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Stability of 180° domain in ferroelectric thin films

Biao Wang^{a)} and C. H. Woo^{b)}

Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

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Ferroelectric random access memory (FRAM) has attracted much attention in the last two decades due to its ideal properties such as nonvolatility, high speed, and low power consumption. There is a strong incentive to develop high-density FRAMs, in which the switched domains, developed under low voltage or short pulses, are necessarily very small, and are therefore usually unstable and suffer from significant backswitching upon removal of the external voltage. In this investigation, a general form of energy expression for a ferroelectric material containing 180° domains is derived, from which evolution equations of the domain are established. By choosing the change in internal energy as the Liapunov function, a general formulation is developed to determine the stability conditions of the switched domain. This is applied to the case of an ellipsoidal 180° domain and yields a criterion for the stability of switched domains. We note that our approach is generally applicable to many other fields, including phase transformation, nucleation, expansion of dislocation loops in thin films, etc. © 2003 American Institute of Physics. [DOI: 10.1063/1.1578529]

I. INTRODUCTION

Ferroelectric materials fall into a special group of polar dielectrics in which the spontaneous polarization can be switched with an external electric field. Different ferroelectric domains have different piezoelectric, pyroelectric, electro-optic, and nonlinear optic constants, and many applications of the ferroelectric materials are derived from this characteristic. Over the last decade, interest in ferroelectrics has dramatically increased due to their wide application in various electronic and optoelectronic devices, and as a result of recent achievements in the processing of ferroelectric thin films.

The unique ability of a ferroelectric film to maintain its polarization even in the absence of an external voltage makes it very useful as a nonvolatile memory device. Random access memory (FRAM) devices made from ferroelectrics have attracted much attention recently, due to their ideal properties such as nonvolatility, high speed, and low power consumption.^{1,2}

The development of high-density FRAMs requires the fabrication of switched domains of very small size under low voltage or short pulses. Recently, atomic-force microscopes (AFMs) have been successfully used to imprint (or “write”) small ferroelectric domains onto the surface of ferroelectric materials.³ Devices prepared in this way have been proposed for possible use as high-density nonvolatile memory because of the very small feature size achievable using this technique. Polarization in AFM writing is accomplished with the high electric field of the AFM tip. There is no need to use a top electrode, like in the usual poling process. However, without electrodes, there is no bound charge to tie the polarization charge. Therefore, the depolarization energy may cause serious depoling when the AFM tip is removed. Li

*et al.*⁴ considered the stability of an electrodeless near-surface ferroelectric domain, and found that the domain is unstable unless the surface charge is compensated. Therefore it is very important for us to know the stability conditions for a domain in the absence of an external electric field. In this regard, the critical dimension of a stable 180° domain (i.e., one that does not switch back after the removal of external voltage), induced by the AFM tip on the surface of a ferroelectric material, is important information for fabricating ferroelectric memories with reliable retention properties.

Due to the direct influence of domain structures on the macroscopic properties of ferroelectric samples, many fabrication techniques are based on domain structure optimization. In general, a 180° domain evolves under combined action of the externally applied electric field, the depolarization field, the surface tension of the domain wall, and an internal electric field that may originate from defects in the material.⁵ Under an external electric field, a 180° domain nucleates and expands, but may shrink back under action of the depolarization field and surface tension when the external field is removed.

Since domain switching has profound effects on the performance of devices made of ferroelectrics, a lot of research work has been done to understand the phenomena. In an early study, Landauer⁶ considered the possible formation of thermally induced, spike-shaped domains of reversed polarization in BaTiO₃. Rickman *et al.*⁷ reported treatment of twin domain formation energetics in ferroelectric materials. Speck *et al.*⁸ described domain formation in epitaxial systems in terms of a defect theory. The kinetics of domain wall evaluation were considered by Loge and Suo.⁹ Gopalan and Mitchell⁵ carried out a systematic study of the switching time, domain wall velocities, and stabilization mechanisms of 180° domains in Z-cut LiTaO₃ crystals. Huo and Jiang¹⁰ and Rosakis and Jiang¹¹ proposed a continuum model for domain switching in polycrystalline ferroelectric ceramics, and studied the morphology of ferroelectric domains. Lynch

^{a)}On leave from Harbin Institute of Technology, Harbin, China; electronic mail: mmwangb@polyu.edu.hk

^{b)}Corresponding author; electronic mail: mmchwoo@polyu.edu.hk

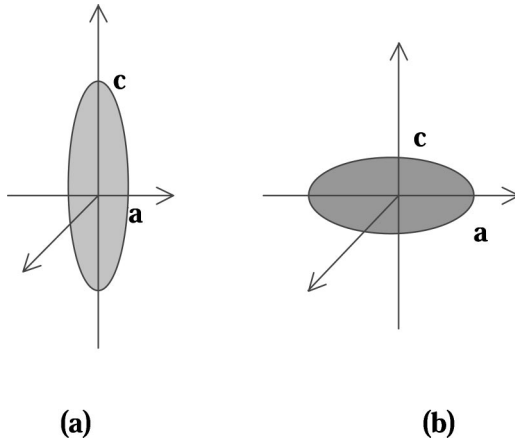


FIG. 1. Schematic of the prolate spheroidal and oblate spheroidal domains.

and co-workers¹² examined the nonlinear behavior of PLZT based on a domain switching mechanism. Wang and Xiao¹³ investigated the dynamic process of domain switching. Yang *et al.*¹⁴ made a direct optical observation of pinning and bowing of a single 180° ferroelectric domain wall under a uniformly applied electric field using a collection mode near-field scanning optical microscope. Li and Weng¹⁵ developed a micromechanical theory for the nonlinear behavior of ferroelectrics. Recently, domain switching and the back-switching process have attracted many researchers. For example, Matyjasek¹⁶ studied the depolarization effect in a telluric acid ammonium phosphate crystal using the nematic liquid-crystal decoration technique; Guo *et al.*¹⁷ studied the domain stability of $(\text{Pb}_{0.76}\text{Ca}_{0.24})\text{TiO}_3$ thin film using piezoresponse microscopy; Gruverman and Tanaka¹⁸ investigated the nanoscale mechanism of retention behavior in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films by piezoresponse scanning force microscopy.

In this article, we intend to establish a general formulation to determine the stability conditions and the stable dimension of a 180° domain in a ferroelectric material to avoid backswitching. An expression for the energy of a ferroelectric material as a function of the domain geometry is first derived. The thermodynamic driving force and the kinetic equations governing the evolution of the domain are then established. Based on the kinetic equations of the domain and using the internal energy change as a Liapunov function, a stability analysis is carried out, and the critical geometry of the domain is determined. Finally, as an example, we consider an ellipsoidal 180° domain in a ferroelectric material. The ranges of its two size parameters for which backswitching will happen are determined.

II. ENERGY EXPRESSION

Assumed as a near-equilibrium thermodynamic process, the speed of domain evolution can be assumed to be proportional to the energy driving force, i.e., the total free energy reduction rate with respect to the change in domain size. For simplicity, the 180° domain is assumed to be in the form of an oblate or prolate spheroid, the geometry of which is describable in terms of two parameters, a and c , where $a = a_1$

$= a_2$ and $c = a_3$. For the prolate case, $a < c$ [Fig. 1(a)], and for the oblate case, $a > c$ [Fig. 1(b)]. Under an applied electrical field, a 180° domain will nucleate and expand. The driving force for domain evolution is the reduction in free energy in the process, which can be calculated by a surface integral derived by Wang and Xiao¹³ for a general shape. In this connection, the electrostatic energy of a ferroelectric material with a general 180° domain depends on the geometry of the domain. The energy driving force can be derived directly by taking the derivative with respect to each parameter governing the geometry. For example, if the domain is assumed to be an oblate or prolate spheroid, we can obtain the driving force directly by taking the derivatives with respect to shape parameters a and c .

Since there is no strain involved in the 180° domain, only the electrostatic energy and domain-wall energy enter into our analysis. The ferroelectric material can be modeled as an ordinary dielectric material with spontaneous polarization $\vec{P}_s$, whereas inside the 180° domain, the spontaneous polarization is $-\vec{P}_s$. This problem can also be considered as two subproblems:¹³ one that is related to a uniform dielectric material with spontaneous polarization $\vec{P}_s$, and the other related to this dielectric material, with an embedded region with spontaneous polarization $\vec{P}^* = -2\vec{P}_s$, corresponding to the 180° domain.

Consider a dielectric body V , containing an inclusion Ω with spontaneous polarization $-2\vec{P}_s$, subjected to an applied electric field. The total electric field is the sum of E_i^0 and E_i , where E_i^0 is the electric field applied in the absence of the inclusion, and E_i is due to the spontaneous polarization prescribed in the inclusion. In the absence of strain, the fundamental work associated with the change in electric field is given by

$$\delta W^* = \frac{1}{2} E \delta D, \quad (1)$$

where D is the electric displacement vector.

Under two different boundary conditions, we can derive the following two different energy expressions for the system.

(1) On boundary S , the electric charge is given by $\rho^0 = n_i(D_i^0 + D_i)$, where D_i^0 and D_i are the electric displacement vectors due to ρ^0 and the inclusion, respectively.

If the internal energy is assumed to be zero when $\vec{D} = \vec{P}$, $E_i^0 = 0$, and the uniform ferroelectric polarization charges were neutralized, the electrostatic energy can be written as

$$W^* = \frac{1}{2} \int \int \int_V [D_i^0 + D_i - P_i^* H(\Omega)] (E_i^0 + E_i) dV, \quad (2)$$

where $H(\Omega)$ is the Heaviside step function in domain region Ω . Since $D_{i,i} = 0$ in V and $n_i D_i = 0$, $n_i D_i^0 = \rho^0$ on S , where n_i is the inward unit normal vector on the boundary, integration by parts gives

$$\begin{aligned}
& \int_V \int_V \int_V D_i(E_i^0 + E_i) d\nu \\
&= \int_V \int_V \int_V \{[D_i(\Phi^0 + \Phi)],_i - D_{i,i}(\Phi^0 + \Phi)\} d\nu \\
&= - \int_S \int n_i D_i(\Phi^0 + \Phi) ds = 0, \tag{3}
\end{aligned}$$

$$\begin{aligned}
& \int_V \int_V \int_V D_i^0 E_i d\nu = \int_V \int_V \int_V \varepsilon_{ij} E_j^0 E_i d\nu \\
&= \int_V \int_V \int_V E_i^0 (D_i - P_i) d\nu \\
&= - \int_\Omega \int E_i^0 P_i^* d\nu. \tag{4}
\end{aligned}$$

Substitution of Eqs. (3) and (4) into Eq. (2) yields

$$\begin{aligned}
W^* &= \frac{1}{2} \int_V \int_V \int_V D_i^0 E_i^0 d\nu - \frac{1}{2} \int_\Omega \int P_i^* E_i d\nu \\
&\quad - \int_\Omega \int P_i^* E_i^0 d\nu. \tag{5}
\end{aligned}$$

Here the first term is the electrostatic energy due to the electric field applied in the absence of the spontaneous polarization inclusion. The second term is the electrostatic energy due to the depolarization field of the spontaneous polarization, and the third term is the interaction energy of the two electric fields. It is interesting to note that the electrostatic energy is not the sum of the two energies due, respectively, to $\vec{E}^0$ and $\vec{P}$, as stated by Colonnetti's theorem in the counterpart elastic problem.^{19,20} Under constant temperature, the electrostatic energy can be treated as the Helmholtz free energy of the body. One needs to subtract the work done by external charges to derive its Gibbs free energy G ,

$$\begin{aligned}
G &= W^* - \int_S \int \rho^0(\Phi_0 + \Phi) ds \\
&= W^* - \int_S \int \rho^0 \Phi_0 ds - \int_S \int \Phi n_i D_i^0 ds \\
&= \frac{1}{2} \int_V \int_V \int_V E_i^0 D_i^0 d\nu - \int_S \int \rho^0 \Phi_0 ds \\
&\quad - \frac{1}{2} \int_\Omega \int E_i P_i^* d\nu, \tag{6}
\end{aligned}$$

where Eqs. (4) and (5) were used to derive Eq. (6). Without the 180° domain, and assuming that a dielectric body is subjected to ρ^0 alone, the Gibbs free energy is given by

$$G_0 = \frac{1}{2} \int_V \int_V \int_V E_i^0 D_i^0 d\nu - \int_S \int \rho^0 \Phi_0 ds. \tag{7}$$

If spontaneous polarization due to inclusions is introduced in V , the Gibbs free energy of the system will increase by

$$\Delta G = G - G_0 = - \frac{1}{2} \int_\Omega \int E_i P_i^* d\nu. \tag{8}$$

One may be puzzled by this surprising result: the change in Gibbs free energy of the system, due to the introduction of inclusions with spontaneous polarization, is just the depolarization energy of the inclusions. There is no interaction between the electric field applied and the spontaneous polarization. In fact, this surprising result is due to the boundary condition we assumed. The electric charges along the boundary remain unchanged when spontaneous polarization inclusions are introduced into the body, which means that the electric charges induced by the inclusions on the boundary have been discharged. Thus, the interaction between the electric field applied and the spontaneous polarization has been eliminated.

It is not easy to fix the electric charge distribution along the boundary during the whole process. The result obtained here in Sec. II suggests that the effect of the electric field applied on domain switching may be eliminated by properly adjusting the boundary conditions. More familiar results can be obtained if the following boundary condition is used instead.

(2) On boundary S , the electric potential Φ^0 is given. One can derive the electrostatic energy using Eq. (2). Thus, since $D_{i,i}=0$, $D_{i,i}^0=0$ in V and $\Phi=0$ on S , integration by parts gives

$$\begin{aligned}
& \int_V \int_V \int_V E_i (D_i^0 + D_i) d\nu = - \int_V \int_V \int_V [\Phi (D_i^0 + D_i)],_i d\nu \\
&= \int_S \int n_i (D_i^0 + D_i) \Phi ds = 0. \tag{9}
\end{aligned}$$

$$\begin{aligned}
& \int_V \int_V \int_V E_i^0 D_i d\nu = \int_V \int_V \int_V E_i^0 (\varepsilon_{ij} E_j + P_i) d\nu \\
&= \int_V \int_V \int_V D_i^0 E_i d\nu + \int_\Omega \int E_i^0 P_i^* d\nu \\
&= \int_\Omega \int E_i^0 P_i^* d\nu. \tag{10}
\end{aligned}$$

Substitution of Eqs. (9) and (10) into Eq. (2) yields

$$\begin{aligned}
W^* &= \frac{1}{2} \int \int \int_V [D_i^0 + D_i - P_i^* H(\Omega)] (E_i^0 + E_i) d\nu \\
&= \frac{1}{2} \int \int \int_V D_i^0 E_i^0 d\nu - \frac{1}{2} \int \int \int_\Omega E_i P_i^* d\nu. \quad (11)
\end{aligned}$$

It is interesting to note that the electrostatic energy here is the sum of two contributions due to ρ^0 and P_i^* , respectively. The increase in Gibbs free energy can be written as

$$\begin{aligned}
\Delta G = G - G_0 &= -\frac{1}{2} \int \int \int_\Omega E_i P_i^* d\nu \\
&\quad - \int \int \int_\Omega E_i^0 P_i^* d\nu, \quad (12)
\end{aligned}$$

where in deriving Eq. (12), we have used Eq. (10) again.

Equations (5), (8), (11), and (12) are general expressions for the electrostatic energy and the changes in energy associated with the introduction of a different ferroelectric domain in a ferroelectric material under different boundary conditions. It can be seen that only the internal electric field inside the domain is needed to evaluate the energy.

A given electric potential is the most common boundary condition used. In this case, Eq. (12) gives the free energy

change associated with the growth of the domain. In the following, we derive the explicit energy expressions for an ellipsoidal domain. We divide the problem of an 180° domain in a ferroelectric body into two subproblems, as mentioned earlier. For an ordinary dielectric material with uniform spontaneous polarization $\vec{P}_s$, the electric field is given by

$$\vec{E}^0 = \vec{e}^0 - \frac{\vec{P}_s}{\epsilon}, \quad (13)$$

where $\vec{e}^0$ is the electric field applied in the dielectric material without spontaneous polarization, which may include internal electric field $\vec{E}^i$ as follows:

$$\vec{e}^0 = E_0 \vec{k} + \vec{E}^i, \quad (14)$$

in which the electric field applied is assumed to be parallel with the z axis, whereas the spontaneous polarization is along the opposite direction of the z axis. When there is a 180° domain with spontaneous polarization $-2\vec{P}_s$ in this dielectric material, the electric field inside the ellipsoidal domain is given by¹³

$$E_3 = -\frac{P_s}{2\pi\epsilon} I_3, \quad E_1 = E_2 = 0, \quad (15)$$

where for ellipsoidal domain, I_3 is given by²¹

$$I_3 = \begin{cases} 4\pi c a^2 \{ \log[c/a + \sqrt{(c/a)^2 - 1}] - \sqrt{c^2 - a^2}/c \} / (c^2 - a^2)^{3/2} & \text{prolate spheroid, } c > a \\ 4\pi/3 & \text{sphere, } c = a \\ 4\pi a^2 c [\sqrt{(a/c)^2 - 1} - \arccos(c/a)] / (a^2 - c^2)^{3/2} & \text{oblate spheroid, } c < a. \end{cases} \quad (16)$$

Substitution of Eqs. (14) and (15) into Eq. (12) yields

$$\begin{aligned}
\Delta G = G - G_0 &= -\frac{1}{2} \int \int \int_\Omega E_i P_i^* d\nu - \int \int \int_\Omega E_i^0 P_i^* d\nu \\
&= \frac{4\pi}{3} c a^2 \left[\frac{P_s^2}{2\pi\epsilon} I_3 - 2(E_0 + E^i) P_s - \frac{2P_s^2}{\epsilon} \right], \quad (17)
\end{aligned}$$

where $\vec{P}^* = 2P_s \vec{k}$, and we assume that the internal electric field acts in parallel with the electric field applied. Equation

(17) gives only the change in electrostatic energy due to the introduction of an 180° domain. One needs to add the surface energy of the wall as follows:

$$\begin{aligned}
\Delta T &= \frac{4\pi}{3} c a^2 \left[\frac{P_s^2}{2\pi\epsilon} I_3 - 2(E_0 + E^i) P_s - \frac{2P_s^2}{\epsilon} \right] \\
&\quad + \Gamma(a, c) \sigma, \quad (18)
\end{aligned}$$

where σ designates the surface energy per unit area of the wall, and Γ is the surface area of an ellipsoidal domain, given by

$$\Gamma(a, c) = \begin{cases} 2\pi a \left[a + \frac{c}{\sqrt{1 - a^2/c^2}} \arcsin(\sqrt{1 - a^2/c^2}) \right], & \text{prolate spheroid, } a < c \\ 4\pi a^2, & \text{sphere, } a = c \\ 2\pi a [a + c/\sqrt{(a/c)^2 - 1} \log(a/c + \sqrt{(a/c)^2 - 1})], & \text{oblate spheroid, } a > c. \end{cases} \quad (19)$$

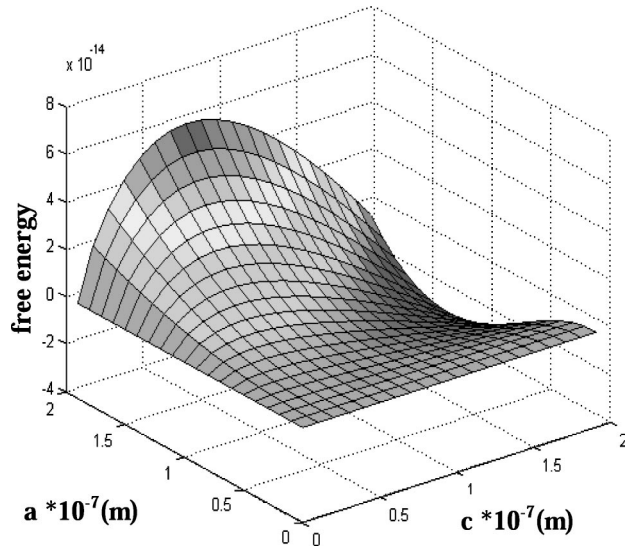


FIG. 2. The free energy as a function of the domain size.

The energy expressions, Eq. (18), derived here can be used to calculate the change in free energy due to the introduction of a ferroelectric domain in a general ferroelectric sample.

We assume that the process is isothermal, so that effects due to a change in entropy can be neglected. Generally speaking, the spontaneous polarization is a decreasing function of the temperature; it approaches zero when the temperature approaches the Curie temperature of the material. Thus the effect of the temperature can be taken into account by substituting the spontaneous polarization as a function of the temperature. In practice, the initial ferroelectric polarization charges on the surface can be neutralized in sufficient time, therefore the third term in the square bracket in Eq. (17) can be omitted.

For PZT thin film, we can use the following material constants:⁴ spontaneous polarization: $P_s = 30 \mu\text{C}/\text{cm}^2$; relative dielectric constant: $\epsilon_r = 1000$; domain wall energy: $\sigma = 4 \text{ mJ}/\text{m}^2$. If electric field $E_0 = 120 \text{ kV}/\text{cm}$ is applied and the internal electric field is assumed to be zero, the change in free energy, Eq. (18), is a function of the 180° domain dimension $\{a, c\}$, as shown in Fig. 2.

It is interesting to note from Fig. 2 that for a given transverse size of the domain once the semiaxis c along the symmetric axis is above a critical value, the free energy of the system will decrease. On the other hand, if one fixes the size of the domain along the symmetry axis, the free energy always increases with an increase in the transverse size of the domain. This provides an explanation for the observation that the 180° domain always develops along the direction of applied electric field first, and then sidewise development follows.¹⁴

III. KINETIC EQUATIONS OF EVOLUTION

For a spheroidal domain, two parameters, a and c , completely describe the geometry of the domain. The rate of evolution of the domain then depends on the driving forces which are the free energy reduction rates accompanying the change of a and c , i.e.,

$$\begin{aligned} f_a &= -\frac{\partial(\Delta T)}{\partial a}, \\ f_c &= -\frac{\partial(\Delta T)}{\partial c}. \end{aligned} \quad (20)$$

As discussed by Loge and Suo,⁹ the evolution rate can be reasonably assumed to be proportional to the corresponding driving force,

$$\begin{aligned} \frac{dc}{dt} &= M f_c = -M \frac{\partial(\Delta T)}{\partial c}, \\ \frac{da}{dt} &= M f_a = -M \frac{\partial(\Delta T)}{\partial a}, \end{aligned} \quad (21)$$

where M is a material constant.

As discussed earlier in Sec. I, investigation on the back-switching process, i.e., shrinking of the switched domains after the removal of the electric field applied, is of both practical and scientific interest. Here, the back-switching process is driven by reduction of the depolarization energy and the domain-wall energy, whereas the internal electric field and the coercive field provide resistance.

Equation (21) is a system of nonlinear differential equations, which we will not attempt to solve. Instead, our interest is in the conditions of stability of the solution. Knowing that $(a, c) = (0, 0)$ is a stationary point, we can determine the condition under which backswitching can be avoided if we can find its area of attraction, because all solutions of Eq. (21) starting in this area will asymptotically approach the stationary point.

Although the Liapunov criterion²² may be used to determine the stability of a stationary point and an associated area of attraction, there is no guarantee that this area contains all the starting points of solutions that eventually end up in the stationary point. In the following, we will determine the area of attraction using the phase diagram of the solution. We can choose the change in internal energy of the system as a Liapunov function:

$$L(a, c) = -\frac{1}{2} \int \int \int_{\Omega} E_i P_i^* d\nu + \Gamma(a, c) \sigma, \quad (22)$$

where the first term comes from Eq. (17) by setting the electric field applied to zero. It is obvious that $L(a, c) > 0$ for all $(a, c) \neq 0$, and $L(0, 0) = 0$. Therefore, the total derivative of the Liapunov function corresponding to Eq. (21) is

$$\frac{dL}{dt} = \frac{\partial L}{\partial a} \cdot \frac{da}{dt} + \frac{\partial L}{\partial c} \cdot \frac{dc}{dt} = M \left(f_a \frac{\partial L}{\partial a} + f_c \frac{\partial L}{\partial c} \right). \quad (23)$$

The stability condition for the stationary point $(0, 0)$ can be identified if $dL/dt < 0$. This can be expressed as

$$\begin{aligned} -\left(\frac{\partial L}{\partial a}\right)^2 - \left(\frac{\partial L}{\partial c}\right)^2 + \frac{\partial L}{\partial a} \frac{\partial}{\partial a} \int \int \int_{\Omega} E_i^0 P_i^* d\nu \\ + \frac{\partial L}{\partial c} \frac{\partial}{\partial c} \int \int \int_{\Omega} E_i^0 P_i^* d\nu < 0. \end{aligned} \quad (24)$$

For an ellipsoidal domain,

$$L(a, c) = \frac{4a^2c}{3\epsilon} P_s^2 I_3(a, c) + \Gamma(a, c) \sigma, \quad (25)$$

$$\int \int \int_{\Omega} E_i^0 P_i^* d\nu = \frac{8\pi}{3} a^2 c (E^0 + E^i) P_s.$$

We set the electric field applied as $E^0 = 0$. Taking PZT material as an example,¹ and assuming an internal field of 60 kV/cm, spontaneous polarization is $P_s = 30 \mu\text{C}/\text{cm}^2$; the relative dielectric constant is $\epsilon_r = 1000$; the domain wall energy is $\sigma = 4 \text{ mJ}/\text{m}^2$. For an ellipsoidal domain, Eq. (24) gives, to good approximation, a linear relation between a and c :

$$c < 3.2a + a_0, \quad (26)$$

where a_0 is about 4 nm. The region given by Eq. (26) includes the stationary point (0, 0). It is obvious that the zero solution is asymptotically stable. Next we need to determine, the area of the origin, which contains all the starting points of solutions that have the origin as a stationary point. If the transverse size a of the ellipsoidal domain is much larger than a_0 , the critical aspect ratio approaches a constant, i.e.,

$$\beta_c = 3.2 + \frac{4 \times 10^{-9}}{a} \approx 3.2. \quad (27)$$

A generalization of Eq. (26) can be written as

$$c = ka + b, \quad (28)$$

where slope k is found to depend on the internal electric field and the spontaneous polarization, and parameter b is found to depend mainly on the wall energy.

Noting that b is very small, we make the approximation that $\beta = c/a$ remains constant. Then Eq. (24) can be written as

$$c \frac{\partial L}{\partial a} \left[\frac{8}{3\epsilon} P_s^2 a I_3(\beta) - \frac{16}{3} \pi a E^i P_s + \sigma \hat{\Gamma}(\beta) \right] + a \frac{\partial L}{\partial c} \left[\frac{4}{3\epsilon} P_s^2 a I_3(\beta) - \frac{8}{3} \pi a E^i P_s + \sigma \hat{\Gamma}(\beta) \right] > 0, \quad (29)$$

where $\Gamma(a, c, c) = a c \hat{\Gamma}(\beta)$. Since $\partial L / \partial a > 0$ and $\partial L / \partial c > 0$, and numerous numerical calculations have shown that the wall energy contribution is small, Eq. (29) can be approximated by

$$\frac{8}{3\epsilon} P_s^2 a I_3(\beta) - \frac{16}{3} \pi a E^i P_s > 0. \quad (30)$$

Since $a > 0$, we have

$$I_3(\beta) > \frac{2\pi\epsilon E^i}{P_s}, \quad (31)$$

in which we have considered that $I_3(\beta)$, $\beta = c/a$ is a monotonic decreasing function of the aspect ratio (Fig. 3). Substitution of the material constants into Eq. (31) gives the critical aspect ratio $\beta_c \approx 3.4$, which agrees very well with our numerical results.

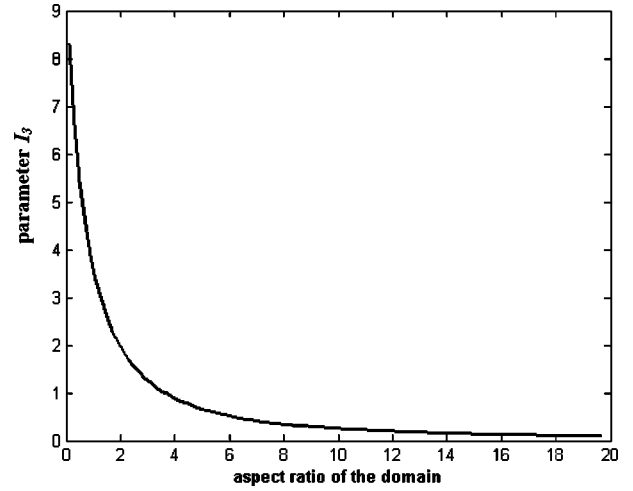


FIG. 3. Parameter $I_3(\beta)$ vs the aspect ratio $\beta = c/a$.

Since Eq. (21) is an autonomous equation with a simple attractor at the origin $(a, c) = (0, 0)$, it is easy to compute its phase diagram based on

$$\frac{dc}{da} = \frac{f_c}{f_a}. \quad (32)$$

From the phase diagram, the region of instability can be determined for PZT material. Any solution that starts from this region will eventually end up in the attractor at the origin, i.e., shrink to zero (Fig. 4).

Experimental results of the aspect ratio of stable 180° domains in a bulk ferroelectric body were always found to be much larger than the critical value. For example, Gopalan and Mitchell⁵ found that the aspect ratio of dagger shape domains for TGS single crystal is 13.6 ± 2.2 . Woo *et al.*²³ found an aspect ratio of 5:14 for the dagger shape domain in PZT thin film. To quantify the back-switching resistance of the domain, one can replace internal electric field E^i by co-

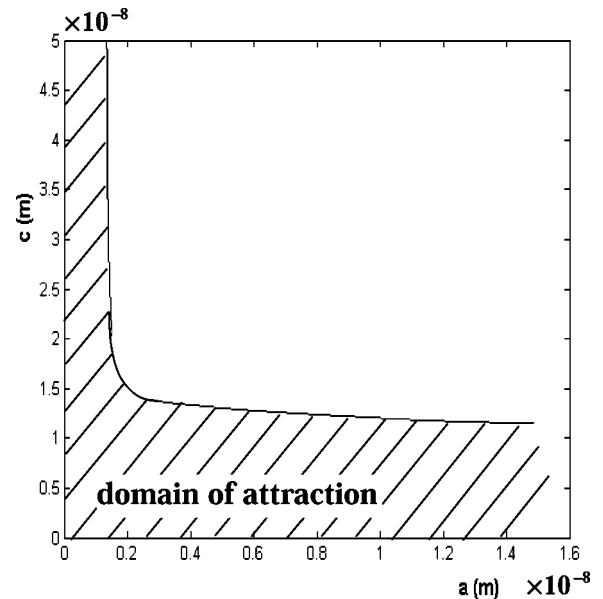


FIG. 4. Unstable area of 180° domain (shaded).

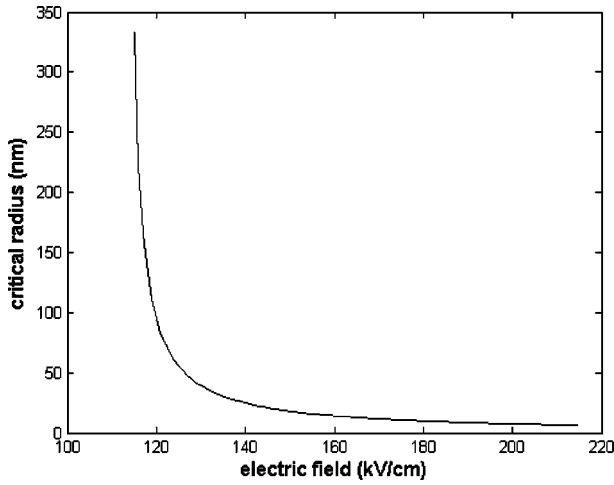


FIG. 5. Critical radius of 180° domain nucleation vs the electric field applied.

ercent field E_c as Li *et al.*⁴ did. However, their stability analysis gave a minimum aspect ratio of a stable domain of the order of 100 for PZT thin film, which is unrealistically too large. It may be worthwhile to redo the stability analysis of the AFM-tip/PZT film/substrate configuration using our formulation.

As a simple example, we consider a spherical domain. We further assume unrealistically that it will expand along the radial direction. In this case, Eq. (18) becomes

$$\Delta T = \frac{4\pi}{3} a^3 \left(\frac{2P_s^2}{3\epsilon} - 2E_0 P_s \right) + 4\pi a^2 \sigma, \quad (33)$$

and the evolution equation becomes

$$\frac{da}{dt} = -M \left[4\pi a^2 \left(\frac{2P_s^2}{3\epsilon} - 2E_0 P_s \right) + 8\pi a \sigma \right]. \quad (34)$$

If we define the stationary points a_c at which driving force da/dt is zero, i.e.,

$$a_{c1} = 0, \quad a_{c2} = \frac{2\sigma}{2E_0 P_s - 2P_s^2/(3\epsilon)}, \quad (35)$$

it is easy to verify that $a_{c1} = 0$ is a stable equilibrium point, whereas a_{c2} is a nonstable stationary point from the sign of the derivative of the right-hand side of Eq. (34). That means if the 180° domain size is in the range of $0 \leq a \leq a_{c2}$, it will shrink to zero, if its domain size is in the range of $a \geq a_{c2}$ will expand to fill the whole sample. Thus a_{c2} is the critical radius of 180° domain nucleation. The variation of critical radius a_c versus the electric field applied E_0 for PZT is shown in Fig. 5. Using Eq. (35), one can also obtain the condition for the electric field applied or the internal electric field, under which the 180° domains will always shrink,

$$E_0^c \leq \frac{P_s}{3\epsilon}. \quad (36)$$

One should bear in mind that the stability analysis for ellipsoidal domain is very different from that for a spherical do-

main. Even if the starting shape of a domain is spherical, it may not keep its spherical shape during the evolution process. The stability analysis should not be performed under the *a priori* assumption of spherical symmetry. For the expansion process of the 180° domain, the driving force comes from the interaction energy of the electric field applied and spontaneous polarization, whereas the resistance is provided by the depolarization energy, domain wall energy, and coercive field. One can also carry out a stability analysis based on the foregoing formulation to determine the critical dimension of the domain, above which it will expand into the whole sample in an unstable manner.

IV. CONCLUDING REMARKS

Based on evolution equations, a general formulation for the investigation of the stability of microstructures has been established. If only one parameter x is needed to describe the kinetic equation,

$$\frac{dx}{dt} = f(x), \quad (37)$$

one can determine its stable point and the associated attraction region by considering its right-hand side. But if more than two parameters are needed to describe the system evolution, one can choose the internal energy change of the system, expressed as a function of the microstructural parameters and environment, as the Liapunov function. The stability properties of the system can then be analyzed readily. As an important application, the method is used to determine the critical dimensions in which switched domains in ferroelectric materials will switch back upon removal of external voltage. Besides the obvious scientific interest, such a theory can be used to provide the necessary guidance for the production of stable switched domains. This is especially important for the fabrication of ferroelectric memory devices. Although the analysis has focused on an ellipsoidal domain in a bulk ferroelectric material in which an explicit expression for the depolarization energy can be derived, it can be extended to cases of more complicated geometry, in which the depolarization field and energy may be evaluated numerically. The effect of the temperature can also be taken into account through the temperature-dependent spontaneous polarization. In this analysis, we assumed the driving force for shrinkage of the domain is the depolarization energy and the domain-wall energy, and that resistance is provided by the internal electric field. However, the reversal of polarization would necessitate domain-wall motion, which is a dissipative process commonly characterized by a coercive field. Thus one can also replace or add the resistant terms by the coercive field in the energy expressions. Furthermore, the analysis is sufficiently general that it can be extended to many similar phenomena, such as phase transformation, dislocation loop nucleation, expansion, etc.

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