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ABSTRACT

An atomistic model approach parameterized from first-principles calculations is used to investigate size and shape effects on the polarization field in isolated stress-free PbTiO_3 nanoparticles. The study was carried out by molecular dynamics simulations in free-standing nanodots of cylindrical, spherical, and ellipsoidal shapes. We show that in cylinders with diameter equal to height, the size-induced transformation from the vortex to the flux-closure domain configuration causes an anomaly in the behavior of the toroidal moment and the volume of the system. During this transformation, the vortex core evolves into domain walls while the resulting structure is stabilized due to the non-homogeneous distribution of polarization and strain inside the domains. A similar behavior is observed in elongated cylinders, spheres, and spheroids. The increment in the diameter/height relation of the nanoparticles gives rise to a succession of topological transformations that include multi-vortex configurations, ferroelectric bubble states, and multi-domain patterns. While the transformation path for flat cylinders is similar to the one previously obtained for cuboids, the thinner edge region of the spheroids prevents the stabilization of one- and two-bubble states. Despite this last difference, our results indicate that the polarization pattern of a nanoparticle depends more on its aspect ratio than on its shape.

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I. INTRODUCTION

Ferroelectric materials at the nanoscale are receiving a great deal of attention due to their potential application in miniaturized devices like random access memories, actuators, infrared sensors, mechanical and solar energy converters, etc.^{1–10} As the size of a ferroelectric structure reduces to the nanoscale, the homogeneously polarized bulk state becomes unstable giving rise to a rich variety of polarization patterns. Domains with alternating polarization, polar vortices, ferroelectric bubbles, multi-vortex states, and skyrmions are representative examples.^{11–17} Recent experimental advances have allowed the synthesis of perovskite nanocrystals with well-defined sizes and shapes, opening the possibility to fabricate nanoparticles with specific polar states that can be used for different applications.¹⁸ The understanding of the formation process and stability of different polar configurations is then essential to gain control over their functional properties.

Particular attention has been devoted to the vortex state since it was predicted to occur in zero-dimensional ferroelectrics.¹² In such

confined systems, the dipoles that are close to a surface tend to align parallel to it in order to reduce the depolarizing field energy, driving a closed-loop configuration with continuous dipole rotation around the core. While several theoretical approaches support the existence of a single vortex state in ferroelectric nanoparticles of a few nanometers size, a direct experimental observation of such a structure has not been realized yet. Instead, quadrant domain arrangements where dipole orientation changes abruptly 90° between domains in a flux-closure configuration have been observed in nanodots.^{19–22} We note that arrangements of vortex were already observed in PbTiO_3 (PTO)/ SrTiO_3 superlattices,¹⁰ but the necessary conditions for their detection in nanoparticles have not been reached.²³ Further investigation is then required to fill the gap between the theory and experiment.

It is known that besides dipole-dipole interactions and depolarization effects; composition, size, shape, strain, and boundary conditions also play important roles in the stability of topological structures.^{24,25} However, even in simple cases, the evolution of the

polarization patterns with those factors is not fully understood. For example, there is a consensus that a single vortex configuration corresponding to dipoles rotating perpendicularly to the rod axis is stabilized in tetragonal ferroelectrics with rod-like geometry. Nevertheless, a variety of different polar configurations was theoretically predicted when the size of the nanorod increased.^{12,13,23,26,27} The distribution of dipoles in flux-closure structures requires further clarification: whether local polarizations vanish or reorient at the center of the configuration remains controversial. Furthermore, experimental observations show that domains accommodate around a loop that has a 180° domain wall at its center.^{3,28} This configuration is often seen as a precursor to the formation of a true vortex state, but an atomic-level description of how the vortex transforms into domains is still lacking. These are just a few examples that indicate that a considerable amount of research is still necessary to fully understand the dipole textures of nano-size ferroelectric structures.

The aspect ratio (i.e., the width–height ratio) of a ferroelectric nanostructure is another key parameter for the stabilization of different polarization patterns. We have found from atomic-level simulations that the topology of the polarization field in PbTiO₃ (PTO) nanoparticles depends on the aspect ratio of the nanostructure.¹⁴ We have shown that size-induced topological transformations lead to the stabilization of a ferroelectric bubble in nanodots of only a few lattice constants in size by the alignment of vortex cores along a closed path. The vortex structure forms a ring-shaped torus, and a ferroelectric bubble develops as a strong resultant polarization concentrated through the center of the ring, directed perpendicular to the plane of the ring. We have also shown that, for sufficiently flat nanostructures, a multibubble state bridges the gap between the theoretical predictions for 0D nanodots and the stripe domain configuration experimentally observed in 2D ultrathin films.¹⁴ This fact gives predictability and reliability to our simulation results. We note that this previous study was carried out for cuboid nanostructures, and whether the topological transformation path depends on the shape of the nanoparticle has become an issue of great importance. In this work, we address that point by extending the research reported in Ref. 14 to cylindrical, spherical, and ellipsoidal shaped nanostructures. The evolution of the polarization pattern with the size and the aspect ratio of the nanoparticles is investigated from elongated nanorods to flat nanoplatelets.

II. MODEL AND COMPUTATIONAL DETAILS

The shell model potential used in the present work was originally developed to study bulk properties of PTO, and it was then successfully used to describe the behavior of surfaces, interfaces, and nanoparticles.^{29,30} In the shell model approach, each atom is described as two charged and coupled particles: a massive core and a massless shell. The potential energy is then expressed as

$$V = V_{CS} + V_{LR} + V_{SR},$$

where V_{CS} represents the contribution of the interatomic core–shell coupling, V_{LR} contains the long-range electrostatic interactions among cores and shells of different atoms, and V_{SR} represents the contributions of short-range interactions between shells. In the present case, two different types of short-range potentials are

considered: a Rydberg potential [$V(r) = (a + br) \exp(-r/\rho)$] is used for the Pb–Ti, Pb–O, and Ti–O pairs, and a Buckingham potential [$V(r) = a \exp(-r/\rho) + c/r^6$] is used for O–O interactions. The coefficients of the interactions were fitted to first principle results. The input data included phonon frequencies and eigenvectors along high symmetry directions, and the energy and atomic forces at different relevant configurations. See Ref. 29 for further details.

We use molecular dynamics simulations to determine the polarization patterns of isolated stress-free PTO nanodots under ideal open-circuit boundary conditions. The simulations are carried out using the DL-POLY package,³¹ and the runs are performed employing a constant temperature algorithm. The nanoparticles are surrounded by vacuum without using periodic boundary conditions. The long-ranged electrostatic energy and forces were calculated by the Wolf direct sum method. The time step was 0.4 fs, which provided enough accuracy for the integration of the shell coordinates. The total time of each simulation, after 5 ps of thermalization, was at least of 40 ps. In order to avoid high-energy metastable states,

FIG. 1. Particles' shape considered in this study: (a) cylinders with different diameter/height (D/H) aspect ratios, and (b) sphere and spheroids with $D < L$ (prolate) and $D > L$ (oblate).

successive heating and cooling steps were performed. The presented results correspond to equilibrated configurations at $T = 50$ K. The investigated nanodots have cylindrical, spherical, and ellipsoidal shapes (see Fig. 1). The different particles were constructed from elementary perovskite unit-cells centered on Ti atoms with axes along pseudocubic directions (x , y , and z axes lie along the $[100]$, $[010]$, and $[001]$ directions, respectively). In addition, we consider that all surface faces consist of PbO planes. As a result, the (curved-) boundaries of the constructed objects are not smooth. The cylinders are characterized by the D diameter and the H height, and the cylinder axis is chosen to be along the z -direction. The size of each sphere is described by its diameter, and spheroids are represented by diameter in the (x,y) plane, and the length L along the z -direction. The dimensions of the particles are expressed in terms of the number of unit-cell lattice constants. Since the net polarization in zero-dimensional dots under an ideal open-circuit boundary condition is null, we adopted the local polarization (i.e., the polarization of a perovskite unit-cell) to map polar distributions and the toroidal moment per unit volume $\vec{g}$ to quantify single vortex-like configurations. The local polarization considers contributions from all atoms in the conventional cell and atomic positions with respect to Ti at its center: $\vec{p} = \frac{1}{v} \sum_k \frac{1}{\omega_k} z_k (\vec{r}_k - \vec{r}_{Ti})$,³² where v is the volume of the cell; z_k and $\vec{r}_k$ denote the charge and the position of the k particle, respectively; and ω_k is the weight factor equal to the number of cells to which the particle belongs. The second parameter is defined as $\vec{g} = \frac{1}{2Nv} \sum \vec{r}_i \times \vec{p}_i$,¹² where $\vec{p}_i$ represents the dipole of cell i located at position $\vec{r}_i$, N is the number of cells of the system, and v is the cell volume.

To improve the characterization of nanocylinders, we extend the microscopic analysis to other relevant quantities, such as energy, volume, and stress. We define the local energy as the energy of a perovskite unit cell evaluated from the contributions of the atoms associated to that cell: $e = \sum E_k / \omega_k$, where the energy of the k -atom E_k is the sum of the kinetic and potential parts. The second contribution corresponds to half of the sum of the interactions of the atom with the rest of the ions. Local values of the stress tensor components, $s^{\alpha\beta}$, are obtained following a similar procedure: $s^{\alpha\beta} = \sum S_k^{\alpha\beta} / \omega_k$, where $S_k^{\alpha\beta}$ represents stress tensor components of the k -atom. $S_k^{\alpha\beta}$ has a kinetic and a virial contribution due to atomic interactions. In the case of the volume, we consider a Wigner–Seitz cell located at its center of mass. All these magnitudes were computed with the LAMMPS code.³³

III. RESULTS AND DISCUSSION

A. Cylindrical nanoparticles with diameter equal to height

We first investigated the evolution of the polar patterns corresponding to cylinders with equal diameter and height, $D = H$. Figure 2 shows the components of the toroidal moment obtained from simulations as a function of the size, for D varying from 6 to 34. In the smaller particles, the atomic displacements are completely dominated by surface relaxations, and the absence of order is attributed to negligible values of local polarizations. The first sign of the toroidal order is observed at $D = 8$, where one of the components, g_z , starts to increase. The non-zero value of g is

FIG. 2. Toroidal moment and average local polarization (inset) as a function of diameter in $D = H$ nanocylinders.

driven from the simultaneous increment of polar distortions (inset of Fig. 2) and the correlation among dipoles. The polarization pattern corresponds to a single vortex configuration with its core along the cylinder axis. Figure 3(a) shows how local dipoles rotate from cell to cell at the central xy -plane of a $D = 10$ nanocell. The vortex structure remains quite homogeneous along the entire height of the cylinder, while the polarization along the z -direction is practically zero. The obtained single vortex structure is then in agreement with earlier theoretical predictions.^{12,13} Besides, we note that the direction of the vortex axis ($\langle 001 \rangle$) in cylinders differs from the one previously obtained with the same model for nanocubes ($\langle 111 \rangle$),¹⁴ which indicates that the vortex configuration depends on the nanoparticle geometry.

The magnitude of local dipoles and g_z increase with the size of the nanocylinders, except from $D = 20$ to $D = 22$. This anomaly reflects a transformation to a different configuration. The emerged polar arrangement maintains the flux-closure structure, but g_z decreases slightly since local polarizations are not necessarily oriented perpendicularly to the radial vector from the core to the dipole. As a result, the nearly continuous dipole rotation evolves into four regions with a rather uniform polar orientation, as shown in Fig. 3(b), for a $D = 34$ cylinder. In each region or domain, local dipoles adopt one of the four equivalent $\langle 100 \rangle$ crystallographic directions, and they rotate 90° from one domain to the other, forming a closed-loop structure. The configuration, however, does not correspond to a classical closure configuration with all domains converging into a central point. Instead, a distorted core region with two domain wall junctions and an additional domain wall between them is observed. The resulting domain structure is formed by two halves of a closure quadrants, and it is similar to domain patterns observed in tetragonal BaTiO_3 ,^{19,34,35} $\text{PbZr}_{0.42}\text{Ti}_{0.58}\text{O}_3$,²⁰ $[\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.88}-[\text{PbTiO}_3]_{0.12}$,³⁶ and in strained PTO films.²²

Closure domain configurations are often seen as precursors for vortex formation, since the coalescence of the two 3-fold wall junctions into a vortex configuration is expected.^{35,37,38} In other

FIG. 3. Local polarization pattern at the central xy -plane in $D=H$ cylinders showing (a) a vortex-like structure at $D=10$ and (b) a closure domain configuration at $D=30$. Values are obtained at $T=50$ K.

words, the vortex state transforms into a closure domain configuration when the size of the nanoparticle increases, as we obtain in the simulations. Figure 4 shows the evolution of the polar patterns for cylinders with intermediate sizes. To better visualize the core transformation process, we plotted the central region of each nanostructure using the same spatial and polar scales. That is, each polar pattern corresponds to a region of 16×16 unit cells, and arrows are proportional to the polarization magnitude. At $D=14$, the vortex

core is constituted by four cells with dipoles pointing in the equivalent $[110]$ directions, similar to the $D=10$ vortex showed in Fig. 2. The core distorts when the size of the cylinder increases. It stretches first along the $[010]$ direction for $D=20$ [Fig. 3(b)] and then along $\sim[110]$ direction for $D=24$, generating 90° domain walls [Fig. 3(c)]. From this size, the core distortion increases with the appearance of the 180° domain wall between the junctions [Figs. 3(d)–3(e)]. It can be seen in the figure that the resulting

FIG. 4. Size-induced evolution sequence that leads the vortex-like structure to the closure domain configuration in cylinders with $D=H$ for (a) $D=14$, (b) $D=20$, (c) $D=24$, (d) $D=30$, and (e) $D=34$. Each polar pattern corresponds to a central xz -plane region of 16×16 unit cells. Arrows are proportional to the polarization magnitude.

angles between walls in the junctions differ from those originally proposed of 135° and 90° between $180^\circ/90^\circ$ and $90^\circ/90^\circ$ domain walls, respectively.³⁷ This is because the 180° domain wall in the present simulations is not parallel to the domain's polarization. It is noteworthy that the topological winding number of +1 characteristic of the vortex structure³⁹ breaks up into two defects, each one with a winding number of +1/2 across the transformation. Then "net winding number" is preserved if we consider a pathway loop enclosing both domain junctions.

The transformation of the polar structure partially describes the evolution of the state of the nanocylinders with size. To understand more deeply the size effects on the behavior, we compute the surface energy E_{surf} and the volume of the nanoparticles. E_{surf} can be defined as the energy difference between the nanoparticle and a region with the same number of atoms in an infinitely extended solid.⁴⁰ Since the simulated nanoparticles are nonstoichiometric, we adopt the following expression:

$$E_{surf} = \frac{E_{tot} - \sum n_i E_i^{bulk}}{A},$$

where E_{tot} and A are the total energy and the surface area of the nanoparticle and n_i is the number of i -type atoms in the particle, while E_i^{bulk} corresponds to its energy in the reference bulk ground state. Regarding the surface area, it is calculated from the polygons forming the outer Pb ions of the particle. Figure 5 shows the dependence of E_{surf} as a function of nanocylinder size. The surface energy decreases monotonically from $0.536 \text{ eV}/\text{\AA}^2$ at $D=10$ to $0.150 \text{ eV}/\text{\AA}^2$ at $D=34$, indicating that surface effects are relevant in all simulated nanoparticles. Since, to the best of our knowledge, there are no previous reports on E_{surf} in ferroelectric nanoparticles, we compare E_{surf} with the surface energy of the PbO-terminated (001) surface. The reported value of $0.068 \text{ eV}/\text{\AA}^2$ ²⁴¹ is approximately half of that obtained for the $D=34$ cylinder, and it could be considered as a lower limit for convergence. It is worth mentioning

FIG. 5. Surface energy and relative volume as a function of size in $D=H$ cylinders.

that E_{surf} will be reduced if the extension of the electronic cloud is considered in the determination of the surface area of the nanoparticles.⁴² This correction (5% and 1% for the smallest and largest cylinders, respectively) does not modify the qualitative behavior described here. Figure 5 also includes the behavior of the volume of the nanocylinders, which suffers strong variations with respect to the reference bulk. Volume reductions of about 4% for $D=10$ and 1.5% for $D=34$ are obtained. In contrast to E_{surf} , the behavior of the volume presents a kink similar to that observed in g_z (Fig. 2) when the domains start to develop. This anomaly indicates an elastic rearrangement of the cells when domains are formed. It also highlights the relevance of the coupling between polarization and strain in the stability of the nanoparticles.

Figure 6 allows us to compare the distribution of the local energy between a vortex and a closure domain configuration. According to the histogram in Fig. 6(a), local energies display a broad distribution in the configuration where polar direction changes continuously from cell to cell (vortex state). The distribution in the larger particle [Fig. 6(b)] is sharpened, and it is displaced toward lower energies because the proportion of cells with polarization along the tetragonal axis increases. The peak corresponds to cells polarized along (001) directions, and its position shifts from 0.055 eV ($D=14$) to 0.025 eV ($D=34$).

Energy, polarization, volume, and stress are inhomogeneously distributed across a nanoparticle, as shown in Fig. 7, for the $D=34$ closure domain configuration. The energy map showed in Fig. 7(a) is consistent with the domain structure observed in the polarization profile [Fig. 3(b)]. Low energy cells are located inside the domains,

FIG. 6. Local energy interval histogram $[h(e)]$ corresponding to $D=H$ cylinders with (a) $D=14$ and (b) $D=34$.

while the high-energy values correspond to cells at domains walls and near the surface, whose polarization deviates from the (001) axis. In addition, the local energy in the wall decreases with the distance to the domain junction. Simulations also show that the amplitude of the local polarization is proportional to cell volume regardless its cell energy. Contrary to what it is expected,^{43,44} cells with large relative values of volume and polarization are located near the domain walls (including the central region), while smaller values correspond to cells far from the walls [Figs. 7(b) and 7(c)].

Figure 7 also allows to get an insight on how domains accommodate under the imposed boundary conditions. According to Figs. 7(b) and 7(c), the volume and polarization of cells inside a domain decrease toward the edge of the nanoparticle, while the stress components indicate that the compression is mainly along the polar axis. This effect can be observed in the σ_{xx} map [Fig. 7(d)] for the x -polarized domains (top and bottom), and in σ_{yy} [Fig. 7(e)] for the y -polarized domains (left and right). This modulation makes it possible to keep 90° walls in (011) planes, and it is an effective way to minimize the energy associated with the disclination strain of tetragonal domains in a quadrant arrangement.¹⁹ In addition, cells in the 90° wall region display shear distortions [Fig. 7(f)] compatible with their polar direction.

B. Cylindrical nanoparticles with diameter different to height

The polar behavior described above is also observed in elongated cylinders. Such structures were simulated with D ranging from

15 to 30 and H from 15 to 70. In all cases, the toroidal moment lies along the cylinder axis, while the vortex-like structure depends only on D . The situation changes when H is reduced below D . In this case, we found a sequence of topological transformations analogous to the one observed in nanocuboids,¹⁴ and they occur at quite similar aspect ratios. To illustrate, we present results for cylinders with $H = 10$ in Fig. 8. The increment in the aspect ratio favors the appearance of polar components along the z -direction and vortices with cores parallel to the flat surface. These complex dipole structures cannot be properly described with the toroidal moment, and other order parameters should be used.^{45,46} The first transformation to a four-vortex state observed at $D = 17$ gives rise to four z -polarized domains, two pointing up and two pointing down [Fig. 8(a)]. This state transforms into a ring-shaped torus when the nanodisk diameter exceeds a critical value of $D = 23$. This occurs due to the alignment of the vortex cores along a closed path, generating a strongly polarized region (ferroelectric bubble) at the center of the ring [Fig. 8(b)]. A further increment of the nanodisk diameter leads to the formation of multibubble states. The initial ferroelectric bubble splits into two oppositely polarized bubbles as the diameter increases [Fig. 8(c)]. Bubbles elongate to accommodate the geometry of the system and take an increasingly lengthened shape as their number increases [Fig. 8(d)]. In this way, the polarization profile of a nanodisk with a large diameter resembles the striped domain configuration observed in PTO ultrathin films.^{11,14} The width of the domains also rapidly converges to the value of the film. While the “width” of the single bubble is around 12–13 unit cells, it stabilizes in approximately eight unit cells in nanodisks with three or more

FIG. 7. Spatial distribution of local values at the central xy -plane in $D = H$ cylinder with $D = 34$. (a) Energy, (b) relative volume, (c) polarization, and (d) and (e) stress components σ_{xx} , σ_{yy} , and σ_{xy} .

FIG. 8. Size-induced transformations in selected ten unit-cell thick nanodisks at $T = 50$ K. P_z polarization maps (in $\mu\text{C}/\text{cm}^2$) correspond to (a) four-vortex state at $D = 17$, (b) ferroelectric bubble at $D = 23$, (c) stabilized two-bubble state at $D = 31$, and (d) five stripe-shaped bubbles with alternating polarity at $D = 49$.

bubbles. This width agrees with the value reported for PTO thin films with a ten unit-cell thickness.¹¹ A similar behavior is obtained in nanoparticles with a different height, and it is equivalent to the one obtained in nanocuboids. Thus, our results reveal the existence of a critical aspect ratio below which domains do not behave as they do in films, and they are consistent with the anomalous domain periodicity observed in PTO nanodots with a few numbers of domains.⁴⁷ They also indicate that the effects originated in the lateral surface of the dots are confined to the border region, and the characteristics in the interior resemble those of the film. Then, our results suggest that domains in nanoparticles with D/H larger than ~ 4 will behave according to Kittel's scaling law⁴⁸ regardless of their thickness.

C. Spherical and ellipsoidal nanoparticles

To gain a deeper insight into the dependence of the topological transformation path on the nanostructure shape, we investigated the evolution of the polarization pattern in spheres and spheroids. The absence of flat surfaces in those geometries provides an additional degree of complexity to the stability of the possible polar structures. The simulated spheres, with diameters between 15 and 41, display all a single vortex-like configuration, with the vortex axis along one of the equivalent $\langle 001 \rangle$ directions. The texture in the planes perpendicular to the vortex axis depends on the distance to the equatorial plane. For example, the pattern of Fig. 9(a) corresponds to the equatorial plane in a $D = 41$ sphere, and it is similar to the closure domain structure observed in a $D = 41$ cylinder. The diameter of the circular section decreases when the distance to the equatorial plane increases,

and the polar distribution of each slice resembles the pattern observed in $D = H$ cylinders with the same diameter. In particular, the core distortion follows the behavior shown in Fig. 4 for different diameters. The vortex-like configuration of the spheres agrees with the configuration obtained in recent Ginzburg–Landau–Devonshire simulations of PTO spheres embedded in a low-permittivity dielectric medium.⁴³ Both results, however, differ in the central region. While the polarization is suppressed according to the phase-field approach, our atomic level description indicates that the system prefers to sustain the polarization by distorting the central core.

Spheroids are obtained by deforming spheres along the z -axis. In the limits of large distortions, the spheroids approach to a

FIG. 9. Local polarization configuration in a $[001]$ plane for (a) $D = 41$ sphere and (b) $D = 15$, $H = 39$ prolate spheroid.

FIG. 10. Size-induced transformation in oblate nanospheroids with 11 unit-cell in thickness. P_z polarization maps (in $\mu\text{C}/\text{cm}^2$) showing (a) a four-vortex state at $D=25$, (b) a three-bubble configuration at $D=29$, and (c) a multi-bubble state at $D=51$.

cylinder-like shape. Therefore, in those limits, we can expect polarization patterns similar to the ones obtained for the cylinders. That is a single vortex-like configuration for elongated spheroids and a stripe domain pattern for squashed geometries. The situation is straightforward in the case of prolate spheroids (spheres elongated from the top), which display one-vortex structures similar to the ones observed in spheres. Figure 9(b) shows the vortex structure obtained for a spheroid of $D=15$ and $L=39$, where local polarizations rotate around the longer $\langle 001 \rangle$ axis.

The evolution of the polarization field in oblate spheroids (spheres squashed from the top) is different from the one obtained for cuboid and cylindrical nanostructures. The increase in the aspect ratio produces transformation from a single- to a four-vortex state, similar to the other two cases. This state, however, subsists for aspect ratios greater than those obtained in cylinders. For $L=11$, for instance, the four-vortex state is stable up to $D=25$ [Fig. 10(a)], while the one bubble state is stabilized in a disk of similar dimensions. The stability of the four-vortex state at larger diameters can be attributed to a smaller effective aspect ratio due to the decrease in height toward the border of the nanoparticle. Surprisingly, the ferroelectric bubble state is not stabilized when the aspect ratio is further increased. Instead, we observed a direct transformation from the four-vortex to the three-bubble configuration [Fig. 10(b)]. That is, in no case, we detect the stabilization of one- and two-bubble states in oblate spheroids. In this instance, the thinner region of the nanoparticle edge prevents the stabilization of a robust ring-shaped

torus, which is necessary for the development of a polarized region concentrated on the center of the nanodot. The previous four-vortex state transforms into another four-vortex state but with toroidal moments parallel to the $\langle 100 \rangle$ direction and alternating chirality, generating the three-bubble state. A further increment of the diameter increases the number of bubbles [Fig. 10(c)], and spheroids with large aspect ratio behave like flat disks.

D. Conclusions

We applied an atomistic approach to investigate the topology of the polarization field in isolated PTO nanoparticles with cylindrical, spherical, and spheroidal shapes. We found that a single vortex structure is observed in small $D=H$ cylinders. The increment of polarization with the size of the cylinders produces the distortion of the central core and the formation of a domain structure in a flux-closure configuration. As a result, the vortex configuration transforms into a closure domain structure for diameters above 20 unit-cells. This transition was observed by the presence of anomalies in the toroidal moment and relative volume. While elongated cylinders, spheres, and prolate spheroids show similar single vortex-like configurations, the polarization pattern on flat particles is more complex and strongly depends on its aspect ratio. In nanodisks, a rich variety of polar configurations is observed when the aspect ratio increases. The sequence of the topological transformations includes the formation of four-vortex, ferroelectric bubble,

and multi-bubble states. This transformation path is similar to the one previously observed in nanocuboids.¹⁴ In oblate spheroids, however, the evolution is different. The one- and two-bubble states do not stabilize, and a direct transformation from the four-vortex state to the three-bubble configuration takes place. Despite this last difference, our results indicate that the aspect ratio is more important than the particle shape to determine the polarization pattern of a nanostructure. We finally point out that we defined and calculated local values of energy, volume, and stress, which have provided useful information about the behavior of $D=H$ nanodisks. This information constitutes another step to link first-principles, classical atomic level and Landau–Ginzburg–Devonshire phenomenological approach in a multi-scale description.

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REFERENCES

- ¹N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. Taganste, D. V. Taylor, T. Yamada, and S. Streiffer, *J. Appl. Phys.* **100**, 051606 (2006).
- ²J. F. Scott, *Ferroelectric Memories* (Springer, Berlin, 2000).
- ³C. T. Nelson, B. Winchester, Y. Zhang, S. J. Kim, A. Melville, C. Adamo, C. M. Folkman, S.-H. Baek, C.-B. Eom, D. G. Schlom, L.-Q. Chen, and X. Pan, *Nano Lett.* **11**, 828 (2011).
- ⁴R. W. Whatmore, Q. Zhang, C. P. Shaw, R. A. Dorey, and J. R. Alcock, *Phys. Scr.* **T129**, 6 (2007).
- ⁵C.-B. Eom and S. Trolier-McKinstry, *MRS Bull.* **37**, 1007 (2012).
- ⁶M. Algueró and J. M. Gregg, *Nanoscale Ferroelectrics and Multiferroics* (John Wiley & Sons, Ltd., 2016).
- ⁷C. R. Bowen, H. A. Kim, P. M. Weaver, and S. Dunn, *Energy Environ. Sci.* **7**, 25 (2014).
- ⁸S. P. Alpay, J. Mantese, S. Trolier-McKinstry, Q. Zhang, and R. W. Whatmore, *MRS Bull.* **39**, 1099 (2014).
- ⁹J. Seidel and L. M. Eng, *Curr. Appl. Phys.* **14**, 1083 (2014).
- ¹⁰A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. D. Clarkson, C. M. Schlepütz, A. R. Damodaran, P. Shafer, E. Arenholz, L. R. Dedon, D. Chen, A. Vishwanath, A. M. Minor, L. Q. Chen, J. F. Scott, L. W. Martin, and R. Ramesh, *Nature* **530**, 198 (2016).
- ¹¹D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, *Science* **304**, 1650 (2004).
- ¹²I. I. Naumov, L. Bellaiche, and H. Fu, *Nature* **432**, 737 (2004).
- ¹³L. Lahaoche, I. Luk'yanchuk, G. Pascoli, L. Lahoeche, I. Luk'yanchuk, and G. Pascoli, *Integr. Ferroelectr.* **99**, 60 (2008).
- ¹⁴M. G. Stachiotti and M. Sepiarsky, *Phys. Rev. Lett.* **106**, 137601 (2011).
- ¹⁵Y. Nahas, S. Prokhorenko, L. Louis, Z. Gui, I. Kornev, and L. Bellaiche, *Nat. Commun.* **6**, 8542 (2015).
- ¹⁶A. Gruverman and A. Kholkin, *Rep. Prog. Phys.* **69**, 2443 (2006).
- ¹⁷S. Prosandeev, I. I. Naumov, H. Fu, L. Bellaiche, M. P. D. Campbell, R. G. P. McQuaid, L. Chang, A. Schilling, L. J. McGilly, A. Kumar, and J. Marty Gregg, "Ferroelectric vortices and related configurations," in *Nanoscale Ferroelectrics and Multiferroics: Key Processes Characterization Issues, and Nanoscale Effects*, edited by M. Algueró, J. M. Gregg, and L. Mitoseriu (John Wiley & Sons, Ltd, 2016), pp. 701–728.
- ¹⁸D. Caruntu, T. Rostamzadeh, T. Costanzo, S. Saleemizadeh Parizi, and G. Caruntu, *Nanoscale* **7**, 12955 (2015).
- ¹⁹A. Schilling, D. Byrne, G. Catalan, K. G. Webber, Y. A. Genenko, G. S. Wu, J. F. Scott, and J. M. Gregg, *Nano Lett.* **9**, 3359 (2009).
- ²⁰L. J. McGilly and J. M. Gregg, *Nano Lett.* **11**, 4490 (2011).
- ²¹R. G. P. McQuaid, A. Gruverman, J. F. Scott, and J. M. Gregg, *Nano Lett.* **14**, 4230 (2014).
- ²²Y. L. Tang, Y. L. Zhu, X. L. Ma, A. Y. Borisevich, A. N. Morozovska, E. A. Eliseev, W. Y. Wang, Y. J. Wang, Y. B. Xu, Z. D. Zhang, and S. J. Pennycook, *Science* **348**, 547 (2015).
- ²³A. R. Balakrishna and J. E. Huber, *Appl. Phys. Lett.* **106**, 092906 (2015).
- ²⁴C. M. Wu, W. J. Chen, Y. Zheng, D. C. Ma, B. Wang, J. Y. Liu, and C. H. Woo, *Sci. Rep.* **4**, 3946 (2015).
- ²⁵K. C. Pitike, J. Mangeri, H. Whitelock, T. Patel, P. Dyer, S. P. Alpay, and S. Nakhmanson, *J. Appl. Phys.* **124**, 064104 (2018).
- ²⁶J. Slutsker, A. Artemev, and A. Roytburd, *Phys. Rev. Lett.* **100**, 087602 (2008).
- ²⁷I. Naumov and A. M. Bratkovsky, *Phys. Rev. Lett.* **101**, 107601 (2008).
- ²⁸C.-L. Jia, K. W. Urban, M. Alexe, D. Hesse, and I. Vrejoiu, *Science* **331**, 1420 (2011).
- ²⁹M. Sepiarsky, Z. Wu, A. Asthagiri, and R. E. Cohen, *Ferroelectrics* **301**, 55 (2004).
- ³⁰M. Sepiarsky, M. G. Stachiotti, and R. L. Migoni, *Phys. Rev. Lett.* **96**, 137603 (2006).
- ³¹I. T. Todorov, W. Smith, K. Trachenko, and M. T. Dove, *J. Mater. Chem.* **16**, 1911 (2006).
- ³²M. Sepiarsky and R. E. E. Cohen, *J. Phys. Condens. Matter* **23**, 435902 (2011).
- ³³S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).
- ³⁴L. J. McGilly, A. Schilling, and J. M. Gregg, *Nano Lett.* **10**, 4200 (2010).
- ³⁵R. G. P. McQuaid, L. J. McGilly, P. Sharma, A. Gruverman, and J. M. Gregg, *Nat. Commun.* **2**, 404 (2011).
- ³⁶L. W. Chang, V. Nagarajan, J. F. Scott, and J. M. Gregg, *Nano Lett.* **13**, 2553 (2013).
- ³⁷D. J. Srolovitz and J. F. Scott, *Phys. Rev. B* **34**, 1815 (1986).
- ³⁸G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, *Rev. Mod. Phys.* **84**, 119 (2012).
- ³⁹N. D. Mermin, *Rev. Mod. Phys.* **51**, 591 (1979).
- ⁴⁰D. Vollath, F. D. Fischer, and D. Holec, *Beilstein J. Nanotechnol.* **9**, 2265 (2018).
- ⁴¹B. Meyer, J. Padilla, and D. Vanderbilt, *Faraday Discuss.* **114**, 395–405 (1999).
- ⁴²D. Holec, F. Dieter, and D. Vollath, *Comput. Mater. Sci.* **134**, 137 (2017).
- ⁴³J. Mangeri, Y. Espinal, A. M. Jokisaari, S. Pamir Alpay, S. Nakhmanson, O. G. Heinonen, S. P. Alpay, S. Nakhmanson, and O. G. Heinonen, *Nanoscale* **9**, 1616 (2017).
- ⁴⁴J. Mangeri, S. P. Alpay, S. Nakhmanson, and O. G. Heinonen, *Appl. Phys. Lett.* **113**, 092901 (2018).
- ⁴⁵M. G. Stachiotti and M. Sepiarsky, *Ferroelectrics* **427**, 41 (2012).
- ⁴⁶S. Prosandeev and L. Bellaiche, *J. Mater. Sci.* **44**, 5235 (2009).
- ⁴⁷J. Y. Son, S. Song, J. Lee, and H. M. Jang, *Sci. Rep.* **6**, 26644 (2016).
- ⁴⁸C. Kittel, *Phys. Rev.* **70**, 965 (1946).