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Critical size in ferroelectric nanostructures

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Abstract. **Recently, several attempts have been made to determine the critical size in ferroelectricity. Due to the development of ferroelectric nanostructure technology, this fundamental problem had also become crucial for applied research. It is shown that although the theory predicts the existence of a finite critical size, ferroelectric polarization and its switching can be observed in monolayer films, at least in the case of ferroelectric vinylidene fluoride-trifluoroethylene copolymer P[VDF – TrFE] films prepared by the Langmuir – Blodgett method. The experimental search for the critical size in perovskite ferroelectrics is briefly reviewed. It is shown that the Landau – Ginzburg theory predicts the critical size to be infinitely small if the extrinsic effect of the film – electrode strain mismatch is taken into account. Special features of the switching dynamics of ultrathin ferroelectric films are also considered.**

1. Introduction

The critical size L_{cr} is defined as the maximal thickness of a film or the maximal size of a crystal at which ferroelectricity is impossible.

In 1944, Onsager, using the Ising model, demonstrated the existence of spontaneous polarization for a two-dimensional cubic lattice with dipoles (spins) in the vertices and showed that such a monolayer nonoriented phase becomes oriented as a result of a second-order phase transition [1]. Later, Landau and Vdovichenko formulated this conclusion in a simpler mathematical way [2]. These works, however, cannot be considered to prove that ferroelectricity is possible for a single monolayer (or a single primitive cell) because they do not take the mechanisms responsible for the existence of the critical size into account.

At the end of the 1940s, V L Ginzburg developed a phenomenological model of ferroelectricity [3, 4] based on Landau's theory of second-order phase transitions. As a result, two parameters determining the critical size were discerned, the surface energy and the screening energy. When the film is so thin that one of these energies becomes larger than the lattice energy, ferroelectricity disappears.

The same parameters are responsible for the so-called size effect, i.e., the continuous change in the properties of a ferroelectric (for instance, the decrease in the Curie temperature) due to the reduction of its size. The experimental search for the critical size became one of the fundamental problems in the physics of ferroelectrics. Dozens of papers were devoted to this problem. Still, up to the end of the 1990s, no direct observations of the critical size were reported. As an example, Fig. 1 shows the low-temperature shift of the Curie point in lead titanate crystals due to the reduction of their size [5]. The critical size was estimated in Ref. [5] by extrapolating the size dependence of T_{C} near absolute zero. One can see from Fig. 1 that extrapolation to $T = 0$ yields the critical size value $L_{\mathrm{cr}} \approx 20$ nm. We show in what follows that recent measurements on perovskite ferroelectric films give smaller values for L_{cr}. This is probably because these measurements are performed not on free particles but on electrode-coated films, in which the screening energy can be considerably reduced. It should also be taken into account that the Curie temperature $T = T_{\mathrm{C}}$ was measured in Ref. [5] through the measurement of the soft-mode frequency. We show below that the soft mode may disappear as the film becomes thinner than some critical size l_{cr} and, in principle, $l_{\mathrm{cr}} \neq L_{\mathrm{cr}}$.

Some progress materialized at the beginning of the 1990s, when the first Langmuir – Blodgett (LB) ferroelectric films were prepared. In 1993, ferroelectricity was discovered in 30-monolayer (15 nm) LB films prepared from a vinylidene fluoride-trifluoroethylene copolymer P[VDF – TrFE] [6].

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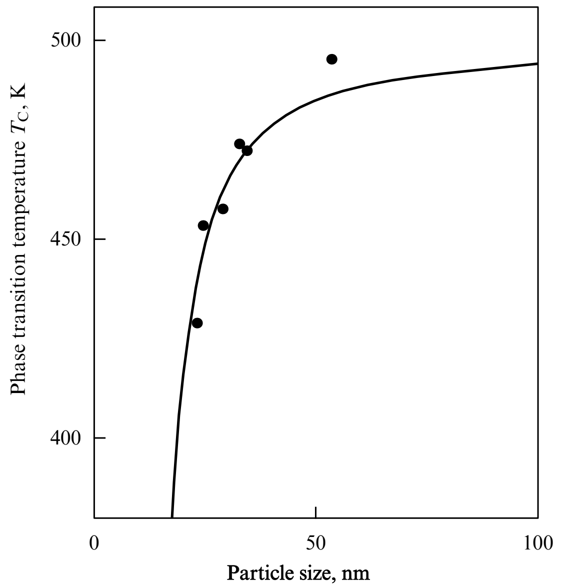

Figure 1. The critical size in ground $PbTiO_3$ crystals [5].

Later, ferroelectric switching was observed in two-monolayer (1 nm) [7, 8] and single-monolayer (0.5 nm) [9] films. It was thus shown that the ferroelectric copolymer has $L_{cr} = 0$. These papers probably stimulated the search for the critical thickness in other ferroelectrics, first and foremost, ones with the perovskite structure. For perovskite films, the critical thickness turned out to be nonzero.

Observation of single-monolayer ferroelectricity (i.e., the absence of the critical thickness) in copolymer ferroelectric films made by the LB method was certainly possible because in the LB method, the thickness of a film can be permanently increased with the accuracy of a single monolayer. On the other hand, possible differences between the switching mechanisms in polymer and perovskite ferroelectrics (and the resulting differences in their switching kinetics) seem to be unable to influence the critical thickness. The latter, as we have mentioned above, is determined by the surface energy and the screening energy, which do not directly depend on the switching mechanism. However, one should take into account that the size effect and the critical size in ultrathin films can be affected by nanodomains [10], their existence or absence. Nanoscopic domains have been observed in perovskite films, while in ultrathin ferroelectric films of the copolymer, they have not been observed and are probably absent. We return to this point in the Conclusion.

In any case, it has been shown that the critical thickness can, in principle, be absent in ferroelectric films. In this paper, we do not review the diverse variety of original and generalizing works on the size effect (see, e.g., reviews [11, 12]). The search for the critical size has been carried out over the last thirty years and has essentially been related to the development of the technology (mostly, epitaxial) of obtaining ferroelectric thin and ultrathin films (mostly, with the perovskite structure, $L \leqslant 10$ nm).

Figure 2 demonstrates that up to the beginning of the 1990s, studies only involved films of thickness $L \geqslant 100$ nm [13–15] and it was only at the end of the 1990s that the manufacturing and study of ferroelectric nanostructures ($L \leqslant 10$ nm) was actually started [16–22].

2. Critical size in ferroelectric P[VDF–TrFE] copolymer films prepared by the Langmuir–Blodgett method

Preparation, structure, phase transition, and ferroelectric properties of vinylidene fluoride–trifluoroethylene P[VDF–TrFE] films prepared by the Langmuir–Blodgett method were described in detail in Ref. [23]. Similarly to bulk (spinning) P[VDF–TrFE] films studied in detail in earlier works (see, e.g., Ref. [24]), they manifest spontaneous polarization $P_s \sim 0.1$ C m^{-2} in the polar orthorhombic phase 2 mm, and at 80–100 °C (depending on the proportion of VDF to TrFE), pass into a nonpolar phase (probably, a hexagonal 6:m one) via a first-order phase transition. The structure of LB films has been studied by means of X-ray and neutron diffractometry, as well as scanning tunnel microscopy (STM) [23].

The copolymer consists of carbon chains with the distance between CH_2-CF_2 groups being ~ 2.6 Å. The dipole moment is directed normally to the chains (and normally to the film surface). An LB film is formed by transferring the copolymer chains from the water surface to the surface of glass coated with aluminum or platinum as an electrode (the bottom electrode). When the film is prepared, it is coated by the top Al or Pt electrode. The thickness of the transferred monolayer is of the order of 0.5 nm and can be controlled by

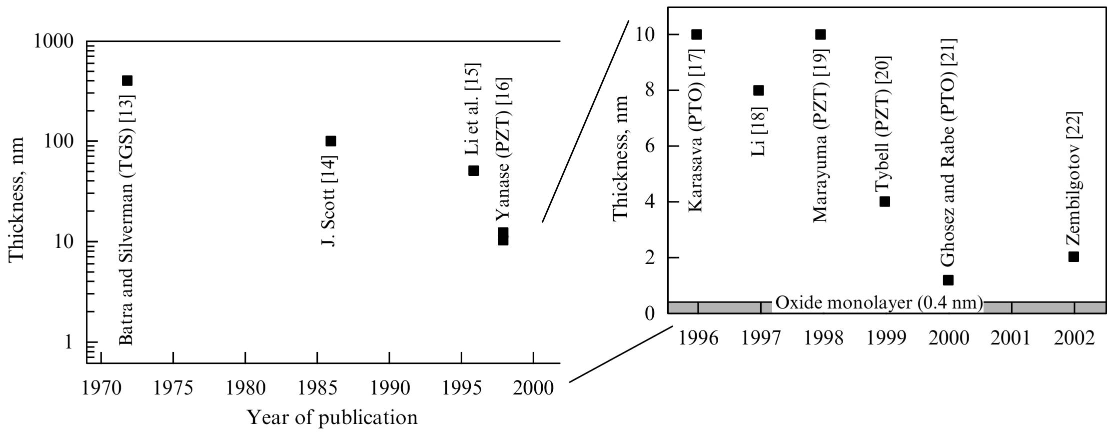

Figure 2. Thickness of nanostructure ferroelectric films studied over the last 30 years [12].

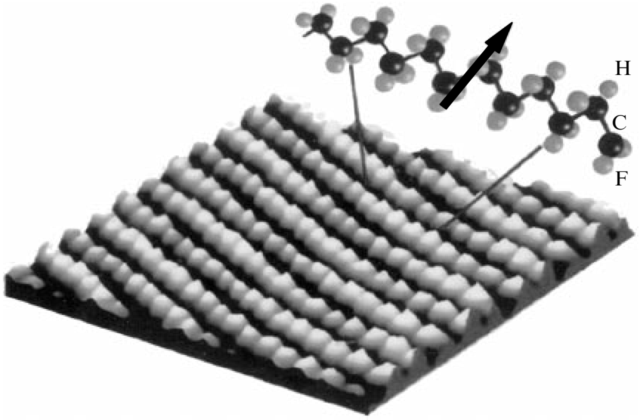

Figure 3. STM image of two P[VDF – TrFE (70 : 30)] monolayers on a graphite substrate. The structure of carbon chains in the ferroelectric phase [8].

an ellipsometer. [1] In Ref. [7], dielectric hysteresis loops were observed for films of thickness from 30 to 2 monolayers (15 – 1 nm). The switching of ferroelectric polymer ultrathin films has been observed in an STM for two monolayers (1 nm) [8]. For this, two monolayers were coated on a graphite substrate (Fig. 3). Figure 4 shows the borders between the regions of a film oppositely switched at a voltage of 0.57 V. Finally, in Ref. [9], hysteresis loops have been obtained for a single monolayer (Fig. 5). The film was a sandwich prepared by the LB method and consisting of two polymer monolayers separated by a layer of anthraquinone, which is not ferroelectric (Fig. 5a). Figure 5b shows the hysteresis loop, which apparently relates to a single monolayer (0.5 nm). It is important that the spontaneous polarization of a single monolayer was much less than 0.1 C m^{-2}, while its relaxation time was about $10^2 - 10^3$ s and depended on the polarization direction. This fact can be easily understood by taking the conditions at the monolayer boundaries into account. The role of the boundary conditions in the framework of the phenomenological approach is discussed below.

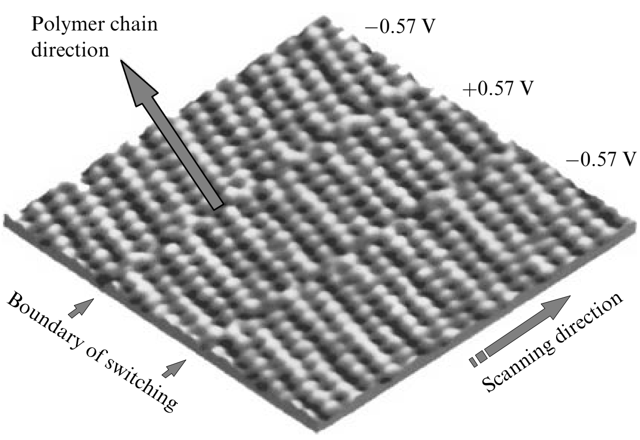

Figure 4. Boundaries between oppositely switched regions of two copolymer layers. As shown in the figure, the boundaries are created because of the monomer reorientation. The image was obtained using STM [8].

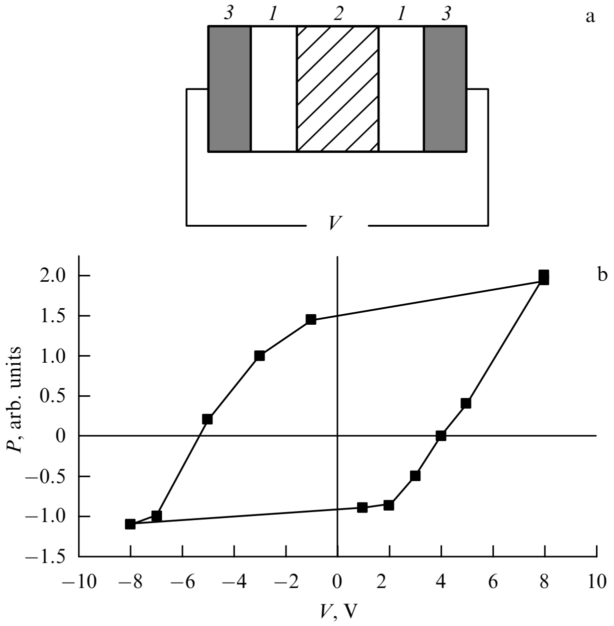

Figure 5. (a) Sandwich consisting of two copolymer monolayers (*1*) separated by an anthraquinone monolayer (*2*) and coated with aluminum electrodes (*3*). (b) The hysteresis loop obtained by the switching of a single monolayer (*V* is the bias voltage on the sandwich) [9].

3. Critical size in perovskite ferroelectrics

One of the first attempts to discover the critical size of thin perovskite films was made in Ref. [20]. Using atomic-force and piezoelectric microscopy, it was shown that for $Pb(Zr_{0.2}Ti_{0.8})O_3$ ferroelectric films grown on niobium-doped $SrTiO_3$ (001) crystals by magnetron sputtering, ferroelectricity is maintained down to thicknesses of 4 nm (ten primitive cells). However, the authors of Ref. [20] do not consider this value to be the critical thickness. Paper [25] provides a review of experimental data on $BaTiO_3 - SrTiO_3$ and $CaTiO_3 - SrTiO_3 - BaTiO_3$ superlattices, as well as other structures where ferroelectricity can be found in ultrathin films; however, no critical thickness has been observed.

The same method of atomic-force microscopy was applied in Ref. [26] to study the switching of PZT films epitaxially grown on $SrTiO_3$. For films with the thickness $L = 15$ nm, square, well-filled loops have been obtained (Fig. 6). However, no reliable switching was observed for L as small as 10 nm, probably because of the charge leakages. Hence, this work also failed to allow achieving the critical thickness.

Paper [27] reported observation of the critical thickness for epitaxial $PbTiO_3$ films grown on the (001) face of $SrTiO_3$. According to Ref. [27], $L_{cr} = 1.2$ nm (3 primitive cells). The conclusion that the critical thickness existed was based on observing X-ray diffraction. The authors assumed that the film contained antiparallel domains (Fig. 7) causing satellites in the diffraction pattern. Therefore, Fig. 7 also illustrates the size effect. For two primitive cells, ferroelectric domains are not observed below $T = 311$ K. For three primitive cells, satellites appear at $T = 463$ K. If we assume that the satellites are indeed related to the antiparallel domain structure, then the critical thickness for $PbTiO_3$ is $L_{cr} = 1.2$ nm.

The critical thickness L_{cr} for $BaTiO_3$ was obtained in Ref. [28] using the direct method of hysteresis loops. The sample under study was a $SrRuO_3 - BaTiO_3 - SrRuO_3$ heterostructure grown epitaxially on an $SrTiO_3$ (001) substrate.

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[1] In the LB technology, it is possible to transfer not just one monolayer but also two or three monolayers.

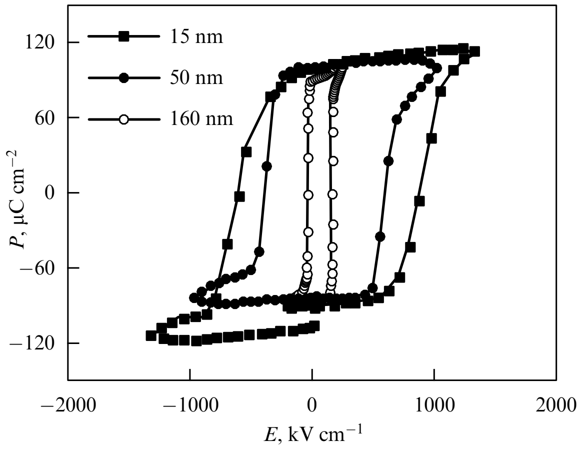

Figure 6. Hysteresis loops obtained with an atomic-force microscope in PZT films.

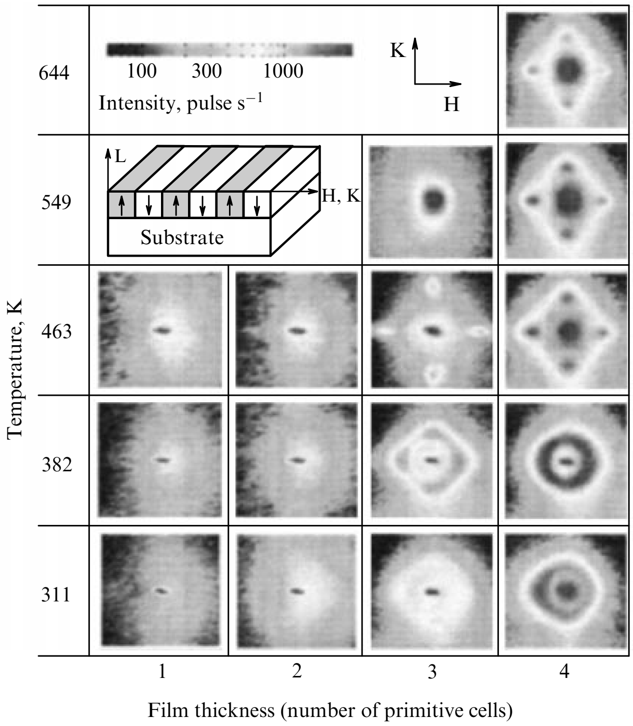

Figure 7. Diffraction pattern for PbTio$_3$ films depending on the thickness (number of primitive cells) and the temperature [27].

Hysteresis loops in BaTiO$_3$ were observed for thicknesses down to $L_{\text{cr}} = 5$ nm (Fig. 8), the polarization relaxation time P_{s} at the thickness $L = 6.5$ nm being $\sim 10^{-3}$ s (Fig. 9).

Recently, ferroelectricity has been observed in Pb(Zr,Ti)O$_3$ solid solution nanotubes and nanodiscs with the diameter 3.2 nm [29]. In Ref. [29], the toroidal moment of ferroelectric nanoparticles was also measured. The toroidal moment was introduced into the mean field theory as an order parameter in Ref. [30].

4. Critical size in ferroelectrics predicted by the Landau – Ginzburg theory

From the review given above, it is clear that the Onsager theory cannot be a proof for ferroelectricity existing in a single monolayer, because the Ising model takes neither the screening energy nor the surface energy into account.

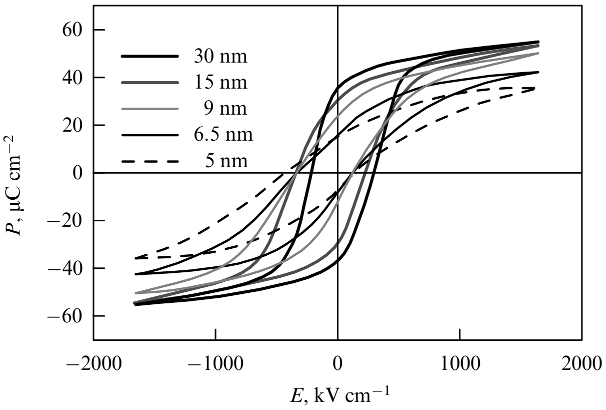

Figure 8. Hysteresis loops in SrRuO$_3$ – BaTiO$_3$ – SrRuO$_3$ heterostructures with various thicknesses of a BaTiO$_3$ film. No loops were observed for thicknesses below $L = 5$ nm [28].

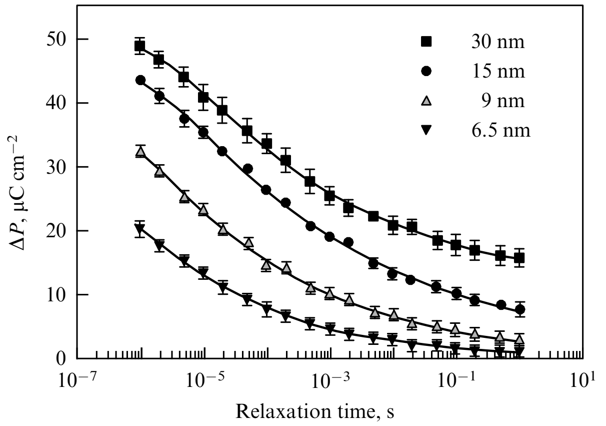

Figure 9. Polarization relaxation in BaTiO$_3$ ultrathin films [28].

An attempt to describe the size effect and to estimate the critical thickness by taking the screening and surface energies into account in the framework of the Landau – Ginzburg theory was made in Refs [31 – 34].

We first consider the size effect related to the surface energy in the absence of the depolarizing field.

For a ferroelectric film of thickness L with the spontaneous polarization P orthogonal to its surface and having coordinates $z = \pm L/2$, the free energy in the absence of the field ($E = 0$) is given by [32]

$$G = F_0 + \frac{1}{L}\int_{-L/2}^{+L/2}\left[\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \frac{D}{2}\left(\frac{\partial P}{\partial z}\right)^2\right]\mathrm{d}z + \frac{D}{2\delta}\left(P_+^2 + P_-^2\right), \qquad (1)$$

where D is the correlation factor, δ is the decay length determining the strength of coupling in the surface layer, $P_\pm$ are the values of spontaneous polarization for $z = \pm L/2$, and α, β, and γ are the Landau – Ginzburg coefficients. The equation of state obtained from free energy (1) has the form of the Euler – Lagrange equation,

$$D\,\frac{\partial^2 P}{\partial z^2} = \alpha P(z) + \beta P^3(z) + \gamma P^5(z) - \frac{4\pi}{L}\int_{-L/2}^{+L/2} P(z)\,\mathrm{d}z. \qquad (2)$$

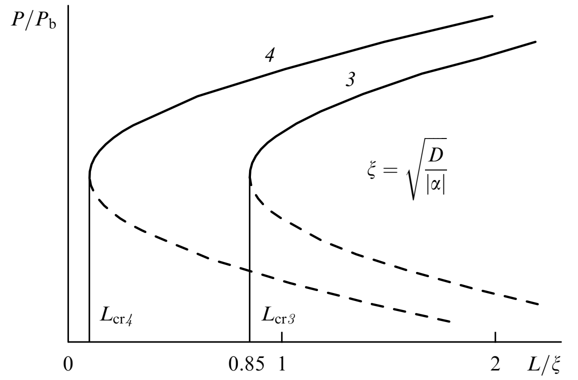

Figure 10. The size effect and the critical thickness in mean field theory.

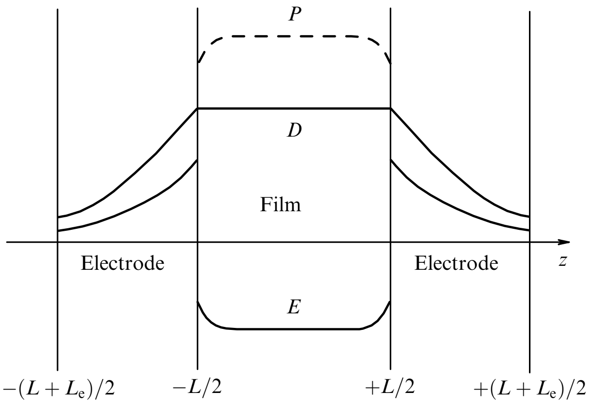

Figure 11. Scheme of polarization screening in the electrodes [32].

The boundary conditions were considered in Refs [29–32] in the form

$$\frac{\partial P}{\partial z} \pm \frac{1}{\delta} P(z) = 0 \,, \quad z = \pm \frac{L}{2} \,. \tag{3}$$

If the coupling strength in the surface layer is positive ($\delta > 0$), then both P and the phase transition temperature T_C decrease as L decreases. Figure 10 (curve *3*) demonstrates the size effect for $\delta > 0$ in the form of the polarization P dependence on the film thickness L. Here, P_b is the spontaneous polarization in a bulk crystal ($L = \infty$) and the thickness L is normalized to the correlation length $\xi = (D/|\alpha|)^{1/2}$. The lower branch of the numerical solution shown in Fig. 10 is unstable. From Fig. 10, we can see that there exists a critical thickness L_{cr3} at which the spontaneous polarization disappears:

$$L_{cr3} \cong 0.85\xi = 0.85\left(\frac{D}{|\alpha|}\right)^{1/2} . \tag{3'}$$

Assuming $D \sim 3 \times 10^{-18}$ m^2 and $|\alpha| \geqslant 10^{-1}$ ($T = 300$ K) for perovskites [35], we obtain $L_{cr3} \leqslant 5$ nm. Thus, the Landau–Ginzburg theory can explain both the size effect and the existence of the critical thickness but, naturally, the value of L_{cr} depends on the accuracy of estimating the correlation factor D and the coefficient δ [35].

We now show the role of the second parameter, i.e., the influence of the depolarizing field on the size effect [32]. The term in free energy (1) taking the depolarizing field into account leads to an additional size effect, which is the decrease in the polarization P and the phase transition temperature T_C as the films becomes thinner. We consider a ferroelectric film of thickness L with metal electrodes of thickness $L_e/2$, as shown in Fig. 11. If the electrodes are shortcircuited, the spontaneous polarization of the film is screened in the metal at the depth given by the Thomas–Fermi value l_s. This leads to an additional contribution to free energy (1),

$$\Delta G_s = -\int_{-L/2}^{L/2} \left[\frac{V}{L+L_e} P(z) + \frac{1}{2} E_d(z) P(z)\right] dz \,, \tag{1a}$$

where V is the voltage between the electrodes and E_d is the depolarization field satisfying the Poisson equation (the film is supposed to contain no free charges):

$$\frac{dE_d}{dz} = -\frac{1}{\chi} \frac{dP}{dz} \,, \quad |z| \leqslant \frac{L}{2} \,, \tag{1b}$$

where χ is the polarizability of the ferroelectric.

This should be combined with the boundary condition

$$\int_{-(L+L_e)/2}^{(L+L_e)/2} E(z) \, dz = V \tag{1c}$$

and the Thomas–Fermi equation for screening in the electrodes,

$$\frac{d^2 E}{dz^2} = \frac{E}{l_s^2} \,, \quad \frac{L}{2} < |z| < \frac{L+L_e}{2} \,. \tag{1d}$$

Analysis of the solution of Eqn (1d) [32] shows that the depolarizing field leads to a renormalization of the coefficients in Eqn (1) and, hence, to an additional size effect. If only a single term with the depolarizing field is kept in Eqn (1), then the critical thickness of the film is

$$L_{cr} = \frac{2\chi C}{T_b \varepsilon_0} l_s \,, \tag{1e}$$

where T_b is the phase transition temperature in the bulk material. Figure 12 shows the normalized temperature $t = T_C/T_b$ of the phase transition in the film as a function of the normalized film thickness $x = L/L_{cr}$.

If the electrodes are made of gold ($l_s \approx 0.8$ Å), the critical temperature given by Eqn (1e) for a ferroelectric-like barium

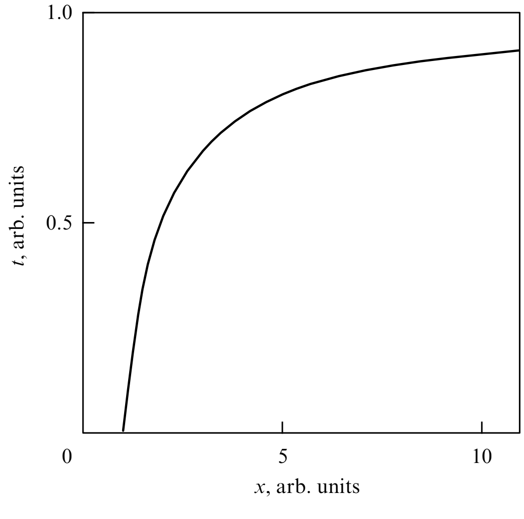

Figure 12. The size effect and critical thickness for the Thomas–Fermi polarization screening in the electrodes [32].

titanate ($C = 1.8 \times 10^5$ K, $\chi = 134$, $T_b = 403$ K [35]) is $L_{cr} \sim 0.5$ nm. For polyvinylidene fluoride and its copolymers, according to Eqn (1e), we have $L_{cr} \sim 0.1$ nm, which is less than the monolayer thickness. Thus, in the framework of the Thomas – Fermi model, screening in the electrodes has negligible influence on L_{cr}. The same conclusion was made by the authors of Ref. [12]. Of course, this conclusion depends on the estimate for the screening length l_s, which is rather crude. The screening energy can certainly have a dominating influence on L_{cr} if there are dielectric gaps between the film and the electrodes, but this case is not considered here.

The size effect in ferroelectric films has also been studied within the framework of the transverse Ising model, which was suggested in its general form in Ref. [36] and applied to ferroelectrics in Refs [33, 37]. Using this model is basically justified for ferroelectrics with hydrogen bonds, like KDP. Similarly to the previous case, the Ising model also leads to a dependence of T_C and P on the film thickness and predicts the existence of a critical thickness L_{cr}. Because the interaction between neighboring protons on the surface can be much different from their interaction in the bulk of the film, tunneling of protons from one minimum of a double-well potential to the other destroys the ordering and makes the transition to the ferroelectric phase impossible. Therefore, no ferroelectricity appears in a critical-thickness film.

We have already mentioned the role of boundary conditions in the size effect and the estimate of the critical size. The authors of Refs [12, 38] considered Eqn (1) and boundary conditions (3) taking into account the polarization P_m caused by the incompatibility of the ferroelectric and electrode lattices (or the lattices of the ferroelectric and sublattice material at the boundary), thermal expansion coefficients, and mechanical strain at the boundary (the mismatch effect).

Mechanical (misfit) strain S_m interacts with the polarization in ultrathin films and, due to the electrostriction effect, leads to an additional contribution to polarization (as happens in extrinsic ferroelastics). In the literature, this effect is called the extrinsic size effect [12, 36, 37] or the mismatch effect [38]. In Refs [12, 38], the mismatch effect was assumed to be responsible for ferroelectricity in ultrathin films; the conclusion was that the critical size can have extrinsic origin. With an account for polarization P_m, Eqn (1) and boundary conditions (3) take the form

$$G = F_0 + \frac{1}{L}\int_{-L/2}^{+L/2}\left[\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \frac{D}{2}\left(\frac{\partial P}{\partial z}\right)^2 - P(z)\,E\right]\mathrm{d}z + \frac{D}{2\delta}\left[(P_+ + P_m)^2 + (P_- + P_m)^2\right], \qquad (1')$$

$$\frac{\partial P}{\partial z} \pm \frac{1}{\delta}\,P(z) = -P_m\,, \quad z = \pm\frac{L}{2}\,. \qquad (4)$$

Figure 10 (curve *4*) shows the mismatch-caused size effect calculated numerically from Eqns (1′) and (4). From this dependence, the possibility that $L_{cr\mathit{4}} \ll L_{cr\mathit{3}}$ follows:

$$L_{cr\mathit{4}} \leqslant 10^{-8}\left(\frac{P_b}{P_m}\right), \ \mathrm{m}\,. \qquad (4')$$

If we assume that $P_b/P_m = 10^{-1}$, then $L_{cr\mathit{4}} \leqslant 1$ nm and, hence, the critical size L_{cr} can in principle be equal to the size of a monolayer (or a primitive cell), which means that it is absent.

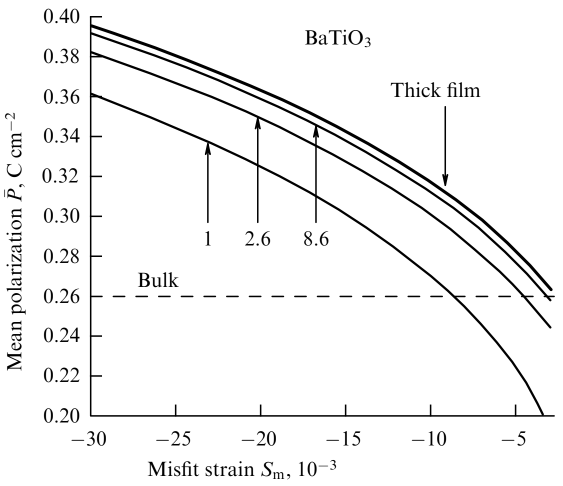

Figure 13. Polarization in BaTiO$_3$ films as a function of the mechanical (misfit) strain S_m. The parameter of the curves is the film thickness normalized to the correlation length [12].

As already mentioned, the extrinsic nature of the size effect and the influence of the mismatch effect have been pointed out in Ref. [12]. Figure 13 shows the phenomenological dependence of polarization in BaTiO$_3$ films on the squeeze strain S_m caused by the mismatch effect [12]. The parameter of the curves is the film thickness normalized to the correlation length, L/ξ.

In some papers [27, 28, 39], it was suggested that one cannot expect the size effect to be revealed and the critical size to be estimated in the framework of mean field theory. As we see, by taking surface strains and the extrinsic mismatch effect into account, one can not only describe the size effect in the framework of a phenomenological theory but also explain the existence of such a small critical size in ferroelectric LB films. In the general case of mean field theory, as already mentioned, L_{cr} depends on certain phenomenological parameters such as D, δ, and P_m. In addition, the values of D and δ in nanofilms may differ from the values given in the literature for usual films and crystals, and there is no information about the asymptotic behavior of these parameters as $L \to 0$.

Applying Ginzburg's concept of the soft mode to (1′) and (4), we can see that for the displacing phase transition in a thin film, the soft mode disappears at

$$l_{cr} \approx \frac{2\delta}{\alpha\lambda}\,\frac{P_m}{P}$$

and in the general case, $l_{cr} \neq L_{cr}$ [40].

5. Critical size calculated ab initio

In Refs [41, 42], an effective Hamiltonian was constructed, which was used to obtain, by means of the Kohn density functional, the ferroelectric phase transition in an ionic crystal, in BaTiO$_3$ in particular. Later, an ab initio method was developed [43, 44] for determining the critical thickness in perovskites. However, these calculations did not correctly take the boundary conditions into account and assumed that the screening field did not exist in the bulk of the ferroelectric. As a result, these calculations led to the incorrect conclusion that perovskites have no critical thickness.

In Ref. [45], the density functional method was applied to calculating the critical thickness for ultrathin BaTiO$_3$ (BTO)

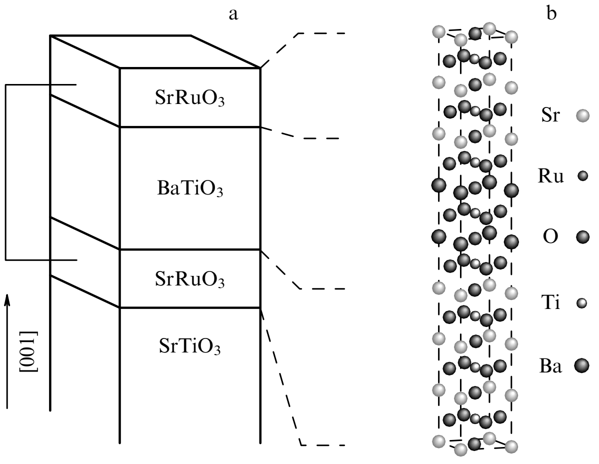

Figure 14. Structure of the shortcircuited capacitance SRO – BTO – SRO (a). Atomic structure of the superlattice for $m = 2$ (b) [45].

crystals placed between shortcircuited $SrRuO_3$ (SRO) metal electrodes grown epitaxially on an $SrTiO_3$ substrate (Fig. 14). In addition, the finite screening field in $BaTiO_3$, which depended on the Thomas – Fermi screening length in SRO and the polarization in the ferroelectric, was taken into account. The results of the calculations are shown in Fig. 15 as the energy of the system versus the shift ξ of a Ba atom, which is proportional to the polarization. For the curves, the parameter is the number of $BaTiO_3$ primitive cells. We see that the critical thickness indeed exists and is equal to six primitive cells ($L_{\mathrm{cr}} = 2.4$ nm). It follows that L_{cr} depends on the electrode material (on the screening length). In the case of complete screening and the absence of surface dopants and strains, $L_{\mathrm{cr}} = 0$, as was supposed in Refs [43, 44].

Certainly, this theory considers $BaTiO_3$ as an ideal dielectric with no defects and, hence, no internal screening or leakages. All these additional reasons (and, in the case of LB films, also the influence of the substrate orienting the dipoles) lead, as we have already mentioned, to polarization relaxation in ultrathin films. For instance, it was shown in [12] that for 6 nm $BaTiO_3$ films in the SRO – BTO – SRO sandwich, tunnel current can have a considerable influence on hysteresis loops already at the voltage ~ 1 V. This, in particular, can explain the discrepancy between the estimate of the critical thickness in Ref. [45] and the experimental results in Ref. [28].

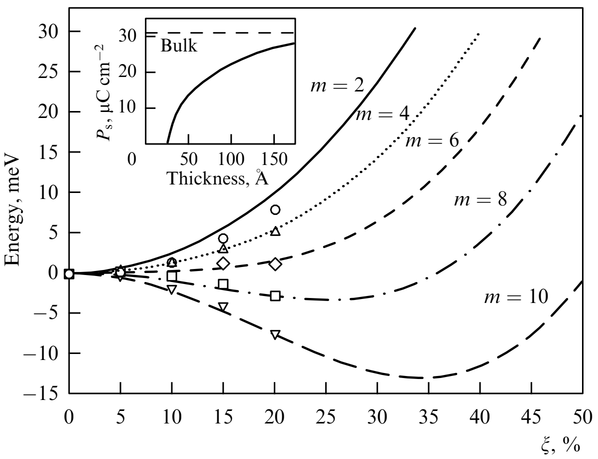

Figure 15. The energy of a $BaTiO_3$ film in the SRO – BTO – SRO heterostructure as a function of the polarization P_s, proportional to the shift ξ. The parameter of the curves is the number of $BaTiO_3$ primitive cells. The inset shows the dependence of the polarization P_s, found from the minima of the curves, on the number of cells [45].

The ab initio calculations of L_{cr} have just started. For polymer nanofilms, no calculations have been made so far. Therefore, at present, it is difficult to make a reliable comparison of these data with experiment.

6. Special features of switching in ultrathin films

In several recent papers, some special features of switching in ferroelectric nanostructures have been observed [46, 47, 49 – 52].

The kinetics of switching in ferroelectric crystals and films are known to be well described by the Ishibashi – Avrami – Kolmogorov (IAK) theory [48]. In Ref. [46], it was shown for the first time that switching in ultrathin PZT films does not obey this theory but is caused by other polarization processes having a broad distribution of relaxation times. Switching in PZT films of thickness $L = 135$ nm, studied in Ref. [47] within a broad time interval, did not follow the IAK theory either. To explain this behavior, the authors used the classical IAK model of inverse domain nucleation and growth, but the film and the nucleation probability distribution were assumed to be inhomogeneous. The switching kinetics were well described with the help of the nucleation probability distribution function introduced for the film regions with independent switching dynamics.

It is worth noting that for all crystals and films, including those obeying the IAK mechanism and those whose switching kinetics deviate from it, the coercitive voltage V_{c} (or coercitive field E_{c}) is many orders of magnitude less than the value predicted by the Landau – Ginzburg theory. As we know, this is caused by the domain switching mechanism and by the fact that the mean field theory does not take domains into account.

It was in ultrathin ferroelectric LB copolymer films that the measured coercitive field, $E_{\mathrm{c}} \sim 10^9$ V m^{-1}, for the first time coincided with the prediction by the Landau – Ginzburg theory (if the values of α, β, and γ, measured independently, are included into the theory) [23]. From this fact, one could suggest that the switching of ultrathin LB films is not connected with the domain mechanism or domains do not play a significant role in switching.

The switching kinetics of copolymer ferroelectric films with thicknesses varying from 1 to 100 monolayers were studied in Refs [49 – 52]. Films whose thicknesses range from 1 to 30 monolayers manifest quite unusual switching kinetics. Two special features can be pointed out. The switching occurs only at the voltage $V > V_{\mathrm{c}}$. At $V < V_{\mathrm{c}}$, the film is not switched, while as $V \to V_{\mathrm{c}}$, the switching has a critical behavior and the switching time τ grows to infinity. Figure 16 demonstrates this critical switching behavior in ultrathin LB copolymer films of the thickness of 30 monolayers [50]. The critical behavior is only observed for ultrathin copolymer films, up to 30 monolayers. For thicker films (for instance, for 100 monolayers), the switching time τ depends on V exponentially, and the switching curves have no singularities at $V = V_{\mathrm{c}}$ and agree well with the IAK theory [49].

In Refs [49 – 52], an attempt was made to describe this behavior with the help of the Lagrange equation, often called the Landau – Khalatnikov (LK) equation [53].

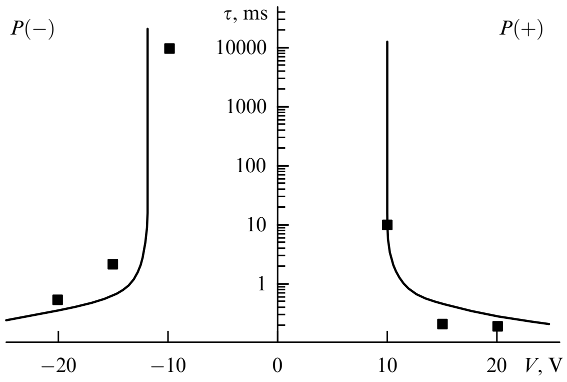

Figure 16. Dependence of the copolymer LB film switching time τ on the voltage V for two switching directions, $|V_c| = 10$ V (30 monolayers). For $|V| < |V_c|$, there is no switching [50].

In Ref. [49], a solution of the LK equation was obtained in the case of switching in a ferroelectric with a first-order phase transition. In this case, the LK equation has the form

$$\xi \frac{dP}{dt} = -\frac{\partial F}{\partial P} = -\alpha P - \beta P^3 - \gamma P^5 + E \,, \tag{5}$$

where P is the spontaneous polarization, F is the free energy, α, β, and γ are the known Landau – Ginzburg coefficients, and ξ is a phenomenological parameter (the damping constant) that determines the switching time. The LK equation (5) describes the kinetics of intrinsic switching, which is not related to the domain kinetics.

By solving Eqn (5), we obtain the critical behavior of the ferroelectric switching at $V = V_c$ [49]:

$$\tau^{-1} = \frac{\beta^2}{6.3\gamma\xi}\left(\frac{V}{V_c} - 1\right)^{1/2} . \tag{6}$$

It follows from (6) that there is no switching for $V < V_c$ and the switching time tends to infinity as $V \to V_c$. The analysis of the LK equation shows that switching occurs only for $V > V_c$.

Figure 17 shows the experimental points and the theoretical dependence of τ^{-1} on V/V_c for LB films consisting of 10, 30, and 100 monolayers (solid lines). For films of 10 and 30 monolayers, the theoretical curve is calculated from Eqn (6) and for the 100-monolayer film, from the IAK theory. Clearly, the thick film shows no special behavior at $V = V_c$.

Thus, the LK equation provides a good description for the above-mentioned special features of the switching kinetics in ultrathin polymer films. We also mention that the increase in the film thickness not only changes the switching dynamics but also leads to a decrease in τ.

We also note that in inhomogeneous LB films, the critical behavior is smeared by the distribution of ξ and V_c over the surface. As a result, the singularity at $V = V_c$ may not manifest itself. Such cases have been observed in experiment [54, 55]. The switching dynamics of such films should probably be described using the approach in Ref. [47].

The switching dynamics of ultrathin perovskite ferroelectric films (with a near-critical thickness) have not been studied so far. Therefore, it is not clear whether the results obtained for the polymer are valid in the general case.

However, the coercitive fields E_c for PZT films ($L = 15$ nm) and for barium titanate films ($L = 5$ nm) are much smaller than the values predicted by the mean field theory (Figs 6, 8). This indicates that the switching of ultrathin perovskite films is likely to have a domain mechanism. The same reason can probably explain the difference in the times and kinetics of the switching. The switching time of PZT nanofilms ($L \sim 5 - 15$ nm), although being somewhat larger than that of thick films, is still within the range $10^{-6} - 10^{-5}$ s [28]. The switching of polymer nanofilms ($L \sim 1 - 15$ nm) is much slower. In the critical range, $E \sim E_c$, their switching times are $\tau \sim 10^2$ s or larger. For $E \gg E_c$, $\tau \sim 10^{-3} - 10^{-4}$ s. As we have already mentioned, this may be caused by inhomogeneous switching.

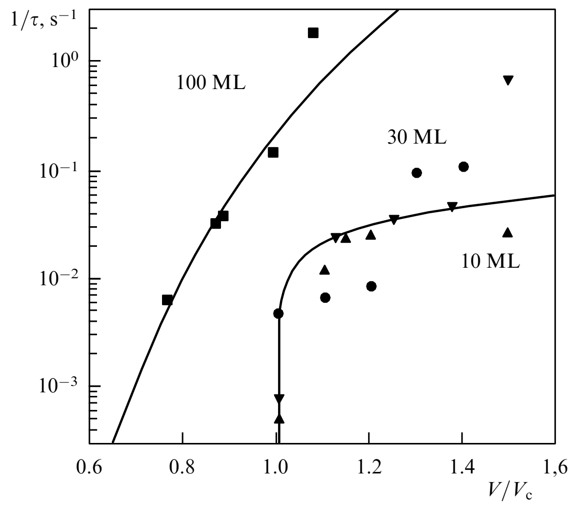

Figure 17. Dependence of the copolymer LB film inverse switching time τ^{-1} on V/V_c. For $V < V_c$, 10- and 30-monolayer films manifest no switching [49]. The parameter of the curves is the number of monolayers.

7. Conclusion

What causes such different behaviors of perovskite and polymer ferroelectrics with respect to both their critical size and their switching kinetics? (The switching kinetics of perovskite films with near-critical thicknesses has not been studied so far but, as we have already mentioned, it is likely to have a domain mechanism.)

It seems that the answer could be given by an ab initio theory. Although the crystal structure of the ferroelectric P[VDF – TrFE] copolymer has been studied sufficiently well [23], it is probably difficult to construct the appropriate Hamiltonian because the chemical bond of the polymer is a mixed one. Anyway, such calculations have so far been absent in the literature.

We believe that the answer to this question is essentially based on the fact that perovskite films have a nanoscopic domain structure, while ultrathin polymer films probably do not have such a structure. According to the Janovec – Kay – Dahn mechanism [10], the length of a nanodomain l in the direction of the field and the field E are related as

$$l \sim E^{-3/2} \,. \tag{7}$$

Equation (7) predicts both the size effect, $E_c \sim L^{-2/3}$ (E_c being the coercitive field and L the film thickness), and the critical size, $L_{cr} \sim E^{-3/2}$, because the critical size L_{cr} cannot be less than the nanodomain length l and is limited by the breakdown resistance of the film. In Ref. [10], other mechanisms limiting the nanodomain size have also been suggested. A depletion layer can be formed near the electrode, with the length l depending on the film polarization and the donor concentration. If nanodomains are formed within this depletion layer, then $L_{\mathrm{cr}} \approx l$. Here,

$$l \approx \frac{\varepsilon\varepsilon_0}{eN_{\mathrm{d}}} E_{\mathrm{s}} , \qquad (8)$$

e and N_{d} being the charge and concentration of the donors, ε the dielectric permittivity of the ferroelectric, and E_{s} the field in the depletion layer. The same mechanism should lead to the size effect in ultrathin perovskite films with a nonzero critical thickness.

As was shown in Ref. [23], the size effect $E_{\mathrm{c}} = E_{\mathrm{c}}(L)$ is absent in copolymer films of thickness $L = 1-15$ nm. Meanwhile, the coercitive field, $E_{\mathrm{c}} \sim 10^9$ V m^{-1}, which is independent of the film thickness, coincides with the value given by the Landau – Ginzburg theory. This fact, as well as the kinetics of switching in ultrathin copolymer films, probably indicates the absence of nanodomains. In addition, no nanodomains have been experimentally observed in ultrathin copolymer films. If this assumption is correct, copolymer nanodomains do not determine the critical thickness.

Although research on ferroelectric nanostructures is relatively recent, the data obtained so far allow several conclusions to be made.

1. The Landau – Ginzburg theory and the microscopic ab initio theory indicate that the critical size L_{cr} may be present in ferroelectricity. In the framework of the phenomenological approach, the critical size L_{cr} depends on the correlation factor D and the extrapolation length δ, which largely depends on the material.

With the extrinsic effects related to the incompatibility of the nanofilm and substrate lattices and the misfit deformations (the mismatch effect) taken into account in the framework of the mean field theory, one obtains extremely small values of L_{cr}, including $L_{\mathrm{cr}} = 0$.

2. Experiment has shown that there is no critical size for polymer ferroelectric films grown by the Langmuir – Blodgett method. This conclusion can be made even though the literature provides no information about the role of the electrodes (up to now, only Al and Pt electrodes have been used) and ultrathin films have the tunnel current (which provides STM observations of switching).

For perovskite ferroelectrics, the experimental data obtained by various authors yield the values of L_{cr} in the range 1.2 – 5 nm. The role of electrodes has not been studied sufficiently well here, either; mostly, it is the case of epitaxial $\mathrm{SrRuO_3}$ on a $\mathrm{SrTiO_3}$ substrate that has been studied. In addition, the existence of the tunnel current may distort the hysteresis loops and therefore lead to overestimated values of L_{cr}. The measurement results are also influenced by the defect structure and the leakages, which accelerate polarization relaxation.

3. Perovskite and polymer nanofilms demonstrate different behaviors with respect to both the critical size and the switching kinetics. At present, it is difficult to formulate a definite reason for this difference. Probably, the main role is played by the nanodomain structure, which is present in perovskite nanofilms and apparently absent in copolymer nanofilms.

The present review is only aimed at discussing some achievements in the development of a new area, the physics of ferroelectric nanostructures, and does not pretend to give a complete explanation of all the results described above. The importance of this new field of research was pointed out by Ginzburg in his list of the most crucial areas of modern physics [56, 57].

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