

NONLINEAR AND NONLOCAL CONTINUUM THEORY ON DOMAIN WALLS IN FERROELECTRICS

WENWU CAO AND L. E. CROSS

Materials Research Laboratory, The Pennsylvania State University,
University Park, PA 16802

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Abstract The domain structures in ferroelectrics can be described by a Landau-Ginzburg type theory with the twin and twin band (domain) structures being nonlinear and nonlocal excitations of the ferroelectric phase. The polarization gradients in the theory reflect the degree of nonlocal coupling along different crystallographic orientations. These gradient parameters can be obtained either from the dispersion surface of the soft mode or through fitting the polarization profile measured by the holographic electron microscopy.

INTRODUCTION

The understanding of domain structures is essential for the design and applications of ferroelectrics. It has been long recognized that the piezoelectric and dielectric properties of ferroelectric ceramics are mainly determined by the behavior of domain structures. The formation of domains in ferroelectrics is due to the existence of multi-variants in the ferroelectric phase. Atomic coherency is usually maintained across the domain boundaries, which make it possible to switch domain orientations from one to the other using external (either mechanical or electrical) fields. This switching gives rise to the so called extrinsic contributions to the materials properties. The formation of domain walls in ferroelectrics may be treated in terms of solitary wave excitations in a nonlinear and nonlocal system. Single kink-like and periodic solitary wave solutions for the twin and periodic domain structures can be derived using the continuum theory.¹⁻⁴ Since all the expansion coefficients in the Landau-Devonshire model can be expressed in terms of measurable macroscopic quantities, the continuum theory can give quantitative description of the domain wall properties, including the profile of polarization across the domain wall, domain wall width, energy stored in the multi-domain structure, and the stress build up at the domain wall region, once the polarization gradient coefficients are obtained.

THE MODEL

The Landau-Devonshire type phenomenological theory for ferroelectrics has been developed for the ferroelectric phase transition.^{5,6,7} For a cubic system, such as perovskite ferroelectrics, the elastic Gibbs free energy can be expressed in the following form:

$$G = G_p + G_{el} + G_c \quad (1)$$

$$G_p = A (P_1^2 + P_2^2 + P_3^2) + B (P_1^4 + P_2^4 + P_3^4) + C (P_1^6 + P_2^6 + P_3^6) \\ + D (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + E (P_1^4 P_2^2 + P_1^2 P_2^4 + P_2^4 P_3^2 + P_2^2 P_3^4 \\ + P_3^2 P_1^4 + P_1^2 P_3^4) + H P_1^2 P_2^2 P_3^2 \quad (2)$$

$$G_{el} = -\frac{s_{11}}{2} (X_{11}^2 + X_{22}^2 + X_{33}^2) - s_{12} (X_{11}X_{22} + X_{22}X_{33} + X_{11}X_{33}) \\ - \frac{s_{44}}{2} (X_{12}^2 + X_{13}^2 + X_{23}^2) \quad (3)$$

$$G_c = Q_{11} (X_{11} P_1^2 + X_{22} P_2^2 + X_{33} P_3^2) + Q_{12} [X_{11} (P_2^2 + P_3^2) + X_{22} (P_1^2 + P_3^2) \\ + X_{33} (P_1^2 + P_2^2)] + Q_{44} (X_{12} P_1 P_2 + X_{13} P_1 P_3 + X_{23} P_2 P_3) \quad (4)$$

where A, B, C, D, E, H are the linear and nonlinear dielectric constants, s_{ij} are the elastic compliance coefficients, Q_{ij} are the electrostriction constants, P_i and X_{ij} are the components of polarization and stress, respectively. All the coefficients are assumed to be independent of temperature except A which is a linearly function of T,

$$A = \alpha (T - T_0) \quad (5)$$

In a homogeneous system, a paraelectric-ferroelectric phase transition occurs at T_c . Under stress free condition, the phase transition temperature T_c and the spontaneous polarization P_c at the transition can be derived by minimizing Eq. (1),

$$T_c = T_0 + \frac{B^2}{4 C \alpha} \quad (6)$$

$$P_c^2 = \frac{-B}{2 C} \quad (7)$$

One of the low temperature ferroelectric phases is the tetragonal phase. There are six energetically degenerate variants in the tetragonal phase: $(\pm P_s, 0, 0)$, $(0, \pm P_s, 0)$ and $(0, 0, \pm P_s)$, where P_s is the spontaneous polarization given by

$$P_s = \sqrt{\frac{-B + \sqrt{B^2 - 3 AC}}{3 C}} \quad (8)$$

These energetically degenerate variants can coexist in the ferroelectric phase to form the twin structures. Electron microscopy reveals that the ionic coherency is maintained across domain walls, but domain walls are not atomically sharp. Domain wall width is determined by the nonlocal coupling strength of the ferroelectric system.

Since the nonlinearity has been included in the model [see Eqs. (1)-(4)], if we add the contributions of nonlocal coupling, then from soliton theory, we may expect solitary wave excitations in the ferroelectric phase. These excitations are in deed found and they represent the ferroelectric domain walls.

For a perovskite system, the symmetry of the high temperature phase is cubic, therefore, the Gibbs energy representing the nonlocal coupling can be written as follows:²

$$G_g = \frac{1}{2} g_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + g_{12} (P_{1,1} P_{2,2} + P_{1,1} P_{3,3} + P_{2,2} P_{3,3}) + \frac{1}{2} g_{44} [(P_{1,2} + P_{2,1})^2 + (P_{1,3} + P_{3,1})^2 + (P_{2,3} + P_{3,2})^2] \quad (9)$$

here the indices after the comma represent derivatives with respect to space variable along that axis. Upon the minimization of the total free energy of the system Eqs. (1) and (9), one can obtain the solutions for the domain walls.²

90° DOMAIN WALLS

There are two types of domain walls in the tetragonal ferroelectrics. One is the 180° domain wall which divides a twin domain with identical strain but opposite polarization, and the other is the 90° domain wall which divides two domains whose polarization and spontaneous strain are nearly 90° from each other. Solutions for the 180° domain walls can be easily obtained since the problem is one-dimensional.² Here we only solve the problem of 90° domain walls for which the problem can be rendered to quasi-one-dimensional.

From transmission electron microscopy studies, domain walls tend to broaden or bent near the surface, however, inside the sample they have well defined wall-like

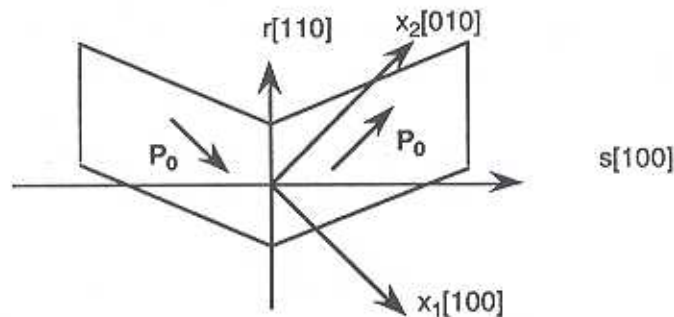


FIGURE 1. A tetragonal twin structure and the coordinate system used in this paper.

structure with translational symmetry parallel to the wall plane. Therefore, while dealing with a <110>-type domain walls in tetragonal ferroelectrics we can rotate the x_1, x_2 coordinates about the x_3 coordinate by 45° so that the properties of the domain walls only depend on one space variable (s -coordinate as indicated in Fig. 1) only.

In the new coordinate system the equilibrium conditions are governed by the following equations:²

$$\frac{\partial}{\partial x_j} \left[\frac{\partial G}{\partial P_{i,j}} \right] - \frac{\partial G}{\partial P_i} = 0, \quad (i,j = s, r, 3) \quad (10)$$

$$X_{ijj} = 0, \quad (i,j = s, r, 3) \quad (11)$$

and we also need the elastic compatibility relations

$$\epsilon_{ikl} \epsilon_{jmn} x_{ln,km} = 0 \quad (i,j,k,l,m,n = \hat{s}, r, 3) \quad (12)$$

to insure the elastic continuity since in our model the domain walls are intrinsic excitations, no defects are created in the domain wall region. x_{ln} is the component of elastic strain tensor and ϵ_{ikl} is the Levi-Civita density.

Eqs (11) and (12) has three nontrivial solutions:

$$X_{r3} = 0 \quad (13)$$

$$X_{rr} = \frac{1}{2(s_{11}s_{ss} - s_{12}^2)} \{ [2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12})]P_0^2 - [2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} - Q_{44})]P_s^2 - [2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} + Q_{44})]P_r^2 \} \quad (14)$$

$$X_{33} = \frac{1}{2(s_{11}s_{ss} - s_{12}^2)} \{ [s_{12}(Q_{11} + Q_{12}) - 2s_{ss}Q_{12}]P_0^2 - [s_{12}(Q_{11} + Q_{12} + Q_{44}) - 2s_{ss}Q_{12}]P_r^2 - [s_{12}(Q_{11} + Q_{12} - Q_{44}) - 2s_{ss}Q_{12}]P_s^2 \} \quad (15)$$

where

$$s_{ss} = \frac{1}{2}(s_{11} + s_{12} + \frac{s_{44}}{2}).$$

It can be easily verified that the two stress components X_{rr} and X_{33} are nonzero only in the vicinity of the domain wall. These nonzero stress components near the domain wall region is the cause of the faster etching rate which makes the domain walls visible through chemical etching technique.

In order to see the general trend of the variation of polarization profile without specifying the coefficients to a particular system, we normalize the polarization and the space variable s into dimensionless forms by the following substitutions:

$$P_r = \sqrt{-\frac{B}{2C}} f_r = P_c f_r \quad P_s = \sqrt{-\frac{B}{2C}} f_s = P_c f_s \quad (16a,b)$$

$$s = \gamma \xi, \quad \gamma = \left(\frac{G_{ss} G_{rs}}{4 A_c^2} \right)^{1/4} \quad (17a,b)$$

where

$$G_{ss} = \frac{1}{2}(g_{11} + g_{12} + 2g_{44}), \quad G_{rs} = \frac{1}{2}(g_{11} - g_{12}),$$

and define the dimensionless temperature as

$$\tau = \frac{T - T_0}{T_c - T_0} \quad (18)$$

then the equilibrium condition Eq. (10) can be written in the following form for a 90° twin structure,

$$a f_s \xi_s^2 = \tau_s f_s + b_s f_s^3 + c f_s f_r^2 + d f_s^5 + (8 - \frac{2}{3}d) f_s^3 f_r^2 + (4 - \frac{1}{3}d) f_s f_r^4 \quad (19)$$

$$\frac{1}{a} f_r \xi_s^2 = \tau_r f_r + b_r f_r^3 + c f_r f_s^2 + d f_r^5 + (8 - \frac{2}{3}d) f_r^3 f_s^2 + (4 - \frac{1}{3}d) f_r f_s^4 \quad (20)$$

where the coefficients are given by

$$a = \sqrt{\frac{G_{ss}}{G_{rs}}} \quad (21)$$

$$\tau_s = \tau \frac{(1 + \sqrt{1 - \frac{3}{4}\tau})}{3(s_{11}s_{ss} - s_{12}^2)B} \{ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12}) - 2s_{ss}Q_{12}] \} \quad (22)$$

$$\tau_r = \tau \frac{(1 + \sqrt{1 - \frac{3}{4}\tau})}{3(s_{11}s_{ss} - s_{12}^2)B} \{ (Q_{11} + Q_{12} + Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12}) - 2s_{ss}Q_{12}] \} \quad (23)$$

$$b_s = -2 \frac{D}{B} + \frac{1}{2B(s_{11}s_{ss} - s_{12}^2)} \{ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} - Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} - Q_{44}) - 2s_{ss}Q_{12}] \} \quad (24)$$

$$b_r = -2 \frac{D}{B} + \frac{1}{2B(s_{11}s_{ss} - s_{12}^2)} \{ (Q_{11} + Q_{12} + Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} + Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} + Q_{44}) - 2s_{ss}Q_{12}] \} \quad (25)$$

$$c = -6 + \frac{D}{B} + \frac{1}{2B(s_{11}s_{ss} - s_{12}^2)} \{ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} + Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} + Q_{44}) - 2s_{ss}Q_{12}] \} \quad (26)$$

$$d = \frac{3}{4} \left(1 + \frac{E}{C} \right) \quad (27)$$

RESULTS AND DISCUSSIONS

Using the normalized equations, we can study the influence of different parameters to the polarization profile and obtain a conceptual understanding on the nature of the polarization variation in the domain wall region. Fig. 2 shows the variation of the polarization components with the parameter a across a 90° domain wall. One can see that the domain wall becomes wider as a increases. In real dimensions, because the scaling factor of the space variables, γ , is directly related to the product $G_{SS} * G_{RS}$ [see eq.(17)], domain wall becomes wider as the gradient coefficients become larger.

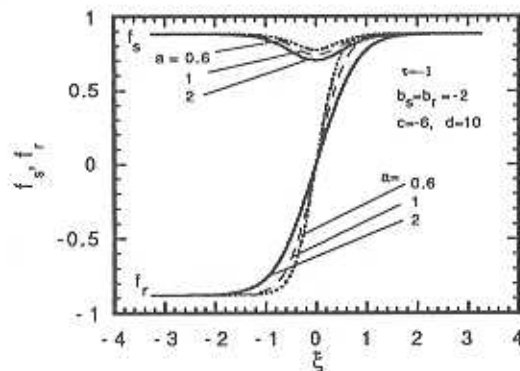


FIGURE 2. Variation of polarization components f_s and f_r induced by the change of parameter a across a 90° domain wall. The gradient parameter a determines the width of the domain wall.

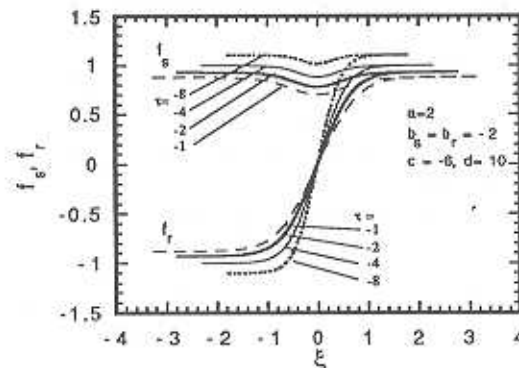


FIGURE 3. Variation of polarization components f_s and f_r with temperature τ across a 90° domain wall. The asymptotic values of the polarization components increase and the domain wall width decrease while lowering temperature.

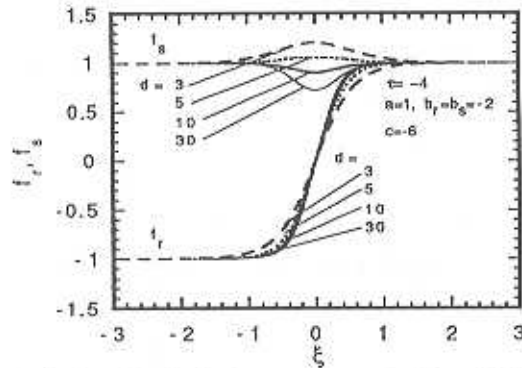


FIGURE 4. Variation of polarization components f_s and f_r induced by the change of parameter d across a 90° domain wall. The nonlinear parameter d influences the magnitude of the polarization variation in the domain wall region.

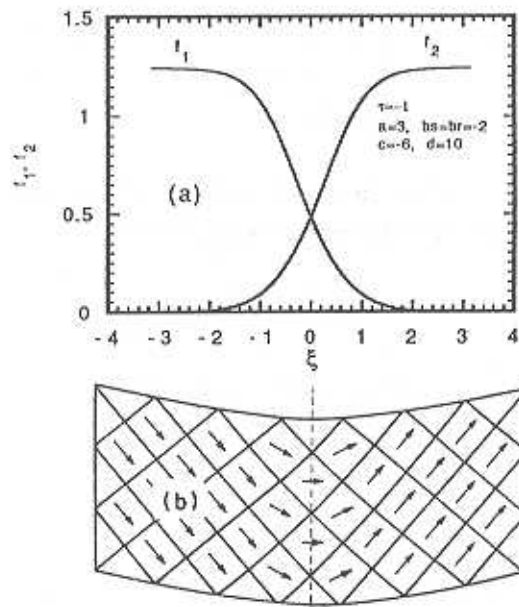


FIGURE 5. (a) Polarization components f_1 and f_2 across a 90° domain wall, and (b) Illustration of the variations of the polarization vector and the unit cell distortion across a 90° domain wall.

Fig. 3 shows the variation of the polarization with temperature τ . The asymptotic values of the magnitude of the polarization components increase and the domain wall thickness decreases as the temperature is lowered. The temperature dependence is strong near the transition and gradually becomes insensitive when the temperature is far below T_c . Fig. 4 shows the variation of the polarization components f_s and f_t induced by the change of parameter d . We can see that the magnitude of f_s is very sensitive to d while the domain wall thickness is relative insensitive to d . We can also calculate the polarization components f_1 and f_2 in the original coordinates. One example is given in Fig. 5 (a) for a set of chosen parameters. The corresponding unit cell distortion and the polarization variation across the domain wall are illustrated in Fig. 5(b). The polarization vector rotates gradually from one orientation into the other accompanied also by a change of the magnitude.

All properties of the domain walls can be quantitatively calculated using this model once the expansion coefficients are known. As we have mentioned above that the polarization gradient coefficients are most crucial for the study of domain walls, which may be derived from the measurements on the dispersion surface of the soft mode.^{8,9} In general, inelastic neutron scattering to probe the soft mode may be difficult due to the relatively high transition temperature in many systems of interest and in some cases, the soft mode is over damped. An alternative way to obtain these coefficients would be to probe the polarization profile across the domain wall and then fitting the unknown coefficients using the differential equations (19) and (20). The recently emerged new technique, electron holography, may offer an option to this end.^{10,11}

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