Scale effects and the formation of polarization vortices in tetragonal ferroelectrics

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Abstract

Vortices consisting of 90° quadrant domains are rarely observed in ferroelectrics. Although experiments show polarization flux closures with stripe domains, it is as yet unclear why pure single vortices are not commonly observed. Here we model and explore the energy of polarization patterns with vortex and stripe domains, formed on the square cross-section of a barium titanate nanowire. Using phase-field simulations, we calculate the associated energy of polarization patterns as a function of nanowire width. Further, we demonstrate the effects of surface energy and electrical boundary conditions on equilibrium polarization patterns. The minimum energy equilibrium polarization pattern for each combination of surface energy and nanowire width is mapped for both open-circuit and short-circuit boundary conditions. The results indicate a narrow range of conditions where single vortices are energetically favorable: nanowire widths less than about 30nm, open-circuit boundary condition, and surface energy of less than 4N/m. Short-circuit boundary conditions tend to favor the formation of a monodomain, while surface energy greater than 4N/m can lead to the formation of complex domain patterns or loss of ferroelectricity. The length scale at which a polarization vortex is energetically favorable is smaller than the typical size of nanoparticle in recent experimental studies. The present work provides insight into the effects of scaling, surface energy and electrical boundary conditions on the formation of polarization patterns.

Introduction

Although vortices of magnetic domains have been experimentally observed in ferromagnets [1][2], it is intriguing to note that the analogous simple polarization vortices are not seen in ferroelectrics. Models such as the time-dependent Ginzburg-Landau theory suggest that polarization vortices should form under certain conditions [3][4].

Polarization vortices possess tremendous potential for the design of nanoscale devices such as memory elements [10][13] and transducers [6][14][15]. With the progressive miniaturization of electronics, the functional properties of ferroelectric domain patterns are of increasing importance [16][20]. Hence much current research is directed towards finding polarization vortices and studying their nanoscale properties in detail [21][31].

Polarization flux closures in the form of bundles of 90° stripe domains oriented to form a vortex have been imaged by McGilly and Gregg in PbZr(T(0.43))Ti(0.58)O3 nanodots [25]. Similar stable flux closures have been observed by McQuaid et al. in BaTiO3 [28]. However, these flux-closures consist of 90° stripe domains [23][30] and so differ from the classic polarization vortex consisting of 90° quadrant domains, which is well-known in ferromagnetic materials [22][33]. Polarization vortex patterns consisting of dipole flux closures [26][28] or quadrupole chains [26], have been observed. However, these vortices have 180° domain walls at their core and so differ from the classic polarization vortex in small particles as predicted by Kittel [1]. Although, the direct observation of polarization rotation which facilitates the formation of a vortex has been established [24], the classic vortex polarization pattern continues to be elusive [22]. This leads us to consider the question – Why are these polarization vortices not seen in experiments?

In the present work, a BaTiO3 nanowire in the tetragonal phase, with square cross-section is modelled in isothermal conditions. The wire is assumed to extend indefinitely out of the model plane, such that plane strain and plane electric field conditions apply. Minimum cross-sectional widths of 20nm were considered, noting that ferroelectricity has been observed in BaTiO3 structures from a few nanometers in size upwards [24][29]. The wire is assumed to be simply supported, with traction free surfaces. We consider two distinct electrical boundary conditions: open-circuit and short-circuit, by applying zero normal component of electric displacement and zero voltage boundary conditions, respectively.

A phase-field model previously developed by Landis and co-workers [37][39] calibrated for BaTiO3 is used to find equilibrium states. This model has been applied as a design tool [6][11] and to study domain wall interactions in ferroelectrics [37][38]. The model describes the Helmholtz free energy, \( \psi \) as a function of polarization, \( P_i \), which is the order parameter, strain, \( \epsilon_{ij} \) and electric displacement, \( D_i \) [37]:

\[
\psi = \psi_g + \psi_d
\]

\[
\psi_g = \frac{1}{2} \epsilon_{ijkl} P_i P_j P_k P_l
\]

\[
\psi_d = \frac{1}{2} \pi_{ij} P_i P_j + \frac{1}{4} \eta_{ijkl} P_i P_j P_k P_l + \frac{1}{6} \pi_{ijklmn} P_i P_j P_k P_l P_m P_n
\]

where \( \pi_{ij} \), \( \eta_{ijkl} \), and \( \pi_{ijklmn} \) are the elastic constants, the magnetic dipole energy and the trigonal elastic constants of the material respectively. The elasticity tensor, \( \epsilon_{ijkl} \), is given by:

\[
\epsilon_{ijkl} = \frac{1}{2} \kappa_0 (D_i - P_i)(D_j - P_j)
\]
The form of Eq. 1-3 is identical to that in the work of Landis and co-workers [37,39] where the detailed meaning of the specific terms and material properties are explained. For our purposes, we note that the gradient energy, $\psi_g$, includes energy due to polarization variation at domain walls or surfaces. The domain energy, $\psi_d$, accounts for the elastic, piezoelectric and dielectric energy due to distortion away from the spontaneously polarized state. The domain evolution follows a generalized Ginzburg-Landau equation [37]:

$$\frac{\partial \psi}{\partial t} = \beta \frac{\partial^2 \psi}{\partial P^2},$$

(4)

where $\beta$ is the polarization viscosity, which was controlled as a relaxation parameter in the simulation to allow equilibrium states $\beta = 0$ with to be found. In the simulation, the polarization vector is constrained to lie in-plane with no other boundary conditions applied; it is governed by Eq. 4.

The phase-field model is solved using finite element methods with the element size chosen such that a 180° domain wall spans four elements. The nodal displacements enable the strain and polarization gradient to be computed; hence the energy density was found from Eq. 1-3.

To identify commonly occurring domain arrangements, the initial state of the model was set by assigning random polarization values, $-P_0 \leq P_i \leq P_0$, at each node. Wire cross-sections in the size range 20nm $\leq L \leq 40$nm were simulated. From this random starting state the simulation converged on equilibrium states, which frequently resulted in one of the three types of domain arrangement shown in Fig. 1(a-c); see also Xue et al. [10] where similar structures were found using Monte Carlo methods. Type I [Fig. 1] consists of a classic vortex while Type II is identified with two vortices and stripe domains [Fig. 1]. This structure is closely related to the double-closure pattern with domain wall vertices as observed by McQuaid et al. [29]. Type III is a more complicated pattern of domains forming a flux closure [Fig. 1].

Having established three types of polarization patterns with vortex and stripe domains [Fig. 1(a-c)] that can typically form on the cross-section of a nanowire, these patterns were studied further to establish the size dependency of their stability. Nanowire cross-sections of size 20-80nm were simulated with initial conditions that forced each of the three patterns of Fig. 1 to form. This was achieved by initializing the simulation with the polarization at each node set to match one of the domain patterns in Fig. 1 while the nodal displacements and electric potential were initialized at zero. If the simulations reached equilibrium without pattern change, this indicated the stability of the pattern and the associated energy was thus found as a function of size. As the size was increased, the type I pattern remained stable, but other patterns became energetically favorable.

The resulting free energy for each of the three types of polarization patterns obtained from the phase-field simulations is shown in Fig. 2(a) as a function of nanowire width, $L$. The energy per unit volume, $\psi$, is normalized as $(\psi_0 - \psi)/\psi_0$ where $\psi_0$ corresponds to the energy per unit volume of a monodomain element in a spontaneously polarized state. The energy curves of type I and type II cross at $L = 34$nm indicating a dependence of minimum energy state upon nanowire width. The type III pattern is not stable for $L < 35$nm: even if the simulation is started with polarization matching the type III pattern, other flux closures with lower energy form. The lower size limit for stability of the type III pattern is indicated by “A” in Fig. 2. Also shown in Fig. 2 are the results obtained from starting the simulations with randomly polarized states. These data jump back and forth between the main three types of polarization pattern indicating that the stable state found is highly dependent on the starting conditions.

Since the model size is much larger than the intrinsic length scale due to domain wall width, the total energy in volume $V$ due to polarization gradient, $\int \psi_d dV$, scales approximately with domain wall area whereas domain energy, $\int \psi_g dV$, scales with the volume of polarized domains. Then, defining the total free energy $\psi_{tot} = \int \psi_d dV$, and defining the volume to have an out-of-plane depth $D$, the energy of a given pattern is:

$$\psi_{tot} = aLD + bL^2D$$

(5)

where, the coefficients $a$ and $b$ for each pattern are estimated using linear regression of the data in Fig. 2b. [see Fig. 2b].

For a given nanowire width, $L$, the gradient energy, $\psi_g$ of the three types of polarization patterns is governed by coefficient $a(\times 10^{-8}J/m^2)$ which is related by type III $> \text{type II } > \text{type I}$. While $\psi_d$ is governed by coefficient $b(\times 10^{-8}J/m^2)$ and follows the
reverse order type I > type II > type III. Thus the multidomain patterns reduce their domain energy at the cost of increased gradi-

tent energy. When $L < 34 \text{nm}$, the percentage contribution of $\psi_b$ to $\psi$ is sig-
nificant (25–30%), causing polarization patterns with greater do-
main wall area to possess greater energy [Fig. 2(a)]. This makes the
classic polarization vortex (type I) energetically favorable when
$L < 34 \text{nm}$. However, for $L > 50 \text{nm}$, $\psi_b$ dominates the energy.
Thus, for $L > 50 \text{nm}$, polarization patterns with stripe domains
become favorable. The balance of energy contributions: $\psi_g$, $\psi_d$
and nanowire width, $L$ determines the minimum energy polarization
pattern [Fig. 2(a–b), Eq. 5]. Noting that the energy is well

$$\frac{\psi}{L}$$

Then in the limit as $L$ becomes large, $\frac{\psi}{L \to b}$. Hence the curves in Fig. 2a asymptotically approach a
constant energy per unit volume. This suggests that the type III
domain pattern will become favorable at larger scales. However in
the present study calculations did not go beyond $L = 80 \text{nm}$; it is
likely that other low energy patterns will become favorable before
the cross-over from type II to type III is reached.

Up to this point, surface energy was neglected and only open-
circuit boundary conditions were considered. However, at the
nanoscale, both surface energy, $\gamma$ [41, 43] and electrical bound-
ary conditions [36, 44] affect the formation of ferroelectric domains.
For BaTiO$_3$ nanowires, experiments and theoretical considerations
suggest $\gamma$ values of about 0.68N/m, [36, 44] however the presence
of depolarization field and surface layer effects can cause local vari-
ation in $\gamma$ values and have led to greater estimates of $\gamma$, around
10N/m [14]. Other authors found values within this range de-
dering on shape and surface conditions including chemical en-
vironment [12, 43]. Hence, we allow surface energy values in the
range 0N/m $\leq \gamma \leq$ 10N/m in the model. Morozovska et al. [45, 47]
have modelled the effect of a surface tension proportional to lo-
cal curvature of cylindrical nanoparticles and nano-rods, via the
free energy function. For our case involving a square cross-section
nanowire we approximate the effect of surface tension by apply-
ing surface force boundary conditions at corners only, neglecting
second order effects on surface curvature due to deformation. The
surface effect on the Helmholtz free energy $\psi$ in a narrow region
near the nanowire surface is also neglected. Local polarization
orientation relative to the surface also affects the value of $\gamma$, and
indeed the relation between the surface energy and the resulting
surface stresses is expected to be anisotropic. However since this
study focuses on flux closures, we expect polarization to be paral-
lel to the surface and so neglect this effect. We further consider
short-circuit or open-circuit boundary conditions. A “phase dia-
gram” mapping the minimum energy equilibrium state for each
combination of $\gamma$ and $L$, with open-circuit and short-circuit bound-
ary conditions is shown in Fig. 3(a–b). Boundaries on the diagram
indicate approximately the location of points where the patterns
associated with the adjacent regions have equal energy; markers
show specific points calculated on each boundary.

In nanowire cross-section with open-circuit boundary conditions
[Fig. 3(a)], type I polarization pattern is the minimum energy ar-
angement in a region with 10nm $L < 30 \text{nm}$ approximately,
and surface energy, $\gamma < 4 \text{N/m}$. At greater values of surface en-
ergy, complex patterns with multiple domains are favored, while
nanowire widths $L > 30 \text{nm}$ favor the type II pattern as the low-
est energy state. BaTiO$_3$ nanowires with open-circuit boundary
condition are non-ferroelectric for combinations of high values of
surface energy, $\gamma > 4 \text{N/m}$ and low values of width, $L < 10 \text{nm}$.
This is manifested in the model by the disappearance of tetra-
gonal (e$_{11} = e_{22} = 0$) and polarization $P_1 = P_2 = 0$. By con-
trast, in a nanowire with short-circuit boundary condition [Fig. 3(b)],
a monodomain state is favored at low values of surface energy
$\gamma < 2 \text{N/m}$, when $L > 2 \text{nm}$. There is a narrow region where po-
larization patterns with band-like domains and complex patterns
with multiple domains are observed, with 10nm $< L < 20 \text{nm}$
and $\gamma > 4 \text{N/m}$. Finally, the model suggests that BaTiO$_3$ nanowires
with short-circuit boundary condition are non-ferroelectric when
$L > 8.5 \times 10^6 \text{N/m}^2$.

The phase diagrams in Fig. 3 are consistent with several aspects
of experimental observations. The lack of experimental observa-
tions of the classic (type I) polarization vortex is explained by
two factors. First, scale effects are important in that typical ex-
periments which map in-plane polarization patterns use sample
sizes of order 100nm upwards [25, 27, 30, 32]. The simulations sug-
gest that the type I vortex is a high energy state at this scale.
Second, surface environments in experiments often include polar
or ionic species that may act as charge carriers, providing some
conductivity [21, 30, 36, 48, 49]. Again, the simulations suggest
that the type I vortex is unlikely to form in conductive environ-
ments. Other features that agree with experiment include the loss
of tetragonality at small scales; this has been observed in barium
titanate nanowires at scales of 10nm or less [50–52]. Meanwhile in
nanowires with short-circuit boundary conditions, ferroelectricity
has been observed down to the nanometer scale provided the sur-
face energy is low, consistent with Fig. 3. At greater length
scales, 80nm upward, complex domain patterns including several
or many domains are typical [25, 27, 30, 32].

In conclusion, we used a phase-field simulation to study the effects
of scale and surface conditions on the polarization patterns that
can form in BaTiO$_3$ nanowires. There exists a narrow range of
scale and surface conditions for which the classic single polarization
vortex is likely to form. The study thus provides an insight into
the absence of experimental observation of classic polarization vortices
of the form described by Kittel: typical experiments in nanowires
and nanoparticles do not operate in the regime where such vortices
are energetically favorable. At scales on the order of a hundred
nanometers, the classic single vortex is unlikely to appear because of high domain energy, which is lowered in multiple domains. At smaller scales, ferroelectricity is plagued by surface energy and surface conductance that affect the formation of a single vortex, making it elusive.

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