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Surface state on first-order ferroelectrics

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Abstract. In the presence of a surface the Landau-Devonshire equations of ferroelectricity must be extended to include a boundary condition. For a ferroelectric with a second-order transition in the case when the polarization $p(z)$ increases at the surface, it is well known that a surface state occurs in a range of temperature above the bulk critical temperature t_{CB}. Here we explore the corresponding effect for a first-order ferroelectric. We show that a surface state can occur, but only if the surface effect is sufficiently strong. Analytic expressions are derived and illustrated for $p(z)$, the surface value $p_S = p(0)$ and the free energy. The transition from the paraelectric state ($p = 0$) to the surface state is first order, and for completeness we establish the dependence of the three critical temperatures (supercooling, thermodynamic and superheating) on a boundary-condition parameter y. In a final section, we derive and illustrate expressions for $p(z)$in the temperature range $t < t_{CB}$.

PACS. 77.80.Bh Phase transitions and Curie point – 68.35.Rh Phase transitions and critical phenomena – 73.20.-r Electron states at surfaces and interfaces

1 Introduction

The technology of ferroelectric memories has seen tremendous progress, which is actually made possible as the results of the exploitation of the characteristics properties of ferroelectrics particularly thin film ferroelectrics [1,2]. Important advances in recent years in the physics of thin-film ferroelectrics, particularly its oxides, have been reviewed recently by Dawber et al. [3]. As the trend of device fabrication is to have higher packing density per area, it therefore leads to the reduction in size of the individual component. In particular, miniaturization of the components results in aggravating the surface and size effects that influence the extrinsic properties of ferroelectric thin film such as dielectric properties, critical temperature, and etc. [1,2]. These effects may ultimately affect the quality and efficiency of devices. The influence of surface in particular is a fundamental problem that has to be addressed in order to improve further on device performance. In order to gain a deeper understanding of the underlying physics, the problem is best considered normally from the first-principle calculations but they are usually quite computer demanding [3–7]. Hence, other theoretical and computer simulation approaches are more often exploited to study the surface influence. Examples of these approaches are the Landau-Ginzburg (LG) theory [8–10], the Ising model in a transverse field [11,12], the mean-field theory [13], and an atomic-level simulation technique [14].

The presence of surfaces in thin films leads to the possibility of a surface-ordered state. In the surface-ordered state, the transition temperature is higher than the critical temperature for bulk ferroelectrics and the spontaneous polarization becomes a function of distance from the surface. It is found experimentally that the polarization can be suppressed or even enhanced in FE materials with reduced spatial dimension [15,16]. The extent of the distance dependence is known to be related to the surface parameter, and thus for a very thin film, the effect could alter the polarization profile significantly and could have a dramatic influence not only on the intrinsic characteristics but also on the dynamics properties of the film. We have studied this further by investigating the properties of the surface-ordered state for single surface ferroelectrics undergoing first-order phase transition. The single surface problem is chosen because of the simplicity in understanding the physics and the effects found can easily be related to the effects existed in ferroelectrics films. Furthermore, there are many materials undergoing a first-order paraelectric to ferroelectric transition and we mention in particular $BaTiO_3$ and $Bi_4Ti_3O_2$.

The Landau-Devonshire (LD) form of mean-field theory is widely used to model the phase transition to ferroelectricity [17]. The free energy F is expanded as a power

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series in the components of the polarization $\mathbf{P}$. In the simplest form of the theory the expansion is truncated at quartic terms and the expressions derived for equilibrium quantities such as the static polarization describe a second-order thermodynamic transition. In practice, most transitions to ferroelectricity are first order and to describe these, the expansion of F must be continued to include sixth-order terms in $\mathbf{P}$.

The possibility of a surface-ordered state with a transition temperature higher than the critical temperature for bulk ferroelectricity was considered by Kretschmer and Binder [18] using the extension of Landau theory that had previously been applied to magnetic surfaces by Lubensky and Rubin [19]. In the surface state, since $\mathbf{P}$ is a function of distance z from the surface, thust F must be written as an integral over z, with the integrand including a term in $|\nabla\mathbf{P}|^2$. The minimum of F that corresponds to the equilibrium state $P(z)$ is then determined by an Euler-Lagrange equation. This can only be solved with the aid of a boundary condition which is derived from the lowest-order surface invariants in F. Kretschmer and Binder [18] derived analytic forms for $P(z)$ and for the surface critical temperature T_{CS}. Despite the importance of first-order transitions in ferroelectricity, comparatively little has been done to extend this form of study to first-order materials. And the first question is: does a surface state occur at all?

Interestingly, any work on first-order surfaces would have been thought to be numerical in nature, however here, we show that in fact analytic expressions in terms of elementary functions can be found for $P(z)$ and related quantities for the surface state on a first-order ferroelectric. The transition from the high-temperature paraelectric phase into the surface state is first order. We give analytic results for the supercooling and superheating temperatures in terms of the parameter y (inverse extrapolation length) that characterizes the surface, and we show a numerically calculated curve for the y dependence of the thermodynamic critical temperature. From the latter we are able to prove that the surface state exists only for $y > y_C$, where the critical value is $y_C \cong 0.37$. In addition to the main work on the surface state, we also derive expressions for the surface modification of $P(z)$ when the temperature is below the bulk critical temperature.

2 Formalism and reduced units

We start by reviewing the LD theory and introduce the dimensionless units which can be used to derive quasi-universal results. For a bulk material the LD free-energy density may be written in terms of the polarization P (dipole moment per unit volume) as [20]

$$F_B = \frac{A}{2\varepsilon_0}P^2 + \frac{B}{4\varepsilon_0^2}P^4 + \frac{C}{6\varepsilon_0^3}P^6, \quad B < 0, \quad C > 0. \quad (1)$$

Here A, B and C are phenomenological constants. The powers of ε_0 in the denominators are not always used, but they are convenient for some purposes, for example the calculation of nonlinear-optical coefficients [21,22]. In order to reproduce the experimental behaviour, in particular the susceptibility and specific heat, A is taken to depend on temperature T:

$$A = a\,(T - T_0)\,. \quad (2)$$

Here we introduce the units that have been used previously [23,24] and are similar to those used by Lines and Glass [20] in their discussion of the dielectric hysteresis loop. We define

$$p = P/P_0 \quad \text{with} \quad P_0^2 = \varepsilon_0\,|B|\,/2C, \quad (3)$$

$$f_B = F_B/F_0 \quad \text{with} \quad F_0 = |B|^3\,/8C^2, \quad (4)$$

and a reduced temperature

$$t = \frac{4aC\,(T - T_0)}{|B|^2}\,. \quad (5)$$

Note that (5) is a scaling of $T - T_0$ and not merely of T. In consequence, negative values of t can occur. Furthermore, the value of t corresponding to $T = 0$ is a material-dependent parameter, so the results to be derived are quasi-universal rather than universal.

Substituting (3) to (5) into (1) we find

$$f_B = \frac{1}{2}tp^2 - \frac{1}{2}p^4 + \frac{1}{6}p^6\,. \quad (6)$$

Solution of $\frac{df}{dp} = 0$ for non-zero p yields an expression for the bulk polarization p_B:

$$p_B^2 = 1 + (1 - t)^{1/2}\,. \quad (7)$$

Following a common procedure, we find the thermodynamic critical temperature $t_{CB} = 0.75$, where the free energies of the paraelectric and ferroelectric phases are equal. The ferroelectric phase can persist as a metastable phase (local, but not global, minimum) up to a critical superheating temperature $t_{SHB} = 1.0$. Likewise the paraelectric phase can persist as a metastable phase down to the critical supercooling temperature $t_{SCB} = 0$. In summary,

$$t_{SCB} = 0, \quad t_{CB} = 0.75, \quad t_{SHB} = 1.0. \quad (8)$$

We add B for bulk to distinguish these from the corresponding surface values, which will be found later.

The new results to be presented later are for the surface of a first-order ferroelectric. For a semi-infinite sample we use the obvious generalization of the form applied for second-order materials [18,19,25,26], namely

$$F = \int_0^\infty \left[\frac{A}{2\varepsilon_0}P^2 + \frac{B}{4\varepsilon_0^2}P^4 + \frac{C}{6\varepsilon_0^3}P^6 + \frac{D}{2\varepsilon_0}\left(\frac{dP}{dz}\right)^2\right]dz + \frac{1}{2\delta}P_S^2, \quad (9)$$

where P_S is the value of P at the surface. We define dimensionless units by means of (3) and (5) together with

$$\zeta = \frac{B}{2C^{1/2}D^{1/2}}z \quad (10)$$

to find

$$f = \int_0^{\infty} \left[\frac{1}{2}tp^2 - \frac{1}{2}p^4 + \frac{1}{6}p^6 + \frac{1}{2}\left(\frac{dp}{d\zeta}\right)^2 \right] d\zeta + \frac{1}{2\eta}p_S^2, \tag{11}$$

where the dimensionless p_S is the surface value of p,

$$f = \frac{4C^{3/2}}{D^{1/2}B^2}F \tag{12}$$

and

$$\eta = \frac{B}{2C^{1/2}D^{1/2}}\delta. \tag{13}$$

Variation of f with respect to p gives the Euler-Lagrange equation

$$\frac{d^2p}{d\zeta^2} - tp + 2p^3 - p^5 = 0 \tag{14}$$

together with the boundary condition

$$\frac{dp}{d\zeta} = \frac{1}{\eta}p \quad \text{at} \quad \zeta = 0. \tag{15}$$

We shall also make use of the first integral of (14), which is

$$\frac{1}{2}\left(\frac{dp}{d\zeta}\right)^2 = \frac{1}{2}tp^2 - \frac{1}{2}p^4 + \frac{1}{6}p^6 + c = f_B(p) + c, \tag{16}$$

where c is the constant of integration and $f_B(p)$ is the bulk free energy as defined in (6).

Equations (14) to (16) set out the mathematical framework for the questions to be discussed in subsequent sections. As in second-order materials [18], negative η gives an increase in p at the surface and is therefore a candidate for a surface state. Usually it is the inverse of η that enters, so instead of η we use the parameter $y = -1/\eta$. We show in Section 3 that a surface state does occur, but only for y larger than a critical value y_C, that is, for a sufficiently strong surface effect. Not surprisingly, the transition from the paraelectric phase to the surface state is first order, so we find three critical temperatures t_{SCS}, t_{CS} and t_{SHS}, all of which are functions of y. In the second part of Section 3 we discuss the polarization profile, that is, the function $p(\zeta)$, for the surface state. For $t < t_{CB} = 0.75$ the stable bulk state has p equal to p_B as given by (7). However, because of the boundary condition (15) p differs from p_B near the surface, increasing for positive y and decreasing for negative y. This surface modification of the bulk ferroelectric phase is discussed in Section 4.

3 Surface state

We now show that for y positive and sufficiently large, corresponding to an increase in p at the surface relative to the bulk value, in some temperature range $t > t_{CB} = 0.75$ there is a solution of (15) and (16) in which p takes a nonzero value p_S at $\zeta = 0$ and $p \to 0$ as $\zeta \to \infty$. This is the Kretschmer-Binder [18] surface state with a ferroelectric surface ($p \neq 0$) on the bulk paraelectric phase ($p = 0$).

Since for an assumed surface state both $p \to 0$ and $\frac{dp}{d\zeta} \to 0$ as $\zeta \to \infty$, the constant of integration c in (16) is zero. Hence the polarization profile is given by

$$\int_{p_S}^{p} \frac{dp}{p\left(t - p^2 + \frac{1}{3}p^4\right)^{1/2}} = -\zeta \tag{17}$$

where the negative sign is taken for the square root of (16) because p is a decreasing function of ζ. In (17) the upper limit p of the integrand is the value at position ζ. From (17) we obtain

$$p = \left\{ \frac{2t}{1 + \Delta^{1/2}\sinh(Z)} \right\}^{1/2}, \tag{18}$$

where

$$\Delta = \frac{4}{3}t - 1, \quad Z = 2t^{1/2}(\zeta - \zeta_0), \tag{19}$$

and ζ_0 is a function of the lower limit p_S, that is, a constant of integration, which will be determined from the boundary condition. The solution (18) is valid for $t > t_{CB} = 3/4$ which is the temperature region where surface ordering should be found.

Substitution of (18) into the boundary condition (15) gives the equation for ζ_0 which takes the form

$$t^{1/2}\Delta^{1/2}\cosh\left(2t^{1/2}\zeta_0\right) = y\left[1 - \Delta^{1/2}\sinh\left(2t^{1/2}\zeta_0\right)\right], \tag{20}$$

in which it will be recalled that $y = -1/\eta$. As can be seen from (18) the surface value p_S is related to ζ_0 by

$$p_S = \left[\frac{2t}{1 - \Delta^{1/2}\sinh\left(2t^{1/2}\zeta_0\right)} \right]^{1/2}. \tag{21}$$

The free energy may be found by substitution of (18) in (11). However, it is convenient to express the free energy in terms of p_S. Since the constant of integration c in (16) is zero, the polynomial in p in (11) can be expressed in terms of $\frac{dp}{d\zeta}$ to bring f into the form

$$f = \int_0^{\infty} \left(\frac{dp}{d\zeta}\right)^2 d\zeta + \frac{1}{2\eta}p_S^2 = \int_{p_S}^{0} \frac{dp}{d\zeta}dp + \frac{1}{2\eta}p_S^2$$
$$= \int_0^{p_S} p\left(t - p^2 + \frac{1}{3}p^4\right)^{1/2} dp + \frac{1}{2\eta}p_S^2, \tag{22}$$

which can be reduced to [27]

$$f = \frac{1}{8}\left\{ a_s^2\left(t - p_S^2 + \frac{1}{3}p_S^4\right)^{1/2} + 3t^{1/2} + \frac{3^{3/2}}{2}\Delta \right.$$
$$\left. \times \left[\sinh^{-1}\left(\frac{a_s^2}{3(\Delta)^{1/2}}\right) + \sinh^{-1}\left(\frac{1}{\Delta^{1/2}}\right)\right] - 4yp_S^2 \right\}. \tag{23}$$

where $a_s^2 = 2p_s^2 - 3$.

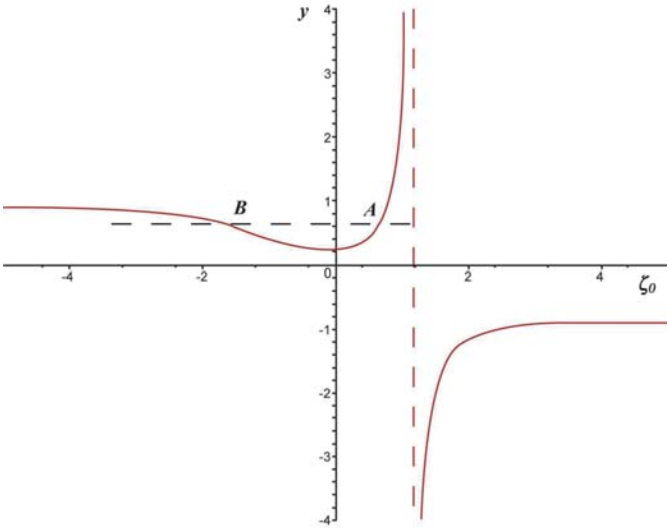


Fig. 1. Example graph of equation (20): y versus ζ_0 for $t = 0.8$. The graph is used to find ζ_0, given y, and as illustrated over some range of y there are two solutions for ζ_0.

The results we require are derived from equations (18), (20), (21) and (23). Before we discuss these we review the calculation of the supercooling temperature for the paraelectric phase. Assume that the paraelectric phase $p = 0$ persists as a metastable phase in some temperature interval below the thermodynamic critical temperature t_{CS}. At the supercooling temperature t_{SCS} the paraelectric phase changes from metastable (local energy minimum) to unstable (local energy maximum). At this temperature the phase is unstable against infinitesimal changes in p. Consequently t_{SCS} is the temperature at which the linearised Euler-Lagrange equation has a solution. The linearized form of (14) is

$$\frac{d^2p}{d\zeta^2} - tp = 0 \qquad (24)$$

and this is to be solved with the boundary condition (15). The solution of (24) that satisfies $p \to 0$ as $\zeta \to \infty$ is simply a decreasing exponential and substitution into (15) gives

$$t_{SCS} = y^2. \qquad (25)$$

This is identical to the equation for the critical temperature of the surface state on a second-order material [18]. The limits of (25) are $t_{SCS} = 0$ for $y = 0$ and $t_{SCS} \to \infty$ as $y \to \infty$. For the former the boundary condition is $\frac{dp}{d\zeta} = 0$ so that there is no increase in p at the surface and t_{SCS} coincides with t_{SCB}.

We now turn to the boundary condition (20). In the physical problem y is a material constant so (20) determines the constant of integration ζ_0 as a function of t. However, it is easier to start by finding ζ_0 as a function of y. An example of the corresponding graph is shown in Figure 1. The asymptotic values are $y \to \mp t^{1/2}$ as $\zeta_0 \to \pm\infty$ The infinity in y is at $\zeta_0 = -\frac{1}{2t^{1/2}} \sinh^{-1}\left(\Delta^{-1/2}\right)$ and the minimum is at $\zeta_0 = -\frac{1}{2t^{1/2}} \sinh^{-1}\left(\Delta^{1/2}\right)$with value $y = (t - 3/4)^{1/2}$. The surface state occurs only for positive y, so we are concerned with the left-hand portion of the graph. It is seen from this that for sufficiently large y there is just one solution for ζ_0, for an intermediate range of values of y, as illustrated in Figure 1, there are two solutions, and for small y there are no solutions. For later reference, we mark the root to the right of the minimum as A and the root to the left as B. The relevant inequalities, expressed in terms of t, are:

$$t > y^2 + 3/4 \qquad \text{no solutions,} \qquad (26)$$

$$y^2 < t < y^2 + 3/4 \qquad \text{two solutions,} \qquad (27)$$

$$t < y^2 \qquad \text{one solution.} \qquad (28)$$

It is seen from (25) that the inequality (28) is the same as $t < t_{SCS}$ and correspondingly we use (26) to identify the superheating temperature t_{SHS} for the surface state as

$$t_{SHS} = y^2 + 3/4. \qquad (29)$$

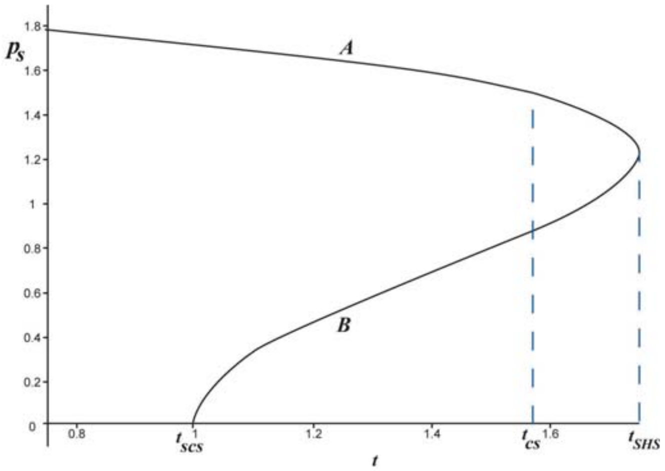


Fig. 2. Graph of surface polarization p_S versus t for $y = 1$, drawn from (20) and (21).

Given the solution of (20), (21) may be used to draw p_S versus t for given y and an example is shown in Figure 2. As marked, the upper part of the curve corresponds to root A in Figure 1 and the 'return portion' to root B; sections A and B meet at $t = t_{SHS}$ and B terminates on the line $p_S = 0$ at $t = t_{SCS}$. The line $p_S = 0$ for $t > t_{SCS}$ is the paraelectric phase, first metastable and then stable. The curve in Figure 2 is typical of first-order transitions and we may anticipate that portion B is unstable, while A is stable at low t and metastable at a higher range of t. As indicated in Figure 2, the equilibrium phase transition takes place at the thermodynamic critical temperature t_{CS}, intermediate between t_{SCS} and t_{SHS}.

In order to find t_{CS} it is necessary to evaluate the free energy f from (23). For a given value of y, (21) gives p_S as a function of t, so that (23) gives f as a function of t. An example of this graph is shown in Figure 3, which like Figure 2 is in the characteristic form for a first-order transition. As anticipated, portion B is unstable ($\frac{d^2f}{dt^2} > 0$) and t_{CS} is the point $f = 0$ on portion A.

Repeated calculation of curves like Figure 3 enables us to find t_{CS} numerically as a function of y; this is shown in

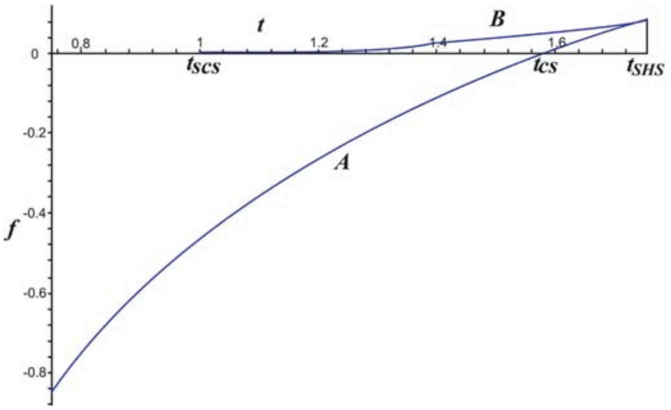


Fig. 3. Graph of free energy f versus t for $y = 1$, drawn from (23). A and B correspond to the marked portions of the p_S curve in Figure 2, and the three critical temperatures are marked.

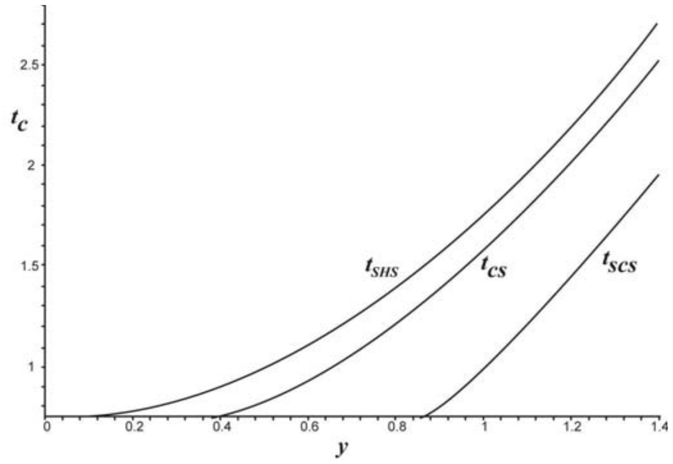
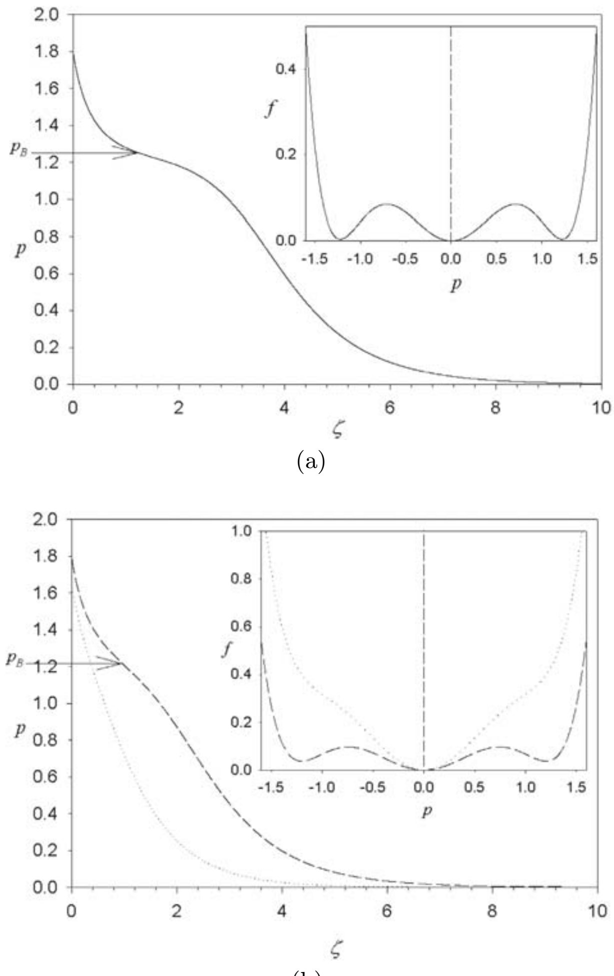


Fig. 4. The three critical temperatures t_{SCS}, t_{CS} and t_{SHS} as functions of y.



(a)

(b)

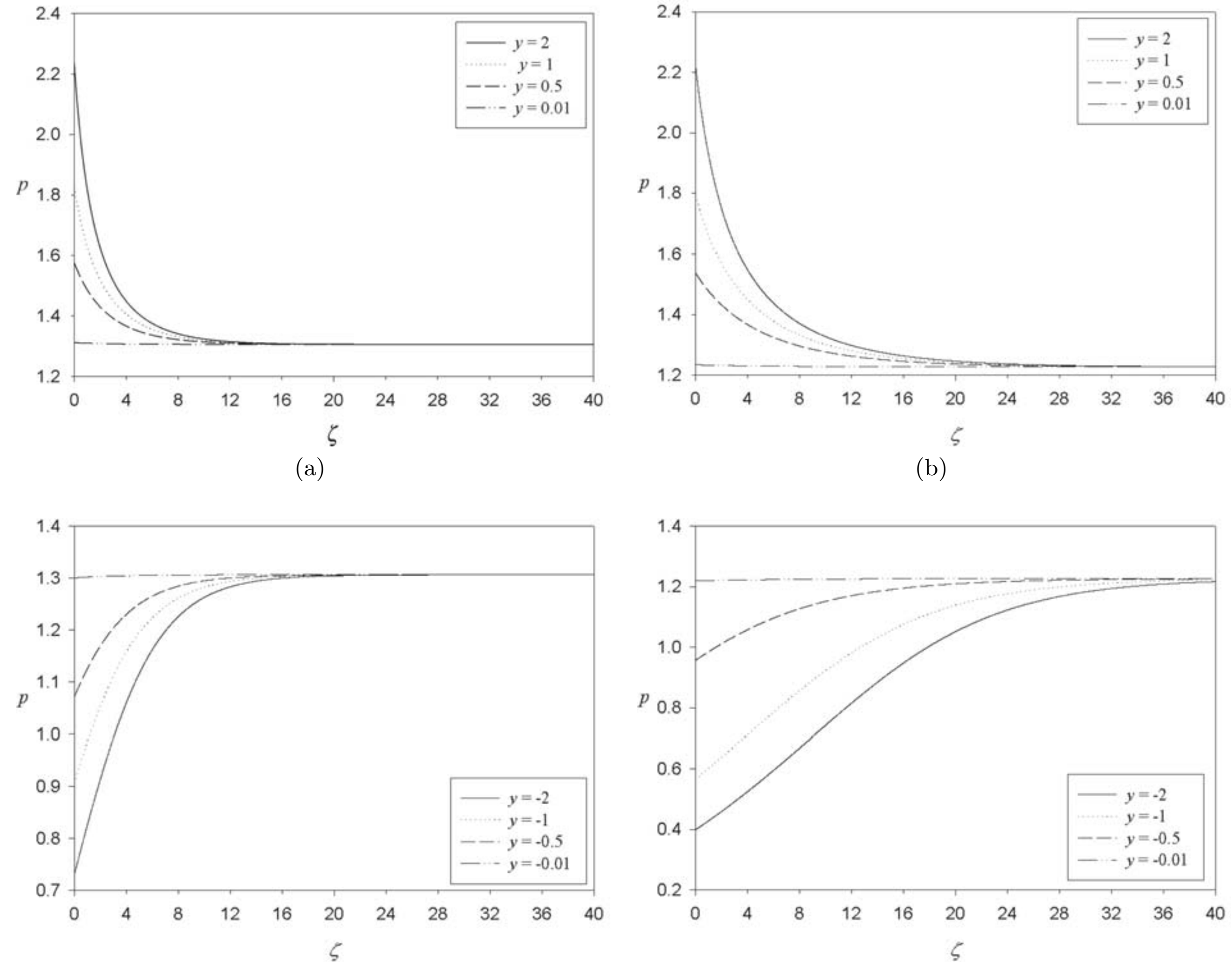
Fig. 5. Surface-state polarization profiles $p(\zeta)$ for $y = 1$. (a) $t = 0.755$, (b) $t = 0.8$, and $t = 1.3$. For $t = 0.755$ and $t = 0.8$ the values of p_B, as in (7), are marked. The insets show the p dependence of the bulk free energy $f_B(p)$.

Figure 4 together with the curves for t_{SCS} and t_{SHS} taken from (25) and (29). It will be recalled that the formalism of this section holds only for $t > 0.75$, since $t_{CB} = 0.75$ is the bulk thermodynamic critical temperature. The graphs in Figure 4 are therefore drawn for this range, and it is seen that there is a solution for t_{CS} only if $y > y_C$, where the critical value is $y_C \cong 0.37$. In this way the first-order material differs from the second-order, for which there is a surface state for all values of y [18].

Finally in this section we show, in Figure 5, examples of the polarization profile $p(\zeta)$, drawn from (15), (16), (18) and (21) for the value $y = 1$. For the highest temperature, $t = 1.3$ (Fig. 5b), $p(\zeta)$ decreases in a simple way from p_S to zero. However, for t near to 0.75, the curve has a more complicated form with a plateau a little distance in from the surface. This is seen prominently for $t = 0.755$ (Fig. 5a) and in a minor way for $t = 0.8$ (Fig. 5b). The reason can be seen from the insets to Figures 5a and 5b. $t_{CB} = 0.75$ is the bulk thermodynamic critical temperature, and for t just above 0.75 the bulk ferroelectric phase is metastable, nearly stable. The curve for $p(\zeta)$ is therefore 'pulled' by the bulk value p_B; to clarify this the values of p_B at $t = 0.755$ and $t = 0.8$ are indicated on the vertical scale. Algebraically, the condition for a zero in the second derivative $\frac{d^2(p^2)}{d\zeta^2}$ is $\sinh Z = \varDelta^{1/2}\left(\cosh^2 Z + 1\right)$, where $Z = 2t^{1/2}(\zeta - \zeta_0)$ as in (19), and this condition can be satisfied for some value of Z in the temperature range under discussion. With reference to Figure 4, the 'plateau' form is seen for all values of y in a narrow strip of t values just above $t = 0.75$; $y = 1$ is typical.

4 Surface modification of bulk states

For $t < t_{CB}$, where $t_{CB} = 0.75$ is the bulk critical temperature, the polarization p has the bulk value p_B, given by (7), for ζ remote from the surface. The effect of the boundary condition (15) is that p changes near to the surface, increasing for positive y and decreasing for negative y. This change does not alter the values of the critical temperatures because the volume of the surface region in which $p \neq p_B$ is negligible compared with the total volume. The only physical effect is the surface profile of p, and this is what we discuss in this section.



(a) (b)

(c) (d)

Fig. 6. Surface modification of the bulk phase, $p(\zeta)$ versus ζ. (a) $t = 0.5$, positive y; (b) $t = 0.745$, positive y; (c) $t = 0.5$, negative y; (d) $t = 0.745$, negative y.

To find $p(\zeta)$ we solve (14) with boundary condition (15). Since now $p \to p_B$ as $\zeta \to \infty$ the constant of integration in (16) is no longer zero; instead (16) takes the form

$$\frac{1}{2}\left(\frac{dp}{d\zeta}\right)^2 = f_B(p) - f_B(p_B), \tag{30}$$

where $f_B(p)$ is the bulk free energy introduced in (6). Equation (30) leads to

$$\int_{p_S}^{p} \frac{3^{1/2} dp}{\left(p^2 - p_B^2\right)\left(p^2 + 2p_B^2 - 3\right)^{1/2}} = -\zeta, \tag{31}$$

and the upper limit of the integral is the value of p at position ζ. The result follows from evaluating the integral [27]:

$$\frac{1}{2p_B\tau^{1/2}}\left\{\sinh^{-1}\left[\frac{a_B^2 + pp_B}{a_B\left(p - p_B\right)}\right] - \sinh^{-1}\left[\frac{a_B^2 - pp_B}{a_B\left(p + p_B\right)}\right]\right\} = \zeta - \zeta_0, \tag{32}$$

where

$$\tau = p_B^2 - 1 = (1 - t)^{1/2}, \quad a_B^2 = 2p_B^2 - 3. \tag{33}$$

In (32) we have used the form of the integral that applies for $\tau > 1/2$, i.e. $t < 0.75$. This is the temperature range in which the bulk ferroelectric phase is stable. In a similar way to what was done in (18), the contribution from the lower limit of the integral in (31) has been taken into the constant of integration ζ_0.

Substitution of (32) into the boundary condition (15) gives

$$\frac{1}{\left(a_B^2 + p_B^2\right)^{1/2}\left(p_S^2 - p_B^2\right)} = \frac{1}{3^{1/2}\left|y\right| p_S} \tag{34}$$

and as before p_S is $p(\zeta = 0)$, the value of p at the surface.

Equations (32) and (34) can be used to draw the polarization profile $p\left(\zeta\right)$ for given y and t; examples are shown in Figure 6. Figures 6a and 6b are for positive values of y, the first for t well below t_{CB} and the second for t near t_{CB}; both show a monotonic decrease from p_S to p_B. It is seen from the comparison of these two figures that the modification of p_B extends further from the surface for t near t_{CB}; this is the usual increase of the temperature-dependent coherence length. Figures 6c and 6d, y negative and $p_S < p_B$, are drawn for the same temperatures. The low-temperature curve, Figure 6c, shows a simple monotonic increase from p_S to p_B. For t near t_{CB}, Figure 6d, and the smaller values of $|y|$, the profiles are similar to those in Figure 6c, except that as in Figure 6b the surface modification extends further in. For t near t_{CB} and larger $|y|$, $y = -2$, $p(\zeta)$ retains a low value for an extended range of ζ near the surface. For such temperatures, the paraelectric phase $p = 0$ is metastable, nearly stable, so that over some range of ζ $p(\zeta)$ remains close to zero. This 'attraction' of the metastable phase is similar to that shown for the surface state for t just above 0.75 in Figure 5; it is characteristic of a first-order phase transition. For $y < 0$ the polarization profile is part of the complete solution of (31) with the asymptotic limits $p \to p_B$ as $\zeta \to \infty$ and $p \to -p_B$ as $\zeta \to -\infty$. This has been applied previously [28] to describe 180° domain walls in first-order material.

5 Conclusion

We have given a complete account of the theory of surface states on first-order ferroelectrics within the model defined by the free-energy expression (9). All of the necessary results are given analytically in terms of elementary functions. In Section 3 we discussed the surface state that is found for positive y ($p(\zeta)$ increasing at the surface) in a certain range of temperature above the bulk critical temperature, t_{CB}. This state is found only when the surface effect is sufficiently strong ($y > 0.37$). The transition from the surface state to the paraelectric state ($p = 0$) is first order; the temperature dependences of the surface value p_S and the free energy f are of the characteristic form for first-order transitions. For most of the temperature range the polarization profile resembles that for a second-order material [2] but in a narrow temperature interval near t_{CB} a clear indication is seen of the presence of a metastable state characteristic of a first-order transition. The surface modification of the bulk polarization $p = p_B$ for $t < t_{CB}$ is discussed in Section 4. Here also, the results are analytic and in fact the form of $p(\zeta)$ is identical to part of a 180° domain wall [28]. For negative y, $p_S < p_B$, and t near t_{CB} the influence of the metastable paraelectric phase is clearly seen.

In their paper on surface states on second-order ferroelectrics, Kretschmer and Binder [18] devote a section to the critical region of temperature near to the surface transition temperature. In this region, which in practice for ferroelectrics is usually very small, mean-field theory does not hold because of strong thermodynamic fluctuations in the order parameter p. However, fluctuations have a negligible effect on first-order transitions, and there is therefore no need to extend Kretschmer and Binder's renormalization-group analysis to the present case.

It is important to note here that the main purpose of this paper is not to present results to compared with experimental findings directly. Instead, it is aimed at a systematic investigation, via analytical expressions, to look for qualitative surface effects and to illustrate general dependencies of polarization at the surface on the essential model parameters: "y". The results obtained may be of particularly importance in the understanding of surface ferroelectricity. In this case, the model that has been constructed for the case with negative y might be physically relevant to the degradation of polarization at the surface found experimentally in most perovskite ferroelectrics [29]. In addition, it is also quite similar to the results obtained by the shell model calculation [14] and quantum mechanical approach [30] for $BaTiO_3$ films. Recently, enhancement of polarizations at the surface of $PbTiO_3$ films was evidenced by X-ray photoelectric diffractions [31]. The results simply indicate the possible existence of positive y surfaces. An increase in polarization at the surface of a $PbTiO_3$ film predicted theoretically by first-principle calculations [31,32] further supports the validity of a positive y surface.

The present model mainly considers the properties of surface corresponding to a single slab of ferroelectric materials, i.e. the surface of a semi-infinite medium. For layered structures such as heterostructures of films grown on substrate and multilayers, the effects of interface and coupling between neighboring constituents may affect the behaviors of the structure and must be considered. In other words, the properties of layered ferroelectrics may be determined by the interface region — "interface structure". The nature of interfacial coupling on the static and dynamic properties of an interface structure formed between two semi-infinite ferroelectric constituents was recently constructed and discussed carefully using the Landau-Ginzburg theory [9,33–35]. Recently, there has also been published work on studies of interface effects using first-principle calculations [36], and other works have also been reviewed [3].

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