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Effect of Electric Field on Surface and Center of Ferroelectric Film

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Abstract: Size, surface and temperature effects of first and second order phase transition of ferroelectric (FE) thin films have been discussed in detail in the literature. However, the reversal of polarization by an applied electric field in FE materials is an important phenomenon to the industrial and technological applications, and it is an active research area for experimentalists as well as for theories. The Tilley-Zeks model has well described the polarization profiles of FE thin films in the absence of electric field. Hence, we adopt the Tilley-Zeks model of free energy expression and a term $P.E$, which gives the energy due to the interaction of electric field E and polarization P , included in the free energy expression. We study the effects of electric field on polarization profile for second order FE thin films with different surface parameters for the case when the direction of electric field is along the direction of polarization (induced polarization phenomenon) and the case when the electric field is in opposite direction with the polarization (polarization reversal phenomenon). We have found that the switching time decreases with increasing the value of external electric field.

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Keywords: Polarization reversal; Tilley-Zeks model; Electric field; Switching time.

Introduction

Due to the recent development in thin-film fabrication techniques, there is an increasing number of applications of ferroelectric materials in microelectronics, such as nonvolatile memory, random access memory, microwave devices and micro-electro-mechanical systems. A number of advantages are expected from thin film based devices; for example, light weight, small volume, high density, high switching speed and low power consumption [1, 2].

Experimentally, finite size effect has long been studied since the 1960s. Various techniques including x-ray diffractometry (XRD), Raman scattering, second harmonic generation (SHG), differential scanning calorimetry (DSC), specific heat, dielectric constant and static polarization measurements have been employed [3-10].

Distinct physical properties have been observed in thin film from these experiments which are completely different from their counterparts in bulk form. Consequently, thickness dependence of various physical properties in ferroelectric films has been extensively studied [1].

Ferroelectricity is a result of collective behavior of many interacting dipoles. For a bulk sample, this interaction is so strong that the surface effect can be ignored. The size effect can be visualized as the influence due to the presence of a surface layer with completely different properties from those in the interior layers of the film^[11-15] and the introduction of inhomogeneous polarization profile $(dp/dz)^2$ incorporation of the extrapolation length δ such that $dp/dz = \pm p/\delta$ [16, 17].

Landau Devonshire (LD) theory is successfully applied to bulk ferroelectrics [18, 19]. Kretschmer and Binder [20] set out a framework for finite material in which polarization (p) is treated as a function of coordinate (z) normal to the film. Tilley and Zeks [16] and Ong *et al.* [21] showed that the polarization profile $p(z)$ within the film can be expressed in terms of Jacobi elliptic functions for the symmetric second-order films. Tan *et al.* [22, 23] numerically studied the first order transition for thin film in detail. However, a group of authors investigated the properties of the polarization reversal of ferroelectric film for second order phase transition based on Tilley-Zeks model by using step field, sinusoidal and bipolar electric field [24-27]. For completeness, in this paper we study the effect of electric field on polarization profile when the electric field is in the same and the opposite direction to the polarization.

Theory and Modeling

In this paper, we study the effect of electric field on polarization, so we consider a symmetric thin FE film of thickness L extending along the z axis, from $-L/2$ to $L/2$. The FE material is assumed to undergo a second-order phase transition. The model is one-dimensional with polarization and related physical quantities varying as a function of z . The direction of polarization may be parallel to the film surface, so the effect of the depolarization field is negligible. We can also assume an FE film with a polarization direction normal to the film surface where we can ignore the depolarization field for FE materials with finite conductivity [28] or for FE materials in short-circuited capacitors [29]. The Landau-Devonshire free energy per unit area for the thin film with thickness L under an action of an electric field E is expressed as [16, 30]:

$$\frac{G}{S} = \int_{-L/2}^{L/2} \left[\frac{a(T-T_c)}{2\epsilon_0} P^2 + \frac{B}{4\epsilon_0^2} P^4 + \frac{D}{2\epsilon_0} \left(\frac{dP}{dz} \right)^2 - EP + \frac{D}{2\epsilon_0 \delta} (P_-^2 + P_+^2) \right] dz; \quad (1)$$

where S is the cross-sectional area of the film with plane surface at $z = \pm(L/2)$ and $P_{\pm} = (\pm L/2)$ is the polarization value at the boundaries. Here, a and B are temperature-independent parameters. For a second-order phase-transition material, B has a positive value and T_c is the Curie temperature of the material. The coefficient D is associated with the spatial variation of P along the z direction. The factor of ϵ_0 in Eq. 1 is to ensure that a , B and D have simple mechanical dimensions [31]. The effect of electric field is included in $-EP$ term. The inhomogeneity of the film, where the polarization varies as a function of distance (z) across the film thickness, can be represented by the term $(dp/dz)^2$. The surface and size effects of the film are studied by introducing the so-called extrapolation length δ leading to the boundary conditions.

$$\frac{dP}{dz} = \pm \frac{P}{\delta} \text{ at } z = \pm \frac{L}{2}. \quad (2)$$

For a positive δ , the polarization is depressed at the surface and for a negative value, it is enhanced [16]. For numerical presentation, it is convenient to scale all variables. We let $t = T/T_c$, $p = P/P_0$ with $P_0^2 = \epsilon_0 a T_c / B$ and $e = E/E_0$ with $E_0^2 = 4a^3 T_c^3 / 27 \epsilon_0 B$. P_0 and E_0 are the equilibrium bulk polarization and the bulk coercive field at $T = 0$, respectively. With this scaling, we then have the reduced free energy as:

$$F = \int_{-l/2}^{l/2} \left[\frac{1}{2}(t-1)p^2 + \frac{1}{4}p^4 + \frac{1}{2} \left(\frac{dp}{d\zeta} \right)^2 - \frac{2}{3\sqrt{3}} ep + \frac{1}{2\delta_r} (p_-^2 + p_+^2) \right] d\zeta; \quad (3)$$

where:

$$F = BG / a^2 T_c^2 \xi_0 S, \quad \zeta = a^{1/2} T_c^{1/2} z / D^{1/2},$$

with $\xi_0^2 = D / a T_c$ corresponding to the characteristic length of the material. $\delta_r = \delta / \xi_0$ and l is related to L in the same

way as ζ to z . The scaled boundary conditions now become:

$$\frac{dp}{d\zeta} = \pm \frac{p}{\delta_r} \text{ at } \zeta = \pm \frac{l}{2}. \quad (4)$$

This scaling has the advantage that all FE materials in the same class are represented by the same universal curves. For a film, the basic assumption is that the equilibrium $p(\zeta)$ corresponds to a minimum of F , so that $p(\zeta)$ is a solution of the Euler Lagrange equation:

$$\frac{d^2 p}{d\zeta^2} = (t-1)p + p^3 - \frac{2}{3\sqrt{3}}ep. \quad (5)$$

We solve Eq. 5 numerically by the use of an error controlled fourth-order Runge-Kutta (RK) routine [32], and the forming of polarization profile will obey the boundary conditions in Eq. 4. The polarization reversal is studied by using the phenomenological Landau-Khalatnikov (LK) equation which can be written as [33]:

$$\left. \begin{aligned} \gamma \frac{\partial P}{\partial \tau} &= -\frac{\partial (F/S)}{\partial P} \\ &= -\frac{A(T-T_C)}{\varepsilon_0}P - \frac{B}{\varepsilon_0^2}P^3 \\ &\quad + \frac{D}{\varepsilon_0} \frac{d^2 P}{dz^2} + E \end{aligned} \right\} \quad (6)$$

where τ is the time. The scaled form of LK equation is:

$$\left. \begin{aligned} \frac{\partial p}{\partial \tau_r} &= -\frac{\partial f}{\partial p} \\ &= (1-t)p - p^3 \\ &\quad + \frac{d^2 p}{d\zeta^2} + \frac{2}{3\sqrt{3}}e \end{aligned} \right\} \quad (7)$$

where the reduced time τ_r is given by $\tau_r = \tau(AT_C\zeta_0/\varepsilon_0\gamma)$. The delay in domain movement is represented by the parameter γ , the coefficient of viscosity. The kinetic term $m(\partial^2 P/\partial t^2)$ is neglected in the LK equation, because it only contributes to phenomena in the higher frequency range.

The global order parameter is the average polarization of the film which can be written as:

$$\bar{p} = \frac{1}{l} \int_{-l/2}^{l/2} p(\zeta) d\zeta \quad (8)$$

The free energy of the bulk is:

$$F = \frac{A(T-T_C)}{2\varepsilon_0}P^2 + \frac{B}{4\varepsilon_0^2}P^4 - EP, \quad (9)$$

and in the reduced form is:

$$f = [(t-1)/2]p^2 + (1/4)p^4 - \frac{2}{2\sqrt{3}}ep. \quad (10)$$

At equilibrium; $df/dp = 0$, $d^2f/dp^2 = 0$, the coercive field of the bulk can be derived as:

$$E_C = \frac{2}{3\sqrt{3}} \left[\frac{A^{3/2}(T_C-T)^{3/2}}{\varepsilon_0^{1/2}\beta^{1/2}} \right]. \quad (11)$$

The reduced form of coercive field is:

$$e_{cb} = (\sqrt{1-t})^3. \quad (12)$$

Results and Discussion

Fig. 1 shows the effect of electric field e on polarization profile in an FE film of thickness $l = 1.5$ with positive extrapolation length $\delta_r = 4.0$. The direction of the electric field is the same as the direction of polarization. The electric field induces polarization inside the film, and it is observed that by increasing the value of e , the polarization increases in the film center and on the film surface. In Fig. 1, we can see that the effect of e on the polarization at film center is different from the effect of e on the polarization on the film surface, so we manifest the difference in Fig. 2 for a wide range of e values. Fig. 2 shows that the polarization increment at the film center is slightly larger than the polarization increment on film surface and this increment increases with increasing the value of e .

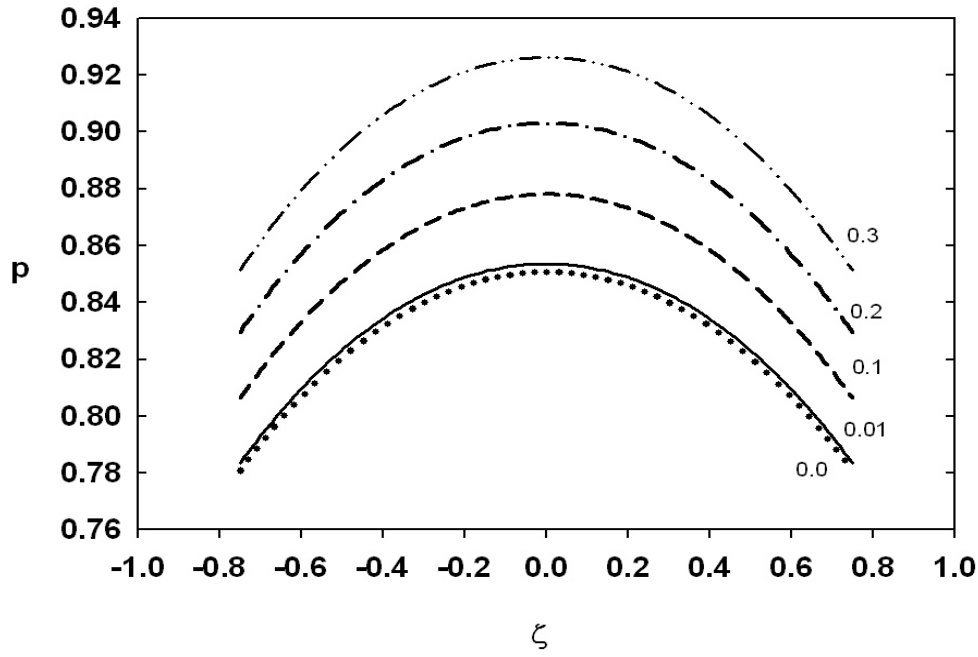


FIG. 1. Polarization p versus ζ for electric field e equal to 0.0, 0.01, 0.1, 0.2 and 0.3. Thickness $l = 1.5$, extrapolation length $\delta_r = 4.0$, temperature $t = 0.0$.

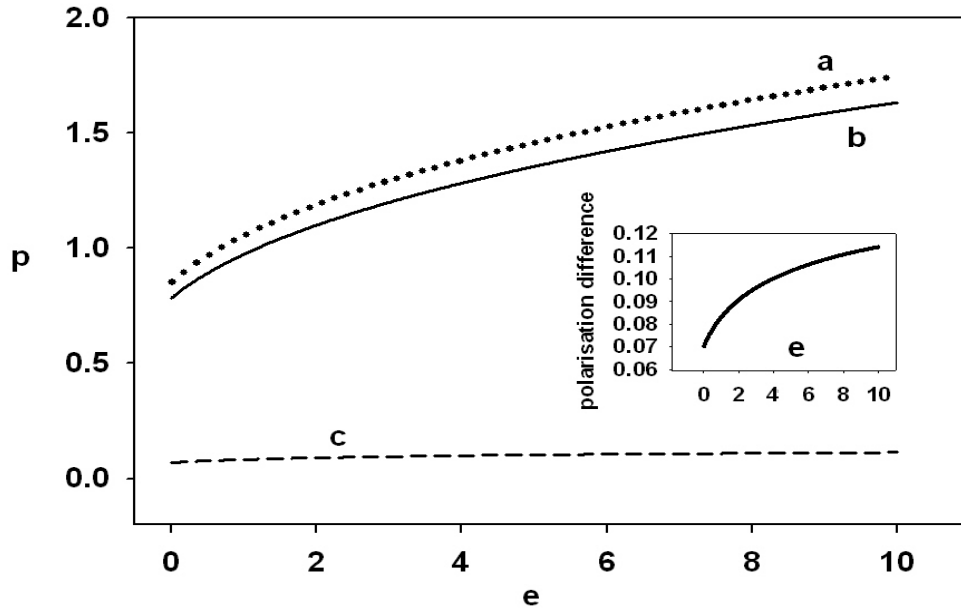


FIG. 2. Polarization p versus electric field e . Curve (a) corresponds to electric field effects at the film center, curve (b) corresponds to the electric field effects on the film surface, curve (c) represents the difference between curves (a) and (b). Film thickness $l = 1.5$, extrapolation length $\delta_r = 4.0$, temperature $t = 0.0$. Curve (c) zoom in inset.

Fig. 3 shows the electric field e effect on polarization of an FE film with a thickness $l = 1.5$ with negative extrapolation length $\delta_r = -4.0$. The electric field direction is the same as the direction of polarization. Hence e induces polarization inside the film, so by increasing e the polarization increases. The figure shows that there is a difference in

increment of induced polarization between the film center and the film surface which can also be visualized in Fig. 4. In the contrary to a film with positive extrapolation length (Fig. 2), the polarization increment on the film surface is slightly greater than the polarization increment at the film center for films with negative extrapolation lengths.

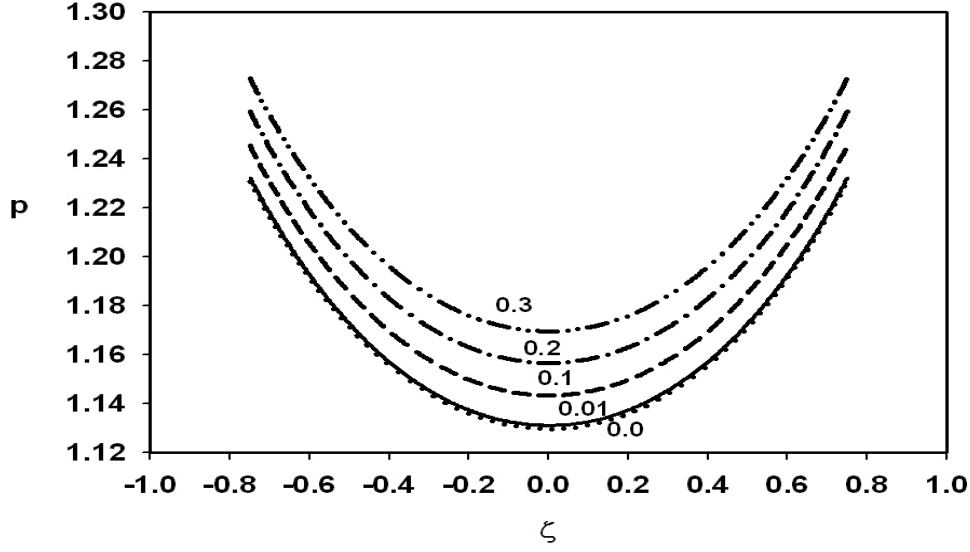


FIG. 3. Polarization p versus ζ for electric field e equal to 0.0, 0.01, 0.1, 0.2 and 0.3. Thickness $l = 1.5$, extrapolation length $\delta_r = -4.0$, temperature $t = 0.0$.

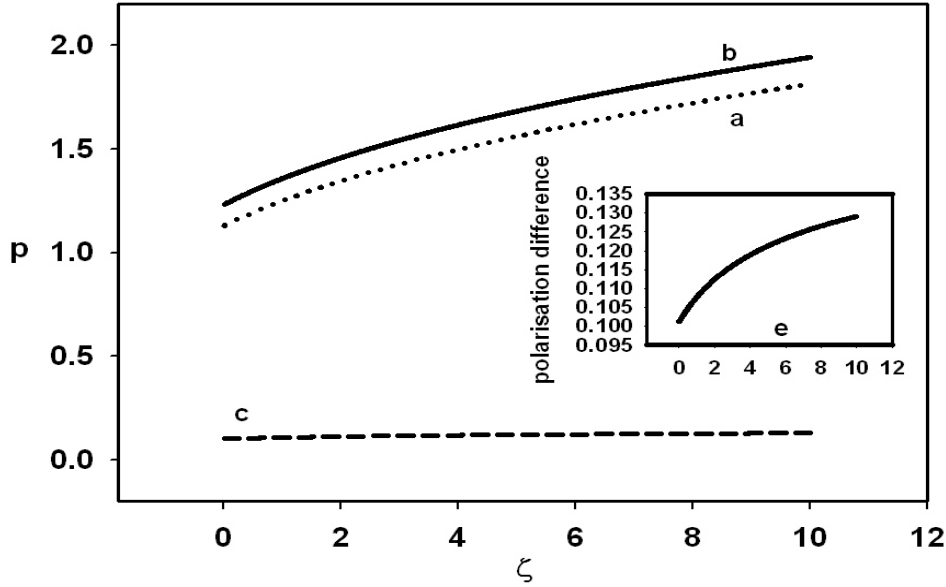


FIG. 4. Polarization p versus electric field e . Curve (a) corresponds to electric field effects at the film center, curve (b) corresponds to the electric field effects on the film surface, curve (c) represents the difference between curves (b) and (a). Film thickness $l = 1.5$, extrapolation length $\delta_r = -4.0$, temperature $t = 0.0$. Curve (c) zoom in inset.

The polarization reversal of FE films is studied by applying the step electric field that is usually used in experiments [34]. The most significant quantity in polarization reversal is the switching time τ_s . There are several definitions of switching time in the literature [18, 35-41]. In this study, we adopt the switching time τ_s to be the time taken when the switching current J drops to 90% of its maximum value $J_{\max}$ [38-40]. The initial

polarization in the film is switched from its negative value in all the simulations. The form of the step field is:

$$e = e_0 \theta(\tau_r) \quad (13)$$

where $\theta(\tau_r)$ is a step function defined as:

$$\theta(\tau) = \begin{cases} 1 & \text{for } 0 \leq \tau_r < \tau_0 \\ 0 & \text{for } \tau_0 \end{cases} \quad (14)$$

where τ_0 is the time when the field is switched off and e_0 is the amplitude of the electric field. By applying the step electric field, we present the effects of electric field on the switching of ferroelectric films.

The study on domain formation and its movement in ferroelectricity is one of the important and complicated problems in switching phenomena. Under a certain applied field at any time during switching, the polarization profile can be simulated from Eq. 7. This polarization profile during switching for an FE film with $\delta_r = +2$ and a film thickness $l = 5.4$ is analyzed from the graphs in Fig. 5 and Fig. 6 by applying electric fields $e = 0.9e_c$ and $e = 5e_c$, respectively at $t = 0.0$ for both films. e_c is the coercive field of the bulk given in Eq. 12. A close look at Fig. 5 and Fig. 6 shows that the dipole moments on the surface are switched before the dipole moments in the film interior. This is because the polarization on the film surface is less than that at the film centre for an FE film with $+\delta_r$ (see Fig. 1). Hence, the polarization on the film surface would switch before that at the film center. Experimentally, it is well known that polarization switches first on the

film surface then in the bulk [42]. Fig. 5 and Fig. 6 show that by increasing the applied electric field e , the switching time τ_s decreases for a film of thickness $l = 5.4$ at $t = 0.0$. It can be seen in Fig. 6 that the initial polarization of an FE film with $+\delta_r$ can be completely reversed by the applied electric field $e = 0.9e_c$. This value of e is less than the bulk coercive field e_c . The reason for that the film is switched by the electric field less than the value of e_c can be explained based on the curves in Fig. 1 for $p(\zeta)$ of a film with positive δ_r . The polarization is suppressed on the surface compared with the value at the center, and even at the center, polarization is lower than that of the bulk case, $p = 1$ for bulk at $t = 0$ and at $e = 0$ (Eq. 10). In this respect, the value of average polarization (Eq. 8) of this film is less than the value of bulk polarization. Hence, we may deduce that switching would take place more readily in the film with $+\delta_r$ than in the bulk at lower applied field ($e < e_c$).

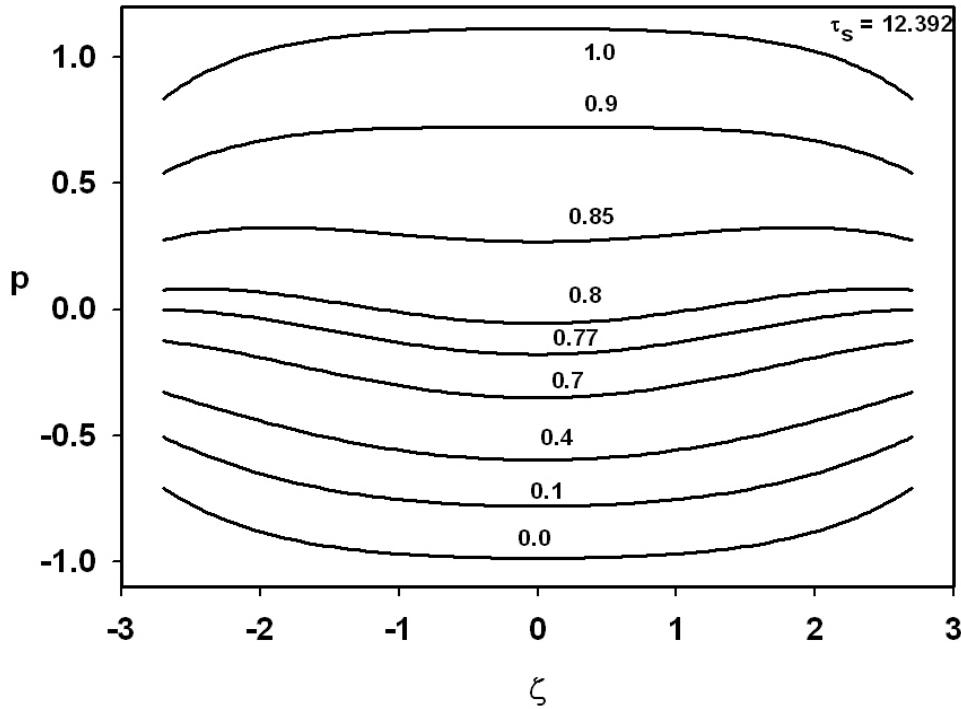


FIG. 5. Polarization profile $p(\zeta)$ during switching for thin film. $l = 5.4$, $\delta_r = +2$, $e = 0.9e_c$, $t = 0.0$. The number at each curve represents the time taken to reach the stage in terms of fraction of $\tau_s = 12.392$.

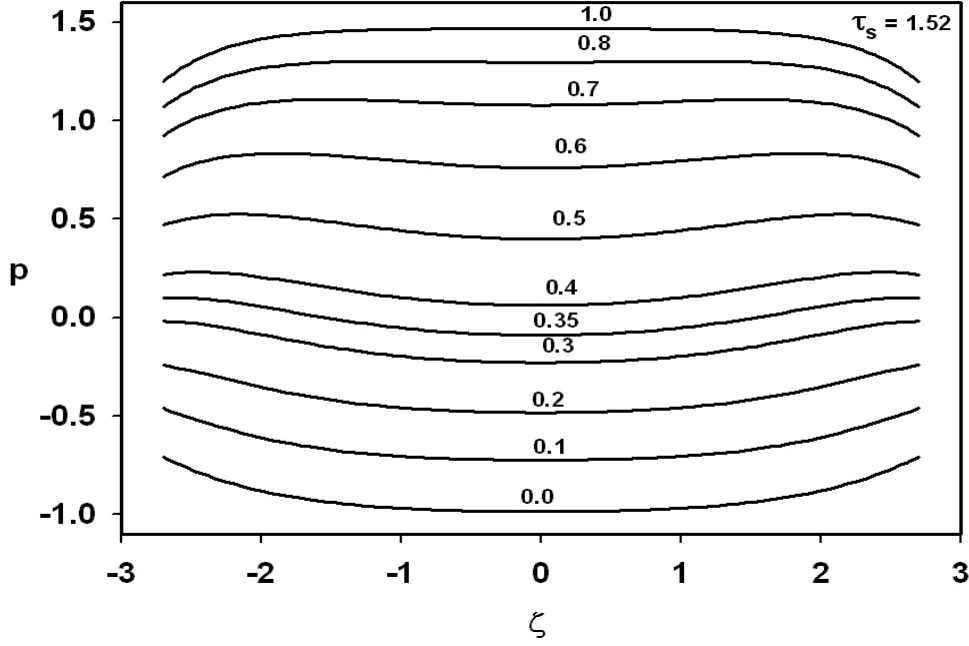


FIG. 6. Polarization profile $p(\zeta)$ during switching for thin film. $l = 5.4$, $\delta_r = +2$, $e = 5e_c$, $t = 0.0$. The number at each curve represents the time taken to reach the stage in terms of fraction of $\tau_s = 1.52$.

Fig. 7 and Fig. 8 show the polarization profile during switching for an FE film with a negative extrapolation length $\delta_r = -2$ for film thickness $l = 5.4$ at temperature $t = 0$. It is obvious that switching of dipole moments at the film center takes place before that on the film surface. This phenomenon is

contrary to what we observed in the FE film with $+\delta$ (Fig. 5 and Fig. 6); that is switching happens on the surface before at the film center. For an FE film with $-\delta_r$, the polarization on the surface is greater than that at the center due to the surface effect with negative extrapolation length (See Fig. 3).

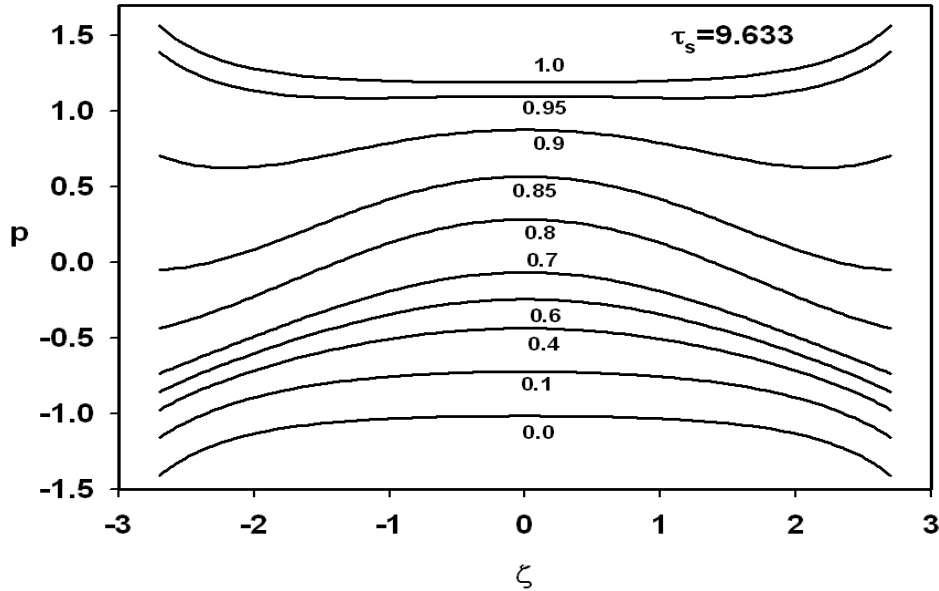


FIG. 7. Polarization profile $p(\zeta)$ during switching for film thickness $l = 5.4$, $\delta_r = -2$, $e = 1.5$, $t = 0.0$. (Film parameters are the same as those of a film with $+\delta_r$, see Fig. 5). Polarization profile stages are taken from bottom to top at 0.0, 0.1, 0.4, 0.6, 0.7, 0.8, 0.85, 0.9, 0.95 and 1.0 in terms of fraction of $\tau_s = 9.633$.

Fig. 7 and Fig. 8 indicate that the switching time τ_s of an FE film with a negative extrapolation length decreases with increasing the value of the applied external electric field. This result is the same as that for an FE film with positive extrapolation length. The switching time ($\tau_s = 1.52$) of an FE film with $l = 5.4$ and $\delta_r = +2$ is less than the switching time ($\tau_s = 1.661$) of an

FE film with $l = 5.4$ and $\delta_r = -2$ at $t = 0$ by applying the same value of electric field $e = 5e_c$ as shown in Fig. 6 and Fig. 8, respectively. The author in Ref. [25] shows that for an FE film with a positive extrapolation length, the switching time and coercive field decrease with decreasing film thickness, and these characteristics may be useful for memory devices.

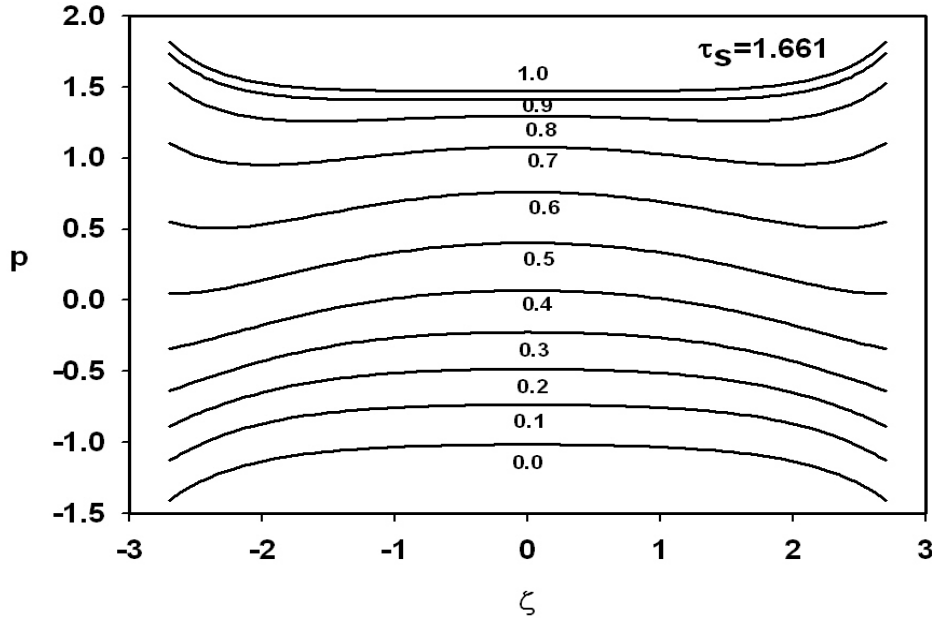


FIG. 8. Polarization profile $p(\zeta)$ during switching for film thickness $l = 5.4$, $\delta_r = -2$, $e = 5e_c$, $t = 0.0$.

(Film parameters are the same as those of a film with $+\delta_r$, see Fig. 5). Polarization profile stages are taken from bottom to top at 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 in terms of fraction of $\tau_s = 1.661$.

Conclusion

Landau-typed TZ model is used to study the intrinsic switching phenomenon of a free standing FE film. We study the effects of electric field on polarization in FE films on the surface and at the center of the film. Two directions of applied electric field with respect to the polarization direction are taken into account. It is found that switching time decreases with increasing the value of the applied field for FE films with positive and negative extrapolation lengths. Polarization switching takes place on the film surface

before that at the film center for an FE film with a positive extrapolation length, while for an FE film with a negative extrapolation length the matter is reversed. When the direction of the applied field is in the direction of polarization, we found that the increment of induced polarization of an FE film due to applied field on film surface is different from that at the film center for both FE films with different signs of extrapolation length.

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