Novel High-Temperature Ferroelectric Domain Morphology in PbTiO$_3$ Ultrathin Films

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Exotic domain morphologies in ferroic materials are an exciting avenue for the development of novel nanoelectronics. In this work we have used large scale molecular dynamics to construct a strain-temperature phase diagram of the domain morphology of PbTiO$_3$ ultrathin films. Sampling a wide interval of strain values over a temperature range up to the Curie temperature $T_c$, we found that epitaxial strain induces the formation of a variety of closure- and in-plane domain morphologies. The local strain and ferroelectric-antiferrodistortive coupling at the film surface vary for the strain mediated transition sequence and this could offer a route for experimental observation of the morphologies. Remarkably, we identify a new nanobubble domain morphology that is stable in the high-temperature regime for compressively strained PbTiO$_3$. We demonstrate that the formation mechanism of the nanobubble domains morphology is related to the wandering of flux closure domain walls, which we characterise using the hypertoroidal moment. These results provide insight into the local behaviour and dynamics of ferroelectric domains in ultrathin films to open up potential applications for bubble domains in new technologies and pathways to control and exploit novel phenomena in dimensionally constrained materials.

INTRODUCTION

Domain walls in thin films have shown promising functionalities, such as induced electric and magnetic properties, and the formation of unusual controllable phases that are not observed in the bulk samples [1–4]. Recent direct observation of so-called wandering domain walls in thin films [5], whereby the direction of the domain wall tangent significantly varies along the wall length, and the ability to control the direction of the domain wall suggests viable mechanisms for tuning intrinsic ferroelectric and piezoelectric properties [6, 7].

The orientation of the polarisation in ferroelectric films is influenced by a delicate balance between the epitaxial strain and screening of the depolarising field. The misfit strain from growth substrates has been shown to promote exotic polar orientations that are not observed in bulk samples [8, 9]. Similarly, compensation of the intrinsic depolarising field through screening has been shown to induce the formation of novel ordered domain structures [10]. A rich variety of new closure domain morphologies, such as Landau-Lifshitz stripe domains [11, 12], vortex and triclinic domains [13], have been predicted in PbTiO$_3$, and BaTiO$_3$ films under open-circuit boundary conditions using density functional theory, effective Hamiltonian and interatomic potential models [14, 15]. Tantalising experimental evidence for these closure domains in platlets and dots of BaTiO$_3$ has been presented in the form of 90$^\circ$ stripe super-domains bifurcated by 180$^\circ$ domain walls [16–18] and recent direct observation of vortices in PbTiO$_3$/SrTiO$_3$ superlattices [19].

The insight into the atomistic mechanisms of formation of dense domain morphologies is fundamentally and industrially important for the next generation of emergent technologies. Density functional theory (DFT) calculations have been extensively applied to various ferroelectric materials and these have provided fundamental insight into the origin of ferroelectricity, domain wall behaviour, grain boundaries and interfacial phenomena [20–23]. However, modelling of domain wall dynamics at DFT level is computationally challenging since this requires large ensembles and long computation times. Semi-empirical forcefields, parametrised to reproduce materials properties, provide robust tools for modelling long timescale dynamics and dense sampling of strain values.

In this paper we model domain morphologies formed in PbTiO$_3$ films using molecular dynamics and calculate the misfit-strain–temperature (Pertsev diagram [8]) of symmetrically terminated PbTiO$_3$ films for a wide range of strain and temperature values. We identify the effect on the domain structure on the ferroelectric-antiferrodistortive coupling at the films surfaces and found that epitaxial strain induces the formation of a variety of closure- and in-plane domain morphologies. Remarkably, we identified a new nanobubble domain morphology that was stable in the high-temperature regime. We demonstrate that the formation mechanism of the novel nanobubble domain morphology is related to the wandering of flux closure domain walls.
METHODOLOGY

We studied (001) properties of strained PbTiO$_3$ ultra-thin films under open circuit conditions using molecular dynamics as implemented in the DL_POLY code [24]. We used the adiabatic core-shell forcefield derived in Gin-dele et al., that reproduces the structural parameters of the cubic and tetragonal phases, the Born effective charge tensors, the elastic properties and soft phonon modes of PbTiO$_3$ in excellent agreement with density functional theory (DFT) calculations [25]. Furthermore, the model correctly describes the enhanced antiferrodistortive c(2x2) surface relaxation of PbTiO$_3$ in agreement with ab initio calculations [26, 27].

We use a large supercell of size 10x10x10 (z=10 layer PbO only) to create a symmetrically terminated film containing 4700 atoms (and larger in some cases, explicitly mentioned) with three dimensional periodic boundary conditions. A 100 Å vacuum gap in the growth direction [001]$_p$ was imposed on the system so the film is continuous and infinite along the pseudocubic [100]$_p$ and [010]$_p$ directions. The homogeneous biaxial misfit strain was defined as

$$ \eta = \frac{a_s}{a_f} - 1 $$

where $a_f$ is the cubic lattice parameter at the Curie temperature $T_c$. The properties of the system were calculated at different values of strain via variation of the effective substrate lattice parameters $a_s$ in the range $3.8 < a_s < 4.05$ (Å). The misfit strain was imposed by a Nosé-Hoover canonical (NVT) ensemble with a 10 fs relaxation constant. For each misfit strain the system was heated over a temperature range of $25 < T < 1000$ (K) in 25 K increments; equilibrated at each temperature for 20 ps using a 0.2 fs timestep, with statistics gathered over a subsequent 60 ps production run. To confirm the consistency of our results we repeated several calculations using random selections of misfit strains within a set of larger systems ($10 \leq N_{x,y} \leq 26$). We note a small variation (within 10%) of the temperature and strain values of phase changes with larger systems and attribute this to the competitive energy balance between an increase of the domain volume against the domain wall area.

The initial slab configuration was prepared to include two anti-aligned out-of-plane ideal Kittel domains with imposed ferroelectric displacements within each domain. To satisfy periodic boundary conditions the film contained two domain walls centred on the PbO(100) planes whose surface normal was parallel to the pseudocubic [100]$_p$ direction.

We define the effective local polarisation as the dipole per unit volume of a Ti centred conventional unit cell [TiPb$_8$O$_6$], delimited by 8 Pb cations with 6 oxygen on the trigonal faces forming a complete octahedral cage about the Ti cation [25]. The contributions from the dipoles separating all cores and shells in the cell are considered with reference to the Ti core site:

$$ \vec{P}_i = \frac{1}{\nu^i} \sum_{j=1}^{29} \frac{1}{\omega^i} q^i (\vec{r}^{j,i} - \vec{r}^i) $$

where $\nu^i$ is the volume of the cell calculated via the local lattice vectors, $\vec{r}^{j,i}$ is the position vector of the $i^{th}$ particle in the $j^{th}$ unit cell with respect to the supercell origin, $q^i$ is the charge of the $i^{th}$ particle species and $\omega^i$ is a weight to normalise the charge of the $i^{th}$ particle with respect to the number of cells it is shared amongst.

RESULTS AND DISCUSSION

Figure 1a presents the results of the observed domain morphologies over the full temperature and strain range considered. Our results are in excellent agreement with observations from other theoretical methods [6, 28] so we adopt the nomenclature of Jiang et al. whereby a,b,c label principle axes along which the polarisation is finite. A superscript $d$ indicates the out-of-plane polarisation is in the form of periodic domains. The definition of each phase in relation to behaviour of the local and macroscopic polarisation is summarised in Table I and characterised from the polarisation profile which is shown.

FIG. 1: Domain morphology dependence on misfit strain and temperature. (a) Pertsev diagram for 3.8 nm thick (001)PbTiO$_3$ calculated using the core-shell model. (b) Macroscopic polarisation dependence on temperature for $\eta = -2.25\%$. 


due to the depolarising field P that the local out-of-plane polarisation can be non-zero, but walls which converge to produce † face layers due to surface relaxations. (†) For all phases necessary from the open-circuit boundary conditions. The local polarisation criteria are not applied to the surface and 1st subsurface layers due to surface relaxations. (†) Wandering domain walls which converge to produce c\textsuperscript{d} domains.

TABLE I: Morphological definitions based on microscopic polarisations of each local unit cell P\textsubscript{k} and the overall macroscopic polarisation P = \sum P\textsubscript{k}/N. P\textsubscript{k} \neq 0 is the criterion that the local out-of-plane polarisation Pz = 0 for all cases necessary from the open-circuit boundary conditions. The local polarisation criteria are not applied to the surface and 1st subsurface layers due to surface relaxations. (†) Wandering domain walls which converge to produce c\textsuperscript{d} domains.

| Domain | Total Polarisation | Local Polarisation | |
|--------|--------------------|--------------------|
| c\textsuperscript{d} | P\textsubscript{x} = P\textsubscript{y} = P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0 |
| bc\textsuperscript{d} | P\textsubscript{x} = P\textsubscript{y} = P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0 |
| abc\textsuperscript{d} | P\textsubscript{x} \neq P\textsubscript{y} \neq P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0 |
| aac\textsuperscript{d} | P\textsubscript{x} = P\textsubscript{y} \neq P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0 |
| p | P\textsubscript{x} = P\textsubscript{y} = P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0 |
| (†) | P\textsubscript{x} = P\textsubscript{y} = P\textsubscript{z} = 0 | P\textsubscript{z} \neq 0, P(x, y, z) \neq P(x, y', z) |

in Figure 1b for \eta = -2.25%. We observe three distinct ferroelectric domain morphologies: aa, c\textsuperscript{d} and abc\textsuperscript{d} (shown in Figure 2, of which we henceforth loosely refer to as phases). Between these distinct phases we find two strain induced transitional ferroelectric phases bc\textsuperscript{d} and aac\textsuperscript{d}. A paraelectric phase p exists for all phases above the Curie temperature T\textsubscript{c}(\eta). Remarkably, in addition to the three distinct phases, we have identified a fourth previously unreported misfit-strain domain phase at high temperatures which we refer to as nanobubble domains c\textsuperscript{b}.

aa Domains

Under tensile strain (\eta > 0) below the paraelectric transition temperature, with corresponding substrate lattice parameters a\textsubscript{s} > a\textsubscript{0}, the polarisation is oriented parallel to the substrate interface [29, 30]. Domains form with ordered regions polarised along the a and b principle axes separated via 90° domain walls (Figure 2a). As the magnitude of the polarisation in each domain is equivalent the domains are classified as aa and are similar to those presented by Kouser et al. using a model Hamiltonian [28].

c\textsuperscript{d} Domains

Under compressive strain (\eta < 0) we observe the formation of closure domains that consist of periodic 180° out-of-plane stripe domains c\textsuperscript{d} (Figure 2b-c). This is consistent with experimental XRD results for PbTiO\textsubscript{3} films of similar thickness [31, 32] and PbTiO\textsubscript{3}/SrTiO\textsubscript{3} superlattices [19, 33, 34]. Morphologically, these are Landau-Lifshitz domains having 90° closure domain caps at the surface as previously observed in theoretical studies of PbTiO\textsubscript{3} films using interatomic potentials [11, 35].

A film thickness dependence has previously been identified by Belletti et al. for the c\textsuperscript{d} phase showing the 180° domain walls (see Figure 2c) to vanish into a vertex as the film thickness is decreased [11]. Our simulations reproduce this dependence which further validates our model. By comparing the configurational energy per unit cell when increasing the supercell dimensions and film thickness (N\textsubscript{z}), we further demonstrate our model satisfies the Kittel scaling law, obeying a linear dependence between the optimal domain width and the square root of the thickness. For films using a\textsubscript{s} = 3.99 Å at 25 K the law is satisfied for N\textsubscript{z} \geq 5 (001)PbO layers (2 nm) which returns a periodicity of 4.0 nm in agreement with experiment [31]. For thinner films the out-of-plane components of polarisation vanishes [32] but we observe that ferroelectricity is maintained with the polarisation reoriented in-plane (a-domain). Such reorientation has also been shown for PbTiO\textsubscript{3} films using DFT [36].

FIG. 2: Domain morphologies of PbTiO\textsubscript{3} ultrathin films. Each unit cell is represented by a cube coloured proportional to the polarisation. TiO\textsubscript{2} stack layers index the (001) TiO\textsubscript{2} planes defined from the film base. Bracketed numerals define (100) columns of unit cells along \hat{x}. (a) Perspective view of the aa domains. (b) x-z cross-section of the film with the c\textsuperscript{d} domain morphology. (c) Perspective view of the c\textsuperscript{d} domains. (d) x-z cross-section of the film with the abc\textsuperscript{d} domain patterning.
Under sequentially decreased compressive strains, components of polarisation can condense first parallel to the domain walls and then parallel to the domain periodicity (Figure 1) forming bc\(^d\), abc\(^d\) and finally aac\(^d\) domains through second order transitions. For each of these domains, out-of-plane stripe domains persist with the additional components superimposed. The x-z profile of the bc\(^d\) is identical to that of the c\(^d\) (Figure 2b).

For compressive strains between 1 < \(\eta\) < 3.75 (%) the \(P_x\) component also condenses forming abc\(^d\) domains (Figure 2d). The symmetry breaking between the \(P_z\) and \(P_y\) critical temperatures (Figure 1b) occurs due to the requirement for dipoles to reorientate to form the closure domains parallel to the direction of domain periodicity [6, 28]. Our simulations show that the 180\(^\circ\) domain walls of the adjacent bc\(^d\) phase collapse into to a vertex creating infinitely long cylindrical chiral tubes[37] as the polarisation parallel to the domain periodicity (\(P_x\)) stabilises further reducing the symmetry. This is consistent with observations in theoretical studies on PZT films[37]. Further to previous investigations, we observe that these chiral tubes propagate towards the film surface as the epitaxial compression is reduced further.

Our model shows a critical misfit strain of 1% upon which the chiral tubes reach the surfaces of the film and dissipate, equalizing the macroscopic in-plane polarisation components whilst maintaining distinct out-of-plane stripe domains, aac\(^d\) domains. The aac\(^d\) domains have a similar cross-section to the abc\(^d\) domains in Figure 2d with the quantitative exception \(P_x = P_y\) and the loss of the chiral centres such that there is no remnant of the 90\(^\circ\) domain caps (as weakly exists for the abc\(^d\) domains observable in Figure 2d above the chiral centre pointer). For compressive strains in the range 0 < \(\eta\) < 1 (%) the magnitude of \(P_z\) in the aac\(^d\) domains reduce continuously to a limiting vanishing point of freestanding films upon which the aa domain pattern is recovered. Second order transitions of the polarisation by means of continuous dipole rotation with the local structure transitioning through low symmetry triclinic phases such as we observe have similarly been been identified in an effective Hamiltonian simulation on PZT subjected to variations in the depolarising field strength [10].

### Dielectric Response

To reduce the error in our domain transition temperatures we evaluate the characteristic dielectric response of the films as it is known that susceptibility of ferroelectrics exhibits a divergent Curie-Weiss behaviour at the phase transition temperature. The susceptibility \(\chi_{\alpha\beta}\) and dielectric \(\epsilon_{\alpha\beta}\) tensors are calculated from fluctuations in the total polarisation[38, 39]:

\[
\chi_{\alpha\beta} = \frac{\langle V \rangle}{\epsilon_0 k_B T} (\langle \vec{P}_\alpha \cdot \vec{P}_\beta \rangle - \langle \vec{P}_\alpha \rangle \cdot \langle \vec{P}_\beta \rangle)
\]

where \(k_B\), \(T\) and \(\epsilon_0\) are the Boltzmann constant, simulation temperature and permittivity of free-space, respectively and \(\langle V \rangle\) is the time-averaged volume of the film. \(\alpha\) and \(\beta\) correspond components of the basis vector having labels of \(x\), \(y\) or \(z\) which define the tensor element. The bulk high-frequency (optical) susceptibility \(\chi_\infty\) for PbTiO\(_3\) is 8.24 and, therefore, negligible in relation to the static component [40].

We find that both the \(c^b \rightarrow bc^d\) and \(bc^d \rightarrow abc^d\) transitions are accompanied by large dielectric response. Indeed, Figure 3 shows asymptotic behaviour for \(\chi_{xx}\) and \(\chi_{yy}\) corresponding to the condensation of \(P_x\) and \(P_y\) components, respectively.

![FIG. 3: Temperature dependence of the static dielectric constant of a PbTiO\(_3\) film for \(\eta = -2.26\%\) identifying transition to different ferroelectric domains. A divergent response is observed for the \(c^b \rightarrow bc^d\) transition \((\epsilon_{yy})\) and \(bc^d \rightarrow abc^d\) \((\epsilon_{xz})\) transitions. Inset: Inverse dielectric constant with linear extrapolation from the high temperature response providing a more accurate estimation of the domain phase transition temperatures.](image)

The transition temperature between the domain phases are then determined from the linear high temperature dependence of the inverse dielectric constant \(\epsilon^{-1}\) (Figure 3-inset). For \(\eta = -2.26\%\) shown in Figure 3, the transition temperatures from the extrapolation are 0.27\(T_c\) and 0.36\(T_c\) for the \(bc^d \rightarrow abc^d\) and \(c^d \rightarrow bc^d\) transitions, respectively, with an uncertainty of \(\pm4.4\%\). Our studies are performed for the system under open circuit electrical boundary conditions which results in the presence of a strong depolarising field. The latter prevents the formation of an out-of-plane dielectric response \((\epsilon_{zz} = 0)\). A corresponding increase in \(\chi_{zz}\) would be expected for imperfect screening approaching the Curie temperature[28].
Novel Properties of bc\textdagger and abc\textdagger Domains

Theoretical studies have previously shown PbTiO$_3$ films to have different critical temperatures of the in-plane components of macroscopic polarisation [6, 28]. This results in the abc\textdagger $\rightarrow$ bc\textdagger $\rightarrow$ cd\textdagger transition sequence under the compressive strain regime, but knowledge of the behaviour of the local polarisation within each domain remains limited. To address the lack of knowledge about the polar behaviour with domain morphology we have analysed the in-plane components of polarisation within each of the closure domain morphologies ($\eta < 0$) at $\eta = -2.15\%$.

In the bc\textdagger domain phase, our simulations reveal the in-plane dipole rotations are not homogeneous throughout the film. The $P_y$ component (perpendicular to both the domain wall and surface normals), has a maximum value within unit cells constituting the domain walls (cell stacks (i), (ii), (vi) and (vii) in Figure 4a) and reduces sharply for cells further from the domain wall, reorientating along the c-axis of the centre of the film away from surface effects. The polar rotations at the surface layers act to change the anisotropy, forcing the domain walls to be more characteristic of magnetic Bloch-Néel walls than the distinctly Ising form in bulk [41]. Evidence for the existence of mixed Ising and Bloch-Néel character domain walls in ferroelectrics has recently been proposed in PbTiO$_3$ and LiNbO$_3$ from \textit{ab initio} calculations [42]. Such dipolar rotations can cause band bending of the conduction states across the domain wall and may be a contributory cause for recent experimental observations of conductive domain walls [43].

We further identify the $P_y$ component of local polarisation in the abc\textdagger domains have a maximum magnitude about the chiral centres producing concentric tubes of increasing in-plane ferroelectricity (Figure 4b). The cd\textdagger domains exhibit no macroscopic or local polarisation parallel to [010], only supporting rotations tangent to the (010) plane which are required to close flux at surface layers.

The coupling between antiferrodistortive (AFD) rotations and the local dipole moments are rarely investigated, yet such interactions have been shown to influence Curie temperatures and phases that can produce improper ferroelectrics [12, 44]. It has recently been proposed that control of AFD chiralities could be used in novel technologies such as four-state memory making the identity of methods to control AFD behaviour at atomic scales paramount [45]. Here, we demonstrate the effects of ferroelectric-antiferrodistortive coupling between the c(2x2) AFD surface reconstruction and the ferroelectric (FE) closure domain patterns at the surface of the PbTiO$_3$ film [26, 27]. This is characterised by the rotation of the equatorial oxygen atoms about the titanium, with simultaneous out-of-plane distortions which vary along the direction of the domain wall normals [001]. The TiO$_6$ octahedral rotations are averaged over the full trajectory and through [010], and are presented in Figure 5a for the cd\textdagger, bc\textdagger and abc\textdagger domain configurations along both the surfaces.

For the cd\textdagger domains a sinusoidal dependence is noted with a maximum rotation at the centre of the domain when the polarisation is pointing out-of-plane and minimised when the polarisation points into the plane (Figure 5a). Due to the symmetry of the domain pattern, the profiles of the rotation angle $\Phi$ for the top and bottom surface are identical, albeit inverted for any given point along [100]. The same relation has previously been noted for films with a cd\textdagger domain configuration modelled using a shell model which sampled three points along

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**FIG. 4:** (Color online). In-plane polarisation angle ($\phi = \tan^{-1}(P_y/P_x)$) and relative intensity of local polarisation chains in different PbTiO$_3$ domain morphologies confirming the domain wall in bc\textdagger and chiral centre in abc\textdagger domains are vortex centres in films. Bracketed Roman numerals index the unit cell column relative to the domain walls as defined in Figure 2. TiO$_2$ stack layers 1 and 9 are the rows of unit cells on the bottom and top surfaces, respectively. [010] polarisation maximised through 180$^\circ$ domain walls and the chiral centres.

**FIG. 5:** FE-AFD coupling on the surface of a 3.8 nm thick PbTiO$_3$ ultrathin film with different ferroelectric closure domain configurations. (a) Rotation angle ($\Phi$) on the top (diamond) and bottom (triangle) surfaces for each closure domain configuration. The arrows represent the out-of-plane domain orientation. (b) Local strain along the top surface (pentagon), bottom surface (triangle) and centre (diamond) of the film with the cd\textdagger domain morphology. (bii) Cartoon illustrating the local strain dependence on polarisation orientation at the top and bottom surface.
The angle variations for the other domain phases have not previously been reported, nor has direct explanation for the mechanism changing the rotation angle.

For both $bc^d$ and $abc^d$ the maxima and minima occur at the centre of the domains for the polarisation pointing out and in, respectively, although there is a slight shift in the absolute position along $[100]_p$ in the case of the $abc^d$ domain due to change from $180^\circ$ domain walls to chiral centres moving from the film centre (Figure 2d). However, due to the change of symmetry of the domain patterns, at a given point along $[100]_p$ the top and bottom of the film no longer share inversion symmetry, breaking this relationship in the $\Phi$ profile. Further, the magnitude of the rotation increases upon transition into the successive domain phases ($c^d$(red) $\rightarrow bc^d$ (blue) $\rightarrow abc^d$ (purple)).

A DFT study into the AFD modes of bulk PbTiO$_3$ has previously shown a direct strain dependence on the rotation angle, showing for strains larger than a critical value, the angle increases with tensile strain [46]. We show the local strain profile of a chain of unit cells along $[100]_p$ at the top, bottom and centre of the film in Figure 5b for the $c^d$ phase. Comparison of the strain-profile to Figure 5a(red) shows a clear relationship between local strain and $\Phi$, as is observed in bulk. Increases in local tensile strain enhance the rotation angle, whereas compressive strains suppress the rotation. A cartoon depicting the top and bottom surfaces is shown in Figure 5b(ii) demonstrating the strain-polarisation coupling acting as the mechanism promoting the variation in rotation angle. The transition from $c^d \rightarrow bc^d \rightarrow abc^d$ occurs with positive increases in strain (at a fixed temperature, Figure 1a) revealing the cause for the increase in rotation angle with the domain phase sequence.

**New High Temperature Nanobubble Domain Morphology**

In addition to the previously predicted phases, our model finds an entirely new phase at temperatures above the $c^d$ phase but below $T_c$. Our simulations show that in the compressive strain regime, in the vicinity of the effective Curie temperature, the homogeneity of the stripe $c^d$ domains along the easy axis, the in-plane [010]$_p$ direction, breaks down. This is due to diffuse nucleation and growth of the reverse domain on the domain walls (Figure 6a), shown previously as a growth mechanism in bulk prototypical systems under an activation field using a Landau-Ginzburg-Devonshire model [47]. This first presents by the distortion of the 180° domain wall alignment with [100]$_p$ planes (Figure 6a-d), so-called ‘wandering’ [5, 6]. Here we observed that, with further temperature increases leading to polarisation reduction, the degree of the anisotropy increases resulting in the domain wall pattern changing from linear stripe domains into nanobubble domains (Figure 6e). To confirm the prediction of this domain pattern, films of the same thickness were modelled using a larger simulation cell. Constructing the film using $26 \times 26 \times 10$ unit cells, the $c^b$ domains were shown to persist, forming through the same mechanism and therefore not a consequence of the chosen supercell size (Figure 6 f-g).

![FIG. 6: New ferroelectric domain morphology - nanobubble domains $c^b$. Out-of-plane polarisation profile at the centre ($N_z=5$) of the PbTiO$_3$ film for (a) 180° domain wall along easy axis (b) wandering 180° domain wall. (c,d) Cartoons depicting the 180° domain wall structures near film centre. (e) Cartoon of the predicted $c^b$ domain. Out-of-plane polarisation profiles from unit cells on the $N_z=5$ (i) and $N_z=2$ (ii) (001) planes of a $10 \times 10 \times 10$ simulation cell. Dotted lines define the interpolated $P_z=0$ isoline. (f) Large scale simulation showing the local dipoles of $c^b$ domains in compressively strained PbTiO$_3$ calculated using a $26 \times 26 \times 10$ cell containing 31772 atoms - for clarity only local dipoles with $P_z^j > 0$ are plotted leaving voids where $P_z^j < 0$. (g) Out-of-plane polarisation contour map of the centre (001) plane of (f) - red $P_z > 0$, blue $P_z < 0$.](image)
have not previously been identified in pure PbTiO$_3$ or for the condition of open circuit boundaries. The faceting instabilities of the nanobubble domains (Figure 6e-f) are analogous to those that occur from surface tension instabilities in thin magnetic films [48].

The presence of nanobubble domains is generally difficult to detect as there is no change to the total polarisation (Figure 1b), nor is there an accompanied dielectric response (Figure 3). To address this difficulty a new order parameter, the hypertoroidal moment $\vec{h}$, was proposed[49]:

$$\vec{h} = \frac{1}{2V} \sum_j \vec{r}^j \times \vec{T}^j = \frac{1}{4V} \sum_j \vec{r}^j \times (\vec{r}^j \times \vec{P}^j)_{t}$$

(4)

where the index $j$ spans all unit cells, $V$ is the supercell volume and $\vec{r}^j$ is the position vector of the $j^{th}$ unit cell relative to a chosen origin with coordinates transformed to set the origin at the centre of the supercell. $\vec{T}^j$ and $\vec{P}^j$ are the transverse components of the local toroidal and dipole moments where we make the approximation of the domains (the turning points along [100] (001) on coordinates corresponding to an xy sample the surface of $\vec{h}$). We note that the hypertoroidal moment surface (Figure 7a, dashed line) is clearly evident at $0.167T_c$ but deformations to the sine wave are evident above $0.5T_c$, which is lower than the temperature at which deformations in the domain walls can start to be observed in the polarisation map (Figure 6a, 0.8$T_c$). To guide the eye to these subtle deformations, a sinusoid (dotted) has been fitted to the $h_z$ surface cross-sections. We assert that the kinks are evidence of small statistical variations in the polarisation from the $180^\circ$ walls into the domains, which lead to the wandering domain wall phenomenon.

**CONCLUSIONS**

In this paper we have calculated the domain morphologies which condensate under varying homogeneous strains and temperatures within ultrathin films of PbTiO$_3$ using molecular dynamics with a shell model interatomic potential. We investigated the local behaviour of polarisation with the domains and identified a previously unreported high temperature nanobubble domain pattern. We have found that, in the vicinity of the Curie temperature, the $180^\circ$ domain walls wander from the easy axis, leading to the formation of this new domain morphology. We characterised the nanobubble domains using the hypertoroidal moment surface ($h_z$) for the first time and showed that it can be used to identify minute changes in the polarisation profile which signalled the domain wall transitions. Ferroelectric-antiferrodistortive coupling was observed at the film surface. The rotation angle of the octahedral cages was determined to be dependent upon the local strain, increasing with tensile strain and consequently enhanced along the strain mediated transition sequence $\Phi_{\text{max}}(\text{ed}) < \Phi_{\text{max}}(\text{bed}) < \Phi_{\text{max}}(\text{abc})$. Such surface properties provide a alternative means for experimental verification of the underlying domain structures.

In summary, the results from the forcefield calculations give unprecedented details about the response of the local polarization in ultrathin ferroelectric films to variations in strain and temperature, leading to the identification of a novel high temperature nanobubble domain pattern. Our studies provide guidance for the application of strain...
FIG. 7: Surface of the out-of-plane component of the hypertoroidal moment ($h_z$) evaluated for the central (001) plane of the PbTiO$_3$ ultrathin film for (a) $c^d$ domain configuration, (b) $c^b$ domain configuration, (c) Cross section of the out-of-plane component of the hypertoroidal moment surface evaluated for domain configurations as a function of temperature. Data points correspond to supercell origins which centre on titanium coordinates in the simulation cell. The dotted lines are sinusoids of the form $h(x) = A \sin(2\pi x/L_x + \phi)$ fit by method of least squares to the $h_z$-surface cross-sections of the closure-domains. Arrows show kinks in the surface.

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