Landau theory of $180^\circ$ domain walls in $BaTiO_3$ type ferroelectric particles: microcomposite materials

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Abstract

The Landau theory of 180° domain walls in \emph{BaTiO}_3 type ferroelectric particles is presented. Results of exact description of domain walls in bulk enabled us to formulate variational approach to theory of domain walls in corresponding small particles. The depolarization field effects and the space-charge layers are taken into account in the samples of the cube form. It was found that at low temperatures well known hyperbolic tangent wall profile is a good approximation for description of domain walls in particles. Near the transition temperature it is more and more appropriate to speak about two walls separating ferroelectric, paraelectric and ferroelectric domains correspondingly as a result of splitting of a single ferroelectric wall into two subwalls in small \emph{BaTiO}_3 particles. Domain wall energy density, average interwall distance and change of the dielectric response of thick walls in small ferroelectric particles in microcomposites is qualitatively found. Our results qualitatively describe observed dependencies better than those theories which exist up to date. In temperature region near transition from the ferroelectric to paraelectric phase in microcomposites our quantitative results for response, for Curie-like transition temperature and other parameters may be verified.
1 Introduction

The transition temperature of the ferroelectric phase - paraelectric phase phase transition decreases with decreasing particle diameter in BaTiO$_3$ [1], PbTiO$_3$ [2] and in KDP [3] microcomposites. It was found experimentally that there is no phase transition bellow a critical size of a particle in the microcomposite. It was observed also that a higher phase transition temperature in smaller particles sometimes occurs. In thin films of KNbO$_3$ [4] and TGS [5, 6] both increase and decrease of the transition temperature were observed with decreasing particle size. In PbTiO$_3$ microcomposites [7] the dielectric constant decreases with decreasing particle size, probably due to the gradual creation of a multidomain state in larger particles. An unusual peak of dielectric constant versus particle size was observed in BaTiO$_3$ [8].

There are two main theoretical approaches to explanation of the size effects in the ferroelectric - dielectric microcomposites of the above type. The significance of depolarization field that tries to break up the ferroelectric particle into domains with different polarizations. The multidomain state then exhibits higher permittivity, but its creation becomes difficult for small enough particles [9]. Another possibility is that a surface layer with different transition temperature than that in the bulk is phenomenologically considered without the depolarization field explicitly taken into account. Then a shift of the phase transition temperature in the particle is present as well as the inhomogeneous distribution of the polarization [10]. In [10] the static properties of such particles is studied by numerical calculations only. The ferroelectric phase transition in small spherical particles was studied in [11]. Size effects were studied analytically as concerning temperature effects and polarization profile. Our model in [11] did not take into account depolarization fields, assuming full compensation of surface charges. The dynamic susceptibility deviates from Debye-like behaviour then and exhibits a broadening at higher frequencies. The Curie-Weiss law is exhibited by the static susceptibility, there exists a divergency at the point of the size-driven transition. Dielectric response of microcomposite ferroelectrics was studied in [12]. A two-phase composite of ferroelectric and dielectric materials was described, and studied by different effective medium theories (isolated particles, Maxwell-Garnet theory, the effective medium approximation and the Bergman representation of the effective dielectric function). There are present modes due to geometric resonances which lead to new low-frequency absorption peaks near the percolation threshold of the ferroelectric material. Those peaks are always located higher than the peak of the transverse polar mode of the bulk component. The soft mode with renormalized mode strength but unchanged frequency exists only in the composite with percolated ferroelectric clusters. Below the percolation threshold the finite clusters of the ferroelectric material soften only to some degree, there is no soft mode. Results of exact description of domain walls in bulk have been found and were preliminary published in [13]. They enabled us to formulate variational approach to the theory.
of domain walls in corresponding small particles.

In this paper we study a Landau theory of 180° domain walls in BaTiO$_3$ type ferroelectric particles. The depolarization field effects and the space-charge layers are taken into account in the samples of the cube form. We have found that at low temperatures well known hyperbolic tangent wall profile is a good approximation for description of domain walls in particles. Nearly the first-order transition temperature a free energy contribution due to paraelectric domain state within a wall center becomes important leading to unusually large wall thickness. Approaching the transition temperature it is more and more appropriate to speak about two walls separating ferroelectric domains as a result of splitting a single ferroelectric wall into two walls with a paraelectric phase between them. Consequently the primary ferroelectric domain wall width becomes very large which influences also size dependence and other characteristics of the ferroelectric transition to the paraelectric phase in small BaTiO$_3$ particles. Domain wall energy density, average interwall distance and change of the dielectric response of thick walls in small ferroelectric particles is qualitatively described and quantitatively approximately found in this temperature region.

2 Domain walls configurations in a BaTiO$_3$ particle

The free energy density $F$ expansion into polar mode amplitude $\mathbf{P}$ following [14] has the form

$$F = \frac{\alpha}{2} \mathbf{P}^2 + \frac{\beta}{4} \mathbf{P}^4 + \frac{\sigma}{6} \mathbf{P}^6 + C |\nabla \mathbf{P}|^2.$$  

(1)

where the coefficient is given by $\alpha = a_0(T - T_{0\infty})$, here $a_0$ is a constant, $T_{0\infty}$ is the Curie-Weiss temperature for the bulk phase transition.

Numerical values of the coefficients of the Landau free energy expansion (1) of BaTiO$_3$ are given in [14].

Assuming the domain wall localized at $x=0$, the polarization $\mathbf{P}$ oriented in the z-direction and that this polarisation changes in the x direction, $P(x)$, the domain-wall energy $\gamma$ is defined by

$$\gamma = \int_{-\infty}^{+\infty} \Delta F(P(x)) dx,$$

(2)

where $\Delta F(P(x)) = F(P(x)) - F(P)$ is the difference of free energy densities between the state with a domain-wall configuration $P(x)$ and the equilibrium state with a homogeneous polarization $P$.

The single domain-wall configuration $P(x)$ in BaTiO$_3$ was in [14] described approximately by the following well-known profile

$$P(x) = P \tanh \left( \frac{x}{\xi} \right),$$

(3)
with P and ξ as variational parameters. The domain-wall configuration P(x) in a BaTiO₃ particle has a wall energy density which may be approximately calculated as in [14] by
\[ \gamma = \int_{-D}^{+D} \Delta F(P(x))dx, \] (4)
with 2D a distance between two neighbouring walls. It is a variational parameter. After calculating the wall energy density γ one can then easily incorporate space-charge layer effects, characterised by a parameter t, in the same way as in [14], too.

3 Exact solution for wall configurations

Let us transform the free energy part (1) describing local potential of the sixth order in the polarization P to a more transparent form
\[ V(P) = b\left[\frac{P^6}{6} - (a^2 + c^2)\frac{P^4}{4} + a^2c^2\frac{P^2}{2}\right]. \] (5)
The coefficients a, b and c above and the free energy density expansion coefficients α, β, γ are connected by relations:
\[ a^2 = \frac{1}{2}\frac{\beta}{\sigma} + \sqrt{\frac{\beta}{\sigma} - \frac{4\alpha}{\sigma^2}}, \] (6)
\[ c^2 = \frac{1}{2}\frac{\beta}{\sigma} - \sqrt{\frac{\beta}{\sigma} - \frac{4\alpha}{\sigma^2}}, \]
\[ b = \sigma. \]

To discuss properties of the local effective potential (5) it is convenient to introduce a dimensionless parameter ρ
\[ \rho = \left(\frac{c}{a}\right)^2, \] (7)
which we will assume to be a nonnegative quantity. The case of negative values leads to a two well potential of the sixth order, which is similar to the well-known double-well potentials.

The local potential V(P) has two absolute minima at ±a and there is a local maximum at P=0 for ρ = 0. The potential V(P) has two absolute minima ±a and there is a local minimum at P=0, and at ±c there are two local maxima for 0 < ρ < \frac{1}{4}. The potential V(P) has three absolute minima at ±a and at P=0, in ±c there are two local maxima for ρ = \frac{1}{4}. The potential V(P) has only single absolute minimum at P=0, at ±a there two local minima and in ±c there are two local maxima for \frac{1}{4} < ρ < 1. For ρ > 1 the situation just described repeats with the reversed role of the a and c constants.
The Lagrange-Euler equation for configurations of polarization $P$ which extremize the free energy (1) has the form

$$2C \frac{dP}{dx} = bP(P^2 - a^2)(P^2 - c^2).$$

We assume that $a > c$, the equilibrium state configurations then realizes at points $\pm a$ (ferroelectric phase) or at $P=0$ (paraelectric phase).

Several years ago [18] we succeeded to find exact solutions of the equation (8). Similar solutions in different forms were obtained also elsewhere, [19] and [20]. For $0 \leq \rho < \frac{1}{3}$ the walls are described in the form

$$P(x) = \pm a \sqrt{q \tanh(x) + R} \sqrt{1 + q - \tanh^2(x) + R)}$$

where $R$ is an arbitrary constant, describing the position of the center of the wall, and where we define $q = \frac{1-3\rho}{3}$. These walls interconnect two ferroelectric domains with opposite polarization.

The parameter $\xi$ describes the rate of change of the polarization at the wall configuration and is given by

$$\xi = \frac{1}{\sqrt{1 + q} \sqrt{\frac{a^4}{2C}}}.$$  

4 180° domain wall configurations

The exact solution (9) describes a profile of a domain wall. It is convenient to rewrite the form (9) into a more transparent form

$$P(x) = P_0(x) \tanh(x) + R),$$

where the first factor in (11) we call a ”modulated amplitude” $P_0(x)$ of the wall configuration $	anh$. It is given by

$$P_0(x) = \pm a \sqrt{q \tanh(x) + R} \sqrt{1 + q - \tanh^2(x) + R)}.$$  

While at larger distances from the center of the wall, localized at $x = 0$ for $R=0$, the ”modulated amplitude” takes the equilibrium configuration values

$$P_0(\pm \infty) = \pm a.$$  

at the center of the wall this amplitude decreases its value to

$$P_0(x = 0) = \pm a \sqrt{q \tanh^2(x) + R} \sqrt{1 + q - \tanh^2(x) + R)}.$$  

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It is clear from (14) that the nearer we are to the phase transition the nearer the constant \( \rho \) to the value \( \frac{1}{3} \), and consequently the smaller "modulated amplitude" of the wall at the center. This decrease reflects the increasing role of the paraelectric phase region in the center of the wall.

The wall thus consists of two subwalls connecting domains with nonzero polarization with a region with almost zero polarization. At temperatures near the phase transition temperature the distance \( d_w \) between the two subwalls (walls separating the ferroelectric domains and the paraelectric phase domain in the center) becomes larger. One can find that at this temperature region we have the distance \( d_w \) given by

\[
d_w = -\frac{\xi}{2} \ln \left( \frac{1 - \sqrt{3\rho}}{1 + \sqrt{3\rho}} \right),
\]

(15)

which describes logarithmic divergence of the distance \( d_w \), because the nearer we are to the phase transition the nearer the constant \( \rho \) to the value \( \frac{1}{3} \).

On the other hand the lower temperature the larger the "modulated amplitude" \( P_0(x = 0) \), approaching the same value as the amplitude at domains \( P_0(\pm \infty) \). One can find that in this temperature region

\[
d_w = \xi \sqrt{3\rho},
\]

(16)

which is a finite quantity.

One can easily estimate temperature region in which the condition \( 0 < \rho < \frac{1}{3} \) is satisfied and thus in which very thin walls may exist the distance \( d_w \) of which logarithmically divergences. Using parameters for \( BaTiO_3 \) from [14] we found that the mentioned inequalities are equivalent with temperature region \( 112.24^\circ C < T < 121.48^\circ C \). In this region thus the ferroelectric domain wall has in the center the large paraelectric region and consists of two walls /subwalls/ connecting this region with the corresponding ferroelectric region.

From this result it follows that at \( 25^\circ C \) the "tanh" wall profile, used in [14] for approximate calculations, is an adequate approximation. At this lower temperatures this material is characterized by an effective potential with only two absolute minima. Near phase transition from the ferroelectric phase to the paraelectric phase in the temperature region \( 112.24^\circ C < T < 121.48^\circ C \) the "tanh" wall profile used for approximate calculations is an inadequate approximation. Our exact description of the domain wall is more appropriate in this region.

5 The dielectric response of a ferroelectric particle

The dielectric response of a ferroelectric particle at temperature region near the transition temperature, where the wall width behaves according to (16), may be estimated in the following way. The effect of the depolarization field and
of the space-charge layer may be taken into account using the same variational approach as in [14]. However, as the wall thickness parameter the domain subwall distance as a domain wall width \( d_w \) instead of \( \xi \) from [14] is taken.

This approach leads to the following wall energy density \( \gamma \)

\[
\gamma \approx \frac{8cP^2}{3d_w}. \tag{17}
\]

The equilibrium interwall distance \( 2D \) between two ferroelectric walls in a particle of a cube form with the side width \( L \) is found to be given by

\[
D = \sqrt{\frac{8c}{5.1d_w t} L}. \tag{18}
\]

where \( t \) characterizes changes of the polarisation near the surface. We see that increasing temperature to the transition temperature the domain wall width measured by the subwall distance \( d_w \) increases while the interwall distance \( D \) decreases. Remaining structure consists of strips of ferroelectric phase domains separated by wide regions (domains) of the paraelectric phase.

If both characteristic lengths, the interwall distance characteristic quantity \( D \) and the subwall distance characteristic quantity \( d_w \) become comparable, \( D \approx d_w \), then the ferroelectric domains become very narrow and almost vanish with respect to usual situation in which ferroelectric domain wall width is very small with respect the ferroelectric domain width. The corresponding temperature is slightly below the transition temperature at which \( \rho = \frac{1}{3} \).

In the regime in which \( \xi \ll D \), one finds the Curie-Weiss law with renormalised transition temperature

\[
\alpha' = \alpha + 3.4 \frac{Dt}{L^2} + \left[ -2d_w \frac{\alpha}{D} + \frac{8c}{3d_w} \right]. \tag{19}
\]

From this expression one finds that the temperature coefficient \( \alpha \) is multiplied by \( 1 - \frac{8c}{3d_w} \) giving \( \alpha' \).

The critical Curie-Weiss temperature becomes

\[
T_0 = T_{0,\infty} - \frac{1}{\alpha'} \left[ 3.4 \frac{Dt}{L^2} + \frac{8c}{3d_w} \right]. \tag{20}
\]

If the wall thickness (15) increases increasing temperature there will be much stronger renormalization of the temperature coefficient to zero approximately for those wall configurations at which the the interwall distance \( 2D \) becomes comparable with the width parameter \( d_w \). From (20) it follows that simultaneously the Curie-Weiss temperature reduces to zero quickly, the ferroelectric phase vanishes even before the wall thickness becomes comparable with the interwall distance characteristic length \( D \). It is also clear that the existence of the ferroelectric phase becomes more sensitive to the length \( L \) of the crystal due to
decreased value of the temperature coefficient $a'$ and due to the domain wall width $d_w$ dependence of the interwall distance $2D$ (18).

For thin walls ($d_w < \frac{D}{8}$) the transition temperature dependence coefficient on the particle size $L$ is larger for the domain walls as described in our paper than for those described approximately by simple $tanh$ dependence used in [14] to qualitatively describe transition temperature dependence on $L$. Experimentally found transition temperature dependence on $L$ is steeper than that predicted by the simple $tanh$ wall model [14]. Our exact description of domain walls for the bulk free energy potential in $BaTiO_3$ describing the first order phase transition which is near the second order phase transition and used for the description of the particle domain structure as in [14] is more appropriate for real crystals $BaTiO_3$. Note that for thick walls ($d_w > \frac{D}{8}$) the transition temperature dependence coefficient on the particle size $L$ is smaller for the domain walls as described in our paper than for those described approximately by simple $tanh$ dependence. Thus mechanism of the increasing domain wall width due to splitting of the domain wall into two walls (sequence ferroelectric - paraelectric - ferroelectric domains) may explain much more abrupt change of the Curie-Weiss temperature at low $L$ values unexplained by the spontaneous strain mechanism in [14].

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