Analytical description of domain morphology and phase diagrams of ferroelectric nanoparticles

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Abstract
Analytical description of domain structure morphology and phase diagrams of ferroelectric nanoparticles is developed in the framework of Landau-Ginzburg-Devonshire approach. To model realistic conditions of incomplete screening of spontaneous polarization at the particle surface, it was considered covered by an ultra-thin layer of screening charge with effective screening length. The phase diagrams, calculated for spherical Sn2P2S6 nanoparticles in coordinates "temperature" and "effective screening length" by finite element modelling, demonstrate the emergence of poly-domain region at the tricritical point and its broadening with increasing the screening length for the particle radius over a critical value. Metastable and stable labyrinthine domain structures exist in Sn2P2S6 nanoparticles with radius (8-10) nm and more. We derived simple analytical expressions for the boundaries between paraelectric, single-domain and poly-domain ferroelectric phases, tricritical point and the necessary condition for the appearance of labyrinthine domains, and demonstrated their high accuracy in comparison with finite element modelling results.

Analytical expressions for the dependence of the ferroelectric-paraelectric transition temperature on the particle radius in the single-domain and poly-domain states of the particle were compared with analogous dependences experimentally measured for SrBi2Ta2O9 nanoparticles and simulated for Sn2P2S6 nanocrystals by Monte Carlo method within the framework of axial next-nearest-neighbours Ising model. The analytical expression for the ferroelectric-paraelectric transition temperature in the poly-domain state quantitatively agrees

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with experimental and simulated results, and it accurately reproduces empirical Ishikawa equation at all temperatures, justifying it theoretically. Analytical description shows that phase diagrams and domain morphologies, which are qualitatively similar to the ones calculated in this work, can be expected in other ferroelectric nanoparticles covered by the screening charges, being rather different for the ferroelectrics with the first and second order ferroelectric-paraelectric transitions respectively.

**Keywords:** ferroelectric nanoparticles, surface screening, domain morphology, phase diagrams

I. INTRODUCTION

Nanoscale ferroelectrics are unique model objects for fundamental studies of polar surface properties, various screening mechanisms of spontaneous polarization by free carriers and possible emergence of versatile multi-domain states [1, 2], including their complex morphologies [3, 4, 5, 6]. Ferroelectric nanoparticles can demonstrate perfect possibilities of polar-active properties control, which attract permanent attention of researchers. Classical examples are nontrivial experimental results of Yadlovker and Berger [7, 8, 9], who revealed the enhancement of polar properties of cylindrical nanoparticles of Rochelle salt. Frey and Payne [10], Zhao et al [11], Drobnich et al [12], Erdem et al [13], Shen et al [14] and Golovina et al [15, 16, 17] demonstrated the possibility to control by finite size effects the phase transition temperatures and other peculiarities, including the appearance of new polar phases for BaTiO$_3$, S$_2$P$_2$S$_6$, PbTiO$_3$, SrBi$_2$Ta$_2$O$_9$ and KTa$_{1-x}$Nb$_x$O$_3$ nanopowders and nanoceramics, respectively. Increasing interest is related with the impact of surface conditions and finite size effects on the photorefractive properties of S$_2$P$_2$S$_6$ or BaTiO$_3$ ferroelectric nanoparticles suspended in nematic liquid crystals (see [18, 19] and refs therein).

The continuum phenomenological Landau-Ginzburg-Devonshire (LGD) approach combined with the electrostatic equations allows one to establish the physical origin of the anomalies in the polar and dielectric properties, and calculate the phase diagrams changes appearing under the decrease of ferroelectric particle sizes. For instance, using the LGD approach Niepce [20], Huang et al [21, 22], Glinchuk et al [23, 24], Ma [25], Khist et al [26], Wang et al [27], Morozovska et al [28, 29, 30, 31] and Eliseev et al [32, 33, 34] have shown, that the changes of the transition temperatures, enhancement or weakening of spontaneous polar or/and magnetic order in a single-domain spherical, ellipsoidal and cylindrical nanoparticles of sizes (4 – 100) nm are conditioned by the various physical mechanisms, such as surface tension, correlation effect, depolarization field, flexoelectricity, electrostriction, magnetoelectric coupling, magnetostriction, rotostriction and Vegard-type chemical pressure. We emphasize that the applicability of the LGD approach for ferroelectric nanoparticles with sizes about (4-8) nm or more (i.e. 10 lattice constants or more) is corroborated by the fact, that the critical sizes for the appearance of the long-range order and the properties calculated for thin films or nanoparticles from atomistic [35, 36, 37, 38, 39] and phenomenological [32-30, 40, 41] theories are in a good
agreement with each other, as well as with experimental results for nanosized ferromagnetics [42] and ferroelectrics [7-11, 13, 43]. As a mean-field approach, LGD can lose its validity below 5-10 unit cells due to the vanishing of long-range order correlations.

Incomplete screening of spontaneous polarization causes depolarization fields, which in turn can lead to the appearance of ferroelectric domains in the particle, decreasing the positive energy of the depolarization fields [26, 27, 33, 34, 44]. Incomplete screening conditions of the spontaneous polarization also lead to the decrease of ferroelectric transition temperature due to the depolarization field effect [26, 27, 33, 34]. Yet the vast majority of theoretical models (both LGD-based and \textit{ab initio}) consider the particles covered with perfect electrodes, stabilizing their single-domain state (see e.g. [20-32]). Only several LGD-based theoretical studies did consider the incomplete screening of spontaneous polarization in ferroelectric nanoparticles [26, 27, 33, 34, 45, 46] and their domain structure [47]. In particular, Wang et al [47] used phase field modelling to calculate the domain structure evolution and its complex morphology in multiaxial ferroelectric PbTO$_3$ nanowires, nanorods and nanodiks placed in vacuum. Eliseev et al [45] calculated the phase diagram and domain structure morphology in spherical nanoparticles of uniaxial ferroelectric CuInP$_2$S$_6$ covered by a layer of screening charge with finite screening length. They revealed that a regular stripe domain structure transforms into a labyrinth pattern when the gradient term decreases below the critical value, and classified the event as a gradient-induced morphological transition.

Under incomplete screening conditions, the analytical description of the domain structure morphology changes and phase diagrams of ferroelectric nanoparticles is absent. In particular, any sort of analytical expressions for the transition temperatures between different poly-domain, single-domain and paraelectric phases is absent. The available analytical expressions for the transition between single-domain ferroelectric and paraelectric phases give significantly overestimated values of the particle critical sizes [33]. To fill the knowledge gap, here we propose LGD-based analytical description of domain structure morphology and phase diagrams of ferroelectric nanoparticles. To model realistic conditions of spontaneous polarization incomplete screening at the particle surface, it was regarded covered by an ultra-thin layer of screening charge with effective screening length.

The manuscript is structured as follows. Free energy and basic equations with boundary conditions are discussed in section II. Analytical expressions for the phase boundaries separating single-domain, poly-domain and paraelectric phases are listed and analyzed in section III. Phase diagrams of ferroelectric nanoparticles covered by sluggish screening charges are analyzed in section IV with the special attention to domain morphologies changes and temporal evolution of striped and labyrinthine domains. Comparison with available experiments [14] for SrBi$_2$Ta$_2$O$_9$ nanoparticles and independent Monte Carlo (MC) simulations within axial next-nearest-neighbours Ising (ANNNI) model [12] for S$_2$P$_2$S$_6$ nanocrysts is presented in section V. Section VI is a brief discussion with
conclusive remarks. Electrostatic problem, justification of effective screening charge model, derivation of analytical expressions and phase diagrams calculated for nanoparticles of different radius are given in Appendixes A, B and C in the Supplement, respectively.

II. PROBLEM STATEMENT

Let us consider a ferroelectric nanoparticle of radius $R$ with a one-component ferroelectric polarization $P_3(r)$ directed along the crystallographic axis 3 [Fig.1(a)]. At the same time we can assume that

$$P_i = \varepsilon_0 \varepsilon_b E_i$$

where $P_i$ is an isotropic relative permittivity of background [48], and $\varepsilon_0$ is a universal dielectric constant. Since the ferroelectric polarization component $P_3(r)$ contains background and soft mode contributions, electric displacement vector has the form $D = \varepsilon_0 \varepsilon_b E + P$ inside the particle. Outside the particle $D = \varepsilon_0 \varepsilon E$, where $\varepsilon - 1$ is the relative dielectric permittivity of external media (air or vacuum). Electric field components $E_i$ are related with electric potential $\varphi$ as

$$E_i = -\partial \varphi / \partial x_i.$$

The potential $\varphi$ satisfies a Poisson equation inside the particle and Laplace equation outside it:

$$\varepsilon_0 \varepsilon_b \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) \varphi = \left( \frac{\partial P_3}{\partial x_3}, \quad r < R, \right.$$

$$\left. 0, \quad r > R \right).$$

Equations (1) are supplemented by the conditions of potential continuity at the particle surface, $\varphi_{ext}(r=R) = \varphi_{int}(r=R)$ and its vanishing either at infinity, $\varphi_{ext}(r=\infty) = 0$, or at the surface of remote electrode located at the boundaries of the computation cell. The boundary condition for the normal components of electric displacements is

$$\left( n(D_{ext} - D_{int}) + \sigma_S \right)|_{r=R} = 0,$$

where the "effective" surface charge density $\sigma_S$ is introduced to model realistic conditions of spontaneous polarization incomplete screening at the particle surface and depends on its ambient (vacuum, air, inert or chemically active gases, liquids, semiconductor or imperfect electrode cover). Several theoretical studies [26, 33, 34, 45] use the linear dependence of the charge density $\sigma_S$ on electric potential excess $\delta \varphi = \varphi_{int}(r=R) - \varphi_{ext}(r=\infty)$ at the surface of ferroelectric nanoparticle:

$$\sigma_S(\varphi) \approx -\varepsilon_0 \frac{\delta \varphi}{\Lambda},$$

where $\Lambda$ is an "effective" screening length.

Noteworthy, the expression (1b) is approximate because it includes as "effective" screening charge, while the real space charge is distributed in the ultrathin layer near the interface [49]. The first justification of Eq.(1b) was proposed by Batra et al [50], who showed that the space charge
distribution in the imperfect electrodes with nonzero screening length could be reproduced by the model in which ideal conducting electrodes are separated from the ferroelectric by a vacuum gap, and all bound and free charges are located at the interfaces (see also Appendix A.II in Supplementary Materials). Later on Stengel et al [51, 52] have shown that the concept of effective screening length can be generalized for a given ferroelectric/electrode interface, at that the interfacial capacitance per unit area is proportional to $\varepsilon_0/\Lambda$. Introduction of the interfacial capacitance $C_{IF} = \varepsilon_0\varepsilon_{IF}S/\Lambda$ (in a flat capacitor approximation) allows one to justify the origin of Eq.(1b) in a simple way, because the product $C_{IF}\,q_{IF}^{\|_{R=\infty}}$ is the total value of the interfacial space charge, $q = \sigma_sS$, and therefore

$$\sigma_s = \frac{C_{IF}\,q_{IF}^{\|_{R=\infty}}}{S} \approx -\varepsilon_0\,\frac{q_{IF}^{\|_{R=\infty}}}{\Lambda}$$

if the strict inequality $R >> \Lambda$ is valid and the interfacial dielectric permittivity $\varepsilon_{IF}$ is close to unity, $\varepsilon_{IF} \approx 1$ (otherwise $\Lambda$ can be redefined as $\Lambda/\varepsilon_{IF}$).

To fulfill the inequality $R >> \Lambda$ reliable estimates of $\Lambda$ value should be used. Following Wang et al. [27], who considered ferroelectric nanoparticles, the effective screening length $\Lambda$ that characterizes the effective thickness of the double electric layer formed by the bound and free charges [53], should be much smaller than 1 Å (about 0.1 Å) in accordance with ab initio estimates [53, 54] and early quantum-mechanical calculations [55]. That say $\Lambda$ is much smaller than a lattice constant $a$~0.5 nm in ferroelectric nanoparticles and almost temperature-independent. One of the reasons why $\Lambda<<a$ is a high relative dielectric permittivity $\varepsilon$ in the double electric layer (in=(10 – 100)), because the effective thickness is proportional to the ratio of the physical thickness to $\varepsilon$ (see e.g. Appendix A in Ref.[56]).

In many other cases the screening charges can be localized at Bardeen-type surface states [57] caused by the strong band-bending via depolarization field [58, 59, 60, 61, 62]. For the case the grounds of Eq.(1b) applicability follows from Eq.(17) and Fig.3 in Ref.[57], where the separation $\Lambda$ (letter "a" in Bardeen's designations) has an angstrom order.

Another important case (relevant to the nanoparticles suspension in gases and liquids) is the Stephenson-Highland (SH) ionic adsorption at the ferroelectric surface [63, 64]. Within SH model the dependence of the surface charge density $\sigma_s[\phi]$ on electric potential excess $\delta\phi$ at the free surface is controlled by the concentration of positive and negative surface charges $\theta_i[\phi]$ in a self-consistent manner via Langmuir adsorption isotherms [65]:

$$\sigma_s[\phi] = \sum_i \frac{eZ_i\theta_i[\phi]}{A_i} = \sum_i \frac{eZ_i}{A_i} \left(1 + q_i \exp\left(\frac{\Delta G_{i0}^{00} + eZ_i\delta\phi}{k_B T}\right)\right)^{-1},$$  \hspace{1cm} (1c)

where $e$ is the electron charge, $Z_i$ is the ionization number of the surface ions, $T$ is the absolute temperature, $1/A_i$ are the saturation densities of positive and negative charge species ($i=1,2$), $\Delta G_{i0}^{00}$ are the formation energies of the surface ions at normal conditions and the factors $q_i$ are the partial
pressures ratios. Considering the simplest case $q_i = 1$, the linearization of expression (1c) for small built-in potential $\frac{eZ_i\delta\Phi}{k_BT} < 1$ leads to the Eq.(1b) for the effective surface charge density $\sigma_s$ with the effective screening length $\Lambda$ given by expression:

$$\frac{1}{\Lambda} \approx \sum_i \frac{(eZ_i)^2}{4e_0\alpha_i k_BT} \left[ 1 - \tanh^2 \left( \frac{\Delta G_i^{\text{ref}}}{2k_BT} \right) \right].$$

(1d)

Since we would not like to restrict by the definite model further, we performed calculations for $\Lambda$ changing in the range $(10^{-3} – 10)$ Å.

![Diagram](image)

**FIG. 1.** Domain stripes calculated in a spherical Sn$_2$P$_2$S$_6$ nanoparticle of radius $R=10$ nm, effective screening length $\Lambda=0.15$ Å and room temperature. The polar cross-section (a), hemispherical view (b) and equatorial cross-section (c) are shown.

LGD free energy functional $G$ additively includes 2-4-6 Landau expansion on polarization powers, $G_{\text{Landau}}$, polarization gradient energy contribution, $G_{\text{grad}}$, electrostatic contribution $G_{\text{el}}$, elastic, electrostriction and flexoelectric contributions $G_{\text{el, flexo}}$. Following Ref.[45] it has the form:

$$G = G_{\text{Landau}} + G_{\text{grad}} + G_{\text{el}} + G_{\text{el, flexo}},$$

(2a)

$$G_{\text{Landau}} = \int_{|r|<R} d^3r \left( \frac{\alpha}{2} P_3^2 + \frac{\beta}{4} P_3^4 + \frac{\gamma}{6} P_3^6 \right),$$

(2b)

$$G_{\text{grad}} = \int_{|r|<R} d^3r \left( \frac{g_{11}}{2} \left( \frac{\partial P_3}{\partial x_3} \right)^2 + \frac{g_{44}}{2} \left( \frac{\partial P_3}{\partial x_2} \right)^2 + \left( \frac{\partial P_3}{\partial x_1} \right)^2 \right),$$

(2c)

$$G_{\text{el}} = \int_{|r|<R} d^3r \left( \frac{P_3 E_3 + \frac{\varepsilon_0 \varepsilon_b}{2} E_i E_j}{2} \right) - \frac{1}{|r|<R} \int d^3r \frac{\sigma_x \Phi}{2} - \frac{\varepsilon_0 E_v}{2} \int_{|r|<R} d^3r,$$

(2d)

$$G_{\text{el, flexo}} = \int_{|r|<R} d^3r \left( -\frac{S_{ijkl}}{2} \sigma_{y} \sigma_{kl} - Q_{ij} p_3^2 - F_{ykl} \left( \sigma_{y} \frac{\partial p_3}{\partial x_l} - P_3 \frac{\partial \sigma_{y}}{\partial x_k} \right) \right).$$

(2e)
The coefficient $\alpha$ linearly depends on temperature $T$, $\alpha = \alpha_T (T - T_c)$, where $T_c$ is the Curie temperature and $\alpha_T$ is the inverse Curie-Weiss constant. The coefficient $\beta$ is regarded temperature-independent. It is positive if the ferroelectric material undergoes a second order transition to the paraelectric phase at $T_c$ and negative otherwise. Higher nonlinear coefficient $\gamma$ and gradient coefficients $g_{11}$ and $g_{44}$ are positive and regarded temperature independent. $\sigma_{ij}$ is the stress tensor in Eq. (2e).

We omit the explicit form of the $G_{ex+flexo}$ for the sake of simplicity; it is listed in Refs. [66, 67, 68]. Since the values of the electrostriction and flexoelectric tensor components, $Q_{ijkl}$ and $F_{ijkl}$, and surface tension coefficient $\mu$ are unknown for most of ferroelectrics, we performed numerical calculations with the coefficients varied in a physically reasonable range ($|F_{ijkl}| \leq 10^{11}$ m$^3$/C, $|Q_{ijkl}| \leq 0.1$ m$^4$/C$^2$). The obtained results proved the insignificant impact of electrostriction and flexoelectric coupling on domain morphology for the uniaxial ferroelectrics Sn$_2$P$_2$S$_6$ and SrBi$_2$Ta$_2$O$_9$ considered below.

Notably that the surface tension (also referred as intrinsic surface stress for solids [69]) induces additional surface stresses proportional to the surface tension coefficient $\mu$ and equal to $\sigma_{11} = \sigma_{22} = \sigma_{33}|_{r=R} = -\frac{2\mu}{R}$ for a spherical nanoparticle of radius $R$. The stresses affect the Curie temperature and ferroelectric polarization behaviour due to the electrostriction coupling [28-31, 33, 47]. In the considered case of a uniaxial ferroelectric the renormalization of Curie temperature, $T_c \to T'_c$, acquires the following form [29, 33]:

$$T'_c(R) = T_c \left( 1 - \frac{Q}{\alpha_T T_c^2} \frac{2\mu}{R} \right), \quad (2f)$$

where $Q = Q_{33} + Q_{12} + Q_{13}$, $Q_{ij}$ is the bulk electrostriction tensor in Voigt notations.

The value of $T'_c$ can be calculated from Eq.(2f) for known parameters. Since we did not find neither $Q_{ij}$ nor $\mu$ value for Sn$_2$P$_2$S$_6$ nanoparticles, for which we performed numerical modeling, we made estimations for typical parameter range. The sum $Q$ of electrostriction tensor components is rather small and positive for e.g. ferroelectric perovskite Pb$_x$Zr$_{1-x}$TiO$_3$ with cubic m$\bar{3}$m symmetry in the paraelectric phase, namely $0.004 < Q < 0.04$ m$^4$/C$^2$, since $Q_{11} > 0$, $Q_{12} = Q_{13} < 0$ and $0.01 \leq 2|Q_{12}| \leq |Q_{11}| \leq 0.1$ m$^4$/C$^2$ for the material and other typical perovskites. In contrast to earlier theoretical suggestions [28-31], recent experiments tell us that $\mu$ is relatively small for the most of ferroelectric perovskites, not more than $(1 - 2)$ N/m for PbTiO$_3$ [25]. Using the reasonable estimate
µ ≤ 1N/m and 0 < Q < 0.025 m⁴/C² one can calculate that \( \frac{2\mu Q}{\alpha_\gamma T_C} \leq 10^{-10} \) m for e.g. Sn₂P₂S₆ with \( \alpha_\gamma = 1.6 \times 10^6 \text{C}² \cdot \text{m J/K} \) and \( T_C = 336 \) K. So that the surface tension contribution to the renormalized Curie temperature \( T_C^* \) is proportional to \( \mu / R \) and not more than \((2 − 1)%\) for a \((5 − 10) \text{ nm} \) Sn₂P₂S₆ nanoparticle, respectively. However this relatively small change should be accounted in the analytical expressions derived below for accurate comparison with experiments. Also it is not excluded that the surface tension contribution can be important for other spherical nanoparticles with higher electrostriction and/or higher surface tension coefficients (see e.g. Refs. [31, 33, 47]).

Allowing for Khalatnikov mechanism of polarization relaxation, minimization of the free energy (2) with respect to polarization \( P(r) \) leads to time-dependent LGD-equation [45]:

\[
\Gamma \frac{\partial P_3}{\partial t} + \alpha_\gamma \left( T - T_0^* \right) P_3 + \beta P_3^3 + \gamma P_3^5 - g_{44} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) P_3 + g_{11} \frac{\partial^2 P_3}{\partial x_3^2} = E_3. \tag{3}
\]

The Khalatnikov coefficient \( \Gamma \) determines the relaxation time of polarization \( \tau_K = \Gamma / |\alpha| \), that typically varies in the range \((10^{-11} - 10^{-13}) \text{ s} \) far from \( T_C \). The boundary condition for polarization at the spherical surface \( r = R \) is natural, \( \partial \tilde{P}_3/\partial n |_{r=R} = 0, \) \( n \) is the outer normal to the surface.

III. ANALYTICAL EXPRESSIONS FOR THE PHASE BOUNDARIES

Phase diagrams of spherical ferroelectric nanoparticles covered by a screening charge have several phases, namely paraelectric (PE) phase, single-domain ferroelectric (SDFE) phase and poly-domain ferroelectric (PDFE) phase including various domain morphologies [45]. Our target is to derive enough accurate approximate analytical expressions for the phase boundaries and compare the analytical formulas with finite element modelling (FEM).

Approximate expression for the nanoparticle transition temperature from SDFE to PE phase is

\[
T_{PE-SDFE}(R, \Lambda) = T_0^* (R) - \frac{1}{\alpha_\gamma \varepsilon_0 \left[ \varepsilon_r + 2 \varepsilon_\epsilon + (R/\Lambda) \right]}, \tag{4}
\]

Here the first term \( T_0^* (R) \) is a Curie temperature renormalized by the surface stress in accordance with Eq.(2f). The second term originates from a depolarization field. The term, depending on the ratio \( (R/\Lambda) \), strongly decreases the PE-SDFE transition temperature for small nanoparticles and vanishes for big particles being proportional to \( (\Lambda/R) \). Derivation of Eq.(4) is given in Ref. [33] and also listed in Appendix A.I. of Supplementary Materials. Notably that the expression (4) is exact for the natural boundary conditions at the particle surface, \( \partial \tilde{P}/\partial n |_{r=R} = 0 \), and becomes high-accuracy approximation for more general boundary condition, when \( \tilde{P} + \lambda \partial \tilde{P}/\partial n |_{r=R} = 0 \), where the so-called
extrapolation length $\lambda$ [70, 71] is regarded positive and typically exceeds $(1 - 2)\text{ nm}$ [72]. Hence Eq.(4) can be used to check the FEM simulations accuracy and convergence rate for the natural boundary conditions used hereinafter.

Approximate analytical expression for the nanoparticle transition temperature from PDPE to PE phase can be found using calculations in the Appendix B of Supplementary Materials, namely:

$$T_{PE-PDPE}(R, \Lambda) = \begin{cases} T_c'(R) - \frac{g_{44}}{\alpha_T R} \left( \frac{1}{\sqrt{\varepsilon_0 (\varepsilon_b + 2\varepsilon_e) g_{44}}} + \frac{1}{\xi R \varepsilon_{cr} (\Lambda)} - \frac{1}{\xi R} \right), & R > R_{cr}^e, \\
absent, & R < R_{cr}^e. \end{cases} \tag{5a}$$

Where the critical radius is

$$R_{cr}^e(\Lambda) = \left( \frac{\xi}{\sqrt{\varepsilon_0 (\varepsilon_b + 2\varepsilon_e) g_{44}}} - \frac{1}{(\varepsilon_b + 2\varepsilon_e) \Lambda} \right)^{-1}. \tag{5b}$$

Three terms in parentheses on the right-hand side of Eq.(5a) originated from the correlation effect and depolarization field energy of the domain stripes. Parameter $\xi$ is a sort of geometrical factor that is close to 0.5 for domain stripes onset in the $\{x,y\}$ cross-section of the spherical particle.

The minimal spatial wave number $k_{min} = \sqrt{k_x^2 + k_y^2}$ and period $D_{max}$ of the domain structure onset in the $\{x,y\}$ cross-section are radius-dependent and temperature-independent,

$$k_{min}(R, \Lambda) = \frac{1}{\xi R} \sqrt{\frac{R}{R_{cr}^e(\Lambda)} - 1}, \quad D_{max} = \frac{2\pi}{k_{min}}. \tag{6}$$

Notably, that the identical form of Eq.(5a) can be rewritten via $k_{min}$ as

$$T_{PE-PDPE} \approx T_c \left( 1 - \frac{Q}{\alpha_T T_c} \frac{2\mu}{R} \right) - \frac{1}{\alpha_T} \left( g_{44} k_{min}^2 + \frac{\varepsilon_{-1}}{R/\Lambda + (\varepsilon_b + 2\varepsilon_e) \left( 1 + (\xi R)^2 k_{min}^2 \right)} \right) \tag{5a}$$

(see Appendix B in Supplementary Materials for details). Expressions (5)-(6) are valid under the condition

$$\frac{\xi}{\sqrt{\varepsilon_0 (\varepsilon_b + 2\varepsilon_e) g_{44}}} \geq \frac{1}{R} + \frac{1}{(\varepsilon_b + 2\varepsilon_e) \Lambda}. \tag{7}$$

Equation (7) means that the critical value of the gradient coefficient exists at fixed other parameters, $g_{44}^* (R, \Lambda) = \frac{\xi^2}{\varepsilon_0 (\varepsilon_b + 2\varepsilon_e) \left( \frac{1}{R} + \frac{1}{(\varepsilon_b + 2\varepsilon_e) \Lambda} \right)^{-2}}$, and domains appears at $g_{44} < g_{44}^* (R, \Lambda)$. At fixed gradient coefficient $g_{44}$ the equality in Eq.(7) means that the relation between the particle radius $R$ and effective screening length $\Lambda$ should be valid for the domain onset.

The fulfilment of the equality in Eq.(7) corresponds to the transition to a single domain state that occurs in a three-critical point on the phase diagram, where the energies of SDFE and PDPE phases are equal to zero energy of PE phase. In the three-critical point $k_{min} = 0$ and
allowing for Eqs.(5)-(6). After substitution into Eq.(4), the radius dependence of the tricritical point temperature \(T_{tcr}(R)\) and effective screening length \(\Lambda_{tcr}(R)\) can be found exactly as

\[
T_{tcr}(R) = T_c \left(1 - \frac{Q}{\alpha_T T_c} \frac{2\mu}{R} - \frac{\sqrt{\epsilon_0 \epsilon_0 + 2\epsilon_0 \epsilon_e} g_{44}}{\alpha_T \epsilon_0 (\epsilon_0 + 2\epsilon_e) \xi R} \right),
\]

(8a)

\[
\frac{1}{\Lambda_{tcr}(R)} = \left(\epsilon_0 + 2\epsilon_e\right) \left(\frac{\xi}{\sqrt{\epsilon_0 (\epsilon_0 + 2\epsilon_e) g_{44}}} - \frac{1}{R}\right).
\]

(8b)

From these expressions the radius dependences \(T_{tcr}(R)\) and \(\Lambda_{tcr}(R)^{-1}\) scales as \(1/R\).

Approximate analytical expression for the nanoparticle transition temperature from PDFE to SDFE phase can be estimated from the free energy equality of the phases, since the transition is of the first order. Using the speculations we derived the expansion

\[
T_{PD-SD}(R, \Lambda) \approx T_{tcr}(R) - \Delta T(R) \left(1 - \frac{\Lambda}{\Lambda_{tcr}(R)}\right)^\delta.
\]

(9)

Power \(\delta\) is related with the critical index of the phase transition and hence \(\delta\) should be radius-independent. The radius dependence of the temperature shift \(\Delta T(R)\) can be established from FEM. Notably Eqs.(9) is valid only when inequality in Eq.(7) is fulfilled.

IV. PHASE DIAGRAMS FOR \(\text{Sn}_2\text{P}_2\text{S}_6\) NANOPARTICLES

LGD parameters for a bulk ferroelectric \(\text{Sn}_2\text{P}_2\text{S}_6\) (SPS) were collected from Refs.[73, 74] and references therein. They are listed in Table I.

<table>
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<th>(\epsilon_b)</th>
<th>(\alpha_T (\text{C}^2 \cdot \text{m} \cdot \text{J}))</th>
<th>(T_c) (K)</th>
<th>(\beta) (\text{C}^4 \cdot \text{m}^2 \cdot \text{J})</th>
<th>(\gamma) (\text{C}^6 \cdot \text{m}^4 \cdot \text{J})</th>
<th>(g_{11}) (m^3/F)</th>
<th>(g_{44}) (m^3/F)</th>
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<td>7</td>
<td>1.6\times10^6</td>
<td>336</td>
<td>7.42\times10^8</td>
<td>3.5\times10^{10}</td>
<td>3.0\times10^{-10}</td>
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</tbody>
</table>

In Appendix C of Supplementary Materials we presented the phase diagrams of SPS nanoparticles with radius \(R = (2 - 10)\) nm calculated in coordinates "temperature \(T\)" and "effective screening length \(\Lambda\" for the gradient coefficients \(g_{44}=10^{-11} \text{ m}^3/\text{F}\) and \(g_{44}=10^{-10} \text{ m}^3/\text{F}\), which are one order of magnitude different. Numerical results become independent on the surface tension coefficient \(\mu\) and electrostriction combination \(Q\) for \(\mu \leq 0.5\text{N/m} \leq 0.025 \text{ m}^4/\text{C}^2\) and \(R \geq 5\) nm. For radii smaller than 5 nm the surface tension contribution can decrease the transition temperature to paraelectric phase on 5% and more for \(\mu = 0.5\text{N/m}, Q = 0.025 \text{ m}^4/\text{C}\) (used hereinafter).
The particles with radius less than 4 nm are either paraelectric or single-domain for all \( \Lambda \) values changing in the range \((10^{-3} - 1) \, \text{Å}\) [see Fig. S1 in Appendix C of Supplementary Materials]. Different domain morphologies appear for \( R=4 \, \text{nm} \) and bigger particles with \( \Lambda \) increase of more than 0.1 Å and \( g_{44}=10^{-11} \, \text{m}^3/\text{F} \) [see Fig. S2-S3 in Appendix C of Supplementary Materials]. Note that since the problem (1)-(3) together with boundary conditions is axially symmetric with respect to polar axes \( x_3 \), at first we specified the initial distribution of the domain structure in the form of axially symmetric distributions (e.g. in the form of coaxial cylinders) in order to probe the stability of the axially-symmetric solution. It appeared that the radial structures are less stable than the domain stripes or irregular (labyrinth-like) structures presented in the phase diagrams [we compared the energies of the final states]. Since radial distributions can relax to more stable distributions, next we used the random seeding for initial polarization distribution.

A typical phase diagrams of 10-nm SPS nanoparticles calculated in coordinates "temperature \( T \)" and "effective screening length \( \Lambda \)" are shown in Fig. 2. Fig. 2(a) corresponds to the gradient coefficient \( g_{44}=10^{-11} \, \text{m}^3/\text{F} \) and in Fig. 2(b) is for \( g_{44}=10^{-10} \, \text{m}^3/\text{F} \). At small \( g_{44} \) the phase diagram has much wider region of stable poly-domain states (PDFE) separating the single-domain ferroelectric (SDFE) and nonpolar paraelectric (PE) phases [compare Fig. 2(a) and 2(b)]. Abbreviation "trc" denotes the tricritical point at the diagram. The tricritical point has coordinates \( \{ \Lambda_{trc}, T_{trc} \} \).

Labyrinthine domain (LD) region exists for small gradient coefficient \( g_{44} \leq 10^{-11} \, \text{m}^3/\text{F} \) and is absent for its higher values, \( g_{44} \geq 10^{-10} \, \text{m}^3/\text{F} \). Since LDs exist over all computation time, they are at least metastable. However the absolute stability of LDs is questionable, because we cannot make a sweep over all possible domain configurations to choose the one or several equivalent ones, whose energy reaches an absolute minimum [45].

The bottom row (I) in Fig. 2 shows the typical changes of polarization distribution in the equatorial cross-section of the 10-nm nanoparticle, which happens with \( \Lambda \) increase. A SDFE state is stable at very small \( \Lambda\textless 0.1 \, \text{Å}, \) two-domain and poly-domain states are stable in the interval \( 0.11 \, \text{Å} < \Lambda < 0.14 \, \text{Å}. \) Coexistence of PDFE with mixture of domain stripes, LD and PE state appears at \( 0.145 \, \text{Å} < \Lambda < 2 \, \text{Å} \) and is followed by the size-induced phase transition into a stable PE at \( \Lambda > 10 \, \text{Å}. \)

The bottom row (II) in Fig. 2 illustrates the polarization distributions in the stable (SLD) and metastable (MLD) labyrinthine domains calculated with temperature \( T \) increase from 230 K to 260 K in the equatorial cross-sections of the nanoparticles with radius \( R=10 \, \text{nm}, \) \( g_{44}=10^{-11} \, \text{m}^3/\text{F} \) and \( \Lambda=0.3 \, \text{Å}. \) LDs are stable at \( T<240\, \text{K}, \) become metastable at higher temperatures \((240 \, \text{K} < T < 260 \, \text{K})\) and then transforms into a PE phase at \( T \geq 260 \, \text{K}. \) In the temperature range \((240 \, \text{K} < T < 260 \, \text{K})\), where LDs are metastable, the stable are domain stripes coexisting with PE phase at the particle boundary. Notably
the metastability or stability of LDs and stripes were concluded from the comparison of the free energies corresponding to these domain morphologies.

**FIG. 2.** Phase diagram of SPS nanoparticles in coordinates "temperature $T$" and "effective screening length $\Lambda$" calculated for the particle radius 10 nm, gradient coefficient $g_{44}=10^{-11}$ m$^3$/F (a) and $g_{44}=10^{-10}$ m$^3$/F (b), ambient permittivity $\varepsilon_e=1$. The ferroelectric single-domain (SDFE), ferroelectric poly-domain (PDFE), labyrinthine domain (LD) and paraelectric (PE) phases are stable. Abbreviation "trc" denotes the tricritical point with coordinates $\{\Lambda_{trc}, T_{trc}\}$. Solid curves corresponding to the SDFE-PE, PDFE-PE and SDFE-PDFE phase boundaries are calculated from Eqs.(4), (5) and (9), respectively. The bottom row (I) shows typical polarization distributions in the equatorial cross-sections of the nanoparticles with radius $R=10$ nm and different values of $\Lambda$ (in Å) for plot (a). The bottom row (II) illustrates the polarization distributions in the stable (SLD) and metastable (MLD) labyrinthine domains calculated with temperature increase from 230 K to 260 K in the
equatorial cross-sections of the nanoparticles with radius $R=10$ nm, $g_{44}=10^{-11}$ m$^3$/F and $\Lambda=0.3\text{Å}$. SPS parameters are listed in Table I.

The temporal evolution of LDs in the 10-nm SPS nanoparticle, calculated using Landau-Khalatnikov relaxation in time-dependent LGD equations [2], is shown by the top row in Fig. 3. LDs growth up from a random distribution of small polarization [see Fig.3(a)] that’s periphery at first becomes paraelectric with time [see Figs.3(b)-(e)], and only then the random domains in the central part start growing and transforming into the labyrinth with computation time increase [see Figs.3(f)-(h)]. At the same other conditions multiple domain stripes can occur from the two-domain configuration shown in Fig.3(i). The stripes evolution is shown in the bottom row in Figs. 3(j)-(p).

Notably that the energy values computed for the metastable multiple domain stripes [shown in Fig.3(p)] and the labyrinthine domain structure [shown in Fig.3(h)] are rather different, $G=-4.18\times10^{-19}$ J for stripes and $G=-7.62\times10^{-19}$ J for LDs. Thus the labyrinthine structure has essentially smaller energy than domain stripes corresponding the optimal balance between the gradient-correlation energy (2c) tending to minimize the area of the domain walls (and hence to decrease the number of them) and electrostatic energy (2d) decreasing with reducing domain width. Note that the walls of LDs are uncharged in the central part of the particle and become charged and broadened near its poles [see light regions near the poles in Figs. 1(a)], since their broadening causes the decrease of depolarization field [75].

![Image](image.png)

**FIG. 3.** Temporal evolution of polarization distribution in the equatorial cross-section of the SPS nanoparticle with $R=10$ nm, $\Lambda=0.1\text{Å}$, $g_{44}=2\times10^{-11}$ m$^3$/F and $T=200$ K calculated starting from random seeding [plots (a) – (h)] and starting from the two domain configuration [plots (i) – (p)]. Several moments of dimensionless time $t$ (in the units of Landau-Khalatnikov relaxation time $\tau_k$ ) are shown. SPS parameters are listed in Table I.

We leave for further studies the question how the ranges of LDs stability and metastability at phase diagram can be derived analytically (i.e. the boundary between SLD and MLD regions is guided
by eye). However the necessary conditions of LDs appearance were derived analytically with the numerical factor estimated from FEM results allowing for the fact that the wave number $k_{\text{min}} = \sqrt{k_x^2 + k_y^2}$ given by Eq.(6) is not limited to the description of domain stripes with e.g. $k_x^2 = 0$ and $k_{\text{min}} = |k_y|$. Since LDs onset presents an instability in both x- and y-directions (somehow similar to the "chess structure" of its Fourier principal components), corresponding instability condition can be described by Eqs.(7), but with geometrical factor different from $\xi$. Hence the necessary conditions of LDs appearance that impose inequalities on the radius $R$, lengths $\Lambda$ and gradient coefficient $g_{44}$, have the form

$$\frac{1}{\Lambda} \leq \frac{\eta\sqrt{\epsilon_b + 2\epsilon_e}}{\sqrt{\epsilon_0 g_{44}}} - \frac{\epsilon_b + 2\epsilon_e}{R} \quad \text{at fixed } R \text{ and } g_{44},$$  

(10a)

$$\frac{1}{R} \leq \frac{\eta}{\sqrt{\epsilon_0 (\epsilon_b + 2\epsilon_e) g_{44}} - \frac{1}{(\epsilon_b + 2\epsilon_e)\Lambda}} \quad \text{at fixed } \Lambda \text{ and } g_{44},$$  

(10b)

$$g_{44} \leq \frac{\eta^2}{\epsilon_0 (\epsilon_b + 2\epsilon_e)} \left( \frac{1}{R} + \frac{1}{(\epsilon_b + 2\epsilon_e)\Lambda} \right)^{-2} \quad \text{at fixed } R \text{ and } \Lambda.$$  

(10c)

Here the parameter $\eta$ has the same sense that the geometrical factor $\xi$ in Eqs.(5), but it appeared close to $1/2\pi$. Inequalities (10) are equivalent to the inequality (7) with the substitution $\xi \rightarrow \eta$, and so they are also temperature-independent. Notably that equality in Eq.(10a) reached at

$$\Lambda = \Lambda_{LD} = \frac{\eta\sqrt{\epsilon_b + 2\epsilon_e}}{\sqrt{\epsilon_0 g_{44}}} - \frac{\epsilon_b + 2\epsilon_e}{R}$$  

determines the almost vertical boundary between the stable LD and domain stripes corresponding to normal PDFE in Fig.2(a).

Noteworthy that the equality in Eq.(10c) gives the critical value of gradient coefficient $g_{44}^{LD} = \frac{\eta^2}{\epsilon_0 (\epsilon_b + 2\epsilon_e)} \left( \frac{1}{R} + \frac{1}{(\epsilon_b + 2\epsilon_e)\Lambda} \right)^{-2}$ for LDs onset. Actually LDs can exist at $g_{44} < g_{44}^{LD}$. The analytical expression for $g_{44}^{LD}$ corroborates the conclusion made in Ref.[45] about the gradient-induced nature of morphological transition from domain stripes to LDs. However, as it follows from Eqs.(10a) and (10b), the conclusion [45] is incomplete, primary because the inequalities (10) relate all three values, $R$, $\Lambda$ and $g_{44}$. Obtained analytical results lead to the conclusion that more correct statement is that the nature of morphological transition from domain stripes to LDs in ferroelectric nanoparticles underlies in the interplay between the 2D instability of domain splitting induced by incomplete screening of polarization facilitated by small enough gradient energy and high enough particle size to prevent the effect of geometric catastrophe. Quantitative criteria of LDs appearance based on Eqs.(10)
has the form $g_{44}\left(\frac{1}{R} + \frac{1}{\varepsilon_b + 2\varepsilon_e}\Lambda\right)^2 \leq \frac{\eta^2}{\varepsilon_0(\varepsilon_b + 2\varepsilon_e)}$. Since $\frac{1}{R} \ll \frac{1}{\varepsilon_b + 2\varepsilon_e}$ for typical values $R \geq 4$ nm, $\Lambda \approx 1\text{Å}$ and $\eta \approx 1/2\pi$, the latter inequality reduces to $\frac{L_d}{\Lambda} \leq \sqrt{\frac{\varepsilon_b + 2\varepsilon_e}{2\pi}}$, where $L_d = \sqrt{\varepsilon_0 g_{44}}$ is the depolarization length. The physical sense of the condition is that the ratio of depolarization length to effective screening length should be smaller than effective "geometrical factor" $2\pi\sqrt{\varepsilon_b + 2\varepsilon_e}$.

Analytical expressions for the PE-SDFE, PE-PDFE and SDFE-PDFE boundaries at the phase diagrams have been listed in the section III and below we demonstrate their accuracy in comparison with numerical results.

Solid curves in Fig.2(a) corresponding to the SDFE-PE, PDFE-PE and SDFE-PDFE phase boundaries are calculated from Eqs.(4), (5) and (9) respectively. The simple analytical expression (4) for the PE-SDFE transition temperature is exact for the natural boundary conditions at the particle surface, and this is the case illustrated in Fig.2 and Figs.S1-S4 in Appendix C of Supplementary Materials. The relatively simple analytical expressions (5) for the PE-PDFE transition temperature have very high accuracy and corresponding curves look almost exact in comparison with the PE-PDFE boundary simulated numerically. Expressions (5) contain only one fitting parameter $\xi$ originated from the spherical geometry of the particle. We additionally checked that the obtained value $\xi \approx 0.5$ is not material specific, because it is the same for SrBi$_2$Ta$_2$O$_9$, CuInP$_2$S$_6$ or LiNbO$_3$ nanoparticles. So that Eq.(5) can be used for description of PE-PDFE transition in other nanoparticles of uniaxial ferroelectrics. Analytical expressions (8) for the radius dependence of the critical point temperature $T_{cr}(R)$ and effective screening length $\Lambda_{cr}(R)$ are almost exact. Analytical expression (9) quantitatively describes the boundary between SDFE and PDFE phases with two fitting parameters, temperature change $\Delta T(R)$ and critical index $\delta$, which depend on the material parameters, and therefore this expression is not universal. Parameters $\xi$, $\Delta T(R)$ and power $\delta$ have been extracted from FEM results shown in Figs.S1-S3 in Appendix C of Supplementary Materials. It turned out that the critical index $\delta = 3/2$.

Radius dependences of the dimensionless geometrical factor $\xi$ and temperature $\Delta T(R)$ are shown in Figs.4(a)-(b), respectively. As one can see from Fig. 4(a) the geometrical factor $\xi$ slightly increases from 0.44 to 0.49 with the particle radius $R$ increase from 4 nm to 10 nm and then saturates rapidly to the value around 0.5 with further increase of $R$. The slight increase and the fast saturation of $\xi(R)$ mean that the fitting parameter is chosen enough successfully. Additional calculations proved that the value $\xi(R) \approx 0.5$ can be used for description of the size effects in other spherical nanoparticles of uniaxial ferroelectrics such as SrBi$_2$Ta$_2$O$_9$, CuInP$_2$S$_6$ or LiNbO$_3$. 


As one can see from Fig. 4(b) the temperature $\Delta T(R)$ decreases rapidly from 105 K to 50 K with increasing the particle radius $R$ from 4 nm to 10 nm and then continues to decrease with further increase of $R$. The rapid decrease of $\Delta T(R)$ and the absence of its saturation with $R$ increase means that the choice of this fitting parameter is not optimal. However its noticeable decrease with $R$ increase appeared universal for the spherical nanoparticles from other ferroelectric materials.

![Graphs showing temperature and radius dependencies](image)

**FIG. 4.** Radius dependences of the dimensionless geometrical factor $\xi(R)$ (a) and temperature $\Delta T(R)$ (b), tricritical screening length $\Lambda_{trc}(R)$ (c) and tricritical temperature $T_{trc}(R)$ (d) calculated at $g_{44}=10^{-11}$ m$^3$/F. The tricritical values have been calculated from Eqs.(8). Parameters $\xi(R)$, $\Delta T(R)$, tricritical point coordinates (symbols) and critical index $\delta = 3/2$ have been extracted from **FEM results**. Solid curves in plots (a) and (b) are guided by eye. SPS parameters are listed in **Table 1**. Vertical dashed lines indicate the particle size $2R=10$ unit cells (7.3 nm for SPS), above which LGD theory is valid quantitatively. SDFE state (dotted vertical line) becomes stable for $R \leq 3$ nm.
Radius dependences of the effective screening length $\Lambda_{\text{tr}}(R)$ and tricritical temperature $T_{\text{tr}}(R)$ are shown in Figs. 4(c)-(d), respectively. The tricritical values have been calculated from exact analytical expressions (8) in the range of particle size $2R$ more than 10 unit cells (~7.3 nm for SPS), where the results obtained within continuum LGD approach is valid quantitatively. From Fig. 4(c) the value $\Lambda_{\text{tr}}(R)$ very slightly decreases from 0.067 Å to 0.066 Å with $R$ increase from 4 nm to 100 nm, at that the saturation value 0.066 Å is reached for $R \geq 100$ nm as anticipated from Eq.(8b) for SPS parameters. From Fig. 4(d) the value $T_{\text{tr}}(R)$ rapidly increases from 200 K to 320 K with $R$ increase from 4 nm to 100 nm, then saturates and tends to $T_C$ for $R \geq 100$ nm as anticipated from Eq.(8a). The vertical dashed lines $R=3.7$ nm in Fig. 4(c)-4(d) indicate the size limit above which LGD theory is quantitatively valid. Note that the size $R=3.7$ nm is very close to the boundary of SDFE stability $R=3$ nm [see dotted vertical lines in Fig. 4(c)-4(d) and FEM results shown in Fig. SI of Supplementary Materials]. Since the SDFE state becomes absolutely stable for $R \leq 3$ nm in comparison with PDFE, the continuation of red solid curves loses its physical sense for $R<3.7$ nm.

Note that the increase of $T_{\text{tr}}(R)$ above room temperature occurring in SPS particles with $R$ increase of more than 50 nm is likely an artifact of the oversimplified LGD free energy expansion on 2-4-6 polarization powers given by Eq.(2b). Actually Eq.(2b) does not contain 8-th and 10-th powers of polarization, which are relevant for precise quantitative description of the Sn$_2$P$_2$(S,Se)$_6$ (see e.g. [76]). In fact, for a bulk sample under the normal pressure, there is the second-order phase transition, and the tricritical point is achieved by compressing (or replacing tin with lead) and lowering the temperature to 250 K [77]. Such a change in the transition order with the decreasing temperature is typical for the case of a three-well local potential (Blume-Emery-Griffiths model [78]) that can be taken into account in the Landau theory by adding the invariants of the 8-th and 10-th polarization powers [76]. Yevych et al also tried to describe the situation using the model of quantum anharmonic oscillators [76, 79]. When the shape of the three-well potential changes under e.g. compression of the crystal, the transition becomes of the first-order and metastable states appear. If the model is supplemented with different ratios of the interactions between the first and the next neighbors [80], it becomes equivalent to the ANNNI model [12], and there will be antiferroelectric ordering and metastable states. The inter-cells interactions can be considered more accurately by taking into account the gradient invariants of higher order in Eq.(2c).

V. COMPARISON WITH EXPERIMENT

As it was argued in the introduction, derived analytical expressions should be compared with experimental results for nanoparticles of uniaxial ferroelectrics. Our first choice is SrBi$_2$Ta$_2$O$_9$ nanoparticles, for which the dependence of ferroelectric transition temperature on the particles' average
radius was measured in Ref. [14] by XRD and in situ Raman scattering. The experimental data [14] is described by empirical Ishikawa equation [81],

$$T_{Ish}(R) = T_C \left(1 - \frac{\Delta R}{R - r_{cr}}\right), \quad (11)$$

with the bulk Curie temperature $T_C = 605$ K, critical radius $r_{cr} = 1.05$ nm and $\Delta R = 1.90$ nm [compare the diamonds with the dashed red curve in Fig. 5(a)]. One can see from Fig. 5(a) that the analytical expression (5) for the radius dependence of the poly-domain particle (black solid curve) accurately reproduces empirical Ishikawa equation (dashed red curve) at all temperatures entire the range of LGD theory quantitative applicability at $2R \geq 10$ unit cells [equal to 5.6 nm for SrBi$_2$Ta$_2$O$_9$]. Note that the value of effective screening length $\Lambda = 0.11$ Å corresponding to the best fit of experimental data [14] is in a surprisingly good agreement with ab initio calculations performed by Tagantsev et al. (see Table II in ref.[53]). The best fit corresponds to the parameter $Q\mu = 0.025 \times m^3 N/C^2$ that is the product of the surface tension and electrostriction coefficients. The fit relatively weakly depends on the $Q\mu$ value until it does not exceed $0.03 \times m^3 N/C^2$. The surface tension can affect significantly on the fitting curves for SrBaTi$_2$O$_9$ at $Q\mu > 0.04 \times m^3 N/C^2$.

Earlier we tried to reproduce Ishikawa fit (11), that is an accurate interpolation of experimental data [14] for transition temperature of SrBi$_2$Ta$_2$O$_9$ nanoparticles, from Eq.(4) valid in the assumption that the particles are single-domain (see e.g. Fig.3 in Ref.[33]). This appeared quite possible, but the fitting value of $\Lambda = 0.04$ Å recalculated from Eq.(4) is significantly smaller than $\Lambda = 0.11$ Å obtained from Eq.(5) for poly-domain particles. At that the poly-domain fit at $\Lambda = 0.11$ Å has lower energy at radii more than 5 unit cells ($R > 2.8$ nm) than the single-domain fit at $\Lambda = 0.04$ Å and the same radii $R > 2.8$ nm. Since the experimental points are absent at $R < 2.8$ nm we concluded the PDFE fit with more realistic values of $\Lambda$ and lower energy better agrees with experimental results [14].

Formally Eqs.(5a) looks very different from Ishikawa equation (11). However both equations can be rewritten in a similar form for particle radii close to the critical value. Actually, Eq.(11) can be presented in the identical form as $T_{Ish}(R) = T_C \frac{R - R_{Ish}}{R - r_{cr}}$, where $R_{Ish} = r_{cr} + \Delta R$. For the particle radii $R \rightarrow R_{Ish}$ the Ishikawa formulae can be approximated as $T_{Ish}(R) \sim T_C \frac{R - R_{Ish}}{R}$ under the condition $R_{Ish} >> r_{cr}$, whose validity should be verified in each concrete case. At $R > R_{cr}$ Eq. (5a) can be presented in the form, $T_{PE-PDFE}(R) = T_C \frac{(R - R_1)(R - R_2)}{R^2}$, where $R_1 = \frac{\Delta r_2}{2} - \sqrt{\frac{\Delta r_1^2}{4} - \Delta r_2^2}$ and $R_2 = \frac{\Delta r_1}{2} + \sqrt{\frac{\Delta r_1^2}{4} - \Delta r_2^2}$ are real roots of the quadratic equation $R^2 - \Delta r_1 R + \Delta r_2^2 = 0$. Parameters
\[ \Delta r_i(\Lambda) = \frac{2\mu Q}{\alpha_T T_c} + \frac{g_{44}}{\alpha_T T_c \xi} \left( \frac{1}{\varepsilon_b (\varepsilon_b + 2\varepsilon_k) g_{44}} + \frac{1}{\xi R_e(\Lambda)} \right) \] and \[ \Delta r_2^2 = \frac{g_{44}}{\alpha_T T_c \xi^2} \]. The obvious inequality, \[ R_i \leq R_2 \], is valid for the case of positive determinant \( \frac{\Delta r_2^2}{4} - \Delta r_2^2 > 0 \) considered hereinafter. When the particle radius is close to the larger root \( R_2 \) of the quadratic equation, \( R \to R_2 \), the transition temperature can be approximated as \( T_{PE-PDFE}(R) \sim T_c \left( \frac{R - R_2}{R} \right) \) under the condition \( R_i \ll R_2 \). Thus for the particular case \( R_i \ll R_2 \), \( R_{lh} \approx R_2 \) and \( R_{lh} \gg r_{ce} \), the approximate expression for \( T_{PE-PDFE}(R) \) is similar to Ishikawa expression, \( T_{lh}(R) \sim T_c \left( \frac{R - R_{lh}}{R} \right) \), at \( R \to R_{lh} \). The similarity explains the proximity of solid and dashed curves in Fig. 5(a), and, more important, gives theoretical grounds to the empirical Ishikawa expression.

Since we analyzed phase diagrams and domain structure of the Sn$_2$P$_2$S$_6$ nanoparticles in the previous section, it would be logical to compare the theoretical dependences with experimental ones. To the best of our knowledge, corresponding experiments are still absent, only MC simulations within the framework of ANNNI model was done in Ref. [12] for SPS nanocrystals. Nanocrystals had different sizes from 9 to 67 unit cells (u.c.) and were imposed to the periodic boundary conditions (see Fig.6 in Ref.[12]). To recalculate the unit cell into a physical size for SPS, we used the pseudo-orthorhombic setting (see e.g. [82]) with the lattice parameters \( a = 0.9318 \) nm, \( b = 0.7463 \) nm and \( c = 0.6518 \) nm at 358 K. Since the cubic cells was used in Ref.[12], we regarded that a unit cell parameter is approximately equal to \( \sqrt[3]{abc} = 0.7323 \) nm. Thus LGD theory is valid quantitatively for \( 2R > 7.3 \) nm, that is about 10 unit cells for SPS.

Diamonds in Fig. 5(b) are MC simulation results from Ref. [12]. The dashed curve represents empirical Ishikawa equation \( T_c = 337(1 - 1.48/(R - 0.4)) \). Solid black curve in Fig. 5(b) is the fit with Eq.(5) for the material parameters of SPS, \( T_c = 337 \) K, \( \alpha_T = 1.6 \times 10^6 \) C$^{-2}$·mJ/K, \( g_{44} = 2.3 \times 10^{-12} \) m$^3$/F, \( \varepsilon_b = 7 \), geometrical factor \( \xi \approx 0.50 \) and effective screening length \( \Lambda = 0.3 \) Å. The value of \( \Lambda \) is in a reasonable agreement with \textit{ab initio} calculations [53]. When fitting the data, we assumed that the surface tension coefficient is negligibly small and put \( \mu = 0 \), because MC simulations performed in Ref. [12] does not account for the surface tension effect. We also note that only when the product \( Q\mu \) exceeds \( 0.2\times m^3N/C^2 \), the joint action of surface tension and electrostriction begin to affect significantly on the fitting curves for SPS.

As one can see from the Fig. 5(b) analytical expression (5a) for the radius dependence of the poly-domain particle (black solid curve) reproduces empirical Ishikawa equation (dashed red curve) and MC simulations in the entire range of radii \( R \geq 3.7 \) nm, where LGD theory is quantitatively valid.
Note that it is possible to reproduce Ishikawa fit for SPS nanoparticles from Eq.(4), but the fitting value of $\Lambda=0.045$ Å appeared significantly smaller than $\Lambda=0.3$ Å obtained by fitting from Eq.(5). At that the poly-domain fit at $\Lambda=0.3$ Å has lower energy at radii $R>3.7$ nm than the single-domain fit at $\Lambda=0.045$ Å and the same $R>3.7$ nm. Since MC data are absent at $R<3.7$ nm we can conclude that the PDFE fit with more realistic values of $\Lambda$ and lower energy better correlates with MC simulations [12].

FIG. 5. (a) Dependence of PE-FE transition temperature on the radius of SrBi$_2$Ta$_2$O$_9$ particles. Diamonds are experimental data from Ref. [14]. Solid black curve is the fit from Eq.(5) for parameters $T_c=608$ K, $\alpha_T=4.06 \times 10^5$ C$^2$·mJ/K, $g_{44}=2.5 \times 10^{-12}$ m$^3$/F, $\epsilon_b=10$, $\xi \approx 0.5$, $\Lambda=0.11$ Å, and $Q\mu=0.025$×Nm$^3$/C$^2$. Dashed curve is empirical Ishikawa equation $T_c=605(1-1.90/(R-1.05))$ with radius $R$ in nanometers. (b) Dependence of PE-FE transition temperature on the radius of Sn$_2$P$_2$S$_6$ particles. Diamonds are MC ANNNI modelling simulation results from Ref. [12]. Solid black curve is the fit from Eq.(5) for parameters $T_c=337$ K, $\alpha_T=1.6 \times 10^6$ C$^2$·mJ/K, $g_{44}=2.3 \times 10^{-12}$ m$^3$/F, $\epsilon_b=7$, $\xi \approx 0.50$, $\Lambda=0.3$ Å and $\mu=0$. Dashed curve is empirical Ishikawa equation $T_c=337(1-1.48/(R-0.4))$ with radius $R$ in nanometers. Vertical dotted lines indicate the particle size $2R=10$ unit cells, above which LGD approach is valid quantitatively. The SDFE becomes stable at $R<3$ nm.
Temperature dependence of the spontaneous polarization in the nanoparticles can be estimated from the expression

\[ P_s(R, \Lambda, T) = \frac{1}{\sqrt{2\gamma}} \left( \beta - \sqrt{\beta^2 + 4\gamma \alpha_r (T_{cr}(R, \Lambda) - T)} \right) \approx \frac{\alpha_r}{\beta} (T_{cr}(R, \Lambda) - T), \]  

(12)

where \( T_{cr}(R, \Lambda) \) is given by Eq.(4) for a single-domain case or can be estimated from Eqs.(5) for a poly-domain case in the sense of maximal value (because the average value is zero in a poly-domain particle).

The temperature dependence of the spontaneous polarization calculated by MC simulations in SPS particles with different radii \( R \) is shown in Fig. 6 by diamonds. Solid curves is the fit from Eq.(12) for the same parameters as in Fig.5(b). From Fig.6 we conclude that Eq.(12) can describe semi-quantitatively the polarization temperature behaviour in the vicinity of FE-PE phase transition, but not the polarization saturation far from the transition. Most likely the discrepancy is related with the principal differences between the continuous Landau free energy expansion on 2-4-6 polarization powers that is applicable to the ferroelectric phase transitions of displacement type and ANNNI model that rather describes the order-disorder phase transitions (see also remark at p.17 and Refs.[76-79]).

**FIG. 6.** Temperature dependence of the spontaneous ferroelectric polarization in the Sn\(_2\)P\(_2\)S\(_6\) particles with different radiuses \( R \) (in unit cells described in the text). Diamonds are MC simulations from Ref. [12]. Solid curves is the fit from Eq.(12) for the same parameters as in Fig.5(b). A unit cell (u.c.) parameter is approximately equal to 0.7323 nm.

**VI. DISCUSSION**

In the framework of LGD approach we evolved analytical description of domain structure morphology and phase diagrams of ferroelectric nanoparticles covered by an ultra-thin layer of screening charge characterized by effective screening length \( \Lambda \). The phase diagrams, calculated by FEM in coordinates "temperature \( T \)" and "effective screening length \( \Lambda \)" for spherical Sn\(_2\)P\(_2\)S\(_6\) nanoparticles with radius \( R \),
demonstrate the appearance of poly-domain region in the tricritical point and its broadening with $\Lambda$ increase above 0.1 Å and $R$ increase above 4 nm. Typically the poly-domain ferroelectric region (PDFE) of triangular-like shape separates the single-domain ferroelectric (SDFE) and paraelectric (PE) phases.

Labyrinthine domains (LD) region was revealed in 10-nm Sn$_2$P$_2$S$_6$ nanoparticles, similarly to the case of CuInP$_2$S$_6$ nanoparticles considered previously [45]. These LDs are expected to be a long-living stable (or at least metastable) configuration in Sn$_2$P$_2$S$_6$ nanoparticles undergoing the second order phase transition at Curie temperature. Earlier the LD structure was predicted theoretically in thin films of incommensurate ferroelectrics [83] and bi-layered ferroelectrics [84], being similar to those observed in ultrathin magnetic films [85]. Notably, fractal domain structures are sometimes observed in multiferroic thin films [86], near the surface of relaxors close to relaxor-ferroelectric boundary [87], but the stable LD with a single characteristic length scale were observed by Vectorial Piezoresponse Force Microscopy (V-PFM) [88] in ergodic relaxors only [89]. Metastable labyrinthine domains can coexist with classical ferroelectric domains [90, 91].

That say, our theoretical prediction of either stable or metastable LDs appearance requires experimental verification. V-PFM can be an appropriate method for the 3D visualization of the labyrinthine domain structure with nanoscale resolution (see e.g. Refs. [88, 89, 92, 93, 94, 95, 96] and refs therein), because stable surface-induced labyrinthine domain structures were revealed by PFM in ferroelectrics relaxors [89]. Noteworthy different domain morphologies inside the small nanoparticles ($R < 10$ nm) can be probed by abbreviation corrected high resolution scanning transmission electron microscopy (STEM) [3 - 5].

We leave for further studies the question how the ranges of LDs stability and metastability at phase diagrams can be derived analytically. However the necessary conditions of LDs appearance was derived analytically with the numerical factor estimated from FEM results. Obtained analytical results lead to the conclusion that the nature of morphological transition [45] from domain stripes to LDs in ferroelectric nanoparticles underlies in the interplay between the 2D instability of domain splitting induced by incomplete screening of polarization facilitated by small enough gradient energy and high enough particle size to prevent the effect of geometric catastrophe. Quantitative criteria of LDs appearance has the form $\frac{L_d}{\Lambda} \leq \psi$, where $L_d = \sqrt{\varepsilon_0 g_{44}}$ is the depolarization length and $\psi = 2\pi\sqrt{\varepsilon_b + 2\varepsilon_v}$ stands for effective "geometrical dielectric factor". The physical sense of the condition is that the ratio of depolarization length to effective screening length should be smaller than $\psi$.

Also we derived analytical expressions for all other boundaries at the phase diagrams and demonstrated their high accuracy by comparison with numerical results. Notably that the simple
analytical expression (4) for the PE-SDFE transition temperature, that is exact for the natural boundary conditions at the particle surface, depends on the ratio \( R/\Lambda \) only. The relatively simple analytical expressions (5) for the PE-PDFE transition temperature appear to have very high accuracy and contain only one fitting parameter \( \xi \) that’s value \( \xi \approx 0.5 \) is conditioned by the spherical geometry of the particle. Since the value \( \xi \approx 0.5 \) is not material specific, Eq.(5) can be used for description of PE-PDFE transition in other nanoparticles of uniaxial ferroelectrics (e.g. for SrBi\(_2\)Ta\(_2\)O\(_9\), CuInP\(_2\)S\(_6\) or LiNbO\(_3\)). Analytical expression (9) quantitatively describes the boundary between SDFE and PDFE phases with two extra fitting parameters, the temperature shift \( \Delta T \) and critical index \( \delta = 3/2 \), which depend on the material parameters, and therefore this expression is not universal. Analytical expressions (8) for the dependence of the critical point temperature \( T_{\text{cr}}(R) \) and effective screening length \( \Lambda_{\text{cr}}(R) \) on the particle radius are almost exact and universal, showing that the dependences \( T_{\text{cr}}(R) \) and \( \Lambda_{\text{cr}}(R) \) scales as \( 1/R \) for ferroelectric nanoparticles.

The derived analytical expressions were compared with the dependence of FE-PE transition temperature on the radius of SrBi\(_2\)Ta\(_2\)O\(_9\) nanoparticles experimentally measured in Ref.[14], and with the analogous dependence for Sn\(_2\)P\(_2\)S\(_6\) nanocrystals simulated by MC method within the framework of ANNNI model in Ref. [12]. The comparison demonstrates that the analytical expression (5) for the radius dependence of the FE-PE transition temperature in a poly-domain nanoparticle quantitatively agrees with experimental [14] and simulated [12] results, as well as it accurately reproduces empirical Ishikawa equation at all temperatures. More important, the analytical expression gives theoretical grounds to the empirical Ishikawa expression. At the same time the PE-FE transition temperature calculated from Eq.(4) in the assumption that the particles are single domain can describe experimental results for significantly smaller values of the fitting parameter \( \Lambda \), at that corresponding SDFE state has higher energy than PDFE state at particle sizes \( 2R > 10 \) unit cells (corresponding to the lowest limit of LGD approach quantitative applicability).

Temperature dependence of the Sn\(_2\)P\(_2\)S\(_6\) nanocrystals spontaneous polarization was calculated by Drobnich et al using MC method and ANNNI model [12]. Derived analytical expression (12) can describe semi-quantitatively the polarization temperature behaviour in the vicinity of FE-PE phase transition, but not its saturation far from the transition. Most likely the discrepancy is related with the principal differences between the continuous Landau free energy expansion on polarization powers, that is applicable to the ferroelectric phase transitions of displacement type, and ANNNI model that describes the order-disorder phase transitions.

To resume, we can conclude that phase diagrams including the wide regions of stripe and labyrinthine domains, which are qualitatively similar to the ones calculated in this work, can be realized in other uniaxial ferroelectric nanoparticles, such as SrBi\(_2\)Ta\(_2\)O\(_9\) and LiNbO\(_3\), with the sizes...
near the PE-FE transition. Notably, the domain morphologies and phase diagrams of nanoparticles are rather different for the uniaxial ferroelectrics with the first and second order PE-FE transitions. Much more complex situation (corresponding to the balance of labyrinthine domains in the bulk and vortices at the surface) are expected in multiaxial ferroelectric nanoparticles with polarization rotation allowed, such as BaTiO$_3$, (Pb,Zr)TiO$_3$ and BiFeO$_3$. Actually, vortices and vertices composed by the closure of four domain walls have been observed experimentally by STEM [3 - 5, 97] and PFM [98, 99, 100], and described theoretically [101] in a bulk and nanosized multiaxial ferroelectrics.

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**Authors' contribution.** A.N.M. generated research idea, stated the problem, derived analytical expressions jointly with E.A.E., interpreted results, compared with experiment and MC simulations and wrote the manuscript. E.A.E. wrote the codes and performed numerical calculations. Y.M.F. tested the codes and assisted E.A.E. with simulations. P.M. and Yu.M.V. densely worked on the results discussion and manuscript improvement.
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**SUPPLEMENTARY MATERIALS**

**APPENDIX A**

I. Derivation of PE-SDFE transition temperature

Let us consider the spherical ferroelectric particle with polarization $\mathbf{P}$ pointed along one of the principal crystallographic axis, denoted below as $z$. Here we also introduce an isotropic background permittivity $\varepsilon_b$ of ferroelectric. The media outside is a dielectric with permittivity $\varepsilon_e$. Electrical displacement is $\mathbf{D}_i = \varepsilon_0 \varepsilon_b \mathbf{E}_i + \mathbf{P}$ and $\mathbf{D}_e = \varepsilon_0 \varepsilon_e \mathbf{E}_e$, where the subscript “$i$” means the physical quantity inside the particle, “$e$” – outside the particle; $\varepsilon_0$ is a universal dielectric constant. We introduce electric field $\mathbf{E} = -\nabla \phi$ via electrostatic potential $\phi$, which should satisfy Poisson and Laplace equations inside and outside the particle, respectively

$$
\varepsilon_0 \varepsilon_b \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi_i = -\frac{\partial P}{\partial z} \quad \text{inside particle} \quad (A.1a)
$$

$$
\varepsilon_0 \varepsilon_e \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi_e = 0 \quad \text{outside particle} \quad (A.1b)
$$

supplemented by the interface conditions of potential continuity at the particle surface $S$ both for potential and normal components of electrical displacement:

$$
\left[ \phi_e - \phi_i \right]_S = 0; \quad \phi_e^n = 0, \quad (A.2a)
$$

$$
\left[ (\mathbf{D}_e - \mathbf{D}_i) \mathbf{n} + \varepsilon_0 \frac{\phi_i}{\Lambda} \right]_S = 0. \quad (A.2b)
$$

Here $\mathbf{n}$ is the outer normal to the particle surface. In Eq.(A.2) we take into consideration the effective screening charge density, proportional to the surface potential and inversely proportional to effective screening length $\Lambda$. Below we suppose that polarization $\mathbf{P}$ is independent on the coordinates; there is homogeneous external electric field $E_0$ far from the particle. This problem is reminiscent of text-book ones (see e.g. [i]) but without screening charges, which makes the problem solution non-trivial.

For a spherical particle the general solutions of Eqs.(A.1) could be expanded into the series on Legendre polynomials. For the considered problem few terms are sufficient, namely

$$
\phi_e = E_e \frac{R^{s+1}}{r^s} \cos \theta, \quad \phi_i = -E_i r \cos \theta. \quad (A.3)
$$

Here $\theta$ is the polar angle for spherical coordinate system, $r$ is the corresponding radial coordinate. $s=1$ and $s=2$ are for and cylindrical polar and spherical coordinate systems respectively. $E_e$ and $E_i$ are the constants to be determined from the boundary conditions (A.2). Application of Eqs.(A.2) to (A.3) leads to condition
\[
E_r \frac{R_{e+1}}{R} \cos \theta = -E_i R \cos \theta \quad \Rightarrow \quad E_r = -E_i
\]  
(A.4)

Radial components of field could be obtained from (A.3) as follows

\[
\begin{align*}
\left( E_r \right)_r &= sE_e \frac{R_{e+1}}{R_{e+1}} \cos \theta, \\
\left( E_i \right)_r &= E_i \cos \theta.
\end{align*}
\]  
(A.5)

Corresponding displacement is

\[
\begin{align*}
\left( D_r \right)_r &= \varepsilon_0 \varepsilon_s E_e \frac{R_{e+1}}{R_{e+1}} \cos \theta, \\
\left( D_i \right)_r &= \varepsilon_0 \varepsilon_b E_i \cos \theta + P \cos \theta
\end{align*}
\]  
(A.6)

Application of Eq.(A.2) to Eq.(A.3) and (A.6) leads to conditions

\[
\begin{align*}
\varepsilon_0 \varepsilon_s E_e \cos \theta - \varepsilon_0 \varepsilon_b E_i \cos \theta - P \cos \theta - \frac{E_i R \cos \theta}{\Lambda} &= 0. \\
\Rightarrow \varepsilon_s E_e - \left( \varepsilon_b + \frac{R}{\Lambda} \right) E_i &= \frac{P}{\varepsilon_0}.
\end{align*}
\]  
(A.7a)

The solution of the linear system (A.4) and (A.7) have the form:

\[
\begin{align*}
E_i &= -\frac{P}{\varepsilon_0 \varepsilon_b + \varepsilon_s s + (R/\Lambda)}, \\
E_e &= \frac{P}{\varepsilon_0 \varepsilon_b + \varepsilon_s s + (R/\Lambda)},
\end{align*}
\]  
(A.8)

with \( s=2 \) for a sphere and \( s=1 \) for a cylinder. Below we use the expression (A.8) for the formulation of the phenomenological equations of state. Including internal electric field (A.8) into the LGD equation one obtain for the sphere

\[
\left( \alpha_T \left( T - T_c^s(R) \right) + \frac{1}{\varepsilon_0 \left( \varepsilon_b + 2 \varepsilon_s + (R/\Lambda) \right)} \right) P + \beta P^3 = 0
\]  
(A.9)

II. Justification of the boundary condition (A.2b)

Let us consider a ferroelectric layer of thickness \( h \) with polarization \( \mathbf{P} \) pointed along polar axis, denoted below as \( z \). An isotropic background permittivity of ferroelectric is \( \varepsilon_b \). The ambient media has relative dielectric permittivity \( \varepsilon_e \). Therefore, electrical displacement could be introduced as \( \mathbf{D}_i = \varepsilon_0 \varepsilon_b \mathbf{E}_i + \mathbf{P} \) and \( \mathbf{D}_e = \varepsilon_0 \varepsilon_e \mathbf{E}_e \), where the subscript "i" means the physical quantity inside the ferroelectric, "e" – outside it; \( \varepsilon_0 \) is a universal dielectric constant. We introduce electric field \( \mathbf{E} = -\nabla \varphi \) via electrostatic potential \( \varphi \), which satisfies Poisson and Debye-Hückel equation

\[
\begin{align*}
\varepsilon_0 \varepsilon_b \frac{\partial^2 \varphi_1}{\partial z^2} &= -\frac{\partial P}{\partial z} \quad \text{inside ferroelectric}, \\
\varepsilon_0 \varepsilon_e \left( \frac{\partial^2 \varphi_e}{\partial z^2} - \frac{\varphi_e}{R_d^2} \right) &= 0 \quad \text{outside ferroelectric},
\end{align*}
\]  
(A.10a,b)
supplemented by the interfacial conditions of potential and normal components of electrical
displacement continuity at the (locally) flat interface \( z=0 \):

\[
\begin{align*}
(\varphi_e - \varphi_i)_{\mid z=0} &= 0; \\
\left[ (\mathbf{D}_e - \mathbf{D}_i) \mathbf{n} + \varepsilon_0 \frac{\varphi_e}{\Lambda} \right]_{\mid z=0} &= 0.
\end{align*}
\] (A.11a) (A.11b)

Here \( \mathbf{n} \) is the outer normal to the ferroelectric surface. In Eq.(A.11b) we take into consideration
the surface screening charge density, proportional to the surface potential and inversely
proportional to the so-called effective screening “length” \( \Lambda \). Other boundary conditions
 correspond to the grounded electrodes:

\[
\varphi_e \big|_{z=-d} = 0, \quad \varphi_i \big|_{z=h} = 0
\] (A.11c)

The formulated problem is reminiscent to the text-book ones, but without surface screening
charge from Eq.(A.11b), which makes problem non-trivial. Let us consider several limiting cases
below.

II.A. Dielectric dead layer of finite thickness without surface charges \(( R_d \to \infty \text{ and } \Lambda \to \infty )\)

The general solutions of Eqs.(A.10) are

\[
\varphi_e = -(z + d) E_e, \quad \varphi_i = -(z - h) E_d - \frac{1}{\varepsilon_0 \varepsilon_b} \int_{z}^{h} P(z) \, dz.
\] (A.12)

Note that solution (A.12) already satisfies Eqs.(A.11c). Electric displacements and fields are

\[
\begin{align*}
D_e &= \varepsilon_0 \varepsilon_e E_e, \quad \frac{\partial \varphi}{\partial z} = E_e, \quad D_i &= \varepsilon_0 \varepsilon_b E_d, \quad \frac{\partial \varphi}{\partial z} = E_i = E_d - \frac{P(z)}{\varepsilon_0 \varepsilon_b}.
\end{align*}
\] (A.13)

The constants \( E_e \) and \( E_d \) should to be determined from the boundary conditions (A.11a) and
(A.11b):

\[
E_e d + E_d h = \frac{1}{\varepsilon_0 \varepsilon_b} \int_{0}^{h} P(z) \, dz, \quad \varepsilon_e E_e = \varepsilon_b E_d
\] (A.14)

The solution of the linear system (A.14) could be easily found, so that the electric field inside the
ferroelectric has the following form:

\[
\begin{align*}
\varphi_i &= \frac{1}{h/\varepsilon_b} \frac{(z-h)}{(h/\varepsilon_b) + (d/\varepsilon_e)} A_e  \varepsilon_b - \frac{1}{\varepsilon_0 \varepsilon_b} \int_{z}^{h} P(z) \, dz, \\
E_i &= - \frac{P(z) - \langle P \rangle}{\varepsilon_0 \varepsilon_b} - \frac{(d/\varepsilon_e)}{(h/\varepsilon_b) + (d/\varepsilon_e)} \frac{\langle P \rangle}{\varepsilon_0 \varepsilon_b},
\end{align*}
\] (A.15a) (A.15b)
where the average polarization \( \langle P \rangle = \frac{1}{h}\int_{0}^{h} P(z)dz \) is introduced. Here the first term is field in the ideal case (Kretschmer & Binder solution), while the latter term is the influence of dead layer.

II.B. Infinite semiconducting dead layer \( (d \to \infty) \) without surface charges \( (\Lambda \to \infty) \)

In this case the general solution of Eqs.(A.10) vanishing at infinity has the form:

\[
\varphi_e = -\exp\left(-\frac{z}{R_d}\right)R_d E_e, \quad \varphi_i = -(z-h)E_d - \frac{1}{\varepsilon_0 \varepsilon_b} \int_{z}^{h} P(z)dz E_z.
\]  

(A.16a)

Corresponding electric displacement and field are

\[
D_e = \varepsilon_0 \varepsilon_e E_e \exp\left(-\frac{z}{R_d}\right), \quad -\frac{\partial \varphi_e}{\partial z} = \exp\left(-\frac{z}{R_d}\right)E_e \quad D_i = \varepsilon_0 \varepsilon_n E_i, \quad -\frac{\partial \varphi_i}{\partial z} = E_d - \frac{P(z)}{\varepsilon_0 \varepsilon_b}
\]

(A.16b)

Constants \( E_e \) and \( E_d \) should be determined from the boundary conditions (A.14):

\[
E_e R_d + E_d h = \frac{h}{\varepsilon_0 \varepsilon_b} \langle P \rangle, \quad \varepsilon_e E_e = \varepsilon_b E_d
\]

(A.17)

The solution of the linear system (A.17) could be easily found; this solution allows one to write electric potential and field inside the ferroelectric in the following form:

\[
\varphi_i = -\frac{(h/\varepsilon_b)(z-h)}{(h/\varepsilon_b)+(R_d/\varepsilon_e)\varepsilon_0 \varepsilon_b} \langle P \rangle - \frac{1}{\varepsilon_0 \varepsilon_b} \int_{z}^{h} P(z)dz E_z,
\]

(A.18a)

\[
E_i = -\frac{P(z)-\langle P \rangle}{\varepsilon_0 \varepsilon_b} = \frac{R_d \varepsilon_e}{(h/\varepsilon_b)+(R_d/\varepsilon_e)\varepsilon_0 \varepsilon_b} \frac{\langle P \rangle}{(h/\varepsilon_b)\varepsilon_0 \varepsilon_b}.
\]

(A.18b)

II.C. Dielectric ambient \( (R_d \to \infty) \) and \( d \gg \Lambda \)

Electric potential, field and displacement are given by Eqs.(A.12)-(A.13). Constants \( E_e \) and \( E_d \) should be determined from the boundary conditions (A.11):

\[
E_e d + E_d h = \frac{h \langle P \rangle}{\varepsilon_0 \varepsilon_b}, \quad 0 = \varepsilon_e E_e - \varepsilon_d E_d + \frac{E_e d}{\Lambda}.
\]

(A.19)

The solution of (A.19) is

\[
E_d = \frac{E_e}{\varepsilon_b} \left(\varepsilon_e + \frac{d}{\Lambda}\right)^{-1} \left(\varepsilon_e + \frac{d}{\Lambda}\right) \frac{\langle P \rangle}{\varepsilon_0 \varepsilon_b} \approx \frac{(h/\varepsilon_b)}{(h/\varepsilon_b)+\Lambda \varepsilon_e \varepsilon_b} \frac{\langle P \rangle}{\varepsilon_0 \varepsilon_b},
\]

(A.20a)

\[
E_e = \left(\varepsilon_e + \frac{d}{\Lambda}\right)^{-1} \frac{\langle P \rangle}{\varepsilon_0} \approx \frac{(h/\varepsilon_b)\Lambda}{(h/\varepsilon_b)+\Lambda d} \frac{\langle P \rangle}{\varepsilon_0}.
\]

(A.20b)

Approximate equalities are valid when \( \varepsilon_e \ll \frac{d}{\Lambda} \). Under the reasonable assumption electric potential and field inside the ferroelectric are
\[ 
\varphi_i \approx -\left(\frac{h}{\varepsilon_b}\right)(z - h) \langle P \rangle - \frac{1}{\varepsilon_0 \varepsilon_b} \int_z^h \langle \rho \rangle \, dz, 
\]

\[ 
E_i = -\frac{\partial \varphi_i}{\partial z} \approx -\frac{P(z) - \langle P \rangle}{\varepsilon_0 \varepsilon_b} - \frac{\Lambda}{(h/\varepsilon_b) + \Lambda} \langle P \rangle.
\]

It is seen that in all three limiting cases the expressions (A.15), (A.18) and (A.21) for the field and potential inside the ferroelectric are equivalent up to parameters substitution

\[ 
\frac{d}{\varepsilon_c} \leftrightarrow R_d \leftrightarrow \Lambda
\]

It should be noted, that electric field outside the ferroelectric film is very different in all three above-considered cases and could not easily transformed one into another. In fact Eq. (A.22) justifies the effective boundary condition (A.2b) for the analytically solvable cases of dielectric gap of thickness \(d\) and semiconducting ambient with Debye-Hückel (or by extension Tomas-Fermi) screening radius \(R_d\) for a locally flat ferroelectric layer.

**APPENDIX B. Derivation of PE-PDFE transition temperature**

The linearized system of equations for polarization and electric potential inside the ferroelectric nanoparticle and outside it has the following form

\[ 
\alpha P_3 - g_{11} \frac{\partial^2 P_3}{\partial z^2} - g_{44} \left( \frac{\partial^2 P_3}{\partial x^2} + \frac{\partial^2 P_3}{\partial y^2} \right) = -\frac{\partial \varphi}{\partial z},
\]

\[ 
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \varphi^{(in)} = \frac{1}{\varepsilon_0 \varepsilon_b} \frac{\partial P_3}{\partial z}, \quad \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \varphi^{(out)} = 0,
\]

with appropriate boundary conditions at the particle surface \(S\):

\[ 
\left. \left( \frac{\partial P_3}{\partial r} \right) \right|_{r=R} = 0, \quad \left. \left( -\varepsilon_0 \varepsilon_b \frac{\partial \varphi^{(in)}}{\partial r} + P_3 + \varepsilon_0 \varepsilon_c \frac{\partial \varphi^{(out)}}{\partial r} - \varepsilon_0 \frac{\varphi^{(in)}}{\Lambda} \right) \right|_{r=R} = 0.
\]

Let us consider harmonic like fluctuations

\[ 
P_3 = P_k(z) \exp(i k \vec{r}), \quad \varphi^{(in)} = \varphi^{(in)}_k(z) \exp(i k \vec{r}), \quad \varphi^{(out)} = \varphi^{(out)}_k(z) \exp(i k \vec{r}).
\]

Equations for amplitudes

\[ 
\left( \alpha + g_{44} k^2 \right) P_k - g_{11} \frac{\partial^2 P_k}{\partial z^2} = -\frac{\partial \varphi_k}{\partial z},
\]

\[ 
\frac{\partial^2 \varphi_k^{(in)}}{\partial z^2} - k^2 \varphi_k^{(in)} = \frac{1}{\varepsilon_0 \varepsilon_b} \frac{\partial P_k}{\partial z}, \quad \frac{\partial^2 \varphi_k^{(out)}}{\partial z^2} - k^2 \varphi_k^{(out)} = 0.
\]

Where \(k^2 = k_x^2 + k_y^2\). Differentiation the Eqs. (B.3) gives
\[
\left(\frac{\partial^2}{\partial z^2} - k^2\right) \left(\alpha + g_{44}k^2\right) P_k - g_{11} \frac{\partial^2 P_k}{\partial z^2} = \left(\frac{\partial^2}{\partial z^2} - k^2\right) \left[ -\frac{\partial \phi_k}{\partial z} \right],
\]  
\[
\frac{\partial}{\partial z} \left(\frac{\partial^2}{\partial z^2} - k^2\right) \phi^{(in)}_k = \frac{1}{\varepsilon_o \varepsilon_b} \frac{\partial^2 P_k}{\partial z^2}.
\]

Hence, one could exclude the potential amplitude from Eq. (B.4a) and get the single equation for polarization amplitude in the form:

\[
\left(\frac{\partial^2}{\partial z^2} - k^2\right) \left(\alpha + g_{44}k^2\right) P_k - g_{11} \frac{\partial^2 P_k}{\partial z^2} = -\frac{1}{\varepsilon_o \varepsilon_b} \frac{\partial^2 P_k}{\partial z^2}
\]

Let us look for the solution of (B.5) in the form \( P_3 \sim \exp(qz) \), where inverse characteristic length \( w \) satisfies the following equation:

\[
q^4 \left( \frac{\alpha + g_{44}k^2}{g_{11}} + k^2 + \frac{1}{\varepsilon_o \varepsilon_b g_{11}} \right) q^2 + \frac{\alpha + g_{44}k^2}{g_{11}} k^2 = 0
\]

Its solutions could be written as

\[
q_{1,2} = \frac{1}{2} \left[ \frac{\alpha + g_{44}k^2}{g_{11}} + k^2 + \frac{1}{\varepsilon_o \varepsilon_b g_{11}} \pm \sqrt{\left( \frac{\alpha + g_{44}k^2}{g_{11}} + k^2 + \frac{1}{\varepsilon_o \varepsilon_b g_{11}} \right)^2 - 4 \frac{\alpha + g_{44}k^2}{g_{11}} k^2} \right]
\]

It should be noted, that in the most cases \( \varepsilon_o \varepsilon_b g_{11} \ll \left| k^2, g_{11} \right|, g_{44} \right|, \) hence the following approximations are valid

\[
q_1 \approx \sqrt{\frac{\left( \frac{\alpha + g_{44}k^2}{g_{11}} \right) k^2}{\alpha + g_{44}k^2 + g_{11} k^2 + \frac{1}{\varepsilon_o \varepsilon_b} \left[ \frac{\alpha + g_{44}k^2}{g_{11}} \right] k^2}} , \quad q_2 \approx \frac{1}{\sqrt{\varepsilon_o \varepsilon_b g_{11}}}
\]

Now we could write the general solution of Eq.(B.5) in the form:

\[
P_3 = s_1 \sinh(q_1z) + s_2 \sinh(q_2z) + c_1 \cosh(q_1z) + c_2 \cosh(q_2z)
\]

The four constants \( s_i \) and \( c_i \) should be found from boundary conditions (B.2). Formal solution is zero, since we have the system of homogeneous linear equations for \( s_i \) and \( c_i \), but we are interested in the stability analysis, hence we should look for zero point of the corresponding determinant of the linear equations system for \( s_i \) and \( c_i \). Since counter domain walls are charged and hence have much higher energy in comparison with parallel ones, the antisymmetric part of the solution corresponding to nonzero \( s_i \) is always unstable from energetic considerations.

Unfortunately exact solution for the constants \( c_i \) in the functions \( P_3 = c_1 \cosh(q_1z) + c_2 \cosh(q_2z) \) and constants \( f_i \), \( f \) in electric potentials \( \phi^{(in)}_k = f_i \sinh(q_1z) + f_2 \sinh(q_2z) \) and \( \phi^{(out)}_k = f \exp(-k|z-h|) \) are impossible to find in a finite
form. Assuming that in the vicinity of the particle poles \( z = \pm R \), the curvature of the spherical
surface can be neglected, we obtained the system of four linear equations
\[
c_i q_1 \sinh(q_1 h) + c_2 q_2 \sinh(q_2 h) = 0, \quad f_1 \sinh(q_1 h) + f_2 \sinh(q_2 h) - f = 0, \quad c_i = \varepsilon_0 \varepsilon_b \frac{q_i^2 - k^2}{q_i}
\]
\[
-B_0 \varepsilon_b (q_1 f_1 \cosh(q_1 h) + q_2 f_2 \cosh(q_2 h)) + (c_1 \cosh(q_1 h) + c_2 \cosh(q_2 h)) - |k| \varepsilon_0 \varepsilon_c f - \varepsilon_0 \frac{f}{\Lambda} = 0.
\]
(A.8b)

After cumbersome calculations of the conditions of its zero determinant can be simplified under
the validity of strong inequalities \(|k| \varepsilon_c \Lambda \ll 1\) valid for most cases, therefore, recalling the
condition \( q_2 >> |k| \),
\[
\alpha + g_{44} k^2 + \frac{1}{e_0 \varepsilon_b (\varepsilon_0 + (R/\Lambda) + \varepsilon_b (\xi R)^2)} \approx 0
\]
(B.9a)

This expression for the critical point should be further minimized with respect to wave vector \( k \).
\[
\left( \frac{g_{44} - \frac{(\xi R)^2}{e_0 \varepsilon_b \left( 1 + \varepsilon_b^{-1} (R/\Lambda) + (\xi R \cdot k)^2 \right)^2} \right) 2k = 0
\]
(B.9a)

Since zero root \( k=0 \) of Eq.(B.9) corresponds to single domain state, we neglected it and obtained
the following value of domain structure wave vector at the transition point
\[
k_{\text{min}}(R, \Lambda) = \left\lfloor \frac{1}{\sqrt{e_0 \left( \varepsilon_b + 2 \varepsilon_c \right) g_{44} \xi R}} - \left( 1 + \frac{R}{\left( \varepsilon_b + 2 \varepsilon_c \right) \Lambda} \frac{1}{\xi R} \right)^2 \right\rfloor
\]
(B.10)

It is valid under the condition
\[
\frac{\xi}{\sqrt{e_0 \left( \varepsilon_b + 2 \varepsilon_c \right) g_{44}}} \geq 1 + \frac{1}{R \left( \varepsilon_b + 2 \varepsilon_c \Lambda \right)}.
\]
With respect to Eq. (B.10),

Eq.(B.8) could be further simplified to
\[
\alpha + \frac{\varepsilon_0 \varepsilon_b g_{44}}{e_0 \varepsilon_b} \frac{2}{\xi R} - g_{44} \left( 1 + \frac{R}{\varepsilon_b \Lambda} \right) \frac{1}{\xi R} \approx 0.
\]

Hence approximate analytical expression for the transition temperature of the spherical nanoparticle from
the PDFE to PE phase is:
\[
T_{\text{PE-PDFE}}(R, \Lambda) \approx T^*_c(R) - \frac{1}{\alpha_T} \left( g_{44} k_{\text{min}}^2 (R, \Lambda) + \frac{e_0^{-1}}{\left( R/\Lambda \right) + (\varepsilon_b + 2 \varepsilon_c) \left( 1 + k_{\text{min}}^2 (R, \Lambda) (\xi R)^2 \right)} \right)
\]
(B.11a)

Here the first term originated from the correlation effect and the second one is from
depolarization field energy of the domain stripes. Parameter \( \xi \) is a sort of geometrical factor that
is close to unity. Its origin is related to the corresponding spherical eigen functions.
Corresponding wave vector \( k_{\text{min}} \) and period \( D_{\text{max}} \) of the domain structure onset are
\[
k_{\text{min}}(R, \Lambda) = \frac{1}{\sqrt{e_0(e_b + 2e_e)g_{44}}} \left( 1 + \frac{R}{e_b + 2e_e} \Lambda \right)^2 \left( \frac{1}{\xi R} \right)^2, \quad D_{\text{max}} = \frac{2\pi}{k_{\text{min}}}. \quad (B.11\text{b})
\]

Substitution of Eq.(B.11b) into Eq.(B.11a) and elementary transformations leads to the evident expression for the PE-PDFE transition temperature radius dependence,

\[
T_{\text{PE-PDFE}}(R, \Lambda) \approx \begin{cases} 
T_c'(R) - \frac{g_{44}}{\alphapsilon R} \left( \frac{1}{\sqrt{e_0(e_b + 2e_e)g_{44}}} + \frac{1}{\xi R\Lambda} - \frac{1}{\xi R} \right), & R > R_c^\varepsilon, \\
0, & R < R_c^\varepsilon.
\end{cases} \quad (B.11\text{c})
\]

Where \( R_c^\varepsilon(\Lambda) = \frac{\xi}{\sqrt{e_0(e_b + 2e_e)g_{44}}} - \frac{1}{(e_b + 2e_e)\Lambda} \) and \( k_{\text{min}}(R, \Lambda) = \frac{1}{\xi R\sqrt{R_c^\varepsilon(\Lambda)}} - 1 \).

Expressions (B.11) are valid under the condition

\[
\frac{\xi}{\sqrt{e_0(e_b + 2e_e)g_{44}}} \geq \frac{1}{R} + \frac{1}{(e_b + 2e_e)\Lambda} \quad (B.12)
\]

That means that the critical value of the gradient coefficient exists at fixed other parameters,

\[
g_{44}^{\varepsilon}(R, \Lambda) = \frac{1}{e_0(e_b + 2e_e)} \left( \frac{1}{\xi R} + \frac{1}{\xi (e_b + 2e_e)\Lambda} \right)^{-2}
\]

, and domains appears at \( g_{44} < g_{44}^{\varepsilon}(R, \Lambda) \). At fixed gradient coefficient \( g_{44} \) the equality in Eq.(B.12) means that the relation between the particle radius \( R \) and screening length \( \Lambda \) should be valid for the domain onset. Namely the fulfillment of the equality

\[
\frac{1}{R} + \frac{1}{(e_b + 2e_e)\Lambda} = \frac{\xi}{\sqrt{e_0(e_b + 2e_e)g_{44}}}
\]

corresponding to the transition to a single domain state that occurs in a three-critical point on the phase diagram in coordinates e.g. \( T \) and \( \Lambda \).

The stability of a PDFE state in comparison with a SDFE state depends on the balance between depolarization field energy (appearing from incomplete screening of the spontaneous polarization characterized by effective screening length \( \Lambda \)) and the domain walls energy (proportional to the gradient coefficient \( g_{44} \)). The domain splitting starts when it becomes energetically preferable. On the threshold of the domain formation the energy of SDFE state \( G_{SD} \) includes the sum of electrostatic energy (2d) and Landau energy (2b) of a homogeneously polarized nanoparticle,

\[
G_{SD} = G_{el} + G_{\text{Landau}} \rightarrow \frac{\alpha R}{4\beta} V \quad (where \quad V = \frac{4\pi}{3} R^3 \quad and \quad \alpha_R = \alpha_T (T - T_{\text{SDFE-PPE}}(R)))
\]

b) becomes equal the energy of the particle with domain walls. The gradient energy (2c) is formally equal to the energy of the domain walls, \( G_{\text{grad}} = G_S = \psi S_{DW} \),
where $\psi_s$ is the surface energy of the domain wall and $S_{DW}$ is the area of domain walls. For infinitely thin domain walls $\psi_s$ is related with LGD coefficients as $\psi_s = \frac{2\sqrt{-2\alpha g_{44}}}{3\beta}$ [ii]. In accordance with Virial's theorem, the equality $|G_{SD}| = G_S$ leads to the equality

$$\frac{2\alpha^2_r V}{4\beta} S_{DW} = \frac{2\sqrt{-2\alpha g_{44}}}{3\beta} S_{DW}$$

that's identical form is

$$T_{PDE-SDFE} = T_{SDFE-PE}(R) - \frac{2g_{44}}{\alpha_r} \left( \frac{8S_{DW}}{3V} \right)^2$$

APPENDIX C. Phase diagrams of nanoparticles for different radius

FIG. S1. Phase diagram of SPS nanoparticles in coordinates "temperature T and screening length $\Lambda$" calculated for particle radius 3 nm, gradient coefficient $g_{44}=10^{-11}$ m$^3$/F (left) and $g_{44}=10^{-10}$ m$^3$/F (right). The ferroelectric single domain (SDFE) and paraelectric (PE) phases are stable. Solid curves corresponding to the phase SDFE-PE boundaries are calculation from Eq.(4).
FIG. S2. Phase diagram of SPS nanoparticles in coordinates "temperature $T$ and screening length $\Lambda$" calculated for different particle radius 4, 5 and 6 nm, gradient coefficient $g_{44}=10^{-11}$ m$^3$/F (left row) and $g_{44}=10^{-10}$ m$^3$/F (right row). The ferroelectric single domain (SDFE), ferroelectric poly domain (PDFE) and paraelectric (PE) phases are stable. Solid curves corresponding to the SDFE-PE, PDFE-PE and SDFE-PDFE phase boundaries are calculated from Eqs.(4), (5) and (9), respectively.
FIG. S3. Phase diagram of SPS nanoparticles in coordinates "temperature $T$ and screening length $\Lambda$" calculated for different particle radius 8 and 10 nm, gradient coefficient $g_{44} = 10^{-11}$ m$^3$/F (left row) and $g_{44} = 10^{-10}$ m$^3$/F (right row). The ferroelectric single domain (SDFE), ferroelectric poly domain (PDFE) and paraelectric (PE) phases are stable. Solid curves corresponding to the SDFE-PE, PDFE-PE and SDFE-PDFE phase boundaries are calculated from Eqs.(4), (5) and (9), respectively.
**FIG. S4.** Energy map in coordinates "temperature $T$ and screening length $\Lambda$" calculated for the particle radius 10 nm and gradient coefficient $g_{44}=10^{-11}$ m$^3$/F. Energy scale is $10^{-19}$ J. The ferroelectric single domain (SDFE), ferroelectric poly domain (PDFE) and paraelectric (PE) phases are stable. Solid curves corresponding to the SDFE-PE, PDFE-PE and SDFE-PDFE phase boundaries are calculated from Eqs.(4), (5) and (9), respectively.

**REFERENCES**
