

Curie temperature and critical thickness of ferroelectric thin films

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The dynamic Ginzburg–Landau theory is applied to establish the critical conditions that control the transition between the paraelectric and ferroelectric states. Analytic expressions of the para-ferroelectric transition temperatures in a thin film under various electromechanical surface conditions are derived via a linear stability analysis of the evolutionary trajectory of the system for both first- and second-order transitions. Explicit expressions are then derived for the critical thickness, below which the thin film is paraelectric for all temperatures. For first-order transitions, the difference between the superheating and supercooling transition temperatures is found to be insensitive to the film thickness and surface boundary conditions. From these expressions, the relative importance on ferroelectricity in thin films due to applied mechanical constraints on the transformation strain and the depolarizing effect of surface charges is discussed and compared with experimental data. © 2005 American Institute of Physics. [DOI: 10.1063/1.1861517]

I. INTRODUCTION

Ferroelectricity is a collective phenomenon, the characteristics of which depend on the combined effects of many factors, such as the ambient temperature, boundary conditions, sample dimensions, misfit epitaxial stresses, etc. Studies of the effects of sample dimensions on the Curie temperature and the critical thickness of thin films have been conducted for the last several decades.^{1–7} Recently, research in this area has found renewed relevance due to the surge of technological interest in ultraminiaturized electronics, ultrahigh-density memory devices, and nanotechnologies in general.

Characteristics governing the para-ferroelectric transitions in a film have been investigated within the framework of both thermodynamic theory and first-principles calculations. However, various discrepancies between experimental measurements and theoretical calculations and among the theoretical calculations themselves may be the result of incomplete understanding. As an example, the critical thickness of PbTiO₃ thin films at room temperature has been estimated at ~5.5 nm, within the phenomenological theory.⁷ However, recent experimental measurements show that stable polarization orthogonal to the surface can exist down to a 4-nm-thick lead zirconate titanate (PZT) film.³ First-principles calculations² even found that an orthogonally polarized ferroelectric state can be maintained under short-circuit electric boundary conditions, even for a film as thin as 1.2 nm (three unit cells). Despite extensive investigations^{1–8} that have been carried out on the size-dependent Curie temperature and critical thickness, its nature and the physical reason of its existence remain uncertain. For example, although it is fairly plausible that the critical thickness origi-

nates from the depolarizing effect of the film surface, information on the details of the competing mechanisms, their relative importance, and their relations with various electromechanical surface conditions are still needed. Except for the simplest cases, numerical calculations using either first-principles² or thermodynamic approaches^{7,8} are the main theoretical tools for explorations in this area. In the latter case, characteristics of the para-ferroelectric transformation have often been obtained from the condition of phase equilibrium at the transition point. This approach has been proven effective for continuous (second order) phase transitions, where the order parameter is continuous and well defined at the point of transition. However, the case is more complicated for discontinuous (first order) transitions, where the order parameter is discontinuous and not well defined at the point of transition.

Alternatively, phase transition may also be described in terms of the time evolution of the order parameter as an irreversible dynamical process governed by the evolution equation. The latter can be formulated using the Ginzburg–Landau functional⁹ expressed in terms of a set of control parameters $\{\lambda\}$, including the ambient temperature, boundary conditions, surface characteristics, sample dimensions, misfit epitaxial stresses, etc. Within the dynamical description,¹⁰ the evolution of the system can be pictured as the trajectory of a moving “particle” in the order-parameter space, starting from an initial point (i.e., the order parameter at $t=0$) representing the initial state and ending towards a point representing the final state (i.e., the order parameter at $t=\infty$). The trajectory and the final state are functions of $\{\lambda\}$, obtained by solving the evolution equation. This operation, however, is generally rather difficult because of the nonlinear nature of the problem.¹⁰ While the numerical approach has been followed for focused problems involving a relatively small number of control parameters, the comprehensive understanding of a multiparameter, multimechanism system is not easily achievable outside an analytic approach.

It is clear that the final state is a stationary state (i.e.,

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with a fixed order parameter) that must be asymptotically stable.¹⁰ In this regard, analytic techniques in nonlinear mathematics exist, with which the stability of the stationary states, i.e., stationary solutions of the Ginzburg–Landau equation (GLE), can be determined without the explicit solution of the system of nonlinear differential equations.^{9–11} Without loss of generality, we focus on the paraelectric to ferroelectric transformation for easy discussion. In this case, the GLE has two stationary solutions, with order parameters corresponding to the two states. Suppose we start with an initial state that is paraelectric. If the corresponding stationary solution is asymptotically stable, the final state must remain paraelectric, and no transition to the ferroelectric state will occur. This is the case even if both the paraelectric and the ferroelectric states are asymptotically stable at the same time. Thus, a necessary condition for the transition to occur is that the stationary paraelectric solution is unstable. This provides us with the means to determine the range of $\{\lambda\}$, within which the paraelectric state is stable, and outside which the paraelectric state may transform into the ferroelectric state, i.e., the phase diagram. The foregoing approach allows important characteristics of a ferroelectric thin film, such as the transition temperatures, critical thicknesses, domain morphology, substrate nature, etc., to be related through the instabilities of the initial state, the linear nature of which opens the system to many established analytic techniques.

In the present paper, we follow the analytic approach described in the foregoing to establish conditions of the stability of the paraelectric versus ferroelectric phases in a thin film. The polarizing/depolarizing effects due to the presence of the film surface, namely, the surface lattice relaxation, the restraint of the transformation strain, the electromechanical surface conditions involving the epitaxial stress, and the induced surface charges, are taken into account. Expressions for the para-ferroelectric transition temperatures as a function of film thickness and the corresponding critical thickness are derived, and the complex relation of the critical thickness with the various parameters discussed. Both first-order and second-order transitions are considered.

II. THE EVOLUTION EQUATION AND STABILITY OF THE STATIONARY STATES

We consider a thin film of ferroelectric material of dimensions of $\infty \times \infty \times h$, h being the film thickness. The origin of the coordinate system is at the center of the cell. We assume that P , the single polarization component normal to the surface of the film, is the order parameter to describe the phase transition. In general, the transition between the cubic and tetragonal phases involves three polarization components related through a system of three coupled nonlinear differential equations, which have to be analyzed together. Nevertheless, this is beyond the scope of the present paper.

Noting that a para-ferroelectric transformation is caused by a transformation between a central symmetric and a non-central symmetric lattice structure, the transition is always accompanied by a transformation strain. When the ferroelectric state under consideration has a tetragonal lattice structure, the transformation strain in the plane of the film can be expressed in the form of $\varepsilon^T = \varepsilon_{xx}^T = \varepsilon_{yy}^T = QP^2$, where Q is the

electrostrictive coefficient. Accordingly, the free energy of a ferroelectric thin film is made up of mechanical and electrical components. The mechanical component contains the elastic self energy due to the transformation strain and the interaction energy between the applied stress and the transformation strain. For rigid substrates, the transformation strain is fully constrained, and the elastic self energy is given by $F_e = GQ^2 \iint_V P^4 dV$, where $G = (C_{11} + C_{12} - 2C_{12}^2/C_{11})$, C_{11} and C_{12} being components of the elastic modulus of the film and V the volume of the film. We note that due to the free upper surface of the films, the component ε_{xx}^T of the transformation strain does not contribute to the elastic energy. Fabrication processes often leave a residual stress distribution in the film due to the lattice mismatch, the epitaxial stress. Its interaction with the transformation strain is given by

$$\begin{aligned} F_i &= - \iint_V \int_V \sigma_{ij} \varepsilon_{ij}^T dv = - \iint_V \int_V (\sigma_{xx} \varepsilon_{xx}^T + \sigma_{yy} \varepsilon_{yy}^T) dv \\ &= - 2 \iint_V \int_V \sigma_r \varepsilon^T dv, \end{aligned}$$

where $\sigma_{xx} = \sigma_{yy} = \sigma_r$.

The electrical component of the free energy can be expressed in terms of the order parameter P and the temperature using the Ginzburg–Landau functional⁹ of the bulk material. Including the effects of the depolarization field $\bar{E}_d = (0, 0, E_d)$ and the surface effects, the Ginzburg–Landau free energy in the neighborhood of the transition point can be expressed as

$$\begin{aligned} F_l &= \iint_V \int_V \left[\frac{A}{2} (T - T_{c0}) P^2 + \frac{B}{4} P^4 + \frac{C}{6} P^6 + \frac{D}{2} \left(\frac{\partial P}{\partial z} \right)^2 \right. \\ &\quad \left. - \frac{1}{2} E_d P \right] dv + \iint_S \frac{D \delta^{-1}}{2} P^2 dx dy, \end{aligned}$$

where A , B , C , and D are the expansion coefficients of the corresponding bulk material under the zero-stress state. T_{c0} is the cooling phase-transition temperature of the bulk crystal, S represents the upper and lower surface planes that cover the entire surface of the film, and δ is the extrapolation length that measures the effect of lattice relaxation on the surface or the change of the polarization due to the surface effect.^{4,12} The total Ginzburg–Landau free energy of the cell can be written as a sum of the electrical and mechanical components,⁷

$$\begin{aligned} F &= \iint_V \int_V \left[\frac{A}{2} (T - T_{c0}) P^2 + \frac{B + 4GQ^2}{4} P^4 + \frac{C}{6} P^6 \right. \\ &\quad \left. + \frac{D}{2} \left(\frac{\partial P}{\partial z} \right)^2 - \frac{1}{2} E_d P - 2\sigma_r \varepsilon^T \right] dv \\ &\quad + \iint_S \frac{D \delta^{-1}}{2} P^2 dx dy. \end{aligned} \quad (1)$$

Two separate cases may be considered: the more common $\delta > 0$ case, corresponding to a reduction of self-polarization on the surface, and the rarer $\delta < 0$ case, corresponding to an enhancement. We note that in general δ is not an absolute

constant. Furthermore, effects of the epitaxial stress and the surface lattice relaxation may contribute to or against the transformation.

Another important surface effect is the depolarization field that comes from the polarization-induced surface charges, which is governed by the electric boundary conditions. In this paper, we consider two cases: (a) the ferroelectric film is sandwiched between two metallic electrodes in short-circuit conditions and (b) the ferroelectric film is sandwiched between two dielectric substrates.

Although perfect screening is not achieved even under the short-circuit condition, partial compensation by the electrodes still reduces the depolarization field, due to the variation of the spontaneous polarization in the z direction. In this case, the relation between the depolarization field E_d and the spontaneous polarization P is given by¹²

$$E_d = -\frac{1}{\varepsilon} \left(P - \frac{1}{h} \int_{-h/2}^{h/2} P dz \right), \quad (2)$$

where ε is the dielectric constant of the film, and the second term on the right-hand side is due to the compensating charges on the upper and lower metallic electrodes. For dielectric substrates, there are no compensation charges, and the corresponding relation is given by (see the Appendix)

$$E_d = -\frac{P}{\varepsilon}. \quad (3)$$

We may write down a general expression that encompasses both contact conditions,

$$E_d = -\frac{1}{\varepsilon} \left(P - \frac{\phi}{h} \int_{-h/2}^{h/2} P dz \right), \quad (4)$$

where ϕ takes on the value of 0 or 1 depending on the contact condition as discussed in the foregoing.

Using Eqs. (1) and (4), the time evolution of the system is governed by the time-dependent Ginzburg–Landau equation:^{7,8}

$$\frac{\partial P}{\partial t} = -M \frac{\delta F}{\delta P} = M \left[-A(T - T_{c0})P + 4Q\sigma_r P - \frac{P}{\varepsilon} - (B + 4GQ^2)P^3 - CP^5 + D \frac{\partial^2 P}{\partial z^2} + \frac{\phi}{\varepsilon h} \int_{-h/2}^{h/2} P dz \right], \quad (5)$$

where M is the kinetic coefficient related to the domain-wall mobility. The surface term in Eq. (1) yields the boundary conditions,

$$\frac{\partial P}{\partial z} = \mp \frac{P}{\delta} \quad \text{for } z = \pm \frac{h}{2}. \quad (6)$$

Equation (5) has a trivial stationary solution, $P=0$, representing the paraelectric state. As discussed in the Introduction, to be able to transform from the initial paraelectric ($P=0$) state to the ferroelectric ($P \neq 0$) state, the paraelectric stationary state must become unstable. The same also applies to the reverse transformation.

The dynamic stability of the stationary states can be probed by applying an infinitesimal perturbation Δ to

the corresponding stationary solution of Eq. (5). The dynamics of Δ follows from Eq. (5) by retaining only the terms linear in Δ , which are given by

$$\frac{\partial \Delta}{\partial t} = M \left[-A(T - T_{c0})\Delta + 4Q\sigma_r \Delta - \frac{\Delta}{\varepsilon} - 3(B + 4GQ^2)P^2 \Delta - 5CP^4 \Delta + D \frac{\partial^2 \Delta}{\partial z^2} + \frac{\phi}{\varepsilon h} \int_{-h/2}^{h/2} \Delta dz \right]. \quad (7)$$

The boundary condition is the same as Eq. (6), only with P replaced by Δ . For a symmetric configuration, the condition $d\Delta/dz=0$ at $z=0$ must also hold.

This equation governs the stability of the stationary solution of Eq. (5). It is a linear equation of Δ . Its analysis in the context of phase stabilities, without having to resort to a solution of the nonlinear equations [Eq. (1) or (5)], is our main aim. It is obvious from Eq. (7) that the equation governing Δ in the paraelectric and ferroelectric states are different in general, from which it follows that the stability conditions for the two branches are also different. However, as we shall see, for second-order transitions, P is continuous at the transition point. The ferroelectric and paraelectric branches are both unstable when crossing this point from opposite directions and transform into one another. The Curie temperature and the critical thickness are then independent of the initial state and are thus well defined.

For first-order transitions, on the other hand, P is discontinuous across the transition temperature. The paraelectric ($P=0$) and the ferroelectric ($P \neq 0$) branches obey different stability conditions due to the difference in the governing equations of Δ in Eq. (7). Suppose the paraelectric branch is dynamically stable for temperatures down to T_c and the ferroelectric branch ($P \neq 0$) is dynamically stable for temperatures up to T_{ch} , then the two critical temperatures are likely to be unequal. Indeed, depending on the direction of the transformation between the two states, T_c is called the supercooling transition temperature and T_{ch} the Curie temperature (superheating transition temperature).

III. STABILITY OF THE PARAELECTRIC STATE AND CRITICAL CHARACTERISTICS

In view of its simplicity, the case in which the initial state is paraelectric, i.e., $P=0$, is considered first. Transition from the ferroelectric state ($P \neq 0$) will be considered in Sec. IV, where it will be shown that the two transition temperatures are related by a constant shift. We do not differentiate between the first- and second-order transitions, to which this analysis applies equally. In the following, the cases $\delta > 0$ and $\delta < 0$ are separately considered.

A. Reduced surface polarization: The $\delta > 0$ case

In most ferroelectric materials, lattice relaxation weakens the polarization on the surface, and $\delta > 0$. Using the method of separation of variables and taking into account $d\Delta/dz=0$, at $z=0$, Eq. (7) can be separated into time-

dependent and time-independent parts, connected by the eigenvalue. For $P=0$, the solution can be written as

$$\Delta_c(z,t) = e^{\omega_c t} \varphi_{\omega_c}(z) = \Delta_0 e^{\omega_c t} [\cos(kz) + R], \quad (8)$$

where ω_c is the eigenvalue and $\varphi_{\omega_c}(z)$ the corresponding eigenfunction of Eq. (7),

$$\omega_c = M[-A(T - T_{c0}) + 4Q\sigma_r - \varepsilon^{-1} - Dk^2], \quad (9)$$

and R a constant given by

$$R = -\frac{2M\phi}{\varepsilon h k \{M[4Q\sigma_r - A(T - T_{c0})] - \omega_c\}} \sin\left(\frac{kh}{2}\right). \quad (10)$$

The $P=0$ solution is unstable when $\omega_c > 0$, because in this case, Δ increases exponentially with time. It can be seen from Eq. (9) that when the temperature T is sufficiently high, $\omega_c < 0$, and the paraelectric state is stable. When T is sufficiently low, ω_c turns positive and the paraelectric state is no longer stable, since any small perturbation Δ will grow exponentially beyond all bounds. The critical condition $\omega_c = 0$, yields, in this case, the supercooling transition temperature T_c of the film,

$$T_c = T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} - \frac{D}{A} k_c^2, \quad (11)$$

where the first term on the right-hand side is related to the bulk ferroelectric property, the second term to the misfit of the substrate, the third term to the induced surface charges, and the fourth term to the lattice relaxation on the surface. While the last two terms act against the transformation by lowering the transition temperature, the second term can act either way, depending on the direction of the misfit, i.e., the sign of σ_r . Here k_c depends on the film thickness h , the extrapolating length δ , and the electric boundary condition through ϕ , as the smallest nonzero root of the equation,

$$\cot\left(\frac{k_c h}{2}\right) = k_c \delta + \frac{2\phi}{\varepsilon k_c h [4Q\sigma_r - A(T_c - T_{c0})]}. \quad (12)$$

The general relation between T_c and the film thickness h can be obtained by solving Eqs. (11) and (12) simultaneously. Equation (12) is a transcendental equation that can easily be solved numerically in general. Furthermore, as we shall show in the following, simple analytic approximations can also be derived in many important cases. The cooling critical thickness (CCT) of the film h_{cc} , below which ferroelectric transition by cooling is not possible, can be derived by putting $T_c = 0$ in Eq. (11), yielding the following expression for the corresponding k_c^2 , which we denote by k_{cc}^2 in terms of the material properties of the film:

$$k_{cc}^2 = \frac{1}{D} \left(AT_{c0} + 4Q\sigma_r - \frac{1}{\varepsilon} \right). \quad (13)$$

h_{cc} can then be obtained by solving for h as the smallest positive root of Eq. (12) corresponding to $T_c = 0$, with k_{cc} given by Eq. (13). Since h_{cc} varies inversely with k_{cc} according to Eq. (12), Eq. (13) then requires that the CCT for these materials increase with decreasing bulk transition temperature and substrate constraint, and with increasing depolarization field. We further note that, for k_{cc} to be real, $\varepsilon(AT_{c0}$

$+4Q\sigma_r) > 1$ must be satisfied, putting a necessary condition on the possibility of the cooling transition from the paraelectric state.

1. Asymptotic solutions for thin films (i.e., $h \ll \delta$)

When $hk_c \ll 1$, Eq. (12) can be solved via a series expansion of the left-hand side, yielding

$$k_c^2 \approx \frac{2 - \phi G_c}{h(\delta + h/6)}, \quad (14)$$

from which T_c is given by

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} - \frac{D(2 - \phi G_c)}{Ah(\delta + h/6)}, \quad (15a)$$

where G_c is a function of T_c ,

$$G_c \equiv \frac{2}{\varepsilon[4Q\sigma_r - A(T_c - T_{c0})]}. \quad (15b)$$

When $h \ll \delta$, the condition $k_c h \ll 1$ is satisfied from Eq. (14). Thus, T_c in Eq. (15a) can be solved explicitly to give

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} - \frac{2D}{Ah(\delta + h/6)} \quad \text{for } \phi = 0, \quad (16a)$$

and

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{2D}{Ah(\delta + h/6)} \quad \text{for } \phi = 1. \quad (16b)$$

Thus, independent of the contact condition, the critical temperature decreases monotonically as the film thickness h decreases. The corresponding CCT can be obtained by putting $T_c = 0$ in Eqs. (16a) and (16b), and solving for h ,

$$h_{cc} \approx \frac{2D}{\delta[(4Q\sigma_r + AT_{c0}) - \varepsilon^{-1}]} \quad \text{for } \phi = 0 \text{ (dielectric contacts)}, \quad (17a)$$

$$h_{cc} \approx \frac{2D}{\delta(4Q\sigma_r + AT_{c0})} \quad \text{for } \phi = 1 \text{ (short-circuit electrodes)}. \quad (17b)$$

Equations (17a) and (17b) show that the CCT decreases with decreasing surface relaxation (i.e., increasing extrapolation length δ), for both contact conditions. In addition, the short-circuit boundaries, with a smaller depolarization field, gives a lower CCT than the dielectric boundaries. Furthermore, h_{cc} may become negative if σ_r is negative and large. Both results can be predicted from physical considerations.

2. Asymptotic solutions for thick films (i.e., $h \gg \delta$) with $\phi G_c \ll 1$

In the neighborhood of $k_c h \approx \pi$, the left-hand side of Eq. (12) can be approximated by $\cot(x) \approx (\pi/2) - x$. This approximation yields

$$k_c \approx \frac{\pi}{h+2\delta} - \frac{2\phi G_c}{\pi h}. \quad (18)$$

Since the condition $k_c h \approx \pi$ is satisfied when $h \gg \delta$ and $\phi G_c \ll 1$, k_c in Eq. (18) is a solution of Eq. (12) for thick films with a small depolarization field. In this case, an explicit relation of T_c can be obtained from Eq. (11), which, taking into account $\delta \ll h$ and $\phi G_c \ll 1$, can be solved for T_c to give

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{D}{A} \left(\frac{\pi}{h} \right)^2. \quad (19)$$

The behaviors of T_c in Eqs. (16a), (16b), and (19) are similar. As the film thickness h is reduced, its critical temperature decreases monotonically.

The corresponding CCT is given by

$$h_{cc} \approx \sqrt{\frac{\pi^2 D}{4Q\sigma_r + AT_{c0}}}. \quad (20)$$

It is interesting to note that, even for thick films, the constraint of the substrate and the surface relaxation cannot be neglected as long as there is a surface in the sample. Furthermore, h_{cc} may become imaginary if σ_r is negative and sufficiently large.

B. Enhanced surface polarization: The $\delta < 0$ case

In rare cases, polarization may be enhanced, instead of reduced, on the surface of some materials. In this case, $\delta < 0$, and, similar to the $\delta > 0$ case, discussed in the foregoing, the solution of Eq. (7) can be written as

$$\Delta = e^{\omega_c z} \varphi_{\omega_c}(z). \quad (21)$$

The eigenvalue ω_c is given by

$$\omega_c = M \left[-A(T - T_{c0}) + 4Q\sigma_r - \frac{1}{\varepsilon} + Dk^2 \right]. \quad (22)$$

The eigenfunction is given by $\varphi_{\omega_c}(z) = \Delta_0 [\cosh(kz) + R]$, with

$$R = -\frac{2M\phi}{\varepsilon h k \{M[4Q\sigma_r - A(T - T_{c0})] - \omega_c\}} \sinh\left(\frac{kh}{2}\right). \quad (23)$$

The cooling critical temperature T_c is obtained by putting $\omega_c = 0$ in Eq. (22),

$$T_c = T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} + \frac{D}{A} k_c^2, \quad (24)$$

where k_c is related to the film thickness through the boundary conditions in (6), as the largest root, corresponding to the highest T_c , of the equation

$$k_c h \coth\left(\frac{k_c h}{2}\right) = k_c^2 h \gamma + \frac{2\phi}{\varepsilon [4Q\sigma_r - A(T_c - T_{c0})]}, \quad (25)$$

where we have defined $\gamma = -\delta > 0$. Similar to the $\delta > 0$ case, h and k_c can be shown to vary inversely with each other in general. This behavior in Eq. (24) leads to a value of T_c that decreases as the film thickness h increases, i.e., opposite to the $\delta > 0$ case. Physically, the reason for this behavior is clear, as caused by the enhanced polarization on the surface.

The major difference between the $\delta > 0$ and $\delta < 0$ cases lies in the sign for the polarization gradient in the two cases. In the $\delta < 0$ case, the enhanced surface polarization, as represented by the positive gradient term, together with the misfit interaction of the transformation strain (if $\sigma_r > 0$), favors the ferroelectric state over the paraelectric state. From Eq. (24), it is clear that unless the depolarization field caused by the surface-induced charges (the ε^{-1} term) is sufficiently large, T_c cannot be zero as long as a solution of k_c in Eq. (25) exists, independent of the film thickness.

The foregoing results show that, if the polarization is enhanced on the surface, i.e., $\delta < 0$, a positive value of the CCT in ferroelectric materials need not exist, and in such a case, the transition to the ferroelectric state by cooling is always possible. In this case, the existence of the CCT depends on whether the depolarization field due to the surface-induced charges is sufficiently large. For the more common $\delta > 0$ case, on the other hand, this condition does not have to hold for the CCT to exist.

1. Asymptotic solutions for thin films, i.e., $h \ll \gamma$

Similar to the case of $\delta > 0$, analytic approximations of the cooling transition temperature and the CCT can also be derived.

When $hk_c \ll 1$, expanding the left-hand side of Eq. (25) to second order in hk_c , the solution can be written as

$$k_c^2 \approx \frac{2 - \phi G_c}{h(\gamma - h/6)}, \quad (26)$$

so that

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} + \frac{D(2 - \phi G_c)}{Ah(\gamma - h/6)}. \quad (27)$$

The validity of solution (26) is satisfied when $h \ll \gamma$. An explicit solution of T_c from Eq. (27) is given by

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\varepsilon} + \frac{2D}{Ah(\gamma - h/6)} \quad \text{for } \phi = 0, \quad (28a)$$

and

$$T_c \approx T_{c0} + \frac{4Q\sigma_r}{A} + \frac{2D}{Ah(\gamma - h/6)} \quad \text{for } \phi = 1. \quad (28b)$$

These expressions show explicitly that, independent of the contact condition, the critical temperature increases monotonically as the film thickness h decreases. This is opposite to the $\delta > 0$ case. At the same time, T_c for $\phi = 1$ is positive definite for any film thickness $h < \gamma/6$. In such a case, the CCT does not exist.

From Eq. (28a), when the depolarization field is sufficiently large, i.e., $(AT_{c0} + 4Q\sigma_r) < \varepsilon^{-1}$, a solution of h_{cc} for $T_c = 0$ exists when $\phi = 0$. This is given by

$$h_{cc} \approx \frac{2D}{\gamma[\varepsilon^{-1} - (4Q\sigma_r + AT_{c0})]} \quad \text{for } \phi = 0 \text{ (dielectric boundaries)}, \quad (29)$$

if $\gamma/h_{cc} \gg 1/6$.

It can be seen from the foregoing that the behavior of h_{cc} depends strongly on the boundary contact conditions in this case of $\delta < 0$.

2. Asymptotic solutions for thick films ($h \gg \gamma$) with $\phi G_c \ll 1$

When the solution lies in the neighborhood of $k_c h > \pi$, the left-hand side of Eq. (25) can be approximated by $\coth(x) \approx 1$. This approximation yields

$$k_c^2 \approx \left(\frac{1}{\gamma} - \frac{\phi G_c}{h} \right)^2, \quad (30)$$

that satisfies $k_c h > \pi$ when $h \gg \gamma$ and $\phi G_c \ll 1$. An explicit expression of T_c can be derived by substituting into Eq. (24),

$$T_c = T_{c0} + \frac{4Q\sigma_r}{A} - \frac{1}{A\epsilon} + \frac{D}{A\gamma^2}, \quad \text{for } \phi = 0 \text{ and } \phi = 1. \quad (31)$$

In both cases, T_c is independent of h , and the critical thickness does not exist.

At this point, we note that the analytic results for second-order transitions,⁸ obtained using the static Ginzburg–Landau equation, are consistent with the present results. Our results are also applicable to first-order transitions from the paraelectric branch to the ferroelectric branch, yielding, instead of the Curie temperature, the stability limit of the paraelectric phase during cooling, i.e., the supercooling transition temperature. To obtain the Curie temperature and the critical thickness, in the following, we will analyze the stability of the ferroelectric branch and investigate the stability limit of the ferroelectric phase on heating, i.e., transitions from the ferroelectric branch to the paraelectric branch.

IV. STABILITY OF THE FERROELECTRIC STATE AND TRANSITION CHARACTERISTICS

In the ferroelectric state, the stationary polarization field $P(z)$ is nonzero, and the corresponding stability equation [Eq. (7)] is no longer the same as that in the paraelectric state. Treating the P -dependent terms as a perturbation and expanding in terms of the complete orthonormal set of eigenfunctions of the unperturbed equation, Eq. (7) can be solved within the first-order perturbation approximation. The eigenvalue ω_h in this case is given by

$$\omega_h = A(T - T_c) + 3(B + 4GQ^2)\langle P^2 \rangle + 5C\langle P^4 \rangle, \quad (32)$$

where T_c is the supercooling temperature obtained in the foregoing section, and $\langle P^n \rangle$ is the expectation value of P^n given by

$$\langle P^n \rangle = \frac{\int_{-h/2}^{h/2} P^n(z) \varphi_{\omega_c}^2(z) dz}{\int_{-h/2}^{h/2} \varphi_{\omega_c}^2(z) dz}, \quad (33)$$

where φ_{ω_c} is the eigenfunction of the unperturbed state. Since both P and φ peak at $z=0$, we may approximate $\langle P^n \rangle$

by $P_0^n = P^n(0)$. This approximation is also valid when P is a slowly varying function. Thus, we may write

$$\begin{aligned} \omega_h &= A(T - T_c) + 3(B + 4GQ^2)P_0^2 + 5CP_0^4 \\ &= (P_0^2 - p_1^2)(P_0^2 - p_2^2), \end{aligned} \quad (34)$$

where p_1^2 and p_2^2 are the two roots of Eq. (34) for $\omega_h = 0$. We note that p_1^2 and p_2^2 can be both real or are complex conjugates. In the simplest case that they are real, the stability condition of the ferroelectric state is satisfied if P_0^2 lies between p_1^2 and p_2^2 . In the following, we will consider several specific cases.

Let us first consider the case in which $C > 0$. We can write down the solutions as

$$p_1^2 = -\frac{3(4GQ^2 + B) + d}{10C}, \quad p_2^2 = -\frac{3(4GQ^2 + B) - d}{10C}. \quad (35)$$

Here d^2 is the discriminant of the quadratic in Eq. (34), given by

$$d^2 = 9(4GQ^2 + B)^2 - 20AC(T - T_c). \quad (36)$$

Note that the roots p_1 and p_2 are both functions of temperature through d . Let us define a temperature T_{ch} by

$$T_{ch} = T_c + \frac{9(4GQ^2 + B)^2}{20AC}. \quad (37)$$

For temperatures above T_{ch} , $d^2 < 0$ and ω_h has the same sign as $A(T - T_c)$, i.e., positive definite. Thus, the ferroelectric system will be unstable at temperatures above T_{ch} .

In the temperature range $T_c < T < T_{ch}$, the product $p_1^2 p_2^2$, from Eq. (34), is equal to $A(T - T_c)/5C$, which is positive definite ($C > 0$). In this temperature regime, it can be shown that $d^2 > 0$, and the roots in Eq. (35) are real and have the same sign. In addition, if $4GQ^2 + B < 0$, it can be seen from Eq. (35) that both roots are positive. In this case, both p_1 and p_2 are real, and the ferroelectric state is stable when P_0 lies between p_1 and p_2 . We note that at $T = T_{ch}$, $d_2 = 0$ and $p_1 = p_2$ so that P_0 is uniquely defined. At $T = T_c$, the smaller solution becomes zero. Within this temperature regime, which is above the cooling para-ferroelectric transition temperature T_c , the ferroelectric state is still stable, and T_{ch} can be identified as the superheating transition temperature. This difference between the heating-up and cooling-down behaviors is well known for first-order phase transformations near the critical point, and is caused by the restraint on the realization of the transformation strain, in the present case by the rigidity of the substrate through the $4GQ^2$ term.

In the case when $4GQ^2 + B > 0$, both p_1^2 and p_2^2 are negative, and P_0 has no real solution in this temperature regime. In this case, the ferroelectric state does not exist for temperatures above T_c , and the ferroelectric state cannot be superheated beyond the cooling transition temperature T_c . We note that when $T = T_c$, the largest solution is zero.

At temperatures below T_c , the product of the two roots is negative, and thus only one of them, the largest one, can be positive. For the ferroelectric state to be stable, P_0 must be smaller than the only real root. The system here then behaves as a typical second-order system.

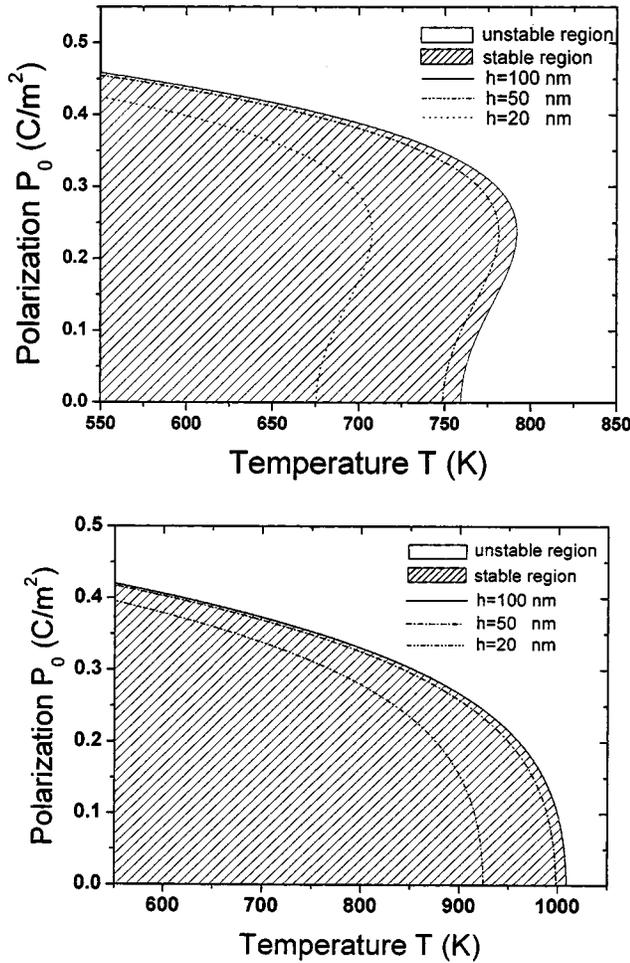


FIG. 1. (a) The stable area of the ferroelectric to paraelectric transition of a freestanding PbTiO_3 film. (b) The stable area of the ferroelectric to paraelectric transition of a PbTiO_3 film on a SrTiO_3 substrate.

Thus, in the case $C > 0$, the order of para-ferroelectric transition in a thin film depends not on the sign of B but on the sign of $B + 4GQ^2$. Since $4GQ^2$ is positive, a film made of a first-order bulk material may exhibit a second-order transition behavior if the constraint due to the substrate is sufficiently large.

Plotted in Figs. 1(a) and 1(b) as a function of temperature for various film thicknesses are the regions of stability of P_0 for PbTiO_3 according to the condition $p_2 < P_0 < p_1$ from Eqs. (35) and (36). Figure 1(a) shows the case of a freestanding film, whereas Fig. 1(b) shows the film on a SrTiO_3 substrate. It is obvious that the constraint of the substrate weakens the polarization of the ferroelectric state, reduces the Curie temperature, and changes the first-order transition of the ferroelectric material into a second-order one.

It is interesting that the difference between the superheating and supercooling transition temperatures is insensitive to the film thickness h . This behavior is also seen in the numerical solution of the static Ginzburg–Landau equation for the first-order phase transition of a freestanding ferroelectric film.¹³ These results show that the two temperatures, plotted as a function of film thickness, are practically parallel.

TABLE I. Phenomenological parameters of PbTiO_3 and BaTiO_3 (in cgs unit).

Material	T_{c0} (K)	$A \cdot 10^{-5}$	$D \cdot 10^{-15}$	δ (nm)	ϵ
PbTiO_3	763 ^a	8.37 ^b	3 ^b	5 ^b	210 ^c
BaTiO_3	397 ^a	7.4 ^b	0.5 ^b	0.5	200 ^d

^aReference 6.

^bReference 7.

^cReference 15.

^dReference 16.

The case of materials with $C=0$ can also be easily analyzed using Eq. (34), which becomes

$$\omega_h = A(T - T_c) + 3(B + 4GQ^2)P_0^2. \quad (38)$$

If $B + 4GQ^2 > 0$, ω_h is positive definite for $T > T_c$, and the system is unstable. For $T < T_c$, the system is stable as long as $P_0^2 < A(T_c - T)/(3(4GQ^2 + B))$. This system behaves like a second-order system. For the rare case in which $B + 4GQ^2 < 0$, the ferroelectric state is stable in the temperature range $T < T_c - 3(B + 4GQ^2)/A$, which is above the supercooling transition temperature T_c . This system thus behaves like a first-order system, with a superheating temperature $T_{ch} = T_c - 3(B + 4GQ^2)/A$. The case $C < 0$ rarely happens and will not be considered. At any rate, the foregoing analysis can be repeated easily for this case also.

Analytic expressions of the Curie temperature and the corresponding critical thickness for first-order transitions can thus be obtained by replacing T_{c0} with $T_{c0} + 9(B + 4GQ^2)^2/20AC$ in the respective equations in Sec. III.

V. DISCUSSIONS

The following discussions refer to the specific examples of PbTiO_3 and BaTiO_3 . Straightly speaking, the foregoing results only apply to uniaxial ferroelectrics and not so much to cubic perovskites such as PbTiO_3 and BaTiO_3 . However, even for these perovskite ferroelectric thin films, the polarization field is often found to be perpendicular to the surface due to the mechanical constraint of the substrate.¹⁴

The material parameters for the free energy expressions of PbTiO_3 and BaTiO_3 film are listed in Table I. The critical thickness of the thin film at $T_c=0$ can be calculated using Eqs. (11) and (12), following the usual assumption of a reduced polarization field on the surface, i.e., $\delta > 0$.

We consider a BaTiO_3 film, epitaxially grown on a thick $\text{SrRuO}_3/\text{SrTiO}_3$ substrate. In SI units, the elastic compliance components of a BaTiO_3 film are¹⁶ $s_{11}=s_{22}=s_{33}=8.3 \times 10^{-12}$, $s_{13}=s_{13}=s_{23}=-2.7 \times 10^{-12}$, and $Q=-0.043$. If stress relaxation during fabrication is neglected, the misfit strain can reach 2%, corresponding to a misfit compressive stress of 3.57 GPa. From the second term of Eq. (11), this large compressive misfit stress may raise the Curie temperature by an unrealistic value of 900°. Experimentally, Yanase *et al.*¹⁷ measured a Curie temperature of 350 °C. Compared with an inherent Curie temperature of BaTiO_3 of 130 °C, one may estimate that the Curie temperature is raised only by 220 °C, corresponding to a misfit stress and strain to be 852 MPa and 0.00477, respectively. In the first-principles calculation of Junquera and Ghosez,¹ the critical thickness of BaTiO_3 under

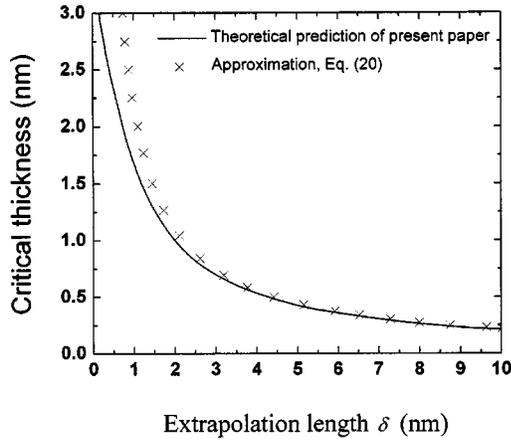


FIG. 2. The critical thickness vs the extrapolation length for BaTiO₃, where '+' describes the approximation $h_c(\text{nm})=2.2/\delta$.

short-circuit boundary conditions was found to have a value of about 2.4 nm. The corresponding extrapolating length can be estimated by numerically solving Eqs. (11) and (12) simultaneously, giving a value of $\delta \approx 0.5$ nm, which satisfies $\delta \ll h$. We note that the small extrapolating length physically means that the tetragonal phase on the surface becomes almost central symmetric due to lattice relaxation, resulting in a large reduction in the polarization on the surface. The depolarizing effect so arises does not come from the usual depolarization field due to induced electric charges on the surface. Indeed, Eq. (20) shows explicitly that this is the case. Thus, even with zero depolarizing charges, i.e., both the third term on the right-hand side of Eq. (11) and the last term in Eq. (12) vanish, a solution of h_c for these equations may still exist, as can be seen explicitly in Eqs. (17a) and (17b), which is independent of the depolarization field. This conclusion is independent of the contact conditions.

From the numerical solution of Eq. (13), the relation between the critical thickness and the extrapolation length of BaTiO₃/SrRuO₃/SrTiO₃ is shown in Fig. 2. The decrease of the extrapolation length δ decreases the surface polarization and causes the critical thickness to increase. The corresponding analytic approximations for the cases of $\delta > 0$, and $h_c \ll \delta$ or $h_c \gg \delta$ are derived in Eqs. (17) and (21), respectively. Using values from Table I, these equations give $h_c(\text{nm}) = 3.5 - 2\delta$ and $h_c(\text{nm}) = 2.2/\delta$, respectively. Despite their simple forms, these expressions give a very good description of the system, as shown by comparing with the numerical solution in Fig. 2.

In the first-principles calculations of Ghosez and Rabe² for (001) PbTiO₃ films, a stable nonferroelectric ground state cannot be observed for films with thicknesses down to ≈ 1.2 nm (three unit cells), suggesting the possibility that the critical thickness may not exist in this case. Ghosez and Rabe's work² also showed that the calculated polarization was enhanced on the surface, implying a value of $\delta < 0$. Our analysis in Sec. III B shows that in such cases, a critical thickness indeed may not exist for the short-circuit boundary conditions. Furthermore, in such a case, the Curie temperature should increase with decreasing thickness. Since surface stress relaxation in this calculation has not been taken into

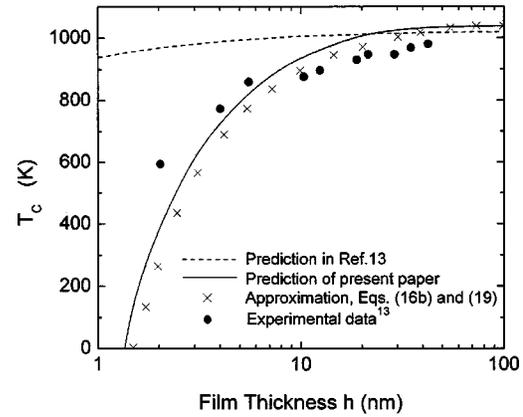


FIG. 3. The Curie temperature vs thickness h .

account, it is not unreasonable to speculate that the surface polarization calculated in Ref. 2, may be overestimated. A proper treatment of the relaxation may produce a positive value of δ . Indeed, Streiffer *et al.*,¹⁴ who measured the Curie temperatures as a function of film thickness up to 50 nm of epitaxial films of PbTiO₃, grown on a SrTiO₃ (001) substrate (i.e., $\phi=0$), found that the Curie temperature decreased with decreasing film thickness, indicating a reduced polarization on the surface corresponding to a positive value of δ .

Assuming the film is fully strained epitaxially, with a compressive epitaxial strain of $\epsilon_{xx} = \epsilon_{yy} = 1.2\%$,¹⁴ and elastic compliance components of $s_{11} = 8.3 \times 10^{-12}$ N/m² and $s_{12} = -2.5 \times 10^{-12}$ N/m²,¹⁸ the epitaxial stresses can be calculated to be $\sigma_r = \sigma_{xx} = \sigma_{yy} = -2.4293 \times 10^9$ N/m². Substituting the epitaxial stresses into Eq. (11) with the parameters in Table I and using the electrostrictive coefficient $Q = -0.026$ (in SI unit),¹⁸ the Curie temperature is found to increase by about 335 K. The transition temperature is a function of film thickness (in nanometers), as given by Eqs. (11) and (12) (for $\phi=0$). The results are shown in Fig. 3, together with the experimental points of Streiffer *et al.*¹⁴ The transition temperature can be calculated analytically using Eqs. (16b) and (20) for large and small values of h , respectively. For PbTiO₃ these equations can be put into the simple forms $T_c = 1041 - 36000/h^2$ for $h > 20$ nm, and $T_c = 1041 - 1440/h$ for $h < 20$ nm, h being in units of nanometer, using the parameters in Table I. It can be seen that this simple relationship describes the experimental data very well. Plotted together in the dotted line is the theoretical prediction used for comparison by Streiffer *et al.*¹⁴ The difference between the two theoretical results in the small film thickness regime is obvious. We note that in the foregoing analysis the elastic strain energy, being proportional to $\epsilon_0^2 \sim P^4$, is assumed negligible in comparison with the interaction energy between the epitaxial stress and the transformation strain. The calculated Curie temperature versus thickness for PbTiO₃ thin films under the two contact conditions is shown in Fig. 4. For films with the same thickness, those on the dielectric substrates have Curie temperatures slightly lower than on short-circuit electrodes due to the screened depolarization effect in the latter case.

VI. SUMMARY AND CONCLUSIONS

A thermodynamic model has been developed to describe the critical parameters in the ferroelectric transformation in

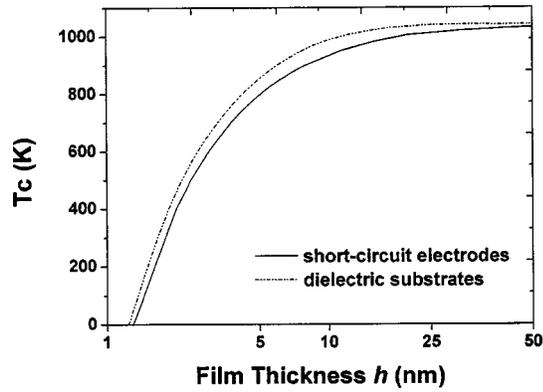


FIG. 4. The Curie temperature vs thickness under different boundary conditions.

thin films, such as the Curie temperature and critical thickness. By analyzing the conditions of dynamic instability of the time-dependent Ginzburg–Landau equation, we obtain analytic expressions for both first-order and second-order transitions for the relationship among the epitaxial stresses, the surface-charge-induced depolarization, the electromechanical contact conditions, the film thickness, and the Curie temperature. From this relation, analytic expressions for the critical thickness are also derived. Despite the simple form of these expressions, they give very good description of the system, as shown by comparing with the numerical solutions.

Our analysis yields the following conclusions:

- (1) Four factors influence the dependence of the paraferroelectric transition on film thickness in thin films: (a) surface lattice relaxation, (b) induced surface charge, (c) interaction of epitaxial stress with transformation strain, and (d) restraint of the transformation strain.
- (2) The restraint of the transformation strain due to the rigidity of the substrate weakens the polarization of the ferroelectric state, reduces the Curie temperature, and may even cause a thin film made of first-order ferroelectric material to undergo a second-order transition.
- (3) Enhanced or reduced polarization on the surface due to the effects of the lattice relaxation and the epitaxial stress plays an important role in determining the Curie temperature and the critical thickness. In the case where surface polarization is enhanced, the Curie temperature is increased and the critical thickness reduced, as the film thickness decreases. It opposes the effect of the depolarization field due to the induced surface charges, the sole presence of which is not sufficient to guarantee the existence of a positive value of the critical thickness. In the reduced case, the opposite is true.
- (4) For first-order transitions, the difference between the superheating and supercooling transition temperatures is found to be insensitive to the film thickness and surface boundary conditions.

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APPENDIX: DEPOLARIZATION FIELD IN THE FERROELECTRIC THIN FILM BETWEEN TWO DIELECTRIC SUBSTRATES

The thin film is assumed to be infinite along the x and y directions with a thickness h . Consider a unit positive charge acting at (z', r', θ') in the film, the electric potential at (Z, R, θ) in the film has been derived by Wang and Woo as follows:¹⁹

$$G(\vec{x}, \vec{x}') = \frac{1}{4\pi\alpha} \frac{1}{[(Z - z')^2 + r^2]^{1/2}} + \frac{1}{4\pi\alpha_0} \sum_{n=0}^{\infty} \left\{ \frac{c_1}{[(z_1 + 2nh)^2 + r^2]^{1/2}} + \frac{c_2}{[(z_2 + 2nh)^2 + r^2]^{1/2}} + \frac{c_3}{[(z_3 + 2nh)^2 + r^2]^{1/2}} + \frac{c_4}{[(z_4 + 2nh)^2 + r^2]^{1/2}} \right\} \beta^n, \quad (\text{A1})$$

where, α_0 , α_2 , and α are the dielectric constant of the upper and lower substrates and of the film, respectively,

$$c_1 = \frac{(1 - \alpha/\alpha_0)(\alpha_0/\alpha - \alpha_0/\alpha_2)}{(1 + \alpha/\alpha_0)(1 + \alpha/\alpha_2)},$$

$$c_2 = \frac{(1 - \alpha_0/\alpha)}{(1 + \alpha/\alpha_0)},$$

$$c_3 = -\frac{(1 - \alpha_0/\alpha)(1 - \alpha/\alpha_2)}{(1 + \alpha/\alpha_0)(1 + \alpha/\alpha_2)}$$

$$c_4 = \frac{(\alpha_0/\alpha_2 - \alpha_0/\alpha)}{(1 + \alpha/\alpha_2)},$$

$$\beta = \frac{(1 - \alpha/\alpha_0)(1 - \alpha/\alpha_2)}{(1 + \alpha/\alpha_0)(1 + \alpha/\alpha_2)}, \quad (\text{A2})$$

and

$$z_1 = 2h + Z - z',$$

$$z_2 = Z + z',$$

$$z_3 = 2h - Z + z',$$

$$z_4 = 2h - (Z + z'). \quad (\text{A3})$$

$$r = [R^2 + (r')^2 - 2Rr' \cos(\theta - \theta')]^{1/2}. \quad (\text{A4})$$

From Eq. (A1), one can derive the electric potential at (Z, R, θ) in the film if a unit dipole along the z axis acts at (z', r', θ') in the film as

$$G_p(\vec{x}, \vec{x}') = \frac{\partial G(\vec{x}, \vec{x}')}{\partial z'} \quad (\text{A5})$$

This result for a single dipole can be readily generalized to a distribution of polarization $P(z')$ as follows:

$$\begin{aligned} \Phi_d &= \int \int_{\Omega} \int G_p(\vec{x}, \vec{x}') P(\vec{x}') d\vec{x}' \\ &= \int \int_{\Omega} \int \frac{\partial G}{\partial z'} P(z') d\vec{x}' \\ &= \int \int_{\Omega} \int \left\{ \frac{\partial}{\partial z'} \left[\frac{\partial G}{\partial z'} \int_0^{z'} P(\chi) d\chi \right] \right. \\ &\quad \left. - \frac{\partial^2 G}{\partial (z')^2} \int_0^{z'} P(\chi) d\chi \right\} d\vec{x}' = E_0 + \frac{1}{\alpha} \int_0^z P(\chi) d\chi, \quad (\text{A6}) \end{aligned}$$

and E_0 is a constant. In fact, the first integral in Eq. (A6) can be reduced to a surface integral on the upper and lower surfaces of the film. By integrating r from zero to infinity, it becomes a constant. As for the second integral in Eq. (A6), since $\partial^2 G / \partial (z')^2 = \delta(\vec{x} - \vec{x}') / (4\pi\alpha)$, one can derive the result easily. The depolarization field can be derived as follows:

$$E_d = - \frac{\partial \Phi_d}{\partial z} = - \frac{P}{\alpha}. \quad (\text{A7})$$

One should bear in mind that the expansion (A1) is not suitable for the case with upper and lower electrodes for which $\alpha_0, \alpha_2 \rightarrow \infty$ and $\beta=1$.

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