Theory and Modeling of Polarization Switching in Ferroelectrics

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Abstract. Thermodynamic approach of ferroelectrics is reconsidered in recourse to thermal activated nature of polarization switching under arbitrary driving voltage. This analysis heavy relies on transformation of the problem to imaginary time Schrödinger equation and its integration by means adopted from pure quantum problems. It turns out that this nonadiabatic treatment reveals non-equilibrium properties directly relevant to essential application-grade performance specifications like hysteresis and spatial inhomogeneity.

Keywords: hysteresis, spatial inhomogeneity, symplectic integration

1.INTRODUCTION

The response of dynamical metastable systems in general and the polarization response of ferroelectrics in particular is an active field of study, both at the theoretical and experimental levels. A large amount of work in ferroelectrics has been devoted to understanding the impact of finite size, spatial inhomogeneity, and high driving. In its simplest form, this approach is based on variation of Ginzburg-Landay type energy functionals resulting in linear response and adiabatic solutions for the polarization field. Less attention has paid to the modeling of nonstationary polarization response due the very complex mathematical technique specific for this kind of analysis. Formally, thermodynamic properties of a ferroelectric have a close resemblance to the energy functionals being nonconservative, nonlocal, and nonlinear in the sense that the phase transition is associated with bifurcation of the ground state solutions. Valuable analytical results concern some idealized cases of metastable systems applicable in case of spin systems[1,] metastable systems in semiadiabatic limit[2], zero field and weak nonlocality[3], strong nonlocality[4], spatio-temporal correlations[5,6] and global stability of stationary solutions[7,8]. Another line of developments concern quantum statistics[9,10], namely, the symplectic integration of time dependent Schrödinger equations. With application to dynamical metastable systems this approach[9] yields effective numerical calculations of the density distribution of polarization and its potential is far beyond the existing kinetic methods. What is missing is the connection between the Fokker-Planck - imaginary time Schrödinger equation for aforementioned nonconservative, nonlocal, and nonlinear energy functionals and the technique of its symplectic integration.

Selection of symplectic integration is argued by its norm conserving property for an auxiliary function providing stable and accurate simulation even under alternate driving voltage and in a long time slice both essential for simulations over long time duration. In this work we deal with nonequilibrium polarization response on arbitrary driving field in the local and weak nonlocal limits. Our main results concern dynamic hysteresis and the relaxation rate found gradient specific and favored in the vicinity of boundaries.

On application grade level the study of stochastic dynamics is stimulated by its nontrivial and contraintuitive behavior as originated by cooperative effect of noise and driving. Examples for technological applications and materials research are the noise controlled resonant trapping effect and noise activated sensors[11,12] to mention only few. More outstanding challenges appear if accounting for finite size effects. Between other the stochastic approach reveals the long-standing problem of ferroelectric domain switching that appears far bellow the classic coercive voltage.

This work is structured as follows. In Sect. 2 we give definitions for Ginzburg-Landau energy functional and related quantities including the recurrence matrix relation for large scale computing and an example solution. Step-by-step formulation of this method is given in[10,13]. In Sect.3 a new auxiliary function is introduced as based on[14] and accounting for first neighbor interaction. A first-hand estimate is given. Summary and discussion in Sect.4 concern further developments as based on alternative[7,8] energy functional and relevant heavy nonlinear Fokker-Planck model.

2.DEFINITIONS AND CONCEPTS: DYNAMIC HYSTERESIS

Definitions start with Ginzburg-Landau energy functional for a double well potential routinely applied to uniaxial ferroelectics, the Langevin kinetic equation with δ-correlated Gaussian noise term and Fokker-Planck equation for probability density of polarization

$$\dot{\rho}(P,t) = \frac{\partial}{\partial P}\left(\frac{\partial U}{\partial P}\rho(P,t)\right) + \Theta\frac{\partial^2 \rho(P,t)}{\partial P^2} \tag{1}$$

Here P is dimensionless polarization, $U(P,t) = -\frac{1}{2}P^2 + \frac{1}{4}P^4 + \frac{1}{2}(\nabla P)^2 - h\,\lambda(t)\,P$ is dimensionless energy density, Θ is diffusion coefficient (noise strength) condensing parameters of the system, and $h\lambda(t)$ specify the time dependent driving voltage. The concept is transforming Eq.1 in imaginary time Schrödinger equation and its integration in the technique borrowed from pure quantum problems. To this end we use the standard ansatz[15] $\rho(P,t) = \exp[-U(P)/2\Theta]G(P,t)$ mapping Fokker-Planck and imaginary time Schrödinger equations. What we search is the auxiliary function

$$\frac{\partial G(P,t)}{\partial t} = \left[\Theta\frac{\partial^2}{\partial P^2} - V(P)\right]G(P,t) \tag{2}$$

In case of time dependent driving voltage the potential operator $V(P)$ reads as

$$V(P,t) = -\frac{1}{4\Theta}\left[h\,\lambda(t) - U'(P)\right]^2 + \frac{1}{2}U''(P) - \frac{P\,h\,\lambda'(t)}{2\Theta} \tag{3}$$

and the G - function is returned by recurrence matrix relation with time increment Δt

$$\begin{aligned}&\left[1 - \frac{\Theta\partial^2}{\partial P^2}\right]G(P,t+\Delta t) = \\ &\exp\left[\frac{1}{\Theta}\left(\frac{\Delta t}{2}V + \frac{\Delta t^3}{48}[V,[T,V]]\right)\right]\left[1 + \frac{\Theta\partial^2}{\partial P^2}\right]\exp\left[\frac{1}{\Theta}\left(\frac{\Delta t}{2}V + \frac{\Delta t^3}{48}[V,[T,V]]\right)\right]G(P,t)\end{aligned} \tag{4}$$

here the commutator $[V,[T,V]] = (\nabla V)^2$, time argument of the potential operator is $t := t + \Delta t/2$, dimensionality of matrices is determined by the polarization mesh, and the integration starts with initial condition $G(P,0)$ derived from a unique stationary solution of Eq.1. Types of problems solvable within this symplectic integration technique are induced polarization (restricted noequilibrium) under a static field, relaxation toward zero ground state, and polarization response under alternate driving field (dynamic hysteresis[1]). Nevertheless the bifurcation property of polarization states and divergence of relaxation time at some critical parameters is lost as a result of the linearity of Fokker-Planck equation Eq.1 for standard Ginzburg-Landau energy functional. Accordingly, all solutions of this type exhibit only a uniquely determined zero ground state and are valid if the nonequilibrium stationary states play no major role as it is expected for constrained nonequilibrium and dynamic hysteresis. The plot of dynamic hysteresis modeled by symplectic integration is shown in Fig. 1 (dots) and compared with well developed semiadiabatic solution[2] proceeded in Floquet function technique.

3.WEAK NONLOCALITY: POLARIZATION SWITCHING

A more realistic approach comprises weak nonlocality as formally introduced by the gradient term $\frac{1}{2}(\nabla P)^2$ in energy density that results in $\frac{\delta U[P(x)]}{\delta P(x)} = U'[P(x)] - P''(x)$ variational derivative comprising a supplementary $P''(x)$ term in the classic ansatz extended for weak nonlocality

$$\rho[P(x),t] = \exp\left[-\frac{U[P(x)]}{2\Theta} + \frac{P(x)P''(x)}{2\Theta}\right] G[P(x),t] \qquad (5)$$

Subsequent transformations in Langevin, Fokker-Planck, and imaginary time Schrödinger equation yields

$$\dot{G}(P,t) = \left(\Theta \frac{\partial^2}{\partial P^2} + \begin{bmatrix} -\frac{1}{4\Theta}\left(\frac{\partial U[P(x)]}{\partial P(x)}\right)^2 + \frac{1}{2}\left(\frac{\partial^2 U[P(x)]}{\partial P(x)^2}\right) \\ -\frac{1}{4\Theta}\left(\frac{\partial^2 P(x)}{\partial x^2}\right)^2 + \frac{1}{2\Theta}\frac{\partial U[P(x)]}{\partial P(x)}\frac{\partial^2 P(x)}{\partial x^2} \end{bmatrix} \right) G(P,t) \qquad (6)$$

In Eq.6 the two last terms in square brackets are assigned to the impact if weak nonlocality (first neighbor interaction) and the initial condition $G(P,0)$ is derived considering constrained equilibrium field at $t < 0$. We precede first-hand estimation considering a boundary $x = 0$ between two regions with opposite polarization and $P > 0$ at $x > 0$. Obviously $P(0) \equiv P''(0) \equiv 0$ and the potential is symmetric as shown by (thin) plot A in Fig.2. A negative driving field $\lambda < 0$ distorts the potential as shown by the medium plot in Fig.1 and as a result the polarization is relaxing toward a negative value. Accounting for $\frac{1}{2\Theta}\frac{\partial U[P(x)]}{\partial P(x)}\frac{\partial^2 P(x)}{\partial x^2}$ term in Eq.5 one can find the impact of $\frac{1}{4\Theta}\left(\frac{\partial U[P(x)]}{\partial P(x)}\right)^2$ term enhanced in vicinity of the boundary at which $P''(x)$ exhibit a maximum and enlarges the asymmetry of V -potential as shown by (bold) plot B. Consequently, the polarization switching is initialized in vicinity of domain walls that agree well with nucleation and domain wall motion mechanism studied in particular cases by another techniques[3].

With symplectic integration in mind we introduce spatial mesh $x = x_{\min} + \Delta x(m-1) \equiv x_m$, $m = 1,2,\ldots,M$, $\Delta x = (x_{\max} - x_{\min})/M$ transforming Eq.5 in

$$\rho(P_1, P_2, \ldots, P_M, t) = \exp\left[\sum_{n=1}^{M} \frac{-U(P_n) + P_n P_n''}{2\Theta}\right] G(P_1, P_2, \ldots, P_M, t) \tag{7}$$

Here the auxiliary function reads as

$$\begin{aligned} &\dot{G}(P_1, P_2, \ldots, P_M, t+\Delta t) = \\ &\left(\begin{aligned} &\Theta \sum_{m=1}^{M} \frac{\partial^2}{\partial P_m^2} + \\ &\sum_{m=1}^{M} \left[-\frac{[U'(P_m)]^2}{4\Theta} + \frac{U''(P_m)}{2} - \frac{[P_m'']^2}{4\Theta} + \frac{U'(P_m)P_m''}{2\Theta} \right] \end{aligned} \right) G(P_1, P_2, \ldots, P_M, t) \end{aligned} \tag{8}$$

and the sums appear due the generalization of the Fokker-Planck equation to the case of M variables[16] . Transformation of Eq.8 to the recurrence matrix form Eq.4 is straightforward and gives nonstationary solution of the Langevin boundary problem in terms of multivariate distributions.

4.SUMMARY AND DISSCUSSION

We have proposed a mathematical technique modeling temporal polarization response within framework of the most popular Ginzburg-Landau model used to discuss phase transitions. The thermal noise term, which is added to the kinetic equations, makes this model capable of exhibiting dynamic hysteresis and related phenomena, and its extension beyond the demonstrated zero-dimensional examples is obviously.

A problem of mathematical technique that is actualized in this context concern spatial nonlocality being essential for modeling kinetics of spatially inhomogeneous polarization field. We have shown that in case of weak nonlocality no substantional changes are involved in the computing technique except the results are represented by multivariate distribution functions that determines the kinetics of internal structure of a ferroelectric material under alternate driving. Firsthand estimates approve that the polarization switching is initiated at the vicinity of boundaries where the second spatial derivative of polarization reaches maximum. Another problem concern the bifurcation of polarization state and divergence of relaxation time at some critical parameters of Ginzburg-Landau energy functional. Under thermal noise this property is lost, the system exhibits a uniquely determined stationary state and, as a consequence, the aforementioned stochastic approach is valid if the nonequilibrium stationary states play no major role as it is expected for constrained nonequilibrium and dynamic hysteresis. An alternative retaining the bifurcation of polarization state and including a feedback expressed in terms of the first moment of the distribution function generates a more complex energy functional[7,8] and a subsequent heavy nonlinear Fokker-Planck model capable of exhibiting thermodynamic phase transitions. Although the high driving field solutions of this self-consistent nonlinear Fokker-Planck equation is, to date, not known, its integration may be preceded with minimal changes in the aforementioned symplectic integration technique that might help search for more advanced models for polarization kinetics in ferroelectrics.

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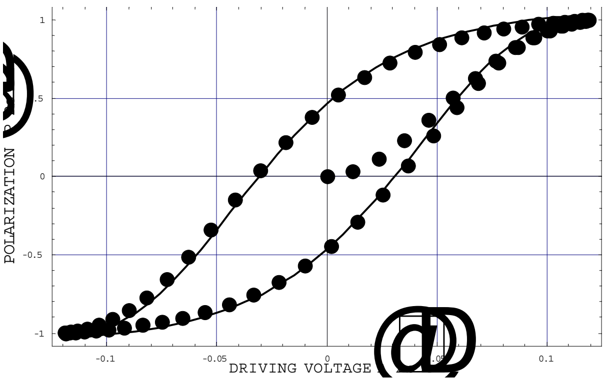

Fig.1 Dynamic hysteresis under harmonic driving: comparison of semiadiabatic approach[2] (line) and symplectic integration (dots). Parameters of the problem: amplitude of the driving voltage $h = 0.309\,h_0$, frequency $\Omega = 10^{-3}$, $\Theta - 1/20$, $\lambda(t) = \sin(\Omega t)$, and $h_0 = 2/\sqrt{27}$ is the static coercive field.

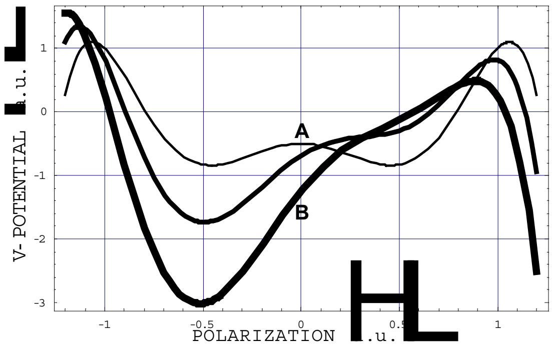

Fig.2 V - potential landscape for variable driving voltage. The thin (A), medium and bold (B) curves match $h=0$, $h=-1/2\,h_0$, and $h=-h_0$, correspondingly. The effect of polarization gradient is proved similarly to enhancement of local applied field.