
**ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM**

Theoretical Model for Thin Ferroelectric Films and the Multilayer Structures Based on Them

A. S. Starkov^{a,*}, O. V. Pakhomov^a, and I. A. Starkov^b

^a*Institute of Refrigeration and Biotechnologies, St. Petersburg National Research University ITMO,
St. Petersburg, 191002 Russia*

^{*}*e-mail: starkov@iue.tuwien.ac.at*

^b*Institute for Microelectronics, Vienna University of Technology, Wien, A-1040 Austria*

Received December 14, 2012

Abstract—A modified Weiss mean-field theory is used to study the dependence of the properties of a thin ferroelectric film on its thickness. The possibility of introducing gradient terms into the thermodynamic potential is analyzed using the calculus of variations. An integral equation is introduced to generalize the well-known Langevin equation to the case of the boundaries of a ferroelectric. An analysis of this equation leads to the existence of a transition layer at the interface between ferroelectrics or a ferroelectric and a dielectric. The permittivity of this layer is shown to depend on the electric field direction even if the ferroelectrics in contact are homogeneous. The results obtained in terms of the Weiss model are compared with the results of the models based on the correlation effect and the presence of a dielectric layer at the boundary of a ferroelectric and with experimental data.

DOI: 10.1134/S1063776113060149

1. INTRODUCTION

Thin ferroelectric films and the multilayer structures based on them attract the attention of scientists due to the possibilities of their diverse applications in designing next-generation memory devices, capacitors, pyroelectric detectors, cooling devices based on the electrocaloric effect, and so on (see, e.g., [1–12]). To describe the electric fields appearing in these thin films is important from the viewpoint of both applied and fundamental science. The latter seems to be very important because of the experimentally detected unique properties of the thin films that distinguish them from bulk ferroelectrics. For example, the differences consist in a shift in the maximum of permittivity and a change in the losses [6, 7]. The dependence of the properties of a film on its thickness is taken to be called the size effect. As a rule, the ferroelectric films produced to date are polycrystalline and consist of granules several tens of nanometers in size. According to the experimental data in [1, 13], each granule is coated with a passive dielectric layer 2–5 nm thick with a permittivity of 40. This dielectric layer substantially changes the properties of the ferroelectric. In particular, if the granule size is smaller than a certain critical value (which is 10 nm for PbTiO_3 and 40 nm for BaTiO_3), spontaneous polarization in such ferroelectrics is absent at room temperature [13]. To describe the size effects in ferroelectric films theoretically, researchers usually apply the Landau theory of second-order phase transitions and add the terms taking into account the surface, deformation, and gradi-

ent effects to the free energy equation [2–12]. It is well known [14] that the Weiss and Ising models serve as the basis for deriving the equation of state of an infinite ferroelectric. The effect of the boundaries of a ferroelectric is thought to be studied in terms of these models as well. It can easily be shown that the Ising model in the simplest version cannot describe the detailed behavior of polarization near a ferroelectric boundary; therefore, the Weiss model should be used to describe a finite ferroelectric. The purpose of this work is to apply the Weiss theory near an interface.

The structure of this work is as follows. In Section 2, we derive (at a mathematical level of rigor) variational principles for ferroelectrics that generalize the variational principles of classical electrodynamics. The possibility of introducing the gradient terms describing the correlation effect and affecting boundary conditions into the Lagrangian is studied in Section 3. In Section 4, we discuss a ferroelectric layer model based on the correlation effect. The dependence of the critical temperature on the film thickness predicted by this model is compared with experimental data.

The simplest two-layer ferroelectric–dielectric system is studied in Section 5 for the case of plane-parallel layers. In contrast to [4, 6–8], we consider the case where the permittivity of the dielectric is variable. In Section 6, the Weiss approach is modified for the case of bounded ferroelectrics. The main subject of inquiry is the temperature dependence of spontaneous polarization. Since the model under study is one-dimen-

sional, the coefficients in the related expansions are scalars; in the general case, they are considered to be tensors. In this work, we touch upon only some problems related to the surface of a ferroelectric. Other problems, such as the formation of domains, the effect of deformation, and the presence of a charge [6, 7, 15] and substance concentration gradients [16], were already resolved. Nevertheless, many phenomena, e.g., thermodeformation and thermoelectric ones, have not been taken into account on describing the boundary of a ferroelectric.

2. VARIATIONAL PRINCIPLES AND MAXWELL EQUATIONS FOR A FERROELECTRIC

To obtain an equation of state for a ferroelectric, researchers as a rule use the condition of the minimum thermodynamic potential at a given field strength [17]. In this approach, the conditions at the interface are partly derived from the Maxwell equations and are partly postulated. In this work, we propose to introduce a thermodynamic potential into a known Lagrangian (action) for an electromagnetic field from the very beginning. We formulate the following natural requirement: the standard Maxwell equations should appear when the nonlinear terms in the equation relating electric field \mathbf{E} to polarization \mathbf{P} disappear. To describe the electromagnetic field in volume Ω , we use scalar ($\varphi(\mathbf{x}, t)$), vector ($\mathbf{A}(\mathbf{x}, t)$), and thermodynamic ($F(\mathbf{P}, t)$) potentials, where t is the time and \mathbf{x} is the radius vector in the coordinate space. The electromagnetic field is a local field whose action S is specified as

$$S = \int_0^t \int_{\Omega} \mathcal{L}(\mathbf{x}, t, \mathbf{P}, T) dx dt. \tag{1}$$

In Eq. (1), the Lagrangian has the form

$$\mathcal{L}(\mathbf{x}, t, \mathbf{P}, T) = \frac{\varepsilon_0}{2}(\nabla\varphi - \mathbf{A}_t)^2 + (\nabla\varphi - \mathbf{A}_t) \cdot \mathbf{P} - \frac{1}{2}[\nabla \times \mathbf{A}]^2 - F(\mathbf{P}, T), \tag{2}$$

where ε_0 is the dielectric constant. The time scale is chosen so that the velocity of light is unity and currents are absent in the system. The magnetic properties of the medium are not taken into account. For them to be taken into account, it is sufficient to add another magnetization-dependent thermodynamic potential to the right-hand side of Eq. (2). Note that the Lagrangian did not contain a thermodynamic potential earlier

[18]. The Euler–Lagrange equations are reduced to the relationships [19]

$$\sum_{i=1}^3 \frac{\partial}{\partial x_i} \mathcal{L}_{\partial\varphi/\partial x_i} = 0, \tag{3}$$

$$\frac{\partial}{\partial t} \mathcal{L}_{\partial A_i/\partial x_i} + \sum_{j=1}^3 \frac{\partial}{\partial x_j} \mathcal{L}_{\partial A_i/\partial x_j} = 0, \quad \frac{\partial \mathcal{L}}{\partial \mathbf{P}} = 0.$$

where x_i and A_i ($i = 1, 2, 3$) are the Cartesian components of vectors \mathbf{x} and \mathbf{A} , respectively, and the subscripts of \mathcal{L} mean the derivatives with respect to these variables. We can easily obtain the explicit form of these equations,

$$\nabla \cdot (\varepsilon_0(\nabla\varphi - \mathbf{A}_t) + \mathbf{P}) = 0, \tag{4}$$

$$\frac{\partial}{\partial t}(\varepsilon_0(\nabla\varphi - \mathbf{A}_t) + \mathbf{P}) - \nabla \times \nabla \times \mathbf{A} = 0,$$

$$\nabla\varphi - \mathbf{A}_t = \frac{\delta F}{\delta \mathbf{P}}. \tag{5}$$

Let electric field be $\mathbf{E} = \nabla\varphi - \mathbf{A}_t$ and magnetic field be $\mathbf{H} = \nabla \times \mathbf{A}$. Then, we have

$$\nabla \cdot (\varepsilon_0 \mathbf{E} + \mathbf{P}) = 0, \quad \varepsilon_0 \mathbf{E}_t + \mathbf{P}_t = \nabla \times \mathbf{H}. \tag{6}$$

It follows from the definition of \mathbf{H} that

$$\nabla \cdot \mathbf{H} = 0; \tag{7}$$

in turn, for \mathbf{E} we can write $\nabla \times (\mathbf{E} + \mathbf{A}_t) = 0$, i.e.,

$$\mathbf{H}_t = -\nabla \times \mathbf{E}. \tag{8}$$

The set of Eqs. (6)–(8) is taken to be the Maxwell equations. The equation

$$E_i = \frac{\delta F}{\delta P_i} \tag{9}$$

should be added to them; this equation is called a constitutive equation [20] and it relates polarization to the electric field. It is the form of this equation that distinguishes a ferroelectric from a dielectric. Note that Eq. (9) cannot be considered irrespective of the set of the Maxwell equations. We choose the thermodynamic potential in the Landau–Ginzburg form [17]

$$F(\mathbf{P}) = \frac{a}{2} \mathbf{P}^2 + \frac{b}{4} \mathbf{P}^4, \tag{10}$$

where a and b are the Landau–Ginzburg coefficients, and obtain the constitutive equation in the form

$$\mathbf{E} = a\mathbf{P} + b\mathbf{P}^3. \tag{11}$$

Thus, action extremum condition (1), (2), and (10) can be used to obtain Maxwell equations (6)–(8) and constitutive equation (11). This derivation is also valid in the case where coefficients a and b are continuous functions of time and space coordinates. These equations should be complemented with boundary conditions for a layered system, where the coordinate dependences of a and b have a jump at the interface. Before performing the required refinements, we present certain generally accepted simplifications in the problem under study. In most cases, the time con-

stant for the processes to be studied is large as compared to the characteristic time for electromagnetic processes (which is determined as the ratio of the characteristic system size to the velocity of light). Therefore, the time derivatives may be neglected because of their smallness and only scalar potential φ is used. As a result of these simplifications, we obtain the following energy functional G :

$$G = \int_{\Omega} \frac{\varepsilon_0}{2} (\nabla\varphi)^2 + \nabla\varphi \cdot \mathbf{P} - F(\mathbf{P}, T) dx, \quad (12)$$

the extremum condition of which yields the desired relationship between \mathbf{E} and \mathbf{P} .

3. BOUNDARY CONDITIONS AT THE FERROELECTRIC INTERFACE

We now pass to discussing the boundary conditions and assume that coefficients $a = a(\mathbf{x})$ and $b = b(\mathbf{x})$ are continuous functions of coordinates in region Ω except for certain surface Σ , where they have a simple discontinuity; that is, Σ is the interface of media with different properties. According to the classical calculus of variations, the Weierstrass–Erdmann conditions [19], which are only determined by the form of functional, must be met at the interface of the media. For action (1), (2), and (10) or functional (12), these conditions are well known and require the continuity of potential φ , the normal component of dielectric displacement vector $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$, and the tangential component of the field on surface Σ .

Since we speak about the Weierstrass–Erdmann conditions, we discuss the possibility of introducing term $g(\nabla\mathbf{P})^2/2$ with certain constant g , as was proposed in [2–4, 8–12, 21], into thermodynamic potential G . Then, Laplacian appears in constitutive equation (11) and a new Weierstrass–Erdmann condition, which consists in the continuity of the normal component of polarization P_n , appears. In this case, the normal components of dielectric displacement \mathbf{D} and polarization \mathbf{P} (hence, electric field \mathbf{E}) should be continuous at interface Σ , which is in conflict with the generally accepted electromagnetic field equations. Therefore, a term with $(\nabla\mathbf{P})^2$ cannot exist in the expression for thermodynamic potential F . The presence of this term causes errors. For example, when calculating the permittivity of thin ferroelectric films, the authors of [21] did not pay attention to the fact that the gradient of piecewise constant polarization \mathbf{P} contains the generalized Dirac delta function. Hence, the integral of $(\nabla\mathbf{P})^2$ diverges in this case. One of the possible versions of retaining a gradient term is the substitution $\nabla\mathbf{P} \rightarrow \nabla\mathbf{D}$, i.e., the choice of a thermodynamic potential in the form

$$F(\mathbf{P}) = \frac{a}{2} \mathbf{P}^2 + \frac{b}{4} \mathbf{P}^4 + \frac{g}{2} (\nabla\mathbf{D})^2. \quad (13)$$

Then, the constitutive equation that relates polarization to electric field takes the form

$$\mathbf{E} = -g\Delta\mathbf{D} + a\mathbf{P} + b\mathbf{P}^3. \quad (14)$$

In this case, the Weierstrass–Erdmann conditions at the interface are consistent with the Maxwell equations. In the next section, we study Eq. (14).

4. PHASE TRANSITION IN A THIN FILM WITH ALLOWANCE FOR THE CORRELATION EFFECT

The polarization in thin films is nonuniform across the film thickness. If axis z is directed across a film, the spatial distribution of polarization modulus $P(z) = |\mathbf{P}|$ with allowance for the correlation effect in the absence of an electric field is determined by solving the equation

$$-g \frac{d^2 P}{dz^2} + aP = bP^3, \quad (15)$$

which is the one-dimensional version of Eq. (14) at $\mathbf{E} = 0$. As boundary conditions, we choose the polarization blocking conditions [22]

$$P(0) = P(h) = 0, \quad (16)$$

where h is the film thickness. We assume that a polarization vector is parallel to the film plane and $\mathbf{P} = \mathbf{D}$. If polarization vector \mathbf{P} is normal to the film plane, the dielectric displacement is constant ($\mathbf{D} = \text{const}$), the polarization equation is not differential, and polarization is uniform across the film thickness. Thus, the correlation effect cannot be used to explain the size effect when polarization is normal to the film plane. The exact solution to this problem was obtained in, e.g., [2, 3]. In the ferroelectric phase ($a < 0$, $T < T_C$), the solution to the set of Eqs. (1) and (16) is expressed through elliptic functions,

$$P(z) = P_S \sqrt{\frac{2m}{1+m}} \sinh\left(\frac{z}{h_0 \sqrt{1+m}}, m\right). \quad (17)$$

where $P_S = \sqrt{-a/b}$ is the spontaneous polarization of a thick film, $h_0 = \sqrt{-g/a}$ is the correlation length, and $\sinh(x, m)$ is the elliptic sine [23]. Parameter m is determined from the transcendental equation

$$h = 2h_0 \sqrt{1+m} K(m), \quad (18)$$

where $K(m)$ is the elliptical integral of the first kind [23]. For $P(z)$ to be real, the condition $0 \leq m \leq 1$ must be met. It follows from the properties of elliptic functions that the limit $m \rightarrow 1$ corresponds to a thick film ($h \gg \pi h_0$) and the limit $m \rightarrow 0$ corresponds to $h \rightarrow \pi h_0$. The existence of this limit demonstrates the presence of a certain critical film thickness $h_c = \pi h_0$ that corresponds to zero spontaneous polarization, and spontaneous polarization is absent at a smaller film thickness. Therefore, the phase transition from a ferroelectric into a paraelectric phase can occur when the

film thickness decreases (thickness-induced phase transition). Phase-transition temperature T_{ch} is lower than Curie temperature T_C . The temperature dependence of T_{ch} follows from Eq. (18) and has the form

$$T_{\text{ch}} = T_C \left[1 - \left(\frac{h_c(0)}{h} \right)^2 \right], \quad (19)$$

$$h_c(0) = \pi \sqrt{\frac{g}{a_0 T_C}},$$

where $h_c(0)$ is the critical film thickness at $T = 0$ and a_0 is the Curie–Weiss constant in the formula that describes the temperature dependence of the Landau–Ginzburg coefficient ($a = a_0(T - T_C)$). At $h \leq h_c(0)$, the film is in the paraelectric phase over the entire temperature range and spontaneous polarization is absent. The main disadvantage of this approach is revealed when Eq. (18) is compared with the experimental dependence of the phase-transition temperature on the film thickness obtained in [24] for barium titanate BaTiO_3 ,

$$T_{\text{ch}} = T_C - \frac{1000}{h}. \quad (20)$$

Formula (19), which describes the quadratic dependence of the phase-transition temperature on the reciprocal film thickness, is in obvious conflict with experimental Eq. (20), where this dependence is linear. Note that the temperature dependence enters into an arbitrary solution to Eq. (15) only through the dependence on h_0 in variable z/h_0 ; that is, quadratic dependence (19) is present in all solutions to Eq. (15) without exception. Of course, the character of this dependence can be slightly changed using, e.g., impedance-type boundary conditions [2, 22]; however, linear dependence (20) cannot be obtained at any boundary conditions. Thus, a comparison of the dependence of phase-transition temperature T_{ch} with the experimental data allows us to conclude that the model under study incorrectly describes the experimental results and that it should be refined. We now pass to studying a simpler model, where the transition layer is modeled by a dielectric layer (passive layer model [6, 15]).

5. PHASE TRANSITION IN A TWO-LAYER FERROELECTRIC–DIELECTRIC SYSTEM

We consider a flat ferroelectric layer of thickness h_f (medium 1) on which a dielectric layer of thickness h_d is placed (medium 2). Hereafter, the quantities belonging to the ferroelectric and dielectric layers are indicated by subscripts “ f ” and “ d ”, respectively. We designate the total layer thickness as $h = h_f + h_d$, direct coordinate z across the layers, and suppose that permittivity $\varepsilon_d(z)$ in medium 2 is variable. We also assume that the outer boundaries of the system have no potential; i.e., spontaneous polarization is sought for. This problem was repeatedly considered but for constant ε_d

[6, 15]. Let E and P with the corresponding subscripts be the projections of field and polarization vectors onto axis z , respectively. Then, the constitutive equations that relate these quantities have the form

$$E_f = aP_f + bP_f^3, \quad P_d = \varepsilon_0(\varepsilon_d - 1)\varepsilon_0 E_d. \quad (21)$$

Apart from Eqs. (21), the field and polarization meet the condition of absent space charges,

$$\frac{d}{dz}(\varepsilon_d(z)E_d(x)) = 0, \quad \frac{d}{dz}(\varepsilon_0 E_f + P_f) = 0. \quad (22)$$

Hence, with allowance for Eq. (20), it follows that $E_f = \text{const}$ and $E_d(x) = E_2/\varepsilon(x)$, where E_2 is the constant of integration unknown at this stage of computations. Moreover, the electric displacement at the boundary $z = h_f$ should be continuous,

$$\varepsilon_0 \varepsilon_d(h_f) E_d = \varepsilon_0 E_f - P_f, \quad (23)$$

and the boundaries $z = 0$ and $z = h$ should have no potential difference,

$$E_f h_f + E_2 \int_{h_f}^h \frac{dz}{\varepsilon_d(z)} = 0. \quad (24)$$

We now designate the ratio of the layer thicknesses as $\kappa = h_d/h_f$ and introduce the effective permittivity of the dielectric as

$$\frac{1}{\varepsilon_{\text{ef}}} = \frac{1}{h_d} \int_{h_f}^h \frac{dz}{\varepsilon(z)}. \quad (25)$$

Then, Eq. (24) can be rewritten in the form

$$E_f + E_2 \varepsilon_{\text{ef}} \kappa = 0. \quad (26)$$

For brevity, we introduce parameter

$$\eta = \frac{\kappa h_d \varepsilon_{\text{ef}}}{\varepsilon_0(\kappa h_d \varepsilon_{\text{ef}} + 1)}. \quad (27)$$

With these introduced designations, we write the solution to problem (21)–(24) as

$$P_f = \sqrt{\frac{a + \eta}{b}}, \quad E_f = -\eta P_f, \quad (28)$$

$$E_d = -\frac{E_f}{\kappa h_d \varepsilon_{\text{ef}}}.$$

Let us discuss these results. The spontaneous polarization of the ferroelectric–dielectric system turns out to be identical to that of a single ferroelectric with Landau–Ginzburg coefficient a replaced by $a + \eta$. This means the displacement of the Curie temperature by

$$\Delta T_C = \eta/a_0. \quad (29)$$

Thus, the decrease in the Curie temperature linearly depends on the dielectric layer thickness and is inversely proportional to the ferroelectric layer thickness. This conclusion is supported by the experimental results in [24]. For a given temperature, there is a critical ratio of the dielectric to the ferroelectric layer thickness κ_c so that the system has no spontaneous polarization at $\kappa > \kappa_c$. Note that, despite a zero poten-

tial, the field is nonzero and its directions in the ferroelectric and dielectric layers are opposite to each other: the field direction in the ferroelectric is opposite to the polarization direction (depolarizing field), and the field and polarization directions in the dielectric coincide with each other. Note also that the derived formulas have no coordinate dependence $\epsilon_d(z)$ in an explicit form and only contain the dependence on the effective permittivity.

6. WEISS FIELD NEAR INTERFACE

Various approaches are used to calculate phenomenological coefficients a and b in Landau–Ginzburg equation (11) [14, 17]. We consider the self-consistent Weiss field approximation as the simplest one. Recall its basic points for infinite ferroelectrics [20]. Self-consistent electric field E_{ef} in a ferroelectric is the sum of true electromagnetic field E and molecular field βP ,

$$E_{ef} = E + \beta P, \tag{30}$$

where β is a certain positive constant characterizing the properties of the ferroelectric. Let N dipoles with constant electric moment p_0 be present in the unit volume of a ferroelectric. We now circumscribe ball B of radius r_0 around a certain arbitrary point in the ferroelectric and designate the polar angle measured from direction \mathbf{E} as θ . The value of r_0 is determined by the characteristic dipole–dipole interaction distance. In the classical Weiss theory, the solution is independent of r_0 . The potential energy of a dipole in an electric field is

$$U = -p_0 E_{ef} \cos \theta. \tag{31}$$

According to the Boltzmann theorem, the distribution of molecules is determined by the equation

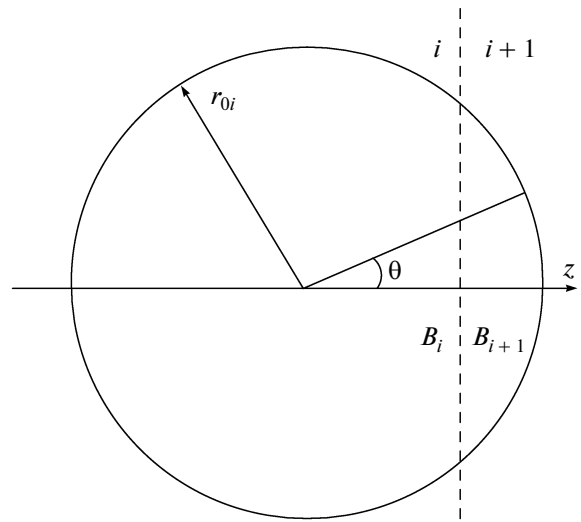
$$\begin{aligned} dN &= c \exp\left(-\frac{U}{k_B T}\right) \sin \theta d\theta \\ &= c \exp(\alpha \cos \theta) d\theta. \end{aligned} \tag{32}$$

Here, k_B is the Boltzmann constant; dN is the number of the dipoles with the angles of their axes falling in the range between θ and $\theta + d\theta$; $\alpha = p_0 E_{ef} / k_B T$; and c is a normalization constant determined from the condition that the total number of dipoles in ball B is VN , where $V = 4\pi r_0^3 / 4$ is the ball volume, or

$$\int_{(B)} dN = VN. \tag{33}$$

Since the integral is

$$\int_0^\pi e^{\alpha \cos \theta} \sinh \theta d\theta = \frac{2 \sinh \alpha}{\alpha}, \tag{34}$$



Position of ball B with respect to the interface of two media.

the constant is found to be $c = \alpha N / \sinh \alpha$. The total dipole moment is $p_0 dN$ and its projection onto direction \mathbf{E} is $p_0 \cos \theta dN$. Therefore, the ferroelectric polarization satisfies the equation

$$\begin{aligned} P &= \int_0^\pi p_0 \cos \theta e^{\alpha \cos \theta} \sin \theta d\theta \\ &= p_0 N \left(\coth \alpha - \frac{1}{\alpha} \right). \end{aligned} \tag{35}$$

At $\beta = 0$, Eq. (33) was first derived by Langevin and the function $L(\alpha) = \coth \alpha - 1/\alpha$ is called the Langevin function. At $E \rightarrow \infty$, polarization asymptotically tends toward its limiting value $P_\infty = p_0 N$. Assuming $E = 0$, we find spontaneous polarization $P_S = P(E = 0)$ by the equation

$$y = L\left(\frac{3T_C}{T} y\right), \tag{36}$$

where normalized pressure $y = P_S / P_\infty$ is unknown and $T_C = p_0^2 \beta N / 3k_B$ is the phase-transition temperature (Curie temperature). At low fields, the Langevin equation transforms into Landau–Ginzburg equation (11) [20].

The computations performed above become invalid near the interface between two ferroelectrics, where part B_1 of the circle is in one medium (medium 1) and part B_2 is in the other medium (medium 2) (see figure). We direct axis z normal to the interface, place its origin at the interface, and assume that the field is parallel to this axis. Note that the result will be different at other \mathbf{E} directions; that is, the permittivity and other medium parameters near the interface depend on both the electric field and its direction.

Hereafter, subscripts 1 and 2 indicate the corresponding media. Polarization near the interface is an unknown function of coordinate z , $P = P(z)$. Obviously, at a distance larger than r_0 from the interface, polarization becomes constant: $P(z) = P_1$ at $z < r_0$ and $P(z) = P_2$ at $z > r_0$, where $P_{1,2}$ is the polarization for an infinite ferroelectric with number 1 or 2. Therefore, we are interested in the behavior of polarization only in the transition layer $|z| < r_0$. Coordinate z is connected with polar radius r and angle θ by the standard relation $z = r \cos \theta$. Formula (32) is valid if α is taken to be a function of coordinate z ,

$$\alpha(z) = \frac{p_0(z)(E(z) + \beta(z)P(z))}{k_B T(z)}, \tag{37}$$

and coefficients $p_0(z)$ and $\beta(z)$ are assumed to be piecewise constant,

$$\beta(z) = \begin{cases} \beta_1, & z < 0, \\ \beta_2, & z > 0, \end{cases} \tag{38}$$

$$p_0(z) = \begin{cases} p_{01}, & z < 0, \\ p_{02}, & z > 0. \end{cases}$$

Here, $\beta_{1,2}$ and $p_{01,2}$ are constants characterizing the media with the corresponding number. Temperature $T(z)$ is considered to be constant, $T(z) = T = \text{const}$, and the thermoelectric effects changing temperature are assumed to be low. Equation (33) is replaced by the equation

$$\int_{(B)} dN = V_1 N_1 + V_2 N_2, \tag{39}$$

where $V_{1,2}$ is the part of ball B located in medium 1 or 2, respectively. With Eq. (39), we can find constant c in Eq. (32). The equation

$$P(z) = \frac{(V_1 N_1 + V_2 N_2) \int \int_{(B)} p_0(z) e^{\alpha(z) \cos \theta} r^2 \sin \theta \cos \theta d\theta dr}{2\pi \int \int_{(B)} e^{\alpha(z) \cos \theta} r^2 \sin \theta d\theta dr}. \tag{40}$$

is a generalization of the Langevin equation. For $P(z)$ to be unambiguously determined from Eq. (40), it should be complemented with a continuity equation relating $E(z)$ to $P(z)$ and a condition for determining $E(z)$ should be formulated. Since the field distribution in an inhomogeneous medium depends strongly on the potential, we consider the simplest case (considered in Section 4) where an applied field is absent and media 1 and 2 have finite temperature hysteresis h_1 and h_2 . In this case, the electric field should meet the condition

$$\int_{-h_1}^{h_2} E(z) dz = 0. \tag{41}$$

The continuity condition is formulated in the standard form

$$\varepsilon_0 E(z) + P(z) = D, \tag{42}$$

where D is a constant electric displacement. Thus, to find polarization $P(z)$ (or electric field $E(z)$), we have to solve nonlinear integral equation (40) along with conditions (41) and (42). In contrast to the case of a homogeneous ferroelectric, problem (40)–(42) is too complex to be solved even numerically and the standard methods of solving integral equations are inapplicable here. The proposed version of generalizing the mean-field theory is the simplest and, of course, has certain disadvantages. For example, the equipotential

surface for the field of an electric dipole is assumed to be a sphere. This assumption holds true only of homogeneous space. Radius r_0 is taken to be independent of the properties of a ferroelectric and to be the same in media 1 and 2. More exact results can be obtained if a more rigorous formula is taken for the dipole field near the interface and integration is performed over the entire space. Nevertheless, the following qualitative conclusions can be drawn from the form of Eq. (40) (or its more exact analog) despite the absence of an exact solution. A transition layer of a certain thickness ($2r_0$ for the model under study) appears at the interface between two ferroelectrics or a ferroelectric and a dielectric. The polarization and electric field are continuous at the interface but change rather sharply within the transition layer. A surface charge density at the interface is absent in the Weiss theory. In this case, the permittivity in this layer depends on the electric field direction even if the media in contact are homogeneous.

Explicit formulas can be written in the case where the transition layer thickness is small as compared to the ferroelectric thickness, $r_0/h \ll 1$. Then, we do not need an explicit form of dependence $P(z)$; as will be shown below, the knowledge of an integral characteristic of this dependence is sufficient. Thus, we now consider the problem of finding spontaneous polarization and its temperature dependence in the two-layer system consisting of a ferroelectric layer of thickness h_f

and a transition layer of thickness $2r_0$, $h_f + 2r_0 = h$. The ferroelectric is assumed to obey the Landau–Ginzburg equations

$$E = aP + bP^3, \quad z \in [0; h_f]. \quad (43)$$

Continuity condition (42) should be met in the entire system. Moreover, the system boundaries should have no potential difference,

$$\int_0^h E(z) dz = 0. \quad (44)$$

We consider the transition layer as a small perturbation of the ferroelectric layer. As a result, we can use the perturbation theory and search for the solution to the problem in the form of the sum of the solution to the unperturbed problem and small correction terms,

$$P = P_S + \delta P, \quad E = \delta E, \quad D = P_S + \delta D, \quad (45)$$

where δP , δE , and δD are small quantities, $O(r_0/h)$. The smallness is understood in an integral sense, i.e.,

$$\int_0^h |\delta P(z)| dz = O(r_0). \quad (46)$$

As a result of elementary manipulations, we obtain the relationship

$$\varepsilon \delta E = -\frac{P_S}{h} \int_0^h \left(1 - \frac{P(z)}{P_S}\right) dz. \quad (47)$$

Equation (47) relates depolarizing field δE to the integral value of polarization in the transition layer. When comparing Eqs. (28) and (47), we can draw the following conclusion: if the dielectric layer thickness and its permittivity satisfy the relationships

$$h_d = 2r_0, \quad \frac{1}{\varepsilon_{ef}} = \frac{1}{2r_0} \int_0^h \left(1 - \frac{P(z)}{P_S}\right) dz, \quad (48)$$

the model of a ferroelectric with a dielectric layer and the Weiss model give the same (accurate to small quantities $O(r_0/h)$) values for the depolarizing field, the polarization, and (hence) the phase-transition temperature. Therefore, the mean-field theory can justify the passive layer model. In both models, the phase-transition temperature depends linearly on the reciprocal layer thickness, which agrees with the experimental data in [24].

7. CONCLUSIONS

We studied the possibility of introducing a term proportional to polarization gradient squared into the Landau–Ginzburg thermodynamic potential and showed that this term $((\nabla P)^2)$ causes boundary conditions that contradict the classical Maxwell electrodynamics. As a consequence, this term should be excluded from consideration or should be replaced by electric displacement gradient squared $(\nabla D)^2$. In turn,

to describe the boundary of a ferroelectric, we propose to use the Weiss mean-field model instead of taking into account the gradient terms. An analysis of the equations following from this model demonstrates the presence of a thin transition layer at the boundary of a ferroelectric. The permittivity of this layer depends on the electric field direction (even in the absence of this dependence in the ferroelectrics in contact), and the polarization and the electric field satisfy a complex nonlinear integral equation, which generalizes the well-known Langevin equation to the case of adjacent media. Since we failed to find an exact solution to this integral equation, we constructed an approximate solution using the smallness of the transition layer thickness as compared to the dielectric layer thickness. The final formulas only include the average polarization in the transition layer. The results obtained by the Weiss model and the passive layer model coincide with each other at a certain set of parameters. In other words, we showed the possibility of simulating the presence of a transition layer in multilayer ferroelectric structures by a thin dielectric layer. This finding makes it possible to substantially simplify the calculations of the physical parameters of materials of this type.

REFERENCES

1. Y. Ishibashi, H. Orihara, and D. R. Tilley, *J. Phys. Soc. Jpn.* **67**, 3292 (1998).
2. L.-H. Ong, J. Osman, and D. R. Tilley, *Phys. Rev. B: Condens. Matter* **63**, 144109 (2001).
3. M. Glinchuk, E. Eliseev, and V. Stephanovich, *Phys. Solid State* **44** (5), 953 (2002).
4. Z.-G. Ban, S. P. Alpay, and J. V. Mantese, *Phys. Rev. B: Condens. Matter* **67**, 184104 (2003).
5. A. L. Roytburd, S. Zhong, and S. P. Alpay, *Appl. Phys. Lett.* **87**, 092902 (2005).
6. N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. Tagansev, D. V. Taylor, T. Yamada, and S. Streiffer, *J. Appl. Phys.* **100**, 051606 (2006).
7. A. K. Tagantsev and G. Gerra, *J. Appl. Phys.* **100**, 051607 (2006).
8. I. B. Misirlioglu, G. Akcay, S. Zhong, and S. P. Alpay, *J. Appl. Phys.* **101**, 036107 (2007).
9. J. H. Qiu and Q. Jiang, *J. Appl. Phys.* **103**, 034119 (2008).
10. X. Lu, B. Wang, Y. Zheng, and C. Li, *J. Phys. D: Appl. Phys.* **41**, 035303 (2008).
11. J. H. Qiu and Q. Jiang, *J. Appl. Phys.* **105**, 034110 (2009).
12. V. M. Fridkin, R. V. Gaynutdinov, and S. Ducharme, *Phys.—Usp.* **53** (2), 199 (2010).
13. K. Ishikawa and T. Uemori, *Phys. Rev. B: Condens. Matter* **60**, 11841 (1999).
14. B. Strukov and A. Levanyuk, *Ferroelectric Phenomena in Crystals: Physical Foundations* (Springer-Verlag, Berlin, 2012).

15. A. Tagantsev, L. Cross, and J. Fousek, *Domains in Ferroic Crystals and Thin Films* (Springer-Verlag, Berlin, 2010).
16. M. Marvan, P. Chvosta, and J. Fousek, *Appl. Phys. Lett.* **86**, 221922 (2005).
17. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 8: L. Landau, E. Lifshitz, and L. Pitaevskii, *Electrodynamics of Continuous Media* (Nauka, Moscow, 1982; Butterworth–Heinemann, Oxford, 1995).
18. I. Savelyev and G. Leib, *Fundamentals of Theoretical Physics* (Mir, Moscow, 1982).
19. N. Akhiezer and M. Alferieff, *The Calculus of Variations* (Taylor and Francis, London, 1988).
20. I. Tamm, *Fundamentals of the Theory of Electricity* (Nauka, Moscow, 1976; Mir, Moscow, 1979).
21. V. N. Nechaev and A. V. Shuba, *Bull. Russ. Acad. Sci.: Phys.* **72** (9), 1230 (2008).
22. O. G. Vendik and S. P. Zubko, *J. Appl. Phys.* **82**, 4475 (1997).
23. H. Bateman, *Higher Transcendental Functions* (McGraw-Hill, New York, 1955).
24. S. T. Davitadze, S. N. Kravchun, B. A. Strukov, B. M. Goltzman, V. V. Lemanov, and S. G. Shulman, *Appl. Phys. Lett.* **80**, 1631 (2002).

Translated by K. Shakhlevich

SPELL: OK