The Effects of the Layer-Dependent Interaction Parameters on the Phase Diagrams and Polarizations of the Ferroelectric Thin Film

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While the exchange interaction and the transverse field parameters are changed with the layers of the ferroelectric thin film, the properties of phase transition of the transverse field Ising model have been studied within the framework of the mean field approximation. The phase diagrams and polarizations of the ferroelectric thin film have been calculated numerically in the different situations of the interaction parameters changed with the layers. The results show that various layer-dependent parameters changed gradually layer by layer have sensitive effects on the phase diagrams and the polarizations of the $n$-layer ferroelectric thin film.

Key words: Ferroelectrics; Layer-dependent Parameters; Phase Diagrams.
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1. Introduction

Although the surface and size effects on the phase transitions in ferroelectrics have been known since the 1950’s, it aroused a renewed interest in recent years due to the development of ferroelectric thin films and composites [1 – 7]. Owing to their special properties, the ferroelectric thin films and superlattices have been widely investigated both experimentally [8 – 11] and theoretically [12 – 23]. The transverse field Ising model (TFIM), introduced firstly by de Gennes [24], was believed to describe reasonably the phase transition properties in potassium dihydrogen phosphate (KDP)-like ferroelectrics [25]. Because TFIM can not be solved exactly, many approximations have been applied to study the transition properties of this model [13 – 23]. Usually, TFIM can be treated with the mean field approximation [12 – 18], the effective-field theory with correlations [26, 27], the decoupling approximation in the differential operator technique [19, 28], and the Green function method [20 – 23]. However, in earlier papers for the transition properties of the ferroelectric thin film [13, 29 – 31], the three interaction parameters in TFIM (the intra-layer and the inter-layer interactions as well as the transverse field parameter) are usually considered as constant ones. In fact, impurities, vacancies, or dislocations etc, are widely present in the thin film. Therefore, the interaction parameters of the ferroelectric thin film materials should be changed with the layers. Recent researches have shown that these defect layers have considerable impact on the phase transformation properties, such as the polarizations, the lattice parameters, the Curie temperature, the spin-wave energies, and the elementary excitations [32 – 37]. The polarization gradients even have detrimental effects on the ferroelectric properties, especially of the ultrathin ferroelectric thin films, due to the coupling of the stress field of the dislocation and the polarization [32]. In this paper, we study the effects of the interaction parameters changed layer by layer on the properties of phase transition of the ferroelectric thin film. Firstly, we consider how the exchange interaction and the transverse field parameters are changed layer by layer and suppose the parameters decrease or increase gradually according to some identical functions from the surface to the interior of the thin film. Then we investigate the impacts of these gradually changed parameters on the properties of phase transition of the ferroelectric thin film. Because the layer-dependent interaction parameters are changed layer by layer, it refers that each layer in the ferroelectric thin film is equivalent to a different defect layer to some extent. Therefore, the investigation to the phase diagrams and polarizations of the $n$-layer ferroelectric thin film while changing the different exchange interactions and the
2. Numerical Results for the Phase Diagrams and Polarizations

The Hamiltonian of the system based on the transverse field Ising model \([12–17]\) is

\[
H = -\sum_i \Omega_i S_{ix} - \sum_{\langle i,j \rangle} J_{ij} S_{ix} S_{jx},
\]

where \(\Omega_i\) is the transverse field, \(S_{ix}\) and \(S_{ix}\) the \(x\) and \(z\)-components of a spin-\(\frac{1}{2}\) operator at site \(i\), \(J_{ij}\) the two-spin exchange interaction between site \(i\) and site \(j\), and \(\sum_{\langle i,j \rangle}\) runs over only the nearest-neighbouring sites. The schematic illustration of the \(n\)-layer ferroelectric thin film is shown in Figure 1. Assuming that the \(z\)-direction is perpendicular to the interface and the polarization is along the \(z\)-direction, the spin average along the \(z\)-direction in the \(i\)th layer can be expressed by \([12–17]\)

\[
\langle S_{iz} \rangle = \frac{\langle H_{iz} / 2 | H_i \rangle}{\langle H_i / k_B T \rangle},
\]

where

\[
H_{iz} = z J_{ii} \langle S_{iz} \rangle + J_{i,i+1} \langle S_{i+1,z} \rangle + J_{i,i-1} \langle S_{i-1,z} \rangle,
\]

\[
|H_i| = \sqrt{\Omega_i^2 + H_{iz}^2},
\]

and \(z\) is the number of nearest-neighbours in the same layer of site \(i\). Considering that \(\langle S_{iz} \rangle\) will be small while the temperature is near the Curie temperature, we have

![Fig. 1. Schematic illustration of the \(n\)-layer ferroelectric thin film.](image)

A set of equations with respect to the reducing arbitrary parameters \(\tau_i\):

\[
\tau_i S_i = z J_{ii} S_i + J_{i,i+1} S_{i+1,i} + J_{i,i-1} S_{i-1,i} - 1,
\]

where

\[
\tau_i = \frac{2 \Omega_i}{J} \coth \left( \frac{\Omega_i / J}{2k_B T} \right),
\]

\[
t_c = \frac{k_B T}{J},
\]

\[
J_{ii} = \frac{J_{ii}}{J},
\]

\[
J_{i,i+1} = \frac{J_{i,i+1}}{J},
\]

\[
J_{i,i-1} = \frac{J_{i,i-1}}{J},
\]

In the following, we will study the phase diagrams and the polarizations while the exchange interactions and the transverse field are changed with the layers of the \(n\)-layer ferroelectric thin film. Because the interaction parameters in the film are layer-dependent, the coefficient determinant with respect to (5) cannot be analytically calculated as usual. So we assume that the two exchange interactions and the transverse field are changed according to some identical functions with respect to the layer number \(n\). Usually, the surface in a material can affect the interior gradually. That means that the parameters in each layer of the thin film are different. So we can assume the parameters in each layer decreasing or increasing from the surface to the interior. Meanwhile the farther the layer is away from the surface, the less the interaction parameters change. And finally the surface in a material has little effect on the most interior when the layer number is large. In order to describe the tendency that the interaction parameters vary layer by layer, we consider that the parameters are changed according to the following decreasing or increasing functions:

a) the slowly and fast decreasing functions:

\[
F_{DS} = D_0 \left( 1 + \frac{\alpha_1}{n} \right) \quad \text{and} \quad F_{DF} = D_0 \left( 1 + \frac{\alpha_2}{n} \right),
\]

b) the slowly and fast increasing functions:

\[
F_{IS} = I_0 \left( 1 - \frac{\alpha_1}{n} \right) \quad \text{and} \quad F_{IF} = I_0 \left( 1 - \frac{\alpha_2}{n} \right),
\]

where \(D_0\) or \(I_0\) denotes \(J_{a0}\), \(J_{e0}\) or \(\Omega_0\).
In this way, the phase diagrams and the polarizations for the \( n \)-layer ferroelectric thin film can be calculated when the interaction parameters are determined by the above functions. Defining three new parameters \( j_a, j_e \) and \( \omega \) as \( j_a = \frac{J_a}{a_0}, j_e = \frac{J_e}{a_0}, \omega = \frac{\Omega}{t} \), the phase diagrams which describe the relations between the Curie temperature and the exchange interactions or the transverse field (\( j_a \sim t_C, j_e \sim t_C \) or \( \omega \sim t_C \)) can be calculated numerically as follows. For simplicity, we study the phase transition properties of a 9-layer ferroelectric thin film.

Based on (5)–(12), the Curie temperature can be derived from the coefficient determinant when the interactions vary according to the functions of \( F_{DS}, F_{DF}, F_{IS}, \) or \( F_{IF} \). The following expressions refer to the situation of the slow decreasing function \( F_{DS} \). Here the symmetry for the upper and lower surface is considered.

\[
\det \begin{bmatrix}
X_1 & -Y_1 & -Y_1 & -X_2 & -Y_2 & -X_3 & -X_3 & -X_4 & -Y_4 \\
-Y_1 & X_2 & X_2 & -Y_3 & X_4 & X_4 & -X_5 & X_5 & -Y_4 \\
-Y_2 & X_3 & X_3 & -Y_4 & X_4 & X_4 & -X_5 & X_5 & -Y_4 \\
-Y_3 & X_4 & X_4 & -Y_4 & X_5 & X_5 & -X_6 & X_6 & -Y_4 \\
-Y_4 & X_5 & X_5 & -Y_4 & X_6 & X_6 & -X_7 & X_7 & -Y_4 \\
-Y_5 & X_6 & X_6 & -Y_4 & X_7 & X_7 & -X_8 & X_8 & -Y_4 \\
-Y_6 & X_7 & X_7 & -Y_4 & X_8 & X_8 & -X_9 & X_9 & -Y_4 \\
-Y_7 & X_8 & X_8 & -Y_4 & X_9 & X_9 & -X_9 & X_9 & -Y_4 \\
-Y_8 & X_9 & X_9 & -Y_4 & X_9 & X_9 & -X_9 & X_9 & -Y_4 \\
-Y_9 & X_9 & X_9 & -Y_4 & X_9 & X_9 & -X_9 & X_9 & -Y_4 \\
\end{bmatrix}
\]

where

\[
X_1 = 2 \cdot \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{4} \right) \right] \cdot \coth \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{2} \right) \right] - 4 \cdot J_{a0} \left( 1 + \alpha \right),
\]

\[
X_2 = 2 \cdot \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{4} \right) \right] \cdot \coth \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{2} \right) \right] - 4 \cdot J_{a0} \left[ 1 + \frac{\alpha}{2} \right],
\]

\[
X_3 = 2 \cdot \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{3} \right) \right] \cdot \coth \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{2} \right) \right] - 4 \cdot J_{a0} \left[ 1 + \frac{\alpha}{3} \right],
\]

\[
X_4 = 2 \cdot \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{4} \right) \right] \cdot \coth \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{2} \right) \right] - 4 \cdot J_{a0} \left[ 1 + \frac{\alpha}{4} \right],
\]

\[
X_5 = 2 \cdot \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{5} \right) \right] \cdot \coth \left[ \Omega_0 \cdot \left( 1 + \frac{\gamma}{2} \right) \right] - 4 \cdot J_{a0} \left[ 1 + \frac{\alpha}{5} \right],
\]

\[
Y_1 = J_{e0} \left( 1 + \beta \right), \quad Y_2 = J_{e0} \left( 1 + \frac{\beta}{2} \right), \quad Y_3 = J_{e0} \left( 1 + \frac{\beta}{3} \right), \quad Y_4 = J_{e0} \left( 1 + \frac{\beta}{4} \right).
\]
Solving the determinant of (13) numerically, the phase diagrams described by the relations between the interaction parameters and the Curie temperature are shown in Figures 2–4. In the calculation we assume the interaction parameters decreasing slowly and fast with the layers, respectively. Obviously, the parameters are largest when the parameters take the values of the first layer from the function of $F_{DS}$ or $F_{DF}$ ($n = 1$), and smallest when the parameters take the values of the fifth layer from the function of $F_{DF}$ ($n = 5$). In order to compare the effect of the layer-dependent parameters on the phase diagrams, we calculate firstly the phase diagrams while the parameters of the ferroelectric thin film are layer-independent. The lines $L_{\text{max}}$ and $L_{\text{min}}$ are referred to the results that the layer-independent parameters take the largest or the smallest ones, respectively. Then we calculate the phase diagrams while the three interaction parameters decrease

Fig. 3. Phase diagram for the inter-layer exchange interaction $j_e$ and the Curie temperature $t_C$ while the exchange interactions and the transverse field decrease with the layers. All curves are for $J_0/J = 1, \Omega_0/J = 10, \alpha = \beta = \gamma = 0.5$.

Fig. 4. Phase diagram for the transverse field $\omega$ and the Curie temperature $t_C$ while the exchange interactions and the transverse field decrease with the layers. All curves are for $J_0/J = 1, J_{e0}/J = 6, \alpha = \beta = \gamma = 0.5$. 
with the layers slowly or fast. The results are shown as $L_{DS}$ and $L_{DF}$. We can see that for the given values of the parameters $J_{d0}/J$, $J_{e0}/J$, or $\Omega_0/J$, the ferroelectric range with respect to $L_{\text{max}}$ is largest and the one with respect to $L_{\text{min}}$ is smallest. While the three parameters decrease with the layers, the ferroelectric range is changed synchronously. Meanwhile, the faster the parameters decrease, the smaller the ferroelectric range is. It indicates that the tendency of the changes for the three parameters has sensitive effects on the phase diagrams.

What effects have the layer-dependent parameters on the phase diagrams while the interaction parameters increase with the layers? The similar results to Figures 2–4 are given in Figures 5–7. Here the parameters are smallest when the parameters take the values of the first layer from the function of $F_{IS}$ or $F_{IS}$ ($n = 1$), and largest when the parameters take the values of the
Fig. 7. Phase diagram for the transverse field $\omega$ and the Curie temperature $t_C$ while the exchange interactions and the transverse field increase with the layers. All curves are for $J_{a0}/J = 3, J_{e0}/J = 1, \alpha = \beta = \gamma = 0.6$.

Fig. 8. Polarization versus the temperature $t$ while the parameters decrease with the layers. $P_{1DS}$ and $P_{1DF}$ are the polarizations of the first layer while the parameters decrease slowly and fast with the layers, and $P_{3DF}$ and $P_{5DF}$ are the polarizations of the third layer and the fifth layer while the parameters decrease fast with the layers, respectively. All curves are for $\alpha = \beta = \gamma = 0.4$ and $J_{a0}/J = J_{e0}/J = \alpha_{0}/J = 1$.

fifth layer from the function of $F_{IF}$ ($n = 5$). We calculate first the phase diagrams while the parameters of the ferroelectric thin film are layer-independent, and use the lines $L_{\text{max}}$ and $L_{\text{min}}$ to show the results that the layer-independent parameters take the largest or the smallest ones, respectively. Then the results for the phase diagrams while the three interaction parameters increase with the layers slowly or fast are shown as $L_{IS}$ or $L_{IF}$. It is obvious that for the given values of the parameters $J_{a0}/J, J_{e0}/J$, or $\Omega_{0}/J$, the ferroelectric range with respect to $L_{\text{max}}$ is largest and the one with respect to $L_{\text{min}}$ is smallest. Meanwhile the ferroelectric range is changed synchronously when the three parameters increase with the layers. That means,
the faster the parameters increase, the larger the ferroelectric range is. Similar results as in Figures 2 – 4 are achieved. Namely, the tendencies of the changes for the three parameters have sensitive effects on the phase diagrams.

The polarizations can be obtained by the iterative calculation based on (2) – (4). First we give out polarizations of the first, the third, and the fifth layers while the parameters decrease fast with the layers. They are expressed as $P_{1DF}, P_{3DF}, \text{and} P_{5DF}$ in Figure 8. Although the polarizations of each layer are different, they have a common Curie temperature. In order to compare the effects of different tendencies for layer-dependent parameters on the polarizations of the thin film, we then calculate the polarizations of each layer while the parameters decrease slowly with the layers. For simplicity, only the polarization $P_{1DS}$ of the first layer is shown in Figure 8. It is obvious that for the
given values, the faster the parameters decrease, the smaller the Curie temperature is. In contrast to the polarizations in Figure 8, we give the polarizations of smaller the Curie temperature is. In contrast to the polarizations in Figure 8, we give the polarizations of smaller the Curie temperature is. Namely, the tendency of the changes for the three parameters has sensitive effects on the polarizations of the ferroelectric thin film, which are in good agreement with the results of Wesselinowa [34], see Figure 10. In fact, the above description of the effect of interaction parameters on the polarizations is also qualitatively coincident with experiments. In experiment, with the increasing Sr concentration to PbTiO₃, the phase transition temperature decreases [36]. That means that the addition of Sr to PbTiO₃ may result in sensitive change for interaction parameters with layers.

3. Conclusions

In summary, we have calculated numerically the phase diagrams and polarizations while the three parameters decrease or increase monotonically with the layers. The results show that various layer-dependent parameters have sensitive effects on the phase diagrams and the polarizations of the n-layer ferroelectric thin film. While the interaction parameters vary layer by layer fast, the ferroelectric range in the phase diagram and the Curie temperature are changed promptly, which are in accordance with the results of the predecessors. It indicates that if the properties of phase transition of the ferroelectric thin film are investigated in the future, the layer-dependent parameters should be involved carefully and some experiments may be explained reasonably.