

Nucleation and growth mechanism of ferroelectric domain-wall motion: Supplementary Online Material

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Growth rates

MD simulations revealed that the growth of critical nuclei is not isotropic, and that the activation barriers for sideways and forward growth are much smaller than for nucleation. The growth rates differ from each other because of different domain wall energies, even though the driving force provided by the interaction with the external field is the same, and they follow the order of $G_{2,2} > G_{1,2} > G_{2,1} > G_{1,1} > G_{0,1} > G_{1,0}$. The observed ratios $G_{m,n}/G_{1,0}$ are shown in Table S1. In the case of $G_{2,2}$, four unit areas of domain walls are eliminated after growth. This growth process is the most exothermic. Following the Brønsted–Evans–Polanyi relation, it has the fastest growth rate. This argument can also be carried further to $G_{1,1} > G_{0,1} > G_{1,0}$, where $G_{1,1}$ does not produce net change in domain wall areas like a half-crystal or kink position, $G_{0,1}$ causes an increase by two unit areas of neutral domain walls, and the $G_{1,0}$ causes an increase by two unit areas of charged domain walls.

Transformation kinetics

Consider a volume in which the new phase β is continuously nucleated at a rate J in the untransformed region α . The new phase that nucleated at time τ then grows with a growth velocity v . The volume V of this new phase at time τ is

$$V = C\nu^d (t - \tau)^d, \quad (1)$$

where d is dimensionality and the prefactor C is either π for two-dimensional systems or $4\pi/3$ for three-dimensional systems.

The number of nuclei that form in a time increment of $d\tau$ will be $Jd\tau$ per unit volume of untransformed α . Ignoring impingement of β , the fraction f of the new phase β at time t is

$$f = CJ\nu^d \int_0^t (t - \tau)^d d\tau = \frac{1}{d+1} CJ\nu^d t^{d+1}. \quad (2)$$

The above estimate overestimates the β fraction since nucleation and growth in the β region should not contribute. Let the true β fraction be F . Then, when f increases by df , the actual increase of F is $(1-F)df$. That is

$$dF = (1 - F)df. \quad (3)$$

Integrating Eq. (3), we obtain

$$F = 1 - \exp\left(-\frac{CJ\nu^d t^{d+1}}{d+1}\right) = 1 - \exp(-(kt)^{d+1}), \quad (4)$$

where k is the rate constant of the overall motion. This is commonly referred to as the Avrami equation.

It is clear from the above equation and the Arrhenius equations for J , ν , and k that the overall activation energy is a weighted energy of the activation energy of nucleation and growth processes. The respective weight factors are $1/(d+1)$ and $d/(d+1)$. This is also consistent with our MD and MC simulations data. In our case the domain wall nucleation and growth processes are two-dimensional, so the respective factors for nucleation and growth are $1/3$ and $2/3$. In reality, in our simulations we often observed

the beginning of second layer nucleation before the growth of the first layer is complete, so that the dimensionality is not exactly 2. Nevertheless, $d=2$ is a good approximation.

Comparing nucleus interface in the MW and LGD models

The boundary between the up domain ($P_z > 0$) and the down domain ($P_z < 0$) is defined by coordinates where $P_z = 0$. This definition is appropriate for both the flat 180° domain wall and for the interface of the nucleus. Note that for flat 180° domain wall, the $P_z = 0$ contour passes through the PbO plane. This is because each Pb atom on the flat wall has an equal number of up and down polarized Ti neighbors, so the symmetry forces the Pb atom to remain at the center of its oxygen cage, hence $P_z = 0$. This is a high-energy bonding configuration since in a PbTiO_3 single crystal the Pb atom displaces by 0.5 \AA away from the center of its O_{12} cage.

In the MW model, the interface contour has a square edge and passes through the Pb atoms at the edge of the nucleus. The additional interface created by the nucleus is therefore proportional to ac (Fig. S3a), where a and c are the lattice constants of the PbTiO_3 unit cell ($\sim 4 \text{ \AA}$). This is so because MW assumes no variation of the magnitude of the polarization during nucleation, allowing only a reversal of the polarization direction at the nucleus interface, so the local symmetry on the nucleus interface is the same as that on the flat 180° domain wall. Therefore, the nucleus interface of $P_z = 0$ coincides with Pb sites in the MW model, as schematically depicted in Fig. 3a of the main text.

In contrast, in our LGD model, the $P_z = 0$ contour is slanted 45° relative to lattice vectors of PbTiO_3 unit cell (Fig. S3b and Fig. S4). The $P_z = 0$ contour on the slanted interface does not pass through any of the Pb atoms, because the Pb atoms located at the edge of the nucleus are actually in an asymmetric environment, with a different number of up and down Ti neighbors. The broken symmetry allows Pb atoms to off-center,

giving rise to finite and oppositely polarized P_z on the two sides of the slanted interface as schematically depicted in Fig. 3b of the main text. A more detailed three-dimensional description of polarization around the nucleus is shown in Fig. S5b using the atomic coordinates of the MD simulation.

Both new features (the 45° tilting of the nucleus interface and the ability of Pb atoms at the edge of the nucleus to go off-center) of the LGD model significantly lower the interface energy density (interface energy per unit length of the nucleus perimeter) and therefore the size and energy of the critical nucleus. The 45° orientation means the additional interface area created by the nucleus is $(\sqrt{2} - 1)ac$, only 41% of the MW estimate. The ability of Pb to off-center means a lower local energy because of more favorable bonding. In addition, the combined effect of both features leads to a smaller gradient energy because the polarization reversal is now more spread out. Taken together, for the LGD model, these effects lead to a total interface energy cost that is a factor of 3-4 lower than the MW estimate. Since the energy of the 2D critical nucleus is roughly proportional to the square of the interface energy density, the factor of 3-4 reduction in interface energy density translates to an order of magnitude smaller activation energy and activation field for our LGD model than that found by MW model.

Estimate of errors

1. Error between DFT and the bond-valence model potential:

Error ($|\Delta E_{\text{DFT}} - \Delta E_{\text{model}}|$) for the 1770 reference structures is 0.01 ± 0.01 eV/(unit cell). See ref. 19 in the main text for more details.

2. Temperature fluctuation during MD runs:

At 240 K, the standard deviation of the temperature is 1.3 K in the Nosé-Hoover thermostat.

3. Error in nucleation rates:

The estimated error in nucleation rates is 6% due to the finite size of the super cell. The error in the mean nucleation rates due to the finite number of measurements (simulations) is estimated using $\sigma_{\text{nuc}}/\sqrt{N_{\text{nuc}}}$, where σ_{nuc} is the standard deviation of nucleation rates and N_{nuc} is the number of measurements. This is between 2.7 and 5.5% in the range of temperatures and electric fields discussed in Table 1 of the main text.

4. Error in growth rates:

The error in the mean growth rates due to the finite number of measurements (simulations) is estimated using $\sigma_{\text{growth}}/\sqrt{N_{\text{growth}}}$, where σ_{growth} is the standard deviation of growth rates and N_{growth} is the number of measurements. This is between 4.7 and 6.5% in the range of temperatures and electric fields discussed in Table 1 of the main text.

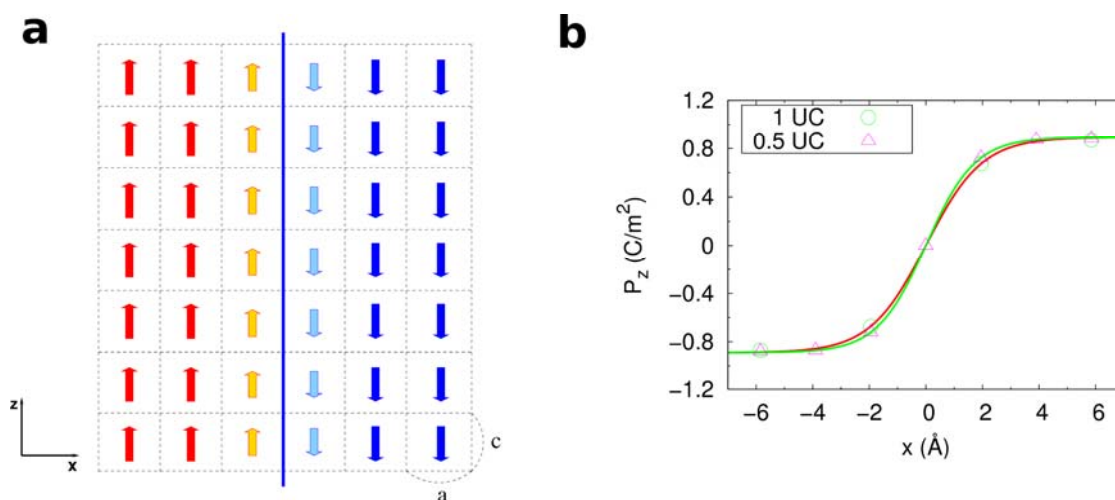


Figure S1. Polarization of the 180° (100) domain wall. **a**, Schematic diagram of polarization around the domain wall. **b**, Polarization P_z profile of the domain wall from the interatomic potential. The green circles are polarization defined from one unit cell, and the triangles are polarization at TiO₂ and PbO layers.

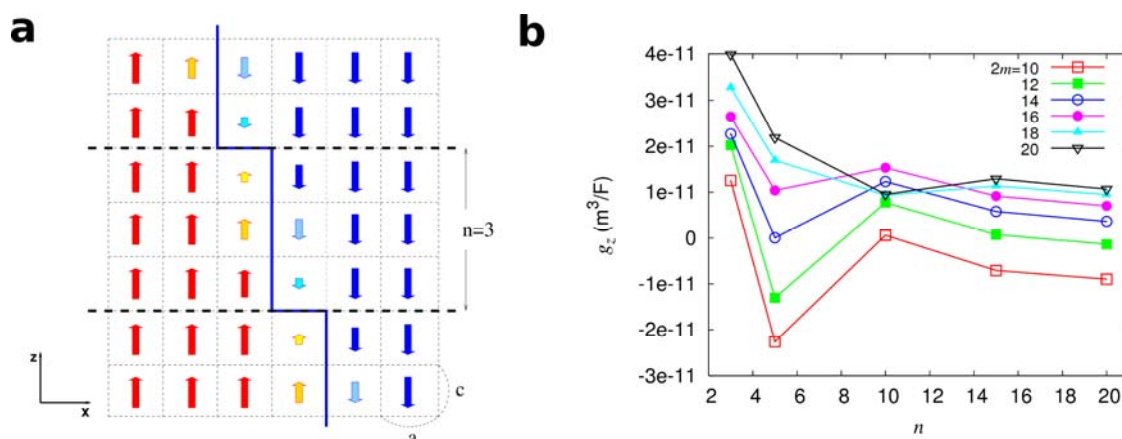


Figure S2. The 180° (*n*01) domain wall. **a**, Schematic diagram of polarization around the (301) domain wall. **b**, The convergence of the gradient coefficient g_z as m and n increase (m is the number of unit cells along the x axis in a supercell).

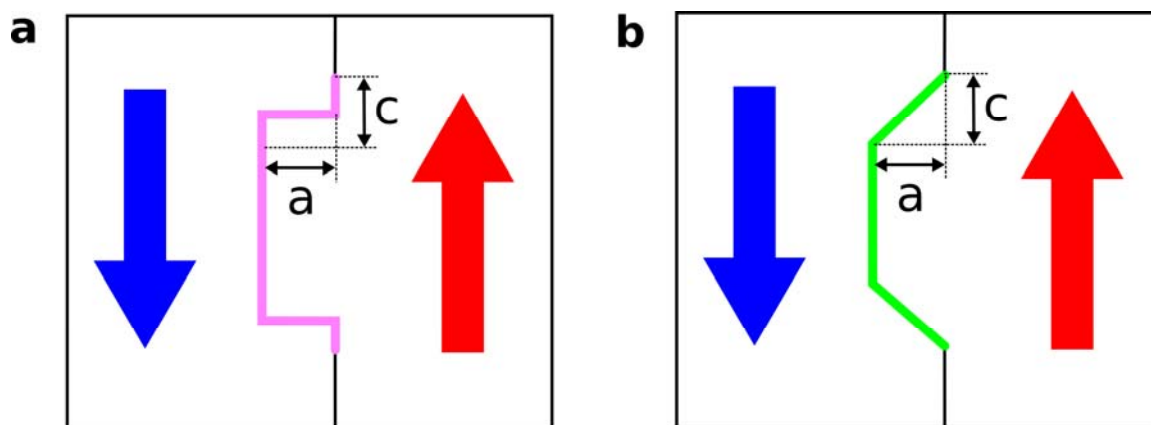


Figure S3. The difference between (a) the MW model and (b) the diffuse boundary model. Pink solid lines and green solid lines describe the boundary around the nucleus in the MW model and the diffuse model, respectively. In the MW model, the additional interface area from nucleation is proportional to $A_{MW}=ac\approx a^2$; in the new model, the additional interface area from nucleation A_D is proportional to $A_D = a(\sqrt{a^2 + c^2} - c) \approx (\sqrt{2} - 1)a^2$. Since A_D is only 41 % of A_{MW} , the interface energy cost is lower in the diffuse boundary model.

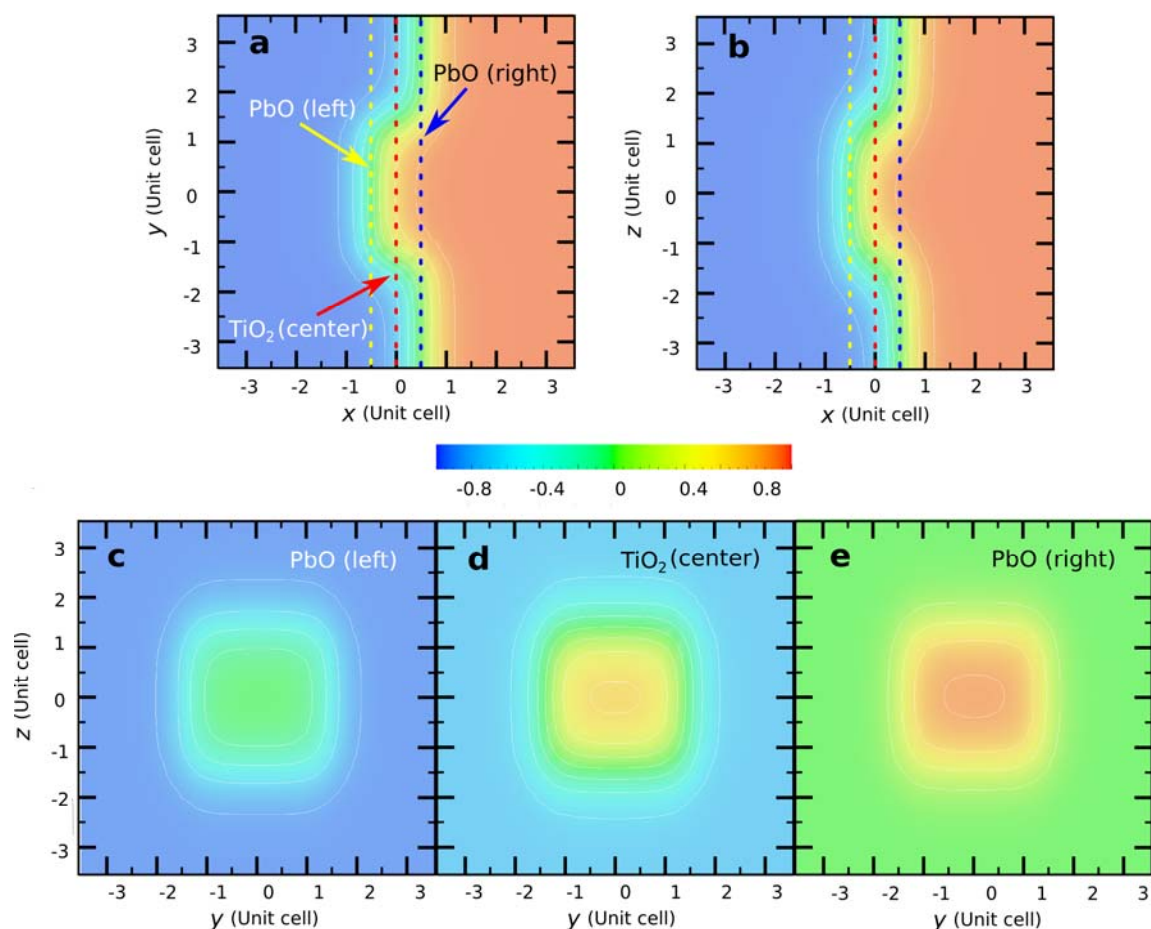


Figure S4. Polarization profiles around a critical nucleus of Eq. M17. **a**, Polarization profile of the TiO₂ x-y plane. **b**, Polarization profile of the TiO₂ x-z plane. **c**, Polarization profile of the PbO y-z plane in the negatively polarized domain next to the PbO plane in the domain wall. **d**, Polarization profile of the TiO₂ y-z plane in the negatively polarized domain next to the PbO plane in the domain wall. **e** Polarization profile of the PbO y-z plane in the domain wall.

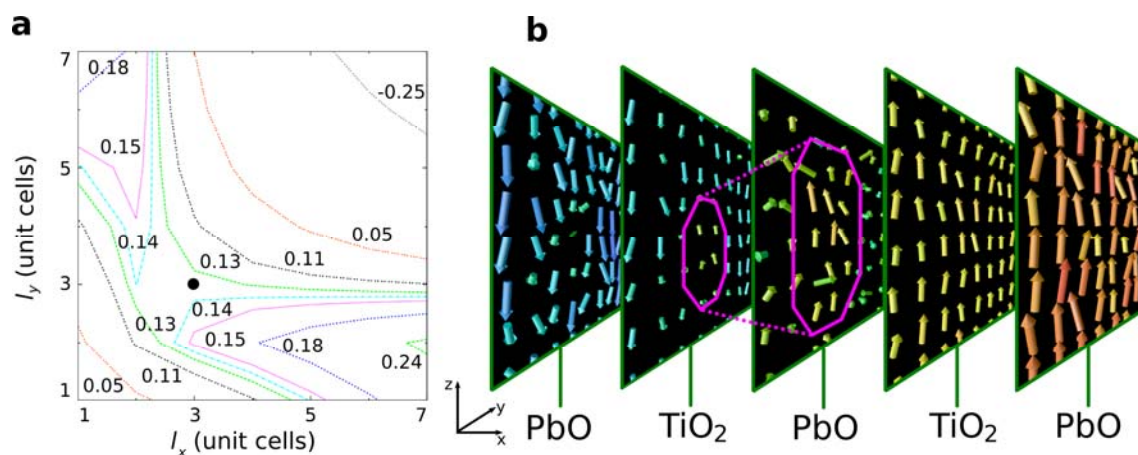


Figure S5. Atomistic-level difference between (a) the MW model and (b) the diffuse boundary LGD model. **a**, Contour diagrams of the free energy difference for PbTiO_3 at 240 K and 0.5 MV/cm. The critical nucleus is denoted by the solid circle. **b**, The actual polarization around a critical nucleus observed in our MD simulations.

Table S1. The growth ratios $G_{m,n}/G_{1,0}$ at $T=240$ K and $E=0.5$ MV/cm.

	1,0	0,1	1,1	2,1	1,2	2,2
$G_{m,n}/G_{1,0}$	1.0	1.5	1.7	2.9	3.4	4.0

$G_{m,n}$ is the rate of polarization switching of a unit cell with m sideway and n forward neighbors polarized along the direction of the external electric field.

Table S2. Polarization across the 180° (100) domain wall at TiO_2 and PbO layers.

x (a)	-2.5	-2.0	-1.5	-1.0	-0.5	0.0	0.5	1.0	1.5	2.0	2.5
	(TiO_2)	(PbO)	(TiO_2)	(PbO)	(TiO_2)	(PbO)	(TiO_2)	(PbO)	(TiO_2)	(PbO)	(TiO_2)
$P_z(x)$	-0.89	-0.89	-0.87	-0.86	-0.73	0.0	0.73	0.86	0.87	0.89	0.89