Three-Dimensional Phase Field Simulations of Hysteresis and Butterfly Loops by the Finite Volume Method *

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Three-dimensional simulations of ferroelectric hysteresis and butterfly loops are carried out based on solving the time dependent Ginzburg–Landau equations using a finite volume method. The influence of externally mechanical loadings with a tensile strain and a compressive strain on the hysteresis and butterfly loops is studied numerically. Different from the traditional finite element and finite difference methods, the finite volume method is applicable to simulate the ferroelectric phase transitions and properties of ferroelectric materials even for more realistic and physical problems.

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Ferroelectricity is one of the fastest growing fields during the past several decades. Interest in this field is attributable to the increasing numbers of practical applications in micro-electromechanical systems, microwave devices, and memory devices. It could be used as pressure sensors, ultrasonic motors, transducers and varied actuators. However, the constitutive relation of ferroelectric materials possesses so strong and complex nonlinear properties that it is difficult to accurately model the hysteresis and butterfly loops.

Thermodynamic phenomenological theory is very convenient and more accurate to describe structural phase transitions compared with other theories, such as first principles calculations or ab initio molecular dynamics simulations. Landau theory has played an important role in understanding the thermodynamics of ferroelectric phase transitions . If the free energy of a ferroelectric system can be constructed accurately, the phenomenological theory can even be used to describe complicated phase transitions that involve the change of unit cell .

Recently there have been a number of two-dimensional computer simulations of domain structure evolution during ferroelectric transitions by using the time-dependent Ginzburg–Landau (TDGL) equation field model . However, most of these previous studies were performed in two dimensions and using the same method: a complicated semi-implicit Fourier-spectral method . Undoubtedly a more realistic 3D simulation and a more flexible method are desirable. In this Letter, a three-dimensional simulation of ferroelectric hysteresis and butterfly loops have been carried out based on solving the time-dependent Ginzburg–Landau equations by using a finite volume method (FVM). The influence of externally mechanical loadings with a tensile strain and a compressive strain on the hysteresis and butterfly loops has also been investigated.

Ferroelectric material possesses spontaneous polarization, spontaneous strain and a domain structure below its Curie–Weiss temperature. In phase field simulations, the temporal evolution of the domain structure is governed by the time-dependent Ginzburg–Landau equation as follows:

\[
\frac{\partial \mathbf{P}(\mathbf{r},t)}{\partial t} = -L \frac{\delta F}{\delta \mathbf{P}(\mathbf{r},t)}, \quad (i = 1, 2, 3)
\]

where \( \mathbf{P} \) is used as the order parameters, \( L \) denotes the kinetic coefficient, \( F \) is the total free energy of the system, and \( \frac{\delta F}{\delta \mathbf{P}(\mathbf{r},t)} \) represents the thermodynamic driving force for the spatial and temporal evolution of the simulated system. In the present study, we adopt Eq. (1) to simulate the spontaneous polarization in a ferroelectric under an applied electrical and mechanical field. The total free energy includes the bulk free energy, the domain wall energy or the polarization gradient energy, the elastic strain energy and the electric energy. The total free energy of the system is given by

\[
F = \int [f_L + f_G + f_E + f_{\text{elec}}]dV.
\]

Bismuth titanate (Bi\(_4\)Ti\(_3\)O\(_{12}\)) is chosen as the system to conduct the simulation. We employ a six-order polynomial for the Landau bulk-free energy density:

\[
f_L(P_1) = \alpha_1(P_1^2 + P_2^2) + \alpha_3P_2^2 + \alpha_{11}(P_1^2 + P_2^2) + \alpha_{33}P_3^4 + \alpha_{31}P_1P_2^2 + \alpha_{32}P_2P_3^2 + \alpha_{12}P_1^2P_2^2 + \alpha_{111}(P_1^4 + P_2^4) + \alpha_{333}P_3^6,
\]

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where $\alpha_1$, $\alpha_3$, $\alpha_{11}$, $\alpha_{13}$, $\alpha_{12}$, $\alpha_{111}$, $\alpha_{333}$ are constant coefficients. For simplicity, the lowest order of the gradient energy density is used here, which takes the form as follows:

\[
\begin{align*}
  f_{G}(P_{i,j}) &= \frac{1}{2} G_{ijkl} P_{i,k} P_{j,l} \\
  &= \frac{1}{2} G_{11} (P_{11}^2 + P_{12}^2 + P_{13}^2 + P_{21}^2 + P_{22}^2 + P_{23}^2 + P_{31}^2 + P_{32}^2 + P_{33}^2),
\end{align*}
\]

where $G_{ij}$ denotes the gradient coefficients. The comma in the subscripts denotes the spatial differentiation. When an external electric field $E_i$ is applied, the additional electrical energy density is given by

\[
f_{\text{elec}}(P_i, E_i) = -E_i P_i = -(E_1 P_1 + E_2 P_2 + E_3 P_3),
\]

Regarding the symmetry of the polarized state, the extension of the elastic energy density takes the following form

\[
f_{E}(P_i, \epsilon_{ij}) = \frac{1}{2} e_{ijkl} (\epsilon_{ij} - \epsilon_{ij}^0) (\epsilon_{kl} - \epsilon_{kl}^0), \tag{6}
\]

where $e_{ijkl}$ is the elastic stiffness tensor, $\epsilon_{ij}$ is the total strain, $\epsilon_{ij}^0$ is the electrostrictive strain caused by the polarization field and it could be expressed as $\epsilon_{ij}^0 = Q_{ijkl} P_k P_l$. The spontaneous strains are linked to the spontaneous polarization components in ferroelectric material in the following form

\[
\begin{align*}
  \epsilon_{11}^0 &= Q_{11} P_{11}^2 + Q_{12} P_{12}^2 + Q_{13} P_{13}^2, \tag{7} \\
  \epsilon_{22}^0 &= Q_{12} P_{12}^2 + Q_{21} P_{21}^2 + Q_{23} P_{23}^2, \tag{8} \\
  \epsilon_{33}^0 &= Q_{13} P_{13}^2 + Q_{23} P_{23}^2 + Q_{33} P_{33}^2, \tag{9} \\
  \epsilon_{12}^0 &= \epsilon_{21}^0 = Q_{44} P_1 P_2, \tag{10} \\
  \epsilon_{13}^0 &= \epsilon_{23}^0 = Q_{44} P_2 P_3, \tag{11} \\
  \epsilon_{31}^0 &= \epsilon_{33}^0 = Q_{66} P_1 P_3, \tag{12}
\end{align*}
\]

where $Q_{ij}$ stands for the electrostrictive constants. The elastic strain energy density can be divided into three parts: the pure elastic energy density, the electrostrictive energy density from the pure polarization and the electrostrictive coupling energy density,

\[
\begin{align*}
  f_{E1}(\epsilon_{ij}) &= \frac{1}{2} C_{11} (\epsilon_{11}^2 + \epsilon_{22}^2 + \epsilon_{33}^2) + 2C_{44} (\epsilon_{22}^2 + \epsilon_{33}^2) \\
  &= + 2C_{66} \epsilon_{12}^2 + \frac{1}{2} C_{33} \epsilon_{23}^2 + C_{12} \epsilon_{11} \epsilon_{12}, \\
  f_{E2}(P_i) &= \beta_{11} P_{11}^2 + \beta_{12} P_{12}^2 + \beta_{31} P_{31}^2 + \beta_{13} P_{13}^2 + \beta_{21} P_{21}^2 + \beta_{23} P_{23}^2 \tag{13} \\
  f_{E3}(\epsilon_{ij}, P_i) &= - (q_{11} \epsilon_{11} + q_{12} \epsilon_{22} + q_{13} \epsilon_{33}) P_{11}^2 \\
  &= - (q_{12} \epsilon_{11} + q_{22} \epsilon_{22} + q_{33} \epsilon_{33}) P_{22}^2 \\
  &= - (q_{13} \epsilon_{11} + q_{32} \epsilon_{22} + q_{33} \epsilon_{33}) P_{33}^2 \\
  &= - q_{44} \epsilon_{12} P_{21} - q_{55} \epsilon_{13} P_{13} P_{31} \\
  &= q_{66} \epsilon_{23} P_{12}, \tag{15}
\end{align*}
\]

where $C_{ij}$ in the energy function should be the components of the elastic stiffness tensor, the coefficients $\beta_{ij}$ are called the electrostrictive constants for constant stress. The coefficients $\beta_{ij}$ and $q_{ij}$ can be written as

\[
\begin{align*}
  \beta_{11} &= \frac{1}{2} C_{11} (Q_{11}^2 + Q_{22}^2) + \frac{1}{2} C_{33} Q_{33}^2 + C_{12} Q_{11} Q_{12}, \\
  \beta_{33} &= C_{11} Q_{11}^2 + C_{22} Q_{22}^2 + \frac{1}{2} C_{33} Q_{33}^2 + 2C_{13} Q_{13} Q_{33}, \tag{16} \\
  \beta_{12} &= C_{12} Q_{11}^2 + 2C_{11} Q_{11} Q_{12} + C_{12} Q_{12}^2 + 2C_{13} Q_{13} Q_{12} + 2C_{14} Q_{14}^2, \\
  \beta_{13} &= C_{11} Q_{11} Q_{13} + C_{12} Q_{11} Q_{12} + C_{13} Q_{13} Q_{13} + 2C_{14} Q_{14} Q_{13} + 2C_{15} Q_{15}^2, \\
  \beta_{23} &= C_{11} Q_{11} Q_{13} + C_{12} Q_{11} Q_{12} + C_{13} Q_{13} Q_{13} + 2C_{14} Q_{14} Q_{13} + 2C_{15} Q_{15}^2, \tag{17} \\
  q_{11} &= q_{22} = C_{11} Q_{11} + C_{12} Q_{12} + C_{13} Q_{13}, \\
  q_{21} &= q_{21} = C_{12} Q_{11} + C_{12} Q_{12} + C_{13} Q_{13}, \\
  q_{13} &= q_{23} = C_{13} Q_{11} + C_{13} Q_{12} + C_{13} Q_{13}, \\
  q_{31} &= q_{32} = C_{13} Q_{11} + C_{12} Q_{13} + C_{13} Q_{33}, \\
  q_{33} &= 2C_{13} Q_{13} + 3C_{33} Q_{33}, \\
  q_{44} &= 4C_{44} Q_{44}, \\
  q_{66} &= 4C_{44} Q_{66}, \tag{20}
\end{align*}
\]

For convenience of simulations, the set of normalized and dimensionless variables, as described in the literature,[16] is employed in the present simulation. In the present study, the TDGL equations are solved by using the cell centered finite volume method.[20] The finite volume method requires dividing the domain of our problem into non-overlapping cells and is capable of numerically solving the canonical governing equation like

\[
\frac{\partial [\rho \psi]}{\partial t} = \nabla \cdot (\mathbf{u} \psi) + [\nabla \cdot (\Gamma \nabla)]_n \psi + S, \quad (n = 1, 2, 3, \ldots) \tag{29}
\]

where $\rho$, $\mathbf{u}$ and $\Gamma$ can be arbitrary functions of any variable of the system, which represent coefficients in the transient, convection and diffusion terms. Equation (29) is a general conservation equation to describe the dynamic process of many physical systems in physics, such as the diffusion process, steady-state convection-diffusion process, and the solidification and dendritic growth of nuclei. It is very important to correlate the variables into the authentic system. For instance, the variables $\rho$ and $\mathbf{u}$ are chosen as the density and velocity of the medium when the equation...
Landau–Devonshire theory, the remanent strain of a ferroelectric film is approximately
proportional to the squared remanent polarization, it could be written as \( \varepsilon_{33}^t = Q_{13} P_3^t \), where \( Q_{13} \) is the electrostriction coefficient. The influences of compressive and tensile mechanical loading on the butterfly and hysteresis loops are simulated. Furthermore, the case with no mechanical loading is also simulated for comparison. The normalized electric field along the \( z \) direction is applied. Figure 2 shows the influence of mechanical loading on (Fig. 2(a)) hysteresis loops and (Fig. 2(b)) butterfly loops. It was found that the influences of compressive and tensile mechanical loading on the hysteresis loop are similar to the result in Fig. 1, while the butterfly loop shows an asymmetric style. The asymmetric behavior could also be observed in other simulated works.\(^{[16,25]}\) It might be attributed to the insufficient number of domains used in the present study.

Temporal evolution of morphological patterns without mechanical loading is shown in Fig. 3. The evolution starts from a noised field, which is represented by a polarization vector field, in which each unit is in a random direction, with a small magnitude. Figure 3 illustrates the polarizations after 50, 100, 200, 300, 400, 500, 600 and 1000 time steps of evolution. It can be seen that the polarization begins to grow and the rudiment of the domain structure starts to appear. After 50 time steps, the polarization is still in nucleation state. After about 100 time steps, the nucleation stage is completed and all four possible domain orientations are present. The evolution of the simulated domain structure shows that the formation of a stable domain experienced three classical processes, i.e., nucleation, growing accompanied with wall moving and the stable stage. These results are consistent with those of the simulations.\(^{[20,27]}\)

In conclusion, the phase field method is a powerful computational method for predicting the ferroelectric properties of processes in numerous materials. Indeed, many research grade computer codes have been developed by academics in separate universities. However, the fact is that there are no portable software tools with user friendly interfaces and the capacity to scale to industrial problems. This work shows that the finite volume method is one of the main computational tools to phase field simulations, which is a robust and cheap method even for more realistic and physical problems. The results in this work are helpful for investigating the macroscopic response of ferroelectrics subjected to external applied electric and mechanical loadings and can give insight into the understanding of domain structures and macroscopic ferroelectrics.

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