Size effects of ferroelectric particles described by the transverse Ising model

C. L. Wang
China Center of Advanced Science and Technology (CCAST), P.O. Box 8730, Beijing 100080, People's Republic of China and Department of Physics, Shandong University, Jinan 250100, People's Republic of China

Y. Xin, X. S. Wang, and W. L. Zhong
Department of Physics, Shandong University, Jinan 250100, People's Republic of China

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The size effects of ferroelectric particles described by the transverse Ising model have been studied taking into account the long-range interactions. The size dependence of the mean polarization, Curie temperature, and the mean susceptibility, as well as the critical size of the particle, have been obtained. The profile of the polarization is given. The size effects of the ferroelectric particle show a strong dependence on the interaction range.

I. INTRODUCTION

Size effects of ferroelectrics were first reported in 1950s,[1,2] and have become a subject of experimental and theoretical studies in recent years. Ferroelectric thin films and particles are two main types of finite-size ferroelectrics that show size effects. Experimentally, Scott *et al.*[3,4] discovered that the ferroelectricity of KNO_3 thin films exists in a much wider temperature range than that of the bulk crystal. Funakuba *et al.*[5] measured the c/a ratio and the dielectric constant of $PbTiO_3$ films. Both the c/a ratio and the dielectric constant decrease with decreasing film thickness. Hayashi *et al.*[6] observed the same feature in $BaTiO_3$ films. The thickness dependence of the Curie temperature of ferroelectric films was also studied.[7,8] Works on the size effects of ferroelectric particles are mainly focused on $BaTiO_3$ and $PbTiO_3$. Ishikawa *et al.*[9] investigated the phase transition in $PbTiO_3$ particles and obtained a critical size of around 12.6 nm. Zhong *et al.*[10] measured the phase transition temperature of $PbTiO_3$ particles of various sizes by specific heat and Raman scattering. They obtained a critical size of about 9.1 nm. Qu *et al.*[11] studied the size dependence of the dielectric constant of $PbTiO_3$ particles at room temperature and observed a dielectric peak at about 40 nm. Schlag *et al.*[12,13] made an intensive study of the size dependence of the phase transition temperature of $BaTiO_3$ particles and found a critical size of about 49 nm. Frey and Payne[14] reported that there is no electric hysteresis at room temperature and there is no Curie peak of the dielectric constant when the grain size of $BaTiO_3$ is 25 nm. Zhong *et al.*[15] obtained the dielectric constant of $BaTiO_3$ particles and found no dielectric anomaly when the particle size is below 105 nm.

Theoretically, Landau-type phenomenological theory and the transverse Ising model are frequently used in studying the size effects in ferroelectrics. Tilley and Zěkš[16] first studied ferroelectric films with a second-order phase transition using a Landau-type theory. Scott *et al.*[3] extended the theory to films of a first-order phase transition. This theory was then applied to ferroelectric particles by Zhong and co-workers.[17,18] They noted that the extrapolation length of a particle should be size dependent. Using the transverse Ising model, Wang *et al.*[19] first studied the phase transition properties of ferroelectric thin films by modifying the exchange strength at the surface. Later this model was applied to ferroelectric particles of a cubic shape.[20,21] In this article, we study the size effects of a spherical ferroelectric particle using this model with the long-range interactions between the pseudospins taken into account. The size dependence of the mean polarization, the Curie temperature, and the mean susceptibility of the particle are presented. The radial profile of the polarization is given.

II. METHODOLOGY

The Hamiltonian of the transverse Ising model has the form[22]

$$H=-\Omega\sum_i S_i^x-\frac{1}{2}\sum_{ij} J_{ij}S_i^zS_j^z-2\mu E\sum_i S_i^z \tag{1}$$

where Ω is the transverse field, and S_i^x and S_i^z are components of a spin-$\frac{1}{2}$ operator at site i. Here J_{ij} is the exchange strength between sites i and j. Also, μ is the effective dipole moment of site i and E is the external electric field. We assume the exchange strength between the ith and jth sites taking the form[23,24]

$$J_{ij}=\frac{J}{r_{ij}^{\sigma}}, \tag{2}$$

where σ is a measure of the interaction range. $\sigma=\infty$ corresponds to the nearest-neighbor model, and $\sigma=0$ corresponds to an infinite-range interaction. In ferroelectrics, the interaction consists of a long-range Coulomb interaction (a small σ) and a short-range repulsion (a larger σ). If the former is treated as a dipole-dipole interaction, the smaller σ should be 3. The σ for the whole interaction in Eq. (2) is therefore greater than 3.

We consider a spherical particle composed of spherical layers, as shown in Fig. 1 schematically. Without loss of generality, we assume that the pseudospins in the same spherical layer have the same value, and N is the total num-

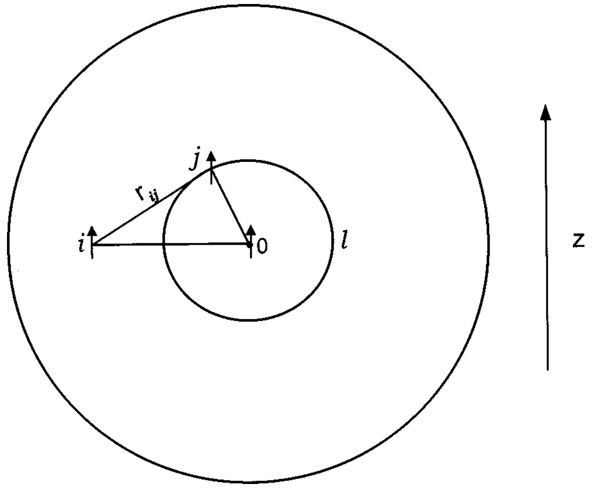

FIG. 1. Model of the ferroelectric particle in our calculations.

ber of spherical layers in the particle. Under a mean-field approximation, the single-particle Hamiltonian of the system can be expressed as

$$H_i = -\Omega S_i^x - S_i^z \sum_j J\langle S_j^z\rangle \Big/ r_{ij}^\sigma = -\Omega S_i^x - S_i^z \sum_{l=0}^{N} J'_{il}\langle S_l^z\rangle \tag{3}$$

where $\langle S_j^z\rangle$ is the thermal average of S_j^z, $J'_{il} = \Sigma_{j\in l} J/r_{ij}^\sigma$, j runs over all the sites in the lth layer of the particle, and J'_{il} represents the summation of the exchange strength between a pseudospin in the ith site and all the other pseudospins in the lth layer of the sphere. $i,j=0$ represents the central site of the particle, and $i,j=N$ represents the surface sites of the particle. Therefore the average value of S_i^z at the nth layer, i.e., $\langle S_i^z\rangle = R_n$, is

$$R_n = \frac{\langle H_n^z\rangle}{2|H_n|}\tanh\left(\frac{|H_n|}{2k_BT}\right), \tag{4}$$

where

$$\langle H_n^z\rangle = \Sigma_{l=0}^N J'_{nl}R_l,$$

$$|H_n| = \sqrt{\Omega^2 + \langle H_n^z\rangle^2}, \tag{5}$$

k_B is the Boltzman constant, and T is the absolute temperature. Equation (4) can be rewritten as

$$\sum_{l=0}^{N} \alpha_{nl}R_l = 0, \tag{6}$$

where $\alpha_{nl} = J'_{nl}$ for $(n\neq l)$, and $\alpha_{nn} = J'_{nn} - \lambda_n$. Here $\lambda_n = 2|H_n|/\tanh(|H_n|/2k_BT)$, and J'_{nn} is the summation of the exchange strength between a pseudospin in the nth layer and all the other pseudospins in the same layer of the particle. As n ranges from 0 to N, Eq. (6) represents a set of simultaneous equations and R_n can be calculated numerically. The mean polarization of the particle is

$$\overline{P} = \frac{2\mu}{Mv}\sum_{n=0}^{N} m_nR_n, \tag{7}$$

where M is the number of the total pseudospins in the particle, μ is the dipole moment of the pseudospin, and v is the volume a dipole possessed. m_n is the number of pseudospins in the nth layer of the particle: in our calculations, we assume that m_n is proportional to the volume of the nth layer.

Near the Curie temperature, R_n is very small, the z component of H_n is approximately zero, and Eq. (4) can be reduced to

$$R_n = \frac{\Sigma_l J_{nl}R_l}{2\Omega}\tanh\left(\frac{\Omega}{2k_BT}\right) \tag{8}$$

and this equation can be rewritten as

$$\sum_{l=0}^{N} c_{nl}R_l = 0, \tag{9}$$

where $c_{nl} = J'_{nl}$ for $(n\neq l)$, $c_{nn} = J'_{nn} - x$, and $x = 2\Omega/\tanh(\Omega/2k_BT)$. Equation (9) represents a set of linearized equations from which the Curie temperature can be determined by its coefficient determinant.

To obtain the dielectric susceptibility χ of the particle, we assume that only R_n is dependent on the electric field, and define a reduced local susceptibility at the ith site:

$$k_i = \chi_i\frac{v}{2\mu} = \frac{v}{2\mu}\frac{\partial P_i}{\partial E} = \frac{\partial R_i}{\partial E}, \tag{10}$$

which satisfies the equation

$$\sum_{l=0}^{N} \gamma_{nl}k_l = 0, \tag{11}$$

where $\gamma_{nl} = J'_{nl}$ for $(n\neq l)$, $\gamma_{nn} = J'_{nn} - 1/b_n$, and $b_n = \partial R_n/\partial|H_n|$. Equation (11) stands for a set of simultaneous equations, and k_n can be obtained by numerical calculations. The mean susceptibility of the particle is defined as

$$\overline{\chi_e} = \frac{1}{M}\sum_{n=0}^{N} m_n\chi_n = \frac{2\mu}{Mv}\sum_{n=0}^{N} m_nk_n. \tag{12}$$

For a ferroelectric material, its bulk Curie temperature is already known; therefore, Ω/J_0 can be obtained. Here $J_0 = \Sigma_{i=1}^{\infty} J'_{0i}$ is the summation of the exchange strength between the central site and all the other pseudospins in a particle with infinite size. In our calculations, we will fix Ω/J_0, and take different values for σ in order to analyze the influence of different interaction ranges.

III. RESULTS AND DISCUSSION

Figure 2 shows the size dependence of the Curie temperature of the particle with different σ at fixed $\Omega/J_0 = 0.35$. The Curie temperature is reduced by $T_{c\infty}$, where $T_{c\infty}$ is the Curie temperature of the bulk material with $\sigma=5$. The Curie temperature of the particle decreases with decreasing size sharply to zero at the critical size. The feature has been observed experimentally in $PbTiO_3$ particles.[10] It is obvious that the critical size of the particle varies with σ at the same value of Ω/J_0. In the case of $\sigma=5$, the Curie temperature increases with increasing size slowly when the particle size is larger than 20 layers and approaches the bulk value when

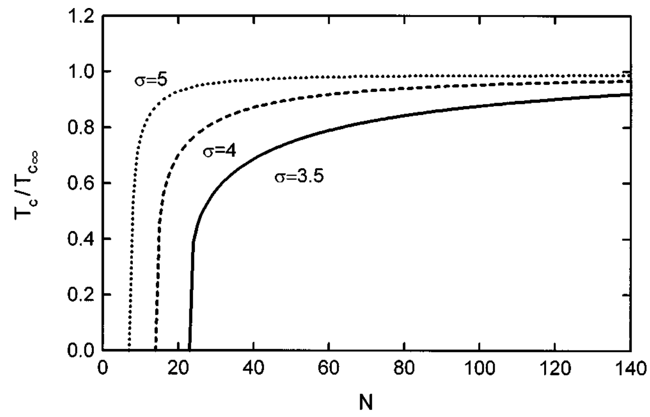

FIG. 2. The size dependence of the Curie temperature of the particle at $\Omega/J_0=0.35$. Here $T_{c\infty}$ is the Curie temperature of the bulk material. The solid line is for $\sigma=3.5$, the dashed line for $\sigma=4$, and the dotted line for $\sigma=5$.

the size becomes infinite, while for $\sigma=3.5$ the Curie temperature increases much faster than those of $\sigma=4$ and $\sigma=5$. This means that the interaction range has a notable influence on the Curie temperature of a particle with finite size. From Fig. 2 we can also see that the smaller the σ, the larger the critical size. This can be ascribed to the fact that a smaller σ corresponds to a longer interaction range, with the decreasing of the particle size, the amount of the pseudospins contributing to the ferroelectricity of the particle decreases quickly. While a larger σ implies a shorter interaction range, only a small amount of pseudospins dominates in contributing to the ferroelectricity of the particle, so the ferroelectricity can persist down to a smaller size.

Figure 3 shows the size dependence of the mean polarization of the particle at a temperature of 0 K with different σ at $\Omega/J_0=0.35$. The mean polarization of the particle decreases to zero at the critical size, which is in accordance with Fig. 2. The mean polarization of the particle with $\sigma=3.5$ increases with increasing size faster than those of $\sigma=4$ and $\sigma=5$; this is reasonable because the stronger the interactions between the pseudospins, the larger the polarization. As a smaller σ corresponds to a longer interaction range, with the increasing of the particle size, the summation of the interactions between the pseudospins increases quickly, so the mean polarization of the particle also increases quickly.

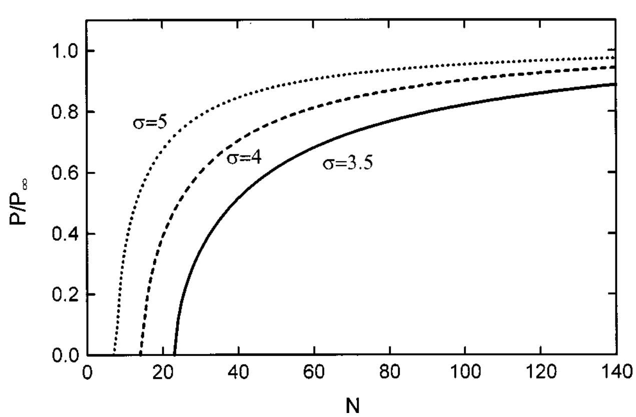

FIG. 3. The size dependence of the mean polarization of the particle at ground state with $\Omega/J_0=0.35$. Here N is the total number of spherical layers in the particle. The solid line is for $\sigma=3.5$, the dashed line for $\sigma=4$, and the dotted line for $\sigma=5$.

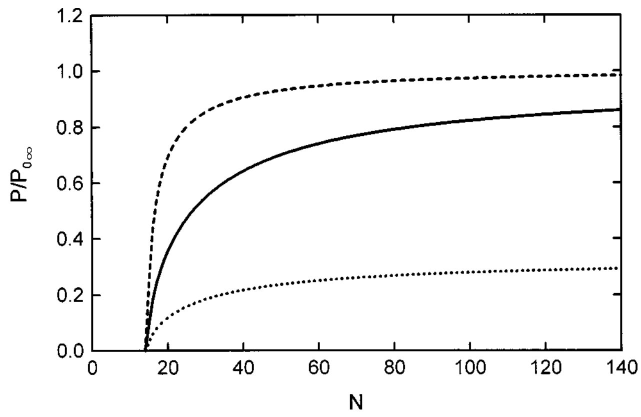

FIG. 4. The size dependence of the ground-state polarization of the particle at $\Omega/J_0=0.38$ and $\sigma=4$. The dashed line is for the central site of the particle, the solid line is for the midlayer between the central site and the surface layer of the particle, and the dotted line is for the surface layer.

Figure 4 shows the size dependence of the ground-state (at a temperature of 0 K) polarization in the particle with $\sigma=4$ and $\Omega/J_0=0.38$. In the figure we present polarization at the central site, the surface layer, and the midlayer halfway between the central site and the surface layer. All three polarizations decrease to zero simultaneously at the critical size of the particle. The polarization of the central site of the particle is larger than those of the other two layers. It is easy to understand because the central site has stronger interactions with the surrounding pseudospins due to its special position.

The radial profiles of the polarization in the particle, with total number of layer of 40, 60, and 80, at temperature of $0.5T_{c\infty}$ are shown in Fig. 5, where $T_{c\infty}$ is the Curie temperature of the bulk material. It can be seen that near the center, the polarization reaches a maximum platform. The polarization of the surface layer is greatly depressed in comparison with those of the other layers. This is easy to understand because the coordinate number for a pseudospin on the sur-

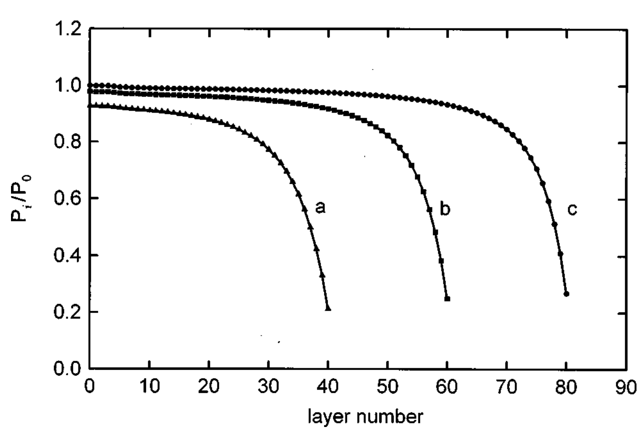

FIG. 5. The radial profile of the polarization in the particle at $0.5T_{c\infty}$. Here $T_{c\infty}$ is the Curie temperature of the bulk material. The line with circles is for a particle with 80 layers, the line with squares is for a particle with 60 layers, and the line with triangles is for a particle with 40 layers. The model parameters are same as Fig. 4.

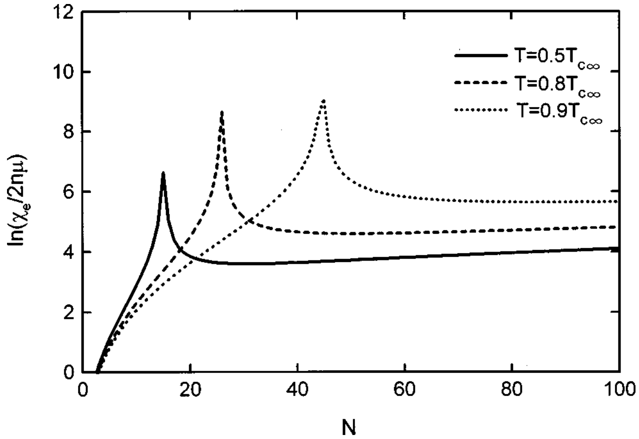

FIG. 6. The size dependence of the mean susceptibility of the particle at different temperatures. The reduced susceptibility of the particle is in natural logarithm scale. The solid lines are for $T = 0.5T_{c\infty}$, the dashed lines are for $T = 0.8T_{c\infty}$, and the dotted lines are for $T = 0.9T_{c\infty}$. The model parameters are same as Fig. 4.

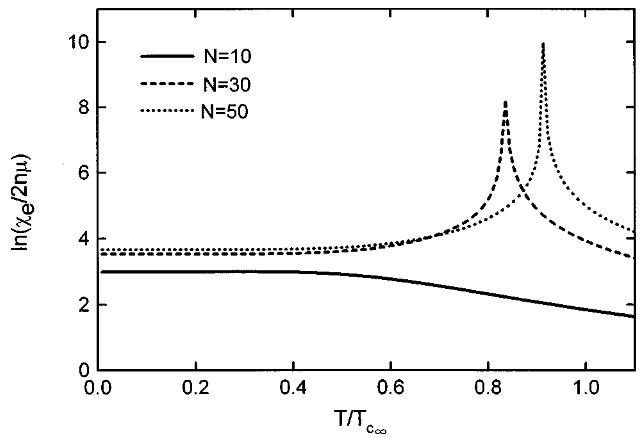

FIG. 7. The temperature dependence of the mean susceptibility of the particle with different sizes. The reduced mean susceptibility is in natural logarithm scale. The solid line is for $N = 10$, the dashed line is for $N = 30$, and the dotted line is for $N = 50$. The model parameters are same as Fig. 4.

face is lower than that for the pseudospins in the interior. Figure 5 also shows that the polarization of each layer in an 80-layer particle is larger than that of the corresponding layer in the 60-layer or 40-layer particle, which obviously results from the strengthening of the interactions in the larger particles.

Figure 6 shows the size dependence of the mean susceptibility of the particle at different temperatures below $T_{c\infty}$. Each curve shows a peak implying a size-driven phase transition. This type of peak was observed in $PbTiO_3$ particles.[11] With the increasing of the temperature, the phase transition size becomes larger. At a temperature of $0.5T_{c\infty}$, the phase transition size occurs at $N = 15$, and at a temperature of $0.8T_{c\infty}$ the phase transition happens at a size of $N = 25$, while at a temperature of $0.9T_{c\infty}$, the phase transition size is $N = 46$. This is understandable because at a lower temperature, the polarization is larger and it can persist down to a smaller size.

The temperature dependence of the dielectric susceptibility of the particle with different sizes is shown in Fig. 7. The particle with 50 spherical layers shows a susceptibility peak at a higher temperature than that with 30 layers. As for the particle with 10 layers, which is smaller than the critical size, the mean susceptibility decreases with increasing temperature monotonically with no peak, which means that there is no phase transition. This kind of feature has been already observed experimentally in the study of $PbTiO_3$ (Ref. 11) and $BaTiO_3$ (Ref. 14) particles.

Our calculations show that σ, as a measure of the interaction range, significantly influences the size effects. As we mentioned in a previous context, in real ferroelectrics, because of the long-range Coulomb interaction, σ should be greater than 3. For a fixed Ω/J_0, which means a fixed Curie temperature of its corresponding bulk system, a smaller σ corresponds to a larger critical size. In other words, in a system with long-range interactions, it needs a large size to establish ferroelectricity; therefore, the critical size increases with increasing interaction range. Because we cannot find two ferroelectrics with the same or close bulk Curie temperature, we choose the experimental results of $BaTiO_3$ and $PbTiO_3$ for a comparison since they are typical ferroelectrics and their bulk properties and size effects are well studied.

The bulk Curie temperature of $BaTiO_3$ (393 K) is above half that of $PbTiO_3$ (763 K), but the critical size of $BaTiO_3$ (around 50 nm) (Ref. 12) is an order of magnitude larger than that of $PbTiO_3$ (around 5 nm).[25] From this comparison, we might say that long-range interactions play a more important role in $BaTiO_3$ than that in $PbTiO_3$. The relatively large critical size of $BaTiO_3$ could be mainly attributed to the long-range interaction (or a smaller σ) if it is not the only contribution. To estimate the value of σ, we may compare the calculated size dependence of the Curie temperature (Fig. 2) or polarization (Fig. 3) with the experimental results. For $PbTiO_3$, the experimental size dependence of the Curie temperature can be found in Ref. 9 or 10. For $BaTiO_3$, similar results can be found in Ref. 26. A comparison of them with the curves in Fig. 2 may give an estimation of σ.

IV. SUMMARY

The size effects of ferroelectric particles described by the transverse Ising model are studied taking into account the long-range interactions. Our results reproduce many features of experimental observations. With a decreasing of the particle size, the mean polarization and the Curie temperature of the particle decrease to zero at the critical size of the particle, which implies a size-driven phase transition from the paraelectric phase to the ferroelectric phase. This is indicative of the fact that long-range interactions are dominant in contributing to the ferroelectricity. A longer interaction range may lead to a larger critical size. For a ferroelectric particle with a shorter interaction range, the size dependence of the ferroelectricity becomes weaker when the size of the particle is large. From our calculation, the loss of the ferroelectricity of a particle below its critical size is mainly caused by the weakening of long-range interactions among the pseudospins in the particle.

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