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EFFECT OF THERMAL FLUCTUATIONS ON FERROELECTRIC RESPONSE: DYNAMIC HYSTERESIS

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Time-dependent Ginsburg-Landau theory is combined with Langevin, Fokker-Planck and nonstationary Schrödinger equation techniques to model impact of thermal noise in kinetics of ferroelectric polarization. A real space/real time method based on Cayley's form and Suzuki's decomposition is implemented for numerically simulating both relaxation of polarization in a static potential and dynamic hysteresis in arbitrary time dependent potential. Results are addressed to high field response and long time dynamics in ferroelectrics.

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1. Introduction

This paper motivated by [1,2,3] presents a systematic analysis of polarization kinetics in presence of high driving field and reports both the relaxation of polarization and dynamic hysteresis modeled within the range of driving voltage far above the validity of routine perturbation theory. The physical model starts with the mean field Ginzburg-Landau energy functional with energy landscape specified by two wells corresponding to two polarization states and a barrier between them preventing a transition from one well to other. This linear response limit is violated at high external fields at which the barrier height is substantially reduced and thermal noise controlled transition appears. A sufficient mathematical model is the imaginary time Schrödinger equation with energy operator derived from the macroscopic Hamiltonian the wave function being paralleled with the probability density of polarization. This similarity holds also for the macroscopic Hamiltonian explicitly depending on time [2,3,4]. The paper is organized as follows. In Section 2 we present denominations for the Ginzburg-Landau theory, Langevin equation, and Fokker – Planck equation. In Sect. 3 we derive the Cayley's form for time independent Ginzburg-Landau Hamiltonian and proceed to a test calculation for polarization relaxation. In Sect. 4 the Cayley's form is extended for the Hamiltonian explicitly depending on time. Dielectric response is modeled both for harmonic driving and pulse shaped driving voltage. The claims, actualized problems and application grade results are emphasized in Conclusions.

2. General theory

Throughout this paper we assume the physics captured by Ginzburg-Landau Hamiltonian and give denominations for Langevin, and Fokker – Planck equations necessary for imaginary time Schrödinger equation and Cayley's form technique. Ginzburg – Landau Hamiltonian reads as

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$$H(P(\mathrm{x}),t)=\int\left[-\frac{\alpha}{2}P^2+\frac{\beta}{4}P^4+\frac{c}{2}(\nabla P)^2-h(t)P\right]dV \tag{1}$$

Here $F=-\frac{\alpha}{2}P^2+\frac{\beta}{4}P^4+\frac{c}{2}(\nabla P)^2-h(t)P$ is the energy density and P is the macroscopic polarization. The amplitude of driving field $h(t)$ is chosen below the static coercive field resulting in two wells of the energy profile. The gradient coefficient c in Eq.1 specifies the energy associated with spatially extended distribution of the polarization. The nonequilibrium case is partially captured by the kinetic (Langevin) equation for the energy functional Eq.1

$$\dot{P}_i(t)=-V\Gamma\frac{\delta F}{\delta P_i}+\eta(t) \tag{2}$$

Here the noise term $\eta(t)$ is assumed to be δ correlated, Gaussian, and independent of polarization. Its detailed dependence on time is replaced by zero mean $\langle\eta(t)\rangle=0$ and $\langle\eta(t)\eta(t')\rangle=2k_B T\Gamma\delta(t-t')$ correlation function in strong sense valid for conservative systems in thermal equilibrium for which the static fluctuation-dissipation theorem (FDT) holds [5,6]. For systems out of equilibrium or under time-dependent external forces the FDT violates [7] and coincidence with the δ correlated correlation function becomes formal [8]. Nevertheless, we follow [2] and consider the deviation from TDT being negligible in the semiadiabatic limit. The kinetic coefficient Γ being, in general, a function of the parameters of theory it is assumed constant at a given temperature. The Fokker-Planck equation for probability density of polarization yields

$$\frac{\partial\rho}{\partial t}=\Gamma V\frac{\partial}{\partial P}\left(\frac{\partial F}{\partial P}\rho\right)+k_B T\Gamma\frac{\partial^2\rho}{\partial P^2} \tag{3}$$

Introducing dimensionless polarization $\tilde{P}=\frac{P}{P_s}$, dimensionless time $\tilde{t}=t\Gamma\alpha V$, the spontaneous polarization $\tilde{P}_s=\sqrt{\frac{\alpha}{\beta}}$, applied field $\tilde{E}=\frac{E}{\alpha P_s}$, and dimensionless frequency $\Omega=\frac{\omega}{\Gamma\alpha V}$ the problem transforms in canonical form

$$\frac{\partial\rho}{\partial\tilde{t}}=-\frac{\partial}{\partial\tilde{P}}\left(\left(\tilde{P}-\tilde{P}^3+\tilde{h}\sin(\Omega\tilde{t})\right)\rho\right)+\frac{k_B T}{\alpha^2 P_s^2 V}\frac{\partial^2\rho}{\partial\tilde{P}^2} \tag{4}$$

with diffusion coefficient $\Theta=\frac{k_B T}{\alpha^2 P_s^2 V}$. The separation of a selected volume in infinite medium is the consequence of Fokker-Planck approach derived originally for Brownian particles. Actually, the choice of a volume is arbitrary. It's enlarging reduces the diffusion coefficient Θ and enlarges the Kramer time $\tilde{t}_{Kr}$ of barrier crossing whereas in physical units the Kramer time $t=\tilde{t}_{kr}/(\Gamma\alpha V)$ remains unchanged. The mark $\langle\sim\rangle$ is omitted and $V=1$ in further calculations. Another feature not accounted for in the monodomainl limit is that the diffusion hops between metastable states modeled by the kinetic coefficient Γ are accompanied with changes in the domain structure. A compromise is in considering the diffusion coefficient as a parameter of theory. Its temperature dependence is given by factor α^2/β in the denominator. This approach is valid within the driving field at which the double well condition $h<h_0, h_0=2/\sqrt{27}\approx 0.4$ holds corresponding to a $E_{\max}=h_0\alpha P_s$ driving field in

physical units. Assuming a ferroelectric medium with $\varepsilon = 1000$ and $P_s = 0.4\left(C/m^2\right)$, and a rough estimate $\alpha = \left(\varepsilon_0 \varepsilon\right)^{-1} \sim 10^8 \left(m/F\right)$ yields the upper limit of driving field $E_{\max} \sim 10^7 \left(V/m\right)$ being far above the validity of the perturbation theory.

3. Thermal noise controlled relaxation

Relaxation of the total polarization from the ordered $P = P_s$ state to the equilibrium state with $\langle P \rangle = 0$ under thermal noise is given by time dependent probability distribution $\rho(P,t)$ reaching the Gibbs-Boltzmann distribution at $t \to \infty$. For arbitrary time this probability distribution is given by the (forward) Fokker-Planck equation

$$\dot{\rho}(P,t) = \frac{\partial}{\partial P}\left(\frac{\partial U}{\partial P}\rho(P,t)\right) + \Theta \frac{\partial^2 \rho(P,t)}{\partial P^2} \tag{5}$$

transformed in imaginary time Schrödinger equation by standard ansatz $\rho(P,t) = \exp[-U(P)/2\Theta]G(P,t)$

$$\Theta \frac{\partial G(P,t)}{\partial t} = \left[\Theta^2 \frac{\partial^2}{\partial P^2} - V(P)\right] G(P,t) \tag{6}$$

with $V(P) = \frac{1}{4}\left[U'(P)\right]^2 - \frac{\Theta}{2}U''(P)$ and the eigenmode equation [1]

$$-\Theta^2 \frac{d^2 \psi_n(P)}{dP^2} + V\psi_n(P) = \lambda_n \psi_n(P) \tag{7}$$

Equilibrium solution is given by zero order eigenfunction [4]

$$\psi_0(P,t) = \left(\int \exp[-U(P)\Theta]dP\right)^{-1/2} \exp[-U(x)\Theta/2] \tag{8}$$

its eigenvalue λ_0 being zero. The conditional probability of polarization initially prepared in the metastable state P_0 is given by eigenfunction expansion

$$\rho\left(P,t|P_0\right) = \exp\left[\left(U(P_0) - U(P)\right)\Theta/2\right]\sum_{n\geq 0} \Psi_n(P_0)\Psi_n(P)\exp\left[-\Theta t\lambda_n\right] \tag{9}$$

Preliminary results of slow relaxation associated with thermal noise controlled barrier crossing accounting for zero Ψ_0 and first order Ψ_1 eigenfunctions [9] and based on analytically derived eigenfunctions [1,2,4] for Hamiltonian Eq.1 shows that solution of imaginary time Schrödinger equation Eq.6 is the key problem for simulating physically meaningful systems. As complementary to [1,2] we adopt the Cayley's form technique [10] derived recently for quantum problems and having a potential to manage long-time behavior of multidimensional systems. With application to the energy operator derived from Ginzburg-Landau Hamiltonian Eq.1 the Cayley's form is given by an exponential operator

$$G(t+t+\Delta t)=\exp[\Theta\Delta t\frac{\partial^2}{\partial t^2}-\frac{V(P)\Delta t}{\Theta}]G(t) \tag{10}$$

The potential operator is decomposed from the potential operator [11]

$$G(t+t+\Delta t)=\exp\left[-\frac{V(P)\Delta t}{2\Theta}\right]\exp[\Theta\Delta t\frac{\partial^2}{\partial t^2}]\exp\left[-\frac{V(P)\Delta t}{2\Theta}\right]G(t) \tag{11}$$

and the exponential of Laplacian is approximated by Cayley's form

$$\exp[\Theta\Delta t\frac{\partial^2}{\partial x^2}]\approx\left(1+\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial x^2}\right)/\left(1-\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial x^2}\right) \tag{12}$$

Substituting Eq.12 for Eq.11 and preceding Suzuki decomposition [16] yields

$$\left[1-\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]G(P+t+\Delta t)=\left[1+\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]G(P,t) \tag{13}$$

The wavefunction $G(P,t)$ is discretized by grid points $P_i=i\Delta P$, $i=0,...,N-1$ where ΔP is the increment of grid points. As a result Eq. 13 becomes a recurrence relationship for matrix equation for the unknown vector $G_i(t+\Delta t)$. The survey starts with initial conditions (in this example found after Eq.9), calculates the distribution density of polarization Fig.1 and the polarization given by its first moment (demonstrated in Fig.2). Features of the system are implemented in two matrices: left-hand $\left[1-\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]$ and right hand $\left[1+\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]$, and two vectors $\exp\left[-\frac{V(P)\Delta t}{2\Theta}\right]$ changing the wavefunction $G(P,t)$ at each grid point. The method is found rather stable in spite of considerable $\Delta t/\Delta P^2>1$ ratio. Fig.1 shows example distribution of density of polarization. The initial polarization is assumed positive, maximal at a given bias voltage, and the corresponding distribution of density of polarization is monomodal. At the moment the bias voltage is removed relaxation starts and the distribution of density of polarization transforms to the nonsymmetrical bimodal (bold). The corresponding polarization determined by the first moment of distribution function is still positive but reduced. The opposite excess of distribution of density of polarization gradually grows (medial plot) and approaches to a symmetric one (thin) as the time goes.

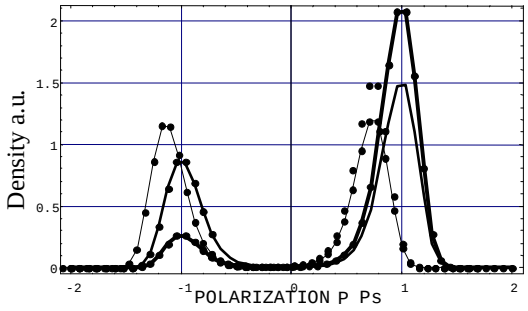

Fig. 1. Model distribution density of polarization illustrating thermal noise controlled relaxation. The initial state $P_{max} > 0$ is specified by unimodal distribution developing toward the bimodal one (bold) ,(medial), (thin) approaching to the symmetric at thermal equilibrium. Diffusion constant $\Theta=1/20$, grid points $N=50$, grid increment $\Delta P=2/25$, time increment $\Delta t=1/100$.

Relaxation patterns evaluated in the Cayley's form technique and in the semiadiabatic technique [1] are shown in Fig. 2.

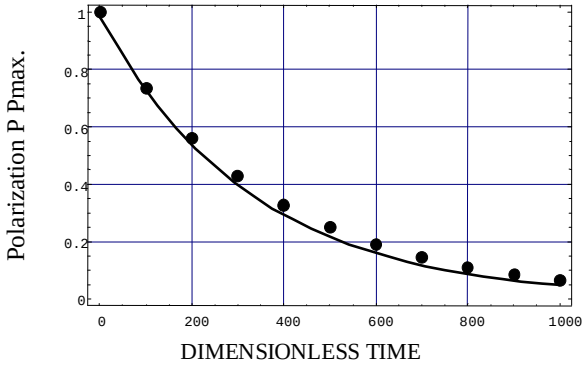

Fig. 2. Comparision of thermal noise controlled relaxation patterns evaluated within semiadiabatic (bold) and Cayley's form (dots) technique. In both cases the relaxation is starting from $P_{\max} > 0$, diffusion constant $\Theta = 1/20$. In Cayley's form the grid points $N = 50$, grid increment $\Delta P = 2/25$, and time increment $\Delta t = 1/100$.

The fit of relaxation patterns in Fig. 2 evaluated in the Cayley's form technique and in the semiadiabatic technique [1] is rather good. This technique that concerns the time independent energy functional comprises the transformation to imaginary time Schrödinger's equation and solution of the eigenfunction problem by approximate analytical methods.

4. Dielectric response at time dependent driving field: dynamic hysteresis

The dielectric response at time dependent driving field is a key problem of the thermodynamic theory and self-consistent solutions for inhomogeneous polarization field including the growth and coarsening of domains are attempted in [12-15]. Nevertheless, at high driving field the barrier height between attractors is reduced and the contribution of thermal noise in long time dynamics becomes essential. Application of the semiadiabatic theory [2] modeling 1D dielectric response at time periodic driving field is given in [9]. This section is focused on extension of the Cayley's form technique demonstrated in Sect. 3 to time-dependent external field. Unlike Eq. 7 the analytically solution is given by Dyson's time ordering operator [3] and the second-order decomposition is given by relationship quite similar to this of Eq.11 except that the potential $V(P)$ in Eq.10 is taken at the specified time $t + \Delta t/2$, namely, Eq. 11 is replaced by

$$G(t+t+\Delta t) = \exp\left[-V\left(P, t+\frac{\Delta t}{2}\right)\frac{\Delta t}{2\Theta}\right]\exp[\Theta\Delta t\frac{\partial^2}{\partial t^2}]\exp\left[-V\left(P, t+\frac{\Delta t}{2}\right)\frac{\Delta t}{2\Theta}\right]G(t) \quad (14)$$

Similarly to the static case the features of system are implemented in two matrices: left-hand $\left[1-\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]$ and right hand $\left[1+\frac{\Theta\Delta t}{2}\frac{\partial^2}{\partial P^2}\right]$, and two vectors $\exp\left[-V\left(P, t+\frac{\Delta t}{2}\right)\frac{\Delta t}{2\Theta}\right]$ comprising the time dependence of potential and changing the wavefunction $G(P,t)$ at each grid point. Comparison of semiadiabatic (bold) and Cayley's form (dots) is shown in Fig. 3.

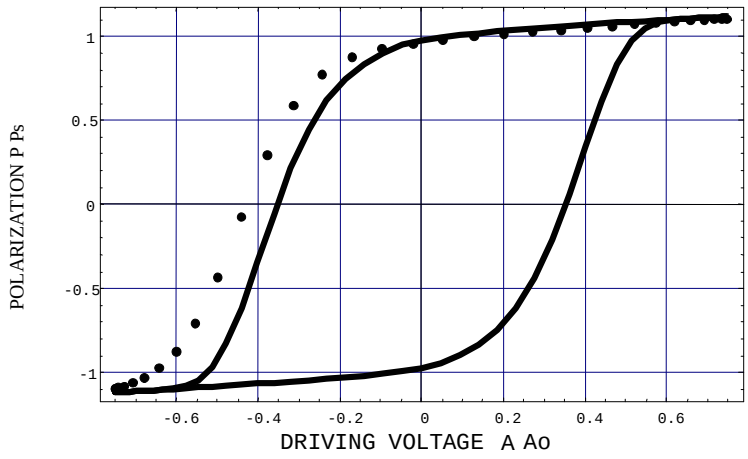

Fig.3 Comparision of dynamic hysteresis patterns modeled in semiadiabatic (bold) and Cayley's form (dots) techniques for applied voltage $A = 3/4A_0 \cos[\Omega t]$, frequency $\Omega - 10^{-3}$, diffusion constant $\Theta = 1/30$. In Cayley's form the grid points $N = 50$, grid increment $\Delta P = 2/25$, and time increment $\Delta t = 1/100$.

A possible origin of minor discrepancies between the hysteresis patterns Fig.3 evaluated in the Cayley's form technique and the semiadiabatic technique [2] is the different rank of approximation if compared to [1]. The technique [2] concerning time dependent energy functional comprises expansion of probability density of polarization in terms of Floquet functions and subsequent expansion of the Floquet functions in terms of instantaneous eigenfunctions of Fokker-Planck operators.

5. Conclusions

We have been concerned on a long-standing objective of thermodynamic theory –the impact of thermal noise in the relaxation and driven dynamics of electric polarization and gave a comparison of results for relaxation and hysteresis obtained analytically with those calculated by one of most promising numerical method for simulating quantum problems. For relaxation patterns (Fig.2) the coincidence is rather good, nevertheless there are minor discrepancies in hysteresis patterns (Fig.3). A possible origin is that neither of these approaches is satisfactory and its level of approximation is different. What we claim is application of the Cayley's form [10] and Suzuki decomposition [16] to imaginary time Schrödinger equation for the potential derived from Ginsburg-Landau energy functional. What we actualize in this work is the development of this technique with application to the Schrödinger equations with multidimensional imaginary time for Fourier amplitudes of polarization. The application grade resulting from this work are addressed to high field response and long time dynamics in ferroelectrics under arbitrary driving voltage.

Acknowledgements

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