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Three-dimensional nonlocal models of deformable ferroelectrics: A thermodynamically consistent approach

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ABSTRACT

Within the framework of continuum thermodynamics, the paper develops a scheme for the study of piezo-ferroelectric materials undergoing large deformations. The ferroelectric polarization is decomposed into the sum of a reversible and a residual part which is considered as an independent variable. The modeling of the constitutive properties is made simpler by using referential, Euclidean invariant quantities. Constitutive functions depend on a set of variables that includes their time derivatives and gradients, and therefore must be consistent with a nonlocal statement of the second law of thermodynamics where the entropy production is represented as the sum of a non-negative supply and a flux. Both terms are also assigned by means of constitutive functions. A new and quite general model relating the residual-polarization rate and the 'electric Gibbs free entropy' is established. This thermodynamic potential is modeled according to the Landau-Devonshire approach and appropriate explicit expressions are proposed for anisotropic materials. Consequently, a new explicit evolution equation for the polarization vector is obtained for both high and low temperatures. In particular, the Landau-Devonshire scalar model is recovered in the isotropic case. Under the assumption of small strains and small polarization gradients, hysteresis and electromechanical coupling are described for a simple one-dimensional model. The advantage of our original approach is that a few constitutive parameters provide a good fit of material behavior.

1. Introduction

Piezo-ferroelectricity is a phenomenon involving the coupling among different physical quantities, like stress, strain, electric field and dielectric polarization. By symmetry considerations, ferroelectric materials are required to be also piezoelectric and pyroelectric at temperatures higher than a critical value, θ_C, called the Curie temperature. They are thus a challenging subject for mathematical modeling in that they exhibit non-linear behavior and hysteresis [1–3]. Moreover, their properties has given rise to a rich variety of technological applications, in particular in the realization of sensors and actuators [4]. Nowadays there is an extensive amount of models for various piezo-ferroelectric phenomena, ranging from micro-mechanical to phenomenological models on a macro scale [5–7].

As well as para-electrics, ferroelectric materials exhibit an electronic, atomic and ionic polarization, but in addition they possess a residual polarization after the removal of the electric field that can be oriented in one direction or another depending on the direction of the applied field. Such materials were called ferroelectrics by analogy to ferromagnetic materials

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which exhibit similar properties (as spontaneous magnetization and hysteresis looping) below the Curie temperature. The physical basis for the ferroelectric transition appears somewhat similar to that for the ferromagnetic transition. Indeed, the transition from a high-temperature para-electric phase to a low-temperature ferroelectric phase is a spontaneous break of the symmetry in the charge distribution inside the crystal cell. Because of this similarity one might think that three-dimensional models for ferromagnetic materials could also be suitable for ferroelectrics. However, there are some elementary aspects that make polarization very different from magnetization.

1.1. Differences between ferroelectrics and ferromagnetics

The difference between polarization and magnetization is mainly due to the fact that the magnetic moment and the electric dipole moment behave differently (see, for instance, [8]). In atoms the magnetic moment $\mathfrak{m}$ associated with an orbiting electron lies along the same direction as the angular momentum of that electron and is proportional to it by a constant known as the *gyromagnetic ratio*[1]. When an external magnetic field not aligned with $\mathfrak{m}$ is applied, the action of the resulting torque on $\mathfrak{m}$ is exactly analogous to the spinning of a gyroscope. So, we observe the precession of the magnetic moment which is named *Larmor precession*. On the contrary, a stationary electric dipole moment $\mathfrak{p}$ consists just in two separated electric charges and is not associated with any angular momentum. When an external stationary electric field not aligned with $\mathfrak{p}$ is applied, the resulting torque will tend to turn $\mathfrak{p}$ towards the field direction. In this case *no precession effects are observed*. This suggests that the evolution of the polarization field in ferroelectrics is different from that of the magnetization in ferromagnets.

1.2. Aim and novelty of the paper

Within the framework of continuum thermodynamics, we propose a phenomenological, non-isothermal, vector-valued model of the ferroelectric phase transition based on a thermodynamic approach. The scheme adopted here applies to piezo-ferroelectric materials undergoing large deformations. It has some features in common with [9–11]: constitutive properties are given by using referential, Euclidean invariant quantities and the ferroelectric polarization is decomposed into a reversible and a residual part which is considered as an independent variable. Instead, the novelty of our approach is based on constitutive functions that depend on a set of variables including the residual polarization gradient as well as their time derivatives. In addition, we apply here a nonlocal statement of the second law of thermodynamics. Notably, the entropy production is represented as the sum of a non-negative supply and a flow term due to an extra-flux vector. Both contributions take into account the exchange of entropy at the interface between ferroelectric domains and are assigned by means of constitutive functions. The resulting original model is able to describe the evolution of both the direction and the modulus of polarization, for both high and low temperatures. Consequently, as the temperature varies, the model describes the polarization vector transition equation. For rigid ferroelectrics, this equation is very close to the Landau-Lifshitz-Bloch equation in ferromagnetism except for the absence of the gyroscopic term.

Throughout the paper the temperature is regarded as a parameter and therefore the heat conduction equation is not involved. The study of the effects of thermal conductivity in ferroelectricity could be addressed for small strains by an eigenvalues approach as in [12,13].

The advantages of our model are twofold. On the one hand it shows that the thermodynamic consistency, in addition to ascertaining the physical admissibility of the constitutive functions, is also a guideline to the setting of the material model. On the other it provides a simple scheme for the selection of the parameters characterizing the material behavior. This work is mainly devoted to the theoretical aspects. A punctual validation of the results presented here requires a comparison with the experimental observations to determine the values of the parameters.

The paper is organized as follows. In the first part (Sect. 2), the Maxwell and balance equations within matter are introduced, jointly with the principle of objectivity and the (nonlocal) second law of Thermodynamics. In Sect. 3 we introduce constitutive equations and scrutinize the thermodynamic restrictions imposed by the second law. The principle of objectivity is satisfied by using invariant fields as independent variables in constitutive functions. By virtue of this, the standard balance of torques (skew part of the stress equal to the skew part of the dyadic product between $\boldsymbol{P}$ and $\boldsymbol{E}$) is a consequence of thermodynamic restrictions. The ferroelectric polarization vector $\boldsymbol{P}$ is decomposed into a reversible (piezoelectric) and a residual (remnant) part (see, for example, [3,14]) and the constitutive functions are assumed to depend on the residual polarization, as well as on the electric field, temperature and deformation of the material. Section 4 is devoted to derive the explicit evolution equation for the polarization vector. After that, in Sect. 5 some appropriate expressions of the polarization free energy are proposed within the Ginzburg-Landau-Devonshire setting, both for isotropic and anisotropic materials. In the isotropic case, the Devonshire scalar model is recovered. Finally, the coupling between electric field and mechanical strain is described in Sect. 6 under the small deformation assumption.

[1] This relation is demonstrated by the Einstein-de Haas effect, discovered in 1915, where a rotation is induced by magnetization, but there is also the reverse effect, known as the Barnett effect, in which magnetization is induced by rotation. Both phenomena demonstrate the connection between the magnetic moment and the angular momentum.

2. Balance laws and basic principles

We consider a body occupying the time dependent region $\Omega \subset \mathbb{R}^3$. The motion is described by function $\boldsymbol{\xi}(\boldsymbol{X}, t)$ providing the position vector $\boldsymbol{x} \in \Omega$ in terms of the position vector $\boldsymbol{X}$, in a reference configuration $\mathcal{R} \subset \mathbb{R}^3$, and the time t, so that

$$\boldsymbol{x} = \boldsymbol{\xi}(\boldsymbol{X}, t), \qquad \Omega = \boldsymbol{\xi}(\mathcal{R}, t).$$

The deformation is described by means of the deformation gradient

$$\boldsymbol{F}(\boldsymbol{X}, t) = \nabla_{\!R}\, \boldsymbol{\xi}(\boldsymbol{X}, t), \qquad \text{(in suffix notation } F_{iK} = \partial_{X_K}\xi_i),$$

satisfying the constraint $\mathcal{J} := \det \boldsymbol{F} > 0$. Here, $\nabla_R := \partial_{\boldsymbol{X}}$ denotes the gradient in the reference configuration $\mathcal{R}$, whereas the symbol $\nabla := \partial_{\boldsymbol{x}}$ denotes the gradient in the current configuration Ω. For any regular vector field $\boldsymbol{w}(\boldsymbol{x}, t)$, they are related as follows

$$\nabla_{\!R}\hat{\boldsymbol{w}} = (\nabla \boldsymbol{w})\boldsymbol{F}, \qquad \nabla \boldsymbol{w} = (\nabla_{\!R}\hat{\boldsymbol{w}})\boldsymbol{F}^{-1},$$

where $\hat{\boldsymbol{w}} = \boldsymbol{w}\big(\boldsymbol{\xi}(\boldsymbol{X}, t), t\big)$. In addition, using the Nanson's formula, we have

$$\nabla_{\!R} \cdot \hat{\boldsymbol{w}} = \mathcal{J}\nabla \cdot \left(\frac{1}{\mathcal{J}}\boldsymbol{F}\boldsymbol{w}\right), \qquad \nabla \cdot \boldsymbol{w} = \frac{1}{\mathcal{J}}\nabla_{\!R} \cdot (\mathcal{J}\boldsymbol{F}^{-1}\hat{\boldsymbol{w}}). \tag{1}$$

Hereafter, a superposed dot denotes the material time derivative, namely

$$\dot{\boldsymbol{f}}(\boldsymbol{x}, t) := \frac{d}{dt} f(\boldsymbol{\xi}(\boldsymbol{X}, t), t) = \partial_t f(\boldsymbol{x}, t) + (\boldsymbol{v} \cdot \nabla) f(\boldsymbol{x}, t),$$

where f is a scalar-, vector- or tensor-valued differentiable function of the current position. The velocity field $\boldsymbol{v}(\boldsymbol{x}, t)$ is such that $\boldsymbol{v}(\boldsymbol{\xi}(\boldsymbol{X}, t), t) = \partial_t \boldsymbol{\xi}(\boldsymbol{X}, t)$ and the velocity gradient $\boldsymbol{L} := \nabla \boldsymbol{v}$ is related to $\dot{\boldsymbol{F}}$ as follows

$$\boldsymbol{L} = \dot{\boldsymbol{F}}\boldsymbol{F}^{-1}. \tag{2}$$

To simplify the description of material properties, throughout the electromagnetic fields are considered at the frame locally at rest with the body (all points of this frame move with the velocity $\boldsymbol{v}$ of the body at the point under consideration). There are different formulations of electromagnetism in matter; different views about the selection of the primary fields lead to seemingly different balance equations in matter. However, since they are equivalent to each other [15], we here follow the Minkowski formulation. Accordingly, $\boldsymbol{E}$ and $\boldsymbol{H}$ denote the electric and magnetic fields, $\boldsymbol{P}$ and $\boldsymbol{M}$ denote the polarization and magnetization vectors, whereas $\boldsymbol{J}$ and q are the electric current and charge, respectively. Inside the ferroelectric solid we assume a paramagnetic relation[2], $\boldsymbol{M} = \chi_m \boldsymbol{H}$, so that the displacement vector $\boldsymbol{D}$ and the magnetic induction $\boldsymbol{B}$ are given by

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P}, \qquad \boldsymbol{B} = \mu_0(1 + \chi_m)\boldsymbol{H},$$

where ϵ_0, μ_0 are positive constants which stand for vacuum permittivity and permeability, respectively. According to § 2.16 of [17], where the Minkowski selection of fields in matter is discussed in connection with the basic balance laws, Maxwell's equations reduces to

$$\nabla \times \boldsymbol{E} + \mu \boldsymbol{H}^{\square} = \boldsymbol{0}, \quad \nabla \times \boldsymbol{H} = \epsilon_0 \boldsymbol{E}^{\square} + \boldsymbol{P}^{\square} + \boldsymbol{J}, \quad \nabla \cdot \boldsymbol{H} = 0, \quad \epsilon_0 \nabla \cdot \boldsymbol{E} + \nabla \cdot \boldsymbol{P} = q, \tag{3}$$

where $\mu = \mu_0(1 + \chi_m)$ and the superposed $^{\square}$ denotes a specific objective time derivative of vectors, namely

$$\boldsymbol{f}^{\square} = \partial_t \boldsymbol{f} + \nabla \times (\boldsymbol{f} \times \boldsymbol{v}) + (\nabla \cdot \boldsymbol{f})\boldsymbol{v} = \dot{\boldsymbol{f}} - \boldsymbol{L}\boldsymbol{f} + (\nabla \cdot \boldsymbol{v})\boldsymbol{f},$$

also referred to as *Truesdell vector rate* (see also $(15)_3$). Since a Galilean transformation is recovered from a Lorentz transformation at the limit of small speeds, relative to the light speed c, the classical form (3) can be obtained as an approximation of the tensor form of Maxwell's equations (see [17, § 2.11]).

Let ε be the specific internal energy, $\boldsymbol{T}$ the mechanical Cauchy stress (which need not be symmetric owing to the polar character of ferroelectrics), $\boldsymbol{q}$ the heat flux vector, ρ the mass density, r the (external) heat supply and $\boldsymbol{b}$ the specific body force (e.g. gravity acceleration).

A thermodynamically consistent derivation of local balance of force and energy is a delicate issue which has been carefully addressed in remarkable research papers (for instance, [17–21]). Referring to the detailed explanation given in [17, § 2.16], the balance equations of linear momentum, angular momentum, and energy can be written in the form[3]

$$\rho \dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b} + q\boldsymbol{E} + \boldsymbol{J} \times \boldsymbol{B} + (\boldsymbol{P} \cdot \nabla)\boldsymbol{E} + \boldsymbol{P}^{\square} \times \boldsymbol{B}, \tag{4}$$

$$\operatorname{skw}\boldsymbol{T} = \operatorname{skw}(\boldsymbol{P} \otimes \boldsymbol{E}), \tag{5}$$

$$\rho \dot{\varepsilon} = \boldsymbol{J} \cdot \boldsymbol{E} + \rho \boldsymbol{E} \cdot \dot{\boldsymbol{p}} + \boldsymbol{T} \cdot \boldsymbol{L} - \nabla \cdot \boldsymbol{q} + \rho r, \tag{6}$$

where $\boldsymbol{p} = \boldsymbol{P}/\rho$ is the *polarization vector per unit mass*, the symbol denotes the dyadic product (in suffix notation $[\boldsymbol{P} \otimes \boldsymbol{E}]_{ij} = P_i E_j$).

[2] Very few materials that are both ferromagnetic and ferroelectric in the same phase exist in nature or have been synthesized in the laboratory [16].

[3] Here $\boldsymbol{E}$ stands for the 'effective electric field' as in [18, eq.(3.12)].

2.1. Entropy principle

Here we need a formulation for the entropy principle that is compatible with the non-local character of the phenomena involved.

Let η be the specific entropy and θ the (positive) absolute temperature. All processes which are compatible with the balance equations (3)-(6) must satisfy the following integral equation

$$\frac{d}{dt}\int_\Omega \rho\,\eta\,dx = -\int_{\partial\Omega} \boldsymbol{h}\cdot\boldsymbol{n}\,da + \int_\Omega \rho s\,dx, \tag{7}$$

where $\boldsymbol{n}$ is the outward normal to the boundary and

$$\boldsymbol{h} = \frac{\boldsymbol{q}}{\theta}, \qquad s = \frac{r}{\theta} + \sigma.$$

Moreover, the quantity σ is said to be the *entropy production* (per unit mass) [22] and is assumed to satisfy the condition

$$\int_\Omega \rho\,\sigma\,dx \geq 0. \tag{8}$$

This statement of the Second Law has a non-local nature since (8) is assumed to be valid only over the entire domain Ω and not point-wise (see, for instance, [22,23]). Let $\boldsymbol{k}$ be an unknown regular field, hereinafter called *entropy extra flux*, such that

$$\int_\Omega \nabla\cdot\boldsymbol{k}\,dx = \int_{\partial\Omega} \boldsymbol{k}\cdot\boldsymbol{n}\,da = 0. \tag{9}$$

Then, (8) can be satisfied by letting

$$\rho\sigma = \rho\zeta - \nabla\cdot\boldsymbol{k}, \tag{10}$$

where ζ is a nonnegative unknown field. If (10) is interpreted as a microscopic local balance, then ζ and $\boldsymbol{k}$ could represent the supply and the entropy flux that is exchanged at the interface between ferroelectric domains (see [24,25] and references therein). By applying the divergence theorem to the nonlocal entropy balance (7) and using (10) we obtain the local form

$$\rho\dot{\boldsymbol{\eta}} + \nabla\cdot\left(\frac{\boldsymbol{q}}{\theta} + \boldsymbol{k}\right) - \frac{\rho r}{\theta} = \rho\zeta \geq 0, \tag{11}$$

that resembles the classical entropy inequality except that the entropy flux vector is redefined by adding the extra contribution $\boldsymbol{k}$. Henceforth, we assume that $\boldsymbol{k}$ and ζ are given as constitutive functions of the assigned set of variables. Upon substitution of $\nabla\cdot\boldsymbol{q} - \rho r$ from the energy equation (6) into (11) and multiplication by θ we obtain the Clausius-Duhem relation

$$-\rho(\dot{\boldsymbol{\psi}} + \eta\dot{\boldsymbol{\theta}}) + \boldsymbol{J}\cdot\boldsymbol{E} + \rho\boldsymbol{E}\cdot\dot{\boldsymbol{p}} + \boldsymbol{T}\cdot\boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta + \theta\nabla\cdot\boldsymbol{k} = \rho\theta\zeta, \quad \zeta \geq 0, \tag{12}$$

where $\psi = \varepsilon - \theta\eta$ denotes the *Helmholtz specific free energy*. Introducing the (electric) *Gibbs specific free energy*,

$$\phi = \psi - \frac{1}{\rho}\boldsymbol{E}\cdot\boldsymbol{P} = \varepsilon - \theta\eta - \boldsymbol{E}\cdot\boldsymbol{p}, \tag{13}$$

upon some rearrangements we rewrite the entropy inequality in the form

$$-\rho(\dot{\boldsymbol{\phi}} + \eta\dot{\boldsymbol{\theta}}) + \boldsymbol{J}\cdot\boldsymbol{E} - \boldsymbol{P}\cdot\dot{\boldsymbol{E}} + \boldsymbol{T}\cdot\boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta + \theta\nabla\cdot\boldsymbol{k} = \rho\theta\zeta \geq 0. \tag{14}$$

Within the isothermal setting, the term $\rho\theta\zeta$ is usually referred to as *rate of (mechanical) dissipation* [26].

2.2. Objectivity

By the principle of objectivity (sometimes referred to as *principle of material frame-indifference* [27,28]) the material properties of a body should not depend on the observer. More precisely, as the statement of the *principle of objectivity* we assume that the constitutive equations are form-invariant within the set of Euclidean frames [29]. Accordingly, they have to be invariant under any change of frame with rotation matrix $\boldsymbol{Q}$,

$$\boldsymbol{x} \to \boldsymbol{x}^*, \quad \boldsymbol{x}^* = \boldsymbol{c}(t) + \boldsymbol{Q}(t)\boldsymbol{x}, \quad \det\boldsymbol{Q} = 1.$$

In particular, vectors $\boldsymbol{E}$ and $\boldsymbol{p}$ transform according to

$$\boldsymbol{E} \quad\to\quad \boldsymbol{Q}\boldsymbol{E}, \qquad \boldsymbol{p} \quad\to\quad \boldsymbol{Q}\boldsymbol{p}.$$

Since $\partial_{\boldsymbol{x}}\boldsymbol{x}^* = \boldsymbol{Q}$, the deformation gradient $\boldsymbol{F}$ transform as a vector, too. It is easy to check that the Cauchy-Green tensor $\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F}$ is an invariant tensor, whereas $\boldsymbol{F}^T\boldsymbol{E}$ and $\boldsymbol{F}^T\boldsymbol{p}$ are invariant vectors (see for instance [10]). Owing to the polar decomposition $\boldsymbol{F} = \boldsymbol{R}\boldsymbol{U}$, $\boldsymbol{R}^T\boldsymbol{E}$ and $\boldsymbol{R}^T\boldsymbol{p}$ are invariant, too. Other invariant vectors are $\boldsymbol{F}^{-1}\boldsymbol{E}$ and $\boldsymbol{F}^{-1}\boldsymbol{p}$. Hereafter, we let

$$\mathcal{E} := \boldsymbol{F}^T\boldsymbol{E}, \qquad \mathcal{P} := \boldsymbol{F}^{-1}\boldsymbol{p} = \boldsymbol{F}^{-1}\boldsymbol{P}/\rho.$$

These fields are strictly related to the electric and polarization fields in the reference configuration, $\boldsymbol{E}_R$ and $\boldsymbol{P}_R$. Indeed, we have $\boldsymbol{E}_R := \boldsymbol{F}^T\boldsymbol{E} = \mathcal{E}$ and $\boldsymbol{P}_R := \mathcal{J}\boldsymbol{F}^{-1}\boldsymbol{P} = \rho_R\mathcal{P}$, respectively [30]. Since they are Lagrangian (or material) fields, their time derivatives,

$$\dot{\mathcal{E}}(\boldsymbol{X}, t) = \partial_t\mathcal{E}(\boldsymbol{X}, t), \qquad \dot{\mathcal{P}}(\boldsymbol{X}, t) = \partial_t\mathcal{P}(\boldsymbol{X}, t),$$

are invariant vectors and their material gradients,

$$\nabla_R\mathcal{E}(\boldsymbol{X}, t) = \partial_{\boldsymbol{X}}\mathcal{E}(\boldsymbol{X}, t), \qquad \nabla_R\mathcal{P}(\boldsymbol{X}, t) = \partial_{\boldsymbol{X}}\mathcal{P}(\boldsymbol{X}, t),$$

are invariant tensors. On the contrary, the standard time derivative of a vector field in the Eulerian (or spatial) description is not objective, since the velocity field depends on the choice of the Euclidean frame.

To construct constitutive equations involving the rates of independent fields it is therefore preferable to follow an invariant formulation using Lagrangian (or material) rather than Eulerian variables. However, the two views are related, since the rates of invariant fields can easily be translated into the spatial description (see for example (16)). For further convenience, we recall here some of the best known objective time derivatives of a vector field $\boldsymbol{u}(\boldsymbol{x}, t)$ occurring in the literature (see, for instance, [31] or, in a more general framework, [29]):

$$\begin{aligned} &\boldsymbol{u}^{\triangledown} = \dot{\boldsymbol{u}} - \boldsymbol{L}\boldsymbol{u} && \text{Oldroyd rate,} \\ &\boldsymbol{u}^{\vartriangle} = \dot{\boldsymbol{u}} + \boldsymbol{L}^T\boldsymbol{u} && \text{Cotter-Rivlin rate,} \\ &\boldsymbol{u}^{\square} = \dot{\boldsymbol{u}} - \boldsymbol{L}\boldsymbol{u} + (\nabla\cdot\boldsymbol{v})\boldsymbol{u} && \text{Truesdell rate.} \end{aligned} \tag{15}$$

3. Constitutive relations and thermodynamic restrictions

Although several other invariant formulations can be used (for instance, [7,32]), from now on we choose $(\boldsymbol{C}, \theta, \mathcal{E}, \mathcal{P})$ as the set of invariant field variables. To express the second law inequality (12) in term of the invariant fields $\mathcal{E}$ and $\mathcal{P}$, we compute their time derivatives,

$$\dot{\mathcal{E}} = \boldsymbol{F}^T\left(\dot{\boldsymbol{E}} + \boldsymbol{L}^T\boldsymbol{E}\right) = \boldsymbol{F}^T\boldsymbol{E}^{\vartriangle}, \qquad \dot{\mathcal{P}} = \boldsymbol{F}^{-1}(\dot{\boldsymbol{p}} - \boldsymbol{L}\boldsymbol{p}) = \boldsymbol{F}^{-1}\boldsymbol{p}^{\triangledown}. \tag{16}$$

In particular we obtain $\dot{\boldsymbol{p}} = \boldsymbol{F}\dot{\mathcal{P}} + \boldsymbol{L}\boldsymbol{p}$ and then

$$\rho\boldsymbol{E}\cdot\dot{\boldsymbol{p}} = \rho(\boldsymbol{F}^T\boldsymbol{E})\cdot\dot{\mathcal{P}} + \rho(\boldsymbol{E}\otimes\boldsymbol{p})\cdot\boldsymbol{L} = \rho\,\mathcal{E}\cdot\dot{\mathcal{P}} + (\boldsymbol{E}\otimes\boldsymbol{P})\cdot\boldsymbol{L}.$$

Applying this result to (12), it follows

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \boldsymbol{J}\cdot\boldsymbol{E} + \rho\,\mathcal{E}\cdot\dot{\mathcal{P}} + \mathcal{T}\cdot\boldsymbol{L} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta + \theta\nabla\cdot\boldsymbol{k} = \rho\theta\zeta, \quad \zeta \geq 0,$$

where, to save writing, we let

$$\mathcal{T} := \boldsymbol{T} + \boldsymbol{E}\otimes\boldsymbol{P}.$$

Then multiplying by $\mathcal{J}$ and using the identities (1), (2) and $\rho_R = \mathcal{J}\rho$, we obtain

$$-\rho_R\left(\dot{\psi} + \eta\dot{\theta} - \mathcal{E}\cdot\dot{\mathcal{P}}\right) + \mathcal{J}(\mathcal{T}\boldsymbol{F}^{-T})\cdot\dot{\boldsymbol{F}} + \boldsymbol{J}_R\cdot\mathcal{E} - \frac{1}{\theta}\boldsymbol{q}_R\cdot\nabla_R\theta + \theta\nabla_R\cdot\boldsymbol{k}_R = \rho_R\theta\zeta, \tag{17}$$

where

$$\boldsymbol{J}_R = \mathcal{J}\boldsymbol{F}^{-1}\boldsymbol{J}, \qquad \boldsymbol{q}_R = \mathcal{J}\boldsymbol{F}^{-1}\boldsymbol{q}, \qquad \boldsymbol{k}_R = \mathcal{J}\boldsymbol{F}^{-1}\boldsymbol{k}.$$

Since (17) must be valid for any thermodynamic process, the functional dependence of the constitutive relations must be subject to thermodynamic restrictions. To be able to determine them, it is necessary to define in advance the set of independent variables.

Taking into account that all the ferroelectric materials exhibit piezoelectric effects[4] due to lack of symmetry [1], we suppose that in the ferroelectric regime $\mathcal{P}$ is partially determined through a constitutive function. Namely

$$\mathcal{P} = \boldsymbol{\Xi}(\theta, \boldsymbol{C}, \mathcal{E}) + \boldsymbol{\Pi}, \tag{18}$$

where $\boldsymbol{\Xi}$ is a differentiable function, which represents the constitutive part of $\mathcal{P}$, while $\boldsymbol{\Pi}$ denotes an independent variable named *residual polarization vector*. The adjective "residual" (or "remanent", as in [3,14]) attributed to $\boldsymbol{\Pi}$ is justified here by assuming that $\boldsymbol{\Xi}$ vanishes when $\boldsymbol{C} = \boldsymbol{1}$ (no deformation[5]) and $\mathcal{E} = \boldsymbol{0}$. Owing to (18) and letting $\mathsf{p} = \boldsymbol{F}\boldsymbol{\Pi}$ (the residual polarization vector in the spatial description) we have

$$\boldsymbol{P} = \rho\boldsymbol{F}\mathcal{P} = \rho\boldsymbol{F}\boldsymbol{\Xi}(\theta, \boldsymbol{C}, \mathcal{E}) + \rho\,\mathsf{p}.$$

[4] The piezoelectric effect occurs only in a few dielectric materials (the 20 piezoelectric point groups) that can be polarized, in addition to an electric field, also by applying a mechanical stress.

[5] Here and in the following $\boldsymbol{1}$ denotes the second-order identity tensor.

Since $\boldsymbol{\Pi}$ is reduced to the so-called *spontaneous* polarization in stationary conditions, it is expected to be negligible in the paraelectric regime where $\theta > \theta_C$. In the ferroelectric regime, where $0 < \theta < \theta_C$, the dependence of the constitutive equations on $\boldsymbol{\Pi}$, as well as on its material gradient $\nabla_R\boldsymbol{\Pi}$, is motivated by the lattice theory of crystals. Therein, the polarization gradient is regarded to model, in the long wave approximation, the shell-shell and core-shell interactions between atoms (see for instance [33]). According to the previous arguments we let

$$\Sigma := (\boldsymbol{C}, \theta, \boldsymbol{\mathcal{E}}, \boldsymbol{\Pi}, \dot{\boldsymbol{C}}, \dot{\boldsymbol{\theta}}, \dot{\boldsymbol{\mathcal{E}}}, \dot{\boldsymbol{\Pi}}, \nabla_R\theta, \nabla_R\boldsymbol{\Pi})$$

be the set of variables involved in any thermodynamic process.

3.1. Thermodynamic restrictions

Now, in order to scrutinize thermodynamic restrictions we let

$$\psi = \psi(\Sigma), \qquad \boldsymbol{k}_R = \boldsymbol{k}_R(\Sigma), \qquad \zeta = \zeta(\Sigma) \geq 0,$$

and assume ψ to be a differentiable function of all its arguments. Upon evaluation of $\dot{\boldsymbol{\psi}}$ and $\dot{\mathcal{P}}$ and substitution into (17) we obtain

$$\begin{aligned}&-\rho_R\big[(\partial_\theta\psi + \eta - \boldsymbol{\mathcal{E}}\cdot\partial_\theta\boldsymbol{\Xi})\dot{\boldsymbol{\theta}} + \big(\partial_{\boldsymbol{C}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{C}}\boldsymbol{\Xi}\big)\cdot\dot{\boldsymbol{C}} + (\partial_{\boldsymbol{\mathcal{E}}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{\mathcal{E}}}\boldsymbol{\Xi})\cdot\dot{\boldsymbol{\mathcal{E}}}\\&+(\partial_{\boldsymbol{\Pi}}\psi - \boldsymbol{\mathcal{E}})\cdot\dot{\boldsymbol{\Pi}} + \partial_{\dot{\boldsymbol{\theta}}}\psi\cdot\ddot{\boldsymbol{\theta}} + \partial_{\dot{\boldsymbol{C}}}\psi\cdot\ddot{\boldsymbol{C}} + \partial_{\dot{\boldsymbol{\mathcal{E}}}}\psi\cdot\ddot{\boldsymbol{\mathcal{E}}} + \partial_{\dot{\boldsymbol{\Pi}}}\psi\cdot\ddot{\boldsymbol{\Pi}} + \partial_{\nabla_R\theta}\psi\cdot\nabla_R\dot{\boldsymbol{\theta}}\\&+\partial_{\nabla_R\boldsymbol{\Pi}}\psi\cdot\nabla_R\dot{\boldsymbol{\Pi}}\big] + (\mathcal{J}\boldsymbol{\mathcal{T}}\boldsymbol{F}^{-T})\cdot\dot{\boldsymbol{F}} + \boldsymbol{J}_R\cdot\boldsymbol{\mathcal{E}} - \frac{1}{\theta}\boldsymbol{q}_R\cdot\nabla_R\theta + \theta\nabla_R\cdot\boldsymbol{k}_R = \rho_R\theta\zeta.\end{aligned} \tag{19}$$

The arbitrariness and the linearity of $\dot{\boldsymbol{\theta}}, \ddot{\boldsymbol{\theta}}, \nabla_R\dot{\boldsymbol{\theta}}, \ddot{\boldsymbol{C}}, \ddot{\boldsymbol{\mathcal{E}}}$ and $\ddot{\boldsymbol{\Pi}}$ imply

$$\psi = \psi(\boldsymbol{C}, \theta, \boldsymbol{\mathcal{E}}, \boldsymbol{\Pi}, \nabla_R\boldsymbol{\Pi}), \qquad \eta = -\partial_\theta\psi + \boldsymbol{\mathcal{E}}\cdot\partial_\theta\boldsymbol{\Xi}. \tag{20}$$

Moreover, using the identities

$$\begin{aligned}\big(\partial_{\boldsymbol{C}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{C}}\boldsymbol{\Xi}\big)\cdot\dot{\boldsymbol{C}} &= 2\boldsymbol{F}(\partial_{\boldsymbol{C}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{C}}\boldsymbol{\Xi})\cdot\dot{\boldsymbol{F}},\\ -\tfrac{\rho_R}{\theta}\partial_{\nabla_R\boldsymbol{\Pi}}\psi\cdot\nabla_R\dot{\boldsymbol{\Pi}} &= -\nabla_R\cdot\Big(\tfrac{\rho_R}{\theta}\partial_{\nabla_R\boldsymbol{\Pi}}\psi\,\dot{\boldsymbol{\Pi}}\Big) + \Big[\nabla_R\cdot\Big(\tfrac{\rho_R}{\theta}\partial_{\nabla_R\boldsymbol{\Pi}}\psi\Big)\Big]\cdot\dot{\boldsymbol{\Pi}},\end{aligned}$$

and letting[6]

$$\Psi_R := \frac{\rho_R}{\theta}\psi, \qquad \delta_{\boldsymbol{\Pi}}\Psi_R := \partial_{\boldsymbol{\Pi}}\Psi_R - \nabla_R\cdot(\partial_{\nabla_R\boldsymbol{\Pi}}\Psi_R),$$

we can rewrite (19) as

$$\begin{aligned}&-\big(\theta\partial_{\boldsymbol{\mathcal{E}}}\Psi_R - \rho_R\boldsymbol{\mathcal{E}}\partial_{\boldsymbol{\mathcal{E}}}\boldsymbol{\Xi}\big)\cdot\dot{\boldsymbol{\mathcal{E}}} + [\rho_R\boldsymbol{\mathcal{E}} - \theta\delta_{\boldsymbol{\Pi}}\Psi_R]\cdot\dot{\boldsymbol{\Pi}} + \boldsymbol{J}_R\cdot\boldsymbol{\mathcal{E}} - \frac{1}{\theta}\boldsymbol{q}_R\cdot\nabla_R\theta\\&+\big[\mathcal{J}\boldsymbol{\mathcal{T}}\boldsymbol{F}^{-T} - 2\rho_R\boldsymbol{F}(\partial_{\boldsymbol{C}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{C}}\boldsymbol{\Xi})\big]\cdot\dot{\boldsymbol{F}} + \theta\nabla_R\cdot(\boldsymbol{k}_R - \partial_{\nabla_R\boldsymbol{\Pi}}\Psi_R\dot{\boldsymbol{\Pi}}) = \rho_R\theta\zeta.\end{aligned} \tag{21}$$

The arbitrariness and the linearity of $\dot{\boldsymbol{F}}$ implies

$$\boldsymbol{\mathcal{T}} = 2\rho\boldsymbol{F}(\partial_{\boldsymbol{C}}\psi - \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{C}}\boldsymbol{\Xi})\boldsymbol{F}^T. \tag{22}$$

As in [24,34] the vanishing of the last addendum in (21) is achieved by assuming

$$\boldsymbol{k}_R(\Sigma) = \partial_{\nabla_R\boldsymbol{\Pi}}\Psi_R(\boldsymbol{C}, \theta, \boldsymbol{\mathcal{E}}, \boldsymbol{\Pi}, \nabla_R\boldsymbol{\Pi})\,\dot{\boldsymbol{\Pi}}, \tag{23}$$

that looks like a constitutive relation for the extra-entropy flux in the material description (see also Remark 3.3). Accordingly, upon division by θ, (21) reduces to

$$\Big[\partial_{\boldsymbol{\mathcal{E}}}\Psi_R - \frac{\rho_R}{\theta}\boldsymbol{\mathcal{E}}\partial_{\boldsymbol{\mathcal{E}}}\boldsymbol{\Xi}\Big]\cdot\dot{\boldsymbol{\mathcal{E}}} + \Big[\delta_{\boldsymbol{\Pi}}\Psi_R - \frac{\rho_R}{\theta}\boldsymbol{\mathcal{E}}\Big]\cdot\dot{\boldsymbol{\Pi}} - \frac{1}{\theta}\boldsymbol{J}_R\cdot\boldsymbol{\mathcal{E}} + \frac{1}{\theta^2}\boldsymbol{q}_R\cdot\nabla_R\theta = -\rho_R\zeta.$$

Remembering that $\phi = \psi - \boldsymbol{\mathcal{E}}\cdot\mathcal{P}$, we introduce[7]

$$\Phi_R := \frac{\rho_R}{\theta}\phi = \Psi_R(\theta, \boldsymbol{C}, \boldsymbol{\mathcal{E}}, \boldsymbol{\Pi}, \nabla_R\boldsymbol{\Pi}) - \frac{\rho_R}{\theta}\boldsymbol{\mathcal{E}}\cdot(\boldsymbol{\Xi}(\theta, \boldsymbol{C}, \boldsymbol{\mathcal{E}}) + \boldsymbol{\Pi}),$$

and we obtain

$$\partial_{\boldsymbol{\mathcal{E}}}\Phi_R = \partial_{\boldsymbol{\mathcal{E}}}\Psi_R - \frac{\rho_R}{\theta}(\boldsymbol{\Xi} + \boldsymbol{\Pi} + \boldsymbol{\mathcal{E}}\partial_{\boldsymbol{\mathcal{E}}}\boldsymbol{\Xi}), \qquad \delta_{\boldsymbol{\Pi}}\Phi_R = \delta_{\boldsymbol{\Pi}}\Psi_R - \frac{\rho_R}{\theta}\boldsymbol{\mathcal{E}}.$$

[6] $\Psi_R := \rho_R\big(\frac{1}{\theta}\varepsilon - \eta\big)$ represents the opposite of the Helmholtz free entropy (also called Massieu potential) per unit volume in the reference configuration, and $\delta_{\boldsymbol{\Pi}}\Psi_R$ denotes its variational (or functional) derivative with respect to $\boldsymbol{\Pi}(\boldsymbol{X})$.

[7] Φ_R denotes the opposite of the (electric) Gibbs specific free entropy in the reference configuration.

According to [35], when thermoelectric effects are ignored, we are allowed to apply Fourier's and Ohm's laws as constitutive relations for $\boldsymbol{q}_R$ and $\boldsymbol{J}_R$,

$$\boldsymbol{q}_R = -\boldsymbol{K}_R \nabla_R \theta, \qquad \boldsymbol{J}_R = \boldsymbol{\Sigma}_R \boldsymbol{\mathcal{E}},$$

$\boldsymbol{K}_R$, $\boldsymbol{\Sigma}_R$ being nonnegative defined second-order tensors[8], so obtaining the final form

$$\left[\partial_{\mathcal{E}} \Phi_R + \frac{\rho_R}{\theta}(\boldsymbol{\Xi} + \boldsymbol{\Pi})\right] \cdot \dot{\boldsymbol{\mathcal{E}}} + \delta_{\boldsymbol{\Pi}} \Phi_R \cdot \dot{\boldsymbol{\Pi}} = -\rho_R \xi, \tag{24}$$

where

$$\xi := \zeta - \frac{1}{\rho_R \theta} \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\Sigma}_R \boldsymbol{\mathcal{E}} - \frac{1}{\rho_R \theta^2} \nabla_R \theta \cdot \boldsymbol{K}_R \nabla_R \theta$$

represents the further production of entropy in addition to that generated by Joule effect and Fourier heat conduction.

Some comments on these results are in order.

Remark 3.1. Constitutive functions for η and $\mathcal{T}$ follow from the electric Gibbs free energy ϕ through the differentiation with respect to θ and $\boldsymbol{C}$, respectively,

$$\eta = -\partial_\theta \phi, \qquad \mathcal{T} = 2\,\rho\, \boldsymbol{F} \partial_{\boldsymbol{C}} \phi \boldsymbol{F}^T. \tag{25}$$

This last condition proves that $\mathcal{T}$ is a symmetric tensor and allows to write $\boldsymbol{T}$ as

$$\boldsymbol{T} = 2\,\rho\, \boldsymbol{F} \partial_{\boldsymbol{C}} \phi \boldsymbol{F}^T - \boldsymbol{E} \otimes \boldsymbol{P}. \tag{26}$$

As a consequence

$$\mathrm{skw}\boldsymbol{T} = -\mathrm{skw}\boldsymbol{E} \otimes \boldsymbol{P} = \mathrm{skw}\boldsymbol{P} \otimes \boldsymbol{E},$$

as it must be in view of (5). A similar result holds within the modified couple stress theory [36].

Remark 3.2. When piezoelectric rather than ferroelectric materials are considered, the dependence on $\boldsymbol{\Pi}$ vanishes, so we have $\mathcal{P} := \boldsymbol{\Xi}$ and (24) boils down to

$$(\partial_{\mathcal{E}} \phi + \mathcal{P}) \cdot \dot{\boldsymbol{\mathcal{E}}} \leq 0.$$

Here $\dot{\boldsymbol{\mathcal{E}}}$ can be chosen arbitrarily and the constitutive equation for $\mathcal{P}$ also follows from a thermodynamic potential, $\mathcal{P} = -\partial_{\mathcal{E}} \phi$.

A dependence of the thermodynamic potentials on the residual polarization gradient, $\nabla_R \boldsymbol{\Pi}$, is compatible with thermodynamics if the extra-entropy flux $\boldsymbol{k}_R$ does not vanish and depends linearly on $\dot{\boldsymbol{\Pi}}$. Moreover, the no-flux condition (9) can be satisfied by assuming the local boundary condition

$$\boldsymbol{k} \cdot \boldsymbol{n}|_{\partial\Omega} = \boldsymbol{k}_R \cdot \boldsymbol{n}_R|_{\partial\mathcal{R}} = 0,$$

which, by means of (23) and the arbitrariness of $\dot{\boldsymbol{\Pi}}$, can be transformed into

$$[\partial_{\nabla_R \boldsymbol{\Pi}} \psi]^T \boldsymbol{n}_R|_{\partial\mathcal{R}} = \boldsymbol{0}. \tag{27}$$

Remark 3.3. Since $\mathbf{p} = \boldsymbol{F}\boldsymbol{\Pi}$, after applying (15) and (16) we transform (23) in the spatial description

$$\boldsymbol{k} := \frac{1}{\mathcal{J}} \boldsymbol{F} \boldsymbol{k}_R = \mathcal{K}\, \mathbf{p}^{\triangledown}, \quad \mathcal{K} = \frac{\rho}{\theta} \boldsymbol{F} \partial_{\nabla_R \boldsymbol{\Pi}} \psi \boldsymbol{F}^{-1}. \tag{28}$$

Since $\mathbf{p}^{\triangledown}$ is an objective rate and $\mathcal{K}$ transforms as an objective tensor, namely $\mathcal{K} \to \boldsymbol{Q}\mathcal{K}\boldsymbol{Q}^T$, (28) can be viewed as the constitutive relation for the extra entropy flux $\boldsymbol{k}$ in the spatial description.

3.2. Local constitutive relations

When the dependence on $\nabla_R \boldsymbol{\Pi}$ is neglected, then $\boldsymbol{k}_R \equiv \boldsymbol{0}$ and (24) reduces to

$$\left[\partial_{\mathcal{E}} \Phi_R + \frac{\rho_R}{\theta} \mathcal{P}\right] \cdot \dot{\boldsymbol{\mathcal{E}}} + \partial_{\boldsymbol{\Pi}} \Phi_R \cdot \dot{\boldsymbol{\Pi}} = -\rho_R \xi. \tag{29}$$

A dissipation-based approach suggests to choose ξ as a nonnegative-valued function. Recently this formulation has given rise to a class of incremental (or rate-type) constitutive relations where $\dot{\mathcal{P}}$ and $\dot{\boldsymbol{\mathcal{E}}}$ turn out to be mutually related (see, for instance, [9,10] and references therein). Such models are able to capture the hysteretic behavior of the $\mathcal{E} - \mathcal{P}$ relationship, but are local in character and therefore are not able to describe the spatial structure of the domains which is typical of hysteresis phenomena.

[8] Although electrically conductive ferroelectric materials are rather rare, the electric conductivity $\boldsymbol{\Sigma}_R$ is considered here for generality; however it can be zero without affecting the main focus of the paper.

Equation (24) can be rewritten in the spatial description by involving $\mathbf{p}$, $\boldsymbol{E}$ and their objective rates [10]. Indeed, after replacing $(16)_1$ into (29), multiplying by θ/ρ_R and exploiting the identities

$$\dot{\boldsymbol{\Pi}} = \boldsymbol{F}^{-1}(\dot{\mathbf{p}} - \boldsymbol{L}\,\mathbf{p}) = \boldsymbol{F}^{-1}\,\mathbf{p}^{\triangledown},$$

$$\partial_{\boldsymbol{E}}\Phi_R = \boldsymbol{F}\partial_{\mathcal{E}}\Phi_R, \qquad \partial_{\mathbf{p}}\Phi_R = \boldsymbol{F}^{-T}\partial_{\boldsymbol{\Pi}}\Phi_R, \qquad \mathcal{P}\cdot\dot{\mathcal{E}} = \boldsymbol{p}\cdot\boldsymbol{E}^{\nabla},$$

we obtain

$$\left[\partial_{\boldsymbol{E}}\hat{\phi} + \hat{\mathbf{p}}\right]\cdot\boldsymbol{E}^{\triangle} + \partial_{\mathbf{p}}\hat{\phi}\cdot\mathbf{p}^{\triangledown} = -\theta\xi/\mathcal{J},$$

where

$$\hat{\phi}(\boldsymbol{F},\theta,\boldsymbol{E},\,\mathbf{p}) = \phi(\boldsymbol{F}^T\boldsymbol{F},\theta,\boldsymbol{F}^T\boldsymbol{E},\boldsymbol{F}^{-1}\mathbf{p}), \quad \hat{\mathbf{p}}(\boldsymbol{F},\theta,\boldsymbol{E},\,\mathbf{p}) = \boldsymbol{F}\boldsymbol{\Xi}(\boldsymbol{F}^T\boldsymbol{F},\theta,\boldsymbol{F}^T\boldsymbol{E}) + \mathbf{p}.$$

The occurrence of the Cotter-Rivlin rate of $\boldsymbol{E}$ and the Oldroyd rate of $\mathbf{p}$ is not a subjective choice. Rather, it is a consequence of the selection of the invariant vector fields $\boldsymbol{\mathcal{E}} = \boldsymbol{F}^T\boldsymbol{E}$ and $\boldsymbol{\Pi} = \boldsymbol{F}^{-1}\mathbf{p}$ as appropriate variables to describe the properties of the material.

4. A vector-valued evolution model for ferroelectrics

Many researches have developed three-dimensional models for the dynamics of the magnetization direction vector (see, for instance, [19,20] and references therein). Although most of them can also be adapted to the evolution of the electric polarization direction, the resulting models are not able to also predict the evolution of its modulus.

Our approach is based on the thermodynamic balance (24). Of course, many different weakly nonlocal models are compatible with this approach. To characterize each of them, all that is needed is to specify constitutive functions ϕ, $\boldsymbol{\Xi}$ and ξ. Notably, ϕ and ξ are allowed to depend on the spatial gradient of $\boldsymbol{\Pi}$. This feature provides an obvious link with phase-field type models.

4.1. The phase-field approach

The constitutive properties of deformable ferroelectrics are often derived applying a variational scheme (see, for instance, [3,14,37] and reference therein). The basic claim of this approach (see, for instance, [38]) is that the equilibrium configurations of a system are determined by finding the critical points of a certain thermodynamic functional $\mathcal{F}$ with respect to the phase-field (for instance, the polarization vector $\boldsymbol{P}$). Accordingly, in isothermal conditions an equilibrium state of the polarization is expected to be the solution of the corresponding Euler-Lagrange equation,

$$\delta_{\boldsymbol{P}}\mathcal{F} = \mathbf{0}.$$

A nonzero value of $\delta_{\boldsymbol{P}}\mathcal{F}$ represents a measure of the departure from equilibrium. Hence the quantity $-\delta_{\boldsymbol{P}}\mathcal{F}$ is regarded as proportional to the appropriate generalized thermodynamic force acting on the system to restore equilibrium. Accepting this point of view, it follows

$$\dot{\boldsymbol{p}} = -\alpha\,\delta_{\boldsymbol{P}}\mathcal{F}, \quad \alpha > 0. \tag{30}$$

In turn, according to the Ginzburg-Landau-Devonshire model [39,40], the functional is given by the sum of the Landau potential, the anisotropic depolarizing contribution and the exchange energy due to gradient terms. The Landau-Devonshire potential is a polynomial of even-order powers of the polarization modulus, usually limited to the sixth order. To account for the transition, the lowest-order term is parameterized by temperature so that the material shows hysteretic properties when the temperature is below the Curie value (see [30, § 69]). At a mesoscopic scale, phase-field models based on this approach are also used to simulate the domain structure of the ferroelectric phase [6,41]. Notably, a different approach based on the Gurtin's variational principle for dipolar bodies [42] could also be applied to ferroelectrics.

In [34] a thermodynamic approach is devised to achieve an evolution equation similar to (30). To describe that procedure with our notations, let $\xi \geq 0$ and assume *a priori* a rate-type constitutive equation for $\boldsymbol{\Pi}$ in the form

$$\dot{\boldsymbol{\Pi}} = \boldsymbol{\mathcal{R}}(\theta,\mathbf{C},\boldsymbol{\mathcal{E}},\boldsymbol{\Pi},\ldots).$$

Upon substitution, $(32)_2$ may be viewed as a thermodynamic restriction on $\boldsymbol{\mathcal{R}}$, namely

$$\delta_{\boldsymbol{\Pi}}\Phi_R\cdot\boldsymbol{\mathcal{R}} \leq 0.$$

This inequality looks like a variational inequality which is typical of the phase-field approach and can be simply satisfied by letting $\boldsymbol{\mathcal{R}} = -\alpha\,\delta_{\boldsymbol{\Pi}}\Phi_R$, α being a positive-valued scalar function. The resulting incremental constitutive equation

$$\dot{\boldsymbol{\Pi}} = -\alpha\,\delta_{\boldsymbol{\Pi}}\Phi_R, \qquad \delta_{\boldsymbol{\Pi}}\Phi_R := \partial_{\boldsymbol{\Pi}}\Phi_R - \nabla_R\cdot(\partial_{\nabla_R\boldsymbol{\Pi}}\Phi_R), \tag{31}$$

provides a three-dimensional evolution equation for $\boldsymbol{\Pi}$. Since (31) looks like the Ginzburg-Landau equation for isothermal phase transitions (see, for instance, [34]), $\boldsymbol{\Pi}$ can be considered as a vector-valued *"phase-field"*.

4.2. Derivation of the model

In this section we derive a quite general three-dimensional evolution equation for the polarization vector $\mathcal{P}$ involving $\delta_{\boldsymbol{\Pi}}\Phi_R$. Our model is a genuinely vector model that relies on a consistent thermodynamic formulation and takes into account the effects due to large deformations. It provides a generalization of (31) and can be viewed either as a rate-type model or as a vector-valued phase-field model in which the residual polarization $\boldsymbol{\Pi}$ is considered an ordering vector instead of the total polarization $\mathcal{P}$.

We start by splitting (24) from the beginning as follows

$$\partial_{\mathcal{E}}\Phi_R + \frac{\rho_R}{\theta}\mathcal{P} = 0, \qquad \delta_{\boldsymbol{\Pi}}\Phi_R \cdot \dot{\boldsymbol{\Pi}} + \rho_R\xi = 0. \tag{32}$$

Taking into account (18), the former assumption yields

$$\partial_{\mathcal{E}}\phi = -\mathcal{P} := -\boldsymbol{\Xi}(\theta, \mathbf{C}, \mathcal{E}) - \boldsymbol{\Pi}, \tag{33}$$

which relates $\boldsymbol{\Xi}$ to the partial derivative of ϕ with respect to $\mathcal{E}$. To scrutinize the latter equality of (32), we choose the entropy production due to polarization in the form

$$\rho_R\xi = \dot{\boldsymbol{\Pi}} \cdot \boldsymbol{A}_R(\mathbf{C}, \theta, \mathcal{E}, \boldsymbol{\Pi}, \nabla_R\boldsymbol{\Pi})\dot{\boldsymbol{\Pi}}, \tag{34}$$

where $\boldsymbol{A}_R$ is assumed to be a positive-definite second-order tensor-valued function so that $\xi \geq 0$. Hence, $(32)_2$ becomes

$$\left(\delta_{\boldsymbol{\Pi}}\Phi_R + \boldsymbol{A}_R\dot{\boldsymbol{\Pi}}\right) \cdot \dot{\boldsymbol{\Pi}} = 0.$$

Since Φ_R and $\boldsymbol{A}_R$ are independent of $\dot{\boldsymbol{\Pi}}$, it follows

$$\dot{\boldsymbol{\Pi}} = -\boldsymbol{A}_R^{-1}\delta_{\boldsymbol{\Pi}}\Phi_R. \tag{35}$$

To properly represent $\boldsymbol{A}_R$, we first introduce some useful notations. Let Π and $\boldsymbol{\pi}$ respectively denote the modulus and director of $\boldsymbol{\Pi}$, namely

$$\Pi = \|\boldsymbol{\Pi}\| = \sqrt{\Pi_1^2 + \Pi_2^2 + \Pi_3^2}, \qquad \boldsymbol{\pi} = \frac{\boldsymbol{\Pi}}{\Pi}.$$

In addition, let $\mathscr{P}_\alpha$ be the positive-definite tensor-valued function such that

$$\mathscr{P}_\alpha(\boldsymbol{\pi}) = \alpha_1\boldsymbol{\pi}\otimes\boldsymbol{\pi} + \alpha_2(\mathbf{1} - \boldsymbol{\pi}\otimes\boldsymbol{\pi}), \qquad \alpha_1, \alpha_2 > 0.$$

Proposition 4.1. *Let α_1, α_2 be positive scalar functions of the temperature θ and let*

$$\boldsymbol{A}_R = \mathscr{P}_\alpha^{-1}(\boldsymbol{\pi}).$$

Then, (35) takes the form

$$\dot{\boldsymbol{\Pi}} = -\mathscr{P}_\alpha(\boldsymbol{\pi})\delta_{\boldsymbol{\Pi}}\Phi_R = \alpha_2\boldsymbol{\pi}\times(\boldsymbol{\pi}\times\delta_{\boldsymbol{\Pi}}\Phi_R) - \alpha_1(\delta_{\boldsymbol{\Pi}}\Phi_R\cdot\boldsymbol{\pi})\boldsymbol{\pi}. \tag{36}$$

Proof. For any vector $\boldsymbol{u}$ we have

$$\mathscr{P}_\alpha(\boldsymbol{\pi})\boldsymbol{u} = \alpha_1\boldsymbol{u}_\parallel + \alpha_2\boldsymbol{u}_\perp, \quad \mathscr{P}_\alpha^{-1}(\boldsymbol{\pi})\boldsymbol{u} = \alpha_1^{-1}\boldsymbol{u}_\parallel + \alpha_2^{-1}\boldsymbol{u}_\perp,$$

where $\boldsymbol{u}_\parallel$ and $\boldsymbol{u}_\perp$ represent respectively the parallel and the perpendicular components of $\boldsymbol{u}$ with respect to $\boldsymbol{\pi}$. By means of the vector triple product identity

$$\boldsymbol{u}_1\times(\boldsymbol{u}_2\times\boldsymbol{u}_3) = (\boldsymbol{u}_1\cdot\boldsymbol{u}_3)\boldsymbol{u}_2 - (\boldsymbol{u}_1\cdot\boldsymbol{u}_2)\boldsymbol{u}_3,$$

we can write

$$\boldsymbol{u}_\parallel = (\boldsymbol{\pi}\cdot\boldsymbol{u})\boldsymbol{\pi}, \qquad \boldsymbol{u}_\perp = \boldsymbol{u} - (\boldsymbol{\pi}\cdot\boldsymbol{u})\boldsymbol{\pi} = -\boldsymbol{\pi}\times(\boldsymbol{\pi}\times\boldsymbol{u}).$$

Hence, (34) gives

$$\rho_R\xi = \dot{\boldsymbol{\Pi}}\cdot\mathscr{P}_\alpha^{-1}(\boldsymbol{\pi})\dot{\boldsymbol{\Pi}} = \alpha_1^{-1}\|\boldsymbol{\pi}\cdot\dot{\boldsymbol{\Pi}}\|^2 + \alpha_2^{-1}\|\boldsymbol{\pi}\times\dot{\boldsymbol{\Pi}}\|^2 \geq 0,$$

and (36) follows from (35). □

Remark 4.2. Coefficients α_1 and α_2 in (36) have the same physical dimension. Moreover, α_1 and α_2 are proportional to the characteristic frequencies of the ferroelectric material and therefore can be determined experimentally. Their reciprocals are proportional to characteristic times, $\tau_\parallel$ and $\tau_\perp$, that are named *ferroelectric longitudinal and transverse relaxation times*, respectively. The larger are the values of α_1 and α_2, the faster is the damping, i.e. the rate at which the parameters tend to their equilibrium values.

By applying the vector triple product identity, we get the alternate form

$$\dot{\boldsymbol{\Pi}} = -\alpha_2\,\delta_{\boldsymbol{\Pi}}\Phi_R + (\alpha_2-\alpha_1)(\delta_{\boldsymbol{\Pi}}\Phi_R\cdot\boldsymbol{\pi})\boldsymbol{\pi},$$

from which it follows that stationary conditions occur if and only if $\delta_{\boldsymbol{\Pi}} \Phi_R = \mathbf{0}$. In the special case $\alpha_1 = \alpha_2$ we obtain

$$\dot{\boldsymbol{\Pi}} = -\alpha_2 \delta_{\boldsymbol{\Pi}} \Phi_R,$$

and then (36) can be viewed as a generalization of (31).

Since $\dot{\boldsymbol{\Pi}} = \dot{\Pi}\boldsymbol{\pi} + \Pi\dot{\boldsymbol{\pi}}$ and $\dot{\boldsymbol{\pi}} \cdot \boldsymbol{\pi} = 0$, the vector-valued equation (36) yields the system

$$\begin{cases} \dot{\boldsymbol{\pi}} &= \dfrac{\alpha_2}{\Pi} \boldsymbol{\pi} \times (\boldsymbol{\pi} \times \delta_{\boldsymbol{\Pi}} \Phi_R), \\ \dot{\Pi} &= -\alpha_1 (\delta_{\boldsymbol{\Pi}} \Phi_R \cdot \boldsymbol{\pi}), \end{cases} \tag{37}$$

where the former equation rules the evolution of the direction $\boldsymbol{\pi}$, the latter rules the evolution of the magnitude Π of the residual polarization. The direction (amplitude) of the polarization is conserved during evolution as long as $\alpha_2 = 0$ ($\alpha_1 = 0$).

Remark 4.3. Eq. (36) is similar to the Landau-Lifshitz-Bloch (LLB) equation introduced by Garanin [43] for micromagnetics (see also [44, eqn.(4.9)]). However, in the LLB equation there is a conservative term involving the gyromagnetic ratio. If a similar term were present in our model it would have the form $\alpha_0 \boldsymbol{\pi} \times \delta_{\boldsymbol{\Pi}} \Phi_R$. Although perfectly compatible with thermodynamics, we avoided introducing in (36) this additional contribution as no precession effects are observed in ferroelectrics (see subsection 1.1).

4.3. Representation of the electric gibbs free energy

As results from (37), the time evolution of the magnitude and direction of $\boldsymbol{\Pi}$ depends mainly on the variational derivative of the electric Gibbs free energy. In this section, according to the Landau-Devonshire approximation in a neighborhood of the Curie point (see, for instance, [45]), we present and discuss the explicit form of ϕ (and therefore of Φ_R) in a anisotropic deformable ferroelectric media.

Piezoelectric effects are taken into account by specializing $\boldsymbol{\Xi}(\theta, \boldsymbol{C}, \boldsymbol{\mathcal{E}})$ in (18). Referring to [3] we let

$$\boldsymbol{P} = \epsilon_0 \chi_e \boldsymbol{E} + \mathbb{D}\, \mathfrak{E} + \rho\, \mathbf{p},$$

and then

$$\rho \boldsymbol{\Xi} = \epsilon_0 \chi_e \boldsymbol{C}^{-1} \boldsymbol{\mathcal{E}} + \boldsymbol{F}^{-1} \mathbb{D}\, \mathfrak{E},$$

where $\mathfrak{E} := \frac{1}{2}(\boldsymbol{C} - \mathbf{1})$ is the Green-St.Venant strain tensor, $\mathbb{D}$ denotes the (third-order) piezoelectric tensor and χ_e stands for the electric susceptibility. Both $\mathbb{D}$ and χ_e can depend on θ and we assume that $\mathbb{D}_{ijk} = \mathbb{D}_{ikj}$. Since $Q_{ij} Q_{ik} = \delta_{jk}$ we have

$$[(\boldsymbol{F}^{-1})^* \mathbb{D}^* \mathfrak{E}^*]_h = (F^{-1}_{hr} Q^{-1}_{ri})(Q_{il} Q_{jm} Q_{kn} \mathbb{D}_{lmn})(Q_{js} Q_{kp} \mathfrak{E}_{sp}) = F^{-1}_{hl} \mathbb{D}_{lmn} \mathfrak{E}_{mn},$$

so that $\boldsymbol{F}^{-1} \mathbb{D} \mathfrak{E}$ is an invariant vector. Accordingly, let $\mathbb{B} = \boldsymbol{F}^{-1} \mathbb{D}$ and consider

$$\rho \boldsymbol{\Xi} = \epsilon_0 \chi_e \boldsymbol{C}^{-1} \boldsymbol{\mathcal{E}} + \mathbb{B} \mathfrak{E}. \tag{38}$$

As required in Sect. 3, $\boldsymbol{\Xi}$ vanishes when both $\boldsymbol{\mathcal{E}}$ and $\mathfrak{E}$ vanish.

Taking into account that $\phi = \psi - \boldsymbol{\mathcal{E}} \cdot [\boldsymbol{\Xi} + \boldsymbol{\Pi}]$, condition (33) can be rewritten as

$$\partial_{\mathcal{E}} \psi = \boldsymbol{\mathcal{E}} \partial_{\mathcal{E}} \boldsymbol{\Xi}(\theta, \boldsymbol{C}, \boldsymbol{\mathcal{E}}),$$

so that applying (38) the specific free energy can be represented as

$$\rho \psi(\theta, \boldsymbol{C}, \boldsymbol{\mathcal{E}}, \boldsymbol{\Pi}, \nabla_R \boldsymbol{\Pi}) = \frac{1}{2} \epsilon_0 \chi_e \boldsymbol{C}^{-1} \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{E}} + \rho \psi^*(\theta, \boldsymbol{C}, \boldsymbol{\Pi}, \nabla_R \boldsymbol{\Pi}). \tag{39}$$

As usual, in purely elastic materials

$$\rho\, \psi^{\mathrm{el}} = \frac{1}{2}\, \mathbb{C}\, \mathfrak{E} \cdot \mathfrak{E},$$

$\mathbb{C}$ being a fourth-order positive-definite tensor possibly dependent on θ and usually referred to as *elasticity tensor*. Accordingly, we split the contribution due to deformation and polarization by choosing

$$\rho \psi^*(\theta, \boldsymbol{C}, \boldsymbol{\Pi}, \nabla_R \boldsymbol{\Pi}) = \frac{1}{2}\, \mathbb{C}\, \mathfrak{E} \cdot \mathfrak{E} + \rho \psi^{\mathrm{pol}}(\theta, \boldsymbol{\Pi}, \nabla_R \boldsymbol{\Pi}). \tag{40}$$

Summarizing,

$$\rho \phi = \frac{1}{2}\, \mathbb{C}\, \mathfrak{E} \cdot \mathfrak{E} - \boldsymbol{\mathcal{E}} \cdot \left[\mathbb{B} \mathfrak{E} + \frac{1}{2} \epsilon_0 \chi_e \boldsymbol{C}^{-1} \boldsymbol{\mathcal{E}} + \rho \boldsymbol{\Pi} \right] + \rho \psi^{\mathrm{pol}}(\theta, \boldsymbol{\Pi}, \nabla_R \boldsymbol{\Pi}). \tag{41}$$

4.3.1. Piezoelectric effects

If the residual polarization $\boldsymbol{\Pi}$ is neglected, $\mathcal{P}$ shortens to $\boldsymbol{\Xi}$ and ψ^{pol} becomes a function that depends only on θ. In this case, constitutive functions provide a simple piezoelectric model when finite deformations are involved. In particular, we have

$$\boldsymbol{E} = \frac{1}{\epsilon_0 \chi_e}[\boldsymbol{P} - \mathbb{D}\,\mathfrak{E}], \qquad \boldsymbol{E} \otimes \boldsymbol{P} = \frac{1}{\epsilon_0 \chi_e}[\boldsymbol{P} - \mathbb{D}\,\mathfrak{E}] \otimes \boldsymbol{P},$$

and from (22) it follows[9]

$$\mathcal{T} = \boldsymbol{F}[\,\mathbb{C}\mathfrak{E} - \mathbb{B}^T\mathcal{E} + \epsilon_0 \chi_e \boldsymbol{C}^{-1}\mathcal{E} \otimes \boldsymbol{C}^{-1}\mathcal{E}]\boldsymbol{F}^T = \boldsymbol{F}[\,\mathbb{C}\mathfrak{E} - \mathbb{D}^T\boldsymbol{E}]\boldsymbol{F}^T + \epsilon_0 \chi_e \boldsymbol{E} \otimes \boldsymbol{E}, \tag{42}$$

where the last dyadic term is referred to as electrostrictive stress. Since $\mathbb{B}^T_{ijk} := \mathbb{B}_{kij}$, the second-order tensor $\mathbb{B}^T\mathcal{E} = \mathbb{D}^T\boldsymbol{E}$ is symmetric and invariant. Finally, taking into account the non-symmetric Cauchy stress tensor, we note that the electrostrictive contribution disappears

$$\boldsymbol{T} = \mathcal{T} - \boldsymbol{E} \otimes \boldsymbol{P} = \boldsymbol{F}[\,\mathbb{C}\mathfrak{E} - \mathbb{D}^T\boldsymbol{E}]\boldsymbol{F}^T - \boldsymbol{E} \otimes \mathbb{D}\,\mathfrak{E}.$$

4.3.2. Polarization effects

Taking into account the effects due to the residual polarization $\boldsymbol{\Pi}$, we have

$$\mathcal{P} = \frac{1}{\rho}\left[\epsilon_0 \chi_e \boldsymbol{C}^{-1}\mathcal{E} + \mathbb{B}\mathfrak{E}\right] + \boldsymbol{\Pi}, \qquad \boldsymbol{P} = \epsilon_0 \chi_e \boldsymbol{E} + \mathbb{D}\,\mathfrak{E} + \rho\,\mathbf{p},$$

and

$$\boldsymbol{T} = \mathcal{T} - \boldsymbol{E} \otimes \boldsymbol{P} = \boldsymbol{F}[\,\mathbb{C}\mathfrak{E} - \mathbb{D}^T\boldsymbol{E}]\boldsymbol{F}^T - \boldsymbol{E} \otimes [\mathbb{D}\,\mathfrak{E} + \rho\,\mathbf{p}]. \tag{43}$$

In order to compute $\delta_{\boldsymbol{\Pi}}\Phi_R$ the key point is then to determine the expression of ψ^{pol} in (41). As previously observed, stationary conditions are characterized as critical points (in the variational sense) of the electric Gibbs free energy functional with respect to $\boldsymbol{\Pi}$, namely

$$\delta_{\boldsymbol{\Pi}}\Phi_R := \delta_{\boldsymbol{\Pi}}\Psi_R^{\text{pol}}(\theta, \boldsymbol{\Pi}, \nabla_R\boldsymbol{\Pi}) - \frac{\rho_R}{\theta}\mathcal{E} = \boldsymbol{0}, \qquad \Psi_R^{\text{pol}} = \frac{\rho_R}{\theta}\psi^{\text{pol}}.$$

On the other hand, in analogy with micromagnetics, it is natural to assume that these critical points correspond to the local vanishing of the invariant *effective electric field*, $\mathcal{E}^{\text{eff}}$, acting on the body. Accordingly, we are led to identify

$$\mathcal{E}^{\text{eff}} = \mathcal{E} - \frac{\theta}{\rho_R}\delta_{\boldsymbol{\Pi}}\Psi_R^{\text{pol}}. \tag{44}$$

After properly introducing $\mathcal{E}^{\text{eff}}$ as a function of $\boldsymbol{\Pi}$ and $\nabla_R\boldsymbol{\Pi}$, this relation allows us to construct a representation of ψ^{pol}. It is worth noting that in homogeneous materials with uniform temperature distribution the factor θ/ρ_R is independent of $\boldsymbol{X}$ and then commutes with $\delta_{\boldsymbol{\Pi}}$, so that

$$\mathcal{E}^{\text{eff}} = -\delta_{\boldsymbol{\Pi}}\phi := \mathcal{E} - \delta_{\boldsymbol{\Pi}}\psi^{\text{pol}}.$$

Like the effective magnetic field (see, for instance, [19–21,46,47]), the effective electric field at a point $\boldsymbol{X}$ of the reference configuration of the body can be represented as the sum of several contributions due to different phenomena. More precisely, we assume

$$\mathcal{E}^{\text{eff}} = \mathcal{E} + \mathcal{E}^{\text{int}} + \mathcal{E}^{\text{an}} + \mathcal{E}^{\text{exc}}, \tag{45}$$

where $\mathcal{E}$ is the external applied field, $\mathcal{E}^{\text{int}}$ is the electric field due to interaction of the polarization field with itself, $\mathcal{E}^{\text{an}}$ is due to anisotropic polarization (which strongly depends on the particle shape) and $\mathcal{E}^{\text{exc}}$ denotes the field arising from exchange neighborhood interactions.

Borrowing some arguments from micromagnetics, we are led to define

$$\mathcal{E}^{\text{int}} = -\mathcal{D}(\theta, \boldsymbol{\Pi})\boldsymbol{\Pi} \tag{46}$$

where $\mathcal{D}$ is a symmetric and invariant tensor-valued function. In absence of an external field, ferroelectric bodies tend to be polarized along precise directions which are called *easy directions*. This is mostly due to the depolarizing effect of spin-lattice coupling in crystals. Therefore, we take this phenomenon into account by adding the field

$$\mathcal{E}^{\text{an}} = -\mathcal{A}(\boldsymbol{\Pi})\boldsymbol{\Pi} \tag{47}$$

where $\mathcal{A}$ is a symmetric, positive semi-definite and invariant tensor-valued function dependent on the shape of the material and on its electric anisotropy.

[9] By virtue of the identity $\partial_{\boldsymbol{C}}\boldsymbol{C}^{-1} = -\boldsymbol{C}^{-1} \boxtimes \boldsymbol{C}^{-1}$; in indicial notation, $(\boldsymbol{C}^{-1} \boxtimes \boldsymbol{C}^{-1})_{ijhk} = \boldsymbol{C}^{-1}_{ih}\boldsymbol{C}^{-1}_{jk}$.

Finally, the exchange field $\mathcal{E}^{\rm exc}$ attempts to make the electric dipole moments lie parallel to one another in the immediately surrounding space. For further convenience we let

$$\mathcal{E}^{\rm exc} = \frac{\theta}{\rho_R}\nabla_R \cdot \left(\frac{\rho_R}{\theta}\mathbb{K}\nabla_R\boldsymbol{\Pi}\right) \tag{48}$$

where the fourth-order invariant tensor-valued function $\mathbb{K}$ is referred to as *exchange stiffness tensor*; it may depend on the temperature θ and the anisotropy of the ferroelectric material [48]. In particular, for homogeneous bodies with uniform temperature distribution in the reference configuration this definition simplifies and reads

$$\mathcal{E}^{\rm exc} = \nabla_R \cdot \left(\mathbb{K}\nabla_R\boldsymbol{\Pi}\right).$$

After collecting (45)-(48) we obtain

$$\mathcal{E}^{\rm eff} = \mathcal{E} - \left[\mathcal{D}(\theta,\boldsymbol{\Pi}) + \mathcal{A}(\boldsymbol{\Pi})\right]\boldsymbol{\Pi} + \frac{\theta}{\rho_R}\nabla_R \cdot \left(\frac{\rho_R}{\theta}\mathbb{K}\nabla_R\boldsymbol{\Pi}\right)$$

so that (44) gives

$$\frac{\theta}{\rho_R}\delta_{\boldsymbol{\Pi}}\Psi_R^{\rm pol} := \partial_{\boldsymbol{\Pi}}\psi^{\rm pol} - \frac{\theta}{\rho_R}\nabla_R \cdot \left(\frac{\rho_R}{\theta}\partial_{\nabla_R\boldsymbol{\Pi}}\psi^{\rm pol}\right) = -[\mathcal{D}(\theta,\boldsymbol{\Pi}) + \mathcal{A}(\boldsymbol{\Pi})]\boldsymbol{\Pi} - \frac{\theta}{\rho_R}\nabla_R \cdot \left(\frac{\rho_R}{\theta}\mathbb{K}\nabla_R\boldsymbol{\Pi}\right).$$

This relationship suggests the following equalities

$$\partial_{\boldsymbol{\Pi}}\psi^{\rm pol} = -[\mathcal{D}(\theta,\boldsymbol{\Pi}) + \mathcal{A}(\boldsymbol{\Pi})]\boldsymbol{\Pi}, \qquad \partial_{\nabla_R\boldsymbol{\Pi}}\psi^{\rm pol} = \mathbb{K}(\theta)\nabla_R\boldsymbol{\Pi} \tag{49}$$

which are simply satisfied by taking the following explicit expression

$$\psi^{\rm pol}(\theta,\boldsymbol{\Pi},\nabla_R\boldsymbol{\Pi}) = \frac{1}{2}\boldsymbol{\Pi}\cdot\mathcal{G}(\theta,\boldsymbol{\Pi})\boldsymbol{\Pi} + \frac{1}{2}\nabla_R\boldsymbol{\Pi}\cdot\mathbb{K}(\theta)\nabla_R\boldsymbol{\Pi} \tag{50}$$

where $\mathcal{G}(\theta,\boldsymbol{\Pi})$ is a symmetric, positive semi-definite, second-order tensor-valued function. In order to satisfy (49), $\mathcal{G}$ is related to $\mathcal{A}$ and $\mathcal{D}$ by the differential relation

$$\mathcal{G}(\theta,\boldsymbol{\Pi}) + \frac{1}{2}\boldsymbol{\Pi}\partial_{\boldsymbol{\Pi}}\mathcal{G}(\theta,\boldsymbol{\Pi}) = -\mathcal{D}(\theta,\boldsymbol{\Pi}) - \mathcal{A}(\boldsymbol{\Pi}). \tag{51}$$

The former addendum in (50) represents the free energy contribution associated with spatially-uniform polarization fields and is referred to as $\psi_1^{\rm pol}(\theta,\boldsymbol{\Pi})$. The latter stands for the interface free energy between polarized domain with different orientations, according to the diffuse interface approach [38]; hereinafter it is referred to as $\psi_2^{\rm pol}(\theta,\boldsymbol{\Pi})$. The subsequent sections provide significant examples of the explicit form of $\psi_1^{\rm pol}$ and $\psi_2^{\rm pol}$.

An application of (50) to the dynamics of $\boldsymbol{\Pi}$, ruled by (37)-(27), yields

$$\begin{cases} \dot{\boldsymbol{\pi}} &= -\dfrac{\rho_R}{\theta}\dfrac{\alpha_2}{\Pi}\boldsymbol{\pi}\times\left(\boldsymbol{\pi}\times\left[\mathcal{E} - (\mathcal{D}+\mathcal{A})\boldsymbol{\Pi} + \dfrac{\theta}{\rho_R}\nabla_R\cdot\left(\dfrac{\rho_R}{\theta}\mathbb{K}\nabla_R\boldsymbol{\Pi}\right)\right]\right), \\ \dot{\boldsymbol{\Pi}} &= \alpha_1\dfrac{\rho_R}{\theta}\left[\mathcal{E} - (\mathcal{D}+\mathcal{A})\boldsymbol{\Pi} + \dfrac{\theta}{\rho_R}\nabla_R\cdot\left(\dfrac{\rho_R}{\theta}\mathbb{K}\nabla_R\boldsymbol{\Pi}\right)\right]\cdot\boldsymbol{\pi}, \end{cases}$$

with the boundary condition

$$[\mathbb{K}\nabla_R\boldsymbol{\Pi}]^T\boldsymbol{n}_R|_{\partial\mathcal{R}} = \boldsymbol{0}. \tag{52}$$

In homogeneous bodies with uniform temperature distribution, θ and ρ_R are independent of the space variable $\boldsymbol{X}$. So, letting $\alpha = \alpha_1\rho_R/\theta$ and $\beta = \alpha_2\rho_R/\theta$ this system simplifies as follows

$$\begin{cases} \dot{\boldsymbol{\pi}} &= -\dfrac{\beta}{\Pi}\boldsymbol{\pi}\times\left(\boldsymbol{\pi}\times\left[\mathcal{E} - (\mathcal{D}+\mathcal{A})\boldsymbol{\Pi} + \nabla_R\cdot(\mathbb{K}\nabla_R\boldsymbol{\Pi})\right]\right), \\ \dot{\Pi} &= \alpha\left[\mathcal{E} - (\mathcal{D}+\mathcal{A})\boldsymbol{\Pi} + \nabla_R\cdot(\mathbb{K}\nabla_R\boldsymbol{\Pi})\right]\cdot\boldsymbol{\pi}. \end{cases} \tag{53}$$

5. Landau-Devonshire (phase-field) models

There are two main categories of ferroelectric materials: those that undergo a second-order transition, like triglycine sulfate, and those that undergo a first-order transition, like BaTiO3 and other perovskites. The Landau-Devonshire theory is able to describe the behavior of these materials by assuming a sixth-order approximation of the specific free energy with respect to a scalar order parameter (see, *e.g*, [49]).

With the aim of generalizing the Landau-Devonshire theory, we suppose that $\mathcal{D}$ and $\mathcal{A}$ are fourth-order even functions of $\boldsymbol{\Pi}$, whose coefficients possibly depend on θ. In particular, we let

$$\mathcal{D}(\theta,\boldsymbol{\Pi}) = \left[D_2\Pi^4 + D_1\Pi^2 - D_0^*(\theta)\right]\mathbf{1}, \qquad D_0^*(\theta) = D_0\frac{\theta_c - \theta}{\theta_c}, \tag{54}$$

where $D_0 > 0$, $D_2 \geq 0$, whereas $D_1 \in \mathbb{R}$. On the other hand, the explicit form of $\mathcal{A}$ is related to the anisotropic properties of materials that are characterized by their symmetry group. In the following subsections we treat several cases and for each we represent its specific free energy ψ^{pol}.

5.1. Isotropic bodies

In continuum mechanics, the largest symmetry group in three-dimensional space includes all orthogonal transformations. It is denoted by $O(3)$ and is referred to as *isotropic*. If this is the case, then $\mathcal{D}$ is given by (54) and

$$\mathcal{A} = \mathbf{0}, \qquad \mathbb{K} = \varkappa_1 \mathbb{I} + \varkappa_2 \mathbf{1} \otimes \mathbf{1}, \tag{55}$$

where $\mathbb{I}$ denotes the fourth-order identity tensor and $\varkappa_1, \varkappa_2 > 0$ are scalars possibly dependent on temperature. By virtue of (51), (54) and (55) we obtain

$$\mathcal{G}(\theta, \boldsymbol{\Pi}) = \left[\frac{D_2}{3}\Pi^4 + \frac{D_1}{2}\Pi^2 - D_0^*(\theta)\right]\mathbf{1}.$$

Consequently, (50) gives

$$\psi_1^{\text{pol}} = -\frac{D_0^*(\theta)}{2}\Pi^2 + \frac{D_1}{4}\Pi^4 + \frac{D_2}{6}\Pi^6, \qquad \psi_2^{\text{pol}} = \frac{\varkappa_1}{2}\|\nabla_R \boldsymbol{\Pi}\|^2 + \frac{\varkappa_2}{2}|\nabla_R \cdot \boldsymbol{\Pi}|^2.$$

Since D_0^* becomes positive as θ lowers below θ_C, the function ψ_1^{pol} with respect to Π changes from convex to non-convex.

In the special case given by (39)-(40) the isotropy of the material gives

$$\mathbb{C} = 2\mu_{\text{el}}\mathbb{I} + \lambda_{\text{el}}\mathbf{1} \otimes \mathbf{1},$$

where $\lambda_{\text{el}}, \mu_{\text{el}}$ denote Lamé's moduli, so that the whole free energy becomes

$$\rho\psi = \frac{1}{2}\epsilon_0\chi_e \boldsymbol{\mathcal{E}} \cdot \mathbf{C}^{-1}\boldsymbol{\mathcal{E}} + \mu_{\text{el}}\mathfrak{E}^2 + \frac{1}{2}\lambda_{\text{el}}[\text{tr}\,\mathfrak{E}]^2 + \rho\psi^{\text{pol}}. \tag{56}$$

A special solution to the polarization dynamics is obtained by assuming that $\boldsymbol{\Pi}$ and $\boldsymbol{\mathcal{E}}$ have a common direction $\boldsymbol{\pi}$ which is fixed and constant, that is independent of time and place. This is consistent with $(53)_1$ provided that $\beta = 0$, namely $\alpha_2 = 0$ (no transversal relaxation). Let $\mathcal{E} = \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\pi}$. After replacing (54)-(55) into $(53)_2$ and taking into account that $\nabla_R \boldsymbol{\Pi} \cdot \boldsymbol{\pi} = \nabla_R \Pi$, we obtain the scalar equation

$$\frac{1}{\alpha}\dot{\boldsymbol{\Pi}} = \mathcal{E} + \Pi\left[D_0^*(\theta) - D_1\Pi^2 - D_2\Pi^4\right] + \nabla_R \cdot \left(\varkappa_1 \nabla_R \Pi\right) + \nabla_R(\varkappa_2 \nabla_R \Pi) \cdot (\boldsymbol{\pi} \otimes \boldsymbol{\pi}).$$

When $\boldsymbol{\Pi}$, as well as $\boldsymbol{\mathcal{E}}$, is a solenoidal field ($\nabla_R \cdot \boldsymbol{\Pi} = 0$), the last addendum at the right disappears and this equation reduces to the unidimensional Landau-Devonshire equation (see, for instance, [34,50]).

5.2. Anisotropic bodies

Although isotropic Landau-Devonshire energy is widely applied and easy to compute, most ferroelectric materials are anisotropic. For instance, anisotropy in ferroelectrics is due to spin-lattice coupling in cubic crystals (as the perovskite system) and transversely isotropic symmetry in piezoelectric thin films. In the former case the group consisting of all proper rotations leaving invariant a cubic lattice is the rotational octahedral symmetry group. If, in addition, we allow reflections, we arrive at the so-called *octahedral symmetry group* which is denoted by O_h. Basically, when cubic anisotropy occurs then three privileged mutually orthogonal material directions exist. On the other case, a *transversely isotropic material* is characterized by symmetry with respect to one selected material direction referred to as principal direction. Properties of a transversely isotropic material remain unchanged by rotations about, and reflections from the planes orthogonal or parallel to, this direction. For the sake of definiteness, in the sequel we give the expressions of the Landau-Devonshire specific free energy related to octahedral and transversely isotropic symmetries.

Let $(\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)$ be a principal material direction basis and $\boldsymbol{\mathcal{S}}_i = \boldsymbol{e}_i \otimes \boldsymbol{e}_i$, $i = 1, 2, 3$, be the related structural tensors so that

$$\boldsymbol{\Pi} = \sum_{i=1}^{3} \Pi_i \boldsymbol{e}_i, \qquad \boldsymbol{\mathcal{S}}_i \boldsymbol{\Pi} = \Pi_i \boldsymbol{e}_i.$$

In particular, $\boldsymbol{\mathcal{S}}_i^n = \boldsymbol{\mathcal{S}}_i$, $n \in \mathbb{N}$, and $\boldsymbol{\mathcal{S}}_i \boldsymbol{\mathcal{S}}_j = \mathbf{0}$ when $i \neq j$. Then for any $n \in \mathbb{N}$ we introduce the family of tensors

$$\mathcal{H}_n(\boldsymbol{\Pi}) = \sum_{i=1}^{3} \Pi_i^n \boldsymbol{\mathcal{S}}_i.$$

After performing a suitable change of coordinates (in the frame locally at rest with the body), $\mathcal{A}$ can be expressed in diagonal form with respect to this basis. Confining our attention to forth-order powers in $\boldsymbol{\Pi}$, we assume

$$\mathcal{A} = \mathcal{A}_0 + \mathcal{A}_1 \mathcal{H}_2(\boldsymbol{\Pi}) + \mathcal{A}_2 \Pi^2 \mathcal{H}_2(\boldsymbol{\Pi}) + \mathcal{A}_3 \mathcal{H}_4(\boldsymbol{\Pi}),$$

where

$$\mathcal{A}_0 = \sum_{i=1}^{3} \ell_i \boldsymbol{\mathcal{S}}_i, \quad \mathcal{A}_1 = \sum_{i=1}^{3} \lambda_i \boldsymbol{\mathcal{S}}_i, \quad \mathcal{A}_2 = \sum_{i=1}^{3} \mu_i \boldsymbol{\mathcal{S}}_i, \quad \mathcal{A}_3 = \sum_{i=1}^{3} \nu_i \boldsymbol{\mathcal{S}}_i.$$

Fig. 1. Graph of the transversally isotropic energy surface, $\psi_1^{\rm pol}=1$, when $0<\theta<\theta_c$: $\ell,\lambda<0$ (left) and $\ell,\lambda>0$ (right).

Constants ℓ_i, λ_i, μ_i, ν_i, $i=1,2,3$, characterize the anisotropy of the body. From (54) we obtain

$$\boldsymbol{\mathcal{D}}(\theta,\boldsymbol{\Pi})\boldsymbol{\Pi}+\boldsymbol{\mathcal{A}}(\boldsymbol{\Pi})\boldsymbol{\Pi}=\big[D_2\Pi^4+D_1\Pi^2-D_0^*(\theta)\big]\boldsymbol{\Pi}+\sum_{i=1}^{3}(\ell_i+\lambda_i\Pi_i^2+\mu_i\Pi^2\Pi_i^2+\nu_i\Pi_i^4)\Pi_i\boldsymbol{e}_i,$$

and applying (51) it follows

$$\begin{aligned}\psi_1^{\rm pol}(\theta,\boldsymbol{\Pi}) &:= \frac{1}{2}\boldsymbol{\Pi}\cdot\boldsymbol{\mathcal{G}}(\theta,\boldsymbol{\Pi})\boldsymbol{\Pi}=\frac{1}{2}\left(\sum_{i=1}^{3}\ell_i\Pi_i^2-D_0^*(\theta)\Pi^2\right)\\ &\quad+\frac{1}{4}\left(D_1\Pi^4+\sum_{i=1}^{3}\lambda_i\Pi_i^4\right)+\frac{1}{6}\left(D_2\Pi^6+\sum_{i=1}^{3}\big[\mu_i\Pi^2\Pi_i^4+\nu_i\Pi_i^6\big]\right).\end{aligned}$$

Then, borrowing the arguments set out in [48] for a cubic perovskite systems, we assume that anisotropy affects $\mathbb{K}$ in a similar way,

$$\mathbb{K}=\varkappa_1\mathbb{I}+\varkappa_2\mathbf{1}\otimes\mathbf{1}+\sum_{i=1}^{3}\lambda_i\boldsymbol{\mathcal{S}}_i\otimes\boldsymbol{\mathcal{S}}_i.$$

Accordingly the second term on the right in (50) becomes

$$\begin{aligned}\psi_2^{\rm pol}(\theta,\boldsymbol{\Pi}) &:= \frac{1}{2}\nabla_R\boldsymbol{\Pi}\cdot\mathbb{K}(\theta)\nabla_R\boldsymbol{\Pi}\\ &= \frac{1}{2}\big(\varkappa_1\|\nabla_R\boldsymbol{\Pi}\|^2+\varkappa_2|\nabla_R\cdot\boldsymbol{\Pi}|^2\big)+\frac{1}{2}\sum_{i=1}^{3}\lambda_i(\boldsymbol{\mathcal{S}}_i\cdot\nabla_R\boldsymbol{\Pi})^2.\end{aligned}$$

5.2.1. Transversely isotropic bodies

If the material is transversely isotropic (it has one easy direction, say $\boldsymbol{e}_3$) we let

$$\ell_1=\ell_2=\ell,\quad \lambda_1=\lambda_2=\lambda,\quad \ell_3=\lambda_3=0,\quad \mu_i=\nu_i=0,\ i=1,2,3,$$

so that it follows

$$\psi_1^{\rm pol}=\frac{1}{2}\big[\ell(\Pi_1^2+\Pi_2^2)-D_0^*(\theta)\Pi^2\big]+\frac{1}{4}\big[D_1\Pi^4+\lambda(\Pi_1^4+\Pi_2^4)\big]+\frac{1}{6}D_2\Pi^6,$$

$$\psi_2^{\rm pol}=\frac{\varkappa_1}{2}\sum_{i,j=1}^{3}(\partial_{X_i}\Pi_j)^2+\frac{\varkappa_2}{2}\left(\sum_{i=1}^{3}\partial_{X_i}\Pi_i\right)^2+\frac{\lambda}{2}\sum_{i=1}^{2}(\partial_{X_i}\Pi_i)^2.$$

Provided that $\theta<\theta_c$, when $D_1>0$ the specific energy $\psi_1^{\rm pol}$ takes nontrivial minima along either the easy direction, if $\ell,\lambda<0$, or the easy plane, if $\ell,\lambda>0$ (see Fig. 1).

5.2.2. Cubic crystals

When the material lattice has cubic symmetry, then $\lambda_i=\lambda$, $\mu_i=\mu$, $\nu_i=\nu$ and $\ell_i=0$, $i=1,2,3$. After introducing proper constants

$$\begin{aligned}\alpha_{10} &= -\frac{1}{2}D_0^*(\theta)=\frac{D_0}{2}\frac{\theta-\theta_c}{\theta_c},\quad \alpha_{11}=\frac{D_1+\lambda}{4},\quad \alpha_{12}=-\frac{\lambda}{2},\\ \alpha_{111} &= \frac{D_2+\mu+\nu}{6},\quad \alpha_{112}=-\frac{2\mu+3\nu}{6},\quad \alpha_{123}=-(\mu+\nu),\\ g_{11} &= \frac{1}{2}(\varkappa_1+\varkappa_2+\lambda),\quad g_{12}=\varkappa_2,\quad g_{44}=\frac{1}{2}\varkappa_1,\end{aligned}$$

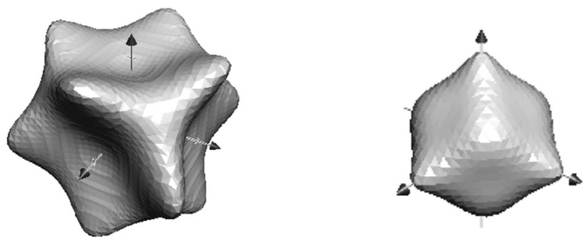

Fig. 2. Graph of the specific energy surface $\psi_1^{\text{pol}} = 1$ with cubic symmetry when $0 < \theta < \theta_c$, and $\lambda + D_1 > 0$: $2\mu + 3\nu > 0$ (left) and $2\mu + 3\nu < 0$ (right).

we obtain (let compare, for instance, with Table 1 in [48])

$$\psi_1^{\text{pol}} = \alpha_{10}\Pi^2 + \alpha_{11}\Pi^4 + \alpha_{12}(\Pi_1^2\Pi_2^2 + \Pi_2^2\Pi_3^2 + \Pi_1^2\Pi_3^2) + \alpha_{111}\Pi^6$$
$$+\alpha_{112}[\Pi_1^4(\Pi_2^2 + \Pi_3^2) + \Pi_2^4(\Pi_1^2 + \Pi_3^2) + \Pi_3^4(\Pi_1^2 + \Pi_2^2)] + \alpha_{123}\Pi_1^2\Pi_2^2\Pi_3^2,$$

$$\psi_2^{\text{pol}} = g_{11}\sum_{i=1}^{3}(\partial_{X_i}\Pi_i)^2 + g_{12}\sum_{i\neq j=1}^{3}\partial_{X_i}\Pi_i\,\partial_{X_j}\Pi_j + g_{44}\sum_{i\neq j=1}^{3}(\partial_{X_i}\Pi_j)^2.$$

Remark 5.1. We observe that α_{12} is negative if $\lambda > 0$, whereas α_{11} is positive provided that $\lambda > -D_1$ and the sign of α_{10} depends on θ. Then, below the Curie temperature $\alpha_{10} < 0$ so that ψ_1^{pol} takes nontrivial minima along the principal material directions provided that $2\mu + 3\nu > 0$, on the contrary it takes maxima along the same directions when $2\mu + 3\nu < 0$ (see Fig. 2). In addition, we observe that α_{111} is positive provided that $\mu + \nu > -D_2$, whereas the sign of α_{112} and α_{123} only depend on the values of μ and ν. All coefficients in ψ_2^{pol} are positive provided that $\lambda > -\varkappa_1 - \varkappa_2$. In all known ferroelectrics, $D_0 > 0$ and $\alpha_{111} > 0$. These coefficients may be obtained experimentally: for ferroelectrics with a first order phase transition, $\alpha_{11} < 0$, whereas $\alpha_{11} > 0$ for a second order phase transition [50].

5.2.3. Cubic crystals with $D_2 = 0$, $D_1 > 0$

The material lattice has cubic symmetry, as above, but a fourth-order approximation of the specific free energy is involved. In this case, from (50) we obtain the customary expressions for the cubic system O_h (see, for instance, [39] and in particular [48], Tables 1 and 2)

$$\psi_1^{\text{pol}} = \alpha_{10}\Pi^2 + \alpha_{11}\Pi^4 + \alpha_{12}(\Pi_1^2\Pi_2^2 + \Pi_2^2\Pi_3^2 + \Pi_1^2\Pi_3^2),$$

whereas ψ_2^{pol} takes the same form as in the general case.

Remark 5.2. We observe that α_{12} is negative, whereas α_{11} is positive provided that $\lambda > -D_1$ and the sign of α_{10} depends on θ. Then, below the Curie temperature, ψ_1^{pol} takes nontrivial minima along the principal material directions provided that $\lambda > 0$, on the contrary it takes maxima along the same directions when $-D_1 < \lambda < 0$ (see Fig. 3).

6. Electro-mechanical effects

The coupling between electric field and mechanical strain shows up experimentally via the classical butterfly loops providing the strain versus the electric field. This is done both in the stress-free state and when the material is subject to a constant stress.

Hereafter we adopt a procedure which is standard in piezoelectricity. Namely, we look now at a simplified version where we describe the (linearized) mechanical properties around the reference configuration. Let $\boldsymbol{u} = \boldsymbol{x} - \boldsymbol{X}$ be the displacement and

$$\boldsymbol{\varepsilon} = \text{sym}\nabla\boldsymbol{u},$$

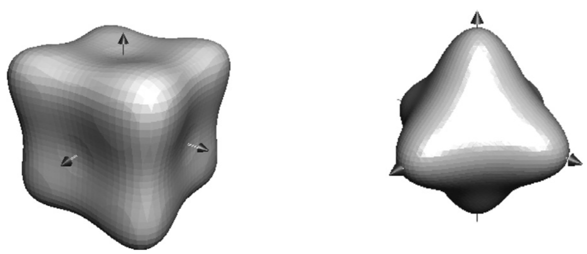

Fig. 3. Graph of the fourth-order specific energy surface $\psi_1^{\text{pol}} = 1$ with cubic symmetry when $D_2 = 0$, $D_1 > 0$ and $0 < \theta < \theta_c$: $\lambda > 0$ (left) and $\lambda < 0$ (right).

be the (infinitesimal) strain. Also by analogy with the literature, we now apply the thermodynamic scheme in the approximation of small deformations, that is when $|\varepsilon_{jk}| \ll 1$ for any jk-component.

Let $\nabla_R \boldsymbol{u}$ the displacement gradient so that $\boldsymbol{F} = \mathbf{1} + \nabla_R \boldsymbol{u}$. Now,

$$\nabla_R \boldsymbol{u} = (\nabla \boldsymbol{u})\boldsymbol{F} = (\nabla \boldsymbol{u})(\mathbf{1} + \nabla_R \boldsymbol{u}) = (\nabla \boldsymbol{u})(\mathbf{1} + (\nabla \boldsymbol{u})\boldsymbol{F}) = \nabla \boldsymbol{u} + o(|\nabla \boldsymbol{u}|),$$

where $|\nabla \boldsymbol{u}| = (\nabla \boldsymbol{u} \cdot \nabla \boldsymbol{u})^{1/2}$. Hence

$$\mathfrak{E} = \tfrac{1}{2}(\boldsymbol{C} - \mathbf{1}) = \boldsymbol{\varepsilon} + o(|\nabla \boldsymbol{u}|).$$

Within this approximation $\rho \simeq \rho_R$ and (41) becomes

$$\rho_R \phi \simeq \frac{1}{2}\,\mathbb{C}\,\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon} - \frac{1}{2}\epsilon_0 \chi_e |\boldsymbol{E}|^2 - \boldsymbol{E} \cdot [\mathbb{D}\boldsymbol{\varepsilon} + \rho_R\, \mathbf{p}] + \rho_R \psi^{\mathrm{pol}}. \tag{57}$$

Accordingly, we obtain the so called *strain-charge form*

$$\mathcal{T} = 2\,\rho \boldsymbol{F}\,\partial_{\boldsymbol{C}} \phi\, \boldsymbol{F}^T \simeq \rho_R \partial_{\boldsymbol{\varepsilon}} \phi = \mathbb{C}\,\boldsymbol{\varepsilon} - \mathbb{D}^T \boldsymbol{E}, \qquad \boldsymbol{P} \simeq \epsilon_0 \chi_e \boldsymbol{E} + \mathbb{D}\,\boldsymbol{\varepsilon} + \rho_R\, \mathbf{p}.$$

Finally, we obtain

$$\boldsymbol{T} := \mathcal{T} - \boldsymbol{E} \otimes \boldsymbol{P} \simeq \mathbb{C}\,\boldsymbol{\varepsilon} - \mathbb{D}^T \boldsymbol{E} - \boldsymbol{E} \otimes (\epsilon_0 \chi_e \boldsymbol{E} + \mathbb{D}\,\boldsymbol{\varepsilon} + \rho_R\, \mathbf{p}). \tag{58}$$

It is worth noting that applying a further linearization with respect to $\boldsymbol{E}$ and $\boldsymbol{P}$, the term $\boldsymbol{E} \otimes \boldsymbol{P}$ is usually ignored. On the contrary, hereafter this term is considered and is shown to be on the basis of the butterfly-shaped hysteresis loops.

We are now interested to study the behavior of the strain $\boldsymbol{\varepsilon}$ in correspondence with the variations of the electric field $\boldsymbol{E}$ and the residual polarization $\mathbf{p}$ when the stress $\boldsymbol{T}$ is constant. As usual, to simplify the computation we assume that $\boldsymbol{T}$ vanishes so that

$$\mathbf{0} = (\mathbb{C} - \boldsymbol{E} \otimes \mathbb{D})\boldsymbol{\varepsilon} - \boldsymbol{E} \otimes (\epsilon_0 \chi_e \boldsymbol{E} + \rho_R\, \mathbf{p}) - \mathbb{D}^T \boldsymbol{E}.$$

Letting

$$\mathsf{D} = \mathbb{D}\,\mathbb{C}^{-1}, \qquad \boldsymbol{\Lambda} = \epsilon_0 \chi_e \mathbf{1} + \mathbb{D}\,\mathbb{C}^{-1}\mathbb{D}^T,$$

we obtain the approximate expressions

$$\boldsymbol{P} = \mathsf{D}\mathcal{T} + \boldsymbol{\Lambda}\boldsymbol{E} + \rho_R\, \mathbf{p}, \qquad \boldsymbol{\varepsilon} = \mathbb{C}^{-1}\mathcal{T} + \mathsf{D}^T \boldsymbol{E}, \tag{59}$$

where the first equation represents the relationship for the direct piezoelectric effect and the latter for the converse piezoelectric effect. In particular, if $\mathbb{C} = \lambda_{\mathrm{el}}\mathbf{1} \otimes \mathbf{1} + 2\mu_{\mathrm{el}}\mathbb{I}$ then

$$\mathbb{C}^{-1} = -\frac{\lambda}{2\mu_{\mathrm{el}}(3\lambda_{\mathrm{el}} + 2\mu_{\mathrm{el}})}\mathbf{1} \otimes \mathbf{1} + \frac{1}{2\mu_{\mathrm{el}}}\mathbb{I}.$$

Using the Mandel-Voigt notation [17, p.691], symmetric second order tensors are represented as vectors of six components, namely

$$\mathfrak{T} = (\mathfrak{T}_1, \mathfrak{T}_2, \mathfrak{T}_3, \mathfrak{T}_4, \mathfrak{T}_5, \mathfrak{T}_6)^T = (\mathcal{T}_{11}, \mathcal{T}_{22}, \mathcal{T}_{33}, \sqrt{2}\mathcal{T}_{23}, \sqrt{2}\mathcal{T}_{13}, \sqrt{2}\mathcal{T}_{12}),$$

$$\boldsymbol{S} = (S_1, S_2, S_3, S_4, S_5, S_6)^T = (\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \sqrt{2}\varepsilon_{23}, \sqrt{2}\varepsilon_{13}, \sqrt{2}\varepsilon_{12}).$$

This means that $\mathfrak{T}$ and $\boldsymbol{S}$ are vectors representing stress $\mathcal{T}$ and strain $\boldsymbol{\varepsilon}$. In the Mandel-Voigt notation, $\mathbb{C}^{-1}$ is represented by the six-by-six tensor S, D by the corresponding six-by-three tensor $\mathfrak{D}$. As a consequence, the strain-charge equations (59) take the form

$$\boldsymbol{P} = \mathfrak{D}\mathfrak{T} + \boldsymbol{\Lambda}\boldsymbol{E} + \rho_R\, \mathbf{p}, \qquad \boldsymbol{S} = \mathsf{S}\mathfrak{T} + \mathfrak{D}^T \boldsymbol{E}.$$

According to the IEEE Standard on Piezoelectricity (IEEE Standards ANSI/IEEE 176 -1987), the strain-charge equations for a poled piezoelectric ceramic (for instance, tetragonal PZT or BaTiO3) are given by

$$\begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & \mathfrak{D}_{15} & 0 \\ 0 & 0 & 0 & \mathfrak{D}_{24} & 0 & 0 \\ \mathfrak{D}_{31} & \mathfrak{D}_{32} & \mathfrak{D}_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \mathfrak{T}_1 \\ \mathfrak{T}_2 \\ \mathfrak{T}_3 \\ \mathfrak{T}_4 \\ \mathfrak{T}_5 \\ \mathfrak{T}_6 \end{bmatrix} + \begin{bmatrix} \Lambda_{11} & 0 & 0 \\ 0 & \Lambda_{22} & 0 \\ 0 & 0 & \Lambda_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} + \rho_R \begin{bmatrix} \mathsf{p}_1 \\ \mathsf{p}_2 \\ \mathsf{p}_3 \end{bmatrix},$$

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} \mathsf{S}_{11} & \mathsf{S}_{12} & \mathsf{S}_{13} & 0 & 0 & 0 \\ \mathsf{S}_{21} & \mathsf{S}_{22} & \mathsf{S}_{23} & 0 & 0 & 0 \\ \mathsf{S}_{31} & \mathsf{S}_{32} & \mathsf{S}_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathsf{S}_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathsf{S}_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(\mathsf{S}_{11} - \mathsf{S}_{12}) \end{bmatrix} \begin{bmatrix} \mathfrak{T}_1 \\ \mathfrak{T}_2 \\ \mathfrak{T}_3 \\ \mathfrak{T}_4 \\ \mathfrak{T}_5 \\ \mathfrak{T}_6 \end{bmatrix} + \begin{bmatrix} 0 & 0 & \mathfrak{D}_{31} \\ 0 & 0 & \mathfrak{D}_{32} \\ 0 & 0 & \mathfrak{D}_{33} \\ 0 & \mathfrak{D}_{24} & 0 \\ \mathfrak{D}_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}.$$

These relations simplify in the special case when $\mathbf{p}$ and $\boldsymbol{E}$ have the same common direction, for instance $\boldsymbol{e}_1$, so that $E_h = \mathsf{p}_h = 0$, $h = 2, 3$, and we let $E_1 = E$, $\mathsf{p}_1 = \mathsf{p}$. Accordingly,

$$P_1 = \mathfrak{D}_{15}\mathfrak{T}_5 + \Lambda_{11}E + \rho_R\mathsf{p}, \quad P_2 = \mathfrak{D}_{24}\mathfrak{T}_4, \quad P_3 = \sum_{i=1}^{3}\mathfrak{D}_{3i}\mathfrak{T}_i, \tag{60}$$

$$S_i = \sum_{j=1}^{3}\mathsf{S}_{ij}\mathfrak{T}_j, \ i = 1, 2, 3, \quad S_4 = \mathsf{S}_{44}\mathfrak{T}_4, \quad S_5 = \mathsf{S}_{55}\mathfrak{T}_5 + \mathfrak{D}_{15}E, \quad S_6 = 2(\mathsf{S}_{11} - \mathsf{S}_{12})\mathfrak{T}_6.$$

Since $\boldsymbol{\mathcal{T}} = \mathrm{sym}(\boldsymbol{T} + \boldsymbol{E}\otimes\boldsymbol{P})$ it follows

$$\mathcal{T}_{ij} = \tfrac{1}{2}[T_{ij} + T_{ji} + E_iP_j + E_jP_i],$$

and then

$$\mathfrak{T}_1 = \mathcal{T}_{11} = T_{11} + EP_1, \ \mathfrak{T}_2 = \mathcal{T}_{22} = T_{22}, \ \mathfrak{T}_3 = \mathcal{T}_{33} = T_{33}, \ \mathfrak{T}_4 = \sqrt{2}\,\mathcal{T}_{23} = \tfrac{\sqrt{2}}{2}\,[T_{23} + T_{32}],$$

$$\mathfrak{T}_5 = \sqrt{2}\,\mathcal{T}_{13} = \tfrac{\sqrt{2}}{2}\,[T_{13} + T_{31} + EP_3], \quad \mathfrak{T}_6 = \sqrt{2}\,\mathcal{T}_{12} = \tfrac{\sqrt{2}}{2}\,[T_{12} + T_{21} + EP_2].$$

We now restrict our attention to the behavior of the linearized strain-vector $\boldsymbol{S}$ in correspondence with the variations of the electric field $E\boldsymbol{e}_1$ and the residual polarization $\mathsf{p}\boldsymbol{e}_1$ when the stress $\boldsymbol{T}$ is constant. In particular, to simplify the computation we assume that $\boldsymbol{T}$ vanishes so that

$$\mathfrak{T}_1 = EP_1, \ \mathfrak{T}_2 = \mathfrak{T}_3 = \mathfrak{T}_4 = 0, \ \mathfrak{T}_5 = \tfrac{\sqrt{2}}{2}\,EP_3, \ \mathfrak{T}_6 = \tfrac{\sqrt{2}}{2}\,EP_2.$$

After replacing these values into (60) we have

$$P_1 = \tfrac{\sqrt{2}}{2}\,\mathfrak{D}_{15}EP_3 + \Lambda_{11}E + \rho_R\mathsf{p}, \quad P_2 = 0, \quad P_3 = \mathfrak{D}_{31}EP_1,$$

and neglecting nonlinear terms in $\boldsymbol{E}$ and $\boldsymbol{P}$ it follows

$$P_1 = \Lambda_{11}E + \rho_R\mathsf{p}, \quad P_2 = 0, \quad P_3 = 0.$$

As a consequence, the non-vanishing components of $\mathfrak{T}$ and $\boldsymbol{S}$ take the form

$$\mathfrak{T}_1 = \Lambda_{11}E^2 + \rho_R E\mathsf{p}, \qquad S_i = \mathsf{S}_{i1}(\Lambda_{11}E^2 + \rho_R E\mathsf{p}), \ i = 1, 2, 3, \qquad S_5 = \mathfrak{D}_{15}E. \tag{61}$$

Now, taking into account that $\boldsymbol{\Pi} \simeq \mathbf{p} = \mathsf{p}\,\boldsymbol{e}_1$, from (53) we obtain the unidimensional (approximate) evolution equation for p,

$$\dot{\mathsf{p}} = \alpha(\theta)\big(E - [\mathcal{D}(\theta, \mathsf{p}) + \mathcal{A}(\mathsf{p})]\,\mathsf{p} + (\varkappa_1 + \varkappa_2 + \lambda)\Delta_R\mathsf{p}\big).$$

In the most general case (see subsection 5.2.2)

$$\mathcal{D}(\theta, \mathsf{p}) + \mathcal{A}(\mathsf{p}) = (D_2 + \mu + \nu)\mathsf{p}^4 + (D_1 + \lambda)\mathsf{p}^2 - D_0^*(\theta).$$

After neglecting the spatial diffusion, we assume $A_1 := D_1 + \lambda > 0$ and $A_2 := D_2 + \mu + \nu > 0$. Hence, setting a temperature $\hat{\theta}$ in the ferroelectric range, $0 < \hat{\theta} < \theta_c$, the approximate evolution equation reduces to

$$\dot{\mathsf{p}} = \alpha(\hat{\theta})\left[E - A_2\mathsf{p}^5 - A_1\mathsf{p}^3 + D_0\frac{\theta_c - \hat{\theta}}{\theta_c}\mathsf{p}\right].$$

The graph of the resulting major hysteresis loop in the (p, E)-plane is qualitatively represented in Fig. 4 on the left, whereas, according to (61), the corresponding butterfly-shaped graph of $S_1 = \varepsilon_{11}$ versus E is provided on the right.

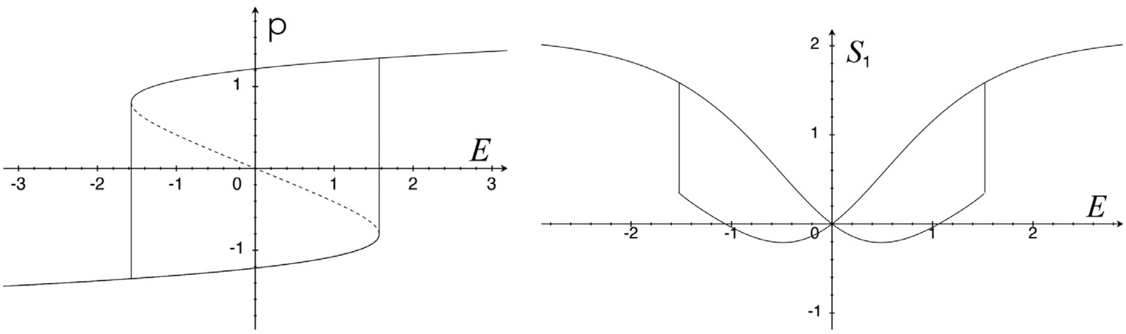

Fig. 4. On the left: the major hysteresis loop in the (E, p) plane ($A_2 = 1, A_1 = 0.2, D_0 = 5, \hat{\theta}/\theta_c = 0.5$). On the right: butterfly-shaped graph of S_1 versus E ($\rho_R = \Lambda_{11} = 1, \mathsf{S}_{11} = 0.7$).

7. Conclusions

In this paper a non-isothermal, vector-valued model for deformable ferroelectric materials is established within the framework of continuum thermodynamics. The scheme adopted here has some features in common with [9,10] for the study of piezo-ferroelectric materials subject to large deformations. In particular, we also use mechanical and electromagnetic variables in the material description, so that the standard balance of torques (5) is a consequence of thermodynamic restrictions. As in [10] we assume that the ferroelectric polarization vector $\mathcal{P}$ is decomposed into a reversible (piezoelectric) component, $\boldsymbol{\Xi}$, and a residual (remnant) part, $\boldsymbol{\Pi}$, which is considered as an independent variable. However, unlike those papers, we take into account the dependence of the thermodynamic potentials on the residual polarization gradient, $\nabla_R\boldsymbol{\Pi}$. This (weakly) nonlocal assumption is compatible with continuum thermodynamics provided that the second law is formulated in a nonlocal form (12), where the entropy production is represented as the sum of a non-negative supply and a flow term due to an extra-flux vector. The entropy extra-flux is assigned in (23) by means of a constitutive function that depends linearly on $\dot{\boldsymbol{\Pi}}$, whereas in (34) the constitutive function of the non-negative supply is assumed to depend quadratically on $\dot{\boldsymbol{\Pi}}$.

Accordingly, we obtain (36), a completely original result regarding the explicit evolution equation of the residual polarization vector, both for high and low temperatures, when large deformations are involved. In particular, the differential system (37) is able to describe the evolution of both the intensity and the direction of $\boldsymbol{\Pi}$. The advantages of our model are twofold. First, it shows that the thermodynamic consistency is a natural guideline to the setting of the material model. Second, it provides a simple procedure for the selection of the parameters characterizing the material behavior. The driving term of the evolutionary system is the variation of the Gibbs free energy functional. Hence, within the Ginzburg-Landau-Devonshire setting, some appropriate expressions of the free energy are proposed. For both isotropic and anisotropic materials the free energy due to polarization is constructed and the nature of the relative maxima and minima is discussed in Remarks 5.1 and 5.2. Finally the coupling between electric field and mechanical strain under the small deformation assumption is described in Section 6. It is worth noting that a typical butterfly-shaped loop is obtained here as a consequence of the non-symmetric, dyadic term $\boldsymbol{E}\otimes\boldsymbol{P}$ that appears in the total stress $\mathcal{T}$ (see eqn.(58)) and acts by deforming the body even if the mechanical Cauchy stress $\boldsymbol{T}$ vanishes.

Data availability

Data will be made available on request.

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Appendix A. List of principal symbols

$\mathcal{R}\subset\mathbb{R}^3$ reference configuration
$\Omega\subset\mathbb{R}^3$ current configuration
t current time
$\boldsymbol{X}$ position vector in $\mathcal{R}$
$\boldsymbol{x}=\boldsymbol{\xi}(\boldsymbol{X},t)$ position vector in Ω
$\boldsymbol{u}=\boldsymbol{\xi}(\boldsymbol{X},t)-\boldsymbol{X}$ displacement vector
$\boldsymbol{v}=\dot{\boldsymbol{u}}$ velocity vector
$\boldsymbol{F}=\nabla_R\boldsymbol{\xi}$ deformation gradient
$\boldsymbol{L}=\nabla\boldsymbol{v}$ velocity gradient
$\mathcal{J}=\det\boldsymbol{F}$ determinant of the deformation gradient
ρ mass density in Ω
$\rho_R=\mathcal{J}\rho$ mass density in $\mathcal{R}$
$\theta,\hat{\theta}$ absolute temperature
θ_c Curie temperature
ϵ_0 vacuum permittivity
μ_0 vacuum permeability
χ_e electric susceptibility
χ_m magnetic susceptibility
ε specific internal energy
η specific entropy
σ,ξ specific entropy production
$\psi=\varepsilon-\theta\eta$ Helmholtz specific free energy

$\psi^{\rm el}$ Helmholtz specific free energy due to elastic deformations
$\psi^{\rm pol}$ Helmholtz specific free energy due to polarization
Ψ_R opposite of the Helmholtz free entropy (Massieu potential) per unit volume in $\mathcal{R}$
$\phi = \psi - \boldsymbol{E}\cdot\boldsymbol{P}/\rho = \psi - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{P}}$ (electric) Gibbs specific free energy
Φ_R opposite of the electric Gibbs free entropy (Planck potential) per unit volume in $\mathcal{R}$
$\boldsymbol{E}$ electric field in Ω
$\boldsymbol{\mathcal{E}} = \boldsymbol{E}_R$ electric field in $\mathcal{R}$
$\boldsymbol{\mathcal{E}}^{\rm eff}$ effective electric field in $\mathcal{R}$
$\boldsymbol{\mathcal{E}}^{\rm int}, \boldsymbol{\mathcal{E}}^{\rm an}, \boldsymbol{\mathcal{E}}^{\rm exc}$ interaction, anisotropic and exchange electric fields
$\boldsymbol{H}, \boldsymbol{M}, \boldsymbol{B}$ magnetic field, magnetization vector and magnetic induction
$\boldsymbol{P}$ polarization vector in Ω
$\boldsymbol{P}_R$ polarization vector in $\mathcal{R}$
$\boldsymbol{p} = \boldsymbol{P}/\rho$, $\boldsymbol{\mathcal{P}} = \boldsymbol{P}_R/\rho_R$ polarization vectors per unit mass
$\boldsymbol{D} = \epsilon_0\boldsymbol{E} + \boldsymbol{P}$ electric displacement vector
$\mathsf{\bf p}$ residual polarization vector in Ω, $\mathsf{p} = |\mathsf{\bf p}|$
$\boldsymbol{\Pi}$ residual polarization vector in $\mathcal{R}$, $\Pi = |\boldsymbol{\Pi}|$
$\boldsymbol{\pi} = \boldsymbol{\Pi}/\Pi$ direction vector for $\boldsymbol{\Pi}$
$\boldsymbol{\Xi} = \boldsymbol{\mathcal{P}} - \boldsymbol{\Pi}$ differentiable function representing the constitutive part of $\boldsymbol{\mathcal{P}}$
$\boldsymbol{J}$ electric current vector in Ω
$\boldsymbol{J}_R$ electric current vector in $\mathcal{R}$
$\boldsymbol{q}$ heat flux vector in Ω
$\boldsymbol{q}_R$ heat flux vector in $\mathcal{R}$
$\boldsymbol{k}$ extra-entropy flux vector in Ω
$\boldsymbol{k}_R$ extra-entropy flux vector in $\mathcal{R}$
$\boldsymbol{\varepsilon} = \frac{1}{2}(\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^T)$ infinitesimal strain tensor
$\boldsymbol{T}$ Cauchy stress tensor
$\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F}$ Cauchy-Green tensor
$\mathfrak{E} = \frac{1}{2}(\boldsymbol{C} - \boldsymbol{1})$ Green-St.Venant strain tensor
$\boldsymbol{1}$ second-order identity tensor
$\mathbb{I}$ fourth-order identity tensor
$\mathbb{C}$ fourth-order elastic tensor
$\mathbb{D}$ third-order piezoelectric tensor

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