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Surface effects and size effects on ferroelectrics with a first-order phase transition

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For ferroelectrics with a first-order phase transition, the contribution of surface to the free-energy expression was examined using transverse Ising model with four-spin interactions taken into consideration. It was shown that a P^4 term should be added to the surface term in the free-energy expression. The surface and size effect on polarization and Curie temperature was studied using the newly developed free-energy expression. Experimental results in the literature were successfully explained using the free-energy expression.

I. INTRODUCTION

Although the explicit size dependence of the Curie temperature and polarization of ferroelectrics has been known since 1950s,[1,2] it has been studied extensively only in recent years since the rapid progress in ferroelectric films and composite materials has made it a subject of great practical importance. As far as the mechanisms leading to the experimental observations[1–7] are concerned, the surface effect, i.e., the modification of polarization near the surface, is considered to be predominant. So far, multiple approaches, including phenomenological theory[8–14] and Ising models,[14–18] have been developed to study the surface and size effects in ferroelectrics. In the phenomenological theory, a parameter δ, called extrapolation length, is introduced to describe the difference between the surface and the interior. When $\delta>0$, polarization is reduced at the surface and the Curie temperature is lower than the bulk value; when $\delta<0$, polarization is enhanced at the surface and it can persist well above the bulk Curie temperature.[12–14] In the transverse Ising model,[14–16] the two-spin interaction constant J and tunneling frequency Ω are modified near the surface, which consequently leads to the size dependence of ferroelectric properties. In the dynamic Ising model,[17] finite-size ferroelectrics were described with finite number pseudospins and the phase-transition properties were studied. As for the connection between the transverse Ising model and the phenomenological theory, Cottam, Tilley, and Zeks[14] have shown that the phenomenological theory can be considered the continuum limit of the transverse Ising model for second-order phase-transition ferroelectrics. These theories[8–10,12–18] have been developed for ferroelectrics with a second-order phase transition whereas most practically used ferroelectrics are those with a first-order phase transition. Phenomenological theory has been applied to ferroelectric films with a first-order phase transition by letting the P^4 term be negative and adding a P^6 term in the free-energy expression with the surface term unchanged.[11] After this modification it successfully explained the observed thickness dependences of the polarization and Curie temperature of KNO_3 films. However, this extension to the first-order phase transition is not satisfactory from both the theoretical and practical viewpoints. On the one hand, it lacks a microscopic verification. On the other hand, there are some experimental observations which cannot be explained. For example, in $BaTiO_3$ ceramics, the polarization decreases while the Curie temperature increases with decreasing grain size.[2] In $PbTiO_3$ films, the surface layer has a higher spontaneous strain but a lower Curie temperature.[6]

In this work, the free energy of ferroelectrics with a first-order phase transition is deduced within the framework of transverse Ising model and mean-field approximation. Using the newly developed free-energy expression, the surface and size dependences of ferroelectric properties are studied, in particular the experimental results reported in Refs. 2 and 6 are successfully explained.

II. METHODOLOGY

For ferroelectrics with a first-order phase transition, the Hamiltonian of the transverse Ising model should include a term of four-spin interactions,[19–21] i.e.,

$$H=-\sum_i \Omega_i S_i^x-\frac{1}{2}\sum_{ij} J_{ij}S_i^z S_j^z-\frac{1}{4}\sum_{ijkl} J_{ijkl}S_i^z S_j^z S_k^z S_l^z \qquad (1)$$

where Ω_i is the tunneling frequency, S_i^x and S_i^z are the x and $\boldsymbol{z}$ components of the spin at lattice site i, J_{ij} and J_{ijkl} are two-spin and four-spin interaction constants, respectively.

Using the mean-field approximation,[22] the entropy of the system can be written as[14]

$$\phi=-k_B\sum_i [2S_i \tanh^{-1} 2S_i+\tfrac{1}{2} \ln(1-4S_1^2)], \qquad (2)$$

where $S_i=(\langle S_i^x\rangle^2+\langle S_i^y\rangle^2+\langle S_i^z\rangle^2)^{1/2}$ ($\langle\ \rangle$ denotes the average value of the quantities). Thus the free energy of the system is

$$F=-\sum_i \Omega_i S_i^x-\frac{1}{2}\sum_{ij} J_{ij}S_i^z S_j^z-\frac{1}{4}\sum_{ijkl} J_{ijkl}S_i^z S_j^z S_k^z S_l^z$$

$$+k_B T\sum_i [(2S_i \tanh^{-1} 2S_i+\tfrac{1}{2} \ln(1-4S_1^2)]. \qquad (3)$$

To derive the Landau free-energy expression from Eq. (3), we expand F to sixth order in $\langle S_i^z\rangle$ and eliminate the noncritical quantities $\langle S_i^x\rangle$ and $\langle S_i^y\rangle$ by minimizing F respect to $\langle S_i^x\rangle$ and $\langle S_i^y\rangle$. That is, $\partial F/\partial\langle S_i^x\rangle=0$, $\partial F/\partial\langle S_i^y\rangle=0$. In this way, we obtain the free energy as a function of the order parameter $\langle S_i^z\rangle$

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$$F=\sum_i \frac{\Omega_i\langle S_i^z\rangle^2}{\tanh(1/2)\beta\Omega_i}-\frac{1}{2}\sum_{ij} J_{ij}S_i^zS_J^Z-\frac{1}{4}\sum_{ijkl} J_{ijkl}S_i^zS_j^zS_k^zS_l^z+\sum_i \frac{\Omega_i\langle S_i^z\rangle^4}{\tanh^3\beta\Omega_i}\left(\frac{\sinh\beta\Omega_i}{\beta\Omega_i}-1\right)$$
$$+\sum_i \frac{2\Omega_i\langle S_i^z\rangle^6}{\tanh^5(1/2)\beta\Omega_i}\left(1-\frac{\sinh\beta\Omega_i}{\beta\Omega_i}+\frac{4\sinh^3(1/2)\beta\Omega_{\mathrm{i}}\cosh(1/2)\beta\Omega_i}{3\beta\Omega_i}\right), \tag{4}$$

where $\beta=1/k_BT$. In the continuum limit, one assumes that $\langle S_i^z\rangle$ changes slowly in space and can be described by a continuous coordinate $r=(x,y,z)$. The summation with respect to i can be replaced by the volume integral

$$\sum_i \rightarrow \frac{1}{a^3}\int dxdydz \tag{5}$$

and $S_{(r)}$ can be expressed as

$$\mathbf{S}_{(\mathbf{r}+\mathbf{a})}=\mathbf{S}_{(\mathbf{r})}+\mathbf{a}\cdot\nabla\mathbf{S}_{(\mathbf{r})}\,. \tag{6}$$

Consider a semi-infinite ferroelectric that occupies the space $z>0$. The spins form a cubic lattice with a lattice constant a. The two-spin interaction constant equals J_s when two spins are on the surface and J otherwise, the four-spin interaction constant equals J_{4s} when four spins are on the surface and J_4 otherwise. The tunneling frequency is Ω_s for spins at the surface and Ω for spins of the interior. For a spin on the surface, the number of surface four-spin coupling is n_{4s} and the number of the others is n_4. For a spin inside, the number of four-spin coupling is n_{40}. The effect of depolarizing field, external electric field and stress are ignored for simplicity, then the free energy of the ferroelectric can be written as

$$F=\int\left[\frac{1}{2}AP^2+\frac{1}{4}BP^4+\frac{1}{6}CP^6+\frac{1}{2}D(\nabla P)^2\right]dv$$
$$+\int D\left(\frac{P^2}{2\delta}+\frac{P^4}{4\delta_4}+\frac{P^6}{6\delta_6}\right)ds, \tag{7}$$

where

$$A=\frac{a^3}{4\mu^2}\left(\frac{2\Omega}{\sinh(1/2)\beta\Omega}-6J\right),$$

$$B=\frac{a^9}{16\mu^4}\left[\frac{4\Omega}{\tanh^3(1/2)\beta\Omega}\left(\frac{\sinh\beta\Omega}{\beta\Omega}-1\right)-n_0J_{40}\right],$$

$$C=\frac{a^{15}}{64\mu^6}\frac{2\Omega}{\tanh^5(1/2)\beta\Omega}\left(1-\frac{\sinh\beta\Omega}{\beta\Omega}+\frac{4\sinh^3(1/2)\beta\Omega\cosh(1/2)\beta\Omega}{3\beta\Omega}\right),$$

$$D=\frac{a^5}{4\mu^2}J, \tag{8}$$

$$\delta^{-1}=\frac{1}{a}\left[\frac{5J-4J_s}{J}+\frac{2}{J}\left(\frac{\Omega_s}{\tanh(1/2)\beta\Omega}-\frac{\Omega}{\tanh(1/2)\beta\Omega}\right)\right.,$$

$$\delta_4^{-1}=\frac{a^6}{4\mu^2}\left\{\frac{n_{40}J_{40}-n_4J_4-n_{4s}J_{4s}}{J}+\frac{1}{J}\left[\frac{4\Omega_s}{\tanh^3(1/2)\beta\Omega}\left(\frac{\sinh\beta\Omega_s}{\beta\Omega_s}-1\right)-\frac{4\Omega}{\tanh^3(1/2)\beta\Omega}\left(\frac{\sinh\beta\Omega}{\beta\Omega}-1\right)\right]\right\},$$

$$\delta_6^{-1}=\frac{a^{12}}{16\mu^6}\left\{\left[\frac{2\Omega_s}{\tanh^5(1/2)\beta\Omega_s}\left(1-\frac{\sinh\beta\Omega_s}{\beta\Omega_s}+\frac{4\sinh^3(1/2)\beta\Omega_s\cosh(1/2)\beta\Omega_s}{3\beta\Omega_s}\right)\right]\right.$$

$$\left.-\left[\frac{2\Omega}{\tanh^5(1/2)\beta\Omega}\left(1-\frac{\sinh\beta\Omega}{\beta\Omega}+\frac{4\sinh^3(1/2)\beta\Omega\cosh(1/2)\beta\Omega}{3\beta\Omega}\right)\right]\right\},$$

and the polarization equals $(2\mu/a^3)\langle S^z\rangle$, μ is the dipole moment of a pseudospin. When $\Omega_s=\Omega$, the coefficients in the surface integral are reduced to a simple form

$$\delta^{-1}=\frac{1}{a}\left(\frac{5J-4J_s}{J}\right),$$

$$\delta_4^{-1}=\frac{a^6}{4\mu^2}\left(\frac{n_{40}J_{40}-n_4J_4-n_{4s}J_{4s}}{J}\right), \tag{9}$$

$$\delta_6^{-1}=0.$$

It should be noted that the effect of fluctuations[18] is suppressed in deriving Eq. (7) since a mean-field approximation is employed. A mean-field approximation is known to be invalid very near the transition temperature and to overestimate the transition temperature. Nevertheless, the temperature range in which the mean-field approximation is invalid is rather small for ferroelectrics, thus the effect of fluctuations is neglected at this stage.

It can be seen from Eq. (7) that the P^4 term in the surface integral cannot be neglected for a ferroelectric with first-order phase transition even if $\Omega_S=\Omega$. While for a ferroelectric with second-order phase transition, this term can be neglected since the polarization is negligibly small near T_c and δ_4^{-1} equals zero when $\Omega_s=\Omega$.[14] In the following, we discuss only the case of $\Omega_S=\Omega$, thus the Gibbs free energy of a semi-infinite ferroelectric can be written as

$$F=\int\int dx\,dy\int_0^\infty[\tfrac{1}{2}\,AP^2+\tfrac{1}{4}\,BP^4+\tfrac{1}{6}\,CP^6+\tfrac{1}{2}\,D(\nabla P)^2]dz+\int\int D\left(\frac{P^2}{2\delta}+\frac{P^4}{4\delta_4}\right)\bigg|_{z=0}dxdy. \tag{10}$$

Compared with the free-energy expression of second-order transition ferroelectrics, a surface term P^4 and a bulk term P^6 are added. Considering the polarization distribution, the minimum principle for free energy yields the following Euler-Lagrange equation

$$D\nabla^2P=AP+BP^3+CP^5 \tag{11}$$

and boundary condition

$$\frac{dP}{dz}=\frac{P}{\delta}+\frac{P^3}{\delta_4}\quad\text{at }\ z=0 \tag{12}$$

from which the polarization distribution near the surface can be calculated.

The above treatments are then extended to ferroelectric films which have two surfaces at $z=\pm d/2$. Assuming that the phenomenological parameters are independent of film thickness, the Gibbs free energy per unit area of a ferroelectric film is

$$\frac{F}{S}=\int_{-d/2}^{d/2}[\tfrac{1}{2}\,AP^2+\tfrac{1}{4}\,BP^4+\tfrac{1}{6}\,CP^6+\tfrac{1}{2}\,D(\nabla P)^2]dz+D\left(\frac{P^2}{2\delta}+\frac{P^4}{4\delta_4}\right)\bigg|_{z=\pm d/2}, \tag{13}$$

where S is the area of the film. The corresponding Euler-Lagrange equation and boundary conditions are

$$D\nabla^2P=AP+BP^3+CP^5, \tag{14}$$

$$\frac{dP}{dz}=\pm\left(\frac{P}{\delta}+\frac{P^3}{\delta_4}\right)\quad\text{at }\ z=\mp\frac{d}{2}. \tag{15}$$

When $\delta_4=\infty$, Eq. (15) is reduced to

$$\frac{dP}{dz}=\pm\frac{P}{\delta}\quad\text{at }\ z=\mp\frac{d}{2} \tag{16}$$

which is the boundary condition used in the literature.[10–14]

Equations (14) and (15) can be solved numerically by finite difference method, thus the polarization profiles in ferroelectric films can be obtained at different temperature. Then the free energy was calculated by Eq. (13) and the temperature at which free energy equals zero, i.e., the Curie temperature, was obtained.

III. RESULTS AND DISCUSSION

It is shown [Eqs. (10) and (13)] that a P^4 term as well as a P^2 term should be included in the surface term of the free-energy expression for the first-order phase-transition ferroelectrics. This is indicative of the complex of the modification on the ferroelectric properties due to the presence of surface. Microscopically, δ and δ_4 are functions of the two-spin and four-spin interaction constants which are different between the surface and the interior. Since the surface two-spin interaction constant J_s and surface four-spin interaction constant J_{4s} depend on both the surface details and the nature of the ferroelectrics, the values of δ and δ_4 are expected to vary with the surface details of the ferroelectrics. In the following, the phenomenological parameters A, B, C, and D of $BaTiO_3$ (Ref. 23) are used. δ is in the order of the correlation length at room temperature as it was chosen in some previous publications.[10–14] Different values of δ_4 are chosen so that its effect on ferroelectric properties becomes significant.

Figure 1 shows the ground-state polarization distribution in a ferroelectric film with a first-order phase transition at different values of δ_4 when $\delta=5\times10^{-7}$ (cgs unit). It can be seen from the figure that the polarization, especially near film surface, increases with the decrease of $1/\delta_4$. When δ_4 is positive, polarization is reduced at the surface. As δ_4 changes from positive to negative, the polarization becomes larger and its profile tends to be flatter. For some values of δ_4, the polarization at the surface can be larger than that of the interior though the extrapolation length δ is positive. When the extrapolation length δ is negative, the polarization in the film also changes with δ_4, and the surface polarization may be smaller than that of interior for some values of δ_4.

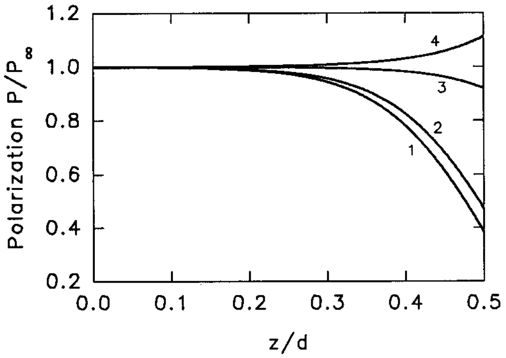

FIG. 1. The polarization profile in a first-order phase-transition ferroelectric film when extrapolation length $\delta = 5\times10^{-7}$ (cgs unit). $T=300$ K. Curves labeled 1, 2, 3, and 4 corresponds to $\delta_4 = 1000$, ∞, -3000, -1000 (cgs unit), respectively. Phenomenological parameters are those of $BaTIO_3$. P_∞ is the polarization of the bulk crystal.

The results are due to the contributions of both P^2 and P^4 terms in the surface integral of the free-energy expression.

For a ferroelectric film with fixed surface parameters $\delta = 5\times10^{-7}$, $\delta_4 = -6.25\times10^2$ (cgs unit), the spatial distribution of polarization at different temperature is illustrated in Fig. 2. The polarization is enhanced at the surface when the temperature is low. As temperature increases, the polarization profile becomes more and more flat. When the temperature is high enough, the polarization at the surface is reduced. If the signs of δ and δ_4 are reversed, contrary results, that is, polarization is reduced at low temperature and enhanced at high temperature, are obtained. The results are due to that the derivative of P depends not only on δ and δ_4 but also on the polarization at the surface [see Eq. (12)]. Since the polarization is a function of temperature, the derivative of polarization, and consequently the profile of polarization, are dependent on temperature.

When both δ and δ_4 have the same sign, polarization is reduced at the surface when they are positive and it is enhanced when they are negative. The temperature dependence of the polarization is similar to that when only P^2 term is included in the surface integral.

Figure 3 shows the temperature dependence of the average value of polarization of a ferroelectric film with a thickness of 100 nm. The polarization of the bulk is also plotted as a comparison. The polarization of the film is smaller than that of the bulk when temperature is low, but persists up to a temperature well above the bulk Curie temperature. The thinner the film is, the lower the polarization at room temperature and the higher the Curie temperature. When the signs of δ and δ_4 are reversed, the converse results were obtained. That is, the polarization of the film is higher than that of the bulk at low temperature but the Curie temperature is lower that of the bulk.

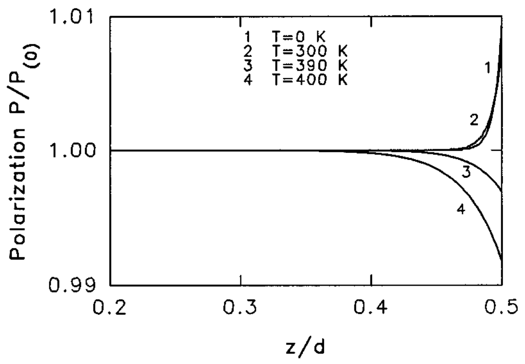

FIG. 2. The spatial distribution of the polarization in films at different temperature. $\delta = 5\times10^{-7}$, $\delta_4 = -625$ (cgs unit). $P_{(0)}$ is the polarization in the center of the film.

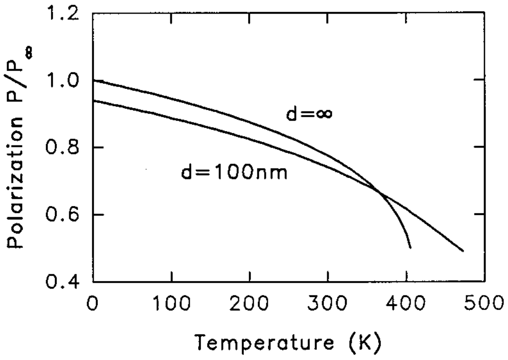

FIG. 3. The temperature dependence of the average value of polarization of a ferroelectric film. $\delta = -5\times10^{-7}$, $\delta_4 = 625$ (cgs unit).

Experimentally, Anliker, Brugger, and Kanzig[2] observed that the polarization of fine-grained $BaTiO_3$ ceramics is lower but the Curie temperature is higher than the bulk material. The smaller the grain size, the lower the polarization and the higher the Curie temperature. On the other hand, glancing-angle x-ray diffraction (XRD) analyses on $PbTiO_3$ films[6] revealed that the surface layer has a larger tetragonal distortion than the interior, which means the polarization at the surface is larger. When the temperature increases, the surface tetragonal distortion decreases quickly and reaches zero at a temperature lower than the interior. These results[2,6] cannot be understood from the earlier theory[10–14] since it predicts that the polarization and Curie temperature must change in the same direction. However, it is clear that the temperature dependence of the polarization of $BaTiO_3$ (Ref. 2) is the same as the dependence in Fig. 3, and the distortion

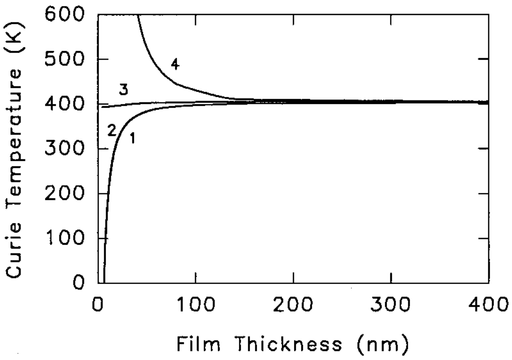

FIG. 4. The thickness dependence of the Curie temperature of a ferroelectric film on the thickness at different surface parameters. $\delta = 1\times10^{-6}$, $\delta_4 = 1000$, ∞, -1000, -500 (cgs unit) for curves 1, 2, 3, and 4, respectively.

(which is proportional to P^2) in $PbTiO_3$ films[6] as a function of temperature is similar to Fig. 2. Therefore the observed peculiar behavior of the polarization and the Curie temperature[2,6] can be understood by taking into account the effects of both P^2 and P^4 terms in the surface integral of the free-energy expression. The former result[2] corresponds to $\delta<0$ and $\delta_4>0$, and the latter result[6] corresponds to $\delta>0$ and $\delta_4<0$.

Figure 4 shows the Curie temperature of a ferroelectric film as a function of the thickness when the extrapolation δ is positive. The Curie temperature decreases with decreasing film thickness when δ_4 is positive, which is similar to the size dependence of Curie temperature of ferroelectric films when only P^2 term is included in the surface integral of the free energy expression.[8–14] When δ_4 is negative and its absolute value is small enough, the Curie temperature will increase with decreasing film thickness (see curve 4). In the case of negative δ, the Curie temperature is also a function of δ_4. The Curie temperature may decrease with decreasing film thickness for certain values of positive δ_4

In summary, the free-energy expression of finite-size ferroelectrics with a first-order phase transition is deduced from the viewpoint of transverse Ising model and mean-field approximation. It is concluded that apart from a P^6 term added in the volume integral, a P^4 term should be added to the surface integral compared with the free-energy expression of a second-order phase transition. Due to the presence of the P^4 term, the size and temperature dependences of polarization and the size dependence of Curie temperature become more complicated.

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