Physics Letters A 372 (2008) 7187–7190

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

# Deterministic and stochastic behavior in ferroelectric particles

Artjom Vargunin, Teet Örd, Risto Tammelo *

*Institute of Physics, University of Tartu, 4 Tähe Street, 51010 Tartu, Estonia*

ARTICLE INFO

*Article history:*
Received 8 September 2008
Accepted 22 September 2008
Available online 16 October 2008
Communicated by V.M. Agranovich

*PACS:*
77.80.-e
64.60.An
05.10.Gg

*Keywords:*
Ferroelectrics
Finite size effects
Stochastic approach
Relaxation

ABSTRACT

The response of a ferroelectric particle to an applied harmonic field is studied using the Fokker–Planck equation approach. The size effect in dielectric susceptibility is interpreted as the complementarity between stochastic resonance and response anomaly of the second-order phase transition. The borderline between stochastic and deterministic behavior is established. Two universal volume-independent ratios of the damping rates are predicted and may be verified in the relaxation experiments. The approach can be generalized also to other finite condensed systems.



## 1. Introduction

The size-induced phenomena in ferroelectrics, discovered about fifty years ago [1,2], have been an object of substantial scientific interest due to their practical importance [3,4]. The critical size, size effect on the transition temperature, size driven diffuseness of the ferroelectric transition, size induced peculiarities of the dielectric properties, and even an interplay between size effects and time of collecting experimental information in various ferroelectric systems have recently been actively investigated (see, for instance, [5–9]).

In the present communication we introduce the stochastic description of finite ferroelectric system based on the Fokker–Planck equation approach. Recently we have demonstrated that stochastic nature of the order parameter plays the essential role on the size-dependent properties of restricted systems with a bulk second-order phase transition [10,11]. It produces the complementarity between stochastic resonance and response anomaly near the phase transformation point, representing particularly the experimentally established fact that system dimension decrease is attended by an increase in the diffuseness of the phase transition. Proposed model predicts also lowering of the critical temperature as the size of the sample decreases. Moreover, the competition of two length scales in the critical behavior was established. The first scale is similar to the correlation length determining the critical behavior in sufficiently large samples. The second scale appears as a consequence of the stochastic nature of the order parameter and controls the transitional features in small samples, particularly, in the vicinity of the critical size [5,12]. We believe that these theoretical findings may be of relevance for the description of the peculiarities of the critical temperature in ferroelectric particles [6,13–15]. Our approach predicts also the enhancement of the susceptibility in small samples due to size stochastic resonance [16,17] relating the latter phenomenon to the existence of the critical size of a ferroelectric particle.

The aim of this work is to establish the borderline between stochastic and deterministic nature of the ferroelectric particles in terms of response to the weak applied periodic field. We will also predict two universal volume-independent ratios of the relaxation times naturally appearing in the ordered and disordered states.

## 2. Stochastic equation of motion for polarization

We model the temporal evolution of the polarization $P$ as an order parameter in an uniaxial ferroelectric restricted in space by the overdamped Langevin equation

$$\frac{dP(t)}{dt} = -\frac{\partial U(P;T)}{\partial P} + E(t) + \sqrt{\frac{T}{V}}\zeta(t). \tag{1}$$

Here $\zeta(t)$ is the zero mean internal Gaussian white noise with the correlation function $\langle\zeta(t)\zeta(t')\rangle = 2\delta(t-t')$, $T$ is temperature, $V$ is the volume of the sample, $E(t)$ is an applied electric field,

* Corresponding author.
*E-mail address:* risto.tammelo@ut.ee (R. Tammelo).

0375-9601/$ – see front matter 
doi:10.1016/j.physleta.2008.09.057

and a temperature-dependent soft potential is taken in the Landau form [18]

$$U(P;T)=\frac{1}{2}a(T)P^2+\frac{1}{4}P^4, \tag{2}$$

with $a(T)=\alpha(T-T_c^\infty)$, where the constant $\alpha>0$, and $T_c^\infty$ is the temperature of the bulk ferroelectric second-order phase transition. The potential $U(P;T)$ is bistable if $T<T_c^\infty$, and monostable if $T>T_c^\infty$.

The smallness of the system implies that its dimensions are smaller than the correlation length of the polarization fluctuations (analogously to zero-dimensional superconductors [19]). In Eq. (1) the finiteness of the particles induces stochastic motion in the system. The latter vanishes in the bulk limit ($V\to\infty$) leaving us with the Landau–Khalatnikov equation which describes the deterministic relaxation of the polarization to its equilibrium value. The size driven crossover from stochastic behavior to deterministic one is a substantial feature of the present model. Note that the consideration stems from the general Landau free energy expansion where the second and the fourth order terms as well as the squared gradient of order parameter are taken into account. In the present approach we neglect the inhomogeneity of fluctuations inside the ferroelectric particle, but incorporate the interwell dynamics in the potential (2). The opposite limiting case corresponds to the Gaussian approximation where the inhomogeneity of fluctuations is taken into account, however, the interwell motions are excluded [20]. For the details of the foundation of the present model see [10,11].

## 3. Dynamic dielectric susceptibility

According to the scheme developed in [21], the stationary autocorrelation function of the polarization $P$ in the asymptotic time limit can be expressed as

$$\langle P(t)P(0)\rangle = g_1 e^{-\lambda_1 t}+g_3 e^{-\lambda_3 t}, \tag{3}$$

where

$$g_1=\langle P^2\rangle_{st}-g_3, \tag{4}$$

$$g_3=\frac{[\lambda_1-a(T)]\langle P^2\rangle_{st}-\langle P^4\rangle_{st}}{\lambda_1-\lambda_3}. \tag{5}$$

Here $\langle\cdots\rangle_{st}=\int_{-\infty}^{\infty}\cdots\Pi_{st}(P)\,dP$, where $\Pi_{st}(P)$ is the stationary probability distribution of the non-perturbed system, and $\lambda_{1,3}$ are the first and third eigenvalues of the non-perturbed Fokker–Planck operator associated with the Langevin equation (1), i.e.,

$$\hat{L}_{FP}(P)=\frac{\partial}{\partial P}\frac{\partial U(P;T)}{\partial P}+\frac{T}{V}\frac{\partial^2}{\partial P^2}. \tag{6}$$

In accordance with Ref. [22] only the odd eigenvalues contribute to (3). In (3), the term proportional to the coefficient $g_1$ describes the contribution from the interwell or hopping dynamics with the characteristic time $\tau_1=\lambda_1^{-1}$, and the term proportional to the coefficient $g_3$ describes the contribution from the intrawell or local dynamics with the corresponding characteristic time $\tau_3=\lambda_3^{-1}$ to the correlation in the bistable regime [21]. We calculate the eigenvalues $\lambda_{1,3}$ numerically, solving the corresponding Schrödinger equation [23] by means of the symplectic method, see e.g. [24].

In the bulk limit, the characteristic time $\tau_1$ diverges below $T_c^\infty$ and $g_1e^{-\lambda_1 t}\to -a(T)$, reflecting the fact that $\tau_3$ governs the leading time dependence of the autocorrelation function (3) of a large system below $T_c^\infty$. Above $T_c^\infty$ this characteristic time represents only a subleading relaxation channel [25]. The relaxation times exhibit substantial changes as the volume of the ferroelectric particle decreases, however, the minimum of $\lambda_3$, appearing as soon as the relaxation rate $\lambda_1$ becomes nonzero, remains an essential feature of the relaxation phenomena in finite particles. This allows one to observe the evolution of the critical temperature (more exactly, pseudocritical temperature [26]) in the considered ferroelectric system [11].

From the correlation function (3) one can derive the linear dynamic dielectric susceptibility by means of the fluctuation–dissipation relation [21], namely

$$\chi(T,\Omega)=\frac{V}{T}\left[\left(\frac{g_1\lambda_1^2}{\lambda_1^2+\Omega^2}+\frac{g_3\lambda_3^2}{\lambda_3^2+\Omega^2}\right)-i\Omega\left(\frac{g_1\lambda_1}{\lambda_1^2+\Omega^2}+\frac{g_3\lambda_3}{\lambda_3^2+\Omega^2}\right)\right], \tag{7}$$

where $\Omega$ is the frequency of the applied periodic field $E(t)$. Correspondingly, in the bulk limit we have

$$\chi(T,\Omega)=\frac{\lambda_{1,3}-i\Omega}{\lambda_{1,3}^2+\Omega^2}, \tag{8}$$

where one must choose $\lambda_1=a(T)$ if $T>T_c^\infty$, and $\lambda_3=-2a(T)$ if $T<T_c^\infty$. Thus, in this limit the conventional Landau phase transition theory realizes with the anomaly of the susceptibility at the phase transition temperature $T_c^\infty$. However, in the finite sample the polarization $P$ becomes a stochastic variable leading to the transformation of this anomaly to the phenomenon of stochastic resonance [10]. The latter peculiarity determines the size driven crossover from stochastic to deterministic nature of the response in the considered ferroelectric systems.

## 4. Size driven crossover from stochastic to deterministic response

In order to demonstrate the stochastic nature of the order parameter $P$ we examine the response of the ferroelectric particle to the weak applied periodic signal. The dependence of dielectric susceptibility on temperature for various values of the volume are displayed in Fig. 1. As one can see, the resonant maximum of $|\chi|$ shifts to higher temperatures if the volume increases, approaching asymptotically the response anomaly at the phase transition point $T_c^\infty$ in the infinite volume limit. This process is accompanied by the decrease in diffuseness as the volume increases, i.e., the corresponding critical exponent $\gamma\approx 1.6$ for $V=0.1$ and $\gamma\approx 1$

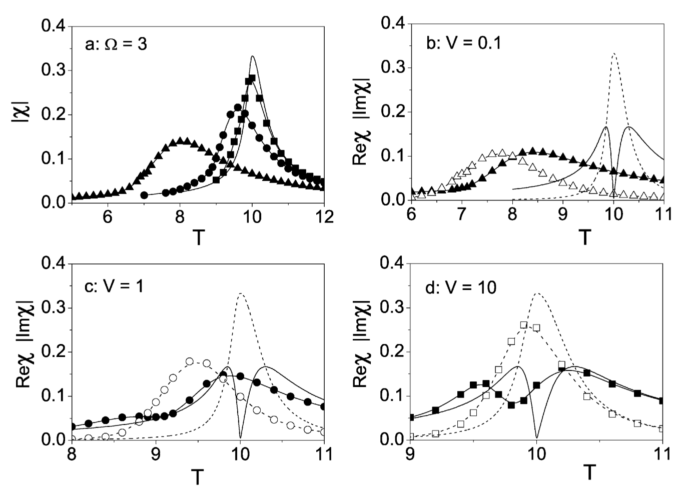


**Fig. 1.** The plots of the dielectric susceptibility vs temperature at frequency $\Omega=3$ for various volumes $V=0.1$ ((a), (b): triangles), $V=1$ ((a), (c): circles), $V=10$ ((a), (d): squares) and the bulk limit ((a)–(d): curves without points). In figures (a)–(d) the modulus of the susceptibility (a), its real part ((b)–(d): solid curves and filled points) and imaginary part ((b)–(d): dashed curves and empty points) are displayed. Here we use $T_c^\infty=10$ and $\alpha=10$.