A phase-field model of relaxor ferroelectrics based on random field theory

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Abstract

A mechanically coupled phase-field model is proposed for the first time to simulate the peculiar behavior of relaxor ferroelectrics. Based on the random field theory for relaxors, local random fields are introduced to characterize the effect of chemical disorder. This generic model is developed from a thermodynamic framework and the microforce theory and is implemented by a nonlinear finite element method. Simulation results show that the model can reproduce relaxor features, such as domain miniaturization, small remnant polarization and large piezoelectric response. In particular, the influence of random field strength on these features are revealed. Simulation results on domain structure and hysteresis behavior are discussed and compared with related experimental results.

Keywords: Phase-field modeling, Relaxor ferroelectrics, Random field theory, Finite element methods

1. Introduction

In contrast with conventional perovskite structured ferroelectrics, relaxor ferroelectrics, also referred to as relaxors, exhibit high permittivity (Park and Shrout, 1997), less hysteresis effect (Shrout and Fielding Jr, 1990) and large piezoelectric response (Cross et al., 1980). The peculiar behavior of relaxors results from the abnormal domain structures, in which the short-range order dominates.

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The origin for the short-range order remains controversial. Besides the concept of polar nanoregions (Bokov and Ye, 2007), the random field model (Glinchuk and Farhi, 1996; Westphal et al., 1992) and the spherical random bond-random field model (Pirc and Blinc, 1999) have been used to explain the properties of relaxors. The random field model was firstly proposed by Westphal et al. (1992), referring to the original idea of Imry and Ma (1975). It was claimed that the relaxor behavior of Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) is due to the quenched random electric fields. These quenched fields can originate from charged compositional fluctuations. In fact, most of the relaxors with the perovskite structure have heterovalent substitutions on the A- and/or B-site. For instance, in AB_1B_2O_3 structure, the differences in the charge and size of B_1 and B_2 cations make the structure asymmetric. When cooling down from high temperature, the concentrations of B_1 and B_2 cation tend to fluctuate and form chemical disorder. This can give rises to random internal electric field (Glinchuk and Farhi, 1996; Westphal et al., 1992). The experiment in linear birefringence supported this theory (Glinchuk and Farhi, 1996; Westphal et al., 1992). Nevertheless the exact mechanism, i.e., how the random field influences the domain structure in relaxors, remains unclear. There are very few theoretical attempts in the literature. For instance, Blinc and Pirc assumed Gaussian random field in their spherical random-bond-random-field model (Blinc et al., 1999; Pirc and Blinc, 1999), and showed analytically that these random fields can prohibit the phase transition from paraelectric phase into ferroelectric one. Instead, a long-range disordered phase forms. Using the same model, the authors also explained the dielectric non-linearity in PMN and predict local polarization distribution. Since the model is based on the Landau theory (Landau and Lifshitz, 1935) with homogeneous domain assumption, it has no access to the domain structure. More recently, Ma et al. (2015) proposed a lattice-based Ginzburg-Landau-type Hamiltonian and performed Monte-Carlo simulations on relaxors, by considering the random field theory. They found that the higher the random field is, the lower the freezing temperature becomes. The influence of the random field on the hysteresis and domain size were also studied. For the best knowledge of authors, there is no model for the study of domain structure on a larger scale and of the electromechanical coupling effect in relaxors.

Phase-field approaches have been successfully applied to model the polarization switching in conventional ferroelectrics (Chen, 2002; Kamlah and Tsakmakis, 1999; Kontsos and Landis, 2009;
Landis, 2004; Liu et al., 2013; Münch et al., 2011; Schrade et al., 2007; Su et al., 2015; Wang et al., 2004; Xiao et al., 2005; Xu et al., 2010b) In particular, Su and Landis (2007) proposed a phase-field model for ferroelectrics based on the microforce theory (Gurtin, 1996). Thereby the total polarization is treated as the order parameter. Recently, Keip et al. (2015) extend the phase-field (Schrade et al., 2014, 2015) simulation of ferroelectric single crystal into composites and polycrystals by homogenization. These models have become a useful tool in the study (Wang and Zhang, 2007) and design (Liu and Wang, 2015) of domain structures in ferroelectrics. However, due to the complexity of relaxors, the phase-field theory has not been applied in this field.

In this paper, we propose for the first time an electromechanical phase-field model for simulation of domain structures in relaxors. A continuum phase-field model is first established in the framework of thermodynamics and the microforce theory. Particularly, static random field is introduced, and its influence on the electrostatic energy is considered. As a result, the evolution equations of the polarization and the constitutive equations are modified accordingly. Following the random field theory (Glinchuk and Farhi, 1996), a Gaussian distribution generator is employed to produce the local random electric field. The Gaussian distribution is generated based on the Box-Muller formula (Box and Muller, 1958). Similar to our previous phase-field model for ferroelectrics (Xu et al., 2010a), the spontaneous polarization, instead of the total polarization, is taken as the order parameter, and the domain wall energy as well as the domain wall thickness appears explicitly as parameters in the model. This phase-field model is implemented in the finite element method (FEM) for its merit of robustness and flexible boundary condition. The model and its implementation are used to analyze the influence of random field on the macroscopic response and domain evolution under mechanical and/or electrical stimulation.

The phase-field model and FEM implementation are elaborated in Section 2 and 3, respectively, whereas Section 4 presents the simulation results based on the model, in order to reveal the influence of random field. In Section 4.1 the dependency of the equilibrium domain structure on the variance of the random field distribution is first revealed by numerical results. The domain structure evolution under bipolar electric field is demonstrated in Section 4.2, along with the dielectric and butterfly hysteresis. Section 4.3 is concerned with ferroelastic switching of the domains in relaxors. Finally the electromechanical loading is considered in Section 4.4. Results
show that the model can predict characteristic features of relaxors, such as domain miniaturization, decreasing of remnant polarization and increased electromechanical effect.

2. Phase-field model

2.1. Governing equations

Denote the space occupied by a relaxor ferroelectric body and its boundary by $B$ and $\partial B$, respectively. At each point in $B$ the mechanical equilibrium

$$\sigma_{ij, i} + f_j = 0 \quad \text{in} \quad B \tag{1}$$

must be satisfied, where $\sigma_{ij}$ is the Cauchy stress in the Cartesian space, and $f_j$ is the body force in the $j^{th}$ direction. Hereafter, the Einstein notation is implied, the Latin symbols $i, j, k, l$ run from 1 to 3, and the comma in the subscript represents the spatial partial derivative. By assuming small deformation, the following strain measures are used

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \tag{2}$$

where $u_i$ the displacement vector. For the point at the boundary surface, displacement or force boundary conditions can be applied,

$$u_i = \bar{u}_i \quad \text{on} \quad \partial B_u, \tag{3a}$$

$$\sigma_{ij} n_i = \bar{t}_j \quad \text{on} \quad \partial B_{\sigma}, \tag{3b}$$

where $n_i$ is the normal vector on the surface, and $t_j$ the traction vector. Moreover, $\bar{u}_i$ denotes the displacement prescribed on the surface part $\partial B_u$, while $\bar{t}_j$ denotes the traction on the surface part $\partial B_{\sigma}$.

The electric quantities such as electrical displacement $D_i$ and volume charge density $q$ are governed by the quasi-static equilibrium derived from Maxwell equations, i.e.,

$$D_{i,i} = q \quad \text{in} \quad B. \tag{4}$$

The electric field can be given as

$$E_i = -\phi_{,i}. \tag{5}$$
in which $\phi$ is the electric potential. The boundary conditions for the electric quantities can be given as

\begin{align}
\phi &= \bar{\phi} \quad \text{on} \quad \partial B_\phi, \\
D_i n_i &= -\bar{\omega} \quad \text{on} \quad \partial B_D,
\end{align}

(6a)  
(6b)

where $\bar{\phi}$ is the surface charge density applied on the surface part $\partial B_\phi$, and $\bar{\omega}$ is the surface charge density applied on the surface part $\partial B_D$.

The microforce theory, originally proposed by Gurtin (1996), is utilized for the derivation of the polarization evolution equation in the following subsection. Thereby the balance law of the microforces is introduced first. In the aimed phase field, the order parameter is chosen to the spontaneous polarization $P_i$. The microforce system associated with $P_i$ is characterized by a generalized stress tensor $\xi_{ij}$ together with related body forces $\pi_i$ and $\gamma_i$ that represent, respectively, the internal and external forces distributed over the volume $B$. Given an arbitrary control volume $\mathcal{R}$ (subregion of $B$), with $n_i$ the unit normal vector on the surface $\partial \mathcal{R}$, the microforce balance holds,

\[ \int_{\partial \mathcal{R}} \xi_{ji} n_j dS + \int_{\mathcal{R}} \pi_i dv + \int_{\mathcal{R}} \gamma_i dv = 0. \]

(7)

By using the Gauss law and noting that Eq. (7) should hold for any arbitrary volume, it yields

\[ \xi_{ji, j} + \pi_i + \gamma_i = 0. \]

(8)

On the boundary, there lays

\[ \xi_{ji} n_j = \bar{\mu}_i \quad \text{on} \quad \partial \mathcal{R}, \]

(9)

where $\bar{\mu}_j$ is the surface microforce applied on the surface part $\partial \mathcal{R}$. In the next section, we will use these microforces to derive the constitutive and the evolution equations.

2.2. Constitutive and evolution equations

In order to get the constitutive relations and evolution equation, thermodynamic relations are considered. According to the second law of thermodynamics, under the isothermal condition, the change rate in the Helmholtz free energy in the control volume should not be greater than the external power expended on the control volume, i.e.,

\[ \{ \int_B \mathcal{H} dv \} \leq W^{ext}. \]

(10)
The free energy \( \mathcal{H} \) is a functional of \( \varepsilon_{ij}, D_i, P_i, P_{i,j} \) and high order items of these parameters. To simplify the model and not lose generality, one can write \( \mathcal{H} \) as

\[
\mathcal{H} = \mathcal{H}(\varepsilon_{ij}, D_i, P_i, P_{i,j}).
\]  

(11)

Applying Taylor expansion and retaining only the first order term, the left hand of Eq. (10) can be written as

\[
\left\{ \int_B \mathcal{H} dv \right\} = \left( \int_B \frac{\partial \mathcal{H}}{\partial \varepsilon_{ij}} \dot{\varepsilon}_{ij} + \int_B \frac{\partial \mathcal{H}}{\partial D_i} \dot{D}_i + \int_B \frac{\partial \mathcal{H}}{\partial P_i} \dot{P}_i + \int_B \frac{\partial \mathcal{H}}{\partial P_{i,j}} \dot{P}_{i,j} \right) dv.
\]  

(12)

\( W^{ext} \) is the power done by external resources, and have components of surface power and body power, and corresponding power to \( P_i \) can be present by microforce mentioned above,

\[
W^{ext} = \int_B (f \dot{u}_i + \phi \dot{q}_i + \gamma \dot{P}_i) dv + \int_{\partial B} (\bar{t} \dot{u}_i + \phi \dot{\bar{\omega}} + \bar{\mu} \dot{P}_i) ds.
\]  

(13)

What should be noticed is that the internal force \( \pi_i \) do not contribute to the external power \( W^{ext} \).

After the Legendre transformation, the electric enthalpy \( \mathcal{H}_2(\varepsilon_{ij}, E_i, P_i, P_{i,j}) \) can be derived as

\[
\mathcal{H}_2 = \mathcal{H} - E_i D_i.
\]

Inserting Eq. (12) Eq. (13) and Eq. (8) into Eq. (10) and applying the divergence theorem, one arrives at

\[
\int_B \left\{ (\sigma_{ji} - \frac{\partial \mathcal{H}_2}{\partial \varepsilon_{ij}}) \dot{\varepsilon}_{ij} - (D_i + \frac{\partial \mathcal{H}_2}{\partial E_i}) \dot{E}_i - (\frac{\partial \mathcal{H}_2}{\partial P_i} + \pi_i) \dot{P}_i + (\xi_{ji} - \frac{\partial \mathcal{H}_2}{\partial P_{i,j}}) \dot{P}_{i,j} \right\} dv \geq 0.
\]  

(14)

From Eq. (14) one can obtain three constitution relations

\[
\sigma_{ji} = \frac{\partial \mathcal{H}_2}{\partial \varepsilon_{ij}}, \quad D_i = -\frac{\partial \mathcal{H}_2}{\partial E_i}, \quad \xi_{ji} = \frac{\partial \mathcal{H}_2}{\partial P_{i,j}},
\]  

(15)

and one inequality

\[
(\frac{\partial \mathcal{H}_2}{\partial P_i} + \pi_i) \dot{P}_i \leq 0
\]  

(16)

due to dissipative process.

To ensure the inequality one can assume that

\[
\frac{\partial \mathcal{H}_2}{\partial P_i} + \pi_i = -\beta \dot{P}_i,
\]  

(17)

where the non-negative constant \( \beta \) indicates the mobility parameter. By applying the balance equation of microforce Eq. (8), one can rewrite Eq. (17) in the following form

\[
\beta \dot{P}_i = -\frac{\partial \mathcal{H}_2}{\partial P_i} + \xi_{ji,j} + \gamma_i = -\frac{\partial \mathcal{H}_2}{\partial P_i} + \left( \frac{\partial \mathcal{H}_2}{\partial P_{i,j}} \right)_{,j} + \gamma_i.
\]  

(18)
2.3. Electrical enthalpy

In our model, the electrical enthalpy consists of five parts, i.e.,

\[ \mathcal{H}_2 = \mathcal{H}_{ela} + \mathcal{H}_{ele} + \mathcal{H}_{coup} + \mathcal{H}_{sep} + \mathcal{H}_{grad}, \]  

(19)

in which \(\mathcal{H}_{ela}\), \(\mathcal{H}_{ele}\), \(\mathcal{H}_{coup}\), \(\mathcal{H}_{sep}\) and \(\mathcal{H}_{grad}\) represent elastic energy density, electrical energy density, electromechanical coupling energy density, domain separation energy density and interface energy density, respectively. The domain separation energy density resembles the Landau-Devonshire free energy, and the interface energy density characterizes to the energy stored in the domain wall by a function of the gradient of the order parameter. These energy terms take the follow specific form,

\[
\begin{align*}
\mathcal{H}_{ela} &= \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \\
\mathcal{H}_{ele} &= - \frac{1}{2} k_{ij} E_i E_j - P_i E_i \\
\mathcal{H}_{coup} &= - b_{ijk} \varepsilon_{ij} E_k \\
\mathcal{H}_{sep} &= \beta_1 (G, \lambda) \psi (P_i) \\
\mathcal{H}_{grad} &= \beta_2 (G, \lambda) P_{i,j} P_{i,j}.
\end{align*}
\]

(20)

The quantities induced in the last equations are explained in the following. Firstly, \(\varepsilon_{ij}\) stands for the elastic strain, which is further given by the difference between the mechanical strain \(\varepsilon_{ij}\) and the spontaneous strain \(\varepsilon_{ij}^0\), i.e., \(\varepsilon_{ij} = (\varepsilon_{ij} - \varepsilon_{ij}^0 (P))\). The spontaneous strain \(\varepsilon_{ij}^0 (P)\) is caused by the spontaneous polarization. According to Huo and Jiang (1997),

\[
\varepsilon_{ij}^0 (P) = \frac{3}{2} \varepsilon_{sat} \frac{\sqrt{P_i P_j}}{P_{0}} (n_i n_j - \frac{1}{3} \delta_{ij}),
\]

(21)

where \(\delta_{ij}\) is the Kronecker delta, \(n_i\) the unit vector of \(P\), \(\varepsilon_{sat}\) the maximum remnant strain, and \(P_{sat}\) the maximum remnant polarization. The stiffness tensor \(c_{ijkl}\) and the permittivity tensor \(k_{ij}\) are assumed to be independent of the polarization. For the piezoelectric tensor \(b_{ijk}\), we used the representation (Kamlah, 2001)

\[
b_{ijk} (P) = \frac{\sqrt{P_i P_j}}{P_{0}} \left\{ d_{33} n_i n_j n_k + d_{31} (\delta_{ij} - n_i n_j) n_k \right\} + \frac{1}{2} d_{15} \left\{ (\delta_{ki} - n_k n_i) n_j + (\delta_{kj} - n_k n_j) n_i \right\},
\]

(22)
in which \(d_{33}, d_{31}, d_{15}\) are linear piezoelectric constants at the poled state. The coefficient functions \(\beta_1\) and \(\beta_2\) are related to the domain wall energy \(G\) and the domain wall thickness \(\lambda\) (Xu et al., 2010b). The function \(\psi(P_i)\) is a Landau-Devonshire free energy function with potential wells. The 2-dimensional form of \(\psi\) is shown in section 3.2.

It should be noted that the electric field has three contributions

\[
E_i = E_i^d + E_i^{ext} + E_i^{random},
\]

where \(E_i^d\) represents the depolarization field, \(E_i^{ext}\) the applied electric field, and \(E_i^{random}\) the random field induced by chemical disorder. In the model, \(E_i^{random}\) is assumed to be static and obeys the Gaussian distribution \(\mathcal{N}(0, \Delta)\). The expectation of the random field Gaussian distribution is set to be zero, while the variance of the distribution is denoted by \(\Delta\). The numerical generation is explained in section 3.2. The two contributions \(E_i^d\) and \(E_i^{ext}\) are calculated from the electric potential \(\phi\) by Eq. (5). To be in accordance with Eq. (5), the sum of \(E_i^d\) and \(E_i^{ext}\) is denoted as \(E_i^\phi\).

It reveals

\[
\begin{align*}
E_i &= E_i^\phi + E_i^{random} \\
E_i^\phi &= \phi_i = E_i^d + E_i^{ext} \\
E_i^{random} &= \mathcal{N}(\mu, \Delta).
\end{align*}
\]

Substituting Eqs. (24) into Eqs. (20) and then (19), one gets the expression of \(\mathcal{H}_2\),

\[
\mathcal{H}_2 = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} k_{ij} (E_i^\phi + E_i^{random}) (E_j^\phi + E_j^{random})
\]

\[
- P_i (E_i^\phi + E_i^{random}) - b_{ijk} \varepsilon_{ij} (E_k^\phi + E_k^{random})
\]

\[
+ \beta_1 (G, \lambda) \psi(P_i) + \beta_2 (G, \lambda) P_{i,j} P_{i,j}.
\]

Inserting the expression into Eqs. (15) and (18) and assuming \(\gamma_i = 0\), the constitutive equations and the evolution equation can be rewritten as,

\[
\begin{align*}
\sigma_{ij} &= c_{ijkl} \varepsilon_{kl} - b_{ijk} E_k^\phi - b_{ijk} E_k^{random} \\
D_i &= k_{ij} E_j^\phi + k_{ij} E_j^{random} + P_i + b_{ijk} \varepsilon_{jk} \\
\beta \dot{P}_i &= E_i^\phi + E_i^{random} - \beta_1 \frac{\partial \psi}{\partial P_i} - \beta_2 \frac{\partial P_{k,l} P_{k,l}}{\partial P_i} + 2 \beta_2 (P_{i,j})_{i,j}.
\end{align*}
\]
3. Numerical implementation

3.1. Weak form

The governing equations for the phase-field model are Eq. (1)-Eq. (9), Eq. (26). To obtain solutions to these equations, the finite element method is adopted. Mechanical displacement, electric potential and spontaneous polarization are chosen as the degrees of freedom, by following the choice of electrical enthalpy as the energy type. The weak form of the field equation can be given as

\[\int_B \beta \dot{P}_i \delta P_i \, dv + \int_B (\sigma_{ji} \delta e_{ij} - D_i \delta E_i + \eta_i \delta P_i + \xi_{ij} \delta P_{i,j}) \, dv = \int_B (f_i \delta u_i - q \delta \phi + \gamma_i \delta P_i) \, dv + \int_{\partial B} (\bar{t}_i \delta u_i - \bar{\omega} \delta \phi + \bar{\mu}_i \delta P_i) \, ds.\]  

(27)

The left-hand of the equation represents the generalized virtual strain energy. The first part of the right-hand stands for the virtual work done in the body, and the second part for the virtual work done on the boundary. The stresses, electric displacements and microforces can be derived from Eqs. (26).

By considering that \(u_i, E_i, P_i\) are the independent variables, one obtains from Eq. (27) the following weak forms,

\[-\int_B \sigma_{ji} \delta e_{ij} \, dv + \int_B f_i \delta u_i \, dv + \int_{\partial B} \bar{t}_i \delta u_i \, ds = 0\]

\[-\int_B D_i \delta E_i \, dv + \int_B q \delta \phi \, dv + \int_{\partial B} \bar{\omega} \delta \phi \, ds = 0\]

\[-\int_B \beta \dot{P}_i \delta P_i \, dv - \int_B (\frac{\partial H}{\partial P_i} \delta P_i + \frac{\partial H}{\partial P_{i,j}} \delta P_{i,j}) \, dv + \int_{\partial B} \bar{\mu}_i \delta P_i \, ds = 0.\]  

(28)

3.2. 2-Dimensional case

The weak form of the field equation is suitable for 3-dimensional cases. However, it is adequate to explore the domain evolution in 2-dimensional, since in the present paper merely qualitative study of the relaxor behavior is intended. Meanwhile, this saves calculation time. It is non-trivial to reduce the 3-dimensional rhombohedral system into a 2-dimensional one, while the tetragonal and the orthorhombic system can be represented in two dimensions by limiting the allowed polarization directions to one principal plane. For tetragonal system, polarization has six possible orientations.
In 2-dimensional case, we focus on one plane with 4 possible orientations, through which both 90° and 180° domain switching can be presented.

The Landau-Devonshire free energy function $\psi$ in 2-dimensional case has a simple form. Here we only chose parts of the Taylor polynomial and expand $\psi$ to the sixth order,

$$
\psi = a_1 + a_2(P_1^2 + P_2^2) + a_3(P_1^4 + P_2^4) + a_4(P_1^2 P_2^2) + a_5(P_1^6 + P_2^6).
$$

The parameters $a_1$ to $a_5$ are chosen properly to allow 90° and 180° domain switching. Meanwhile $\psi$ must guarantee that it takes local minimum at $(\pm P_0,0)$ and $(0,\pm P_0)$. The five parameters used in the simulations are derived from the coefficients published in Bell and Cross (1984).

The discretization of 2-dimensional model is achieved by four-node linear elements. The spontaneous polarization $\mathbf{P}(P_1, P_2)$, the electric potential $\phi$, and mechanical displacement $\mathbf{u}(u_1, u_2)$ are taken as independent variables. Therefore, each node has five degrees of freedom

$$
\mathbf{d}^I = [P_1^I, P_2^I, \phi^I, u_1^I, u_2^I]^T,
$$

in which the superscript $I$ indicates the element nodal number and the underlined bold symbol denotes a matrix. In this section, matrix instead of index notation is used to clearly shows the components of the tensor. A Voigt notation is used in the discretized equations. Detailed components of the matrix can be found in the Appendix. By introducing the shape functions, the values within the element can be expressed by nodal values,

$$
\begin{cases}
\mathbf{u} = \sum_I N^{u}_I \mathbf{u}^I; & \quad \mathbf{\delta u} = \sum_I N^{\delta u}_I \mathbf{\delta u}^I; \\
\phi = \sum_I N^{\phi}_I \phi^I; & \quad \mathbf{\delta \phi} = \sum_I N^{\delta \phi}_I \mathbf{\delta \phi}^I; \\
\mathbf{P} = \sum_I N^p_I \mathbf{P}^I; & \quad \mathbf{\delta P} = \sum_I N^{\delta p}_I \mathbf{\delta P}^I; \\
\dot{\mathbf{P}} = \sum_I N^{\dot{p}}_I \dot{\mathbf{P}}^I.
\end{cases}
$$

The strain, the electric field and the polarization gradient can be calculated by introducing corresponding derivative matrices, and then the stress and the electric displacement can be obtained.
through Eqs. (26),
\[
\begin{align*}
\varepsilon &= \sum_l B^t_l u^l; \quad \varepsilon^e = \varepsilon - \varepsilon^0(P); \quad E = - \sum_l B^t_l \phi^l; \quad \nabla P = \sum_l B^t_l P^l; \\
\sigma &= C \varepsilon - b^T E; \quad D = b \varepsilon + k E + P.
\end{align*}
\]
(31)

From Eqs. (28), the element residuals can be given by the integration over the element area \(B^e\):
\[
\begin{align*}
R_I^u &= - \int_{B^e} B_{Iu}^T \sigma dv \\
R_I^\phi &= - \int_{B^e} B_{I\phi}^T D dv \\
R_I^P &= - \int_{B^e} \{ \beta N_{IP}^T P + N_{IP}^T \partial H \partial P + B_{I\phi}^T \partial H \partial \nabla P \} dv,
\end{align*}
\]
(32)

where
\[
\begin{align*}
\partial H \partial P &= - \partial \varepsilon^T \partial P - (\varepsilon^0 \partial \phi^T \partial P + 1)(E^\# + E_{\text{random}}) + \beta_1 \partial \psi \partial P \\
\partial H \partial \nabla P &= \beta_2 \nabla P.
\end{align*}
\]
(33)

The random field \(E_{\text{random}}\) has two independent components, which are subject to the same Gaussian distribution. According to Box and Muller (1958), the following formula is used
\[
\begin{align*}
E_{\text{random}}^x &= \Delta^2 (-2 \log U_1)^{\frac{1}{2}} \cos 2\pi U_2 + \mu \\
E_{\text{random}}^y &= \Delta^2 (-2 \log U_1)^{\frac{1}{2}} \sin 2\pi U_2 + \mu.
\end{align*}
\]
(34)

Hereby \(U_1, U_2\) are two independent random numbers which obeys the standard uniform distribution, while \(\Delta\) and \(\mu\) govern the variance and the expectation of the Gaussian distribution. The stiffness matrix can be calculated thereafter by
\[
\begin{align*}
K_{uu}^{IJ} &= - \frac{\partial R_I^u}{\partial u^J}; \quad K_{u\phi}^{IJ} = - \frac{\partial R_I^u}{\partial \phi^J}; \quad K_{uP}^{IJ} = - \frac{\partial R_I^u}{\partial P^J}; \\
K_{\phi u}^{IJ} &= - \frac{\partial R_I^\phi}{\partial u^J}; \quad K_{\phi\phi}^{IJ} = - \frac{\partial R_I^\phi}{\partial \phi^J}; \quad K_{\phi P}^{IJ} = - \frac{\partial R_I^\phi}{\partial P^J}; \\
K_{P u}^{IJ} &= - \frac{\partial R_I^P}{\partial u^J}; \quad K_{P\phi}^{IJ} = - \frac{\partial R_I^P}{\partial \phi^J}; \quad K_{PP}^{IJ} = - \frac{\partial R_I^P}{\partial P^J}.
\end{align*}
\]
(35)

For the only time-dependent term \(\dot{P}\), implicit backward Euler time integration method can be
adopted. The non-zero damping matrix $D^{IJ}_{PP}$ can be calculated by

$$
\begin{cases}
\dot{P} = \frac{P^{I+\tau} - P^I}{\tau} \\
D^{IJ}_{PP} = -\frac{\partial R^I_P}{\partial P^J} 
\end{cases}
$$

(36)

where $\tau$ is the time step, and $t$ the current time. With stiffness and damping matrix, the element iteration matrix $S$ can be assembled, in which $S^{IJ}_{PP} = K^{IJ}_{PP} + \frac{1}{\tau}D^{IJ}_{PP}$. For a given sets of nodal values at time $t$, the non-linear algebraic equations can be solved by the Newton-Raphson method. The model is implemented as a user element in the software FEAP (Taylor, 2014).

4. Simulation results and discussion

Four cases are simulated based on the relaxor model presented above. Firstly, the equilibrium domain configurations of a relaxor single crystal with different random fields are simulated. Secondly, the ferroelectric response under bipolar loading is analyzed. Domain evolution with various random fields shows different features. Thirdly, pure mechanical loading is applied, and the influence of random field is demonstrated. Finally, domain evolution under electromechanical loading is discussed. In all the simulations, the body force $f_i$ and charge $q$ are neglected. The parameters used in the simulations are listed in Table 1.

4.1. Equilibrium state of relaxor single crystal

Relaxation process of relaxors is firstly simulated based on this model. The size of the simulated sample is $100 \times 100$ nm$^2$, with mesh size of 1 nm. All the boundaries are traction-free and charge-free. Initial polarization distribution is assumed to be random.

One of the key factors which can influence the domain configuration is the local random field which obeys the Gaussian distribution $N(0, \Delta)$. In the simulation, the mean value of the random fields is set to be zero, to ensure that there is no macroscopic bias field. Thus, the variance $\Delta$ of the Gaussian distribution accounts for the strength of the local random field. Three values of $\Delta$, i.e., 1 kV/mm, 5 kV/mm and 10 kV/mm, are considered. The probability diagram is shown in Fig. 1a, while the random field distribution in the sample for the case $\Delta = 5$ kV/mm is shown in Fig. 1b.
It can be seen that although $\Delta$ is 5 kV/mm, most elements has the random field below 5 kV/mm. The maximum value can reach as high as 10 kV/mm.

| Parameter           | Signal | Value       | Unit   |
|---------------------|--------|-------------|--------|
| Elastic stiffness moduli | $C_{11}$ | $2.11 \times 10^{11}$ | N/m$^2$ |
|                     | $C_{12}$ | $1.07 \times 10^{11}$ | N/m$^2$ |
|                     | $C_{33}$ | $5.62 \times 10^{10}$ | N/m$^2$ |
| Piezoelectric moduli | $d_{31}$ | $-3.88$ | C/m$^2$ |
|                     | $d_{33}$ | $5.48$ | C/m$^2$ |
|                     | $d_{51}$ | $32.6$ | C/m$^2$ |
| Dielectric permittivity | $k_{11}$ | $1.75 \times 10^{-7}$ | F/m |
|                     | $k_{22}$ | $1.75 \times 10^{-7}$ | F/m |
| Domain wall width  | $\lambda$ | $1$ | nm |
| Domain wall energy | $G$ | $0.7 \times 10^{-3}$ | Jm$^2$/C$^2$ |
| Mobility            | $\beta$ | $7 \times 10^{-6}$ | A/Vm |
| Eigenpolarization   | $P_0$ | $0.31$ | C/m$^2$ |
| Eigenstrain         | $\varepsilon_0$ | $0.262$ | % |

**Table 1.** Parameters used in the simulations.

The equilibrium domain configuration for different values of $\Delta$ can be found in Fig. 2. In Fig. 2a-d four colors represent four polarization orientations, respectively. Both 90° and 180° domain walls are visible. Due to the free-force boundary condition, polarization at the edge of the body tends to point parallel to the boundary. By comparing Figs. 2a-d, it can be concluded that the domain size decreases with increasing $\Delta$. Figure 2a is for the case $\Delta = 0$, namely for a conventional ferroelectric without random field. As random field strength is increased, the material behavior becomes more relaxor-like. When $\Delta$ is increased to 5 kV/mm, the domain distribution becomes much randomized, as shown in Fig. 2d. The size of the domain becomes smaller and the shape becomes more twisted.

The domain configuration can be compared with experimental results. In the work by Shvarts-
The surface polarization status of commercial relaxor material Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBNx) at 293 K was studied by Piezoresponse Force Microscopy (PFM). The vertical PFM characterization mode shows the polar structures at the surface of the sample. Fig. 2e and 2f are two PFM images, which demonstrate different domain structures on the surfaces of the sample SBN61 and SBN75, respectively. Thereby, tri-modal color code is used: white stands for up, red for down, and yellow for in-plane. It can be seen that for higher Sr content, the domain size becomes smaller, and the domain boundaries jag more. Comparison between the simulated equilibrium domain structures with the PFM images shows that, Fig. 2b is close to Fig. 2e, while Fig. 2c appears similar to Fig. 2f. It can thus be suggested that the Sr content is positively correlated to the strength of the random field.

4.2. Ferroelectric response

The influence of random field on the macroscopic behavior of relaxor ferroelectrics can be characterized by polarization and strain hysteresis. Here 6 kV/mm bipolar loading is adopted for simulation. Gaussian distribution variance of random field $\Delta$ varies from 0 kV/mm to 50 kV/mm.

In order to reveal the influence of the random field, dielectric hysteresis for the two cases $\Delta =$

![Probability diagram of the local random field distributions with different $\Delta$.](a)

![Random field distribution within the sample for the case of $\Delta= 5$ kV/mm.](b)

Fig. 1. (a) Probability diagram of the local random field distributions with different $\Delta$. (b) Random field distribution within the sample for the case of $\Delta= 5$ kV/mm. Legend unit: V/m.
Fig. 2. (a-d) Equilibrium domain configuration for four cases with different Gaussian distribution variances: (a) $\Delta = 0$ kV/mm; (b) $\Delta = 1$ kV/mm; (c) $\Delta = 5$ kV/mm; (d) $\Delta = 10$ kV/mm. Four colors represent four polarization orientations of domains: yellow-left; green-right; red-top and blue-down. PFM images observed on a c-cut SBN single crystals with various compositions: (e) SBN61 and (f) SBN75. The PFM images are taken from the paper by Shvartsman et al. (2008).
5 kV/mm and 10 kV/mm are compared in Fig. 3. For small $\Delta = 5$ kV/mm, the hysteresis has a rectangular shaped hysteresis, which is typical for a ferroelectric single crystal. Whereas, for large $\Delta = 10$ kV/mm, the hysteresis becomes very slim. Particularly, the remnant polarization $P_r$ almost vanishes. In order to examine this decrease of $P_r$, snapshots of domain structure and electric potential distribution during the poling are compared in Fig. 3. Starting from initially random distribution (Point 1), the polarization is fully poled at maximum field state (Point 2) for both cases. It can be explained by the fact that for both cases the applied electric field is stronger than the local fields at most sites. However, the domain structures at the remnant state (Point 3) are rather different from each other. When the applied field decreases, the influence of random field becomes obvious. Specifically, for $\Delta = 5$ kV/mm, the polarization distribution remains almost unchanged, because the potential barrier prevents the domain switching. However, if the local random field is high enough, e.g. $\Delta = 10$ kV/mm, this barrier can be overcome. Thus the polarization distribution becomes randomized again, which explains the trivial remnant polarization.

In Fig. 4 the influence of the random fields on the dielectric and strain hysteresis is demonstrated in more details. The calculated hysteresis can be classified into three types. If $\Delta$ is less than 5 kV/mm, the remnant polarization ($P_r$) is close to the maximum polarization, while the coercive field ($E_c$) has a relatively high value of 4.5 kV/mm. These two phenomena are commonly found in conventional ferroelectric materials. Moreover, when external field reaches the critical value for the domain switching, the polarization orientation changed simultaneously, which leads to a steep slope at the switching point. This is the typical feature for single crystal (Park and Shrout, 1997). After domain switching process, both polarization and strain is in proportion to the external field.

For the sample with moderate random field, e.g. $\Delta = 10$ kV/mm and $\Delta = 15$ kV/mm, $P_r$ decreases with the increase of random field. The hysteresis feature is less obvious, compared with the cases with lower random field. Due to the lose of hysteresis, the remnant stain becomes smaller, and the difference between maximum stain and remnant stain becomes larger. Hence, the existence of random field makes the high-field piezoelectric coefficient (maximum strain divided by maximum field) larger. Furthermore, strain changes almost quadratically with the applied field, which indicates a typical electrostrictive response.

For the sample with very larger random field, e.g. 50 kV/mm, the material shows a dielectric
Fig. 3. Dielectric hysteresis, snapshots of domain structure and electrical potential distribution for two different cases: $\Delta = 5 \text{ kV/mm}$ (left) and $\Delta = 10 \text{ kV/mm}$ (right).
feature and exhibit a nearly linear response to the external field. The random field in this case is so high that external field has little influence on the polarization distribution. The polarization direction is determined by the local random field distribution, and stays unchanged during the loading.

From the discussion above, a short conclusion can be drawn that with the increase of random field, $P_r$ decreases, the hysteresis effect vanishes gradually, and the material behavior changes from conventional ferroelectric to relaxor type.

![Fig. 4.](image)

**Fig. 4.** (a) Polarization hysteresis and (b) strain hysteresis under bipolar loading for different cases of random field variance.

4.3. Ferroelastic response

In this section the domain switching induced by pure mechanical loading is studied, and the effect of the random field on this response is revealed. Figure 5 shows the evolution of the domain structure and of the stress distribution in a sample under linearly increased stretch up to 0.6% in the vertical direction. Two cases of random fields $\Delta = 1 \, \text{kV/mm}$ and $5 \, \text{kV/mm}$ are considered. Charge-free boundary conditions are prescribed.

In the case of low random field $\Delta = 1 \, \text{kV/mm}$, the initially random distributed polarization vectors tend to align along the stretching direction, as it is demonstrated in Fig. 5a-c. Domains with vertical polarization become larger. Due to the constrain of charge-free boundary conditions, domain structure with multi vertices is formed at the end. This mechanical-induced domain
switching can also be identified by $\sigma$-$\varepsilon$ curve shown in Fig. 5g. The slope of the curve decreases during the stretching loading, which indicates that the domain switching happens in this range. The slope then goes back to its original value after domain switching process is accomplished. It can be explained by the assumption in the model that the stiffness tensor is independent of polarization state. During the unloading process, the slope of the $\sigma$-$\varepsilon$ curve remains constant. Hence the remnant strain emerges, with the value of about 0.1%. This result is close to the experimental measurement on the commercial ferroelectric ceramic PIC 151 (Alatsathianos, 2000).

In the sample with high random field $\Delta = 5 \text{ kV/mm}$, the coarsening of domain is not visible, and the tendency of the vertical polarization is not so obvious, as it can be seen in Fig. 5d-f. Meanwhile, there is hardly slope change of the $\sigma$-$\varepsilon$ curve shown in Fig. 5g. It indicates that there is no apparent mechanical-induced domain switching. The random field counteracts the influence of mechanical loading on polarization switching. Similar phenomenon can be found in the case of compression loading, as it can been seen from the simulated domain structures and the stress-strain curve shown in Fig. 6.

![Fig. 5.](image)

**Fig. 5.** (a-f) Domain structure evolution under uniaxial tensile loading. (g) Mechanical stress v.s. strain curves.
4.4. Electromechanical loading

The hysteresis behavior of mechanically assisted bipolar poling on relaxors is studied. For each of the two random fields with $\Delta = 2.3 \text{ kV/mm}$ and $7.5 \text{ kV/mm}$, three loading scenarios are simulated: 1) only bipolar electric loading, 2) bipolar electric loading combined with mechanical stretching, 3) bipolar electric loading combined with mechanical compression. As illustrated in Figs. 7a and 7b, mechanical loading in the last two scenarios are applied first along the vertical direction. The electric bipolar loading is then applied in the same direction, after the mechanical loading reached a constant. The maximum compression/stretch is 0.6%, and the amplitude of the electric field is 6 kV/mm.

The three hysteresis of the different loading scenarios shown in Fig. 8a are for the random field case $\Delta = 2.3 \text{ kV/mm}$. For this relatively low random field, the polarization at maximum field saturates at all the three loading scenarios, and the polarization is fully poled. However, the remnant states of the compressed and the stretched sample, marked as point 1 and point 2 in Fig. 8a, are rather different, after the external field is removed. It can be seen that the remnant polarization of the compressed sample is much less than that of the stretched one. This feature

![Fig. 6.](image)

Fig. 6. (a-f) Domain structure evolution under uniaxial compression. (g) Mechanical stress v.s. strain curves.
can be well explained by the domain structure at the corresponding remnant states. The domain structure at the remnant state of the compressed sample is shown in Fig. 8c, while that of the stretched sample in Fig. 8d. It is clear that due to the compressive loading, part of the polarization is switched to the lateral directions, which leads to the drop of the remnant polarization, whereas in the stretched loading, the poled state is maintained. Moreover, $E_c$ of the compressed sample is much smaller than that of the stretched one. It can be simply explained by the switching energy criterion (Hwang et al., 1995). The positive mechanical work reduces the work needed from external field for switching. In other words, more energy is needed for compressed sample than for the stretched sample to switch the polarization. Similar results can be found in the work by Soh et al. (2006) on the electromechanical coupling problems of ferroelectrics. Their simulation results show that both $E_c$ and $P_r$ of compressed samples decrease.

In the case of a rather high random field $\Delta = 7.5 \text{ kV/mm}$, different features in these hysteresis are observed, as shown in Fig. 8b. The polarization of the compressed sample at the maximum electric field does not reach the saturation, because the imprint effect of the random field and the effect of the compression loading is strong enough to prevent part of the dipoles switching to the vertical direction. On the other hand, in the stretched sample, the driving force induced by the applied field and by the tensile loading overruns the imprint effect of the random electric field, and thus the polarization is fully poled. The domain structures at this state of the stretched and the compressed sample, shown in Fig. 8e and Fig. 8f, verify this argument. Moreover, not only the compressed sample, but also the free sample has a decreased rem polarization. It implies that the imprint effect of the random field is strong enough, so that part of the dipoles are switched back to the lateral directions. In the stretched sample, the imprint effect of random field is counteracted by the mechanical loading. It explains the large remnant polarization.

In summary, in relaxors the response of mechanically assisted poling can be rather complicated, since the imprint effect of the random field plays also an important role in the domain switching process, in addition to the mechanical loading and the applied electric field. Meanwhile, it can be suggested from these results that if large hysteresis is desired for application, the sample should be stretched along the direction of the applied field. On the other hand, if larger piezoelectric or inversed piezoelectric coefficients are desired, the sample is better to be compressed along
the field direction.

Fig. 7. (a) Illustration of the simulation setup; (b) Electric and mechanical loading history.

Fig. 8. Dielectric hysteresis for three loading scenarios for (a) the random field with $\Delta = 2.3$ kV/mm and (b) the random field with $\Delta = 7.5$ kV/mm. (c) Domain structure at the remnant state of the compressed sample (Point 1). (d) Domain structure at the remnant state Point 2 of the stretched sample (Point 2). (e) Domain structure at the maximum field of the compressed sample (Point 3). (f) Domain structure at the maximum field of the stretched sample (Point 4).
5. Concluding remarks

To conclude, a continuum phase-field model for relaxor ferroelectrics is constructed to simulate the domain structure evolution in relaxor ferroelectrics. Local random fields are introduced according to the random field theory, which can appropriately reflect the influence of chemical disorder in relaxors. The strength of the random field is controlled by the variance of the Gaussian distribution. The simulation results presented in section 4 and the comparison with experimental measurements demonstrate that this model can reproduce typical relaxor features, such as domain miniaturization, small remnant polarization and large piezoelectric response.

Under pure electric loading, domain size decreases and domain configuration is more twisted, as the random field becomes stronger. The remnant polarization decreases with the increase of random fields. Under pure mechanical loading, domains size also become smaller as random field increases, and the strain-induced domain switching can be prevented in the presence of larger random field. When bipolar loading is applied on a preloaded sample, the macroscopic properties such as remnant and maximum polarization can be modified. These results are in consistent with previous study on ferroelectric materials.

This model can be further applied, e.g. to study different relaxor materials by justifying parameters, particularly the variance of Gaussian distribution of random field ($\Delta$). Moreover, if combined with existing phase-field ferroelectric models, relaxor/ferroelectric composites can be simulated. Owing to the advantage of finite element method, structures with complex shapes can be presented.

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Appendix

The specific forms of the vectors and matrices in section 3.2 are given as follows:

\[
\mathbf{u} = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}, \quad \mathbf{P} = \begin{bmatrix} P_1 \\ P_2 \end{bmatrix}, \quad \mathbf{E} = \begin{bmatrix} E_1 \\ E_2 \end{bmatrix}, \quad \mathbf{D} = \begin{bmatrix} D_1 \\ D_2 \end{bmatrix}, \quad \mathbf{n} = \begin{bmatrix} n_1 \\ n_2 \end{bmatrix} = \begin{bmatrix} \frac{p_1}{\sqrt{p_1^2 + p_2^2}} \\ \frac{p_2}{\sqrt{p_1^2 + p_2^2}} \end{bmatrix},
\]

\[
\mathbf{\varepsilon} = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix} = \begin{bmatrix} u_{1,1} \\ u_{2,2} \\ 0.5(u_{1,2} + u_{2,1}) \end{bmatrix}, \quad \mathbf{\varepsilon}^0 = \begin{bmatrix} \varepsilon_1^0 \\ \varepsilon_2^0 \\ \varepsilon_3^0 \end{bmatrix}, \quad \mathbf{\varepsilon}^c = \begin{bmatrix} \varepsilon_1 - \varepsilon_1^0 \\ \varepsilon_2 - \varepsilon_2^0 \\ \varepsilon_3 - \varepsilon_3^0 \end{bmatrix},
\]

\[
\sigma = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix}, \quad \mathbf{C} = \begin{bmatrix} C_{11} & C_{12} & 0 \\ C_{12} & C_{22} & 0 \\ 0 & 0 & C_{33} \end{bmatrix}, \quad \mathbf{k} = \begin{bmatrix} k_{11} & 0 & 0 \\ 0 & k_{22} & 0 \\ 0 & 0 & k_{33} \end{bmatrix}, \quad \mathbf{b} = \begin{bmatrix} b_{111} & b_{122} & b_{112} \\ b_{211} & b_{222} & b_{212} \end{bmatrix},
\]

Here, subscripts 1 and 2 represents x and y directions in 2-dimensional plane, and Voigt notation is utilized. The specific forms of the deformation matrices are given below.

\[
\mathbf{B}_u^l = \begin{bmatrix} N_{1,l}^l & 0 \\ 0 & N_{2,l}^l \\ N_{1,l}^l & N_{2,l}^l \end{bmatrix}, \quad \mathbf{B}_\phi^l = \begin{bmatrix} N_{1,l}^l \\ N_{2,l}^l \\ N_{1,l}^l \\ N_{2,l}^l \end{bmatrix}, \quad \mathbf{B}_y^l = \begin{bmatrix} N_{1,l}^l & 0 \\ 0 & N_{2,l}^l \\ N_{1,l}^l & N_{2,l}^l \end{bmatrix},
\]

where \(N(x,y)^l\) is the shape function of node I. The final iteration matrix \(\mathbf{S}\) have the form of:

\[
\mathbf{S} = \begin{bmatrix} S^{11} & S^{12} & S^{13} & S^{14} \\ S^{21} & S^{22} & S^{23} & S^{24} \\ S^{31} & S^{32} & S^{33} & S^{34} \\ S^{41} & S^{42} & S^{43} & S^{44} \end{bmatrix},
\]

In each component in \(S^{ij}\),

\[
S^{ij} = \begin{bmatrix} S_{uu}^{ij} & S_{u\phi}^{ij} & S_{uP}^{ij} \\ S_{\phi u}^{ij} & S_{\phi\phi}^{ij} & S_{\phi P}^{ij} \\ S_{P u}^{ij} & S_{P\phi}^{ij} & S_{PP}^{ij} \end{bmatrix} = \begin{bmatrix} K_{uu}^{ij} & K_{u\phi}^{ij} & K_{uP}^{ij} \\ K_{\phi u}^{ij} & K_{\phi\phi}^{ij} & K_{\phi P}^{ij} \\ K_{P u}^{ij} & K_{P\phi}^{ij} & K_{PP}^{ij} + \frac{1}{2}D_{PP}^{ij} \end{bmatrix},
\]

24
where the tangent matrices are given by

\[
S_{\alpha u}^{IJ} = \int_{S^e} B_i^{I T} C B_j^{J} dS
\]

\[
S_{\alpha \phi}^{IJ} = \int_{S^e} B_i^{I T} b^T B_j^{J} dS
\]

\[
S_{a u}^{IJ} = -\int_{S^e} B_i^{I T} \left( C \frac{\partial \epsilon^0}{\partial P^j} + b^T \frac{\partial \epsilon^e}{\partial P^j} (E^\phi + E_{\text{random}})^T \right) dS
\]

\[
S_{a \phi}^{IJ} = \int_{S^e} B_i^{I T} b^T B_j^{J} dS
\]

\[
S_{\phi u}^{IJ} = -\int_{S^e} B_i^{I T} k B_j^{J} dS
\]

\[
S_{\phi \phi}^{IJ} = \int_{S^e} B_i^{I T} \left( \frac{\partial b}{\partial P} \epsilon^e + b \frac{\partial \epsilon^e}{\partial P} + 1 N^J \right) dS
\]

\[
S_{P u}^{IJ} = -\int_{S^e} N^I \left( \frac{\partial \epsilon^0}{\partial P^j} C + (E^\phi + E_{\text{random}}) \frac{\partial b}{\partial P} \right) B_j^{J T} dS
\]

\[
S_{P \phi}^{IJ} = \int_{S^e} N^I \left( \frac{\partial \epsilon^0}{\partial P^j} + \frac{\partial \epsilon^e}{\partial P^j} b + 1 \right) B_j^{J T} dS
\]

\[
S_{P \phi}^{IJ} = -\int_{S^e} \left\{ N^I \left( \frac{\partial^2 \epsilon^0}{\partial P \partial P^j} - \frac{\partial \epsilon^0}{\partial P} \frac{\partial \epsilon^0}{\partial P^j} - \frac{\partial \epsilon^e}{\partial P} \frac{\partial \epsilon^e}{\partial P^j} \right) - N^I \left( \frac{\partial \epsilon^0}{\partial P^j} \frac{\partial b}{\partial P} + \epsilon^e \frac{\partial^2 b}{\partial P \partial P^j} + E \frac{\partial^2 \psi}{\partial P \partial P^j} + \beta \frac{\partial^2 \psi}{\partial P \partial P^j} - \frac{\beta^2 \epsilon^0}{\partial P \partial P^j} \right) (E^\phi + E_{\text{random}})^T \right\} dS.
\]
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