

## Smearing of Phase Transition due to a Surface Effect or a Bulk Inhomogeneity in Ferroelectric Nanostructures

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The boundary conditions, customarily used in the Landau-type approach to ferroelectric thin films and nanostructures, have to be modified to take into account that a surface of a ferroelectric is a defect of a field type. The surface (interface) field is coupled to a normal component of polarization and, as a result, the second order phase transitions are generally suppressed and anomalies in response are washed out, as observed experimentally.

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Theoretical studies of phase transitions in thin films and the corresponding size effects within the Landau theory [1] have been undertaken since the 1950s. Recently, the interest in these questions has risen dramatically in view of the applications of ferroelectric thin films [2] and a discovery of various ferroelectric nanostructures [3]. The boundary conditions for thin films were originally discussed by Ginzburg and Landau (GL) in 1950 [4]. It was shown by GL that, if the properties of the boundary layer are the same as of the bulk, one arrives at the condition that the gradient of the order parameter  $\eta$  vanishes at the surface,  $\vec{\nabla}_{\vec{n}}\eta = 0$  (in zero magnetic field,  $\vec{n}$  is the normal to the surface). Starting from a microscopic theory, de Gennes has shown that for a superconductor-metal interface with no current and magnetic field a more general boundary condition applies,  $\vec{\nabla}_{\vec{n}}\eta + \eta/\delta = 0$ , where  $\delta$  is the characteristic length scale describing the proximity effect [5]. These conditions are very general and were introduced phenomenologically by Kaganov and Omelyanchouk for a surface of a ferromagnet [6] (cf. [7]). They assumed that the surface energy was  $\propto \eta^2$ . Kretschmer and Binder [8], using the same boundary conditions, have taken into account the depolarizing field, present for a polarization (magnetization) perpendicular to a surface. These boundary conditions are customarily used in studies of phase transitions in ferroelectric films (see, e.g., [9]).

The choice of a surface energy dependence on the order parameter must be governed by symmetry considerations, as it is for a bulk energy. Surface symmetry is different from a symmetry of the bulk, and this is of special importance for ferroelectrics. A surface eliminates all symmetry elements that change the direction of the normal to the surface. If the order parameter (or one of its components) is a vector perpendicular to the surface, the surface energy contains a linear “field” term reminiscent of a “local field defect” [10]. The “local field” is absent for superconducting or magnetic order parameters because the surface does not break either gauge or time-reversal symmetry. A Coulomb dipole field (double layer), contributing to the

work function [11,12], and structural surface relaxation (see, e.g., [13]) are different aspects of this phenomenological field. If the order parameter is not a vector, the field term may appear in special cases if the surface eliminates appropriate symmetry elements. If the field term is absent, some higher order terms, forbidden in the bulk, can still be allowed by the surface symmetry. We illustrate the effect of new boundary conditions for the thin film of uniaxial ferroelectric (FE). This is relevant also to perovskite ferroelectrics that are cubic in the bulk but become tetragonal in thin films because of elastic misfit with a substrate. Let the surface be perpendicular to the polar axis  $z$ . The Landau-Ginzburg-Devonshire (LGD) free energy for the bulk between electrodes 1 and 2 at  $z = \mp l/2$  is [14,15]

$$F_{\text{LGD}} = \int_2^1 dV \left[ \frac{1}{2}AP^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{2}g\left(\frac{dP}{dz}\right)^2 + \frac{1}{2}D(\nabla_{\perp}P)^2 \right], \quad (1)$$

where  $P \equiv P_z$ , and one adds to it the surface energy which, generalizing Ref. [6], can be written in the form

$$F_s = \int_{1+2} dS \left( \frac{1}{2} \alpha P^2 - wP \right), \quad (2)$$

where  $\alpha$  corresponds to a “temperaturelike” component of the surface energy and  $w$  to its field component. We obtain from Eqs. (1) and (2) the *new correct boundary conditions* for ferroelectrics in the same way as in Ref. [6],

$$\alpha_{1(2)}P + (-)g \frac{dP}{dz} = w_{1(2)}, \quad z = +(-)l/2. \quad (3)$$

In cgs units, one can estimate that  $\alpha \sim d_{\text{at}}$ , where  $d_{\text{at}}$  is the characteristic “atomic” length scale, on the order of the lattice constant. The electric field at the surface [11,12] is on the order of  $\Phi_s/d_{\text{at}} \sim 1 \text{ V}/\text{\AA} \approx 10^8 \text{ V/cm}$ , where  $q\Phi_s \sim 4 \text{ eV}$  is the typical work function for ferroelectrics [2]. The surface field corresponds to a polarization, which is on the order of an atomic polarization  $P_{\text{at}} = q/d_{\text{at}}^2 \sim 200 \mu\text{C/cm}^2$ , so that  $w \sim P_{\text{at}}d_{\text{at}}$ . We expect that the struc-

tural relaxation contribution to  $w$  is of the same order of magnitude: from first-principles calculations at the ideal surfaces of BaTiO<sub>3</sub> and PbTiO<sub>3</sub> the surface polarization  $P_{\text{surf}} \sim 10^{-1} P_{\text{at}}$  [13]. Usually, the top and bottom electrode interfaces to the FE film are dissimilar and the thickness of the surface polarized layers is  $\sim d_{\text{at}}$ . This is enough to produce a considerable field in the film. Indeed, the field in the surface double layer is  $E_1 = -4\pi P_{\text{surf}} \sim -4\pi P_{\text{at}}$ . If, for example, we consider a short-circuited film with strongly asymmetric double layers at the interfaces (so that the voltage drop on the second layer is much smaller than the one on the first layer) the surface voltage drop  $\sim E_1 d_{\text{at}}$  must be compensated by the field in the bulk,  $E_{\text{bulk}} = -E_1 d_{\text{at}}/l = 4\pi P_{\text{at}}/l$ . For example, in a film with a thickness  $l \sim 1000 \text{ \AA}$  we find  $E_{\text{bulk}} \sim P_{\text{at}} d_{\text{at}}/l \sim 300 \text{ kV/cm}$ , which is very strong indeed. In a ferroelectric film this field smears second order transitions and may smear a first order phase transition. In a freestanding FE film the role of electrodes would be played by a surface conductivity and/or atmospheric ions. Note that in a rare case of *symmetric* surfaces the surface dipoles produce no electric field in the film and *no smearing* of the phase transition occurs. The polarization  $P(z)$  is found from the equation of state for (1) and the Poisson equation:

$$AP + BP^3 + CP^5 - g d^2 P/dz^2 = E, \quad (4)$$

$$d(E + 4\pi P)/dz = 0, \quad (5)$$

$$(1/l) \int_1^2 Edz = (\varphi_1 - \varphi_2)/l \equiv E_0, \quad (6)$$

where  $E_0$  is the external electric field. We obtain from Eqs. (5) and (6)

$$E = E_0 - 4\pi[P(z) - \bar{P}], \quad (7)$$

where the overbar means an average over the film, i.e.,  $\bar{f} = (1/l) \int_1^2 dz f(z)$ . One probes experimentally not the actual surface polarization but the net polarization in the sample. Indeed, the experiment measures the surface charge  $\sigma$ , which is equal to the normal component of the displacement field,  $\sigma = D_z/4\pi = E_0/4\pi + \bar{P}$ . Therefore, we need to find an equation for the net polarization  $\bar{P}$ , which, from the symmetry arguments alone, should have the form

$$\check{A}\bar{P} + b\bar{P}^2 + \check{B}\bar{P}^3 + f\bar{P}^4 + \check{C}\bar{P}^5 = E_0 + W/l, \quad (8)$$

since the terms of all powers in  $\bar{P}$  are allowed in a system with asymmetric boundaries. Below, we solve the system (4)–(7) with the boundary conditions (3) and find the coefficients in the generic equation of state (8). To find the net polarization  $\bar{P}$ , we integrate the equation of state (4) over the film with the use of the boundary conditions (3):

$$\begin{aligned} A\bar{P} + B\bar{P}^3 + C\bar{P}^5 + (3B\bar{P} + 10C\bar{P}^3)\overline{\delta P^2} + \\ (B + 10C\bar{P}^2)\overline{\delta P^3} + 5C\bar{P}\overline{\delta P^4} + C\overline{\delta P^5} = E_0 + R/l, \end{aligned} \quad (9)$$

$$R \equiv w_1 + w_2 - \alpha_1 P_1 - \alpha_2 P_2, \quad (10)$$

where  $\delta P = P(z) - \bar{P}$ ,  $P_{1(2)} = P[+(-)l/2]$  is the surface polarization that can be expressed via the coefficients  $c_{1(2)}$  introduced in Eq. (12). To find  $\delta P$ , we subtract Eq. (9) from Eq. (4) and obtain

$$\check{A}\delta P + K_2 + K_3 + K_4 + K_5 - g d^2 \delta P/dz^2 = -R/l, \quad (11)$$

where the cumulants  $K_2 = (3B\bar{P} + 10C\bar{P}^3)(\delta P^2 - \overline{\delta P^2})$ ,  $K_3 = (B + 10C\bar{P}^2)(\delta P^3 - \overline{\delta P^3})$ ,  $K_4 = 5C\bar{P}(\delta P^4 - \overline{\delta P^4})$ , and  $K_5 = C(\delta P^5 - \overline{\delta P^5})$  can be neglected under the conditions used below,  $\check{A} = 4\pi + A + 3B\bar{P}^2 + 5C\bar{P}^4 \approx 4\pi$ , since  $A = (T - T_c)/T_0$  and for displacive systems  $T_0 \sim 10^5 \text{ K}$ , so we are in a regime where  $|A| \lesssim T_c/T_0 \ll 1$ . The solution of the Eq. (11) is

$$\begin{aligned} \delta P = -R/(\check{A}l) + c_1 \exp[-\lambda(z + l/2)] \\ + c_2 \exp[-\lambda(l/2 - z)], \end{aligned} \quad (12)$$

where  $\lambda = (\check{A}/g)^{1/2} \sim d_{\text{at}}^{-1}$ .

The fact of appearance of the atomic length  $1/\lambda \sim d_{\text{at}}$  in our phenomenological treatment is important and was actually noticed in Ref. [8]. Physically, it appears because the spatial changes of polarization lead to bound charges and strong “depolarizing” fields at the interfaces. Strictly speaking, the present phenomenological derivation is valid for models with  $\sqrt{g} > d_{\text{at}}$ . From the data [16] for 90° domain walls in PbTiO<sub>3</sub> we get a typical estimate  $1/\lambda = (g/4\pi)^{1/2} = 0.4\text{--}0.5 \text{ \AA}$ . Therefore, the results below are semiquantitative; the exact values of the coefficients in (8) are to be found from a microscopic theory.

We can find an approximate solution keeping the leading terms linear in  $1/l$ :

$$c_{1(2)} = (w_{1(2)} - \alpha_{1(2)}\bar{P})/(\alpha_{1(2)} + \lambda g), \quad (13)$$

and obtain from the condition  $\int \delta P dz = 0$

$$R = \lambda g \left( \frac{w_1 - \alpha_1 \bar{P}}{\alpha_1 + \lambda g} + \frac{w_2 - \alpha_2 \bar{P}}{\alpha_2 + \lambda g} \right). \quad (14)$$

The averages in Eq. (9) are then easily calculated with the use of (12):  $\overline{\delta P^n} = (c_1^n + c_2^n)/(n\lambda l)$  for  $n = 2\text{--}5$ . Further simplification is possible if we assume that the characteristic length  $\sqrt{g} \gg d_{\text{at}}$ , while  $\alpha \sim d_{\text{at}}$ , meaning that we

have a small parameter  $\alpha/\lambda g \ll 1$ . In this case the terms  $K_{2,\dots,5}$  contain higher powers of the small parameter  $\alpha/\lambda g$  and can indeed be omitted. Expanding the results in terms of the small parameter  $\alpha/\lambda g \ll 1$ , we find

$$\check{A} = A + a/l, \quad (15)$$

$$W = w_1(1 - \alpha_1/\lambda g) + w_2(1 - \alpha_2/\lambda g), \quad (16)$$

$$a = \alpha_1 + \alpha_2 + \beta, \quad (17)$$

$$\check{B} = B + \Delta B, \quad (18)$$

where  $\beta = 3B(w_1^2 + w_2^2)/(2g^2\lambda^3) + 5C(w_1^4 + w_2^4)/(4g^4\lambda^5)$  and  $\Delta B = 5C(w_1^2 + w_2^2)/(g^2\lambda^3l)$ . The terms  $b$  and  $f$  have no effect on a behavior near the phase transition, since they are proportional to  $d_{\text{at}}/l$ , and can be shown to be small. They can be neglected together with the renormalization of the coefficient  $C$ . The dielectric function is

$$\epsilon = 1 + \frac{4\pi}{A + a/l + 3\check{B}\bar{P}^2 + 5C\bar{P}^4}, \quad (19)$$

with  $\bar{P}$  determined from Eq. (8) and has a smooth peak in all systems with nonsymmetric electrodes. In a symmetric case ( $W = 0$ ) the second order transition is shifted down proportionally to  $1/l$ . Indeed, in the Landau theory  $A = (T - T_{c0})/T_0$ , where  $T_0 \sim T_{\text{at}} \sim 10^5$  K in displacive ferroelectrics,  $T_{c0}$  is the phase transition temperature in the bulk, and the transition temperature in the film is

$$T_c - T_{c0} = -aT_0/l. \quad (20)$$

This result is similar to the one after Kretschmer and Binder [8], but what is new here is that the shift depends on surface dipoles via the new term  $\beta$  that pushes the transition temperature down. Indeed,  $B$  is negative but small for weak first order transitions as in perovskites, while  $C$  has the usual atomic value,  $C \sim P_{\text{at}}^{-4}$ . The first order phase transition is pushed closer to the second order, because of positive renormalization of the coefficient  $B \rightarrow \check{B}$ . The shift of temperature of the first order transition in the symmetric case is defined mainly by the renormalization of the coefficient  $A$ . Indeed, the condition of the first order transition  $\check{A}_1 = 3\check{B}^2/16C$  can be presented as

$$A_1 = A_{\text{Ibulk}} - a/l + 3B\Delta B/8C, \quad (21)$$

where  $A_{\text{Ibulk}} = 3B^2/16C > 0$  corresponds to the homogeneous first order transition in the bulk and we have neglected the term  $\propto l^{-2}$ . Note that if, according to Eq. (21),  $A_1$  becomes negative due to the  $-a/l$  term above the temperature of the first order phase transition, it cannot then take place because prior to that transition the system splits into domains. Indeed, it has been shown in Ref. [14] that the ferroelectric transition in a film with perfect metallic electrodes and a “dead layer” (e.g., vacuum layer) proceeds with the domain formation even with dead layers

down to atomic thicknesses. The imperfect screening by metallic electrodes will produce similar results. The strongly polarized surface regions that we consider here are analogous to those dead layers. The value of  $A$  corresponding to the transition with the domain formation depends on the materials parameters and can be roughly estimated as  $A \sim -d_{\text{at}}/(l\epsilon^{1/2})$ , where  $\epsilon$  is the dielectric constant in the direction perpendicular to the polar axis [14,17]. For perovskites, which are uniaxial due to a misfit strain, the value of  $\epsilon$  can be large, so that the condition for the domain formation is  $A < -d_{\text{at}}/(l\epsilon^{1/2})$  and can be met in a tiny temperature interval just below the loss of stability of the paraelectric phase that occurs at the point  $A = 0$ . Therefore, in experiments with symmetric electrodes one would see a phase transition very near  $A = 0$ , which is close to the transition temperature in the bulk, as observed in [18].

The present theory may, at least qualitatively, explain the observed surprisingly strong smearing of the phase transitions in thin films, both epitaxial and polycrystalline [19,20]. Indeed, we made the estimate of the dielectric constants for  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x = 0.3$ ) for thicknesses  $l = 1200$  and  $775$  nm, which is in good semiquantitative agreement with the recent data [20] (Fig. 1). The value of the surface bias field has been in the range  $0.07$ – $0.1$  cgs, which corresponds rather accurately to our above order-of-magnitude estimates. Slower falloff in the data at low temperatures may be related to the usual presence of domains in this temperature region. It is worth mentioning that there have been various hypotheses put forward to explain the observed very strong smearing of the phase transition, like a “dead” layer or the relaxor behavior [19]. We point out that both of those explanations are not likely in the case of epitaxially grown thin films. In particular, the relaxor model would require a presence of strong nano-

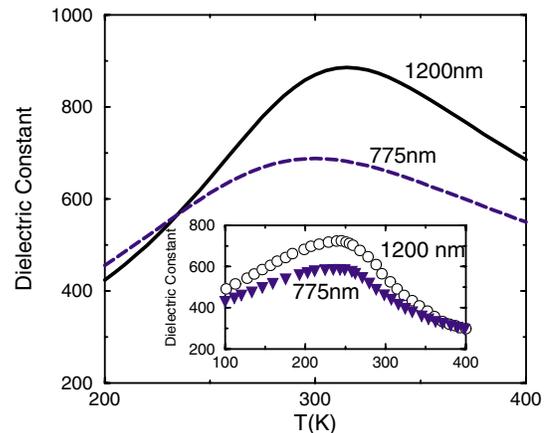


FIG. 1 (color online). Theoretical dielectric constants for films of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  with thicknesses  $l = 1200$  and  $775$  nm showing complete smearing of the phase transition as a result of the surface bias field (see text for discussion). Inset: the data from Ref. [21].

meter scale disorder, whereas in, e.g., epitaxial Pb(Zr, Ti)O<sub>3</sub> films on strontium ruthenate, there is practically an ideal atomic registry with the substrate [21].

The surface polarization discussed above is a special case of a polarization due to gradients of a scalar quantity (concentration  $c$  of, e.g., oxygen vacancies, density, temperature, etc.), and they are accounted for by a term like

$$f_c = -\gamma \vec{P} \vec{\nabla} c, \quad (22)$$

in the free energy, where the coefficient  $\gamma$  is estimated as  $\gamma \sim P_{\text{at}} d_{\text{at}}$  [22–24]. This field should be taken into account in the case of a film with a compositional profile (grading) given by, e.g., the concentration of one of the components of a ferroelectric alloy  $c = c(z)$ . Generally, the other coefficients of the thermodynamic potential also become inhomogeneous. There are FE systems with intentional concentration profile (graded) [25] and unintentional (e.g., with a defect concentration profile) that are currently a focus of research. The equation of state of the graded ferroelectric film with  $c = c(z)$  is

$$A(z)P + BP^3 + CP^5 - g \frac{d^2 P}{dz^2} - D \nabla_{\perp}^2 P = E_0 + 4\pi(\bar{P} - P) + \gamma \frac{dc}{dz}. \quad (23)$$

If it were possible to neglect the inhomogeneity in other coefficients of the thermodynamic potential, we have to simply add an average value of the field  $\gamma dc/dz \sim \gamma \Delta c/l$  to the bias field  $(\tilde{w}_1 + \tilde{w}_2)/l$ , where  $\Delta c$  is the difference of concentration through the sample ( $\Delta c_{\text{max}} = 1$ ). Accounting for the inhomogeneities of the Landau coefficients makes the problem more difficult because even small inhomogeneities of the coefficients have been shown to lead to the domain formation if the bias field is absent [17]. As above, the main effect of the surface bias fields is smearing out of the phase transition into a monodomain state. However, a phase transition with formation of a domain structure remains a possibility. For a special case of stepwise concentration we have found elsewhere [26] that (i) in the case of symmetric boundaries our previous results [17] are not changed essentially by the presence of the interface field  $\gamma$  and the soft part splits into domains. In the case (ii) of asymmetric boundaries the domain formation is possible but only for a much larger compositional inhomogeneity.

We have described a new mechanism of strong phase transition smearing in thin films where surface acts as a defect coupled to the order parameter. Other types of transitions, e.g., antiferroelectric ones, may be smeared by a similar effect. In thicker films, other defects like the grain boundaries would produce the bias field that can be described in the same terms as Eq. (23) and will smear out the transition (as seen in ceramic films). Asymmetric point defects will produce a bias field in the bulk and would contribute to the smearing [10]. However, in thin films one

should expect that the surface effect is the dominant one in smearing the phase transition.

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