and electric fields: (left) defect-free charge neutral systems may anyway host local charges which induce an overall electric field (black arrow), (center) although a large standard deviation (SD(\rho)) of the local dipoles is a necessary condition for the formation of local bound charge it is not a sufficient condition as \( \langle \sigma_i \rangle \) is zero for full correlation along \( z \) (R\text{ }_z = 1), \text{in contrast to (right) where R}\_z < 1 and bound charge is present because of non zero polarization gradient.}\]

B. Evaluation of local charges

Although we focus on an ideal charge-neutral system without defects, the field-driven dipole dynamics can only be fully understood if local (bound) charges dynamics are taken into account. These local bound charges induces large (transitional) depolarization fields \([52]\) and in turn affect the polarization dynamics \([28]\).

Generally charge on a surface with normal along \( i \) is given as \( \sigma_i = \frac{\partial \rho_i}{\partial x_i} \) or for a discrete dipoles \( \Delta \rho_i/\Delta a_i \) with \( \Delta p_i = p_i^a - p_i^{a+1} \) and \( a_i \) is a lattice constant along the \( i \) direction. For the charge neutral system, \( \langle \sigma_i \rangle = 0 \) and the size of the local charges may be estimated by \( \rho_i = \frac{1}{2} \sqrt{\langle \sigma_i^2 \rangle} \neq 0 \), where the prefactor \( \frac{1}{2} \) accounts for the equal amount of positive and negative charges, and \( e \) is charge of an electron.

In the equilibrated tetragonal phase without external field we find \( \rho_x = \rho_y = 45 \cdot 10^{-3} \text{ e/u.c.} \) and \( \rho_z = 50 \cdot 10^{-3} \text{ e/u.c.} \) due to thermal fluctuations of the dipoles at the given temperature. An external field \( E_{\text{ext}} \) along \( z \) does not modify values of \( \rho_x, \rho_y \) as polarization components perpendicular to the field are field independent. Since the applied field affects \( p_z \) component the \( p_z \) experiences time-evolution which is discussed in detail in Sec. III A in relation to statistical properties of \( p_z \) which for we derived the relation 2.

A necessary condition for charge formation along \( z \) by polarization gradients (for the ideal system without defects) is a standard deviation of the local polarization (SD(\( p_z \))). However, this is not a sufficient condition, and the alignment of neighboring dipoles along \( z \) given by their correlation (\( \langle R \rangle \)), determines if variations of \( p_z \) induce local charges, cf. Fig. 2 (center and right figures). For the mean value (\( \langle p \rangle \)) of \( p_z^a \) the Pearson correlation coefficient of nearest dipoles along \( z \) direction can be expressed as \( R_z = (\langle p_z^a - \langle p \rangle \rangle (p_z^{a+1} - \langle p \rangle )) / SD^2(p_z) \) i.e. \( \langle p_z^2 \rangle = SD^2(p_z)R_z + \langle p \rangle^2 \). From the other hand we have \( \rho_z^2 = \frac{\sigma_z^2}{2\epsilon_0} \langle (p_z^a - p_z^{a+1})^2 \rangle = \frac{\sigma_z^2}{2\epsilon_0} \langle (p_z^2) - (p_z^a \cdot p_z^{a+1}) \rangle \).

Therefore the local charges in the system are given as

\[
\rho_z^2 = \frac{\sigma_z^2}{2\epsilon_0} \cdot \text{SD}^2(p_z) \cdot (1 - R_z)
\]

\[
\text{(2)}
\]

III. RESULTS

A. Polarization dynamics

We start our study on ultrafast field application with the limiting case of instantaneous application of the field \( E_{\text{ext}} \). As soon as \( E_{\text{ext}} \) is applied to the bi-domain structure, it imposes an energy penalty to the anti-parallel dipoles and the negative domain vanishes with time.

We are mainly interested in field-induced DW motion and thus focus on the field interval between 15 kV/mm and 40 kV/mm. On the one hand, we observe nucleation within the negative domain for \( E_{\text{ext}} > 40 \text{ kV/mm} \) in agreement to literature \([20]\). On the other hand, 5 kV/mm is the critical field strength for the onset of wall propagation in our simulations and we exclude the field interval \( E_{\text{ext}} < 15 \text{ kV/mm} \) as the speed of the wall scales with the field strength, making the simulations in this interval more time-consuming.

One can depict three different regimes in the time-evolution of the global polarization \( \langle p_z^{\text{total}} \rangle \) for all values of the field, see Fig. 3: (I) Initially, the polarization jumps to a finite value (red arrow). (II) Second, the polarization gradually increases while the DW travels through the system. (III) Finally, to the right of the black arrow, the polarization is constant in the saturated single domain state. This saturated polarization, \( \langle p_z^{\text{sat}} \rangle \), increases linearly with \( E_{\text{ext}} \) due to the well-known linear dielectric response \( \langle p_z^{\text{sat}} \rangle = \epsilon_0 \cdot \chi_{\text{ext}} \) with vacuum electric permittivity \( \epsilon_0 \), and dielectric susceptibility \( \chi_{\text{ext}} \). For the chosen
FIG. 3. Time-evolution of the global polarization $\langle p_{z}^{\text{total}} \rangle$ of the bi-domain structure after the field $E_{\text{ext}}$ has been applied on a semi-logarithmic scale for different field strengths (colors). Arrows separate three regimes: (I) initial jump of polarization (II) gradual increase of $\langle p_{z}^{\text{total}} \rangle$ by DW motion, and (III) constant polarization in the saturated single-domain state.

field interval we estimated $\chi = 63$ which is in the range of reported values for the tetragonal phase of BaTiO$_3$ [12].

Though the initial polarization jump in regime (I) is of the same order of magnitude as this linear dielectric response, it does not scale linearly with the field strength (1.1 $\mu$C/cm$^2$ at 20 kV/mm, 2.0 $\mu$C/cm$^2$ at 30 kV/mm, and 3.2 $\mu$C/cm$^2$ at 40 kV/mm). As discussed below, this switching is a non-equilibrium effect and can be related to a spontaneous alignment of local dipoles with the field direction. With increasing field strength, the percentage of these switched dipoles ($n^\uparrow$) increases exponentially cf. Fig. 4.

These switched dipoles are not localized on the walls in contrast to the polarization switching by DW motion in regime (II). Instead, the polarization of every $x_n$ layer $\langle p_z \rangle$ in the negative domain increases, e.g. by 4 $\mu$C/cm$^2$ for $E_{\text{ext}} = 40$ kV/cm in Fig. 5.

The layer-resolved change of polarization in Fig. 5 furthermore shows that regime (II) can be subdivided into two parts: (IIa) after the initial jump, the magnitude of $\langle p_z \rangle$ in the negative domain increases against the applied field direction until finally in regime (IIb) the layers are consecutively hit by the traveling DW and begin to polarize along the field.

Closier inspection of the regime (IIa) reveals an exponential decay of the initially induced polarization in the next 25 ps. This decay is related to the back-switching of dipoles, cf. Fig. 12 in Appendix V A. Although being counter-intuitive at the first glance, the temporal increase of polarization against the field can be easily explained by the fact that the system is initially driven out of thermodynamic equilibrium. Note that a similar response of the polarization to fast field changes has also been found by phase-field simulations for 90° DWs [10]. Without discussion of the microscopic origin, it has been explained that the temporal increase of the polarization against the field was because of the inability of a small field to overcome the energy barrier for DW shift.

Indeed, for the chosen field interval, the initially switched dipoles in our setup cannot overcome the large energy barrier to form stable nuclei in the negative domain and thus switch back on short time scales. This back-switching is a consequence of the homogeneous dis-
distribution of switched dipoles in the negative domain which results in large bound charge and thus a local depolarization field which may overcompensate the applied field.

To prove this interpretation we refer to Fig. 6 (a) which contains the time evolution of \( \langle p_z \rangle \) with the evolution of \( \rho_z \). Without an external field, thermal fluctuations result in \( \rho_z = 50 \cdot 10^{-3} \, \text{e/u.c.} \) at the considered temperature. After the application of the field, this value is enhanced by: \( 6 \cdot 10^{-3} \, \text{e/u.c.} \) and \( 28 \cdot 10^{-3} \, \text{e/u.c.} \) during the initial switching and and the main switching regimes while the polarization increases by \( 2.9 \, \mu\text{C/cm}^2 \) and \( 27.7 \, \mu\text{C/cm}^2 \), respectively. Thus the ratio between the induced average charge and the change of polarization shows that twice larger charge occur in switched dipoles during the initial stage compared to the main switching regime.

The reason for such charge formation can be understood as an interplay between \( \text{SD}^2(p_z) \) and \( R_z \) which both contribute to the charge formation, cf. Eq. 2. Time evolution of \( \text{SD}^2(p_z) \) and \( R_z \) can be seen in Fig. 6 (b). On the one hand, the maximum value of \( \text{SD}^2(p_z) \) is reached in stage (IIb), when 50 % of dipoles on the layer have switched (\( \langle p_z \rangle = 0 \, \mu\text{C/cm}^2 \)), while the highest value of \( \text{SD}^2(p_z) \) reached in the stages (I-IIa) is an order of magnitude smaller as only around 4 % of dipoles switched during initial switching, see Fig. 4. On the other hand, the correlation \( R_z=0.92 \) is much higher in the (IIb) regime than \( R_z=0.55 \) in the (I-IIb) which drastically reduces bound charge, cf. Fig. 2 (center and right figures). Such a difference in correlations is evidence of small independent cluster switching in the initial regime in contrast to a correlated growth of nuclei in the main stage.

We thus calculated that initial switching is characterized by the formation of small clusters with a large charge density on its surface which results in back-switching of these clusters seen as NC in Fig. 5 and Fig. 12.

FIG. 6. (Color online) Illustration of time-evolution of (a) polarization (\( \langle p_z \rangle \)) along with average charge formation (\( \rho_z \)), and (b) standard deviation (\( \text{SD}^2(p_z) \)) and correlations (\( R_z \)) of \( p_z \) calculated for the layer \( x_{25} \) under instantaneous field \( E_{\text{ext}} = 40 \, \text{kV/mm} \) for four times regimes separated by blue lines: (I) initial switching (0-0.2 ps), (IIa) back-switching (0.2-25 ps), (IIb) main polarization stage (25-33 ps), (III) saturated state (after 33 ps).

The discussed non-equilibrium local dipoles modify DW properties and their dynamics. Before the application of the external field, we observe an atomically flat DW at layer \( x_n = 1 \), represented by blue dots in Fig. 7 [53]. The polarization profile across the wall approximately follows the hyperbolic tangent function [15] and with Eq. 4 we find a DW width of 1.2 u.c in agreement to literature [54].

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B. Domain wall dynamics

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With time, the wall travels to the right. One can note
that the distance, that the wall travels each 13 ps, is becoming shorter with time, meaning that the wall velocity is time-dependent which is untypical for a constant field.

Time dependence of the DW velocity is presented in Fig. 8 for different field strengths. We can see that velocity is indeed higher at the beginning of the journey but approaches a steady-state in the end.

Excitingly, we find that the discussed initial non-equilibrium switching of local dipoles accelerates the DW. First of all, each cluster of initially switched dipoles on the wall may act as a potential nucleation center for dipole switching. One can see this effect comparing propagation of the DW through layers $x_2$ and $x_{10}$ in Fig. 9. The layer $x_2$ exhibits more nucleation centers compared to the layer $x_{10}$. It is thus likely that the DW velocity depends on the number of separate reversed clusters in front of the moving DW.

Indeed we observe similar trend of $v_{DW}$ and $n_{nuc}^{1D}$, cf. Fig. 8 and Fig. 12, namely the time window of near exponential decay of DW velocity coincides with the time window of back-switching. Since the effect of negative capacitance decreases the number of potential nucleation centers it hinders the propagation of a DW. Therefore we conclude that an impact of NC on DW velocity is observed, which was recently experimentally detected for a ferroelectric capacitor under fast field ramping [11]. However, we could relate these two effects as an intrinsic microscopic property of the materials.

While back switching approaches to its end, velocity of a DW is approaching its field-dependent steady state [55, 56]: 480 m/s under 20 kV/mm and 1000 m/s under 40 kV/mm [58]. Globally the width increases linearly with time. Initially, nuclei are 2D objects located on one $x_n$ layer, but with time the nuclei start to grow out of the $x_n$ layer. We can see this when comparing upper and lower rows in Fig. 9: while nuclei in the upper row span over one plane, the nucleus on the lower row is extended to the nearest planes [59]. Superimposed we find broadening during the initial switching when the width is increasing up to 2.25 u.c. and then decreasing to 1.8 u.c. after 25 ps when the process of back-switching was terminated.

We found that initial switching drastically accelerated DW velocity playing a role of potential nucleation centers during DW propagation. Back-switching in its turn reduces the number of potential nucleation centers and brings DW to steady velocity. Furthermore, we find that DW broadening from 1.2 u.c. up to 3 u.c.

### C. Field ramping

So far we have restricted our study to instantaneous field application with an instantaneous onset of the field. Figure 11 summarizes the impact of different ramping rates on DW velocity under $E_{ext} = 40$ kV/mm. First of all, we find the same change of the velocity with time as discussed for instantaneous field application: DW acceleration by the initially switched dipoles, which further decelerates to a steady state (1000 m/s) via back-switching state independent of the ramping time [60]. Second, there is a rate-dependent delay for the onset of DW motion until the critical field strength of 5 kV/mm is reached [61].

While the DW velocity is maximal in the first time steps for instantaneous ramping, the velocity increases during field ramping due to the discussed increase of initially switched dipoles with field strength. We also observe a little shifted (3 ps) of the maximal velocity from ramping time (vertical lines in Fig. 11).

With increasing ramping time, the initial DW acceleration is systematically reduced, i.e. from 2500 m/s for instantaneous ramping to 1800 m/s for 20 ps. Thus, the acceleration is indeed a non-equilibrium effect which disappears with increasing of the ramping time.

The investigation under finite field ramping shows that not only instantaneous field application but also finite ramping induces non-equilibrium dipoles dynamics with DW acceleration and NC effect. This effects are, however, converges with the well-known DW response if ramping times are further increased.

### IV. Conclusion

This work focuses on the impact of ultrafast field ramping on dipoles dynamics and propagation of a $180^\circ$ DW in BaTiO$_3$ using *ab initio* based MD simulations. We find that ultrafast field application can induce an abrupt
FIG. 9. (color online) Change of local polarization in the vicinity of the DW with time $E_{\text{ext}} = 40 \text{kV/mm}$. Snapshots for three consecutive layers at 2 ps (upper row) and 11 ps (lower row). Red and blue dots mark local polarization parallel and anti-parallel to the field respectively. Layers and time steps have been chosen as such that the polarization in the left layer already started to switch parallel to the field and reached a value of $10 \mu \text{C/cm}^2$.

FIG. 10. (color online) Change of the domain wall width ($2d_{\text{DW}}$) with time for the example of $E_{\text{ext}} = 40 \text{kV/mm}$. The three regimes (I) initial switching (IIa) back-switching and (IIb) steady state are separated by vertical black lines. The horizontal red line marks approximate final DW width.

FIG. 11. (color online) Time evolution of the DW velocity for $E_{\text{ext}} = 40 \text{kV/mm}$ for field ramping in the first 0.1 ps (solid vertical line), 10 ps (dashed vertical line), and 20 ps (dotted vertical line), compared with an instantaneous ramping (empty circle).

homogeneous dipole switching in the entire domain accompanied by a twice denser bound charge formation, compared to nucleation and growth process in the main polarization stage.

Surprisingly, the initially switched dipoles that are in a vicinity of a DW can accelerate the wall up to 200%, which is an important finding for a fast DW operation. In contrast, the dipoles located apart from a DW are unstable and switch back with time. An effect of transient

NC is thus observed as an intrinsic property of a bulk ferroelectric material.

In this work, we propose a simple relationship that can be used to relate bound charge formation and spatial dipoles distribution. In particular, we could show that denser bound charge formation during the initial switching is a result of low spatial dipoles correlation.

We believe that the obtained results shed light on a fundamental understanding of ferroelectric response on
ultrafast field application and can be used to improve potential ferroelectric devices operating in pico- nanosecond regimes.

V. APPENDIX

A. Back-switching estimation

Figure 12 shows the layer-resolved time evolution of switched dipoles within the reversed domain for an instantaneously applied field of $E_{\text{ext}} = 40$ kV/mm.

![Diagram showing layer-resolved time evolution of switched dipoles within the reversed domain.](image)

**FIG. 12.** (colour online) Change of amount of positive dipoles in the negative domain with time for $E_{\text{ext}} = 40$ kV/mm given as percentage of positive dipoles ($n^\uparrow_{\text{layer}}$) per layer in the layers from $x_n = 28$ (blue) to $x_n = 40$ (brown) with an increment of 4 (other colors).

Initially most of the dipoles in the reversed domain are polarized against the field ($n^\uparrow_{\text{layer}} = 0$ at $t = 0$). The number of positive dipoles increases by initial switching reaching its maximum in the number of switched dipoles in the first 0.2 ps. After that, the number of positive dipoles is reduced in each layer until it is reached by the moving wall and the whole layer switches polarization. This increase of polarization antiparallel to the external field is clear evidence of back-switching and a transient NC.

B. Modified hyperbolic tangent

The polarization profile across a $180^\circ$ wall approximately follows a hyperbolic tangent profile [15, 62]

$$\langle p_z(x_n) \rangle = p_0 \cdot \tanh \left( \frac{x_n - x_0}{d_{DW}} \right),$$

where $p_0$ is a polarization of single domain crystal without an applied electric field at the given temperature, $x_0$ the center of the wall and $d_{DW}$ half of the DW width.

To describe a two domain system under an ultrafast applied electric field we modified a hyperbolic tangent function 3 used in the works [15] by adding terms responsible for linear dielectric response and NC. The modified function is as follows

$$\langle p_z(x_n) \rangle = p_0 \cdot \tanh \left( \frac{x_n - x_0}{d_{DW}} \right) + p_0 \cdot \Delta^\uparrow + p_0 \cdot \Delta^\downarrow \cdot \Theta \left[ -\tanh \left( \frac{x_n - x_0}{d_{DW}} \right) - \Delta^\uparrow \right]$$

$\Delta^\uparrow$ stands for linear dielectric response, and $\Theta (x)$ is the Heaviside function to include impact of NC ($\Delta^\downarrow$) in the region of the reverse domain.

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[41] We note that a width of a DW depends not only on velocity but also on field strength and is not under our focus at the moment.
[42] We noted that misleading DW acceleration for ramping 10 ps and 20 ps because of the fitting artifact.