Path to finding the critical thickness for memory in thin ferroelectric films

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The finite screening length by real metallic electrodes, albeit very small (< 1 A), results in finite depolarizing field that tends to split the film into domains. In very thin ferroelectric films the domain structure reduces to sinusoidal distribution of polarization considered first in the 1980s. We discuss the phase transition between this structure and a single domain state and show that it is first order, if it exists at all. The alternative possibility is that the single domain state at zero bias voltage would be metastable for all temperatures in most systems. This scenario defines a path towards solution to a problem of finding parameters of a system that can sustain the ferroelectric memory over a desired period of time.

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Stability of ferroelectricity in ultrathin films with electrodes is a topic of intense current interest, as illustrated by numerous papers that appeared recently in the leading journals (see, e.g.\(^1\) 2 3 4 5). In this Letter, we show that all those papers have little or no relevance to the possibility of the ferroelectric (FE) memory since they do not actually address the core issues. We shall formulate the actual problem that has to be resolved in order to answer the question at hand, and indicate possible paths to its solution. Our present formulation builds on an old paper by Chensky and Tarasenko (ChT)\(^6\), which, unfortunately, is rarely mentioned in recent literature. ChT discussed stability of the FE films with respect to small fluctuations of the single and multidomain states in an electroded film of a uniaxial ferroelectric with ‘dead’ layers between the electrodes and the material, Fig.1a (inset). It was already shown that their system satisfactorily models also the FE films without a physical dead layer but real metallic electrodes\(^7\), i.e. it considers the same type of a system as have the recent Refs.\(^1\) 2 3 4 5, which customarily disregard the multidomain region.

The results of ChT and the above authors for stability of homogeneous FE state in the films would only be correct if the phase transitions between the single and multidomain states were second order. In fact, the character of the transition between the ferroelectric single domain state and the multidomain ones was not studied by ChT, and it is one of the main questions we address in this Letter. We find that in the low-T part of the phase diagram the transition is first order. Thus, the stability of the FE state found by ChT means, in fact, its metastability at least in some temperature region. With account of our old result\(^8\), we expect that the single domain state is metastable for all temperatures or, if one studies the FE states at a given temperature but for different film thicknesses, at all film thicknesses. This question has to be studied in more detail, but in any case, the key theoretical problem to be resolved in order to predict feasibility of the FE memories is not that of existence of a solution corresponding to the ferroelectric phase or demonstrating its stability with respect to small fluctuations. For the case of metastability of a single domain state, the key problem is calculating the escape rate from this metastable state. We are not aware of theoretical efforts to solve this problem. Another aspect of the memory problem is to find the conditions of absolute stability of the single domain state under zero external bias voltage.

The single domain FE state is evidently stable in the case of the ideal metallic electrodes (here and below we mean, of course, the ideally homogeneous systems.) For a non-zero dead layer thickness (d) this is not evident anymore, although it is hardly surprising that there exists a “minimal thickness” \(d_m\) such that for \(d < d_m\) the FE single domain phase is stable in the ChT sense, i.e. with respect to small fluctuations, in all the temperature range. The minimal thickness \(d_m\) depends on parameters of the FE material, as well as on the dielectric constant of the dead layer (or, in the case of real metallic electrode, on parameters of both the electrode and the ferroelectric film.) The stability in the ChT sense of single domain FE state does not mean that this state is absolutely stable. According to our result in Ref.\(^8\), at any finite thickness the homogeneously polarized state is metastable far enough from the phase transition (or for thick enough films.) However, it is stable not very far from the transition or for very thin films. This conclusion makes this case attractive from the point of view of memory applications. Unfortunately, the experimental systems of today do not fall into this category\(^8\). It does not seem impossible, at least in principle, to find a suitable system, but we shall not dwell on this issue here, assuming below that \(d > d_m\).

Similar to ChT\(^6\), we consider a uniaxial ferroelectric film under the external bias voltage \(U\) (Fig. 1a, inset).
The free energy of such a film is given by [9]:

\[
\tilde{F} = F_0 + \int_{FE} dV \left\{ \frac{A}{2} P_z^2 + \frac{B}{4} P_z^4 + \frac{1}{2} D_{ij} (\nabla_{i} P_z)(\nabla_{j} P_z) \right. \\
+ \frac{1}{2} \eta (\partial_{k} P_z)^2 + \frac{1}{2} \kappa P_z^2 + \frac{A_{\perp}}{2} P_\perp^2 + \frac{E^2}{8\pi} \left. \right. \\
+ \int_{DL} dV \frac{\epsilon_s E^2}{8\pi} + QU, \tag{1}
\]

where \( F_0 \) is the free energy of the system at \( P = 0 \), with \( P_z \) the ferroelectric (switchable) component of polarization, \( P_{\perp} \) the nonferroelectric part of the polarization perpendicular to the electrodes [3], \( P_{\parallel} \) the in-plane polarization, \( A = \gamma (T - T_c) \), and \( B, D_{ij}, \eta = \text{const.} \), \( \nabla_{\parallel} = (\partial_x, \partial_y) \) is the gradient in the plane of the film, \( i, j = x, y \), and we assume summation over repeating indices, \( A_{\perp} > 0 \), \( \mathbf{E} \) the electric field, \( \epsilon_s \) the dielectric constant of the electrode/dead layer (marked DL), \( Q \approx -p \) the electrode charge, \( p = (P_z) \) is the average polarization in the FE film. We assume that \( D_{ij} = D_{0ij} \), which is valid, in particular, for BaTiO$_3$ or PbTiO$_3$ films grown on (100) SrTiO$_3$ substrate because of a square symmetry in the film plane. The noncritical in-plane and out-of-plane dielectric constants are equal \( \epsilon_{\parallel} = 1 + 4\pi P_z/E_{\parallel} = 1 + 4\pi/A_{\perp} \) and \( \epsilon_{\perp} = 1 + 4\pi/\kappa \), respectively.

The stability of the paraelectric phase is lost with respect to appearance of the “polarization waves” [3, 9]:

\[
\tilde{P}_z(x, z) = a \cos qz \cos kx, \tag{2}
\]

where, for \( d \gtrsim 2d_m \), \( q \approx \pi/d \) and \( k = (4\pi^3/\epsilon_{\parallel} D^2)^{1/4} \) [6, 9]. To find the amplitude of the polarization wave in the external bias field, we use the following approximation valid close to the phase transition (see below):

\[
P_z(x, z) = p + \tilde{P} = p + a \cos qz \cos kx. \tag{3}
\]

In this case, the non-equilibrium free energy per unit area \( \tilde{F}(p, a) \) takes the form:

\[
l^{-1} \tilde{F}(p, a) = \frac{\tilde{A}}{2} p^2 + \frac{\tilde{A}}{8} a^2 + \frac{B}{4} E^4 + \frac{3B}{8} a^2 p^2 + \frac{9B}{256} p^4 - pE_0, \tag{4}
\]

where \( \tilde{A} = A + 2Dk^2 = \gamma (T - T_d) \), \( \xi = 4\pi d/\epsilon_{\parallel} \ell \), \( \eta = 2Dk^2/\epsilon_{\parallel} \ell^2 \), \( E_0 = \epsilon_s U/\epsilon_{\parallel} \ell \) the external field for the usual case of a thin dead layer \( \epsilon_{\parallel} \ell \gg \epsilon_{\perp} d \). At \( \xi > 0 \) (or \( d > d_m \)), according to the above expression for the free energy, the system will undergo a phase transition at \( E_0 = 0 \) and \( \tilde{A} = y = 0 \), i.e. at \( T = T_d \) into the sinusoidal domain phase. At lower temperatures, there may be another transition into a homogeneously polarized state with \( a = 0, p \neq 0 \). The above potential allows one to study both phase transitions also at non-zero external field.

When writing Eq. (3), we have assumed the stripe-like sinusoidal domain structure. This is far from being obvious in our isotropic case, and ChT [6] discussed possibilities of checkerboard and hexagonal sinusoidal domain structures. However, those become irrelevant if one takes into account the elastic strains. Their coupling to the inhomogeneous polarization produces anharmonic terms in Eq. (1), with the renormalized coefficients that now depend on the direction of the “wave vector” \( k \) for any elastically anisotropic medium [10]. For the case of tetragonal uniaxial ferroelectric, the square symmetry tells us that there are at least two orthogonal orientations of stable stripe structures with the same free energy, while a hexagonal domain pattern is clearly impossible. The checkerboard domain lattice should be studied separately, but it is unlikely to be relevant. In the following, we discuss a stripe structure neglecting the elasticity and assuming that its role reduces mainly to selecting the direction of the sinusoidal polarization waves. To be precise, elastic coupling also leads to changes of the coefficient \( B \) in (1), which are slightly different between the third, fourth, and fifth terms there (see Ref. [10]), but this is only a numerical difference that does not affect any of the results below, and we shall not dwell on this issue here.

By minimizing the free energy (1) with respect to \( a \), one finds the equilibrium amplitude of the wave:

\[
a_0 = \left[ -\frac{16}{9B} (\tilde{A} + 3Bp^2) \right]^{1/2} = \frac{4p_c}{3!^2} \sqrt{1 - s^2}, \tag{5}
\]

where \( s = p/p_c \), with \( p_c = \sqrt{-\tilde{A}/3B} \) the characteristic polarization. We finally arrive at the dimensionless free energy, \( f = 3B\xi l^{-1} \tilde{F} \):

\[
f_{\pm} = \left\{ \begin{array}{ll} \frac{1}{2} \frac{y(1 - y)}{2} s^2 + \frac{1}{12} y^2 s^4 - \frac{\sqrt{3}}{2y} s_e & |s| \geq 1, \\
- \frac{y^2}{4} + \frac{y}{2} (1 + \frac{y}{2}) s^2 - \frac{\sqrt{3}}{2y} s_e & |s| < 1, \end{array} \right. \tag{6}
\]

where \( e = E_0/\zeta \) the relative external field, \( \xi = \xi^{3/2}/\sqrt{3B} \) the characteristic electric field, and

\[
y = -\tilde{A}/\xi, \tag{7}
\]

the characteristic temperature (i.e. the relative distance of transition temperature from the paraelectric phase that depends on the film thickness \( l \)). It is easy to see that the free energy is continuous with the first derivative with respect to \( s \), while \( d^2 f/\iota^2 ds^2 \neq d^2 f_+/\iota ds^2 \) at \( s = \pm 1 \).

One of the easiest ways to reveal the order of the transition is to inspect the equations of state curves \( s = s(e) \) obtained from the condition \( df/\iota ds = 0 \), which read:

\[
\sqrt{y} (1 - y) s + \frac{1}{3} y^{3/2} s^3 = e, \quad |s| \geq 1 \tag{8}
\]

\[
\sqrt{y} (1 + \frac{y}{2}) s - y^{3/2} s^3 = e, \quad |s| < 1. \tag{9}
\]
Recall that the given state is (meta)stable only when \( d^2f/ds^2 > 0 \). Several typical \( s(e) \) curves for \( y = 1/4, 1, \) and \( 3 \) are displayed in Fig. 1. We see that at a relatively small \( y = 1/4 \) (not far below \( T_d \) or \( A = y = 0 \)) and in the field \( e > e_c = \sqrt{7} - 2y^{3/2}/3 = 5/12 \) the system is homogeneously polarized. In the lower bias field, it splits via the second order phase transition into domains with zero net polarization at \( E_0 = 0 \). At \( y > 3/8 \), the transition is first order, which is clearly seen for \( y = 1 \), where two metastable solutions exist in the fields \( e_A < E_0/\zeta < e_B \), Fig. 1. The points of the first order phase transitions found from the condition of equal free energies, \( f_+\{s_+(e)\} = f_-\{s_-(e)\} \), are marked in Fig. 1. The first instance when the state with spontaneous net polarization \( p \neq 0 \) at \( E_0 = 0 \) becomes formally possible as a solution to the equations of state is at \( y = 3/2 \). However, this state is unstable \( (d^2f_-/ds^2 < 0 \) at \( s = \pm 1 \), as is evident from the negative slope of the lower branch of \( p - e \) curve at \( s = 1 \) in Fig. 1b in the external fields \( e_A < E_0/\zeta < e_B \). The above tricritical behavior of thin ferroelectric films with real electrodes becomes clear from the phase diagram in \((E_0, y)\) plane, Fig. 2. Indeed, there is a second order phase transition in the interval \( 0 < y < 3/8 \), where the sinusoidal domains form in the fields below \( e = e_A \), where

\[
e_A = E_A/\zeta = \sqrt{y}(1 - 2y/3),
\]

(10)
corresponding to point A in Fig. 1b. In the range \( 3/8 < y < 3/2 \), the same expression gives the line of stability loss of the single domain phase. After passing the tricritical point at \( y = 3/8 \), there appears a line of first order phase transitions \( E_1(y) \), that terminates at \( y = 3 \), and it is bracketed by the lower and higher terminal fields \( e_A \) (10) and \( e_B \), where

\[
e_B = E_B/\zeta = 2(3 + y)^{3/2}/27.
\]

(11)
The physical meaning of these fields is clear from Fig. 2: \( E_A \) is the lowest field where the stability of the homogeneous phase is lost with respect to domains, while \( E_B \) is the highest field where the domain structure still exists. The hysteresis, therefore, is observed in the range of

![Fig. 1: The equation of state for ferroelectric film with dead layer in external field \( E_0 \) for various values of the relative temperature \( y \), Eq. 14. (a) \( y = 1/4 \), (b) \( y = 1 \), and (c) \( y = 3 \). There is a phase transition between the homogeneous state and the one with sinusoidal domains: (a) second order, which becomes first order in cases (b) and (c), where arrows indicate the hysteretic behavior during polarization switching. The terminal external fields for hysteresis are at points A and B. All those cases are very different from the FE film without the dead layer. \( \zeta = \epsilon^{3/2}/\sqrt{AB} \) is the characteristic electric field. Inset (a) shows the schematic of the ferroelectric film with either real electrodes or the dead layer with the thickness \( \lambda \).](image)

![Fig. 2: External field-temperature (thickness) phase diagram of a ferroelectric thin film with real metallic electrodes. The line of stability loss of the homogeneous states \((E_A, E_B)\) has been calculated in Ref. 8. The tricritical point \((y = 3/8)\) and lines \( E_1 \) (line of first order phase transitions), \( E_B \) are from the present work. The point \( y_1 = 1 \) corresponds to the "critical thickness" calculated in Refs. 1, 2, 3, 4 with an account for atomistic structure of the electrodes (additional boundary conditions), \( y_2 = 3/2 \) is the stability point considered in Ref. 8 with an account for elastic strains. The shaded region is area of interest for estimating the retention time of homogeneously polarized state.](image)
fields $E_A < E_0 < E_B$, when $y > 3/8$. Although the approximation of sinusoidal domains becomes rather poor at larger parameters $y \gtrsim y_1 = 1$, it should still correctly grasp the main features of the phase behavior. Note that this result invalidates a long unchallenged claim by Chesn-ky and Tarasenko that one can prepare a monodomain state at $E_0 = 0$, $y > y_2 = 3/2$ (that corresponds to low temperatures well below $T_c$ and $T_d$) by polarizing the system in sufficiently high field and then removing the field.

The present diagram suggests that the homogeneously polarized state will remain metastable (in the present one-sinusoid approximation) only at $y > 3$. There is a metastability of homogeneously polarized state in the region $3/2 < y < 3$. Formally, both the ferroelectric memory and the polarization switching are possible at these temperatures/thicknesses but no conclusion of practical importance can be made before calculating the escape time from the metastable state. At larger $y \gtrsim 3$ (further down from the phase transition with respect to temperature, or for films with thickness exceeding the critical one) the state with the homogeneous polarization in the present single-harmonic approximation, Eq. (3), has the same or lower free energy than the state with $p = 0 : f_+(s_m) \leq f_-(0)$, where $s_m$ are the positions of the minima of the free energy $f_+$ at $E_0 = 0$ (Fig. 3). Note that this result is approximate. The reason is that Eq. (3) is valid near the phase transition point only. The region of validity of this approximation has been estimated in [6] as roughly $-\tilde{A} < Dk_y^2$, which means $y \lesssim 1$ if $4\pi d/(\epsilon_e l)$ and $2Dk_y^2$ are of the same order of magnitude.

We should mention that the second order phase transition into homogeneus FE phase, considered in the prior papers [1,2,3,4], may only occur in zero field, $E_0 = 0$, and it corresponds to $A = 4\pi d/(\epsilon_e l + \epsilon_0 d)$, or, in other words, to the point $y = y_1 = 1$ on the ($E_0, y$) diagram, which is the point that in typical circumstances lies well inside the domain regime and, therefore, is normally unreachable, Fig. 2. On the other hand, Pertsev and Kohlstedt have studied the stability loss of the FE homogeneous state, which corresponds to point $y = y_2 = 3/2$ in the phase diagram. They noted that one should take elastic coupling into account while discussing the stability of the ferroelectric state but, unfortunately, did it in a confusing manner with incorrect conclusions, see analysis in [11]. In a more accurate approximation accounting for higher harmonics to describe the inhomogeneous polarization, the free energy minimum at $s = E_0 = 0$ dips lower than that of the homogeneous state. It is those higher harmonics that convert the sinusoidal domain structure into a conventional one with narrow domain walls. For the parts of the curves corresponding to $|s| \gtrsim 1$, these higher harmonics are not important (they are when an amplitude of the first harmonic becomes substantial) but they will change the curves for $|s| < 1$ substantially. The amplitudes of the higher harmonics are to be considered as new variational parameters for the free energy, and their account will be lowering the estimated free energy. Hence, the minimum at $s = p = 0$ in Fig. 3 is actually deeper, and the homogeneously polarized phase becomes stable not at $y = 3$ but at a larger value (i.e. at a lower temperature or a larger thickness.) Furthermore, it is possible that the homogeneous state would always remain less stable than the polydomain state in that region. Indeed, in the opposite limiting case, i.e. far below the FE transition, it has been shown that for any thickness of the dead layer the multidomain state has lower free energy than the homogeneously polarized state [5]. Anyway, what value of $y$ would correspond to the “critical thickness for the ferroelectricity” within the discussed simple case depends on the desirable memory retention time and should be found by solving a kinetic problem.

The present discussion of an equilibrium problem in the one-sinusoid approximation can be improved. We have already mentioned the effect of coupling of the polarization and the elastic strains, which is unimportant for studying the stability of the paraelectric phase but should be taken into account while considering the multidomain state. This is valid also for the discussion of stability of a single domain FE phase. We can mention also the effect of the additional boundary conditions, apart from electrostatic ones used by ChT, and the effects of higher order terms in the LGD expansion. This, however, would not change the present qualitative conclusions that will apply also to finite FE patches with lateral sizes of 100nm and smaller, which have lateral dimensions still much larger than the domain width, which is just $\sim 1–2$nm in 5nm thick BaTiO3 film [7]. Our discussion above indicates only the first steps on the path to addressing the kinetic problem in a likely scenario that the single domain state is not absolutely stable but.

![Figure 3: The free energy of the FE film with the dead layer for the relative temperature $y = 3$, when the transition between the homogeneously polarized state and sinusoidal domains is first order.](image)

It is evident that switching proceeds through the state with domains with much lower energy barrier for nucleation (top of the barriers indicated by arrows). An account for higher harmonics in Eq. (2) will deepen the energy of the domain state compared with the one shown here and will lower the barrier even further.
metastable.

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