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Energy functions and basic equations for ferroelectrics

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Abstract Energy functions (or characteristic functions) and basic equations for ferroelectrics in use today are given by those for ordinary dielectrics in the physical and mechanical communications. Based on these basic equations and energy functions, the finite element computation of the nonlinear behavior of the ferroelectrics has been carried out by several research groups. However, it is difficult to process the finite element computation further after domain switching, and the computation results are remarkably deviating from the experimental results. For the crack problem, the iterative solution of the finite element calculation could not converge and the solutions for fields near the crack tip oscillate. In order to finish the calculation smoothly, the finite element formulation should be modified to neglect the equivalent nodal load produced by spontaneous polarization gradient. Meanwhile, certain energy functions for ferroelectrics in use today are not compatible with the constitutive equations of ferroelectrics and need to be modified. This paper proposes a set of new formulae of the energy functions for ferroelectrics. With regard to the new formulae of the energy functions, the new basic equations for ferroelectrics are derived and can reasonably explain the question in the current finite element analysis for ferroelectrics.

1 Introduction

Ferroelectric materials such as barium titanate, lead titanate and PZT are ionic crystalline solids that are spontaneously polarized below their Curie temperatures. The spontaneous polarization can take any one of several possible orientations. Moreover, the spontaneous polarization can be switched under an applied electric or mechanical field. Ferroelectric materials show remarkable nonlinear behavior under an electric or mechanical loading due to microscopic domain switching. Ferroelectric ceramics have found wide application as memories, sensors, and actuators in smart components owing to their excellent coupled electromechanical properties [1,2]. Ferroelectric ceramics are mostly exposed to high electrical and mechanical loads during service, so studies on the nonlinear constitutive behavior of ferroelectrics are significant to guide the design of ferroelectric smart components and to analyze and predict their performance.

Many experimental and theoretical studies were devoted to explaining the nonlinear behavior of the ferroelectric ceramics [3–8]. Several nonlinear constitutive models were proposed and these different types of constitutive models for the ferroelectric ceramics can generally fall into two categories [9–27]. One category is based on the micro-electromechanical behavior of grains and another on the macro phenomenological model.

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Chen and his cooperators [9–12] firstly proposed the phenomenological model to describe the electromechanical coupling characters of ferroelectrics. The macro phenomenological models [9–19], which are mainly based on the first and second laws of thermodynamics and the postulate of maximum dissipation, consist of a selection of the internal variables characterizing the thermodynamic state of the material, a description for a switching surface (just analogous to a yield surface in conventional plasticity theory), a flow rule, and a derivation of the evolution equations of these internal variables. They usually give a purely macroscopic picture and do not describe the microstructural changes that accompany the process of polarization and domain switching. Micro-electromechanical models [20–27], which are based on a description of the material element at a unit cell or a domain length scale, include a selection of the internal variables representing the microstructure of the material element, a domain switching criterion and a kinematic description of these internal variables. Some approaches have been made to capture grain-grain interactions such as a mean field theory or a finite element method in some micromechanical models. Then, they can predict the macroscopic response of the material by averaging the response at the micro level. Li and Weng [28–30] studied the nonlinear coupled behavior of ferroelectrics using a micromechanics approach that combines the principle of irreversible thermodynamics and physics of domain switch. And this work was recently expanded to include the effect of temperature to study the shift of the Curie point [31,32] and to calculate the hysteresis behavior of single crystals and the ceramic polycrystal [33,34].

According to the above theories and models, some researchers have simulated the electromechanical coupled nonlinear behavior of ferroelectrics by the finite element method which generally implements the displacement and electric potential as the basic nodal variables [35–43]. In the solution of the finite element formalization, the researchers have found that the equivalent nodal load produced by spontaneous polarization is large enough to cause illogical simulated results [36,41–43]. In order to accomplish the calculation and obtain good simulated results, the finite element formulation should be modified to neglect the equivalent nodal load produced by spontaneous polarization [36,41–43]. Thus, it could not be suitable for finite element computation of ferroelectrics to employ the basic equations for dielectrics. Recently, Li and Rajapakse [44] had provided a detailed physical argument for the above problem in the finite element modeling. They explained that there was the charge-screening effect in real ceramics. That is, for bulk materials, the depolarization field induced by the polarization gradient or polarization change during domain switching is completely compensated by free charges. The free charges are trapped by unbalanced polarization and turn into space charges, which cannot be driven by the applied electric field unless the polarization switches. When domain switching occurs, the space charges are released and move to the surface of a material.

In the finite element modeling of ferroelectrics, each element should be a macroscopic material element and consists of a large number of domains. Thus, the physical quantities of the element are the volume averages of the corresponding quantities of all domains within the element. The depolarization field induced by the polarization gradient among adjacent elements is much larger than the coercive electric field, but it can be compensated by the screening-charges from the physical fundamentals of ferroelectrics according to Li and Rajapakse [44]. Hence, the equivalent nodal load produced by spontaneous polarization could be neglected in the finite element modeling. However, there is not any mathematical verification till now. Meanwhile, we can check the mathematical expressions of energy functions for ferroelectrics. Certain energy functions in use today are not compatible with the constitutive equations of ferroelectrics and need to be modified. This paper proposes a set of new formulae of the energy functions for ferroelectrics with sophisticated consideration. The new basic equations for ferroelectrics are derived in terms of the new formula of the energy functions. The new basic equations for ferroelectrics can overcome the difficulty in the current finite element analysis for ferroelectrics. The good calculation results have been obtained for ferroelectrics using the new basic equations [36,41–43].

2 Current energy functions and basic equations for ferroelectrics

2.1 Current basic equations and variational principle

The current basic equations for ferroelectrics in quasi-static equilibrium mechanically and electrically are given by Newton's and Maxwell's laws. Consider a volume of material, V , bounded by the surface, S , and free of the body force and the free body charge. The field equation is given by [45,46]

$$\begin{aligned}\sigma_{ij,j} &= 0 \\ D_{i,i} &= 0\end{aligned}\tag{1}$$

The mechanical boundary conditions are given by

$$\sigma_{ij}n_j = \bar{t}_i, \quad \text{on } S_\sigma, \quad (2)$$

$$u_i = \bar{u}_i, \quad \text{on } S_u \quad (3)$$

where σ_{ij} is the stress tensor, \bar{t}_i is the traction applied to the surface S_σ , n_i is a unit vector normal to the surface directed outward from the volume, and \bar{u}_i is the displacement on S_u .

The electric boundary conditions are given by

$$D_i n_i = -\bar{\omega}, \quad \text{on } S_\omega, \quad (4)$$

$$\phi = \bar{\phi}, \quad \text{on } S_\phi \quad (5)$$

where D_i is the electric displacement, $\bar{\omega}$ is the prescribed surface free charge per unit area residing on S_ω , and $\bar{\phi}$ is the prescribed electric surface potential on S_ϕ .

The generalized geometric equations are

$$\gamma_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}), \quad (6)$$

$$E_i = -\frac{\partial \phi}{\partial x_i}. \quad (7)$$

If the recoverable strain $\gamma_{ij} - \gamma_{ij}^s$ and the electric field E_i are chosen as the independent constitutive variables, the second type constitutive equation for a linear response of ferroelectrics can be written as [1,47,48]

$$\sigma_{ij} = c_{ijmn}^E (\gamma_{mn} - \gamma_{mn}^s) - e_{kij} E_k, \quad (8)$$

$$D_i = e_{imn} (\gamma_{mn} - \gamma_{mn}^s) + \varepsilon_{ik}^Y E_k + D_i^s$$

where γ_{ij}^s and D_i^s are the spontaneous strain and polarization, c_{ijkl}^E is the elastic modulus tensor measured at constant electric field, e_{kij} is the piezoelectric coefficient tensor at constant strain, and ε_{ij}^Y is the dielectric permittivity tensor measured at constant strain.

Suppose that the displacement u_i and the electric potential ϕ satisfy the boundary conditions (3) and (5), respectively, the field Eq. (1) and the boundary conditions (2) and (4) are equivalent to the following variational equation [49,50]:

$$\int_V (\sigma_{ij,j} \delta u_i + D_{i,i} \delta \phi) dV - \int_{S_\sigma} (\sigma_{ij} n_j - \bar{t}_i) \delta u_i dS - \int_{S_\omega} (D_i n_i + \bar{\omega}) \delta \phi dS = 0. \quad (9)$$

Substituting the constitutive Eq. (8) into the above Eq. (9), we get

$$\begin{aligned} & \delta \left[\int_V \left(\frac{1}{2} c_{ijkl}^E \gamma_{kl} \gamma_{ij} - e_{kij} E_k \gamma_{ij} - \frac{1}{2} \varepsilon_{ij}^Y E_i E_j \right) dV \right] - \int_V \left[C_{ijkl} \gamma_{kl}^s \delta \gamma_{ij} - (e_{ijk} \gamma_{jk}^s - D_i^s) \delta E_i \right] dV \\ & - \int_{S_\sigma} \bar{t}_j \delta u_j dS + \int_{S_\omega} \bar{\omega} \delta \phi dS = 0. \end{aligned}$$

Hence, the total electric entropy potential Ψ of the system can be expressed as

$$\begin{aligned} \Psi = & \int_V \left(\frac{1}{2} c_{ijkl}^E \gamma_{kl} \gamma_{ij} - e_{kij} E_k \gamma_{ij} - \frac{1}{2} \varepsilon_{ij}^Y E_i E_j \right) dV - \int_V \left[C_{ijkl} \gamma_{kl}^s \gamma_{ij} - (e_{ijk} \gamma_{jk}^s - D_i^s) E_i \right] dV \\ & - \int_{S_\sigma} \bar{t}_j u_j dS + \int_{S_\omega} \bar{\omega} \phi dS. \end{aligned} \quad (10)$$

The variational principle is

$$\delta \Psi = 0.$$

Therefore, the standard finite element formulation in which the displacement and electric potential are chosen as the independent parameters can be obtained.

2.2 Finite element formulation

The generalized displacement is

$$\mathbf{u} = [u_1 \quad u_3 \quad u_3 \quad \phi]^T. \quad (11)$$

The generalized strain is

$$\mathbf{\Gamma} = [\gamma_{11} \quad \gamma_{22} \quad \gamma_{33} \quad 2\gamma_{23} \quad 2\gamma_{13} \quad 2\gamma_{12} \quad -E_1 \quad -E_2 \quad -E_3]^T. \quad (12)$$

The generalized stress is

$$\mathbf{\Sigma} = [\sigma_{11} \quad \sigma_{22} \quad \sigma_{33} \quad \sigma_{23} \quad \sigma_{13} \quad \sigma_{12} \quad D_1 \quad D_2 \quad D_3]^T. \quad (13)$$

The relation between the generalized stress and the generalized strain is

$$\mathbf{\Sigma} = \mathbf{C} (\mathbf{\Gamma} - \mathbf{\Gamma}^s) + \mathbf{D}^s \quad (14)$$

where $\mathbf{\Gamma}^s = [\gamma_{11}^s \quad \gamma_{22}^s \quad \gamma_{33}^s \quad 2\gamma_{23}^s \quad 2\gamma_{13}^s \quad 2\gamma_{12}^s \quad 0 \quad 0 \quad 0]^T$,

$$\mathbf{D}^s = [0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad D_1^s \quad D_2^s \quad D_3^s]^T,$$

$$\mathbf{C} = \begin{bmatrix} c_{1111}^E & c_{1122}^E & c_{1133}^E & 0 & 0 & 0 & e_{111} & e_{211} & e_{311} \\ c_{2211}^E & c_{2222}^E & c_{2233}^E & 0 & 0 & 0 & e_{122} & e_{222} & e_{322} \\ c_{3311}^E & c_{3322}^E & c_{3333}^E & 0 & 0 & 0 & e_{133} & e_{233} & e_{333} \\ 0 & 0 & 0 & c_{2323}^E & 0 & 0 & e_{123} & e_{223} & e_{323} \\ 0 & 0 & 0 & 0 & c_{1313}^E & 0 & e_{113} & e_{213} & e_{313} \\ 0 & 0 & 0 & 0 & 0 & c_{1212}^E & e_{112} & e_{212} & e_{312} \\ e_{111} & e_{122} & e_{133} & e_{123} & e_{113} & e_{112} & -\varepsilon_{11}^r & -\varepsilon_{12}^r & -\varepsilon_{13}^r \\ e_{211} & e_{222} & e_{233} & e_{223} & e_{213} & e_{212} & -\varepsilon_{21}^r & -\varepsilon_{22}^r & -\varepsilon_{23}^r \\ e_{311} & e_{322} & e_{333} & e_{323} & e_{313} & e_{312} & -\varepsilon_{31}^r & -\varepsilon_{32}^r & -\varepsilon_{33}^r \end{bmatrix}. \quad (15)$$

The generalized nodal displacement array of an element is \mathbf{a}_e and the matrix of shape functions is \mathbf{N} . The generalized displacement within an element can then be interpolated as

$$\mathbf{u} = \mathbf{N}\mathbf{a}_e. \quad (16)$$

The generalized strain for each element can be derived as

$$\mathbf{\Gamma} = \mathbf{L}\mathbf{u} = \mathbf{L}\mathbf{N}\mathbf{a}_e = \mathbf{B}\mathbf{a}_e \quad (17)$$

where the matrix \mathbf{L} is given as

$$\mathbf{L} = \begin{bmatrix} \partial_x & 0 & 0 & 0 & \partial_z & \partial_y & 0 & 0 & 0 \\ 0 & \partial_y & 0 & \partial_z & 0 & \partial_x & 0 & 0 & 0 \\ 0 & 0 & \partial_z & \partial_y & \partial_x & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \partial_x & \partial_y & \partial_z \end{bmatrix}^T. \quad (18)$$

The total electric entropy potential Ψ can be expressed by the generalized nodal displacement \mathbf{a}_e ,

$$\begin{aligned} \Psi = & \sum \left(\mathbf{a}_e^T \int_{\Omega_e} \frac{1}{2} \mathbf{B}^T \mathbf{C} \mathbf{B} \mathbf{a}_e dV \right) \\ & - \sum \left(\mathbf{a}_e^T \int_{\Omega_e} \mathbf{B}^T (\mathbf{C}\mathbf{\Gamma}^s - \mathbf{D}^s) dV \right) - \sum \left(\mathbf{a}_e^T \int_{S_\sigma} \mathbf{N}^T \bar{\mathbf{T}} dS \right) + \sum \left(\mathbf{a}_e^T \int_{S_\omega} \mathbf{N}^T \bar{\omega} dS \right). \end{aligned} \quad (19)$$

The element nodal displacement \mathbf{a}_e can be expressed by the total nodal displacement \mathbf{a} , thus

$$\mathbf{a}_e = \mathbf{G}\mathbf{a} \quad (20)$$

where \mathbf{G} is a transformation matrix relating the element local displacement and the global displacement. Then, we have

$$\begin{aligned} \Psi = & \sum_e \mathbf{a}^T \mathbf{G}^T \int_{\Omega_e} \frac{1}{2} \mathbf{B}^T \mathbf{C} \mathbf{B} \mathbf{G} \mathbf{a} dV - \sum_e \mathbf{a}^T \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \Gamma^s dV + \sum_e \mathbf{a}^T \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{D}^s dV \\ & - \sum_e \mathbf{a}^T \mathbf{G}^T \int_{S_\sigma} \mathbf{N}^T \bar{\mathbf{T}} dS + \sum_e \mathbf{a}^T \mathbf{G}^T \int_{S_\omega} \mathbf{N}^T \bar{\omega} dS. \end{aligned} \quad (21)$$

According to $\delta\Psi = 0$, Eq. (21) can yield the finite element equation

$$\begin{aligned} \sum_e \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \mathbf{B} \mathbf{G} \mathbf{a} dV = & \sum_e \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \Gamma^s dV - \sum_e \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{D}^s dV \\ & + \sum_e \mathbf{G}^T \int_{S_\sigma} \mathbf{N}^T \bar{\mathbf{T}} dS - \sum_e \mathbf{G}^T \int_{S_\omega} \mathbf{N}^T \bar{\omega} dS. \end{aligned} \quad (22)$$

The second term on the right-hand side of Eq. (22) is the additional nodal load due to the spontaneous polarization, represented by \mathbf{F}^s . Based on Eq. (22), one can carry out the finite element calculation. Unfortunately it is difficult to process the finite element computation further after domain switching occurs for some elements and the computational results are remarkably deviating from the experimental results. Li and Fang [41,42] neglect this term in their finite element computation because they believe that there could be some free charges to balance this term in practical materials. Liu et al. [43] have also encountered the same difficulty in our finite element computation. Therefore, we think that the basic equations should be further discussed.

2.3 Energy functions currently used for ferroelectrics

The state of homogeneous elastic dielectrics can be described by three pairs of variables, the stress $\boldsymbol{\sigma}$ and strain $\boldsymbol{\gamma}$, the electric field \mathbf{E} and electric displacement \mathbf{D} and the temperature T and entropy S . In view of the thermodynamic theories, only one thermodynamic characteristic function is needed to determine the equilibrium of this system after independent variables are identified. Any one of each pair is respectively chosen as the independent variable to construct a characteristic function for dielectrics. The different combination of the independent variables can construct the different energy (or characteristic) function. The energy (or characteristic) functions for dielectrics are the internal energy, electric enthalpy, Gibbs free energy and so on. The internal energy density, electric enthalpy density and Gibbs free energy density are respectively denoted by U , W and G , which are given by [24,40,51]

$$\begin{aligned} U &= \int (T dS + \sigma_{ij} d\gamma_{ij} + E_k dD_k), \\ W &= U - E_k D_k, \\ G &= U - TS - \sigma_{ij} \gamma_{ij} - E_k D_k, \end{aligned} \quad (23)$$

Suo et al. [50] has shown that the total electric entropy potential Ψ of the system in Eq. (10) can be expressed as

$$\Psi = \int_V W dV - \int_{S_\sigma} \bar{t}_i u_i dS + \int_{S_\omega} \bar{\omega} \phi dS. \quad (24)$$

The energy (or characteristic) functions for ferroelectrics in use today are given by those for ordinary dielectrics in the physical and mechanical communications. Neglecting the heat effect, the internal energy density is written as

$$U = \int (\sigma_{ij} d\gamma_{ij} + E_k dD_k). \quad (25)$$

If the stress σ_{ij} and the electric field E_i are chosen as the independent constitutive variables, the first type constitutive equation for a linear response of ferroelectrics can be written as [47,48,52]

$$\begin{aligned}\gamma_{ij} &= \gamma_{ij}^s + s_{ijmn}^E \sigma_{mn} + d_{kij} E_k, \\ D_i &= D_i^s + d_{imn} \sigma_{mn} + \varepsilon_{ik}^\sigma E_k\end{aligned}\quad (26)$$

where s_{ijmn}^E , d_{kij} , ε_{ik}^σ are the components of the elastic compliance, piezoelectric and dielectric permittivity tensors, respectively.

Substituting Eq. (26) into Eq. (25), the internal energy density U for ferroelectrics is described as

$$U = \frac{1}{2} \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) + \frac{1}{2} E_i (D_i - D_i^s). \quad (27)$$

According to Eq. (23), the corresponding electric enthalpy density W and Gibbs free energy density G for ferroelectrics can be expressed as

$$W = \frac{1}{2} \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) - \frac{1}{2} E_i (D_i + D_i^s), \quad (28)$$

$$G = -\frac{1}{2} \sigma_{ij} (\gamma_{ij} + \gamma_{ij}^s) - \frac{1}{2} E_i (D_i + D_i^s). \quad (29)$$

The first term on the right-hand side of Eq. (28) includes $\gamma_{ij} - \gamma_{ij}^s$, but the second on the right-hand side includes $D_i + D_i^s$. Apparently, the expression (28) for W is not compatible with the constitutive equations of ferroelectrics and needs to be modified. Likewise, the expression (29) for G is strange due to two terms $\gamma_{ij} + \gamma_{ij}^s$ and $D_i + D_i^s$.

3 Energy functions and basic equations for ferroelectrics

3.1 Energy functions and basic equations

In contrast to ordinary dielectrics, ferroelectric crystals undergo a phase transition from a cubic unit cell to a tetragonal, orthorhombic, or rhombohedral one when cooling through the Curie point. This leads to the spontaneous polarization D_i^s and strain γ_{ij}^s . If the recoverable strain $\gamma_{ij} - \gamma_{ij}^s$ and the recoverable electric displacement $D_i - D_i^s$ are taken as independent variables, Eq. (25) can be inverted to the form [25,39]

$$\begin{aligned}\sigma_{ij} &= c_{ijkl}^D (\gamma_{ij} - \gamma_{ij}^s) - h_{kij} (D_k - D_k^s), \\ E_i &= -h_{ikl} (\gamma_{kl} - \gamma_{kl}^s) + \beta_{ik}^\gamma (D_k - D_k^s)\end{aligned}\quad (30)$$

where c_{ijkl}^D is an elastic stiffness tensor, h_{kij} is a piezoelectric tensor and β_{ik}^γ is a dielectric permeability tensor. It can be clearly seen that the state variable (σ_{ij}, E_i) is homogeneously and linearly related to the state variable $(\gamma_{ij} - \gamma_{ij}^s, D_i - D_i^s)$. Both the state variable (σ_{ij}, E_i) and the state variable $(\gamma_{ij} - \gamma_{ij}^s, D_i - D_i^s)$ are the one to one correspondence.

According to Lines and Glass [53] and Elhadrouz et al. [54], the Gibbs free energy density G for ferroelectrics can be expressed as

$$G = -\frac{1}{2} \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) - \frac{1}{2} E_i (D_i - D_i^s). \quad (31)$$

The Gibbs free energy density G defined by Eq. (31) is distinct from that defined by Eq. (29).

According to the thermodynamics law [53,54], when temperature is constant, the Gibbs free energy density G is a function of the independent variables (σ_{ij}, E_i) . It infers from Eq. (31) that the state variable $(\gamma_{ij} - \gamma_{ij}^s, D_i - D_i^s)$ is the work conjugate to the state variable (σ_{ij}, E_i) .

According to the above work conjugate law, the electric enthalpy density W and the Gibbs free energy G for ferroelectrics should be defined by

$$W = U - E_i (D_i - D_i^s) = \frac{1}{2} \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) - \frac{1}{2} E_i (D_i - D_i^s), \quad (32)$$

$$G = U - \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) - E (D_i - D_i^s) = -\frac{1}{2} \sigma_{ij} (\gamma_{ij} - \gamma_{ij}^s) - \frac{1}{2} E_i (D_i - D_i^s). \quad (33)$$

One can clearly find that the new G defined by Eq. (33) is the same as that of Eq. (31) defined by Lines and Glass [53] and Elhadrouz et al. [54]. In contrast to Eqs. (28) and (29), Eqs. (32) and (33) are more reasonable from the physical point view. In terms of the electric enthalpy W defined by Eq. (32) the total electric entropy potential Ψ of the system is

$$\Psi = \int_V W dV - \int_{S_\sigma} \bar{t}_i u_i dS + \int_{S_\omega} \bar{\omega} \phi dS. \quad (34)$$

The first variation of the total electric entropy potential of the system is

$$\begin{aligned} \delta\Psi &= \int_V \delta W dV - \int_{S_\sigma} \bar{t}_i \delta u_i dS + \int_{S_\omega} \bar{\omega} \delta \phi dS \\ &= \int_V [\sigma_{ij} \delta \gamma_{ij} - (D_i - D_i^s) \delta E_i] dV - \int_{S_\sigma} \bar{t}_i \delta u_i dS + \int_{S_\omega} \bar{\omega} \delta \phi dS \\ &= \int_V [\sigma_{ij} \delta u_{i,j} + (D_i - D_i^s) \delta \phi_{,i}] dV - \int_{S_\sigma} \bar{t}_i \delta u_i dS + \int_{S_\omega} \bar{\omega} \delta \phi dS. \end{aligned} \quad (35)$$

Based on the principle of stationary total electric entropy potential, one can obtain the following new field equation:

$$\sigma_{ij,j} = 0 \quad (36.1)$$

$$(D_i - D_i^s)_{,i} = 0, \quad \text{in } V \quad (36.2)$$

and boundary conditions (37) and (38)

$$\sigma_{ij} n_j = \bar{t}_i, \quad \text{on } S_\sigma \quad (37)$$

$$(D_i - D_i^s) n_i = -\bar{\omega}, \quad \text{on } S_\omega. \quad (38)$$

3.2 The physical meaning of the new Eqs. (36.1) and (38)

The ferroelectric ceramics consists of numerous domains. Within each single domain, the spontaneous polarization is uniform, hence Eq. (36.1) becomes

$$\begin{aligned} \sigma_{ij,j} &= 0 \\ D_{i,i} &= 0 \end{aligned} \quad \text{in } V. \quad (39)$$

The above equation is identical with Eq. (1). It means that the new field Eq. (36.1) is essentially the same as the original field Eq. (1) of ferroelectrics within each single domain. On the other hand, one can get the following interface condition based on Eq. (36.2):

$$[D_i - D_i^s] n_i = 0 \quad \text{on } S_{in} \quad (40)$$

where S_{in} is the interface (domain wall) between two adjacent domains as shown in Fig. 1. Here, the symbol $[]$ denotes the jump across S_{in} of the quantity within. Equation (40) can be rewritten as

$$\begin{aligned} [D_i] n_i &= -\omega_s \\ \omega_s &= -[D_i^s] n_i \end{aligned} \quad \text{on } S_{in} \quad (41)$$

where ω_s is the interface free charge density induced by the spontaneous polarization gradient. Equation (41) is the actual new equation presented in this paper.

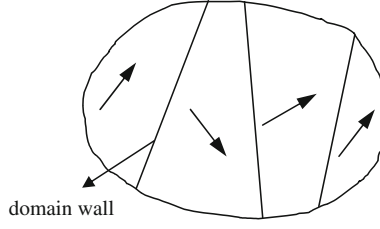


Fig. 1 An aggregate with domains as sub-regions

3.3 Finite element formulations

The 90° domain switch will produce a very thin surface layer on the charge-free boundary of the specimen of ferroelectric ceramics. The recent finite calculations [36,41–43] did not simulate the surface layers. The finite element formulations presented in this paper are also neglecting the surface layers. The reason is given in Appendix A.

Neglecting the body force and free body charge and supposing that the displacement u_i and the electric potential ϕ satisfy the boundary conditions (3) and (5), respectively, the field Eq. (36.1) and boundary conditions (37) and (38) are equivalent to the following variational equation:

$$\int_V \left(\sigma_{ij,j} \delta u_i + (D_i - D_i^s)_{,i} \delta \phi \right) dV - \int_{S_\sigma} (\sigma_{ij} n_j - \bar{t}_i) \delta u_i dS - \int_{S_\omega} [(D_i - D_i^s) n_i + \bar{\omega}] \delta \phi dS = 0. \quad (42)$$

Substituting Eq. (8) into Eq. (42), we get

$$\begin{aligned} \delta \left[\int_V \left(\frac{1}{2} c_{ijkl} \gamma_{kl} \gamma_{ij} - e_{kij} E_k \gamma_{ij} - \frac{1}{2} \varepsilon_{ij}^r E_i E_j \right) dV \right] - \int_V [C_{ijkl} \gamma_{kl}^s \delta \gamma_{ij} - e_{ijk} \gamma_{jk}^s \delta E_i] dV \\ - \int_{S_\sigma} \bar{t}_j \delta u_j dS + \int_{S_\omega} \bar{\omega} \delta \phi dS = 0. \end{aligned} \quad (43)$$

Hence, the total electric entropy potential Ψ of the ferroelectrics can be expressed as

$$\begin{aligned} \Psi = \int_V \left(\frac{1}{2} c_{ijkl} \gamma_{kl} \gamma_{ij} - e_{kij} E_k \gamma_{ij} - \frac{1}{2} \varepsilon_{ij}^r E_i E_j \right) dV - \int_V [C_{ijkl} \gamma_{kl}^s \gamma_{ij} - e_{ijk} \gamma_{jk}^s E_i] dV \\ - \int_{S_\sigma} \bar{t}_j u_j dS + \int_{S_\omega} \bar{\omega} \phi dS. \end{aligned} \quad (44)$$

The variational principle is

$$\delta \Psi = 0. \quad (45)$$

Equation (45) can be written in a discretized form as

$$\begin{aligned} \Psi = \sum_e \mathbf{a}^T \mathbf{G}^T \int_{\Omega_e} \frac{1}{2} \mathbf{B}^T \mathbf{C} \mathbf{B} \mathbf{G} dV - \sum_e \mathbf{a}^T \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \mathbf{r}^s dV - \sum_e \mathbf{a}^T \mathbf{G}^T \int_{S_\sigma} \mathbf{N}^T \bar{\mathbf{t}} dS \\ + \sum_e \mathbf{a}^T \mathbf{G}^T \int_{S_\omega} \mathbf{N}^T \bar{\omega} dS. \end{aligned} \quad (46)$$

Then, Eq. (46) yields the finite element equation

$$\begin{aligned} \sum_e \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \mathbf{B} \mathbf{G} dV &= \sum_e \mathbf{G}^T \int_{\Omega_e} \mathbf{B}^T \mathbf{C} \mathbf{F}^s dV + \sum_e \mathbf{G}^T \int_{S_\sigma} \mathbf{N}^T \bar{\mathbf{T}} dS \\ &\quad - \sum_e \mathbf{G}^T \int_{S_\omega} \mathbf{N}^T \bar{\omega} dS. \end{aligned} \quad (47)$$

In contrast to Eq. (22), the equivalent nodal load \mathbf{F}^s disappears on the right-hand side of Eq. (47). It can confirm that the effect of the spontaneous polarization does not exist really in the new finite element formulation. Now there is not any difficulty in the finite element calculation when the new basic equations derived in this paper are used.

4 Concluding remarks

This paper carefully analyzes the puzzle in the current finite element modeling of nonlinear behavior of ferroelectrics. The puzzle arises from neglecting the equivalent nodal load \mathbf{F}^s induced by the spontaneous polarization [36,41–43]. According to the currently used basic equations, the equivalent nodal load \mathbf{F}^s does exist, and it is very large to cause the illogical computational results [2,36,41–43]. A rigorous mathematical verification is presented to overcome the puzzle. According to the work conjugate law, we modify the formula of certain current energy functions which are incompatible with the constitutive equations of ferroelectrics and propose a set of new formulae of energy functions for ferroelectrics. Based on the new formulae of energy functions, the new basic equations for ferroelectrics are derived. Employing the new basic equations, one can smoothly overcome the difficulty in the current finite element computation for ferroelectrics and obtain good computational results.

Appendix A

Figure 2 shows a specimen of ferroelectric ceramics with single domain. The specimen is subjected to uniform compression on the boundaries BC and DA and satisfies the charge-free condition on the boundaries AB and CD. When the compression is large enough, the 90° domain switch will occur in the body. On the surface AB and CD, the situation will be complicated. The 90° domain switch will produce two very thin surface layers as

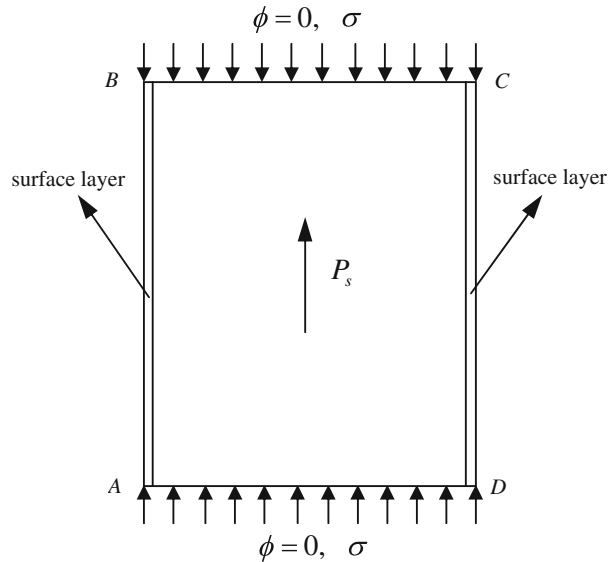


Fig. 2 A specimen with single domain under compression

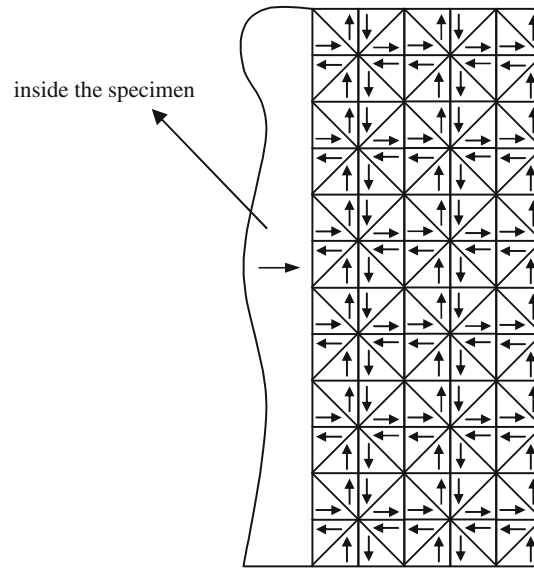


Fig. 3 Domain configurations of the surface layer

shown in Fig. 2. Within the surface layers, the microstructure is much more complicated than inside the body. Figure 3 is an enlargement of the surface layer. A possible microstructure is shown in Fig. 3. The original single domain in the surface layer is divided into small pieces of sub-domains to form complicated domain patterns. The 90° domain switches are accompanied by 180° domain switches in the surface layer. The spontaneous polarization in all sub-domains on the surface is parallel to the surface as shown in Fig. 3, which satisfies the original boundary condition (4). But the spontaneous polarization of the sub-domain within the surface layer may be perpendicular to the surface. If the specimen is a single crystal, such kinds of the domain patterns can propagate into the body with domain wall elongation and propagation. But for the ferroelectric ceramics, thousands of grain boundaries become strong barriers to prevent a continuous movement of the domain wall. Each grain may be divided into several pieces of sub-domains with parallel spontaneous polarization. Across the grain boundary, the spontaneous polarization gradient could be balanced by ω_s .

The recent finite calculations [36,41–43] did not simulate the surface layers. One reason is that the simulation of the surface layers needs too much consuming of computation time. On the other hand, there is not any mechanical principle to deal with the domain patterns in the surface layers. There are thousands of varieties of possible domain patterns. It is nearly impossible to simulate so many possible domain patterns. The recent finite calculations [36,41–43] have neglected the surface layers. This paper provides a mathematical verification for the recent finite calculations [36,41–43].

References

1. Jaffe, B., Cook, W.R., Jaffe, H.: Piezoelectric Ceramics. Academic Press, London (1971)
2. Setter, N., Waser, R.: Electroceramic materials. *Acta Mater.* **48**, 151–178 (2000)
3. Cao, H., Evans, A.G.: Nonlinear deformation of ferroelectric ceramics. *J. Am. Ceram. Soc.* **76**, 890–896 (1993)
4. Lynch, C.S.: The effect of uniaxial stress on the electro-mechanical response of 8/65/35 PLZT. *Acta Mater.* **44**, 4137–4148 (1996)
5. Fang, D.N., Li, C.Q.: Nonlinear electric-mechanical behavior of a soft PZT-51 ferroelectric ceramic. *J. Mater. Sci.* **34**, 4001–4010 (1999)
6. Kamlah, M.: Ferroelectric and ferroelastic piezoceramics—modeling of electromechanical hysteresis phenomena. *Cont. Mech. Thermodyn.* **13**, 219 (2001)
7. Landis, C.M.: Non-linear constitutive modeling of ferroelectrics. *Curr. Opin. Solid State Mater. Sci.* **8**, 59–69 (2004)
8. Huber, J.E.: Micromechanical modeling of ferroelectrics. *Curr. Opin. Solid State Mater. Sci.* **9**, 100–106 (2005)
9. Chen, P.J., Peercy, P.S.: One dimensional dynamic electromechanical constitutive relations of ferroelectric materials. *Acta Mech.* **31**, 231–241 (1979)
10. Chen, P.J., Madsen, M.M.: One dimensional polar response of the electrooptic PLZT7/65/35 due to domain switching. *Acta Mech.* **41**, 255–264 (1981)
11. Chen, P.J., Tucker, T.J.: Determination of the polar equilibrium properties of the ferroelectric ceramics PZT 65/35. *Acta Mech.* **38**, 209–218 (1981)

12. Chen, P.J.: Three dimensional constitutive relations for ferroelectric materials in the presence of quasi-static domain switching. *Acta Mech.* **48**, 31–42 (1983)
13. Kamlah, M., Tsakmakis, C.: Phenomenological modeling of the non-linear electromechanical coupling in ferroelectrics. *Int. J. Solids Struct.* **36**, 669–695 (1999)
14. Kamlah, M., Jiang, Q.: A constitutive model for ferroelectric PZT ceramics under uniaxial loading. *Smart Mater. Struct.* **8**, 441–459 (1999)
15. Huber, J.E., Fleck, N.A.: Multi-axial electrical switching of a ferroelectric: theory versus experiment. *J. Mech. Phys. Solids* **49**, 785–811 (2001)
16. Landis, C.M.: Fully coupled, multi-axial, symmetric constitutive laws for polycrystalline ferroelectric ceramics. *J. Mech. Phys. Solids* **50**, 127–152 (2002)
17. McMeeking, R.M., Landis, C.M.: A phenomenological multi-axial constitutive law for switching in polycrystalline ferroelectric ceramics. *Int. J. Eng. Sci.* **40**, 1553–1577 (2002)
18. Kim, S.J.: A one-dimensional continuum model for ferroelectric ceramics. *Eur. J. Mech. A Solids* **22**, 423–432 (2003)
19. Klinkel: A phenomenological constitutive model for ferroelastic and ferroelectric hysteresis effects in ferroelectric ceramics. *Int. J. Solids Struct.* **43**, 7197–7222 (2006)
20. Hwang, S.C., Lynch, C.S., McMeeking, R.M.: Ferroelectric/ferroelastic interactions and a polarization switching model. *Acta Metall. Mater.* **43**, 2073–2084 (1995)
21. Sun, C.T., Jiang, L.Z.: Domain switching induced stress at the tip of a crack in piezoceramics. In: Proceedings of the 4th ESSM and 2nd MIMR Conference, Harrogate, pp. 715–722 (1998)
22. Chen, X., Fang, D.N., Hwang, K.C.: Micromechanics simulation of ferroelectric polarization switching. *Acta Mater.* **45**, 3181–3189 (1997)
23. Chen, W., Lynch, C.S.: A micro-electro-mechanical model for polarization switching of ferroelectric materials. *Acta Mater.* **46**, 5303–5311 (1998)
24. Lu, W., Fang, D.N., Hwang, K.C.: Nonlinear electric-mechanical behavior and micromechanics modeling of ferroelectric domain evolution. *Acta Mater.* **47**, 2913–2926 (1999)
25. Huber, J.E., Fleck, N.A., Landis, C.M., McMeeking, R.M.: A constitutive model for ferroelectric polycrystals. *J. Mech. Phys. Solids* **47**, 1663–1697 (1999)
26. Huber, J.E., Fleck, N.A.: Multi-axial electrical switching of a ferroelectric: theory versus experiment. *J. Mech. Phys. Solids* **49**, 785–811 (2001)
27. Huber, J.E., Fleck, N.A.: Ferroelectric switching: a micromechanics model versus measured behaviour. *Eur. J. Mech. A Solids* **23**, 203–217 (2004)
28. Li, J., Weng, G.J.: A theory of domain switch for the nonlinear behavior of ferroelectrics. *Proc. R. Soc. Lond. A* **455**, 3493–3511 (1999)
29. Li, J., Weng, G.J.: A micromechanics-based hysteresis model for ferroelectric ceramics. *J. Int. Mater. Syst. Struct.* **12**, 79–91 (2001)
30. Li, W.F., Weng, G.J.: A micromechanics-based thermodynamic model for the domain switch in ferroelectric crystals. *Acta Mater.* **52**, 2489–2496 (2004)
31. Su, Y., Weng, G.J.: The shift of Curie temperature and evolution of ferroelectric domain in ferroelectrics crystals. *J. Mech. Phys. Solids* **53**, 2071–2099 (2005)
32. Su, Y., Weng, G.J.: A self-consistent polycrystal model for the spontaneous polarization of ferroelectric ceramics. *Proc. R. Soc. Lond. A* **462**, 1763–1789 (2006)
33. Srivastava, N., Weng, G.J.: A dual-phase homogenization theory for the hysteresis and butterfly-shaped behavior of ferroelectric single crystals. *Mech. Mater.* **38**, 945–957 (2006)
34. Srivastava, N., Weng, G.J.: A theory of double hysteresis for ferroelectric crystals. *J. Appl. Phys.* **99**, 1–11 (2006)
35. Gong, X., Suo, Z.: Reliability of ceramic multilayer actuators: a nonlinear finite element simulation. *J. Mech. Phys. Solids* **44**, 751–769 (1996)
36. Kalyanam, S., Sun, C.T.: Modeling of electrical boundary condition and domain switching in piezoelectric materials. *Mech. Mater.* **37**, 769–784 (2005)
37. Chen, W., Lynch, C.S.: Finite element analysis of cracks in ferroelectric ceramic materials. *Eng. Fract. Mech.* **64**, 539–562 (1999)
38. Hwang, S.C., Waser, R.: Study of electrical and mechanical contribution to switching in ferroelectric/ferroelastic polycrystals. *Acta Mater.* **48**, 3271–3282 (2000)
39. Landis, C.M.: A new finite-element formulation for electromechanical boundary value problems. *Int. J. Numer. Methods Eng.* **55**, 613–628 (2002)
40. Kim, S.J., Jiang, Q.: A finite element model for rate-dependent behavior of ferroelectric ceramics. *Int. J. Solids Struct.* **39**, 1015–1030 (2002)
41. Li, F.X., Fang, D.N.: Simulations of domain switching in ferroelectrics by a three-dimensional finite element model. *Mech. Mater.* **36**, 959–973 (2004)
42. Fang, D., Li, F., Soh, A.K., Liu, T.: Analysis of the electromechanical behavior of ferroelectric ceramics based on a nonlinear finite element model. *Acta Mech. Sin.* **21**, 294–304 (2005)
43. Liu, F., Li, H.J., Wang, T.C.: Energy principle and nonlinear electric-mechanical behavior of ferroelectric ceramics. *Acta Mech.* **198**, 147–170 (2008)
44. Li, F.X., Rajapakse, R.K.N.D.: A constrained domain-switching model for polycrystalline ferroelectric ceramics. Part I: model formulation and application to tetragonal materials. *Acta Mater.* **55**, 6472–6480 (2007)
45. Pak, Y.E.: Linear electro-elastic fracture mechanics of piezoelectric materials. *Int. J. Fract.* **54**, 79–100 (1992)
46. Parton, V.Z., Kudryavtsev, B.A.: *Electromagnetoelasticity*. Gordon and Breach Science Publishers, New York (1988)
47. Landau, L.D., Lifshitz, E.M.: *Electrodynamics of Continuous Media*. Pergamon Press, Oxford (1960)
48. Eringen, A.C., Maugin, G.A.: *Electrodynamics of Continua I: Foundations and Solid Media*. Springer, New York (1990)
49. Zienkiewicz, O.C., Taylor, R.L.: *The Finite Element Method 1: The Basis*. Butterworth-Heinemann, Oxford (2000)

-
50. Suo, Z., Kuo, C.M., Barnett, D.M., Willis, J.R.: Fracture mechanics for piezoelectric ceramics. *J. Mech. Phys. Solids* **40**, 739–765 (1992)
 51. Zhong, W.L.: *Ferroelectrics Physics*. Science Press, Beijing (in Chinese) (1996)
 52. Bassiouny, E., Ghaleb, A.F., Maugin, G.A.: Thermomechanical formulation for coupled electromechanical hysteresis effect-I. Basic equations, II. Poling of ceramics. *Int. J. Eng. Sci.* **26**, 1279–1306 (1998)
 53. Lines, M.E., Glass, A.M.: *Principles and Applications of Ferroelectrics and Related Materials*. Oxford University Press, Oxford (1977)
 54. Elhadrouz, M., Zineb, T.B., Patoor, E.: Constitutive law for ferroelectric and ferroelastic single crystals: a micromechanical approach. *Comp. Mater. Sci.* **32**, 355–359 (2005)