Fast molecular-dynamics simulation for ferroelectric thin-film capacitors using a first-principles effective Hamiltonian

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A newly developed fast molecular dynamics method is applied to BaTiO3 ferroelectric thin-film capacitors with short-circuited electrodes or under applied voltage. The molecular dynamics simulations based on a first-principles effective Hamiltonian clarify that dead layers (or passive layers) between ferroelectrics and electrodes markedly affect the properties of capacitors, and predict that the system is unable to hop between a uniformly polarized ferroelectric structure and a striped ferroelectric domain structure at low temperatures. Simulations of hysteresis loops of thin-film capacitors are also performed, and their dependence on film thickness, epitaxial constraints, and electrodes are discussed.

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I. INTRODUCTION

Ferroelectric thin films are beginning to see wide-ranging applications, for example in multilayer capacitors, nonvolatile FeRAMs,1 and nanoelectromechanical, and in providing an understanding of how to include surface effects and depolarization fields caused by interface structures. It is well known that the properties of ferroelectric capacitors are highly influenced by the properties of the interface between the ferroelectrics and the electrodes. For example, the fatigue of ferroelectric capacitors is associated with the appearance of dead layers (or passive layers) near the electrodes and imperfect electrodes cannot fully screen the polarization of ferroelectrics,7,8 leading to a finite depolarization field in the ferroelectric film. However, the nanosize effects and temperature dependences of ferroelectric capacitor hysteresis, polarization switching, and dynamics of domain-wall motion remain poorly known. Experimentally, in situ observations are difficult. Theoretically, the long-range Coulomb interaction limits the size and time of molecular dynamics (MD) simulations, and it has been unclear how to include surface effects and depolarization fields caused by interface structures. In 1994, King-Smith and Vanderbilt studied the total-energy surface for zone-center distortions of perovskite-like ferroelectric oxides ABO3 (A is a monovalent or divalent cation and B is a penta- or tetravalent metal) at zero temperature using first-principles calculations with ultrasoft pseudopotentials and a plane-wave basis set.9 Starting from the full symmetric cubic perovskite structure, they define the displacements $v_a$ of atoms $\tau = (a, B, O_1, O_2, O_3)$ in the Cartesian directions $\alpha(x, y, z)$ along the $\Gamma_1$ soft-mode normalized direction vectors $E_\alpha$ as

$$v_a = \begin{pmatrix} u_A^a \\ u_B^a \\ v_{O_1}^a \\ v_{O_2}^a \\ v_{O_3}^a \\ v_{O_4}^a \\ v_{O_5}^a \\ v_{O_6}^a \\ v_{O_7}^a \\ v_{O_8}^a \\ v_{O_9}^a \\ v_{O_{10}}^a \\ v_{O_{11}}^a \\ v_{O_{12}}^a \\ v_{O_{13}}^a \\ v_{O_{14}}^a \\ v_{O_{15}}^a \end{pmatrix} = u_a \xi_\alpha = u_a \begin{pmatrix} \xi_A^a \\ \xi_B^a \\ \xi_{O_1}^a \\ \xi_{O_2}^a \\ \xi_{O_3}^a \\ \xi_{O_4}^a \\ \xi_{O_5}^a \\ \xi_{O_6}^a \\ \xi_{O_7}^a \\ \xi_{O_8}^a \\ \xi_{O_9}^a \\ \xi_{O_{10}}^a \\ \xi_{O_{11}}^a \\ \xi_{O_{12}}^a \\ \xi_{O_{13}}^a \\ \xi_{O_{14}}^a \\ \xi_{O_{15}}^a \end{pmatrix}, \quad (1)$$

with the scalar soft-mode amplitude $u_a$. Under the condition that the strain components $\eta_i (i = 1, \ldots, 6)$ minimize the total energy for each $u = (u_A, u_B, u_{O_1}, \ldots, u_{O_{15}})$, they expressed the total energy as

$$E^{tot} = E^0 + \kappa u^2 + \alpha' u^4 + \gamma' (u_A^2 + u_B^2 + u_{O_1}^2 + u_{O_2}^2 + u_{O_3}^2 + u_{O_4}^2), \quad (2)$$

where $u^2 = u_A^2 + u_B^2 + u_{O_1}^2 + u_{O_2}^2 + u_{O_3}^2 + u_{O_4}^2$, $E^0$ is the total energy for the cubic structure, $\kappa$ is half the eigenvalue of the soft mode, and $\alpha'$ and $\gamma'$ are the constants determined from coupling constants between atomic displacements and strains. Their expression properly describes the coupling of polar atomic displacement and strain degrees of freedom.

In 1994–1997, Zhong, Vanderbilt, and Rabe10,11 and Waghmare and Rabe12 expanded Eq. (2) from a mean-field framework to a local-mode framework, replacing $u$ with $u_k$, where the braces $\{ \}$ denote a set of $u$ in a simulation supercell, and

$$E^{tot} = V_{self}(u_k) + V_{pl}(u_k) + V_{short}(u_k) + V_{elas}(\eta_1, \ldots, \eta_6) + V_{int}(u_k, \eta_1, \ldots, \eta_6). \quad (3)$$

Here $V_{self}$, $V_{pl}$, $V_{short}$, $V_{elas}$, and $V_{int}$ are a local-mode self-energy, a long-range dipole-dipole interaction, a short-range interaction between soft modes, an elastic energy, and an interaction between the local modes and local strain, respectively. They employed Eq. (3) as an effective Hamiltonian for $u_k$ in the supercell, performed Monte Carlo simulations, and demonstrated the ability to describe the phase transitions of bulk ferroelectrics. The coarse-graining that reduces the 15-dimensional atomic displacement vector $v_{O_1}^a$ to a three-dimensional local soft-mode amplitude vector $u_A$ in each unit

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cell was shown to be a good approximation. However, the computation of $V^{\text{pl}}$ was still time-consuming, owing to the long-range Coulomb interaction, thus limiting system size and simulation time that could be handled in practical simulations.

In 2003, Waghmare, Cockayne, and Burton introduced a technique to decrease the computational time for $V^{\text{pl}}$ (or forces exerted on $\{u\}$),\textsuperscript{13} Direct calculation of the forces in real space requires a computational time proportional to $N^2$, i.e., $O(N^2)$, where $N$ is the supercell size ($N=L_x \times L_y \times L_z$). It decreases to $O(N \log N)$ if one calculates the forces in reciprocal space using fast Fourier transform (FFT) methods. This acceleration in computational speed enabled us to perform MD simulations on $\{u\}$ in a large supercell, and was applied to bulk relaxor ferroelectrics.\textsuperscript{13,14}

Here, we explain how the fast MD method for simulating a first-principles effective Hamiltonian can be applied to study ferroelectric thin-film capacitor structures with short-circuited electrodes or external electric fields. This new MD method can simulate perovskite-like ferroelectric thin-film capacitors with dead layers and consequent depolarization fields. The high speed of this MD method enables us to simulate a ferroelectric material for a realistic system size (up to 100 nm) and a realistic time span (>1 ns).

In Sec. II, we explain the formalism of the new MD simulation method for thin-film capacitors. Results of simulations of BaTiO$_3$ bulk and thin-film capacitors are shown in Sec. III. In Sec. III A, we confirm the reliability of our MD program by simulating thermal properties of bulk BaTiO$_3$. The advantage of this MD method compared to the Monte Carlo method is also discussed. In Sec. III B, we perform heating-up and cooling-down simulations for thin-film BaTiO$_3$ capacitors with perfect and imperfect electrodes. Thickness dependence of simulated striped domain structures in thin-film capacitors with imperfect electrodes are analyzed in detail. We have already reported some simulated results of thin-film capacitors of this section and determined thermal properties in Ref. 15 briefly. In Sec. III C, newly obtained simulated results of hysteresis loops of thin-film capacitors are reported. In Sec. IV, we summarize the paper.

We named our MD program FERAM and distribute it as free software through http://loto.sourceforge.net/feram/.

II. FORMALISM AND METHOD OF CALCULATION

A. Effective Hamiltonian

The effective Hamiltonian used in the present MD simulations is basically the same as that in Ref. 13. Here, we present the Hamiltonian with a notation similar to that in Ref. 11 as

$$H^{\text{eff}} = \frac{M^{\text{dipole}}}{2} \sum_{\alpha, \beta} \tilde{u}_\alpha^2(R) + \frac{M^*}{2} \sum_{\alpha} \tilde{w}_\alpha^2(R) + V^{\text{self}}(\{u\})$$

$$+ V^{\text{pl}}(\{u\}) + V^{\text{short}}(\{u\}) + V^{\text{homog}, \text{elas}}(\eta_1, \ldots, \eta_6)$$

$$+ V^{\text{homog}, \text{elas}}(\{w\}) + V^{\text{homog}, \text{elas}}(\{u\}, \{w\}) - Z \sum_R \mathcal{E} \cdot u(R),$$

where $u = u(R)$ and $w = w(R)$ are, respectively, the local soft-mode amplitude vector and the local acoustic displacement vector of the unit cell at $R$, the $\alpha$ component of $R$ runs over

$$R_\alpha = 0, a_0, 2a_0, \cdots (L_\alpha - 1)a_0,$$

$\eta_1, \ldots, \eta_6$ are the homogeneous strain components, and $M^{\text{dipole}}$ and $M^*$ are the effective masses for $u$ and $w$, respectively. Note that $u$ can also be considered as the optical displacement, in contrast to the acoustic displacement $w$, or the dipole moment $Z' u$, where $Z'$ is the Born effective charge associated with the soft mode. In the effective Hamiltonian (4), external electric field $\mathcal{E}$ is taken into account through its vector product with each dipole moment $Z' u$.

To determine the effective mass $M^{\text{dipole}}$, let $e^{\text{dipole}}_{ij}(k,i)$ be a mass-weighted ith eigenvector of the phonon dynamical matrix at wave vector $k$. Its eigenvalue is the corresponding phonon frequency. Moreover, let $d^{\text{dipole}}_{ij}(k,i) = e^{\text{dipole}}_{ij}(k,i) / \sqrt{M}$ be an atomic displacement vector, which is normalized as by adjusting the norm of $e(k,i)$. Here, $M^*$ is the mass of atom $\tau$. Generally, the effective mass of a phonon is $k$- and mode-dependent:

$$M^{k,i} = \sum_{\alpha, \tau} (d^{\alpha}_{\alpha}(k,i))^2 M^*.$$

However, as an approximation, we have to employ a unique effective mass for dipoles in the MD simulation. Thus using the steepest descent $\Gamma_{ij}$ soft-mode normalized direction vectors $\xi_{ij} = (0.20,0.76,-0.21,-0.21,-0.53)$ and $\xi_{ij} = \xi_{ij} = 0$ from Ref. 11, for BaTiO$_3$, we set $M^{\text{dipole}}$ as

$$M^{\text{dipole}} = \sum_{\tau} (\xi_{\tau})^2 M^* = 39.0 \text{ amu}. (7)$$

It should be mentioned that $\xi_{ij}$ is not equal to the $d^{\text{dipole}}_{ij}$ of the $\Gamma_{ij}$ soft mode of phonon, because $M^a$, $M^b$, and $M^c$ are not identical.

The local-mode self-energy $V^{\text{self}}(\{u\})$ is

$$V^{\text{self}}(\{u\}) = \sum_{i=1}^{N} (\kappa_{ij} u^2_i(R) + \alpha w^4_i(R) + \gamma u^2_i(R) u^2_i(R))$$

$$+ u^2_i(R) u^2_i(R) + u^2_i(R) u^2_i(R))),$$

where $u^2_i(R) = u^2_i(R) + u^2_i(R) + u^2_i(R)$.

The long-range dipole-dipole interaction $V^{\text{pl}}(\{u\})$ is

$$V^{\text{pl}}(\{u\}) = \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \sum_{\gamma=1}^{N} u_{\alpha\beta}(R) \Phi_{\alpha\beta}(R_{ij}) u_{\beta\gamma}(R_{ij}),$$

where

$$\Phi_{\alpha\beta}(R_{ij}) = \sum_{n} \frac{\delta_{\alpha\beta} - 3 (R_{ij} + n) G_{R_{ij} + n}}{|R_{ij} + n|^2},$$

$\epsilon$$_\infty$ is the optical dielectric constant (or refractive index squared), $\delta_{\alpha\beta}$ is the Kronecker delta, a hat indicates a unit vector, $n$ is the supercell lattice vector
\[ n_a = \cdots - 2L_a a_0, -L_a a_0, 0, L_a a_0, 2L_a a_0, \cdots, \] (11)

and \( a_0 \) is the equilibrium lattice constant. In Eq. (10), \( \Sigma' \) indicates that the summation does not include terms for which \( R_{ij} = n = 0 \).

We take account of short-range interactions between the optical displacements \( u(R) \) up to third nearest neighbor (3nn) as

\[ V_{\text{short}}(\{u\}) = \frac{1}{2} \sum_{a=1}^{N} \sum_{b} \sum_{j} u_{a}(R) J_{j,i,a,b} u_{b}(R), \]

where \( J_{j,i,a,b} \) is the short-range interaction matrix, which can be classified into 7 independent interaction parameters.\(^{11}\) \( J_{j,i,a,b} = \pm J_{j}(k=1, \cdots, 7) \).

In practice, \( J_{j} \) in Eq. (8), Eq. (9), and Eq. (12), in which \( u_a \) as quadratic, are gathered and calculated in reciprocal space as

\[ V_{\text{quad}}(\{u\}) = \frac{1}{2} \sum_{k} \sum_{a,b} \bar{u}_{a}(k) \Phi_{a,b}^{(0)}(k) \bar{u}_{b}(k), \]

where \( \bar{u}_{a}(k) = \sum_{R} u_{a}(R) \exp(-i k \cdot R), \)

of \( u_{a}(R), \) \( \Phi_{a,b}^{(0)}(k) \) is similarly the Fourier transform of the quadratic interaction matrix (which is only calculated once at the beginning of the simulation\(^{13}\)), and \( k \) is a reciprocal vector in the first Brillouin zone of the unit cell such as

\[ k_{a} = - \frac{2 \pi}{2L_{a} a_0}, \cdots, - \frac{1}{2} \frac{2 \pi}{L_{a} a_0}, 0, \frac{1}{2} \frac{2 \pi}{L_{a} a_0}, \cdots, \frac{1}{2} \frac{2 \pi}{2 a_0}. \]

The homogeneous elastic energy \( V_{\text{elas, homo}}(\eta_{1}, \cdots, \eta_{6}) \) is

\[ V_{\text{elas, homo}}(\eta_{1}, \cdots, \eta_{6}) = \frac{N}{2} B_{11}(\eta_{1}^2 + \eta_{2}^2 + \eta_{3}^2) \]

\[ + N B_{12}(\eta_{2} \eta_{3} + \eta_{1} \eta_{3} + \eta_{1} \eta_{2}) \]

\[ + \frac{N}{2} B_{44}(\eta_{1}^2 + \eta_{2}^2 + \eta_{3}^2), \]

where \( B_{11}, B_{12}, \) and \( B_{44} \) are the elastic constants expressed in energy unit \((B_{11}=a_{0}^{2} C_{11}, B_{12}=a_{0}^{2} C_{12}, \) and \( B_{44}=a_{0}^{2} C_{44})\).

The inhomogeneous elastic energy \( V_{\text{elas, inhomo}}(\{w\}) \) is also calculated in reciprocal space as

\[ V_{\text{elas, inhomo}}(\{w\}) = \frac{1}{2} \sum_{k} \sum_{a,b} \bar{w}_{a}(k) \Phi_{a,b}^{(0)}(k) \bar{w}_{b}(k), \]

For the force constant matrix \( \Phi_{a,b}^{(0)}(k) \), we employed the long-wavelength approximation. For instance, the diagonal part is

\[ \Phi_{a,a}^{(0)}(k) = \frac{1}{N}[k_{x}^{2} B_{11} + k_{y}^{2} B_{12} + k_{z}^{2} B_{44}], \]

and the off-diagonal part is

\[ \Phi_{a,b}^{(0)}(k) = \frac{1}{N}[k_{x} k_{y} B_{12} + k_{x} k_{z} B_{44}]. \]

The coupling between \( \{u\} \) and homogeneous strain is the same as that given in Ref. 9, i.e.,

\[ V_{\text{coup, homo}}(\{u\}, \eta_{1}, \cdots, \eta_{6}) = \frac{1}{2} \sum_{R} \sum_{i=0}^{6} \eta_{i} C_{i j}(u_{j}(R)), \]

Here, \( y_{1}(R) = u_{x}^{2}(R), y_{2}(R) = u_{y}^{2}(R), y_{3}(R) = u_{z}^{2}(R), y_{4}(R) = u_{x}(R) u_{y}(R), y_{5}(R) = u_{y}(R) u_{z}(R), \) and \( y_{6}(R) = u_{z}(R) u_{x}(R), \)

The coupling between \( \{u\} \) and inhomogeneous strain is also calculated in reciprocal space as

\[ V_{\text{coup, inhomo}}(\{u\}; \{w\}) = \frac{1}{2} \sum_{k} \sum_{a,i=1}^{6} \bar{w}_{a}(k) \bar{B}_{a}(k) \bar{y}_{i}(k), \]

where \( \bar{w}_{a}(k) \) and \( \bar{y}_{i}(k) \) are the Fourier transforms of \( w_{a}(R) \) and \( y_{i}(R) \), respectively. For the \( 3 \times 6 \) coupling matrix \( B(k) \), we again employed the long-wavelength approximation

\[ \bar{B}(k) = \frac{1}{N} \begin{pmatrix} k_{x} B_{1xx} & k_{y} B_{1xy} & k_{z} B_{1xz} & 0 & 2k_{x} B_{4yz} & 2k_{x} B_{4yz} \\ k_{x} B_{1xy} & k_{y} B_{1yy} & k_{z} B_{1zy} & 2k_{y} B_{4yz} & 0 & 2k_{x} B_{4yz} \\ k_{x} B_{1xz} & k_{y} B_{1zy} & k_{z} B_{1zz} & 2k_{z} B_{4yz} & 2k_{y} B_{4yz} & 0 \end{pmatrix}. \]

In the present MD simulations of BaTiO\(_{3}\), the parameters from Refs. 10 and 11, which are determined by first-principles calculations, are employed. As mentioned in Refs. 10 and 11, this parameter set leads to an underestimation of
the Curie temperature $T_C$. To correct this underestimation, we follow these references in applying a negative pressure of $p=-5.0$ GPa in all simulations.

### B. Molecular dynamics

MD simulations with the effective Hamiltonian of Eq. (4) are performed in the canonical ensemble using the Nosé-Poincaré thermostat. This simplectic thermostat is so efficient that we can set the time step to $\Delta t=2$ fs. In our present simulations, we thermalize the system for 40,000 time steps, after which we average the properties for 10,000 time steps.

In Fig. 1 we roughly illustrate how to calculate the forces exerted on $u_a(R)$ with $\tilde{F}_a(k)$ in Eq. (13) and how the time evolution is simulated. First, $u_a(R)$ is Fourier transformed to $\tilde{u}_a(k)$, the force $\tilde{F}_a(k)=\Sigma_{\beta} \tilde{F}_{a\beta}(k)\tilde{u}_{\beta}(k)$ is calculated in reciprocal space, and then the force in real space is obtained by the inverse Fourier transform (IFFT) of $\tilde{F}_a(k)$. In practice, updates of $u_a(R)$ and $\tilde{u}_a(k)$ are processed in the manner of the Nosé-Poincaré thermostat.

The homogeneous strain components $\eta_1, \cdots, \eta_6$ are determined by solving

$$\frac{\partial}{\partial \eta_i} \left[ V_{\text{elas,homo}}(\eta_1, \cdots, \eta_6) + V_{\text{coupl,homo}}(u_1, \eta_1, \cdots, \eta_6) \right] = 0$$

(24)

at each time step according to $\{u\}$ so that $\eta_1, \cdots, \eta_6$ minimize $V_{\text{elas,homo}}(\eta_1, \cdots, \eta_6) + V_{\text{coupl,homo}}(u_1, \eta_1, \cdots, \eta_6)$. While the local acoustic displacement $w_a(R)$ could be treated as dynamical variables using the effective mass $M_a^{\text{acoustic}}$, we have instead chosen to integrate out these variables in a manner similar to the treatment of the homogeneous strain. That is, $w_a(R)$ is determined so that $V_{\text{elas,inhom}}(w)$ becomes minimum at each time step according to $u_a(R)$. Technically, the minimization is performed by solving the linear set of equations

$$\tilde{G}_{\text{elas,inhom}}(k)\tilde{w}(k) + \tilde{B}(k)\tilde{y}(k) = 0$$

(25)

for each $k$ in reciprocal space.

### C. Ferroelectric thin films

If a ferroelectric thin film is placed in isolation in vacuum without electrodes as depicted in Fig. 2(a), its spontaneous polarization $P=(P_x, P_y, P_z)$, which is represented by a thick arrow in the figure, induces charges $\pm \sigma_{\text{ind}} = \pm P_z$ at both surfaces, and the induced charges cause a full depolarization field in the thin film, $E_0=-4\pi \sigma_{\text{ind}} = -4\pi P_z$. On the other hand, if the ferroelectric thin film is placed between short-circuited perfect electrodes as depicted in Fig. 2(b), the induced charges are fully canceled by free charges $\sigma_{\text{free}}$ arising at both surfaces of the electrodes. $E_0=-4\pi (\sigma_{\text{ind}} + \sigma_{\text{free}}) \kappa=0$. This geometric circumstance can be simulated with the doubly periodic supercell as depicted in Fig. 2(c), because the two electrodes act as two electrostatic mirrors facing each other, and the mirrors make oppositely charged infinite mirror images beyond the electrodes.

We can also introduce dead layers of thickness $d$ between the ferroelectric thin film and electrodes by constraining the local soft-mode amplitudes to vanish ($u=0$) in these layers, as illustrated in Fig. 2(d). With the dead layers, the infinite mirror images beyond the electrodes become more sparse than images of the without-dead-layer configuration. Consequently, the free charges arising at the electrode surfaces decrease to $\sigma_{\text{free}} = -\frac{d}{l} \sigma_{\text{ind}}$, where $l$ is the ferroelectric film thickness. This simulates short-circuited imperfect electrodes resulting in a depolarization field of

$$E_0 = -4\pi \frac{d}{l+d} P_z.$$  

(26)

We can also use a doubly periodic supercell with dead layers for this case. Physically, the depolarization field of Eq. (26) can arise either from the presence of a dead layer in the ferroelectric near the interface, or from imperfect screening at the metal electrode, or both. We can define an effective screening length for each of these effects, and we interpret...
the “dead-layer thickness” \(d\) of our model as corresponding to the sum of these two physical screening lengths. The screening length associated with the electrode interface appears in Eq. (16) of Ref. 7 and Eq. (1) of Ref. 8 and is discussed for the SrRuO\(_3\)/BaTiO\(_3\) interface in Refs. 17–19. Therefore, while the model does not explicitly incorporate information about the interface screening, this information is effectively included in the definition of the total screening length \(d\) in our model. Thus, for example, simulations at constant \(d\) for various film thicknesses can give the thickness dependence of the properties of capacitors with a certain interface structure.

In the present MD simulations, the local soft-mode amplitude vectors \(\mathbf{u}\) in dead layers are fixed to zero by the infinitely large mass. This infinitely large mass trick is congenial to the Nosé-Poincaré thermostat for maintaining the Nosé-Poincaré Hamiltonian at zero. Moreover, this treatment also has another advantage in that the short-range interactions between the surfaces of ferroelectric thin film and the electrodes are automatically truncated.

The depolarization field \(\mathcal{E}_d\) increases the total energy of the ferroelectric thin film by \(-P \cdot \mathcal{E}_d = 4\pi \varepsilon_0 \mu \mathcal{E}_d^2\). To avoid forming a depolarization field in ferroelectric thin films, it is known that the films often develop striped domain structures.\(^{20–23}\) The introduction of the striped domain structure can eliminate some part of the energy increase \(4\pi \varepsilon_0 \mu \mathcal{E}_d^2\), because \(P\) becomes zero on average. However, the striped domain structure involves an energy cost in the short-range interaction \(V^{\text{short}}(\mathbf{u})\), because it has domain boundaries between which \(\mathbf{u}\) has opposite direction \(\pm \mathbf{e}\). The shorter the wavelength \(\lambda\) of the striped domain structure, the weaker the depolarization field, but the higher the short-range interaction energy. The ground state of a ferroelectric thin film will be decided by a competition between the long-range dipole-dipole interactions which favor a short-period domain structure, and domain-wall energy that arises from the short-range interactions and favors a uniformly polarized structure or a longer-period striped structure. In some previous works,\(^{24–26}\) the imperfect screening was mimicked with a parameter. On the other hand, our method with doubly periodic boundary condition does not require any parameters, because the effect of imperfectness of electrodes is automatically and implicitly included in the long-range dipole-dipole interaction \(V^{\text{dip}}(\mathbf{u})\).

III. RESULTS AND DISCUSSION

A. Bulk BaTiO\(_3\)

We first check the reliability of our MD program by comparing results of our simulations for bulk BaTiO\(_3\) with earlier work based on the same effective Hamiltonian.\(^{10,11}\) We used a system size of \(L_x \times L_y \times L_z = 16 \times 16 \times 16\) and small temperature steps in heating-up (+5 K/step) and cooling-down.
 transition temperature $T_3$=408 K. Our estimates of $\eta_l=1$ and without (d=0) dead layers. This is accomplished through use of doubly periodic boundary conditions as explained earlier.

Both the heating-up and cooling-down simulations are started with an initial configuration of $\langle u_x\rangle=0$, $\langle u_y\rangle=0.07$ Å and $\langle u_z\rangle=0.02$ Å. In the cooling-down simulations, which start at a sufficiently high temperature, the initial configuration changes to an unpolared one ($\langle u_z\rangle=0$) during thermalization. We monitor the temperature dependence of $\langle u_x\rangle$ and $\langle u_y\rangle$ for thin films with thicknesses $l=15, 31, 127$, and 255 with dead layers $d=1$ and a thin film orthorhombic-to-rhombohedral phase transitions is evident in the width of the temperature intervals of hysteresis (see Fig. 3). We note that the ability to simulate time-dependent phenomena is one of the advantages of MD simulations compared to Monte Carlo simulations.

### B. BaTiO$_3$ Ferroelectric Thin-Film Capacitors

We now simulate and analyze the behavior of epitaxially grown films of BaTiO$_3$ on GdScO$_3$ substrates. In our simulations, we represent this with 1% in-plane biaxial compressive strain by maintaining the homogeneous strain $\eta_l=\eta_0=-0.01$ and $\eta_2=0$. In other words, we maintained the average lattice constants $a$ and $b$ at 0.99$a_0$ and angle $\gamma$ at 90°. We use supercell sizes of $L_x \times L_y \times L_z=32 \times 32 \times 2(l+d)$ and $40 \times 40 \times 2(l+d)$ and simulate ferroelectric layers of thickness $l$ sandwiched between two short-circuited electrodes with $(d=1)$ and without (d=0) dead layers. This is accomplished through use of doubly periodic boundary conditions as explained earlier.

Both the heating-up and cooling-down simulations are started with an initial configuration of $\langle u_x\rangle=0$, $\langle u_y\rangle=0.07$ Å and $\langle u_z\rangle=0.02$ Å. In the cooling-down simulations, which start at a sufficiently high temperature, the initial configuration changes to an unpolared one ($\langle u_z\rangle=0$) during thermalization. We monitor the temperature dependence of $\langle u_x\rangle$ and $\langle u_y\rangle$ for thin films with thicknesses $l=15, 31, 127$, and 255 with dead layers $d=1$ and a thin film

### TABLE I. Dependence of the wave vector k/2$\pi$ of the striped domain structure on thickness l in the thin-film BaTiO$_3$ capacitor with a dead layer (d=1).

<table>
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<tr>
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<td>${5/40 5/40 0}$</td>
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<td>${3/32 3/32 0}$</td>
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<tr>
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<td>255</td>
<td>${1/32 0/32 0}$</td>
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FIG. 7. (Color online) Calculated thickness $l$ dependence of wavelength $\lambda$ of striped domain structures in thin film BaTiO$_3$ capacitors with a dead layer (d=1). + marks are from $32 \times 32 \times 2(l+d)$ supercell calculations and × are those of $40 \times 40 \times 2(l+d)$ supercell. Data of $l<127$ are fitted with $\lambda=C\sqrt{l}$ (dotted line). $l=255$ data are omitted, because of their large supercell-size dependence.
with thickness \( l=32 \) without dead layers \((d=0)\) (see Fig. 4 and animations in the EPAPS).\(^{25}\) The behavior of the film with no dead layer is the same in heating and cooling simulations. In contrast, for the films with a dead layer \((d=1)\), the transition behavior exhibited by \((u_\perp)=0\) is rather different in heating and cooling simulations, although the temperature dependence of \((u_\perp)^2\) is almost the same in both kinds of simulations.

In the heating-up simulations, the discontinuity in \((u_\perp)\) as a function of temperature marks a transition from a ferroelectric state with almost uniform out-of-plane polarization [Fig. 5(a)] to one with a striped domain structure [Figs. 5(b) and 5(c)]. We find that this transition temperature, \(T_s(l,d=1)\), exhibits a strong dependence on size \( l \). We note that this transition is missing in the cooling-down simulations; just above \( T_s \), striped domain structures appear and the stripes remain and are frozen at \( T<T_s \). The temperature \( T_c(l,d=1)\) at which \( \sqrt{(u_\perp)^2}(T)\) exhibits a change in its slope marks another transition, namely from a striped domain phase to a paraelectric phase. \( T_c(l,d=1)\) depends relatively weakly on the film thickness. It should be mentioned that the results of heating-up simulations with a phase transition from the single domain state to the striped domain state at \( T_s \) below \( T_c \) agree with thermodynamical treatment of ferroelectric capacitors with dead layers by Chensky and Tarasenko.\(^{28}\)

For films with \( d=1 \), \( T_s \) is 150 and 210 K for \( l=15 \) and \( l=31 \), respectively, which is lower than the bulk transition temperature \( (T_c=320 \text{ K}) \). However, for \( d=1 \) films with \( l=127 \) and \( l=255 \), \( T_s \) is enhanced to 520 and 610 K, respectively, well above the bulk \( T_c \). In the infinite thickness limit \((l\rightarrow\infty)\), it appears that \( T_s(l,d=1)\) tends to the \( T_c \) of thick films with no dead layer \((d=0)\), since \( T_c \) is 650 K for \( l=32 \) and \( d=0 \). In the \( d=1 \) cases with \( l=127 \) and \( l=255 \), the effect arising from the depolarization field weakens significantly, and the enhancement of \( T_s \) results from the in-plane biaxial compressive strain. In the \( d=0 \) case with \( l=32 \), there is no depolarization field and enhancement of \( T_c \) by the in-plane biaxial compressive strain is effective even in very thin

FIG. 8. (Color online) Effective potential surfaces of BaTiO\(_3\) thin-film capacitors with short-circuited electrodes: (a)–(e), under 1% in-plane biaxial compressive strain arising from epitaxial constraints; (f)–(j), without epitaxial constraints (i.e., for “free” films). The thicknesses of ferroelectric films and dead layers are indicated in each panel with \( l \) and \( d \), respectively. Total energies as functions of \( u_\perp \) are compared among striped domain structures with wave vectors \( k \) parallel to \((110)\). \( k=(000)\) corresponds to the uniformly polarized structure. The zero of the energy scale is placed at the total energy of the nonpolarized \( u_\perp=0 \) structure. A negative pressure \( p=-5 \text{ GPa} \) is applied to correct the underestimation in \( T_c \).
films. We note that $\sqrt{\langle u_z^2 \rangle}$ and $\sqrt{\langle u_x^2 \rangle}$ are distinct even at high temperatures [see Fig. 4(e)], indicating that the symmetry of the paraelectric phase is broken by the presence of the epitaxial constraint and the electrodes, as well as correlations between local dipoles and their images.

For films with a dead layer ($d=1$), the striped domain structures appear in the cooling-down simulations at low temperatures for all values of thickness $l$ explored here [see Figs. 5(b) and 5(c)] for the case of $l=15$ with $d=1$, and Fig. 6 for various $l$.

As shown in Table I, the wave vector $k$ of the striped domain, at which $\vec{u}_z(k)$ has the largest amplitude $|[\vec{u}_z(k)]|$, exhibits an interesting dependence on thickness $l$. We have determined $k$ for two supercell sizes, $32 \times 32 \times 2(l+d)$ and $40 \times 40 \times 2(l+d)$, to identify supercell-size effects. It can be seen that, except for the data for $l=255$, $k$ tends to be along the in-plane $\{110\}$ direction, consistent with earlier reports. The simulated striped domain structure for $l=255$, which is parallel to the $\{100\}$ direction, is likely to be an artifact of the finite supercell size: $L_x \times L_y=32 \times 32$ or even $40 \times 40$ are too small to allow for the formation of a sufficiently thick $\{110\}$ striped domain. The wavelength $\lambda=2\pi/|k|$ of dominant periodicity of the domain pattern is shown as a function of thickness $l$ in Fig. 7, where it is evident that the thinner films have smaller $\lambda$ to avoid the stronger depolarization field [Eq. (26)]. The fitting shown in Fig. 7 suggests a square-root dependence on $l$ (the result for $l=255$ is not included in the fit). Extensive simulations at larger length scales would probably be required to clarify further the dependence of the domain period of these striped structures on film thickness and dead-layer thickness.

The stark difference in the behavior of $\langle u_z \rangle$ in heating-up and cooling-down simulations hints that the (almost) uniformly polarized state and the $\langle u_z \rangle=0$ striped domain states are frozen and thermal hopping between them may be almost impossible at low temperatures. To understand why both uniformly polarized and striped domain states are stable and
structure \([k=000]\). However, on the time scale of our simulations \((\sim 1 \text{ ns})\), even at \(T=255\) there is no hopping from the striped domain metastable state to the uniformly polarized ground state \([\text{Fig. } 4(d)]\). It can also be seen in Figs. 8(a)–8(e) that the magnitude of \(u_c\), which gives the minimum-energy ground state becomes larger, and the minimum energy gets deeper, as \(l\) increases, in good correspondence with the thickness dependence of \(T_c\). The trend of \(k\) with \(l\) also shows good agreement with the simulated values shown in Table 1. The simulated stability of the out-of-plane uniformly polarized states against the energetically lower striped-domain states in thinner \((l<127)\) films at low temperature seems to give support to the recent idea of elastic stabilization of a homogeneously polarized state in strained ultrathin films. 30 As shown in Fig. 9(a), the polarization switching in the epitaxially constrained film may be suppressed by the presence of a potential barrier that prevents hopping between the uniformly polarized and striped domain states. For \(l=127\) with \(d=1\), it is expected that a uniformly polarized film would evolve into a striped domain state, or vice versa, over a sufficiently long time at \(T<T_S\). However, the time scale of the evolution might be very much longer than the present simulation time scale \((\sim 1 \text{ ns})\). It might also be expected that, in the cooling-down simulations of films with \(l\geq 127\) and \(d=1\), the uniformly polarized state is obtained at \(T<T_S\). Instead, however, we find that stripes appear.

C. Hysteresis loops

A measurement of polarization typically involves use of a triangle-wave electric field for recording the ferroelectric hysteresis loops \([\text{inset of Fig. } 10]\). The hysteresis loops and coercive fields \(E_c\) depend on the amplitude \(E_0\) and frequency \(f\) of the applied fields. We simulate hysteresis here using triangle-wave with steps \((\text{width } \Delta t_{\text{step}} \text{ and height } \Delta E)\) as sketched schematically in Fig. 10. Thus, the frequency of the applied field in our simulations is \(f=\Delta E/4\Delta t_{\text{step}}E_0\). We used supercell sizes of \(L_x \times L_y \times L_z = 16 \times 16 \times 2(l+d)\) in simulations of hysteresis loops for ferroelectric thin-film capacitors with \(1\%\) in-plane biaxial compressive strain and without constraints of strain \((\text{namely, the “free” film})\) \([\text{see Fig. } 11]\). The temperature is maintained at 100 K through the simulations. For both the epitaxially constrained and “free” films, our simulations confirm that the imperfect screening of
the electrodes decreases the coercive field as the film thickness decreases, as described phenomenologically in Ref. 8. There is a large (order-of-magnitude) difference in the coercive field \( E_c \), between the epitaxially constrained film and the “free” film. This may be because the compressive strain arising from epitaxial constraints prevents the polarization switching, while the inclusion of inhomogeneous strain (i.e., acoustic displacements) eases the switching, as depicted in Fig. 9. The potential barriers themselves are lower in the “free” films than in the epitaxially constrained films (see Fig. 8). We note that hysteresis loops for “free” film capacitors with \( t=63 \) and \( t=127 \) are very similar to the experimentally observed hysteresis loops of a ferroelectric capacitor with damaged electrodes that have “steps” and “plateaus” during polarization switchings.1 This is because, in the “free” film capacitors with imperfect electrodes \( (d=1) \), the configuration with out-of-plane polarization is no longer the ground state. In fact, the ground state has a nonzero in-plane polarization. Thus, the dipoles \( Z^u(R) \) have large in-plane components \( Z^u_x(R) \) and \( Z^u_y(R) \) in the hysteresis-loop simulations (and experiments), as evident in the snapshot shown in Fig. 12.

Unfortunately, attempts to fit our results to the usually assumed Kay-Dunn scaling of the coercive field \( E_c \), with film thickness \( t \) of thicker films,31 were unsuccessful, as were attempts to emulate the relatively weak dependence of \( E_c \) on \( t \) for epitaxially grown high-quality ultrathin films.52-54 The experimentally observed values of coercive fields \( E_c \) for ultrathin BaTiO\(_3\) capacitors range from 200 to 500 kV/cm,32-34 while simulations of epitaxially constrained films largely overestimate \( E_c \), and those of “free” films slightly underestimate \( E_c \). This may be because the switching in real thin-film capacitors is a large-scale (>100 nm) phenomenon involving defect-mediated nucleation mainly at ferroelectric-electrode interfaces,18,31,35-38 as well as the possibility that the strain conditions may be intermediate between the cases of epitaxially constrained and “free” films. Such intermediate strain conditions may be achieved and will be simulated with MD in the future by introducing a mechanical boundary condition such as that presented in Ref. 30. In contrast to our case of ultrathin BaTiO\(_3\) capacitors, it is well known that for ultrathin PbZr\(_{x}\)Ti\(_{1-x}\)O\(_3\) (PZT) capacitors the coercive fields \( E_c \) increase with decreasing film thickness \( t \), and there is an argument whether this strong increase in \( E_c \) is coming from compressive substrate-induced lattice strain16 or not.20 Constructing a first-principles Hamiltonian for PZT and simulations with this MD method will help us to understand this difference between BaTiO\(_3\) and PZT.

IV. SUMMARY

We have developed a robust and highly efficient molecular dynamics scheme, based on a first-principles effective Hamiltonian formulation, for simulating the behavior of the polarization in perovskitelike ferroelectrics. We have applied this approach to study BaTiO\(_3\) ferroelectric thin-film capacitors, with special attention to the dependence on film thickness and choice of electric boundary conditions. We find that striped domain structures tend to form on cooling-down simulations when a ferroelectric dead layer is present near the electrodes, and we study the dependence of the domain period on the conditions of formation. We also study the hysteresis loops for capacitor structures, both with and without such dead layers, and we find dramatic differences in the hysteretic behavior for the cases of elastically constrained or “free” films. Our MD simulator FERAM will be a powerful tool for further investigations of the physical properties of ferroelectric nanostructures that are relevant for a variety of potential device applications.

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See EPAPS Document No. E-PRBMD-78-004830 for animations of the cooling-down and heating-up simulations. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

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