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Thermodynamics and kinetics of switching effects in ferroelectrics

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We present a detailed analysis of thermodynamics and kinetics of switching effects in ferroelectrics with 180° domains. First, the switching effects are investigated by field-theory approaches and, then, within the weak metastability domain they are analyzed by means of classical nucleation theory. All basic characteristics for the switching process are estimated, i.e., evolution of the size distribution function for domains is found and the time dependence of changes in the density of domains and flow of domains during the process is determined. The growing mechanism of domains is investigated. An approach to define certain constants for ferroelectric crystals with respect to analysis of evolution of the switching current is proposed.

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I. INTRODUCTION

Ferroelectric crystals and films are widely employed as storage cells in integrated electronic devices and other areas of technology.[1] The most essential property of the structures is their ability to reverse the direction of polarization.[2] As a result, a switching current appears. Multiple switching caused by alternating pulses brings about a decrease in the switched charge in the systems and, as a consequence, a decrease in the switching current.[1,3–7] The switching phenomenon in ferroelectrics is intensively investigated, both theoretically[7,8,10–15] and experimentally.[3–6,11] For instance, the review of Scott[1] presents a generalized analysis of these studies, and a review of microscopic studies of the structural evolution of domains formed in the process of switching is given in Refs. 3, 5 and 6. References 16 and 17 play an important role in understanding phase transformations in ferroelectrics. They were devoted to the formation of the domain structure in solids under loading.

There are presently two main approaches for the description of the switching kinetics. Both approaches are based on the idea that the switching processes are first-order phase transitions, which result in the nucleation of domains with the polarization opposite to the previous one in the bulk of the ferroelectric. Within the first approach,[1] the parameters determining the time dependence of the current represent a set of empirical fitting quantities. In the second approach,[4,7] the corresponding parameters are expressed in terms of the parameters of the Kolmogorov-Avrami model,[18,19] which is widely used in describing the degree of volume filling by growing crystals. Attempts are presently being made to improve the second approach. In particular, allowances are made for the effects associated with the ferroelectric samples of a finite size,[4] etc.

However, despite all the efforts of the researchers, progress in understanding the switching process is presently lacking. In our opinion, this is associated with the fact that the Kolmogorov-Avrami model is a purely geometric model. The equations used in this model contain parameters such as the nucleation rate of the domains and the rate of their growth. These quantities are not defined within the Kolmogorov-Avrami model and should be found from thermodynamics and kinetic theory. The researchers engaged in the growth of crystals and films from vapor, solution, or melt were faced with the same problems,[20–22] and the Kolmogorov-Avrami model was used in describing the growth of crystals and films.

Presently, the rigorous kinetic theory of first-order phase transitions is available and its results are summed in Refs. 20–22. It was shown[20–22] that the first-order phase transitions are complex multistage processes accompanied by various nonlinear phenomena. The theory developed in Refs. 20–22 permits one to treat the rich diversity of the processes involved within a unified approach and to calculate all important characteristics of a phase transition (the rate of nucleation of the new phase, the nucleus growth rate, the evolution of the nucleus size distribution function, the degree of filling of the sample's volume with nuclei, the interface structure, etc.). We will use the latter approach for a description of the switching processes in ferroelectrics in an electric field. The consideration will be exemplified by an intrinsic ferroelectric crystal of a one-component order parameter with 180° domains. We will consider the process of switching only in monocrystals without impurities and defects. The system of equations describing the switching process will be derived and solved. This system may be applied to thin films and crystals with defects.

II. THERMODYNAMICS OF SWITCHING

Let us consider a ferroelectric crystal in the form of a plate of thickness L placed between the plates of a capacitor in a completely ordered state at a temperature below the Curie point. The polarization axis is directed along the z axis. We assume that the dielectric properties of the crystal along the x and y axes have no anomalies. This means that when considering the thermodynamic properties of such a ferroelectric crystal, it is possible to include only the z component of the polarization vector P_z in the expression for the thermodynamic potential. According to Refs. 2 and 23, the thermodynamic potential of a ferroelectric in an electric field at a temperature near the Curie point can be written as

$$\tilde{\Phi}=\Phi_0(p,T)+a(T-T_c)P_z^2+bP_z^4-E_zP_z-\frac{\varepsilon_0E_z^2}{2} \quad (1)$$

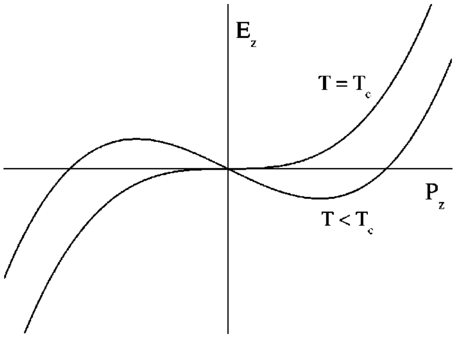

FIG. 1. Dependence of E_z on P_z calculated on the basis of Eq. (2).

where Φ_0 is the part of the thermodynamic potential which does not depend on the degree of polarization *p* and *T* are the pressure and temperature of the medium, E_z is the *z* component of the electric-field strength, T_c is the Curie temperature, *a* and *b* are the coefficients of the thermodynamic potential expansion in powers of P_z, and ε_0 is the permittivity of free space.

Let us consider the temperature region $T < T_c$. Differentiating Eq. (1) at the constant E_z yields the following equation:

$$2a(T-T_c)P_z+4bP_z^3=E_z, \tag{2}$$

which relates the electric-field strength to the polarization of the ferroelectric.[2,23] The form of function $E_z(P_z)$ described by Eq. (2) is shown in Fig. 1. For $T<T_c$ the value $P_z=0$ cannot be related to the stationary state of the ferroelectric. For $E_z=0$, spontaneous polarization of the pyroelectric phase manifests. Then,

$$P_{z1,2,0}=\pm\sqrt{\frac{a(T_c-T)}{2b}}, \tag{3}$$

where P_{z10} and P_{z20} are the equilibrium values of the polarization.

Equation (3) allows one to plot a curve describing equilibrium states in a ferroelectric with the polarization oriented along and opposite to the *z*-axis direction. The curve presenting the equilibrium state of phases is called bimodal (see Fig. 2). To determine the boundaries of the metastability region, we have to find the derivative $(\partial E_z/\partial P_z)_T$ and equate it to zero:

$$P_{1,2s}=\pm\sqrt{\frac{a(T_c-T)}{6b}}. \tag{4}$$

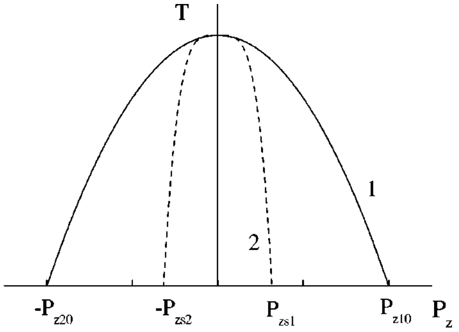

FIG. 2. 1: The phase equilibrium curve of a ferroelectric with P_z, "up" polarization, and $-P_z$; "down" polarization states are shown, 2: The spinodal curve restricting domains, where polarization of a ferroelectric under no circumstances can be uniform; $P_{z1,2s}$ are the metastability domain boundaries.

The curve bounding the metastability region is called the spinodal; it is shown in Fig. 2.

Supersaturation is the most important characteristic of the first-order phase transitions.[20–22] For the description of the switching processes, we can introduce a similar quantity,

$$\xi=1-\frac{P_z}{P_{z10}}, \tag{5}$$

where χ is the permittivity, and ε_0 is the vacuum permittivity. We shall call it the relative repolarization, and

$$\Delta_p=P_{z10}-P_z \tag{6}$$

the repolarization. For the case of small electrical-field strength, the electrical field is directed along the polarization vector $P_z=P_{z10}+\chi\varepsilon_0E_z$.[23] In the opposite case we consider that $P_z=P_{z10}-\chi\varepsilon_0E_z$ [see Eq. (2) and Fig. 1]. Substituting the last expression in Eq. (2) and then in the relationship for Δ_P yields

$$\xi=\frac{\chi\varepsilon_0E_z}{P_{z10}}. \tag{7}$$

As a result we obtain the relationship for the repolarization as a function of an electric-field. For this reason, the electrical field strength in the ferroelectrics switching processes can be considered as an analog of the supersaturation or supercooling in conventional phase transitions. According to Refs. 23, $\chi=[4a\varepsilon_0(T_c-T)]^{-1}$ at $T<T_c$, and from Eq. (7), it follows that at $T-T_c$, the increase in χ is accompanied by an increase in the repolarization.

The quantity

$$\xi_{\max}=1-\frac{P_z}{P_{z1s}} \tag{8}$$

has the meaning of the maximum repolarization. The region $\xi \gg \xi_{\max}$ is called the "weak metastability" region and the region $\xi\to\xi_{\max}$ is called the "strong metastability" region. For $\xi>\xi_{\max}$, the initial orientation of the ferroelectric phase becomes completely unstable. This region of repolarization values corresponds to the spinodal region in the classical thermodynamic theory of phase transitions.[20–22] This region is not considered in the present paper.

III. SWITCHING KINETICS

The most general method for studying phase transitions is field theory,[2,20,24] which allows one to describe first-order phase transitions within a unified approach. In this approach, it is inessential whether the system undergoing the transition is in the region of strong or weak metastability. Nevertheless, this method requires knowledge of the equation of state of the system. If the equation of state is unknown, it can be found in an approximate way by using the Landau expansion for the thermodynamic potential. This expansion (and the equation of state) is valid, only in the vicinity of the second-order phase transition, which narrows substantially the region of its applicability. The interphase energy is necessary in calculating the basic parameters of new-phase nucleation. Usually, this parameter can be found from experimental data. But in the framework of field theory this parameter is not necessary because it can be found analytically. The classical theory makes use of a phenomenological parameter such as surface tension, but it does not permit calculation of the interface structure. The structure of the interface can be calculated in terms of field theory. In our study of the first-order phase transitions in ferroelectrics, we will use both the field approach and the classical theory of nucleation, because the equation of state Eq. (2) is known only in the vicinity of the Curie point. At the same time, we are interested in a description of phase transitions throughout the region of variations in the thermodynamic parameters. We consider first the switching processes in the region of weak metastability.

A. The field theory of the initial stage of nucleation near the critical point

Let us write the Hamiltonian of a ferroelectric near the critical point in the form proposed by Ginzburg and Landau:

$$H\{P_z\}=\int\left[\phi_0+\frac{\delta}{2}(\nabla P_z)^2+\frac{a}{2}(T-T_c)P_z^2+\frac{b}{4}P_z^4-E_zP_z\right]dr. \tag{9}$$

Since we are interested in the relaxation of the order parameter P_z, we have to establish whether the latter is retained in the phase transition or not.

It is well known that ferroelectric crystals are divided into two groups. The first contains crystals in which phase transitions occur by virtue of the displacement of ions belonging to different sublattices. The second one contains crystals in which phase transitions occur by virtue of the ordering in the location of separate ions or molecular groups. Somehow, in ferroelectric crystals of both kinds the dipole moment per one elementary cell tends to zero when its direction reverses. This distinguishes ferroelectric phase transitions from magnetic phase transitions in which the elementary magnetic moment does not vanish when the phase transition takes place. Therefore, the total dipole moment is a conservative parameter for ferromagnetics. So, in the case of ferroelectrics, when the order parameter is a nonconservative parameter, the equation describing the order-parameter relaxation has the following form:[24]

$$\frac{1}{\gamma}\frac{\partial P_z}{\partial t}=-\frac{\delta H\{P_z\}}{\delta P_z}+f, \tag{10}$$

where γ is the kinetic coefficient, $\delta H\{P_z\}/\delta P_z$ is the variational derivative, and f is the external force simulating the thermal ensemble.

Let us introduce dimensionless variables: $\alpha=2a(T_c-T)$, radius $r=\sqrt{2\delta/|\alpha|}\Lambda$, time $t'=|\alpha|\gamma/2t$, polarization $P_z'(\Lambda,t)=P_z(\Lambda,t')/\varphi_S$, $\varphi_S=\sqrt{|\alpha|/b}$, and $z=z'\sqrt{2\delta/|\alpha|}$. For the solution of Eq. (10) we should know the shape of domains. The shape of repolarization nuclei, unlike the nuclei formed during conventional phase transitions, cannot be arbitrary. Obviously, this fact is associated with the solution of the Maxwell equations for a dielectric[23] (on the interface of domains the normal component of an electric induction vector is continuous, as well as the tangential component of field vector $\vec{E}$). It means that phase boundaries between domains of initial and new phases are parallel to the z axis. So, during switching, domains in the form of flat plates or cylinders originate in a ferroelectric crystal and being of such shape, they should extend for the whole crystal thickness. However, as is shown below, in the case of large thickness L the probability of formation of domains tends to zero. This fact is associated with the energy consumption of the system to produce the interphase. In analysis of conventional first-order phase transitions such a problem does not arise, since nuclei are of the form either close to a spherical one or they are two-dimensional cylindrical nuclei with the height H comparable to the interatomic distance.[20] In the general case, it is obvious that the form of domains is not to be retained in the process of switching. In some cases the radius of domains can turn out to be smaller as the domains penetrate deeply into a crystal, while in other cases the domain will become faceted. In our work, to simplify the analysis, we assume that domains of height H with the order of magnitude equal to the size of an elementary crystal cell, $H\sim\omega^{1/3}$, arise across the whole width of the crystal. Further, the domains instantaneously coalesce into a long cylindrical domain. The width and the radius of the domains will change in the course of their nucleation and subsequent evolution. So, when evaluating the variational derivative for the case of cylindrical symmetry and substituting into Eq. (10) at $f=0$, we get

$$\frac{\partial P_z'}{\partial t'}=\frac{\partial^2 P_z'}{\partial\Lambda^2}+2(P_z'-P_z'^3)+E_z+\frac{1}{\Lambda}\frac{\partial P_z'}{\partial\Lambda}+\frac{1}{\Lambda^2}\frac{\partial^2 P_z'}{\partial\Theta^2}+\frac{\partial^2 P_z'}{\partial z'^2}, \tag{11}$$

where Λ is the radius in the cylindrical coordinate system, and Θ is the angle.

According to Ref. 24, this equation can be solved if the width of the nucleus boundary $\Lambda_0(t)$ is small compared to the nucleus size. In this case, Eq. (11) can be rewritten in the form

$$\frac{\partial P_z'}{\partial t'}=\frac{\partial^2 P_z'}{\partial\Lambda^2}+2(P_z'-P_z'^3)+E_z+\frac{1}{\Lambda_0}\frac{\partial P_z'}{\partial\Lambda}+\frac{1}{\Lambda_0^2}\frac{\partial^2 P_z'}{\partial\Theta^2}+\frac{\partial^2 P_z'}{\partial z'^2}. \tag{12}$$

The approximate solution of nonlinear Eq. (12) has the form[24]

$$P_z' = \pm th[\Lambda - \Lambda_0(\Theta,t')] + \frac{E_z'}{4}, \tag{13}$$

where is $E_z' = (2\sqrt{b}/\alpha\sqrt{|a|})E_z$ The velocity of the nucleus boundary motion can be represented in the form

$$\Lambda_0(\Theta,t') = \sum_{n=0}^{\infty} \Lambda_0^n(t')\cos(n\Theta + \beta_n), \tag{14}$$

where $\beta_0 = 0$, $\beta_n = \mathrm{const}$ for $n \geqslant 1$ are determined by the boundary conditions. Substituting Eqs. (13) and (14) in (12) yields

$$\begin{aligned} \frac{d\Lambda_0}{dt'} &= -\frac{1}{\Lambda_0} + \frac{3}{2}E_z', \\ \frac{d\Lambda_0^n}{dt'} &= -\frac{n^2-1}{\Lambda_0^2}\Lambda_0^n. \end{aligned} \tag{15}$$

From here, for $\Lambda_0^n(t')$, we have

$$\Lambda_0^n(t') = \Lambda'(0)\exp\left[-\int_0^{t'} \frac{(n^2-1)}{\Lambda_0(t'')}dt''\right]$$

and for the nucleus growth rate, we obtain

$$\frac{dr_0}{dt} = \Gamma\left(\frac{3}{2}\,\frac{\sqrt{2\delta b}E_z}{\sqrt{\alpha|a|}} - \frac{\delta}{r_0}\right). \tag{16}$$

The quantity $\sqrt{2\delta\alpha|a|}/3\sqrt{b}E_z$ is nothing else but the radius of the critical nucleus, i.e.,

$$R_c = \frac{\sqrt{2\delta\alpha|a|}}{3\sqrt{b}E_z}. \tag{17}$$

We denote

$$r_c = \sqrt{\frac{2\delta}{|\alpha|}}$$

and then,

$$R_c = \frac{2}{3}\,\frac{r_c}{E_z'}.$$

Note that the representation of the Hamiltonian in the form of Eq. (9) becomes possible in the vicinity of the critical point where the Landau mean-field theory is valid. The region of its applicability is specified by the Ginzburg-Levanyuk criterion G_i, subject to the condition that

$$G_i = \frac{(k_BT_c)^2b^2}{\delta^3} \ll |\alpha| \ll 1 \tag{18}$$

and

$$\frac{R_{\max}}{k_BT} \gg 1,$$

where $R_{\max}$ is the maximum work needed to form the new phase. Conditions of Eq. (18) indicate, on one hand, that the Landau theory is valid, and on the other hand, that the system is in the region of weak metastability. Far from T_c, i.e., at $T \ll T_c$, in the region of weak metastability, we cannot, in the general case, use an expansion of Eq. (9) and should use the results obtained in Refs. 20–22.

B. Kinetics of the initial stage of switching in the region of weak metastability (classical approach)

Recall that the polarization P_z used above is defined in the following way:[2,23] $P_z = 1/\omega\Sigma_i e_i r_{zi}$, where ω is the unit-cell volume of the crystal, $p_{zi}' = \Sigma_i e_i r_{zi}$ is the dipole moment of the unit cell in the point-charge approximation, e_i is the charge of the ith ion, and r_{zi} is the z component of the ith charge position vector. From this,

$$p_{zi}' = P_z\omega. \tag{19}$$

We assume the elementary structural units of domains to be the crystal unit cells with the dipole moment p_{zi}. Depending on the type of ferroelectric crystal, atoms also can be elementary structural components. In this case, the volume ω implies the volume per atom. The number of unit cells in a domain of volume V_d is

$$n = \frac{V_d}{\omega}, \tag{20}$$

and for the polarization of this domain, we have

$$P_{zn} = p_{zi}'n. \tag{21}$$

We introduce the distribution function $f(n,t)$ of domains in the number of unit cells they contain, which is normalized against the number of domains $N(t)$ per unit volume of the crystal, that is,

$$N(t) = \int_0^\infty f(n,t)dt. \tag{22}$$

We can change over from $f(n,t)$ to the distribution function of domains in the degree of polarization $f(P_{zn},t)$ using the relationship $f(n,t)dn = f(P_{zn},t)dP_{zn}$ and Eq. (21).

According to the classical theory of nucleation,[20–22] the kinetic equation describing the process of new-phase nucleation can be written in the form

$$\frac{\partial f}{\partial t} = I_{n-1} - I_n, \tag{23}$$

where $f(n,t)$ is the distribution function of the switched domains in the number of unit cells they contain, I_{n-1} is the flux of new-phase nuclei transferring from size $n-1$ to size n, and I_n is the flux of the new-phase nuclei transferring from size n to size $n-1$. Hence, it follows that

$$I_{n-1}=W_{n-1,n}f(n-1,t)-W_{n,n-1}f(n,t),$$

$$I_n=W_{n,n+1}f(n,t)-W_{n+1,n}f(n+1,t),$$

Here, $W_{n-1,n}$, $W_{n,n-1}$, and $W_{n,n+1}$ are the transition probabilities of the nuclei moving from the state with a particular number of unit cells to another. Depending on the actual size of the switching nuclei, they can be divided into two classes: nuclei with $n<n_c$ and those with $n>n_c$, where n_c characterizes the nucleus of a critical size which is in equilibrium with the medium. The nuclei with $n<n_c$ decay, because the medium is ''underswitched'' for them, and those with $n>n_c$ grow, because the medium is ''overswitched.'' Such a size distribution of the nuclei is due to the existence of the interface energy between a nucleus with the polarization vector along the field and the medium with the oppositely directed polarization vector. In the region between the nucleus and the medium, the polarization vector turns, which accounts for the creation of additional energy.

For $n\gg 1$, we can change over from the difference Eq. (23) to a differential one. In this case, we obtain

$$\frac{\partial f}{\partial t}=\frac{\partial}{\partial n}W_{n,n+1}\left[\frac{1}{k_BT}\frac{\partial R_{\min}}{\partial n}f(n,t)+\frac{\partial f}{\partial n}\right], \tag{24}$$

where $W_{n,n+1}$ is the diffusion coefficient of the switching nuclei in the space, $R_{\min}(n)$ is the minimum work done by the system to create the nuclei, and $\partial R_{\min}/\partial n$ is the change in the minimum work due to a change in the number of structural units in a domain at $n<n_c$.

The quantity $(W_{n,n+1}1/k_BT)(\partial R_{\min}/\partial n)$ is the growth rate of nuclei of size *n*, that is,

$$\frac{dn}{dt}=-W_{n,n+1}\frac{1}{k_BT}\frac{\partial R_{\min}}{\partial n}, \tag{25}$$

and the quantity $W_{n,n+1}(\partial f/\partial n)$ describes a random walk of a nucleus in the size space. By solving Eq. (24), we can determine the main characteristics of the switching process, namely, the distribution function $f(n,t)$, as well as the dependence of the number of domains created in the course of the switching, the variation in the domain mean size, and many other parameters of this process.

Any first-order phase transition can be conventionally divided into a number of characteristic time stages[20,21] to facilitate its analysis. In the initial stage, the system undergoing a phase transition does not feel that a new phase has already been formed and its thermodynamic parameters do not change. In the subsequent stages of the phase transition, the thermodynamic parameters of the system vary and this becomes reflected in the nucleation process.

In the initial stage of nucleation, it is sufficient to consider the steady-state Eq. (24) and to determine the stationary flux of the polarization switching nuclei. To find it, we should determine the coefficient $W_{n,n+1}$, the minimum work to be done to produce a nucleus $R_{\min}(n_c)$, and the critical size of the polarization switching nucleus n_c. These quantities can be found in two equivalent approaches. The first one is the classical approach,[22] which requires knowledge of the equilibrium distribution function for the determination of the nucleus flux. The second approach, which was developed in Ref. 25, makes use of certain relationships between the coefficients of absorption, $W_{n,n+1}$, and those of emission, $W_{n+1,n}$. They allow one to derive the expression for the stationary flux of nuclei without recourse to the equilibrium distribution functions. Both approaches yield the same result. We will employ the latter technique to calculate the polarization switching nucleus flux.

For nuclei with $n<n_c$, the distribution function $f(n)\sim\exp(-R(n)/k_BT)$ makes the left-hand side of Eq. (24) vanish, i.e., $\partial f/\partial t=0$. This means that the transition probabilities $W_{n,n+1}$ and $W_{n+1,n}$, which change the nucleus size by one structural unit, are exactly the same as for heterophase fluctuations at equilibrium.

Using the approach developed in Ref. 25, we can obtain relationships between the absorption and emission coefficients, which would be valid for all values of *n*. We consider an auxiliary-ferroelectric crystal with a polarization at which a nucleus of size $n>n_{nc}$ will be in equilibrium with the crystal. The auxiliary-ferroelectric-true ferroelectric system resides in a local thermodynamic equilibrium. Introduction of such an auxiliary system permits one to obtain the relationship

$$\frac{W_{n,n+1}}{W_{n+1,n}}=\begin{cases}\exp\left(\dfrac{-\tilde{R}_{\min}}{k_BT}\right) & n<n_c,\\[2ex] \exp\left(\dfrac{-\tilde{R}_{\min}}{k_BT}\right) & n>n_c,\end{cases} \tag{26}$$

which is valid for all values of *n*.

Let us calculate the minimum work done to create a nucleus of the switched phase with polarization P_{zn} in a ferroelectric crystal. According to Ref. 26 the minimum work required to form a nucleus in a medium is,, $R_{\min}(n)=\Delta W+\Delta_0 W$, where ΔW is the total change in the nucleus energy and $\Delta_0 W$ is the change in the energy of the medium as a result of the nucleus formation. The quantities with the subscript zero refer to the medium, and those without a subscript, to the nucleus. Let us consider the quantity $\Delta_0 W$. As follows from thermodynamics, the change in the energy during the reverse transition from one state to another can be represented in the form

$$\Delta_0 W'=-p_0\Delta_0 V+T_0\Delta_0 S+\mu_0\Delta_0 n. \tag{27}$$

In the case of a ferroelectric in an electric field, the work done by the electric forces should also be taken into account, that is,

$$\Delta_0 W=\Delta_0 W'+E_{z0}\Delta_0 D_{z0}=\Delta_0 W'+E_{z0}\Delta_0 P_{z0}+\Delta_0\left(\frac{\varepsilon_0 E_z^2}{2}\right). \tag{28}$$

In Eq. (27), p_0, T_0, and μ_0 are the pressure, temperature, and chemical potential of the medium, respectively; $\Delta_0 V$ and $\Delta_0 S$ are the corresponding changes in the volume and entropy of the medium; E_{z0} is the electric-field strength in the medium; D_0 is the electric induction of the medium; and P_{z0}

is the polarization of the medium. The quantity $\varepsilon_0 E_z^2/2$ is the work associated with electric—field generation between the capacitor plates. Because we investigate the internal field of a ferroelectric, this quantity will be disregarded and all parameters will be expressed in terms of the polarization rather than through induction.

The pressure, volume, and temperature in the system remain fixed, and hence, $p_0=p$, $T_0=T$, $n_0=n$, and $\Delta_0 V=-\Delta V$. For the change in the entropy, we can write $\Delta S+\Delta_0 S=0$. The polarization components in the medium and the nucleus are oppositely directed, i.e., $\Delta_0 P_{z0}=-\Delta P_z$ and $E_{z0}=E_z$. Then, for $R_{\min}(n)$, we obtain

$$R_{\min}(n)=\Delta(W+p_0V-T_0S-E_{z0}P_z)-\mu_0 n. \tag{29}$$

Because the electric field in a nucleus of size n is E_{zn}, we can rewrite Eq. (29) in a more convenient form. In view of Eq. (28), we come to the relationship

$$\begin{aligned}R_{\min}(n)=\Delta(W+p_0V-T_0S-E_{zn}P_z)\\ +(E_{zn}-E_{z0})P_z-\mu_0 n.\end{aligned} \tag{30}$$

Let us consider the nucleus energy W in Eq. (29). It consists of a volume part of the nucleus energy W_v and a surface part W_s. To calculate them, we have to know the nucleus shape. In this case, $W_s=2(\pi H\omega)^{1/2}\sigma n^{1/2}$, where σ is the surface tension of the domain wall. It is well known that the surface tension of clusters depends on their size. The dependence of surface tension on cluster radius was calculated twenty years ago, but to our best knowledge, in ferroelectric crystals this dependence was discovered recently.[27]

Recall it is assumed above that the height H is comparable with the linear size of an elementary cell with respect to value, $H\sim\omega^{1/3}$. In principle, in each specific case the value is to be additionally determined. Note that the expression under the Δ sign in Eq. (30) is the thermodynamic potential of the nucleus with an internal field E_{zn}, that is,

$$\phi(P_{zn})=\Delta(W+p_0V-T_0S-E_{zn}P_z)=\tilde{\mu}n, \tag{31}$$

Here, $\tilde{\mu}$ is the chemical potential of the new-phase nucleus of size n with inclusion of the surface tension, that is,

$$\left.\frac{\partial\phi(P_{zn})}{\partial n}\right|_{E_z,p,T}=\tilde{\mu}(E_{zn},p,T)=\mu(E_{zn},p,T)+\frac{(\pi H\omega)^{1/2}\sigma}{n^{1/2}}. \tag{32}$$

Now, we can find the quantity $\tilde{R}_{\min}$ entering into formula (26),

$$\tilde{R}_{\min}=\left.\frac{\partial R_{\min}}{\partial n}\right|_{E_z,p,T}=(\tilde{\mu}-\mu_0)+(E_{zn}-E_{z0})\frac{\partial}{\partial n}P_z, \tag{33}$$

where $\partial P_z/\partial n$ is the polarization per structural unit in a nucleus, i.e., the quantity p_{zi} introduced earlier [see Eq. (21)].

Let us write $\tilde{\mu}(E_{zn},p,T)-\mu_0(E_{zn},p,T)$ in an explicit form taking into account that the equilibrium magnitude of the nucleus-medium polarization is given by the expression

$$\tilde{\mu}(E_{zn},p,T)=\mu(E_{zn},p,T)+\frac{(\pi H\omega)^{1/2}\sigma}{n^{1/2}}=\mu_0(E_{zn},p,T). \tag{34}$$

The equilibrium value of the nucleus-medium field $\tilde{E}_z$ (the nucleus of an infinite size $n\to\infty$) can be found from the condition

$$\mu(\tilde{E}_z)=\mu_0(\tilde{E}_z). \tag{35}$$

By subtracting Eq. (34) from Eq. (35) and expanding the left- and right-hand sides of the relationship thus obtained in the vicinity of the $\tilde{E}_z$ point in the small deviation $(E_{zn}-\tilde{E}_z)/\tilde{E}_z$, we obtain for the main part of the nucleus distribution spectrum

$$\frac{\partial\mu}{\partial E_z|\tilde{E}_z}(E_{zn}-\tilde{E}_z)+\frac{(\pi H\omega)^{1/2}\sigma}{n^{1/2}}=\frac{\partial\mu_0}{\partial E_z|\tilde{E}_z}(E_{zn}-\tilde{E}_z). \tag{36}$$

Since the deviation of E_{zn} from $\tilde{E}_z$ is small, we have retained only the first term in the last expansion.

Because $-\partial\mu/\partial E_z|\tilde{E}_z=p_{zi2}=P_{z20}\omega$ and $-\partial\mu_0/\partial E_z|\tilde{E}_z=p_{zi1}=P_{z10}\omega$, where p_{zi1} is the elementary polarization of the medium, and p_{zi2} is the elementary polarization of the nuclei, these quantities are equal in absolute magnitude and have opposite directions. We denote $p_{zi1}=p_{zi}$, then $p_{zi2}=-p_{zi}$, and from Eq. (36), we obtain

$$2(E_{zn}-\tilde{E}_z)p_{zi}=\frac{(\pi H\omega)^{1/2}\sigma}{n^{1/2}}$$

and

$$n^{1/2}=\frac{(\pi H\omega)^{1/2}\sigma}{2p_{zi}(E_{zn}-\tilde{E}_z)}. \tag{37}$$

As is seen from Fig. 2, the equilibrium state of the ferroelectric corresponds to the field $\tilde{E}_z=0$. On the other hand, the critical size of the polarization switching nucleus, which is in equilibrium with the ferroelectric in the switching field, is determined by the relationship $E_{znc}=E_{z0}$.

Taking into account this relationship and $\tilde{E}_z=0$, from Eq. (37), we obtain

$$n_c^{1/2}=\frac{(\pi H\omega)^{1/2}\sigma}{2p_{zi}E_{z0}}\,. \tag{38}$$

Dropping the index "0," which identifies the field with the medium (i.e., with the part of the ferroelectric that has not yet switched), we have

$$n_c^{1/2}=\frac{(\pi H\omega)^{1/2}\sigma}{2p_{zi}E_z}. \tag{39}$$

This relationship determines the number of structural units in the critical switching nucleus. It is similar to the expressions describing the number of structural units in the critical nuclei formed in solutions and melts.[20–22] The electric field plays the role of supersaturation or supercooling.

We rewrite Eq. (39) in terms of the radius of the critical domain radius R_c rather than through the number of unit cells n_c, that is,

$$R_c=\frac{\sigma\omega}{2p_{zi}E_z}. \tag{40}$$

The same result can be obtained by the minimization of the energy of new-phase island formation

$$\tilde{R}_{\min}=2\pi H\sigma R-\frac{\pi R^2 H}{\omega}2E_z p_{zi}. \tag{41}$$

It should be pointed out that the dependence of a critical radius on electrical field as shown in Eq. (40) was obtained in Ref. 16 as well. Now, we can obtain an expression for the work to be done to create a nucleus of the critical size. As follows from Eqs. (30)–(37), it can be written as

$$R_{\min}(n_c)=(\pi H\omega)^{1/2}\sigma n_c^{1/2}. \tag{42}$$

Using the relationships derived above and in Eq. (34), we recast expression Eq. (33) in the form

$$\begin{aligned}\tilde{R}_{\min}=\frac{\partial R_{\min}}{\partial n}&=\mu_0(E_{zn},p,T)-\mu_0(E_{z0},p,T)-(E_{zn}-E_{z0})p_{zi}\\&=\frac{\partial\mu_0}{\partial E_z|_{E_{z0}=E_{zn}}}(E_{zn}-E_{z0})-(E_{zn}-E_{z0})p_{zi}\\&=-2(E_{zn}-E_{z0})p_{zi}.\end{aligned} \tag{43}$$

Note that by introducing an auxiliary ferroelectric and deriving relationships as in Eq. (26), we obtained an expression for $\tilde{R}_{\min}$ which is valid throughout the range of n values near the critical size. As follows from Eq. (43), if $E_{zn}=E_{znc}=E_{z0}$, the derivative $\partial R_{\min}/\partial n$ for a nucleus of critical size is zero. In the next section we shall calculate the polarization switching nucleus flux in the size space.

1. Determination of the diffusion coefficient $W_{n,n+1}$ in the size space

In order to calculate the diffusion coefficient $W_{n,n+1}$ in the size space, we should use Eq. (25). It follows from this equation that the growth rate dn/dt of domain of size n depends both on $W_{n,n+1}$ and on $\partial R_{\min}/\partial n$ [see Eq. (43)]. To find $W_{n,n+1}$, we define the growth rate in a different manner, namely, as

$$\frac{dn}{dt}=[\beta(E_{zn})-\beta(E_{z0})]S, \tag{44}$$

where $\beta(E_{zn})$ is the flux of the switched elementary regions attaching to the side surface of a domain, $\beta(E_{z0})$ is the reverse cell flux bringing about "domain dissolution," E_{zn} is the field in the auxiliary medium which is in equilibrium with a domain of size n, E_{z0} is the field in the medium of the ferroelectric under study, and $S=2(\pi H\omega)^{1/2}n^{1/2}$ is the side surface of a bubble cylindrical domain. Note that we are considering a domain of size $n>n_c$, which is in equilibrium with the auxiliary ferroelectric. We assume that the domain grows through the transfer of atoms in the cells from one state to another directly in the interface separating the domains. In this case, we can determine the $\beta(E_{zn})$ and $\beta(E_{z0})$ fluxes in the following way. If the ferroelectric is in an equilibrium state (no external electric field, and its total polarization is zero), the unit-cell fluxes induced by thermal fluctuations from domains with polarization in the directions along and opposite to the z axis are equal. In a nonequilibrium state, the polarization of the system will change. Consider the quantity

$$\beta_0'=\nu\exp(-V_0/k_BT),$$

where ν is the vibrational frequency of atoms in the unit cells on the domain surface and V_0 is the height of the energy barrier separating the domains located in two symmetric positions with oppositely directed polarizations in the absence of the field. By multiplying β_0' by the number of unit cells N_s on the surface of domains, we can obtain the equilibrium unit-cell flux

$$\beta_0=N_s\nu\exp(-V_0/k_BT).$$

The magnitude of N_s can be estimated as $N_s\sim 1/\omega^{2/3}$, where $\omega^{2/3}$ is the area occupied by a cell on the domain surface.

If the ferroelectric is in an external field, the height of the energy barrier V_0 changes. For each cell in a domain with the polarization aligned along the field, the barrier height decreases to $V_0-p_{zi}E_z$, and for the cells residing in domains with oppositely directed polarization, it increases to $V_0+p_{zi}E_z$. In the presence of a field, the fluxes of cells from the surface of one domain to another are no longer equal. The cell flux from the medium is $\beta(E_{zn})=\beta_0\exp(p_{zi}E_{zn}/k_BT)$, and the cell flux from a nucleus of the critical size is $\beta(E_{z0})=\beta_0\exp(p_{zi}E_{z0}/k_BT)$. If $p_{zi}E_z\ll k_BT$, the exponentials in the expressions for these fluxes can be expanded in a series. Limiting ourselves to linear terms of the expansion in Eq. (44), we obtain the growth rate for the side surface of a domain of the size $n>n_c$,

$$\frac{dn}{dt}=2(\pi H\omega)^{1/2}\beta_0\frac{2\,p_{zi}(E_{zn}-E_{z0})}{k_BT}n^{1/2}. \tag{45}$$

Now, we can determine the diffusion coefficient W_n in the size space. To do this, we compare Eq. (45) with Eq. (25) and recall Eq. (43) to obtain

$$W_n=2(\pi H\omega)^{1/2}\beta_0 n^{1/2}. \tag{46}$$

Then, for a nucleus of the critical size, we have

$$W_{n_c}=2\,(\pi H\omega)^{1/2}\beta_0 n_c^{1/2}. \tag{47}$$

2. The flux of polarization switching nuclei

Using the value of the work needed to create a nucleus of the critical size and the expression for the diffusion coefficient in the size space, and using the standard technique, we can calculate the stationary flux of the polarization switching nuclei passing through the critical barrier. According to Refs. 20–22, this flux can be written as

$$I = W_{n_c} N_v \frac{1}{\sqrt{\pi}} \sqrt{-\frac{1}{2k_B T} \frac{\partial^2 R_{\min}}{\partial n^2|_{n=n_c}}} \exp\left[-\frac{R_{\min}(n_c)}{k_B T}\right], \tag{48}$$

where N_v is number of unit cells per unit volume of the crystal, $N_v = 1/\omega$.

Substituting the values of W_{n_c} from Eq. (47), $R_{\min}(n_c)$ from Eq. (42), and

$$\left.\frac{\partial^2 R_{\min}}{\partial n^2}\right|_{n_c} = -\frac{(\pi H\omega)^{1/2}\sigma}{4n_c^{3/2}}.$$

we finally come to

$$I = \frac{\pi^{1/4} N_v \beta_0 (H\omega)^{3/4} \sigma^{1/2}}{\sqrt{2} n_c^{1/4} \sqrt{k_B T}} \exp\left(-\frac{(\pi H\omega)^{1/2}\sigma n_c^{1/2}}{k_B T}\right). \tag{49}$$

Equation (49) describes the process of homogeneous nucleation. Defects (for instance, charged impuities, twin boundaries, and so on) in ferroelectrics may decrease the nucleation barrier.

We now express the critical radius n_c in Eq. (39) in terms of the field strength according to Eq. (49), that is,

$$I = \frac{N_v \beta_0 (H\omega)^{1/2} (p_{zi} E_z)^{1/2}}{\sqrt{k_B T}} \exp\left(-\frac{\pi H \omega \sigma^2}{2k_B T p_{zi} E_z}\right). \tag{50}$$

Relationship (50) describes the flux of switched domains as a function of the applied field. Next we take the logarithm of expression (50) to obtain

$$\ln I = \ln K - \frac{1}{2} \ln E_z - \frac{\pi H\omega\sigma^2}{2k_B T\, p_{zi} E_z}, \tag{51}$$

where

$$K = \frac{N_v \beta_0 (H\omega p_{zi})^{1/2}}{\sqrt{k_B T}}.$$

Because the logarithm is a slowly varying function, as a first approximation, we assume the second term in expression (51) to be field independent. In this case, we obtain a convenient expression for the estimation of experimental data,

$$\ln I \approx \text{const} - \frac{\pi H\omega\sigma^2}{2k_B T p_{zi} E_z}, \tag{52}$$

where const stands for the first two terms in Eq. (51).

It is easy to see from Eq. (51) that preexponential terms in the nucleation rate are proportional to squared electrical field. And the exponential term itself is proportional to the inverse negative electrical field. All these terms depend on the shape of domains and Eq. (51) is valid for the cylindrical shape only. In the general case it is necessary to use Eq. (48).

Stadler[28,29] showed experimentally that the nucleation rate of domains in $BaTiO_3$ is about proportional to $E^{1.4}$ in the case of strong fields. In the case of weak fields the nucleation rate can be represented as the exponents of inverse negative electrical field. Stadler showed also that in the case of weak fields there is strong dependence of the nucleation rate on the thickness of crystals. Otherwise, this dependence does not take place. This fact is in a good agreement with Eq. (51). $BaTiO_3$ crystals have a multicomponent order parameter, therefore, in the case of strong field the dependence $E^{1.4}$ of nucleation rate on electrical field will be different from our dependence $E^{0.5}$ for one-component crystals and cylindrical domains. We point out once more that Eq. (51) is valid only in the region of weak metastability.

Let us estimate the time of the establishment and existence of a stationary flux of the switching nuclei. The region with $n < n_c$ is determined primarily by heterophase fluctuations of polarization switching. Hence, the existing flux sets in during the time it passes the region δn_0 in the vicinity of the critical point at which the hydrodynamic growth rate of the switching nuclei is zero, i.e., where $dn/dt = 0$ and $\partial R_{\min}(n)/\partial n|n = n_c = 0$. The width of this region is

$$\delta n_0 = \left(-\frac{1}{2k_B T} \frac{\partial^2 R_{\min}(n)}{\partial^2 n}\right)^{-1/2}. \tag{53}$$

It follows that the time required for the stationary flux to set in can be estimated as

$$t \sim \frac{(\delta n_0)^2}{W_{n,n+1}}. \tag{54}$$

The time of the persistence of the stationary flux is determined by the condition that the time required for a nucleus to cross the region δn_0 in the size space should be substantially shorter than that taken for a nucleus of the critical size to emerge from the vicinity of the critical point

$$\frac{(\delta n_0)^2}{W_{n,n+1}} \leqslant \frac{\delta n_0}{dn_c/dt}. \tag{55}$$

Substitution of the corresponding values of δn_0 and $W_{n,n+1}$ in the relationship of Eq. (54) yields

$$t \sim \frac{4k_B T n_c}{\pi H\omega\beta_0\sigma} \tag{56}$$

and, taking into account expression (39) for n_c, we obtain

$$t \sim \frac{k_B T\sigma}{\beta_0 (p_{zi} E_z)^2}. \tag{57}$$

Thus, the time for the stationary flux to set in or the time for the first nucleus to appear is inversely proportional to the squared electric field.

Note that we have found relationships (49) or (50) for the stationary flux of the nucleating domains. There are presently methods permitting one to solve the Focker-Planck nonstationary Eq. (24) and to find the nonstationary flux of polarization switching domains.[30] However, the main process of the formation of the new phase starts in the next stage when the system contains so many nuclei that they change the supersaturation of the system (in our case, the field in the ferroelectric), which results in the nucleus flux becoming dependent on time. This stage will be studied in the future.

3. The flux of polarization switching near the critical point

In the vicinity of the critical point the surface tension is determined as $\sigma=(2\sqrt{2}\delta/3b)\alpha^{3/2}$, and the size of the critical value can be calculated using Eq. (10), where for the coefficients δ and b we used Eq. (17). After substitution of these values in Eq. (49) we obtained the following expression for the flux of the switched domains near the critical point:

$$I=\frac{N_v\beta_0 H^{1/2}\omega^{2/3}\alpha^{1/4}E_z^{1/2}}{\sqrt{k_BT}b^{1/4}}\exp\left(-\frac{4\pi H\delta\alpha^{5/2}}{9b^{3/2}k_BTE_z}\right). \quad (58)$$

Note that Eq. (58) is valid only in the vicinity of the critical point [according to the conditions of the existence of Eq. (4)].

C. Kinetics of bulk polarization switching in a ferroelectric crystal

According to the general theory of phase transitions,[20–22,31] after the maximum in the size spectrum of nuclei has reached the critical size in its evolution, fluctuations no longer affect the growth of nuclei of the new phase significantly. Therefore, the master kinetic equation for first-order phase transitions [see Eq. (24)] can be written in the form

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial n}[V_nf(n,t)]=0, \quad (59)$$

where V_n is the growth rate of a nucleus and $f(n,t)$ is the size distribution function of the switched domains. Thus, the term describing the fluctuations is disregarded in this stage. In this stage of the phase transition, the repolarization in the system is not a constant quantity: it varies in the course of the phase transition, because the formation of polarization switching nuclei changes the overall polarization of the crystal. Hence, Eq. (59) for the distribution function should be complemented by an equation describing the conservation of the total dipole moment in the crystal.

We write this equation in the differential form

$$J(E_z^0)\frac{p_{zi}}{P_{z10}}=\frac{d\xi}{dt}+\frac{p_{zi}}{P_{z10}}\int_0^\infty V_nf(n,t)dn. \quad (60)$$

Here, ξ is the relative repolarization, $J(E_z^0)p_{zi}/P_{z10}$ is the polarization switching source generated by the external field, and $(p_{zi}/P_{z10})\int_0^\infty V_nf(n,t)dn$ is the rate of "polarization consumption" by new-phase domains. Now, we determine the source $J(E_z^0)$. The field applied to a ferroelectric will change the direction of polarization in its cells. In order to find the number of elementary polarization vectors formed per unit volume of the crystal in a unit time, we will proceed as we did when calculating the domain growth rate. Let $J(E_z^0)$ be the number of elementary polarization vectors induced by the field. Using the results, we can immediately write an expression for the number of switched cells appearing in a unit volume of the crystal per unit time, that is,

$$J(E_z^0)=\beta_0'\frac{2p_{zi}(E_z^0-\overline{E}_z)}{k_BT}, \quad (61)$$

where $\beta_0'=N_v\nu\exp(-V_0'/k_BT)$, V_0' is the energy barrier height required for an elementary dipole in a cell to turn from a state with one direction of polarization to another in the absence of an external field, ν is the frequency of atomic vibrations in the cell, and E_z^0 is the external field of the source at the instant of the onset of bulk polarization switching. Recalling that $P_z^0=P_{z10}-\chi\varepsilon_0E_z^0$, where χ is the permittivity and also $p_{zi}=P_{z10}\omega$, we obtain

$$\xi^0=\frac{J(E_z^0)p_{zi}\tau}{P_{z10}}=\frac{\overline{P}_z-P_z^0}{P_{z10}}, \quad (62)$$

where $\tau=k_BT\chi\varepsilon_0/2\beta_0'p_{zi}^2$. In a general case, the source $[J(E_z^0)p_{zi}]/P_{z10}$ can be time dependent. By analogy with Refs. 20 and 21,31, the coupled Eqs. (59) and (60) can be solved numerically for sources of any kind, specifically of pulsed action. We rewrite Eq. (60) in the form

$$\frac{\xi^0}{\tau}=\xi'(t)+\frac{p_{zi}}{P_{z10}}\int_0^\infty V_nf(n,t)dn. \quad (63)$$

If the time τ is short enough to allow neglect of derivative $\xi'(t)$ we obtain

$$\xi^0=\tau\frac{p_{zi}}{P_{z10}}\int_0^\infty V_nf(n,t)dn. \quad (64)$$

Equations (59) and (64) describe the switching kinetics in ferroelectric crystals. In order to solve them, we need to know the expression for the domain growth rate V_n.

As was shown in Refs. 20, 21, and 31, in this stage of the phase transition, the supersaturation (or in our case, repolarization) changes insignificantly and is still large enough for the size n of the forming and growing nuclei to considerably exceed the critical value, i.e., $n\gg n_c$. So we can rewrite Eq. (45) as

$$V_n=2\,\mathrm{const}\,E_z(t)n^{1/2}, \quad (65)$$

where $\mathrm{const}=2\beta_0(\pi H\omega)^{1/2}p_{zi}/k_BT$.

The system of equations is now complete, and we can find its solutions. To accomplish this, we rewrite Eq. (65) in the form

$$V_n=\frac{dn}{dt}=2\frac{\xi(t)}{t_0}n^{1/2}, \quad (66)$$

where t_0 is the characteristic time of growth, $t_0=[2\beta_0(\pi H\omega)^{1/2}p_{zi}P_{z10}/k_BT\chi\varepsilon_0]^{-1}$. Next we introduce the dimensionless radius ρ of the nuclei in order to make the growth rate independent of n, i.e., we transform the variable to $\rho=n^{1/2}$.

Because $f(n,t)dn=g(\rho,t)d\rho$, Eq. (59) and Eq. (60) can be rewritten as

$$\frac{\partial g(\rho,t)}{\partial t}+\frac{\xi(t)}{t_0}\frac{\partial}{\partial \rho}[g(\rho,t)]=0, \tag{67}$$

$$\frac{\xi_0}{\xi(t)}-1=\lambda\int_0^\infty \rho g(\rho,t)\,d\rho \tag{68}$$

with boundary and initial conditions of the form $g(0,t)=I[\xi(t)]t_0/\xi(t)$, $g(\rho,0)=0$ $(\rho>\rho_c)$, where $\lambda=k_B T\chi\varepsilon_0/t_0\beta_0' p_{zi}P_{z10}$.

The coupled Eq. (66)–(68) fully describe the switching kinetics in ferroelectrics in the stage when the maximum in the nucleus size distribution has reached a critical size[20,21,31] and the rate of change of supersaturation is small compared to the flux of switched nuclei entering the system. The system can be solved by the method developed in Ref. 31. The solution has the following form:

$$I(t)=\frac{I(\xi_0)\exp\{-T^k(t)\varphi_k[T(t)]\}}{1+\left(\frac{1}{\Gamma}\right)T^k(t)\varphi_k[T(t)]}, \tag{69}$$

$$N(t)=I(\xi_0)t_k\varphi_k[T(t)], \tag{70}$$

$$\xi(t)=\frac{\xi_0}{1+\left(\frac{1}{\Gamma}\right)T^k(t)\varphi_k[T(t)]}, \tag{71}$$

where $I(t)$ is the flux of the switched domains at the instant of time t; $N(t)$ is the density of the newly formed, switched domains at the instant t; and $\xi(t)$ is the relative repolarization at the instant t. Here, Γ is a parameter[31] defined as

$$\Gamma=-\frac{\xi_0}{k_B T}\frac{dR_{\min}}{d\xi}\bigg|_{\xi=\xi_0},$$

where $R_{\min}$ is the minimum work needed to form new-phase nuclei in a ferroelectric. In this case,

$$\Gamma=\frac{\pi H\sigma^2\omega\chi\varepsilon_0}{2p_{zi}P_{z10}\xi_0 k_B T}.$$

The distribution function of the switched region in the magnitude of polarization can be written in the form

$$f(\rho,t)=\begin{cases}\dfrac{I(\xi_0)t_0}{\xi_0}\exp\left[-\left(T(t)-\dfrac{t_0\rho}{t_k\xi_0}\right)\right]^k\varphi_k\left[\left(T(t)-\dfrac{t_0\rho}{t_k\xi_0}\right)\right] & \rho\leqslant\dfrac{\xi_0 t_k}{t_0}T(t),\\[2ex] 0 & \rho>\dfrac{\xi_0 t_k}{t_0}T(t).\end{cases} \tag{72}$$

Here $I(\xi_0)$ is the flux of nuclei, which is found from Eq. (51),

$$T=\frac{t}{t_k}-\frac{1}{\Gamma}\int_0^T x^k\varphi_k(x)\,dx, \tag{73}$$

$$t_k=\frac{t_0}{\xi_0}\left[\frac{\xi_0}{(k+1)\omega\Gamma I(\xi_0)\tau}\right]^{1/(k+1)},$$

where the auxiliary function $\varphi_k(x)$ is determined from the solution to the equation $d\varphi_k/dx=\exp(-x^k\varphi_k)$ subject to the condition $\varphi_k(0)=0$;[20,21,31] k is a coefficient depending on the mechanism of the nucleus growth.[20,21,31] In this case, $k=1$.

The maximum size of the switched region can be determined from the relationship

$$\rho_{\max}=\frac{\xi_0 t_k T(t)}{t_0},$$

Then,

$$T=\frac{t_0\rho_{\max}}{t_k\xi_0}.$$

The equality can be used as a definition of the renormalized time.

The set of Eq. (59) and (60) describes the nucleation process in crystals without impurities. If crystals contain the current of conductivity, defects, or sources of internal electrical fields, then their influence may be taken into account by additional terms in Eq. (60). We turn now to the study of the later stage in the evolution of an ensemble of switched regions.

D. Ostwald ripening of an ensemble of switched domains

Ostwald ripening is the final stage of a phase transition where no new nuclei are formed and the repolarization tends to zero.[20–22,32–34] In these conditions, a specific interaction sets in among the switched domains. The mean size of the polarization switching nuclei in the ensemble will grow as a result of "dissolution," i.e., the rotation of the polarization vector "against the field" and the growth of large nuclei due to aligning a part of the polarization vectors with the field.

In this process, the average magnitude of repolarization in the crystal will decrease. This is due to the decrease in the free energy of the system as a result of diminishing the interface, and, accordingly, diminishing stresses at the domain walls. In the general case, large domains will absorb small ones. A specific interaction sets in between the polarization switching nuclei, because each domain feels the cooperative polarization field of the whole domain system. This should be connected with the law of conservation of the total polarization in the system, Eq. (60). We rewrite Eq. (59) and Eq. (60) with the variables *R* and *t*, where *R* is the radius of the switched regions. Since

$$f(n,t)dn = f(R,t)dR,$$

we have

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R}[V_R f(R,t)] = 0. \tag{74}$$

In the stage of Ostwald ripening, domains of different sizes compete because of the growth of the critical nuclei in the system, which become comparable in radius to domains.

In the case where the domain's dimensions become comparable with the critical size, we should take into account not only the flux of cells attaching to a domain but the reverse cell flux bringing about dissolution of a domain as well. Therefore, in order to describe the growth rate of domains, we turn to Eq. (45). Recall that E_n can be expressed through the number of particles according to Eq. (39). After simple calculations, we obtain the following equation for the domain growth:

$$V_n = \frac{2\pi H \omega \beta_0 \sigma}{k_B T}\left(\frac{n^{1/2}}{n_c^{1/2}} - 1\right). \tag{75}$$

We now express Eq. (75) not in terms of the number of particles *n* in a domain but through domain radius *R*. As a result, the rate of domain growth by the normal mechanism is represented in the form

$$\frac{dR}{dt} = \frac{\beta_0 \omega^2 \sigma}{k_B T R}\left(\frac{R}{R_c} - 1\right). \tag{76}$$

We turn now to an analysis of the relationship derived. The balance Eq. (60) has the form

$$Q_0 + \int_0^t \xi_0(t')dt' = \frac{P_{z10} - \overline{P}_z(t)}{P_{z10}} + \frac{\pi H p_{zi}}{P_{z10}\omega}\int_0^\infty f(R,t)\, R^2 dR, \tag{77}$$

where

$$Q_0 = \frac{P_{z10} - \overline{P}_{z0}}{P_{z10}} + \frac{\pi H p_{zi}}{P_{z10}\omega}\int_0^\infty f_0(R)\, R^2 dR.$$

As in Refs. 20 and 33, we assume that the source $\int_0^t \xi_0(t)dt$ decays in time and can be approximated by the polynomials $\xi_0(t) = (\xi_0/\tau)t^{n-1}$, where $n \geqslant 0$ is the field growth index. For simplicity, we assume that the source is uniformly distributed in the sample. The coupled of Eqs. (74) and (77), together with Eqs. (71) or (77), which describe the growth rate of nuclei, make up a complete system and formally coincide fully with the equations describing the late stage in first-order phase transitions[33] (the Ostwald ripening stage).

The solution to such a system was obtained by Lifshitz and Slyozov (see Refs. 20, 21, and 33). However, there also exists a different and more rigorous asymptotic treatment[34] (see also Ref. 20), whose results will be used here. The Ostwald ripening stage can occur only in the case when the external field is either turned off after the formation of switched domains or varied with time so that the index *n* in Eq. (77) becomes smaller than $2/p$, where *p* is the growth index, and $p = 2$ for the growth of nuclei (76). Then, the mean size of nuclei varies with time as a result of evolution[20,34] as

$$\vec{R}(t) \rightarrow \text{const}' \cdot t^{1/p}, \tag{78}$$

where $p = 2$. The density of the nuclei varies with time as follows:

$$N(t) \rightarrow \text{const}\, t'' \;\cdot\; t^{(2/p-n)}. \tag{79}$$

The nucleus size distribution functions in dimensionless coordinates have the same form for the late stage of all phase transitions (see, for example, Refs. 20, 33, and 34).

We note in conclusion that because both the mean and critical sizes in the Ostwald ripening stage vary with time according to Eq. (78), the repolarization change with time should be as follows.

$$\xi(t) \rightarrow \text{const}''' \;\cdot\; t^{-1/p}. \tag{80}$$

In Eqs. (78)–(80), const′, const″, and const‴ are constants depending on the actual domain growth mechanism. These constants are readily found in the Lifshitz-Slyozov theory.[20,21,33,34] According to Ref. 34, in a general case, the constants are not determined theoretically and can be found only from comparison of the theoretical expressions with experimental data.

IV. SWITCHING CURRENT IN FERROELECTRICS AND COALESCENCE OF DOMAINS

The dependence of the switching current density on time in a ferroelectric capacitor can be written as follows:[7]

$$J = -2P_{z10}\frac{dQ}{dt}, \tag{81}$$

where dQ/dt is the rate of change in the ferroelectric volume fraction *Q* which has not yet switched and P_{z10} is the starting value of the spontaneous polarization of the ferroelectric. In the earliest switching stage, i.e., in the first stage of the phase transition, which we studied, the switching current should be zero. Indeed, the expression for the nucleus flux *I* derived [in Eq. (46)] describes the switching process only in the case when no noticeable volume fraction of the crystal has become involved in the phase transition and the rate of change in the crystal volume fraction is zero. The main switching current will start to flow when the system enters the stage of bulk polarization switching. The time of the onset and the duration of this stage can be estimated from formula.[18,19] To calculate the switching current in this stage, we pursue the following reasoning. The volume fraction, or the degree of sample volume filled by the nuclei of the new phase, can be calculated using two approaches. One of them is based on the well-known Kolmogorov-Avrami method.[18,19] This method was employed in Ref. 7 to determine the switching current. However, it is known that quantities such as the nucleation rate and the growth rate of the nuclei, which enter into the Kolmogorov-Avrami expression, are not parameters of this theory. They are calculated from other considerations. It is these parameters that we have just found. Now, we can insert them into the Kolmogorov-Avrami expression and calculate the current.

However, the Kolmogorov-Avrami expression is valid in the case when the growth rate of nuclei does not depend on their radiis and the repolarization remains constant throughout the process. As is seen from Eqs. (69)–(71), this is not so. Therefore, application of this theory to the process of transformation is not justified from the physical standpoint. Note that attempts at correcting this drawback have recently appeared.[35] However, we will use another approach, which makes it possible to describe rigorously the process of filling the system volume by growing nuclei with due regard for the change in the repolarization and the dependence of the growth rate of nuclei on their size.

This approach is based on the set of kinetic equations derived above [Eqs. (59) and (60)]. In a general case, the switching domains, as nuclei of the new phase,[20,21,36] can collide with one another and coalesce. If the system is sufficiently tenuous, we can assume the collisions to be primarily binary. To take them into account, we add the collision integral to the right-hand side of Eq. (59). This procedure was employed in Ref. 36 to take into account the collisions between nuclei in volume and surface systems. We can write the equation of evolution for the distribution function of polarization switching domains with inclusion of their possible collisions and coalescence; that is,

$$\frac{\partial f}{\partial t}+\frac{\partial[V_n f(n,t)]}{\partial n}=\frac{1}{2}\int_0^n \beta(n-n',n')\,f(n-n')\,f(n')\,dn' - f\int_0^\infty \beta(n,n')\,f(n')\,dn', \qquad (82)$$

$$f(n_0,t)=I(t)[1-Z(t)]\,V_n^{-1}\big|_{n=n_0},\quad f(n,0)=0, \qquad (83)$$

where $I(t)$ is the rate of nucleation, $Z=1-Q$ is the degree of filling of the ferroelectric volume by the polarization switching domains, and β is the coagulation kernel[36] [it is assumed that $f(n,t)=0$ at $n<n_0$]. Because the functions V_n and $I(t)$ depend on the repolarization $\xi(t)$, Eq. (82) should be complemented by the law of polarization conservation. We rewrite Eq. (63) with due regard for the fact that part of the unit volume of the ferroelectric is already occupied by switching regions. The region filled by the polarization switching nuclei is given by

$$Z(t)=\omega\int_0^\infty n\,f(n,t)\,dn. \qquad (84)$$

Then, the law of conservation Eq. (63), which was written taking into account that nucleation occurs only in empty sites, can be recast as

$$\frac{d\xi}{dt}=\frac{\xi_0}{\tau}-\frac{\xi}{\tau}-\frac{\left(\dfrac{P_{z2}}{P_{z10}}-1-\xi\right)}{(1-Z)}\frac{dZ}{dt}, \qquad (85)$$

where P_{z2} is the absolute value of polarization after switching, taking into account the applied electrical field. By solving the set of Eqs. (82)–(84) with the use of Eqs. (69)–(71), we can find all the main characteristics of the switching process. For some kinds of coagulation kernels, it is possible to obtain the analytic expression. A comprehensive analysis of the system requires knowledge of the mechanisms by which polarization switching domains interact with one another. These coupled equations were analyzed in the specific case of the growth of crystalline new-phase nuclei on the substrate surface.[20,21,36] For rigorous calculation of the switching current, we can use the analogy and invoke these results. We consider the application of this method in the simplest case, without inclusion of domain coalescence, i.e., the integral in the right-hand side of Eq. (82) is taken equal to zero. We write the expression for $Z(t)$ in the variables ρ and t bearing in mind that $\rho=n^{1/2}$ and $f(n,t)dn=q(\rho,t)d\rho$. Differentiating $Z(t)$ with respect to time and transforming it with the use of Eqs. (66), (67), and (49) under the condition that $q(\rho,t)|_{\rho\to\infty}=0$, we obtain

$$\left(\frac{Z'}{\xi}\right)'=\frac{2\omega\xi}{t_0^2}N, \qquad (86)$$

where t_0 is the characteristic growth time introduced earlier [see Eq. (66)] and N is the number of created nuclei. In the latter expression, the prime denotes the time derivative. Differentiating Eq. (86) once more with respect to time yields

$$\left[\frac{1}{\xi}\left(\frac{Z'}{\xi}\right)'\right]'=\frac{2\omega}{t_0^2}I[\xi(t)], \qquad (87)$$

where $I[\xi(t)]$ is the flux of the nuclei.

Since the equation for the switching current contains not Z' but $Q'=(1-Z)'$, the switching current takes the form

$$\left[\frac{1}{\xi}\left(\frac{j}{\xi}\right)'\right]'=-\frac{4\omega P_{z10}}{t_0^2}I(\xi). \qquad (88)$$

Thus, Eq. (88) together with Eq. (84) make up coupled equations for calculating the dependence of the switching current on time and applied field. We transform Eq. (85) to the form

$$j=-\frac{2P_{z10}\left(\dfrac{\xi_0}{\tau}-\dfrac{\xi}{\tau}-\xi'\right)(1-Z)}{\left(\dfrac{P_{z2}}{P_{z10}}-1-\xi\right)}. \qquad (89)$$

Substituting Eq. (89) in Eq. (88) yields

$$\left[\frac{1}{\xi}\left(\frac{\left(\dfrac{\xi_0}{\tau}-\dfrac{\xi}{\tau}-\xi'\right)(1-Z)}{\left(\dfrac{P_{z2}}{P_{z10}}-1-\xi\right)\xi}\right)'\right]'=\frac{2\omega}{t_0^2}I(\xi). \qquad (90)$$

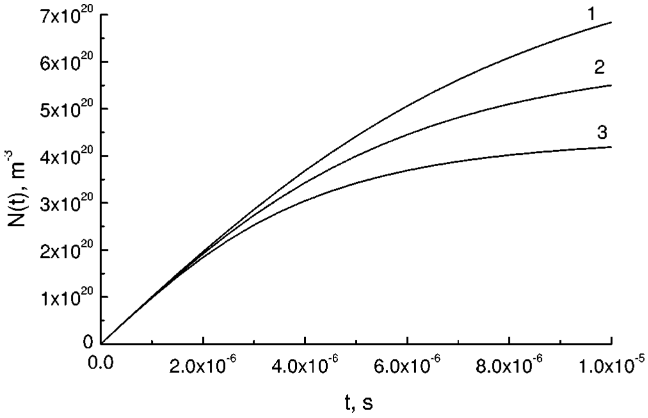

FIG. 3. Dependencies of the density of repolarized domains $N(t)$ versus time for different electrical fields: $1-E_z=10^7$ V m^{-1}, $2-E_z=6\cdot 10^6$ V m^{-1}, and $3-E_z=3\cdot 10^6$ V m^{-1}.

This equation determines the dependence of the supersaturation on time. The initial conditions here are that the switching current, its derivatives with respect to time, and the supersaturation are zero.

The $I(\xi)$ dependence was found earlier in formula (49); we recast in the form

$$I(\xi)=I_0\xi^{1/2}e^{-\alpha/\xi}, \qquad (91)$$

where $I_0=(N_v\beta_0\sqrt{H\omega p_{zi}P_{z10}})/(\sqrt{k_BT\chi\varepsilon_0})$, $\alpha=(\pi H\omega\sigma^2\chi\varepsilon_0)/(2k_BTp_{zi}P_{z10})$.

The constants I_0, t_0, and α entering into the expression for the flux of the nuclei $I(\xi)$ can be determined by comparing the theoretical dependencies of the switching current with the experimental dependencies. These data can be used to obtain a number of the parameters for ferroelectrics (surface tension σ, the kinetic coefficients β_0, etc). Moreover, the equations derived make it possible to determine the flux and the number of the switched domains formed in the course of polarization switching. Thus, investigation of the polarization current in ferroelectrics opens up a unique possibility for studying some parameters of materials, which are difficult to determine otherwise.

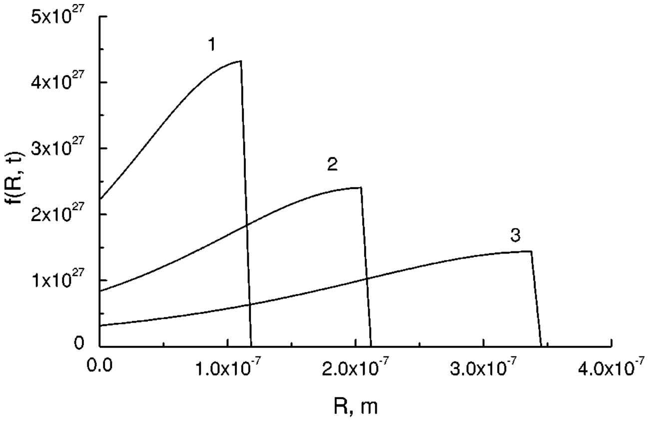

FIG. 4. Distribution function of repolarized domains in size at $t=t_k$ and different electrical fields: $1-t_k=5\cdot 10^{-6}$ s at $E_z=10^7$ V m^{-1}, $2-t_k=7{,}5\cdot 10^{-6}$ s at $E_z=6\cdot 10^6$ V m^{-1}, and $3-t_k=2\cdot 10^{-5}$ s at $E_z=3\cdot 10^6$ V m^{-1}.

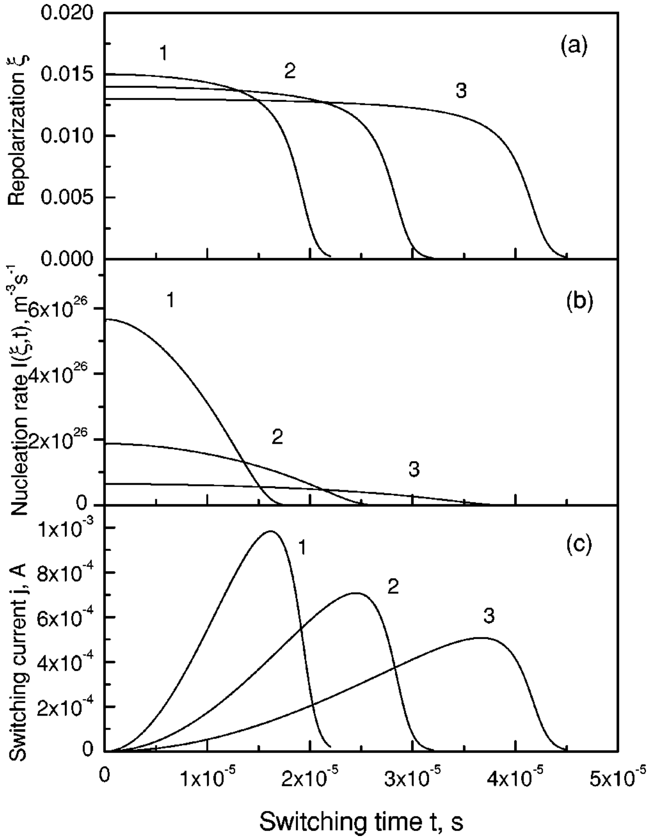

FIG. 5. Repolarization (a), the nucleation rate (b), and switching current (c) versus time and the electrical-field strength ($1-E_z=10^7$ V m^{-1}; $2-E_z=6\cdot 10^6$ V m^{-1}; $3-E_z=3\cdot 10^6$ V m^{-1}) for $I_0\sim 10^{38}$, α=0,2, $\tau=10^{-8}$ s, $t_0\sim 10^{-10}$ s, $P_{z2}/P_{z10}\sim 1{,}2$, and $S=10^{-9}$ m^2, where S is the square of the sample.

Note that if the mechanisms of domain coalescence are known, solving the complete system Eqs. (88)–(90) will provide more complete and accurate information on these constants. It should be remembered that in developing our theory, we assumed that the ferroelectric crystal was a perfect dielectric, the leakage current was zero, and that there were no pinning centers impeding domain-wall motion. Usually, ferroelectric crystals contain defects of various types. Nucleation is known to proceed more intensively at defects. In principle, this can be taken into account. Such a study was performed in the specific case of nucleation of a new phase on the surface of a substrate.[20,21]

V. DISCUSSION OF THE RESULTS AND COMPARISON WITH EXPERIMENTS

Now, we shall estimate some of the relationships obtained for triglycinesulfate crystals with 180° domains. For the Curie point $T_c\sim 322$ K, surface tension at $T\sim 302$ K; $\sigma\sim 0{,}6\times 10^{-3}$ J m^{-2}; $P_{z10}\sim 3\times 10^4$ μ C m^{-2}; $\chi\sim 20$; $\varepsilon_0=8{,}85\times 10^{-12}$ F m^{-1}; and $\omega\sim 6{,}7\times 10^{-28}$ m^3, according to Ref. 6. Hence, in the field $E=10^5$ V m^{-1} the critical size of domains R_c determined by Eq. (40) equals $R_c\sim 10^{-1}$ μm, that is, in close agreement with the data outlined in Ref. 6. Substituting also the data into Eq. (56) and estimating β_0 as $\beta_0 \sim 10^{31}$ m^{-2} s^{-1}, we obtain $t \sim 10^{-9}$ for the setting time of stationary flow in fields $E \sim 10^5$ V m^{-1}. In a similar way, we can estimate the flow value I for nucleating domains by formula (50). Thus, if the switching field equals, for instance, $V \sim 10^7$ then for the crystal being just at the same temperature $I = 10^{44}\sqrt{H}\exp(-H\cdot 10^8)$ m^{-3} s^{-1}. Thus, we set $H \sim 1/\omega^{1/3}$. In the general case, the nucleation frequency, as it can be seen above, may be dependent on the sample thickness. In thin films, which, as a rule, consist of small blocks, the probability of nucleation of repolarization domains will appreciably depend on the sizes of blocks.

In the cases with field values $V \sim 10^7$ V m^{-1}, $I_0 \sim 10^{38}$, $\alpha \sim 0{,}2$, and $t_0 \sim 10^{-10}$ s. Time dependencies of the density of repolarized domains $N(t)$ are given in Fig. 3 and distribution functions [abscissa—radius R, ordinate—$f(R,t) = f(\rho,t)d\rho/dR$] of repolarized domains for TGS crystals at different values of the switching field are given in Fig. 4. The density of repolarized domains was calculated by Eq. (70), the distribution functions by Eq. (72). The switching current, the nucleation rate, repolarization versus time, and the field value for the above values of constants (TGS crystals) are plotted in Fig. 5 in correspondence with Eqs. (89)–(91). It is shown that the curves indicate qualitatively well the dependence of switching current in ferroelectrics.[1,3,4,9]

In conclusion, we note that in similar ways the switching processes can be examined in ferroelectric crystals of a wider class (not only in ferroelectrics with 180° domains). In these cases it is necessary to introduce additional terms into the isobar-isotherm potential dependence and to take into account whether the elastic energy components occurred. In future, we intend to develop this approach. Nevertheless, the equations derived in this work should retain their general form.

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