Intrinsic ferroelectric switching from first principles
Shi Liu, Ilya Grinberg, Andrew M. Rappe

The existence of domain walls, which separate regions of different polarization, can influence the dielectric, piezoelectric, pyroelectric and electronic properties of ferroelectric materials. In particular, domain-wall motion is crucial for polarization switching, which is characterized by the hysteresis loop that is a signature feature of ferroelectric materials. Experimentally, the observed dynamics of polarization switching and domain-wall motion are usually explained as the behaviour of an elastic interface pinned by a random potential that is generated by defects, which appear to be strongly sample-dependent and affected by various elastic, microstructural and other extrinsic effects. Theoretically, connecting the zero-kelvin, first-principles-based, microscopic quantities of a sample with finite-temperature, macroscopic properties such as the coercive field is critical for material design and device performance; and the lack of such a connection has prevented the use of techniques based on ab initio calculations for high-throughput computational materials discovery. Here we use molecular dynamics simulations of 90° domain walls (separating domains with orthogonal polarization directions) in the ferroelectric material PbTiO₃ to provide microscopic insights that enable the construction of a simple, universal, nucleation-and-growth-based analytical model that quantifies the dynamics of many types of domain walls in various ferroelectrics. We then predict the temperature and frequency dependence of hysteresis loops and coercive fields at finite temperatures from first principles. We find that, even in the absence of defects, the intrinsic temperature and field dependence of the domain-wall velocity can be described with a nonlinear creep-like region and a depinning-like region. Our model enables quantitative estimation of coercive fields, which agree well with experimental results for ceramics and thin films. This agreement between model and experiment suggests that, despite the complexity of ferroelectric materials, typical ferroelectric switching is largely governed by a simple, universal mechanism of intrinsic domain-wall motion, providing an efficient framework for predicting and optimizing the properties of ferroelectric materials.

In ferroelectric materials, domain walls separate regions with different polarization orientations. In response to an external perturbation that favours one polarization state over another, the domain wall will move to increase the size of the domain favoured by the perturbation, potentially leading to polarization switching of the whole material. The translational motion of the 180° domain wall has been studied experimentally and theoretically. The dynamical behaviour of a domain wall is usually understood as an elastic interface moving in a fluctuating pinning potential that is created by defects. Under relatively weak electric fields, the propagation of domain walls at finite temperature can be described with a creep process:

\[ v \propto \exp \left( \frac{-U}{k_B T} \left( \frac{E}{E_{CD}} \right)^\theta \right) \]

where \( v \) is the domain-wall velocity, \( U \) is a characteristic energy barrier, \( k_B \) is Boltzmann’s constant, \( E_{CD} \) is a critical field at which depinning occurs at 0 K and \( \mu \) is the dynamical exponent determined by the nature of the defects. The dynamical exponent \( \mu = 1 \) is usually ascribed to the random field defects, which break the symmetry of the ferroelectric double-well potential, whereas \( \mu = 0.5 \) is an indication of random bond disorder, which locally modifies the symmetric ferroelectric double-well potential depth. Another widely used equation that characterizes the switching and domain-wall motion is Merz’s law, which takes the form

\[ v = v_0 \exp \left( -E_a/E \right) \]

where \( v_0 \) is the domain-wall velocity under an infinite field and \( E_a \) is the temperature-dependent activation field. Merz’s law can be viewed as a reformulation of equation (1) with \( \mu = 1 \) and \( E_a = U E_{CD}/(k_B T) \). When the electric field becomes larger than the crossing field \( E_{CD} \), the wall experiences a pinning–depinning transition, with the velocity becoming temperature-independent and given by:

\[ v \propto (E - E_{CD})^\theta \]

where \( \theta \) is a velocity exponent that reflects the dimensionality (\( D \)) of the wall. A classical theory based on a nucleation-and-growth mechanism was developed by Miller and Weinreich to explain the intrinsic origin of Merz’s law and creep behaviour. However, the Miller–Weinreich model assumes the dominant role of depolarization energy during nucleation, which incorrectly leads to an atomically sharp triangular critical nucleus and implausibly high activation fields for nucleation. Multiscale simulations for 180° domain walls in defect-free PbTiO₃ revealed a square critical nucleus with diffusive and bevelled interfaces that substantially reduces the nucleation barrier and hence leads to much lower activation fields for domain-wall motion, suggesting an intrinsic origin for \( \mu = 1 \) (ref. 17). Unlike the motion of 180° domain walls, switching processes in ceramics, thin films and single-crystal ferroelectrics are not well understood. The presence of a variety of extrinsic features, the possible role of ferroelastic effects in non-180° switching and the long (microsecond–millisecond) timescales typically studied for switching make it challenging to relate the observed hysteresis loops to the microscopic properties of ferroelectric materials. Because of the strong clamping effect of the substrate, the intrinsic dynamics of non-180° domain walls cannot be studied in high-quality ferroelectric thin films; instead, most recent experimental and theoretical studies of non-180° domain walls have focused on static properties. Here, we use a multiscale approach to computationally model the switching process. We first obtain the missing quantitative understanding of the intrinsic dynamics of non-180° domain walls and encapsulate it in a simple and general model for domain-wall speed. The model is then used in coarse-grained simulations on long timescales that enable accurate calculation of ferroelectric-switching hysteresis loops and coercive fields.

We quantitatively estimate the velocity of a 90° domain wall in defect-free PbTiO₃ over a wide range of temperatures and electric fields using large-scale molecular dynamics simulations (see Methods). Figure 1 presents the velocity as a function of applied electric field for various temperatures, revealing an intrinsic ‘creep–depinning’ transition. In the low-field region (\( E < 0.5 \) MV cm\(^{-1}\)), the velocity strongly depends on temperature and has a strong nonlinear dependence on the electric field. In the high-field region (\( E > 0.5 \) MV cm\(^{-1}\)), the temperature
dependence of the domain-wall velocity becomes weaker, as seen by
the overlap of the velocity data obtained at different temperatures.
Plotting $\ln(v)$ versus $1/E$ (Fig. 1b), we find that $\ln(v)$ has a linear
relationship with $1/E$ in the low-field region. This confirms that for
relatively low electric fields and high temperatures the velocity of the
90° domain wall follows Merz’s law ($\mu = 1.0$), showing a creep-like
response even in the absence of defects. The inset in Fig. 1b shows the
temperature dependence of the activation field $E_a = U_{\text{Ecyl}}/(k_B T)$
above 140 K. The nearly linear relationship between $E_a$ and $1/T$ shows that
$U_{\text{Ecyl}}/k_B$ is temperature-independent in the creep-like region
with a value of 283 K MV cm$^{-1}$. By fitting the velocity data at 40 K
with equation (2), we find that $\theta = 0.72$ and $E_D = 0.48$ MV cm$^{-1}$.
The crossing field for the 90° domain wall is lower than that for the 180°
domain wall (1 MV cm$^{-1}$) in Pb(Zr, Ti)O$_3$ (PZT) thin films$^{10}$; this is expected, because $ab$ initio calculations have shown that the 90°
domain wall in PbTiO$_3$ is lower in energy than the 180° domain wall
in PZT$^{16}$. The values of the dynamical exponent are the same ($\mu = 1$)
for 90° and 180° domain walls$^{17}$. This indicates a universal intrinsic
response for ferroelectric domains under low driving force. The observed intrinsic creep–depinning transition can be explained with a
nucleation-and-growth mechanism. At low fields, the large size of the
critical nucleus and the high nucleation barrier relative to thermal
fluctuations make nucleation the rate-limiting step and lead to an
Arrhenius dependence of the velocity in the creep region. At high fields,
the nucleus size and nucleation barrier approach zero and the
domain-wall velocity is growth dominated, resulting in near-linear dependence
on electric fields and a weak temperature dependence.

We now develop an analytical model for nucleation at a non-180°
domain wall based on our molecular dynamics simulations for 90°
domain walls. As shown in Fig. 2a, a 90° domain wall in $x$–$y$ coordinates
can be viewed as a special 180° domain wall in $X$–$Y$ coordinates: the polarization component parallel to the domain wall $(P_X)$ is reversed by
180° across the boundary, while the polarization component perpendicular to the domain wall $(P_Y)$ remains almost unchanged (bottom of Fig. 2a). This transformation allows us to treat all types of non-180°
domain walls as a 180° domain wall and allows a convenient estimate of the relative energies of different types of domain walls based on the
Landau–Ginzburg–Devonshire (LGD) expression for the energy per
unit area ($\sigma$) of the 180° domain wall ($\sigma_{\text{LDGW}}$). Detailed examinations
of nucleation events at the domain wall ($X = 0$) at low temperature
($T = 20$ K) reveal a diamond-like nucleus in the $Y$–$Z$ plane (Fig. 2b),
with substantial diffuseness at the boundary characterized by a gradual
polarization change. With this microscopic picture of nucleation, we
use LGD theory to relate the nucleation energy to the fundamental
characteristics of the material (see Methods). The nucleation energy
$U_{\text{nuc}}$ includes two important energy terms: polarization–electric-field
coupling ($PE$) and interface energy. Contrary to the assumption of the
classical Miller–Weinreich model, the depolarization energy is quite
small and does not make a substantial contribution to the nucleation
energy (see Methods for a detailed analysis of elastic and depolarization
energy).

At the lowest approximation, $P_X$ and $P_Z$ remain unchanged across
the domain wall and, therefore, the nucleation energy depends only on $P_Y$. The profile of $P_Y$ for a domain wall containing a nucleus of size
$l_1 \times l_2 \times l_3$ can be described as:

$$P_Y = \frac{2P}{\sqrt{2}} \left( f(X, h_1, h_2) f(Y + Z, \sqrt{2} h_1, h_2) - f(Y - Z, \sqrt{2} h_1, h_2) \right) + \frac{P}{\sqrt{2}} g(X, h_1, h_2)$$

where $f(x, l, \delta) = \frac{1}{2} [\tanh \left( \frac{x + l/2}{\delta/2} \right) - \tanh \left( \frac{x - l/2}{\delta/2} \right)]$, $g(x, l, \delta) = \tanh \left( \frac{x - l/2}{\delta/2} \right)$.

$P$ is the bulk polarization and $\delta$ characterizes the diffuseness of the
nucleus along direction $i$. Figure 2c shows the polarization profile in
the $Y$–$Z$ and $X$–$Y$ planes generated by equation (3). Evaluating this $P_Y$
profile in the LGD energy expression for different parameter values ($l_1$ and $l_2$) allow us to identify the critical nucleus size and to estimate the
nucleation activation energy ($\Delta U_{\text{nuc}}$). According to Avrami theory of
transformation kinetics, $\Delta U_{\text{nuc}}$ can be related to the activation field
in Merz’s law as $E_a \approx \frac{1}{D + 1} \frac{\Delta U_{\text{nuc}}}{l^3}$, where $D$ is the dimensionality$^{17}$. By
applying this relation with $D = 2$ and using parameters (see Methods)
obtained from our classical bond-valence potential, we obtain $E_a$ values
for a range of temperatures. As shown in Fig. 2d, the activation fields
predicted from the analytical model agree well with molecular dynamics
results. To apply the model to other types of non-180° domain walls,
only a simple modification of the input parameters is required, with the
necessary values obtained from first-principles density functional theory
(DFT) calculations of the particular domain wall (see Methods).

The availability of an analytical model that uses DFT inputs enables
rapid estimation of hysteresis loops and coercive fields ($E_c$; see Methods).
Because the structure and polarization of Ti-rich PZT are similar to those of PbTiO$_3$, we compare the simulated values of the PbTiO$_3$ $E_c$ to various experimental values for PZT materials. We find that our theoretical coercive fields (Fig. 3a) using parameters of
90°-domain-wall motion agree well over a large frequency range with the
experimental $E_c$ values (5–20 kV cm$^{-1}$)$^{21–23}$. The $E_c$ values based on
180°-domain-wall motion are quite large and exhibit the correct
frequency dependence (Fig. 3c), in agreement with experimental results
obtained in thin films (with thickness larger than the critical size of the
nucleus)$^{23}$. This suggests that the 180° switching in ceramics proceeds
via sequential 90°-domain-wall motion$^{23}$, owing to the much smaller
Figure 2 | LGD model of nucleation at domain walls. a, Schematic of mapping a 90° domain wall in x–y coordinates to a 180° domain wall in X–Y coordinates. The bottom panel shows the polarization P profile of a 90° domain wall in X–Y coordinates. The change in \( P_x \) across the domain wall (\( X = 0 \)) is small. b, Simulated nucleation process at the domain wall in the Y–Z plane (blue-shaded plane in the schematic). The black arrows scale with the local dipole magnitudes of each unit cell in the Y–Z plane. The background of each arrow is coloured on the basis of the magnitude of the Y component of the local dipole. At \( t = 0 \) ps, the Y–Z interface at \( X = 0 \) has dipoles aligned along –Y. In the presence of electric field, a diamond-like nucleus forms at \( t = 6.5 \) ps. c, Polarization profile of a nucleus generated by equation (3). The size of the nucleus is defined as \( l_3 \times l_2 \times l_1 \). \( \delta_{1,2,3} \) characterize the diffusiveness of the polarization. d, Comparison of the activation fields \( E_a \) obtained from molecular dynamics (MD) simulations with the results of the LGD model. The analytical model reproduces molecular dynamics activation fields using bond-valence-potential-based parameters together with the molecular dynamics temperature dependence of local polarization.

Figure 3 | Hysteresis loops and coercive fields for several materials simulated using first-principles data. a, Simulated frequency dependence of coercive fields \( E_c \) for PZT ceramics for various domain sizes (see legend) at 300 K. Theoretical values are comparable to various experimental values\(^{22–23} \) in ceramics. PZT-4, -5A and -5H refer to different PZT ceramics in ref. 21. b, Hysteresis loops of BaTiO\(_3\) with a domain size of 1 \( \mu \)m (dashed lines) and 10 \( \mu \)m (coarse grain). The green labels refer to experimental values of coercive fields. c, Frequency- and temperature-dependent coercive fields for PZT thin films. Experimental data (solid lines with filled circles and squares) are taken from ref. 25. A domain size of 0.1 \( \mu \)m (vertically dashed lines) and 1 \( \mu \)m (dashed lines) is used to obtain the theoretical values. d, Theoretical coercive fields for different domain walls in BiFeO\(_3\) with a domain size of 0.5 \( \mu \)m (solid lines), 0.05 \( \mu \)m (vertically dashed lines) and 5 \( \mu \)m (dashed lines), compared to experimental values\(^{27–29} \).
intrinsic nucleation barrier at the 90° domain wall. Thus, the switching and coercive fields in PZT are largely determined by the intrinsic properties of the appropriate domain-wall-motion mechanism. Similarly to the PZT results, we find that switching in BaTiO$_3$ ceramics is governed by the motion of 90° domain walls (Fig. 3b), with the predicted coercive field of around 0.1 kV cm$^{-1}$ at 300 K close to the experimental value for coarse-grain BaTiO$_3$ ceramics.\(^{26}\)

Polarization reversal in BiFeO$_3$ is another test of our model, owing to the importance of octahedral rotations and the presence of three types of domain walls in rhombohedrally polarized BiFeO$_3$. DFT calculations revealed that the 71° domain wall has the highest energy, followed by the 180° domain wall, with the lowest energy for the 109° domain wall. The higher energy of the 71° domain wall is attributed to the mismatch of oxygen octahedral rotations across the domain boundary. We introduce a second order parameter (oxygen octahedral rotation, $\theta$) into our LGD-based nucleation-and-growth model (see Methods). Using DFT domain-wall energies, our analytical model predicts that $E_c$ is lowest for the 71° domain wall, followed by the 109° and 180° domain walls. The predicted coercive fields for 180° domain walls are comparable with experimental values in thin films.\(^{27–29}\) The ability of our simple analytical model to estimate $E_c$ accurately indicates that the value of the coercive field is largely determined by the intrinsic properties of the material, with the nucleation barrier on the domain wall controlling the dynamics of polarization reversal.

The dominant role of intrinsic domain-wall motion explains the consistent differences in $E_c$ of the tetragonal and rhombohedral ferroelectrics. For example, an increase in $E_c$ of approximately 80% is observed across the rhombohedral—tetragonal compositional phase transition at the morphotropic phase boundaries in lead-free (Ba, Ca) TiO$_3$-Ba(Zr, Ti)O$_3$ and Bi-rich BiScO$_3$-Bi(Zr, Ti)O$_3$-PbTiO$_3$ ceramic systems.\(^{30}\) Analysis of our LGD nucleation model incorporating the changes in octahedral rotations across the 71° domain wall shows that the ratio of the coercive fields for 90° and 71° domain walls is approximately two (see Methods). This suggests that the switching in rhombohedral and tetragonal ferroelectrics proceeds via a multistep switching mechanism that involves a series of 71° and 90° steps, respectively, and that the higher $E_c$ of the tetragonal ferroelectrics is a direct consequence of the larger nucleation energy for 90°-domain-wall motion. The unified framework presented here relates microscopic zero-kelvin quantities to macroscopic material parameters at finite temperature and thus suggests an avenue for rational material design.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 28 January; accepted 13 April 2016.


Acknowledgements S.L. was supported by the NSF through Grant DMR-1124696, Grant CBET-1159736, and the Carnegie Institution for Science. I.G. was supported by the US ONR under Grant N00014-12-1-1033. A.M.R. was supported by the US DOD through a Challenge Grant from the HPCMO, and by the US DOD through computer time at NERSC.

Author Contributions S.L., I.G. and A.M.R. designed and analysed the simulation approaches. S.L. performed the molecular dynamics simulations. All authors discussed the results and implications of the work and commented on the manuscript at all stages.

Additional Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests: details are available in the online version of the paper. Correspondence and requests for materials should be addressed to S.L. (sliu@carnegiescience.edu) and A.M.R. (rappe@sas.upenn.edu).
LGD nucleation model. The nucleation energy \( U_{\text{nuc}} \) that captures the most important energy terms can be expressed as \( U_{\text{nuc}} = \Delta U_L + \Delta U_I \) where the polarization-field coupling term \( \Delta U_L \) is:

\[
\Delta U_L = -E \int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ \left[ U_{\text{eff}}(X, Y, Z) - U_{\text{DW}}(X, Y, Z) \right]
\]

and the interfacial energy \( \Delta U_I \) is:

\[
\Delta U_I = \int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ \left\{ U_0(P_{\text{nuc}}) + U_{\text{loc}}(P_{\text{nuc}}) \right\}
\]

Here \( P_{\text{nuc}}(X, Y, Z) \) and \( U_{\text{DW}}(X, Y, Z) \) are the polarization profiles of a domain wall with and without the nucleus, respectively. \( U_0 \) is the local energy penalty due to the deviation of the local polarization from the ground-state bulk value \( P_i \), where \( P_i = A_{\text{nuc}} (1 - P_i^{2})^{1/2} \), where \( A_{\text{nuc}} \) is the energy difference between the ferroelectric phase and the paraelectric phase. \( U_0 \) is the gradient energy due to the polarization changes \( \langle \partial P_i / \partial x \rangle \) at the domain wall; \( U_{\text{loc}}(P_i) = \sum_i g_i (\partial P_i) \), where \( g_i \) is the coefficient for the gradient of the \( i \)-th component of \( P \) along direction \( j \). The value of \( g_i \) can be derived from the energy and diffusiveness of the domain wall. The contributions from elastic strain energy \( (\varepsilon^2) \) and strain–polarization coupling \((\varepsilon^2 P^2)\) terms could be implemented into equation (3). However, we find that the elastic energy change is not significant (see below) and is therefore omitted in the following analysis.

Elastic energy contribution to nucleation energy. We calculate the effective lattice constants (defined in Extended Data Fig. 1a) in \( X-Y \) coordinates and find that they remain almost unchanged across the domain wall (Extended Data Fig. 3a). This finding suggests that the elastic energy cost at domain boundaries is not significant in an ideal crystal. Extended Data Fig. 3b, c shows the distributions of strain gradient in the presence of a diamond-like nucleus (illustrated in Fig. 2b). It can be seen that the unit cells of the nucleus have essentially the same lattice constants as the rest of the PbTiO3 unit cells at the domain wall. Therefore, the elastic energy contribution to the nucleation energy (change in elastic energy during nucleation) is negligible and does not have to be treated explicitly. We have therefore omitted explicit strain and strain–polarization coupling terms from our LGD nucleation model at the lowest approximation. Additionally, although the LGD theory presented in the main text does not explicitly refer to elastic interactions, these are included implicitly. It can be shown that inclusion of strain and strain–polarization coupling terms merely renormalizes the fourth-order LGD parameter. Because the parameters for the LGD model are obtained from DFT calculations in which strain polarization coupling is included, these elastic energetics are included in the \( A_{\text{nuc}} \) parameter that specifies the dependence of local energy on local polarization. (Similarly, because the supercell size is allowed to vary in the NPT simulations, elastic energy is taken into account in molecular dynamics simulations as well.) Therefore, a deviation from the preferred value of polarization \( P_i \) suppresses the switching rate of that unit cell parameters, and the energy of this change is included in our model as the local energy penalty \((U_0)\).

Analysis of the Miller–Weinreich nucleation model. The original work of Miller and Weinreich85 (illustrated in Extended Data Fig. 4) is based on the following assumptions: (1) the nucleus boundary is oriented at a 90° angle relative to the original domain wall; (2) the nucleus is located at the surface of the material and has a net non-zero boundary charge \((\rho_+ - \rho_-) > 0\); (3) the boundary of the nucleus has the same interface energy as that of the planar domain wall \((\sigma_{\text{eff}})\) on which the nucleus is located; and (4) the \( \sigma_{\text{eff}} \) parameter that characterizes the strength of the depolarization interactions is large relative to the magnitude of the local interface energy characterized by \( \sigma_{\text{eff}} \). The assumption that \( \sigma_{\text{eff}} \gg \sigma_{\text{loc}} \) leads to the triangular (red) curve in Extended Data Fig. 4, which is an appropriate approximation for the Miller–Weinreich model.

Owing to the lack of reliable experimental or first-principles data for the domain-wall energy, the model was assumed to be correct in ref. 15 and so was used to parameterize the domain-wall energy with the available domain-wall velocity data. This allowed the fitting of the electric-field/domain-wall-velocity relationships in many experiments. Despite this success, two major studies have cast serious doubt on the model. First, first-principles calculations of domain-wall energy per unit area \((\sigma_{\text{eff}})\) were found to be markedly higher than the fit values and, conversely, inserting the accurate, calculated values into the Miller–Weinreich model gave velocities that were markedly lower than those observed experimentally.86 Second, multiscale modelling of the nucleation process on the domain wall for 180° domain walls shows that the critical nucleus is not a tall, narrow, sharp triangle, as suggested in ref. 15. Instead, the observed nucleus is a diffuse, bevelled square.87 We show that rather than \( \sigma_{\text{eff}} \gg \sigma_{\text{loc}} \) limit assumed in ref. 15, the actual nucleation takes place in the \( \sigma_{\text{eff}} \gg \sigma_{\text{loc}} \) limit, with the local interface energy playing the dominant role and governing the energetics of nucleation and growth.
Reduced depolarization energy. For simplicity, we discuss the relative energies of the depolarization and local interface terms adopting the triangular shape and form of the nucleus energy expression of ref. 15 (presented in Extended Data Fig. 4), so that these terms are discussed in the framework traditionally used to model nucleation on the domain wall. Four factors contribute to the reduced role of depolarization energy in nucleation.

First, the bevelled shape of the nucleus effectively reduces $\sigma_p$. Because the depolarization energy of the Miller–Weinreich model arises from the electrostatic interactions between the charges along the boundary of the nucleus, the magnitude of $\sigma_p$ exhibits a logarithmic dependence on the width of the nucleus ($a$). Although the boundary of the nucleus was assumed to be sharp in ref. 15 and at a 90° angle to the domain wall, the actual nucleus boundary has a bevelled shape, as shown in previous molecular dynamics studies. This decreases the effective domain-wall area or, alternatively, the effective local-domain-wall energy ($\sigma_{dw}$) for a given nucleus of width $a$. According to equation (9) in ref. 15 (also presented in Extended Data Fig. 4), the magnitude of the width of the critical nucleus $a'$ is determined by the ratio between $\rho_p$ and the PE terms in the limit $\sigma_p \gg \sigma_{loc}$ and in the limit $\sigma_p \gg \sigma_{eff}$. Thus, for all cases, a decrease in $\sigma_p$ leads to a smaller critical width $a'$ and therefore a smaller critical depolarization energy $\sigma_p$. The logarithmic dependence of $\sigma_p$ is not weak for the small nuclei observed in our molecular dynamics simulations. Therefore, a decrease in the local interface energy due to the bevelled shape of the nucleus, which favours smaller critical nucleus size, also substantially decreases the magnitude of $\sigma_p$.

Second, the dielectric constant is enhanced at the domain wall and therefore the screening at the domain wall is stronger than in the bulk of the material. Recent experimental and theoretical work has shown that the dielectric constant at the domain wall is larger than that in the bulk. This is confirmed by our molecular dynamics simulations that show that the local dipole fluctuations and therefore the dielectric constant at the 90° domain wall are enhanced by a factor of two relative to the bulk value. Owing to the presence of the dielectric constant in the denominator of the formula for $\sigma_p$, the actual $\sigma_p$ value is then reduced by another factor of two relative to the original Miller–Weinreich estimate.

Third, the diamond shape of the nucleus shows an interaction cancellation effect. An additional effect is present for the elongated-diamond-like nuclei found in this work. Unlike the Miller–Weinreich model, which is not charge neutral, the elongated diamond shape observed in our molecular dynamics simulations exhibits both positive ($\rho_1$ and $\rho_2$) and negative ($-\rho_1$ and $-\rho_2$) boundary charges (Extended Data Fig. 5) so that the total charge at the nucleus boundary ($Q_{tot}$) is zero. Therefore, the repulsive energy penalty due to the interaction between $\rho_1$ and $\rho_2$ and between $-\rho_1$ and $-\rho_2$ is cancelled by the attractive energy gain of the interaction between $\rho_1$ and $-\rho_1$ and between $\rho_2$ and $-\rho_2$. This changes the dependence of $\sigma_p$ on $a/n ln(2A/eb)$ to $ln(a/eb)$ (the 4$\rho_p^2 / [ln(2A/eb)]$ contribution in which $\epsilon$ is the dielectric constant) to $\sigma_p$ (see Extended Data Fig. 4 for definitions of $\epsilon$ and $A$) arises from the interaction between the charges on the two opposite sides of the triangle; see the text following equation (4) in ref. 15). Although this change would have a minor effect on the large nucleus assumed in ref. 15, it is highly important for the small nuclei observed in our molecular dynamics simulations.

Finally, the boundary of the nucleus has a much smaller depolarization charge. We find that the average boundary charge between the nucleus and the original domain as integrated from the polarization changes on the 90° domain wall observed in our molecular dynamics calculations (Extended Data Fig. 5) is about two times smaller ($\Delta P = 0.7 C m^{-2}$) than that predicted by the sharp polarization change ($\Delta P = 2P_c = 1.41 C m^{-2}$) that would be used in a Miller–Weinreich-like model. Such a small polarization change is due to the greatly decreased value of $P_l$ at the domain wall relative to the bulk value. First-principles calculations show that the differences of the 90° domain wall means that $P_l$ at the domain wall layer is only slightly smaller than the bulk value. This large decrease in $P_l$ is found in our calculations (Fig. 2a). It is this domain wall layer that undergoes the nucleation and growth process governing the domain-wall motion, and therefore the appropriate value of $P$ to be used for estimating the depolarization charge is much smaller than the Miller–Weinreich estimate based on the bulk value $P_l$. The much smaller charge generated at the boundary of the nucleus decreases the strength of electrostatic interactions and $\sigma_p$ by a further factor of approximately four.

Despite the small $\sigma_p$, our nucleus still exhibits an elongated shape; this is due to the greater magnitude of the local energy $\sigma_{loc}$ for the domain wall at which $P$ changes along the $P$ direction than that for the domain wall at which $P$ changes along a direction transverse to the $P$ direction, as found in ref. 17 for 180° domain-wall motion. This is also unlike the assumption in ref. 15 that $\sigma_p$ is the same as the energy of the flat domain wall for all nucleus boundaries.

In summary, rather than the $\sigma_p \gg \sigma_{loc}$ limit assumed in ref. 15, the actual nucleation takes place in the $\sigma_{loc} \gg \sigma_p$ limit, with the local interface energy playing the dominant role and governing the energetics of nucleation and growth. This not only justifies our analytical model that neglects the small depolarization energy term, but also represents a new understanding of the physics that is important for ferroelectric switching.

Quantitative analysis of $\sigma_p$ reduction. We quantitatively evaluate the impact of the effects described above (bevelled shape, high dielectric constant, cancellation effect and small depolarization charge) on the depolarization energy term ($\sigma_p$). To take the modification of the boundary structure into account, we write down a modified version of the Miller–Weinreich formula:

$$U_{nuc} = -2 \Delta E_{loc} + 2 \sigma_{dw} \epsilon \sigma_{loc} / 2 + U_d$$

$$U_d = 8\epsilon^2 P_l^2 c^2 / f_0 \ln \left( \epsilon \sigma_{loc} / eb \right) = 2\epsilon \sigma_{loc}^2 / l$$

where $\sigma_p$ is the energy of the planar 90° domain wall, $s = 0.41$ is a factor that accounts for the reduction in the interface area of the nucleus due to its bevelled shape, as described previously (ref. $\sigma_{dw} = \sigma_{local} \epsilon$), $f_0$ scales the factor between the actual charge at the nucleus and the boundary charge assumed in the Miller–Weinreich model, $l$ is the scaling factor between the values of the dielectric constant ($\epsilon$) at the domain wall and in the bulk, and $f_0$ is a factor reflecting the effect of the interactions between the charged domain boundaries at the net-neutral ($Q_{tot} = 0$) and net-charged ($Q_{tot} = \pm 0$) boundaries of the nucleus, with $f_0 = 2$ for the original, charged, triangular, Miller–Weinreich nucleus and $f_0 = 1$ for a net-neutral, diamond-like nucleus.

To determine the dimensions and the energy of the critical nucleus, we evaluate $U_{nuc}$ for a wide range of $s$ and $l$ values and identify those that give the lowest energy for each nucleus area $A = a l$. Here, we use the DFT $\sigma_{local}$ value of 35 mJ m$^{-2}$ for the 90° domain wall and standard parameters for PbTiO$_3$ (dielectric constant $\epsilon = 60$, bulk polarization component in the plane of the 90° domain wall $P_l = 0.53 C m^{-2}$, $b = 3.9 \text{Å}, c = 4 \text{Å}$ and $e = 2.718$). The plots of the nucleus energy versus area $A$ for different values of $s$, $f_0$, $f_0$ and $f_2$ under an applied field of 0.1 MV cm$^{-1}$, which is typical of the low range of field magnitudes used in molecular dynamics simulations, are shown in Extended Data Fig. 6. We also show the dependence of the nucleus area $A$ on $s$, $f_0$, $f_0$ and $f_2$.

Extended Data Fig. 6 shows several important differences between the results of the classical Miller–Weinreich approach and the results obtained for a Miller–Weinreich-like nucleus with realistic boundaries. First, even for $s = f_0 = f_2 = 1$, the obtained $s = 12.59$ and $l = 47$ values are relatively small. For such a small $a'$, the dependence of $\sigma_p$ on $ln(a/eb)$ is not weak and, therefore, reduction of $a'$ due to the effects described above (smaller effective domain-wall area due to bevelled shape) has a strong effect on $\sigma_p$. Taken together, the various effects lead to a reduction in $\sigma_p$ by a factor of about 30 relative to the Miller–Weinreich estimate for nucleation at the 90° domain wall under an applied field of 0.1 MV cm$^{-1}$. This results in $\sigma_p \approx 0.7$ mJ cm$^{-2}$, much smaller than the local interface energy characterized by the effective domain-wall energy $\sigma_{dw}$ ($= 15.4$ mJ m$^{-2}$). The small value of $\sigma_p$ justifies our neglect of electrostatic interactions in the analytical model of the nucleus, and the much smaller $\sigma_p/\sigma_{loc}$ ratio corresponds to an aspect ratio of the critical nucleus ($l/a'$) that is close to one.

As illustrated in Extended Data Fig. 7, similar effects can be obtained for nucleation on the 180° domain wall under an applied field of 0.3 MV cm$^{-1}$ using the DFT 180°-domain-wall $\sigma_{local}$ value of 132 mJ m$^{-2}$ and standard parameters for PbTiO$_3$ (dielectric constant $\epsilon = 60$, bulk polarization $P_l = 0.75$ C m$^{-2}$, $b = 3.9 \text{Å}, c = 4 \text{Å}$ and $e = 2.718$).

Model parameters for non-180° domain walls. The nucleation model discussed here is similar to the model in ref. 17. The mapping scheme discussed therein allows the treatment of a non-180° domain wall as a generalized 180° domain wall lying in the $Y-Z$ plane with polarization changing from $+P_l$ to $-P_l$ along $X$. The following five parameters are required to estimate the nucleation energy at the domain wall under a given temperature $T$: $\gamma(T)$, $A_{loc}(T)$, $g_{YX}$, $g_{XY}$ and $g_{YZ}$:

$$P_l(T) = \gamma(B(T))$$

$$A_{loc}(T) = A_{loc}(0) P_l(T) / P_l(0)$$

$$A_{loc}(T) = \gamma(A_{loc}(0))$$

where
Here $P_t$ is the total local polarization, $\gamma$ is the fraction of the polarization variation across the domain boundary (for example, $\gamma = \sqrt{3}/2$ for a 90° domain wall), $A_{loc}$ is the energy difference between the ferroelectric phase and the high-symmetry paraelectric phase, $\sigma_{DW}$ is the energy of a domain wall with normal along X and neighbouring dipoles along Y, and $\delta_Y$ is the polarization diffuseness parameter over which the polarization changes across the domain boundary. By analogy, $\sigma_{DW}^{head-to-head}$ is the energy of a domain wall with normal along Y and neighbouring dipoles along Y (head-to-head or tail-to-tail domain wall), and $\delta_Y$ is the associated diffuseness parameter. $P_t(0)$ and $A_{loc}(0)$ are extracted from zero-kelvin DFT calculations. The temperature dependence of $P_t(T)$ is taken from experiments when available. The values of $\Lambda_{loc}$ and $\delta_Y$ can be determined on the basis of the domain-wall energy ($\sigma_{DW}$ calculated from DFT) or diffuseness parameters ($\delta_Y$ calculated from molecular dynamics). In practice, $g_{XX}$, $g_{YY}$ and $g_{XY}$ are of the same order and therefore $g_{XX} \approx 2g_{YY}$ is a useful approximation.

For Bi$_2$O$_3$, DFT calculations using the PBEsol density functional with $a = 3.986$ Å and $c/a = 1.01$ give $A_{loc}(0) = 3.48 \times 10^{-7}$ J m$^{-3}$, $\sigma_{DW} = 11$ mJ m$^{-2}$, $\sigma_{DW loc} = 3.89$ mJ m$^{-2}$, $P_t(0) = 0.283$ C m$^{-2}$ and $g_{XX} = 0.61 \times 10^{-11}$ m$^3$ F$^{-2}$. These parameters are used for simulating the hysteresis loop in Fig. 3b. For PbTiO$_3$, we use experimental lattice constants ($a = 4.15$ Å for DFT calculations with PBEsol and obtain $A_{loc}(0) = 5.05 \times 10^{-7}$ J m$^{-3}$, $\sigma_{DW loc} = 175$ mJ m$^{-2}$, $\sigma_{DW} = 67$ mJ m$^{-2}$, $g_{XX} = 1.21 \times 10^{-11}$ m$^3$ F$^{-2}$. The temperature dependence of polarization is taken from ref. 35, with $P_t(0) = 0.872$ C m$^{-2}$. These parameters are used for predicting the coercive fields of PbTiO$_3$-based ceramics and thin films in Fig. 3a,c.

**LGD model for BiFeO$_3$ and other rhombohedral ferroelectrics with O$_{6}$ rotations.** 71°, 109° and 180° domain walls are all observed in BiFeO$_3$. The energetics of these three types of domain walls have been investigated with DFT in several studies 36–39. In ref. 36, $\sigma_{DW} = 152$ mJ m$^{-2}$, $\sigma_{DW loc} = 62$ mJ m$^{-2}$ and $\sigma_{DW loc} = 73$ mJ m$^{-2}$ was reported using LDA+U. In ref. 38, $\sigma_{DW} = 128$ mJ m$^{-2}$, $\sigma_{DW loc} = 33$ mJ m$^{-2}$ and $\sigma_{DW loc} = 98$ mJ m$^{-2}$ was reported with GGA+U. From equation (5), we deduce that $\sigma_{DW} / P_t(0)$ $\propto A_{loc} / g_{XX}$. Assuming the polarization gradient coefficient is isotropic, the energy of a non-180° domain wall ($\sigma_{DW}^{head-to-head}$) can be related to that of a 180° domain wall: $\sigma_{DW}^{head-to-head} = \gamma \sigma_{DW loc}$. Therefore, for a given ferroelectric, $\sigma_{DW loc} / P_t(0)$ can be used to separate $\sigma_{DW}^{head-to-head} / P_t(0)$ from $\sigma_{DW loc} / P_t(0)$.

**Comparison of coercive fields for tetragonal and rhombohedral ferroelectrics.** The comparison of coercive fields for tetragonal and rhombohedral ferroelectrics. The values of $P_t$, $A_{loc}(0)$, $\sigma_{DW}$, $g_{XX}$ and $g_{YY}$ are derived from DFT. These parameters are used for predicting the coercive fields and in the calculation of the activation field. The value of $\sigma_{DW}$ is estimated at $0.542$ mJ m$^{-2}$ (as explained above). To account for the possible octahedral rotations across the 71° domain wall, we use the angle constant derived from Bi$_2$O$_3$ when simulating the coercive field for rhombohedral (R) ferroelectrics; we find that the coercive field is not sensitive to the value of $\sigma_{DW}$, as demonstrated by the moderate change in coercive fields in response to orders of magnitude change in $d$ (which is equivalent to changing $v_s$ for fixed $d$) shown in Fig. 3d. This indicates that the magnitude of the coercive field is largely determined by the activation field.

**Effect of supercell size.** We carried out a benchmark study on the effect of supercell size (Extended Data Fig. 8). We calculated the domain wall velocity with 40 × 40 × 40, 50 × 50 × 50, 60 × 60 × 40 and 65 × 65 × 40 supercells at 200 K and 240 K. The key finding is that the values obtained with the 40 × 40 × 40 supercell do not substantially deviate from values found using the larger supercells (within 10% m$^{-1}$). Most importantly, the $V_s$-$E$ slope is similar for supercells of different sizes, showing that the domain-wall dynamics obtained with a 40 × 40 × 40 supercell are robust against supercell size.

Extended Data Figure 1 | Large-scale molecular dynamics simulations of 90°-domain-wall motions. a, Schematic of a $40 \times 40 \times 40$ supercell with 90° domain walls used in molecular dynamics simulations. The colours of the domains correspond to the polarization ($P$) wheel shown at the bottom. White arrows represent the polarization directions of domains. b, Simulated domain evolution under a [100]-oriented electric field ($E$). The dashed yellow lines show the positions of 90° domain walls. The electric field is turned on at time $t_0$. The domain-wall velocity $v_{\text{DW}}$ along [110] (yellow arrows) is estimated on the basis of the change in the supercell dimension ($L_x$) along [100] from $t_0$ to $t_0 + \Delta t$. The black arrows scale with the local dipole of each unit cell. The domain wall motion is achieved via the 90° switching of [100] dipoles to [010] dipoles.
Extended Data Figure 2 | Lattice constants of supercells used in molecular dynamics simulations. a, Pb (orange) and Ti (blue) sublattices in a PbTiO$_3$ supercell with 90° domain walls. The boundaries are marked by green lines. $a_x$ and $a_y$ are effective lattice constants of the domain-wall unit cell defined in the transformed $X$–$Y$ coordinates and shown by the red rectangle. When dipoles in one layer of unit cells switch by 90° ($c \to a$), the wall moves by $(a^2 + c^2)^{1/2}/2$ along the [110] direction. b, Temperature ($T$) dependence of $\sqrt{a^2 + c^2}/[2(c - a)]$ obtained from molecular dynamics simulations (squares). It depends on temperature weakly (blue line). c, Plot of polarization change $(dP_x/dt)$ versus cell-dimension change ($v_x$). The solid curves show linear fits at 100 K (blue) and 240 K (red).
Extended Data Figure 3 | Elastic energy contribution to nucleation energy. a, Effective lattice constants across 90° domain walls. The inset is the top view of the 40 × 40 × 40 supercell used in molecular dynamics simulations; black arrows indicate the polarization direction. The effective lattice constants \(a_X\) and \(a_Y\) are defined in \(X–Y\) coordinates, as explained in Extended Data Fig. 1. The averaged lattice constants for each layer of cells across the domain wall along the \([110]\) direction are plotted. b, c, Distributions of strain gradient at the domain wall in the presence of a nucleus. \(a_Y^0\) and \(a_Z^0\) are the effective lattice constants along \(Y\) and \(Z\) in the absence of nucleus (\(t = 0\) ps in molecular dynamics simulations), respectively.
Extended Data Figure 4 | Schematic of a triangular-shaped nucleus, as in the Miller–Weinreich model. The triangular-shaped nucleus (red) has a polarization direction (white arrows) that is antiparallel to its neighbouring domains (blue). The depolarization charges ρ_{1,2} at two boundaries are of the same sign, giving rise to repulsive energy penalty. The expressions for nucleation energy ($U_{\text{nuc}}$), depolarization energy ($U_D$), depolarization-contributed domain-wall energy ($\sigma_p$) and the dimensions for the critical nucleus $a^*$ and $l^*$ are taken from the original work of Miller and Weinreich, ref. 15; $c$ and $b$ are lattice constants ($c \approx b$ in PbTiO$_3$ and BaTiO$_3$), $e$ is the base of natural logarithm, and $\varepsilon$ is the dielectric constant. The $\sigma_p/\sigma_w$ ratio determines the aspect ratio of the critical nucleus ($l^*/a^*$).
Extended Data Figure 5 | Distributions of polarization gradient at the domain wall in the presence of a nucleus. a, b, The polarization gradients (dP/dY, a; dP/dZ, b) are highest at the boundary of the nucleus. The maximum polarization gradient is around 0.08 C m⁻² Å⁻¹, much smaller than the value estimated by the classical theories in ref. 15 (0.25 C m⁻² Å⁻¹). This difference is due to the diffuse nature of the boundary. The total boundary charge (ρ₁ + ρ₂ + ρ₃ + ρ₄) is zero.
Extended Data Figure 6 | Results for the Miller–Weinreich model of nucleation on the PbTiO$_3$ 90° domain wall using various conditions for the interface boundary. a, Nucleus energy $U$ as a function of Miller–Weinreich nucleus area ($al$, given in terms of the number of unit cells (uc)) for the original Miller–Weinreich model (black) and Miller–Weinreich models with $s = 0.41, f_\varepsilon = 1, Q_{\text{tot}} = 0$ and $f_c = 1$ (red), $s = 0.41, f_\varepsilon = 2, Q_{\text{tot}} = 0$ and $f_c = 1$ (green), $s = 0.41, f_\varepsilon = 2, Q_{\text{tot}} = 0$ and $f_c = 1/2$ (blue), $s = 0.41, f_\varepsilon = 2, Q_{\text{tot}} = 0$ and $f_c = 1/3$ (cyan). Inset, zoomed-out view showing all the curves. b, Aspect ratio of the Miller–Weinreich nucleus ($l^*/a^*$) as a function of the ratio between $\sigma_p$ and $\sigma_w$. The Miller–Weinreich assumption that $l^*/a^*$ is not valid for realistic values of $\sigma_p$ and $\sigma_w$. c, $\sigma_p$ for different interface conditions. The actual $\sigma_p$ is much smaller than the estimate used by Miller and Weinreich (MW; ref. 15).
Extended Data Figure 7 | Results for the Miller–Weinreich model of nucleation on the PbTiO$_3$ 180° domain wall using various conditions for the interface boundary. a, Nucleus energy $U$ as a function of Miller–Weinreich nucleus area (al, given in terms of the number of unit cells (uc)) for the original Miller–Weinreich model (black) and Miller–Weinreich models with $s = 0.41, f_{e} = 1, Q_{tot} = 0$ and $f_{c} = 1$ (red), $s = 0.41, f_{e} = 2, Q_{tot} = 0$ and $f_{c} = 1$ (blue), $s = 0.41, f_{e} = 2, Q_{tot} = 0$ and $f_{c} = 1/2$ (magenta), and $s = 0.41, f_{e} = 2, Q_{tot} = 0$ and $f_{c} = 1/3$ (cyan). Inset, zoomed-out view showing all the curves.

b, $\sigma_{p}$ for different interface conditions. The actual $\sigma_{p}$ is much smaller than the estimate used by Miller–Weinreich (MW; ref. 15).
Extended Data Figure 8 | Test of domain-wall velocity ($v_x$) convergence with supercell size. The colours of the domains in the bottom panels correspond to those in Extended Data Fig. 1. The error bars are standard deviations.