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A nonlinear kinetics phase-field model for ferroelectrics

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Résumé — Ferroelectric ceramics exhibit a spontaneous electric polarization that can be reversed under the application of an electrical or mechanical loading. The method of choice to model the evolution of polarization domains are diffuse-interface models (also called phase-field models), most of them being based on the Allen-Cahn equation. The latter assumes, unlike experimental evidence, a linear relation between the velocity of domain walls and their conjugate driving force. In this work, we develop an alternative phase-field formulation that accounts for the non-linear kinetics of domain walls, an important feature with regards to rate effects in ferroelectrics.
Mots clés — Ferroelectrics, phase-field model, phase transformations.

1 Introduction

Ferroelectric materials have a spontaneous electric polarization that can be reversed under the application of an electrical or mechanical loading. At the mesoscale, polarization is organized in domains of constant polarization (these domains correspond to the different variants of the crystallographic phase) that evolve through nucleation of new domains and their subsequent growth. Simulations of the evolution of polarization domains are based on diffuse-interface models (also called phase-field models) where the electro-mechanical fields evolve steeply but continuously across *domain walls*, the entities that separate different domains.

Diffuse-interface models regularize a corresponding sharp-interface model, i.e., the former approximate the latter in the limit of small interface width. Most of the existing phase-field models are based on the Allen-Cahn equation (also referred to as time-dependent Ginzburg Landau models) which postulates that the time evolution of the order parameter (here polarization $\mathbf{p}$) is proportional to the negative of the variational derivative of the free-energy density Ψ, i.e.,

$$\mu\dot{p} = -\frac{\delta\Psi}{\delta p}, \tag{1}$$

where μ is an inverse mobility coefficient. The sharp-interface model associated with the phase-field model governed by (1) has a domain wall velocity proportional to its conjugate driving traction, i.e., domain wall motion is governed by a *linear kinetic relation*. This assumption contradicts experimental measurements of the velocity of domain walls as a function of the applied electric field, which indicates that domain wall motion is governed by non-linear kinetics [5, 6, 7, 8, 9]. While a proper account of the kinetics of domain walls is unimportant for the modeling of quasi-static domain evolution, it becomes critical when one considers rate effects in general and, more specifically, the step load response of ferroelectrics as well as the effects of electrical loading rate.

2 A sharp-interface model for ferroelectrics

In sharp-interface models of ferroelectrics, domain walls are represented as surfaces of discontinuity for the electro-mechanical fields [1, 4, 3]. We denote by $\Omega \subset \mathbb{R}^3$ the region occupied by the ferroelectrics and $\mathcal{S}(t)$ the surface of discontinuity that represents a domain wall.

Firstly, the sharp-interface model involves the general principles (mechanical balance and electrostatic equations), which furnish field equations in the bulk (i.e., the domains) and jump conditions at the interfaces (i.e., the domain walls). These are completed by the coupled constitutive behavior of each of the different domains and more importantly by a *kinetic relation* that relates the normal velocity of a domain wall to its associated local *driving traction*. The driving traction is derived by computing the rate of entropy production (obtained by combining energy balance and entropy imbalance) at the interface. One can show (see e.g., [4]) that the latter reads as the surface integral (over the surface of the domain wall) of the normal velocity of the interface and a scalar quantity, which defines the *driving traction* governing interface motion.

We summarize below the main equations of a sharp-interface model for ferroelectrics. Mechanical equilibrium reads

$$\begin{cases} \operatorname{div}\boldsymbol{\sigma} = 0 & \text{in} \quad \Omega \setminus \mathcal{S}(t), \\ [\![\boldsymbol{\sigma}]\!]\boldsymbol{n} = 0 & \text{on} \quad \mathcal{S}(t), \end{cases} \tag{2}$$

where $\boldsymbol{n}$ denotes the unit normal to $\mathcal{S}$ and $\boldsymbol{\sigma}(\boldsymbol{x},t)$ is the Cauchy stress tensor. For a field w, $[\![w(\boldsymbol{x},t)]\!] = w^+(\boldsymbol{x},t) - w^-(\boldsymbol{x},t)$ denotes the jump at the interface with the plus side being that where $\boldsymbol{n}(\boldsymbol{x},t)$ points to. For electrostatics, we introduce the electric field $\boldsymbol{e}(\boldsymbol{x},t)$, electric displacement $\boldsymbol{d}(\boldsymbol{x},t)$ and polarization $\boldsymbol{p}_{\text{mat}}(\boldsymbol{x},t)$ related by

$$\boldsymbol{d} = \epsilon_0 \boldsymbol{e} + \boldsymbol{p}_{\text{mat}}, \tag{3}$$

with ϵ_0 the permittivity of vacuum. Gauss' law reads in the absence of free-charges

$$\begin{cases} \operatorname{div}\boldsymbol{d} = 0 & \text{in} \quad \Omega \setminus \mathcal{S}(t), \\ [\![\boldsymbol{d}]\!] \cdot \boldsymbol{n} = 0 & \text{on} \quad \mathcal{S}(t). \end{cases} \tag{4}$$

For the constitutive behavior, each variant α of the ferroelectrics is modeled as a linear elastic material with spontaneous strain (elasticity tensor $\mathbb{C}_\alpha$ and eingenstrain $\boldsymbol{\varepsilon}^s_\alpha$) showing a piezolectric coupling (piezoelectric tensor $\mathbb{D}_\alpha$) and a material permittivity $\boldsymbol{\epsilon}_\alpha$. These different features are combined in the electric enthalpy of variant α :

$$W_\alpha(\boldsymbol{e},\boldsymbol{\varepsilon}) = \underbrace{-\frac{1}{2}\boldsymbol{e}\cdot\boldsymbol{\epsilon}_\alpha\boldsymbol{e} - \boldsymbol{p}_\alpha\cdot\boldsymbol{e}}_{W^{\text{dielec}}_\alpha(\boldsymbol{e})} + \underbrace{\frac{1}{2}(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^s_\alpha):\mathbb{C}_\alpha:(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^s_\alpha)}_{W^{\text{mech}}_\alpha(\boldsymbol{\varepsilon})} \underbrace{-(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^s_\alpha):\mathbb{D}_\alpha\cdot\boldsymbol{e}}_{W^{\text{piezo}}_\alpha(\boldsymbol{e},\boldsymbol{\varepsilon})}, \tag{5}$$

where $\boldsymbol{\varepsilon}$ is the small strain tensor and $\boldsymbol{p}_\alpha$ is the spontaneous polarization (i.e., the polarization at zero stress and electric field) of the variant α. By differentiation, (5) furnishes the constitutive relations :

$$\begin{cases} \boldsymbol{\sigma} = \mathbb{C}_\alpha : (\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^s_\alpha) - \mathbb{D}^T_\alpha\cdot\boldsymbol{e}, \\ \boldsymbol{d} = \boldsymbol{\epsilon}_\alpha\boldsymbol{e} + \boldsymbol{p}_\alpha + \mathbb{D}_\alpha : (\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^s_\alpha). \end{cases} \tag{6}$$

Last, the motion of the domain wall, represented by the surface of discontinuity $\mathcal{S}$ is described by its normal velocity $V_n(\boldsymbol{x},t)$ that follows the kinetic relation

$$V_n = \hat{V}_n(f), \tag{7}$$

where $\hat{V}_n : \mathbb{R} \to \mathbb{R}$ is a function—restricted by the positiveness of the dissipation—that satisfies the condition

$$\hat{V}_n(f)f \geq 0 \quad \text{for all } f \in \mathbb{R}. \tag{8}$$

In (7), $f(\boldsymbol{x},t)$ denotes the driving traction given by

$$f = \boldsymbol{n}\cdot[\![\boldsymbol{C}]\!]\boldsymbol{n} + \gamma\kappa. \tag{9}$$

where $\kappa(\boldsymbol{x},t)$ is twice the mean curvature of $\mathcal{S}$ and $\boldsymbol{C}(\boldsymbol{x},t)$ is the Eshelby tensor defined by

$$\boldsymbol{C} = W_\alpha\boldsymbol{I} - \boldsymbol{\sigma}\cdot\nabla\boldsymbol{u} + \boldsymbol{e}\otimes\boldsymbol{d}, \tag{10}$$

with $\nabla\boldsymbol{u}$ the gradient of the displacement and $\boldsymbol{I}$ the identity tensor.

3 A regularized phase-field model with nonlinear kinetics

In this section, we introduce a phase-field model for the evolution of the polarization in ferroelectrics that retains the nonlinearity of the kinetic relation (7) and allows us to prescribe independently the kinetics of 180° and 90° domain walls. Without loss of generality, we consider a ferroelectrics with tetragonal structure that present spontaneous polarizations $\boldsymbol{p}_\alpha$ in the six orthogonal directions of space. We introduce the multi-phase field $\boldsymbol{\varphi}(\boldsymbol{x},t) \in (0,1)^6$ where $\varphi_\alpha(\boldsymbol{x},t)$ represents the volume fraction of phase α at point $\boldsymbol{x}$ and time t so that the spontaneous polarization reads as

$$\boldsymbol{p}(\boldsymbol{x},t) = \tilde{\boldsymbol{p}}\big(\boldsymbol{\varphi}(\boldsymbol{x},t)\big) = \sum_{\alpha=1}^{6} \varphi_\alpha(\boldsymbol{x},t)\boldsymbol{p}_\alpha. \tag{11}$$

For simplicity of the presentation, we neglect the mechanical coupling, assume isotropic material permittivity and introduce the electric enthalpy Ψ, which regularizes $W(\boldsymbol{e},\boldsymbol{p})$, as

$$\Psi(\boldsymbol{e},\boldsymbol{\varphi},\nabla\boldsymbol{\varphi}) = \underbrace{-\frac{\epsilon}{2}\boldsymbol{e}\cdot\boldsymbol{e} - \Big(\sum_{\alpha=1}^{6}\varphi_\alpha\boldsymbol{p}_\alpha\Big)\cdot\boldsymbol{e}}_{W(\boldsymbol{e},\tilde{\boldsymbol{p}}(\boldsymbol{\varphi}))} + C_s\psi_s(\boldsymbol{\varphi}) + p_0^2 C_g \sum_{\alpha=1}^{6} |\nabla\varphi_\alpha|^2, \tag{12}$$

with C_s and C_g two constants related to the domain wall width and interface energy and ψ_s is a multi-well potential with minima at the spontaneous polarization states. ψ_s is typically a multi-well or multi-obstacle potential defined by

$$\psi_s^{(n)}(\boldsymbol{\varphi}) = \omega_n(\boldsymbol{\varphi}) + \tau(\boldsymbol{\varphi}), \tag{13}$$

with

$$\begin{cases} \omega_n(\boldsymbol{\varphi}) = 4^n \left(\displaystyle\sum_{\{\alpha,\beta\}\in I_{180}} |\varphi_\alpha|^n \left|\varphi_\beta\right|^n + h_{90} \sum_{\{\alpha,\beta\}\in I_{90}} |\varphi_\alpha|^n \left|\varphi_\beta\right|^n \right), \\ \tau(\boldsymbol{\varphi}) = C_t \displaystyle\sum_{\{\alpha,\beta,\gamma\}\in\mathcal{T}} |\varphi_\alpha| \left|\varphi_\beta\right| \left|\varphi_\gamma\right|, \end{cases} \tag{14}$$

where h_{90} is the relative height of the 90° barrier, $C_t > 0$ is a numerical parameter and $\mathcal{T} = \{(\alpha,\beta,\gamma) : \alpha,\beta,\gamma \in \mathcal{D}, \alpha \neq \beta \neq \gamma\}$. The exponent n is taken as 1 for a multiple-obstacle potential and 2 for a multi-well potential, these two possibilities having advantages and drawbacks.

The governing equations consist of the field equations $(4)_1$ (with $(2)_1$ when mechanical couplings are considered) completed with an evolution law for the multi-phase field that implicitly governs the motion of interface and which we postulate as

$$\dot{\varphi}_\alpha = \sum_{\beta=1}^{6} \sqrt{\left|\nabla\varphi_\alpha\cdot\nabla\varphi_\beta\right|}\, G_{\beta\alpha}(h_{\beta\to\alpha}) \quad \text{for} \quad \alpha = 1\ldots6, \tag{15}$$

where $G_{\alpha\beta} = G_{\beta\alpha} : \mathbb{R} \to \mathbb{R}$ is the kinetic function for the transformation between phases α and β, and $h_{\beta\to\alpha}$ is the phase-field driving force for the transformation of phase β to phase α defined as

$$h_{\beta\to\alpha}\left(\boldsymbol{e},\boldsymbol{\varphi},\nabla^2\boldsymbol{\varphi}\right) = -\frac{\delta\Psi}{\delta\varphi_\alpha} + \frac{\delta\Psi}{\delta\varphi_\beta} = -\frac{\partial\Psi}{\partial\varphi_\alpha} + \frac{\partial\Psi}{\partial\varphi_\beta} + \operatorname{div}\left(\frac{\partial\Psi}{\partial\nabla\varphi_\alpha} - \frac{\partial\Psi}{\partial\nabla\varphi_\beta}\right). \tag{16}$$

In practice, the functions $G_{\alpha\beta}$ are two different odd functions, one for 180° domain walls and one for 90° domain walls, denoted as G_{180} and G_{90} respectively. The evolution equation (15) is a generalization to multiple phases of the hybrid model of [2] introduced in the context of stress-driven solid-solid phase transformations for two phases. It is shown by means of asymptotics on the two-phase model in [2] and we verify numerically on the present extended model that the evolution equation (15) furnishes a kinetics of domain walls dictated directly by the functions G_{180} and G_{90}. More specifically, the present phase-field model yields a kinetics of domain walls such that

$$\begin{cases} V_n = G_{180}(f) & \text{for 180° domain walls,} \\ V_n = G_{90}(f) & \text{for 90° domain walls.} \end{cases} \tag{17}$$

4 Results

In this section, we report the velocity of a straight neutral 180° domain wall obtained with the phase-field model introduced in Section 3. In this configuration, the electric field is uniform in the entire simulation cell and the sharp-interface driving traction (9) is proportional to the prescribed electric field. To test the proper functioning of the phase-field model, we consider four kinetic relations which, beyond the linear one $G_{180}^{(1)}(h) = g_0 h$, embed different types of nonlinearity, viz.,

$$
\begin{aligned}
G_{180}^{(2)}(h) &= \begin{cases} g_1 \,\mathrm{sign}(h) \exp\left(\frac{-h_a}{|h|}\right) & \text{for} \quad |h| < h_1, \\ g_1 \,\mathrm{sign}(h) \exp\left(\frac{h_a}{h_1}\right)\left(\frac{|h|}{h_1}\right)^{1.4} & \text{for} \quad |h| \geq h_1, \end{cases} \\
G_{180}^{(3)}(h) &= \begin{cases} 0 & \text{for} \quad |h| < h_2, \\ \mathrm{sign}(h)(|h| - h_2) & \text{for} \quad |h| \geq h_2, \end{cases} \\
G_{180}^{(4)}(h) &= \begin{cases} 0 & \text{for} \quad |h| < h_2, \\ \mathrm{sign}(h)\sqrt{h^2 - h_2^2} & \text{for} \quad |h| \geq h_2, \end{cases}
\end{aligned}
\tag{18}
$$

with g_0, g_1, h_a, h_1 and h_2 numerical parameters.

Figure 1 shows the velocity of the domain wall, as obtained from the phase-field model for different levels of applied electric field. These velocities are compared to the target kinetic relation, chosen as an input in the phase-field model. We can see that the proposed phase-field model adequately accounts for all types of nonlinear kinetic relations.

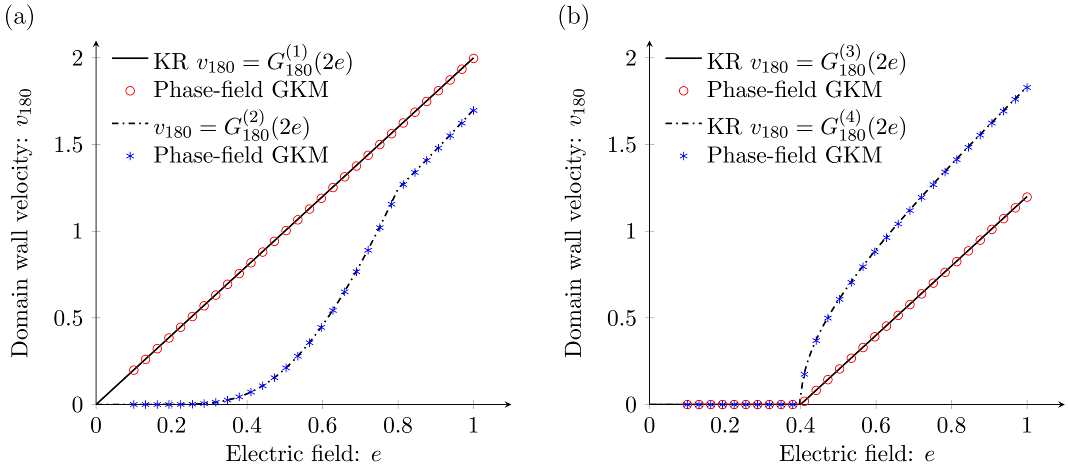

FIGURE 1 – Velocities of straight neutral 180° domain walls obtained with the phase-field model vs. the analytical kinetic relation for four kinetic relations $G_{180}^{(i)}$, $i = 1 \ldots 4$ (arbitrary units).

5 Conclusion

In conclusion, we introduce a new phase-field model for the evolution of polarization domains in ferroelectrics. Unlike Allen-Cahn-based phase-field models, the present formulation conserves the nonlinear kinetics of domain walls in the regularization process of the sharp-interface model. In addition, the kinetics of 180° and 90° domain walls are clearly distinguished. While this model has been devised to investigate rate-effects in ferroelectric switching, it may find applications to other solid-solid multi-phase transformations where the kinetics of the solid-solid interfaces plays an important role.

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