Two-dimensional ferroelectrics and homogeneous switching. On the 75th anniversary of the Landau–Ginzburg theory of ferroelectricity

V S Bystrov, V M Fridkin

Contents

Abstract. **Within the framework of the Landau–Ginzburg (LG) theory, the kinetics of polarization switching in ferroelectric crystals and the transition from domain switching to homogeneous switching in nanosized single-crystal films are considered. It is shown that homogeneous (nondomain) switching can be described in LG theory terms only for two-dimensional ferroelectrics. A review of the experimental results for two-dimensional films of a ferroelectric polymer and barium titanate is given. For ultrathin polymer films, these results are also confirmed by first principles calculations.**

Keywords: ferroelectricity, Landau–Ginzburg–Devonshire theory, domains, two-dimensional ferroelectrics, homogeneous switching

1. Introduction. Ferroelectricity and the Landau–Ginzburg–Devonshire theory

In the Russian scientific literature, the term ferroelectricity (Russian: segnetoelectricity) refers to the appearance of

V S Bystrov [(1, a)], **V M Fridkin** [(2, b)]
[(1)] Institute of Mathematical Problems of Biology,
    Russian Academy of Sciences – branch of the Federal Research Center
    Keldysh Institute of Applied Mathematics
    of the Russian Academy of Sciences,
    ul. Professora Vitkevicha 1, 142290 Pushchino, Moscow region,
    Russian Federation
[(2)] Federal Scientific Research Center Crystallography and Photonics,
    Russian Academy of Sciences,
    Shubnikov Institute of Crystallography
    Leninskii prosp. 59, 119333 Moscow, Russian Federation
E-mail: [(a)] vsbys@mail.ru, [(b)] fridkinv@gmail.com,
       [(b)] fridkin@ns.crys.ras.ru

spontaneous polarization in a crystal (or other material), which was first observed by Valaszek in Rochelle salt (Russian: seignette salt) in 1920 [1, 2]. The ferroelectric properties of barium titanate (BaTiO$_3$) were discovered in 1945 (see, for example, [3] and references in [4]). It became clear that such ferroelectric properties can exist in all crystals belonging to 10-point pyroelectric symmetry groups. In the same year, Ginzburg, and later Devonshire, developed the phenomenological theory of ferroelectricity (mean-field theory) based on the Landau theory of second-order phase transitions [5–7]. The Landau–Ginzburg–Devonshire (LGD) theory explained all the basic properties of ferroelectrics, including polarization switching in an external electric field and the hysteresis loop. It turned out, however, that this theory does not describe the switching of a ferroelectric, since it predicts a value of the coercive field, which is 2–3 orders of magnitude larger than the experimental one. This contradiction remained unresolved for several years.

The large coercive fields predicted by the LGD theory will be referred to in this text as intrinsic fields, and their experimental values as extrinsic.

The intrinsic value of a coercive field can be obtained from the mean-field theory by expanding the thermodynamic potential in series of polarization:

$$\Phi = \Phi_0 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 - EP, \tag{1}$$

where Φ is the thermodynamic potential, P the spontaneous polarization, and E the external field. This leads to the following expression for the intrinsic coercive field E_c:

$$E_c = \frac{P}{\chi_0} f(t), \tag{2}$$

where $f(t)$ is expressed as

$$f(t) = \frac{3}{25} \sqrt{\frac{3}{5}} \left(1 - \frac{25}{24} t\right), \tag{3}$$

and the reduced temperature is given by

$$t = \frac{4\alpha\gamma}{\beta^2} = \frac{4\gamma}{\varepsilon_0 C \beta^2} (T - T_0). \qquad (4)$$

Here, χ_0 is the susceptibility and α, β, γ are the thermodynamic potential expansion coefficients of even order in the polarization, known from the LGD theory. For estimates, one can assume that $E_c \sim P/\chi_0 \sim P/\varepsilon\varepsilon_0$, where ε is the relative permittivity and ε_0 is the vacuum permittivity.

For Rochelle salt, BaTiO$_3$, and other ferroelectric crystals, the intrinsic coercive field E_c defined by Eqn (2) turned out to be several orders of magnitude higher than its experimental (extrinsic) values. It is important to notice that the LGD theory considered the ferroelectric crystal a homogeneous infinite medium.

This contradiction was resolved by the discovery of domains, which were first observed in Rochelle salt [8] and later in barium titanate [9] and other ferroelectrics. It was shown that the switching of the ferroelectric in an external field is related to the domain motion, and the switching kinetics in the Kolmogorov–Avrami–Ishibashi (KAI) theory [10–12] are defined by the dimension and shape of the domains, their size distribution, and the nucleation probability. The dependence of the polarization switching time on the applied voltage $\tau = \tau(V)$ in the KAI theory is close to exponential.

In the absence of external (ion adsorption) and internal polarization screening, the appearance of the domain structure is caused by the thermodynamic potential minimization in the crystal. An extensive overview of theory and experiment related to the nucleation and domain switching in bulk ferroelectrics is given by Cross, Tagantsev, and Fousek [13], and we will not consider domain switching in more detail here.

2. Two-dimensional ferroelectrics

Until the beginning of the 1990s, the available thicknesses of ferroelectric crystals and films were not much smaller than 1 μm. Such samples could be considered to be bulk media, because their thickness was many orders of magnitude larger than the critical domain nucleus, which, according to theoretical estimates, is no more than 10 nm [13–15]. However, already in the 1940s, L Onsager [16] and later N Vdovichenko and G Ryazanov theoretically predicted the possibility of a two-dimensional ferroelectric by considering the interaction of dipoles located in the nodes of a square (two-dimensional) lattice. The coupling of dipoles leads to a spontaneous polarization P and second-order ferroelectric phase transition at the Curie point T_C [17]:

$$P \sim (T_C - T)^{1/2}. \qquad (5)$$

The first experimental observation of two-dimensional ferroelectrics was achieved more than 50 years later using ferroelectric polymer films of polyvinylidene fluoride-tri-fluoroethylene (P(VDF-TrFE)) with a thickness of one-two monolayers (ML) (0.5–1.0 nm) grown by the Langmuir–Blodgett method [18]. Two-dimensional ferroelectrics showed hysteresis loops and an intrinsic coercive field (2), which was several orders of magnitude larger than the extrinsic one known before from crystals and films. The switching kinetics were also significantly different from the well-known domain switching kinetics, which could be described, for example, by the KAI theory.

The first stage of this work was performed in 1993–2003 by one of the authors of this review together with the team at the Laboratory of Liquid Crystals of the Institute of Crystallography of the Russian Academy of Sciences in a collaboration with the laboratory of S Ducharme at the University of Lincoln (USA) [19–21].

The first result was the development of a new growth method for single-crystal ferroelectric films of P(VDF-TrFE) [18, 22–25]. The films in the ferroelectric phase were orthorhombic (point group 2mm), which was confirmed by X-ray and electron diffraction methods, as well as by scanning tunneling microscopy.

The ferroelectric polymer films were grown using the Langmuir–Blodgett (LB) method [18–25], which is based on the transfer of polymer chains from a water surface to a substrate that carries an electrode. Figure 1a, b shows the polymer chains in polar (ferroelectric) and nonpolar (paraelectric) phases. Figure 1c–e shows the transport scheme and chains observed in a tunneling microscope. Langmuir ferroelectric films obtained by this method in 1998 turned out to be record thin. The thickness of a single monolayer (1 ML) was 0.5 nm, which is significantly smaller than the theoretical estimate of the critical domain nucleus size known from literature [13–15]. The thickness of Langmuir polymer films (two-dimensional ferroelectrics) was controlled by ellipsometry and atomic force microscopy. Finally, two-dimensional ferroelectrics consisting of only one monolayer with a thickness of 0.5–1.0 nm were obtained [18].

Since the 1970s, thin single-crystal ferroelectric films (such as barium titanate) have been prepared by laser epitaxy [19]. In the 1990s, the film thickness was not less than several ten nm. The synthesis of Langmuir films in 1998 resulted in record thin ferroelectric films [18] with a thickness smaller than the possible size of the domain nucleus [13–15]. Thus, the development of Langmuir ferroelectrics led to the first observation of two-dimensional ferroelectrics [18].

Figure 2 shows hysteresis loops for Langmuir films P(VDF-TrFE) consisting of different numbers of monolayers, up to 2 ML with a thickness of 1 nm, demonstrating the existence of two-dimensional ferroelectricity [18, 19].

3. Switching kinetics of two-dimensional ferroelectrics (Landau–Khalatnikov kinetics)

The polarization switching kinetics of two-dimensional ferroelectrics was described in [26, 27]. The KAI theory could not be used to explain this phenomenon, since the film thickness was comparable to or even smaller than the domain nucleus size. Of course, the switching can happen in the plane of the two-dimensional ferroelectric, according to the two-dimensional version of the KAI theory [28]. One should also note that, when considering the switching kinetics in two-dimensional ferroelectrics, we were using a phenomenological approach, which (as the LGD mean-field theory itself) does not provide information about the switching mechanism (see also Conclusions).

For this reason, the Landau–Khalatnikov equation [29] was solved in [26, 27] for first-order phase transitions [26, 27, 29]:

$$\xi \frac{dP}{dt} = -\frac{\partial \Phi}{\partial P} = -\alpha P - \beta P^3 - \gamma P^5 + E, \qquad (6)$$

where ξ is the damping coefficient. In the general case, one can take into account the gradient term. Investigation of the
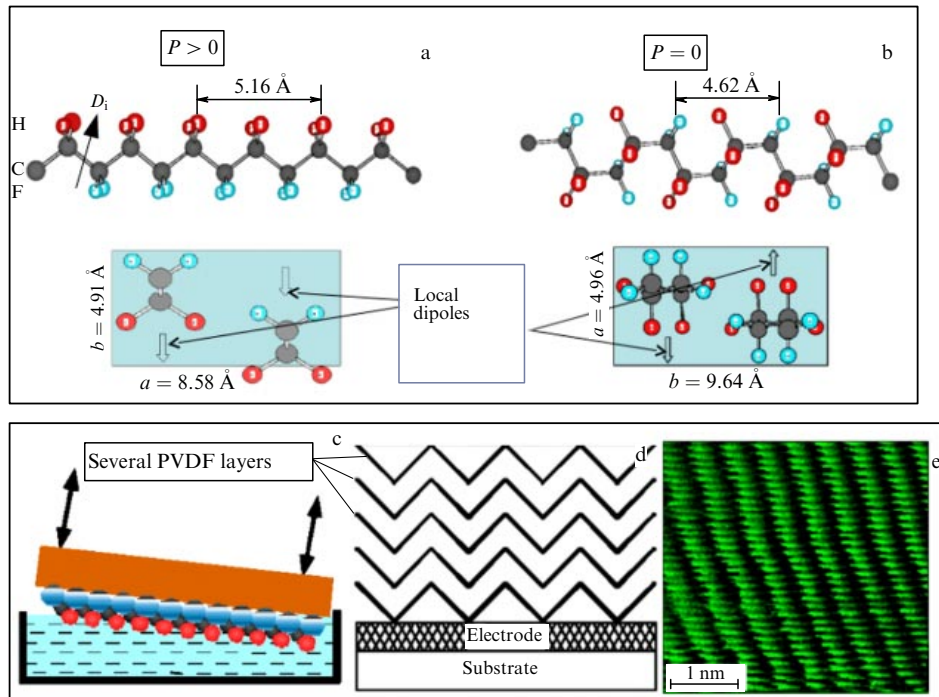
Figure 1. (Color online.) Ferroelectric polyvinylidene fluoride polymer (PVDF): (a) PVDF in polar Trans conformation with net polarization $P > 0$; (b) PVDF in nonpolar Gauche conformation with net polarization $P = 0$; (c) PVDF Langmuir–Blodgett film formation on the water surface; (d) transfer of several PVDF LB film layers on a substrate carrying an electrode; (e) scanning tunneling microscopy image of an LB film P(VDF-TrFE) [18, 19] (taken from [18]).

solution of Eqn (6) has shown that, in the vicinity of the coercive field E_c, the switching time increases indefinitely, and its reciprocal value can be expressed in the following way [26]:

$$\tau^{-1} \simeq \frac{1}{\tau_0} \left(\frac{E}{E_c} - 1 \right)^{1/2}, \tag{7}$$

where $\tau_0 \simeq 6.3\gamma\xi/\beta^2$. Otherwise,

$$\tau^{-2} \simeq \frac{1}{\tau_0^2} \left(\frac{E}{E_c} - 1 \right). \tag{8}$$

In this case, E_c is the intrinsic coercive field of ferroelectric (2) defined by Landau–Ginzburg coefficients.

Experimental results turned out to be in good agreement with the Landau–Khalatnikov kinetics. The critical behavior of τ^{-2} for $E \to E_c$ was directly shown in [30, 31] for P(VDF-TrFE) LB films. Figure 3 shows data for a 10-ML film (5 nm). Here, the dashed curve shows the theoretical result and the triangles indicate the experimental results. For a thicker 30-ML film (15 nm), the dots show the experimental values of τ^{-2} and the dashed curve corresponds to an exponential dependence.

A similar study of P(VDF-TrFE) LB films of different thicknesses was performed in [32] (Fig. 4). It was shown that, for small thicknesses of 2–6 nm, the coercive field E_c is intrinsic and remains almost the same; for thicknesses above 8 nm, a transition region is observed; and for thicknesses larger than 10–12 nm, the intrinsic coercive field E_c becomes extrinsic, with its value defined by the domain mechanism (see Fig. 4).

Thus, it was shown in [19] that the Landau–Khalatnikov kinetics provide a satisfactory description of the switching kinetics in a two-dimensional ferroelectric only if the studied nanocrystal can be considered homogeneous.

Here, by two-dimensional ferroelectric, we mean a nanosized crystal, which can be considered homogeneous in its switching direction. In principle, it can consist of several elementary cells (or monolayers). LG theory phenomenology and the Landau–Khalatnikov equation that follows from it do not include the microscopic mechanism.

4. Homogeneous switching in two-dimensional barium titanate

Since the discovery of homogeneous switching in ferroelectric polymers, it has became clear that a nondomain nature of switching should be exhibited by all nanoscale ferroelectric films with a thickness less than or equal to the size of the domain nucleus. This was shown to be the case by studying the ferroelectric films of barium titanate [19, 20, 33].

The switching kinetics in single-crystal laser-epitaxy films of BaTiO3 with 2–8-nm and 40-nm thicknesses grown on $SrRuO_3/SrTiO_3$ substrate were studied in an $SrRuO_3$–ITO (indium tin oxide) capacitor by atomic force microscopy. A detailed description of the method can be found in [34]. The difference between intrinsic and extrinsic behavior is shown in Fig. 5, which demonstrates the dependence of the switching time τ on the applied voltage V for an 8-nm film in a capacitor (Fig. 5a) or below the tip of an atomic force microscope (Fig. 5b). For comparison, the same dependence is shown for a bulk single-crystal BaTiO$_3$ 1 mm in thickness (Fig. 5c). The dependence $\tau^{-2}(V)$ shown in Fig. 5a, b for barium titanate in a capacitor and in the atomic force microscope agrees well with Eqn (8). Additionally, the experimental results indicate that the coercive field E_c (2) is an intrinsic one. On the contrary, the switching kinetics of a bulk crystal (Fig. 5c) show exponential behavior with a domain nature and, accordingly, the intrinsic
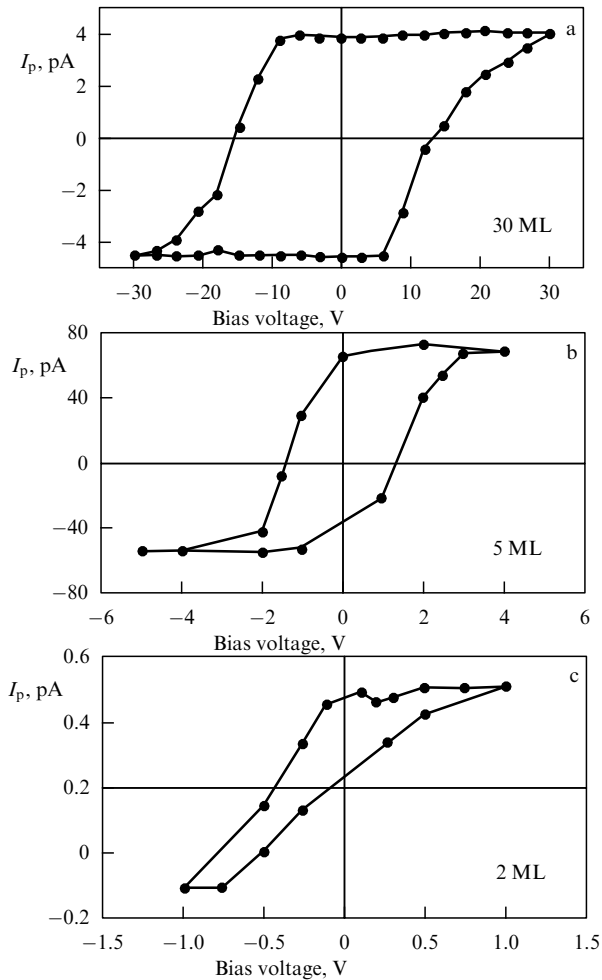
Figure 2. Hysteresis loops at $25\,^{\circ}\mathrm{C}$ measured by the pyroelectric method in LB films P(VDF-TrFE 70:30) with different numbers of monolayers [18, 19]. I_{p} is the pyroelectric current.
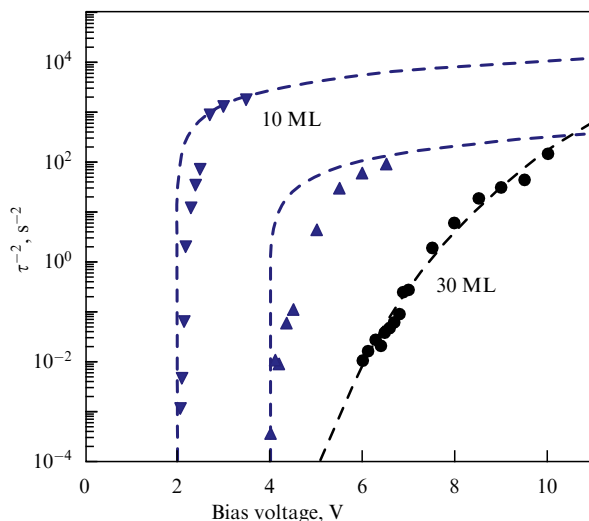

Figure 3. Dependence of τ^{-2} on voltage V for a P(VDF-TrFE) LB film measured by the pulsed-probe method. For a sample with 30 monolayers, the dots correspond to experimental data and the dashed curve indicates correspondence with the exponential dependence. For samples with 10 monolayers, the triangles show the experimental data, while the dashed curves indicate correspondence to equation (8) of the data on the sample [30, 31].
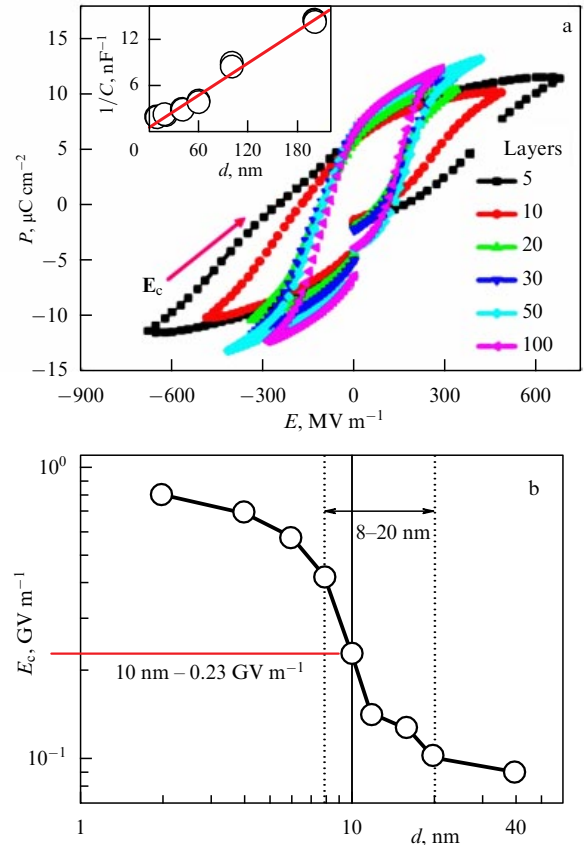

Figure 4. (Color online.) (a) Hysteresis loop for a PVDF LB film [32] with different numbers of monolayers: 5, 10, 20, 30, 50, and 100 ML. The inset shows a linear dependence of the value $1/C$ of reciprocal capacity on the film thickness d. (b) E_{c} as a function of PVDF LB-film thickness (transition region is observed for 8–20-nm thicknesses).

coercive field (2) is two orders of magnitude larger than the extrinsic one.

Figure 5d shows the dependence of the coercive field on the barium titanate film thickness in the range from 3 to 40 nm. One can see that for thicknesses between 3 and 10 nm the coercive field is intrinsic ($E_{\mathrm{c}} \sim 0.12$ GV m) and weakly depends on the thickness, in agreement with the LGD theory. At thicknesses of 40 nm (and larger), the coercive field decreases abruptly, which corresponds to the transition to domain switching. Accordingly, films with 3-nm and 8-nm thicknesses show intrinsic LGD-switching (7), (8), while thicker films exhibit the exponential domain behavior. This data is also in a good agreement with the results for polymer LB-films [32] (see Fig. 4).

In recent years, research interest in nanosized films of silicon-doped hafnium oxide has appeared [35–37]. They were shown to exhibit ferroelectricity, and corresponding hysteresis loops indicate an intrinsic value of the coercive field and, apparently, a homogeneous switching mechanism. One of the authors of the current review received private correspondence from L Collins from Oak Ridge National Laboratory about the ferroelectric properties of Si:HfO₂ films 8 nm in thickness (Fig. 6). One can see from Fig. 6b that for a polarization of $P \sim 0.2$ C m^{-2} the coercive field $E = 0.4 \times 10^{7}$ V cm^{-1} is most probably the intrinsic one (2), and the switching kinetics (Fig. 6c, especially the right-hand branch) is similar to the Landau–Khalatnikov kinetics. Unfortunately, these films are not single crystal and consist of several phases (besides the
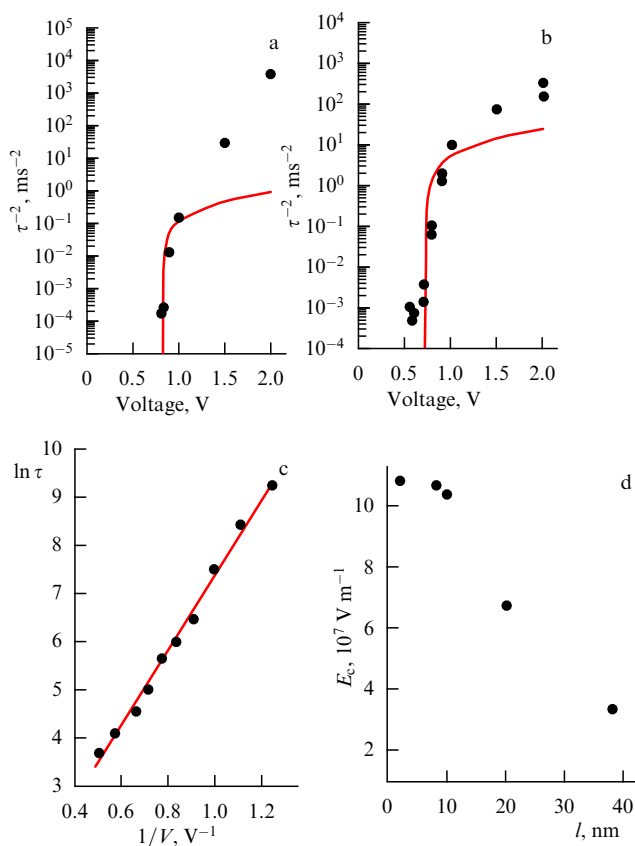
Figure 5. Switching time τ dependence on the voltage for an 8-nm-thick BaTiO$_3$ film [19, 20, 33]: (a) in the capacitor and (b) in the probe mode in an atomic force microscope (curves $\tau^{-2}(V)$ on (a, b) correspond to calculations based on expression (8)); (c) in the case of a BaTiO$_3$ crystal, the curve corresponds to an exponent of $\ln \tau (V^{-1})$ (obtained using the piezo response in an atomic force microscope); (d) dependence of the coercive field E_c on BaTiO$_3$ film thickness.

ferroelectric rhombohedral one, there are also nonpolar ones). It is therefore too early to draw any conclusions about homogeneous switching and its kinetics, but research on these nanosized films is of great interest.

5. Polarization switching in thin ferroelectric polymer films: first principles calculations

In recent years, homogeneous polarization switching in thin ferroelectric films has been obtained from first principles

calculations [38–41]. Ferroelectric polymers based on polyvinylidene fluoride PVDF and its copolymer with trifluoroethylene P(VDF-TrFE) proved to be a convenient object for molecular modeling: they had a fairly clear structure of polymer chains consisting of periodically repeating C$_2$H$_2$F$_2$ units having their own dipole moment. For quantum-mechanical calculations, a semi-empirical method of molecular orbitals with a self-consistent field [42] was used in the PM3 (Parametric Method number 3) parameterization in the Hartree–Fock approximation. The approach itself was developed in detail and tested by Stewart [43, 44], who showed its effectiveness using systems like organic polymers as an example.

In [38–41], the HyperChem software package [45] was used, which contained all the above-mentioned methods. In addition, this package contains some necessary system optimization tools — the conjugate gradient method is used to find the minimum energy of the system. The package can also carry out calculations (runs) by molecular dynamics (MD) methods, using different methods at each step, and allows one to simulate the application of an external electric field. Previously, the applicability of the approach was tested in [46–48] for calculations in PVDF and P(VDF-TrFE) in comparison with the results from [49, 50].

Two main approaches were used to calculate coercive fields and switching times for thin ferroelectric polymer films in an external electric field: 1) calculations based on hysteresis loops, 2) runs and calculations by molecular dynamics methods. Figure 7 shows the scheme of MD calculations for an electric field E together with a typical calculated hysteresis loop and the simplest models of PVDF chains (as an example), as well as change in the orientation of their dipole moment (switching–flipping of a PVDF chain) with a change in the electric field and its passage through the point of the coercive field. On this basis, hysteresis loops were calculated for PVDF and P(VDF-TrFE) chains of various types and with different numbers of chains (as models of LB films with different numbers of monolayers and thicknesses). The MD method calculations were performed in a similar way.

It is important to note that precisely the MD approach allows one to directly determine the switching time τ (flip of a single chain or a group of chains), depending on the magnitude of the applied external electric field, and thereby directly obtain the dependence $\tau(E)$.

Calculations were performed for one, two, four, or more parallel chains for different field values [38–41]. The results showed that the dependence $\tau(E)$ corresponds to the law of
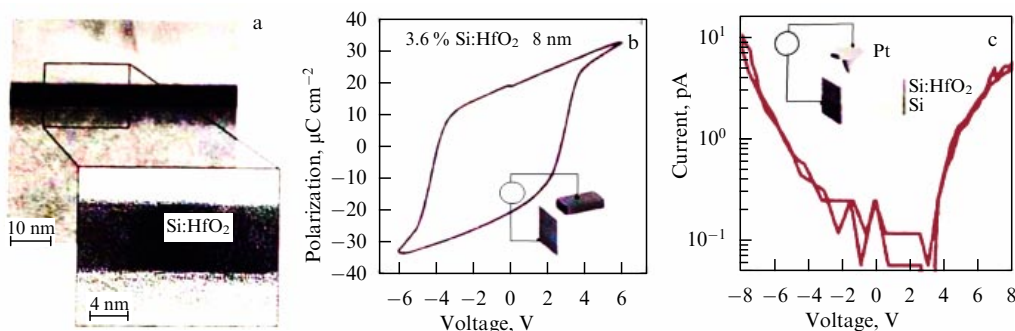

Figure 6. Ferroelectric properties of hafnium oxide nanofilms: (a) illustration of a sample based on 8-nm-thick Si:HfO$_2$ films; (b) hysteresis loop and polarization behavior depending on the voltage for Si:HfO$_2$ films; (c) experimentally obtained dependence of polarization current switching kinetics. (L Collins, private correspondence.)
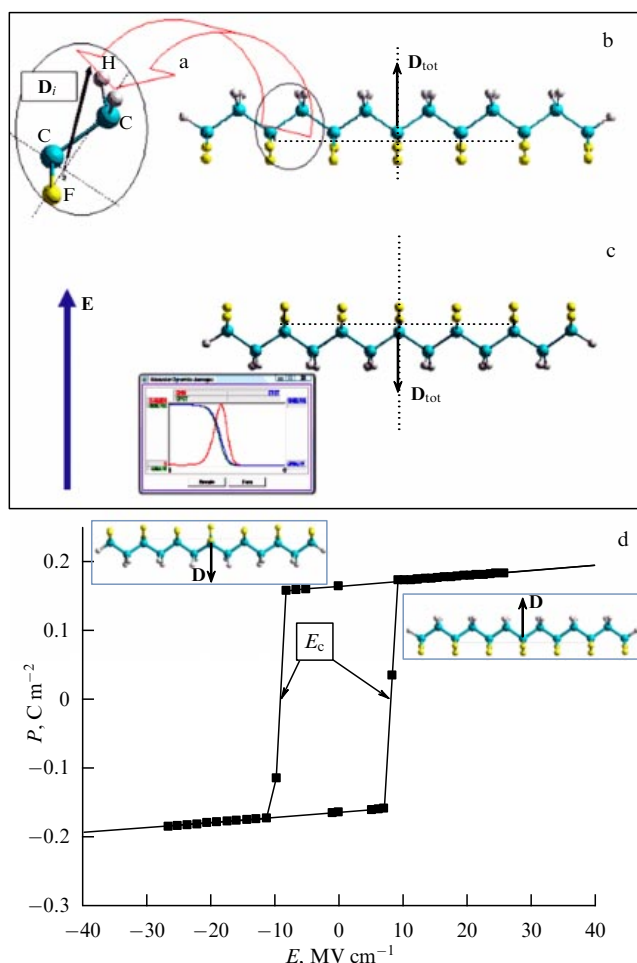
Figure 7. Study of molecular dynamics in electric field **E** and hysteresis loop calculated in steps at each point of field **E** by the PM3 method in the Hartree–Fock approximation. The squares show the calculated points and the curve indicates their approximation. Examples of PVDF models for 6 elements of $C_2H_2F_2$: (a) Single $C_2H_2F_2$ element and its dipole moment $\mathbf{D}_i$; (b) PVDF with a positive direction of the net dipole moment $\mathbf{D}_{tot}$; (c) PVDF with a negative direction of $\mathbf{D}_{tot}$ after its switching (flip of the PVDF chain in an electric field) for $E > E_c$. (d) Calculated hysteresis loop for a PVDF chain of 6 elements.

Figure 8. Calculations by the methods of molecular dynamics (MD-runs) of $\tau^{-2}(E)$ dependence in a logarithmic scale for two and four PVDF chains [38–41], which qualitatively agrees with the data of Fig. 4 [19, 30, 31]. The inset shows linear dependence $\tau^{-2}(E) \sim (E - E_c)$ for $E \to E_c$, fully corresponding to homogeneous switching according to LGD theory (6)–(8). The coercive field $E_c \sim 2.35$ GV m^{-1} is determined from the intersection of the linear fit with the axis E.

homogeneous LG switching and the Landau–Khalatnikov kinetics [26, 29] and satisfactorily corresponds to (8). Figure 8 shows the behavior of $\tau^{-2}(E)$ on a logarithmic scale, which qualitatively coincides with the experimental results [30, 31] (see Fig. 3). The inset in Fig. 8 shows the linear dependence $\tau^{-2}(E)$ (8) near E_c, with extrapolation to the point of intersection with the horizontal axis, which determines the value of the coercive field $E_c \sim 2.4$ GV m^{-1} for 2–4 chains (monolayers).

Taking into account that field E is external and that for thin polymer layers representing monomolecular layers the dielectric constant is $\varepsilon \sim 2.4$ [48, 51] ($\varepsilon = 5$ for thick films), we obtain the limiting maximal value $E_c^{max} \sim E_c/\varepsilon \simeq 1$ GV m^{-1}, which corresponds to all known experimental data [18–22]. Calculations for different numbers of chains and film thicknesses showed that the resulting dependence of the coercive field (Fig. 9) fits well with the experimentally obtained dependence in the film thickness range of 10–12 nm [32] (Fig. 4b).

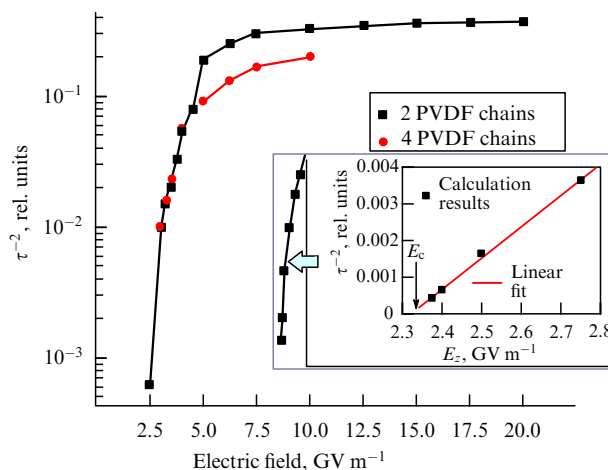This dependence can be conditionally divided into 3 areas: the region of purely homogeneous LG switching (thickness up to 8 nm), the transition region (8–12 nm), where a kind of domain precursor is noted, and the region above 12–16 nm, where the domain mechanism is predominant (the coercive field remains almost unchanged and stays at a low level of $\sim 0.07-0.05$ GV m^{-1}) [32, 38, 39]. This data is also in good agreement with the results for thin $BaTiO_3$ films (Fig. 5d) of other authors, and with a further increase in thickness they correspond to thick films [19–21].

Thus, the calculations of switching in ultrathin polymer ferroelectrics confirm that two-dimensional ferroelectrics can in principle consist of several monolayers or elementary cells.

6. Conclusions

In 1945–1946, the ferroelectric properties of $BaTiO_3$ were discovered, which stimulated the development of the ferroelectricity theory by Ginzburg (the so-called Landau–Ginzburg–Devonshire mean-field theory) [6, 7]. The theory explained all the properties of ferroelectric crystals and films with phase transitions of the first and second kind (in the vicinity of the critical point). However, the switching phenomenon remained unexplained. This situation remained unclear for several years. The discovery of domains indicated the actual heterogeneity of the ferroelectric medium and, accordingly, the inapplicability of the theory developed for an infinite homogeneous medium.

The switching of ferroelectrics was explained by the motion of domains in an external electric field, and the coercive field turned out to be low, in accordance with experimental data.

It would seem that the phenomenological LGD theory cannot explain the switching kinetics of ferroelectrics and predict the correct value of the coercive field. However, this conclusion was premature.

In the 1970s and 1980s, only ferroelectric single crystals were available, and only in the early 1990s did the laser epitaxy fabrication method make perovskite films with a thickness of several ten nm available. The technique of Langmuir ferroelectrics [19–23] led to the discovery of two-
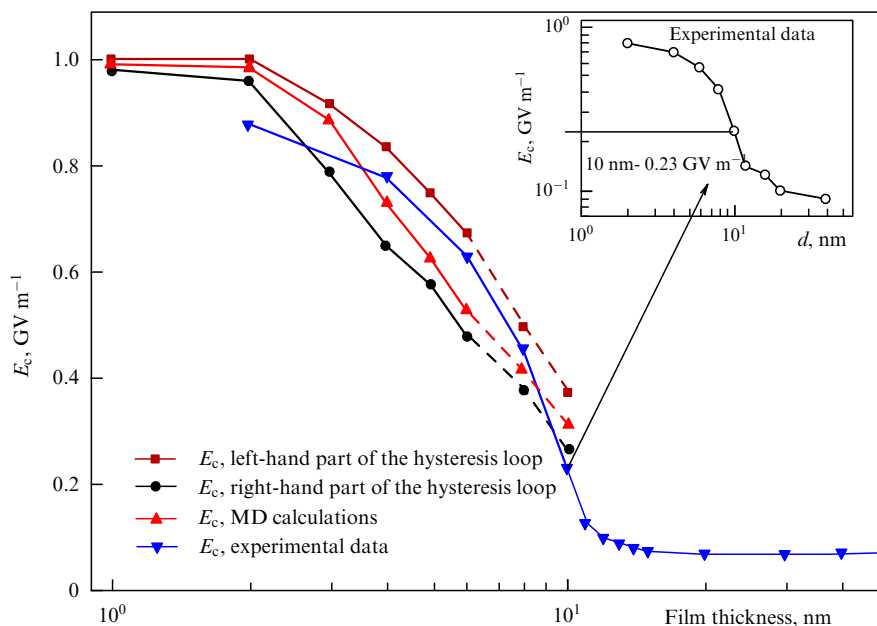
Figure 9. Dependence of the coercive field on the film thickness for a PVDF polymer obtained from calculations using different methods (from hysteresis loops and MD-runs) in comparison with the experimental data of [32], taking into account the dielectric constant of an ultrathin molecular film $\varepsilon = 2.4$.

dimensional ferroelectrics [18], while the investigation of nanoscale perovskite films of barium titanate has shown that they can be two-dimensional. One can assume that other nanosized single-crystals can be two-dimensional and homogeneous. In this case, the phenomenological LGD theory well describes the switching kinetics. Therefore, one should distinguish between the intrinsic coercive field for nanosized homogeneous ferroelectric films E_c (2) and the previously known extrinsic coercive field E_c in thick films and crystals associated with the domain mechanism. Moreover, the intrinsic field is several orders of magnitude larger than the extrinsic one.

The question of the switching mechanism of two-dimensional ferroelectrics is outside the scope of a phenomenological consideration. For bulk ferroelectrics ($l > l^*$, where l^* is the domain size), nucleation and a motion of domains take place. In two-dimensional or nanoscale ferroelectrics ($l \leqslant l^*$), apparently, the rotation of the nuclei occurs. However, a phenomenological theory cannot include this or any other mechanism.

In fact, in nanoscale ferroelectric films, there is a competition between these two mechanisms. As the film thickness increases, the domain mechanism should prevail.

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