Computer Simulation of the Dynamics of 180° Ferroelectric Domains

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A computer simulation technique based on the time-dependent Ginzburg–Landau (TDGL) equations formulated in the reciprocal space was proposed for modeling the dynamics of ferroelectric domain formation and domain-wall motion. The temporal evolution of domain structures with 180° domain walls in a quenched paraelectric phase was studied. Both the long-range electric dipole–dipole interaction energy and the total domain wall energy for any arbitrary distributions of ferroelectric domains were evaluated in the reciprocal space. The effect of free surfaces on the polarization and domain morphologies was discussed. The domain-wall motion under an electric field was investigated.

I. Introduction

A UNIQUE feature common to all ferroelectric ceramics is the formation of domain structures when a paraelectric phase is cooled below the ferroelectric transition temperature. The properties of a ferroelectric material can often be manipulated by controlling its domain structure.[1] The simplest type of ferroelectric domain structure consists of two neighboring domains with opposite alignment of electric dipoles and separated by 180° domain walls. Examples include lead germanate ($Pb_5Ge_3O_{11}$) and gadolinium molybdate ($Gd_2(MoO_4)_3$).[2] It is quite well known that 180° domains arise because of the competition between the depolarization energy and domain-wall energy.[3] The domain-wall energy prefers a single domain whereas the depolarization energy prefers an opposite alignment of dipoles. The more complex type is the 90° domain-wall configuration in which the polarization direction changes 90° from one domain to another across the wall. This is very common in ABO_3 ferroelectric ceramics in which the ferroelectric transition is accompanied by a cubic-to-tetragonal structural transformation resulting in three different orientation variants. The elastic accommodation between different tetragonal variants leads to the formation of 90° domain structures. For example, in $BaTiO_3$ ceramics, both 90° and 180° domains exist.

The static equilibrium polarization profiles across both 90° and 180° domain walls have been quite extensively studied using Ginzburg–Landau phenomenological theories.[3-5] However, the dynamics of domain pattern formation of a quenched paraelectric phase and the evolution dynamics of a domain structure under applied fields are less well understood. It should be emphasized that it is the domain dynamics, not the statics, that is more relevant to the applications of ferroelectric materials. In this short communication, a simple computer simulation technique based on the time-dependent Ginzburg–Landau (TDGL) equations[6] is proposed for studying the dynamics of ferroelectric domains. As a first attempt, we apply it to the

simple case of 180° domains in an idealized two-dimensional system.

The order parameter for describing the proper paraelectric-to-ferroelectric phase transition is the polarization vector, $\vec{P}$. In order to describe the dynamics of ferroelectric domains, we have to consider inhomogeneous systems in which the polarization is not only time-dependent but also space-dependent. The domain dynamics is then characterized by the temporal and spatial evolution of the local polarization profile:[6]

$$\frac{dP_i(\vec{r},t)}{dt} = -L\frac{\delta F}{\delta P_i(\vec{r},t)} + \eta(\vec{r},t) \tag{1}$$

where $P_i(\vec{r},t)$ is the ith component of the local polarization vector at position $\vec{r}$ and time t, L is the relaxation coefficient characterizing the mobility of ferroelectric domain walls, F is the total free energy which is a functional of the local polarization, and $\eta(\vec{r},t)$ is the random thermal noise term with average value 0 and with variance k_BTL.

For an inhomogeneous state with domain walls, the total free energy of the system, F, is given by

$$F = F_L + F_G + F_{ele} + F_{ap} \tag{2}$$

where the first term is the Landau bulk free energy of the system. For simplicity, we assume that the polarization direction is along the x direction and consider a second-order ferroelectric transition in which the local free energy density, $f(\vec{P})$, for the ferroelectric phase can be expanded using only the second- and fourth-order terms with respect to the paraelectric phase, i.e.,

$$f(\vec{P}) = \frac{1}{2}\alpha(T - T_c)P_x^2 + \frac{1}{4}\beta P_x^4 \tag{3}$$

where α and β are phenomenological coefficients, T is the temperature, and T_c is the ferroelectric transition temperature. Therefore, the total Landau free energy is given by

$$F_L = F_0 + \int_v \left[\frac{1}{2}\alpha(T - T_c)P_x^2(\vec{r},t) + \frac{1}{4}\beta P_x^4(\vec{r},t)\right] d^3r \tag{4}$$

where F_0 is the free energy of the paraelectric phase.

The second term in Eq. (2) is the gradient energy or Ginzburg energy associated with the domain wall:

$$F_G = \int_v \frac{\kappa}{2}[\nabla P_x(\vec{r},t)]^2 \, d^3r \tag{5}$$

where κ is the gradient energy coefficient.

The third term in Eq. (2) is the depolarization energy arising from the electrical dipole–dipole interactions. Since the electrical dipole–dipole interaction is a long-range interaction just like elastic dipole–dipole and magnetic dipole–dipole interactions, it is nonlocal and has to be calculated separately from the local Landau free energy and the Ginzburg gradient energy,[7]

$$E_{ele} = \frac{1}{2}\int\int\left[\frac{1}{|\vec{r}_i - \vec{r}_j|^3} - \frac{3(x_i - x_j)^2}{|\vec{r}_i - \vec{r}_j|^5}\right] \cdot P_x(\vec{r}_i,t) \, P_x(\vec{r}_j,t) \, d^3r_i \, d^3r_j \tag{6}$$
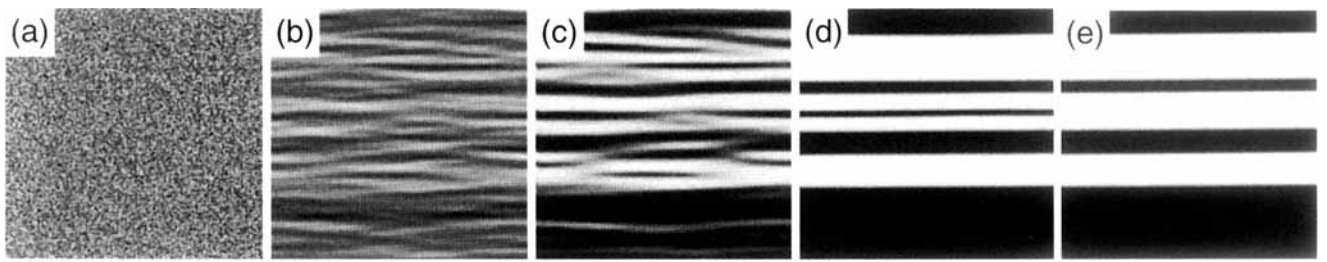
Fig. 1. Temporal evolution of ferroelectric domain structures for a paraelectric phase aged below the ferroelectric transition temperature; $\alpha(T - T_c) = -1.0$, $\beta = 1.0$, $\Delta t = 0.01$, $\eta = 0.0$; (a) $t^* = 0$, (b) $t^* = 0.04$, (c) $t^* = 0.09$, (d) $t^* = 0.39$, (e) $t^* = 2.00$.
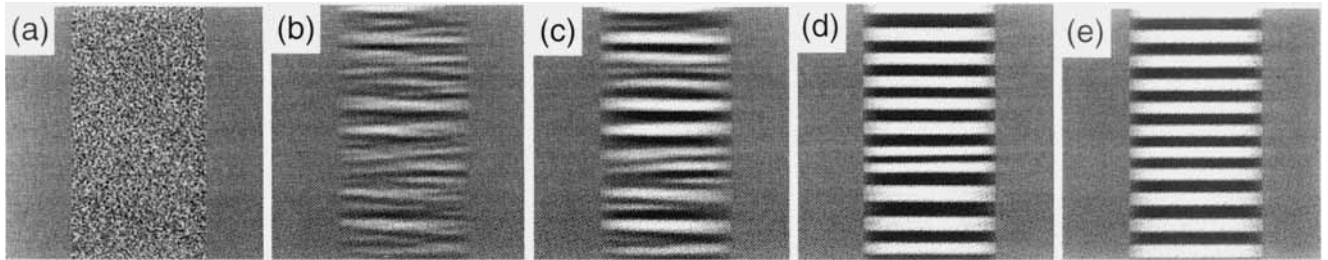

Fig. 2. Temporal evolution of ferroelectric domain structures for a paraelectric thin film aged below the ferroelectric transition temperature; $\alpha(T - T_c) = -1.0$, $\beta = 1.0$, $\Delta t = 0.01$, $\eta = 0.0$; (a) $t^* = 0$, (b) $t^* = 0.04$, (c) $t^* = 0.09$, (d) $t^* = 0.39$, (e) $t^* = 2.00$.

According to Khachaturyan,[8] the double summation in real space in Eq. (6) can be converted to a single summation in reciprocal space,

$$E_{ele} = 2\pi \int \frac{d^3k}{(2\pi)^3} n_x^2 |P_x(\vec{k},t)|^2 \tag{7}$$

where $P_x(\vec{k},t)$ is the Fourier transform of $P_x(\vec{r},t)$ and n_x is equal to k_x/k.

The fourth term in Eq. (2) is the interaction energy of the system with the applied electric field:

$$F_{ap} = -\int_v \vec{E}_a \cdot \vec{P}(\vec{r},t) \, d^3r \tag{8}$$

where $\vec{E}_a$ is the applied electric field.

Substituting Eqs. (2), (4), (5), (7), and (8) into Eq. (1) and Fourier transforming Eq. (1) into the reciprocal space, we have

$$\frac{dP_x(\vec{k}),t}{dt} = -L\{[\alpha(T + T_c) + \kappa k^2 + 4\pi n_x^2]P_x(\vec{k},t)$$

$$+ \beta[P_x^3(\vec{r},t)]_{\vec{k}} - E_{ax}\} + \eta(\vec{k},t) \tag{9}$$

where E_{ax} is the x component of the applied electrical field.

In order to solve the kinetic equation (9) numerically in a computer, we have to discretize it both spatially and temporally. In the computer simulations presented below, the equation is discretized using 256 by 256 reciprocal grid points (or real space grid points). The time derivative of the Fourier components of local polarization at a given reciprocal lattice point is approximated by the explicit Euler technique.

$$P_x(\vec{k},t+\Delta t) = P_x(\vec{k},t) + \frac{dP_x(\vec{k},t)}{dt}\Delta t \tag{10}$$

The temporal evolution of $P_x(\vec{r},t)$, and thus the dynamics of domain evolution, is obtained by Fourier transforming $P_x(\vec{k},t)$ back to the real space at each time step. The initial condition is generated by assigning zero value of local polarization everywhere plus very small random fluctuations. This initial polarization distribution corresponds to the paraelectric state in which the polarization is zero everywhere.

Figure 1 shows the temporal evolution of domain structures when the paraelectric phase is quenched to a temperature below
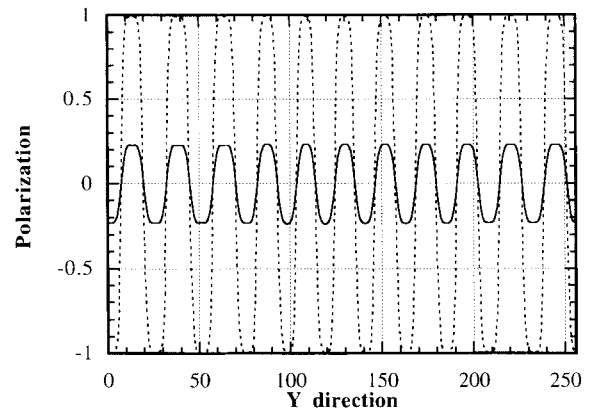

Fig. 3. Variation of local polarization along the y direction. The solid line represents the polarization near the surface; the dotted line represents the polarization in the center of the film.
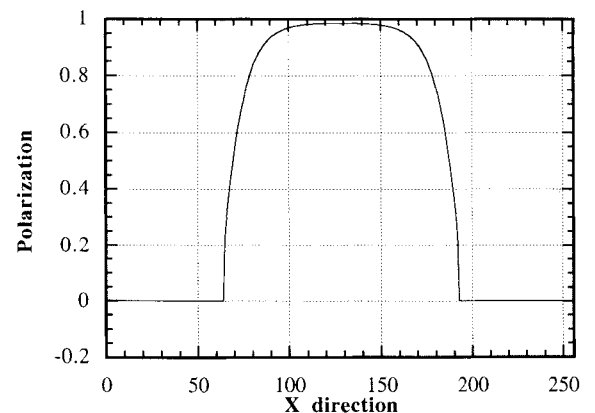

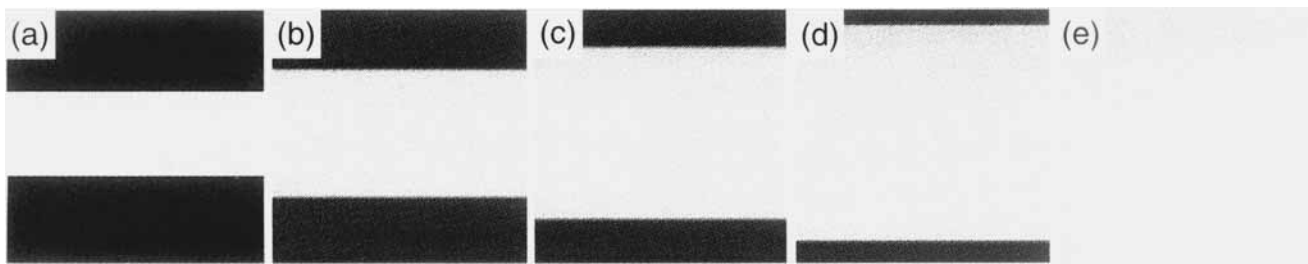**Fig. 4.** Variation of local polarization along x direction.

Fig. 5. 180° ferroelectric domain wall motion under an applied electric field; $\alpha(T - T_c) = -1.0$, $\beta = 1.0$, $\Delta t = 0.01$, $E = 0.30$, $\eta = 0.0$; (a) $t^* = 0$, (b) $t^* = 0.03$, (c) $t^* = 0.06$, (d) $t^* = 0.09$, (e) $t^* = 0.14$.
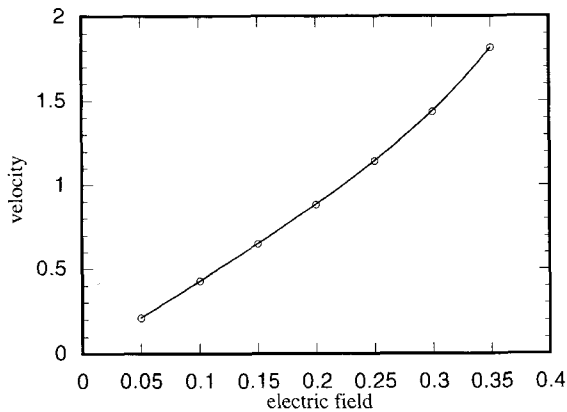

Fig. 6. Speed of domain wall motion as a function of the magnitude of applied electric field.

the ferroelectric transition temperature. Periodic boundary conditions are assumed along both x and y directions. The "gray levels" represent different magnitudes of the polarization. A completely black "gray level" indicates that the polarization is equal to -1 and the polarization direction is along the negative x direction; a completely white "gray level" means that the polarization is equal to 1 and the polarization direction is along the positive x direction. The time is measured in terms of the reduced unit, $t^* = Lt$, where t is real time and L is the kinetic coefficient. It can be clearly seen from Figs. 1(a) and (b) that the initial stage during aging of a paraelectric phase below the ferroelectric transition temperature is the nucleation and growth of ferroelectric domains. As the aging time increases, the ferroelectric domains coarsen and at the same time gradually align along the x direction forming the 180° domain structure (Figs. 1(c), (d), and (f)). The final equilibrium domain structure consists of two domains with the same size and separated by a 180° domain boundary. In this case, the periodicity of the domain structure is fixed by the periodicity of the computation cell in real space.

In real materials, the size of a crystal is always finite and the periodicity of the 180° domain structure depends on the crystal size. Moreover, it is expected that the magnitude of polarization in the bulk will be different from that in the surface regions. Our computer simulation shows that this is indeed the case. For example, in Fig. 2, two surfaces along the y directions are introduced, simulating a thin film situation. The temporal evolution of the domain structure is similar to the case with periodic boundary conditions. However, in this case, the periodicity of the 180° domain structure is not fixed by the computational cell size, but is dependent on the thickness of the film. Figure 3 shows the polarization along the y direction near the surface and in the middle of the film. As expected, the polarization varies nearly periodically along the y direction. The variation of the polarization along the x direction is shown in Fig. 4. From both Fig. 3 and Fig. 4, it can be seen that the polarization in the middle of the film is much larger than that near the surface. We also observed that as the film thickness decreases, the domain

width decreases. In the extreme case, as the film thickness is reduced to a few times (it is about 4.0 times in this particular model) the thickness of the domain boundary, no ferroelectric domains are formed; i.e., there is no ferroelectric phase transition. The reason is that the increase in free energy due to domain boundary formation is larger than the decrease in bulk free energy due to ferroelectric domain formation.

As is well known, the polarization direction can be switched by applying an electric field. An example of domain-wall motion is shown in Fig. 5 for the case in which an electric field is applied to a domain structure consisting of two domains separated by a 180° domain boundary. It is demonstrated that the 180° domain wall moves along its normal until a single domain is formed (Fig. 5(e)). The speed of domain wall motion is shown to depend on the magnitude of the applied electric field (Fig. 6). In the local electric field regime, the dependence is shown to be linear. However, as the electric field increases, the dependence deviates significantly from the linearity. It is emphasized the case discussed here involves a static electric field. If a time-dependent electric field, e.g., a sinusoidal time-dependent electric field, is applied, the domain dynamics are expected to depend on the domain wall mobility characterized by the coefficient L in the kinetic equation and the frequency of an applied electric field, v. For example, if $v \ll L$, the domain switching is expected to be similar to the case of a static electric field. On the other hand, if $v \gg L$, no switching is expected.

In summary, a computer simulation technique based on the TDGL equations has been proposed for modeling the temporal evolution of ferroelectric domain structures. It is demonstrated by using a two-dimensional example that this technique can be employed to model the nucleation and growth of 180° ferroelectric domains in a quenched paraelectric phase, as well as the kinetics of domain coarsening and the domain switching under an applied electric field. With the addition of the elastic energy contribution to the total free energy, this model can also be used to model the dynamics of both 90° and 180° domains with and without applied electric or stress fields.

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