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Phenomenological study of the size effect on phase transitions in ferroelectric particles

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Size effects on the Curie temperature and spontaneous polarization in spherical particles are studied using Landau phenomenological theory. The extrapolation length is shown to be size dependent. The spatial distribution of polarization is obtained. The size dependence of the polarization is calculated whereby a size-driven phase transition is demonstrated. The Curie temperature as a function of particle size is calculated. Theoretical results are compared with the experimental in the literature and good agreement is obtained.

I. INTRODUCTION

Although the size effect on phase transitions in ferroelectrics has been known since the 1950s,[1,2] its study has acquired a great impetus only in recent years. This is mainly due to the development of ferroelectric films and composite materials. Nonvolatile memories and other applications have made ferroelectric films a subject of great practical importance.[3] The Curie temperature, polarization, coercive field, switching speed, etc., depend on the film thickness and grain size.[4] In a composite with a ferroelectric as one of the constituents, for example, the 0-3 type piezoelectric ceramic-polymer composite, the piezoelectric and pyroelectric properties vary with the ceramic particle size.[5] In order to optimize their properties, the size effect must be studied. In addition, phenomena in relaxer ferroelectrics[6] which have very strong electrostriction are closely related to the size dependence of ferroelectricity.

For PZT ($PbZr_xTi_{1-x}O_3$, $0<x<1$) films, Scott[7] reported that the T_C of films is higher than that of the bulk. For $KNbO_3$ films, Scott *et al.*[8] found that some samples exhibit an increase in Curie temperature with increasing film thickness and others show a decrease. The same was observed in TGS [$(NH_2CH_2CoOH)_3{\cdot}H_2SO_4$]. Hadni and Thomas[9,10] reported an increase in T_C with decreasing thickness, whereas Batra and Silverman[11] reported a decreasing T_C with decreasing thickness. The discrepancy emphasizes the effect of surface preparation. Compared with films, the size dependence of the properties in ferroelectric particles has been studied rather extensively.[12-21] Here we only mention the ferroelectric critical size, i.e., the size at which ferroelectricity disappears. For $PbTiO_3$, it was obtained to be 13.8 nm (Ref. 14) or 9.1 nm;[15] for $BaTiO_3$, it was 115 nm.[18]

On the side of theoretical treatment, two main approaches have been used. One is the transverse Ising model,[22-25] and the other is the Landau phenomenological theory.[8,26-33] The latter has been more fruitful. Tilly and Zeks[27] developed the theory and studied in detail the films with a second-order phase transition. Scott *et al.*[8] extended it to a first-order phase transition. Recently, a comprehensive review[32] of the subject was given by Tilly in which depolarization effects were included. A numerical estimate of the critical thickness depending on the Thomas-Fermi screening length of the electrode was made by Tilly and Zeks.[33] To our knowledge, there has been no theoretical treatment of ferroelectric particles. Because ferroelectric particles are important in composite materials and there are more experimental data on particles, it is worthwhile to extend the theories to ferroelectric particles. In the present work, we applied the Landau phenomenological theory to ferroelectric particles. The next section describes the needed modifications. In Sec. III the size dependence of the polarization is calculated whereby a size-driven phase transition is demonstrated. Section IV is devoted to the size dependence of the Curie temperature. The ferroelectric critical size is obtained and compared with the experimental. Some conclusions are given in the final section.

II. THEORY

In order to apply the Landau theory to a finite-size and inhomogeneous ferroelectric, the total free energy instead of the energy density should be used. If the ferroelectric has a second-order phase transition, the total free energy can be written

$$F=\int\left[\tfrac{1}{2}A(T-T_{C\infty})P^2+\tfrac{1}{4}BP^4+\tfrac{1}{2}D(\nabla P)^2\right]dv+\int\tfrac{1}{2}D\delta^{-1}P^2dS\ , \qquad (1)$$

where P is the polarization and $T_{C\infty}$ the Curie temperature of the bulk crystal. The volume and surface integrals give the free energy of the interior and surface, respectively. Compared with the free energy expression of an infinite and homogeneous ferroelectric, a gradient term and a surface term were added. δ is the extrapolation length describing the difference between the surface and bulk. The coefficient B is positive, and D is connected with the correlation length ξ, $D=\xi^2|A(T-T_{C\infty})|$.

The spontaneous polarization must satisfy the following Euler-Lagrange equation and boundary condition to minimize the free energy:

$$D\nabla^2 P = A(T-T_{C\infty})P + BP^3 , \tag{2}$$

$$\frac{\partial P}{\partial n} + \delta^{-1}P = 0 \text{ at the surface} , \tag{3}$$

where n is the unit normal to the surface. For ferroelectric films, Eqs. (2) and (3) have been simplified and solved.[27] For a ferroelectric particle of arbitrary shape, they are very difficult to solve. We therefore made two simplifications. First, the particles are assumed to be spherical and the diameter is d. Second, the polarizations lie in a single direction and their magnitude depends only on the radius r. Then Eqs. (2) and (3) in spherical coordinates become

$$D\left[\frac{d^2P}{dr^2} + \frac{2}{r}\frac{dP}{dr}\right] = A(T-T_{C\infty})P + BP^3 , \tag{4}$$

$$\frac{dP}{dr} + \delta^{-1}P = 0, \quad r = \frac{d}{2} . \tag{5}$$

For ferroelectrics with a first-order phase transition, the free energy should be changed into[8]

$$F = \int \left[\tfrac{1}{2}A(T-T_{0\infty})P^2 + \tfrac{1}{4}BP^4 + \tfrac{1}{6}CP^6 + \tfrac{1}{2}D(\nabla P)^2\right]dv + \int \tfrac{1}{2}D\delta^{-1}P^2 dS , \tag{6}$$

where a term in P^6 with a positive coefficient is added and the coefficient B is negative. $T_{0\infty}$ is the bulk Curie-Weiss temperature, which is lower than the Curie temperature $T_{C\infty}$. As in the case of second-order phase transitions, we considered a ferroelectric particle of diameter d and assumed that the magnitude of the polarization is a function of only the radius r. The Euler-Lagrange equation and the related boundary condition are

$$D\left[\frac{d^2P}{dr^2} + \frac{2}{r}\frac{dP}{dr}\right] = A(T-T_{0\infty})P + BP^3 + CP^5 , \tag{7}$$

$$\frac{dP}{dr} + \delta^{-1}P = 0, \quad r = \frac{d}{2} . \tag{8}$$

A significant modification occurs to the extrapolation length. δ describes the difference between the surface and bulk; it depends not only on the different interaction constants at the surface and in the bulk, but also on the coordination number at the surface. For pseudospins forming a simple cubic lattice with a lattice constant a_0, if the interaction constant is J_s for both pseudospins on the surface and is J otherwise, then δ can be expressed as[22]

$$\frac{1}{\delta} = \frac{5J-4J_s}{a_0 J} . \tag{9}$$

In ferroelectric films, the coordinate number on the surface is always 4; if J_s and J are kept constant, then δ is thickness independent. In a spherical particle of diameter d, even if J_s and J are size independent, δ will depend on size because the coordination number on the surface will be smaller for a smaller d. Considering $d \gg a_0$, the average surface coordinate number can be written

$$n_{\text{av}} = 4\left[1 - \frac{a_0}{d}\right] . \tag{10}$$

Thus we have

$$\frac{1}{\delta} = \frac{5J - n_{\text{av}}J_s}{a_0 J} = \frac{5}{d} + \frac{1}{\delta_\infty}\left[1 - \frac{a_0}{d}\right] , \tag{11}$$

where δ_∞ is the extrapolation length when $d=\infty$. It can be seen that even if $\delta_\infty < 0$, δ will become positive when

$$d < 5|\delta_\infty| + a_0 . \tag{12}$$

The size dependence of δ will lead to some interesting features different from ferroelectric films.

To get the spatial distribution of the polarization, Eqs. (4) and (5) (for second-order phase transitions) or Eqs. (7) and (8) (for first-order phase transitions) must be solved. Although they have been simplified, they are still difficult to solve analytically. Therefore we solved them numerically using the finite-difference method. The sphere was divided into 1000 sections. The accuracy of P is 10^{-7}; the accuracy of F and T_C is about 10^{-5}.

III. SIZE-DRIVEN PHASE TRANSITION

The spatial distribution of the polarization at different δ is calculated first for ferroelectrics with a second-order phase transition. Figure 1 is the polarization profile for a positive δ; Fig. 2 is that for a negative δ. When $\delta > 0$, the polarization at the surface is reduced compared with that in the bulk. When $\delta < 0$, it is enhanced. The reduced temperature $T/T_{C\infty}$ is labeled on each curve. With decreasing temperature, the polarization at the center approaches the bulk value P_∞, and the difference between the polarization at the center and on the surface is enhanced. In the case of $\delta < 0$, polarization can exist above the bulk Curie temperature. These are similar to ferroelectric films.[27]

For ferroelectrics with a first-order phase transition, the spatial distribution of the polarization is also calculat-

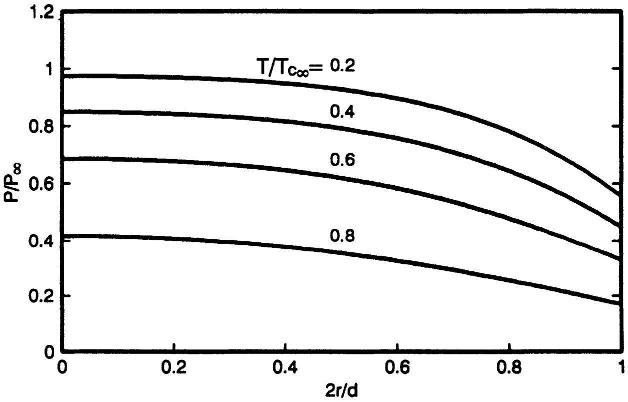

FIG. 1. Spatial distribution of the polarization in a spherical particle. $A=1$, $B=1$, $D=100$, $\delta=15$, $d=40$.

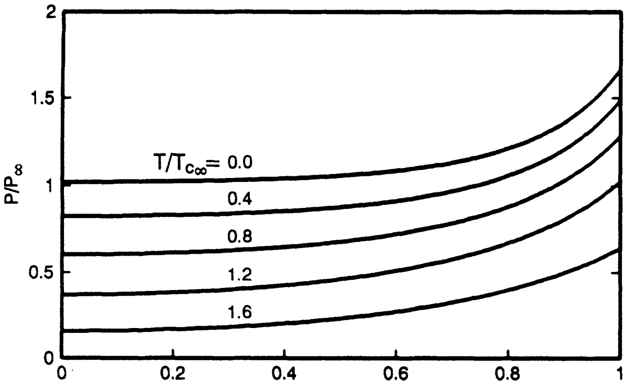

FIG. 2. Spatial distribution of the polarization in a spherical particle. $A=1, B=1, D=100, \delta=15, d=40$.

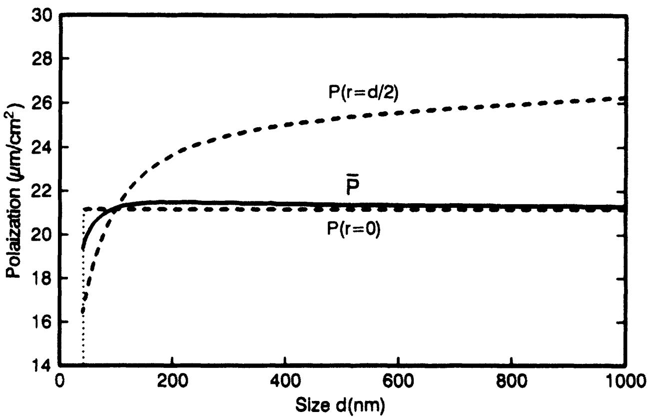

FIG. 4. Same as Fig. 3, but $\delta_\infty=-43$ nm.

ed and a similar result is obtained. In films with a first-order phase transition and negative δ, Scott *et al.*[8] revealed that when $|\delta|\leq\xi$ and thickness $d\gg\xi$, there will be a surface transition at $T\approx T_{C\infty}[\frac{3}{4}+(\xi/\delta)^2]$, where surface ordering suddenly takes place and the polarization far from the surfaces is exponentially small. In our calculation of the polarization profile in Fig. 2, we took diameter $d=40$, $\delta=-15$, $T/T_{C\infty}=0-1.6$. Since ξ is a function of T, at some T in this range, we will have $|\delta|\leq\xi$, but d is not large enough ($d/|\delta|=2.6$). This is why the calculation did not reveal a surface transition. In fact, when d is large, a state of surface order similar to that of films[8] was obtained.

The polarization at 0 K as a function of particle size is then calculated. For a ferroelectric particle with a first-order phase transition, Fig. 3 shows the polarization at the center, on the surface, and the average value for $\delta_\infty>0$; Fig. 4 shows them for $\delta_\infty<0$. When $\delta_\infty>0$, the polarization at the surface is always lower than that at the center. In the case of $\delta_\infty<0$, P $(r=d/2)$ is higher than P $(r=0)$ when d is large, but is lower than P $(r=0)$ when d is small. The crossover is a result of the size dependence of δ. It happens at $d=5|\delta_\infty|+a_0$ [Eq. (12)], where δ changes from negative to positive. Below this size, the polarization at the surface is reduced. This is contrary to ferroelectric films with $\delta<0$, in which the polarization at the surface is always higher than that in the center.[8,27]

Another feature in Fig. 4 is that the average polarization exhibits a slight increase when d is large and a drastic decrease when d is small. It is attributed to the surface layer and the sign change of δ. When d is large and decreases, δ hardly changes, but the volume fraction of surface layer increases. This layer has a higher polarization; thus, P slightly increases. When d is small, δ becomes positive; the polarization behaves similarly for $\delta_\infty>0$.

In any case, the polarization becomes zero when the particle is small enough. It is indicative of a size-driven ferroelectric-paraelectric phase transition. The size at which the phase transition takes place is the smallest size that can sustain ferroelectricity, i.e., the ferroelectric critical size. In the calculation of Fig. 3, we used the param-

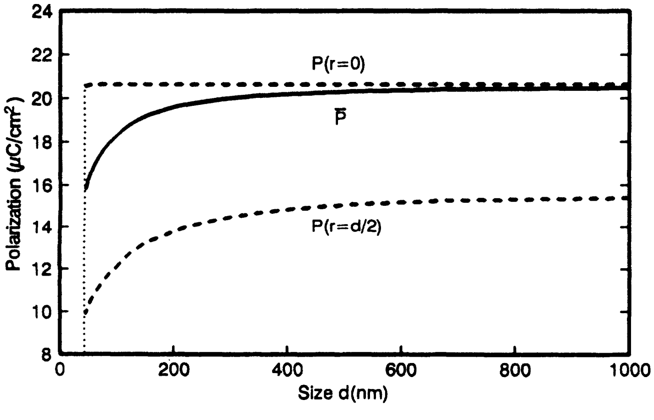

FIG. 3. Size dependence of the polarization of a ferroelectric particle with a first-order phase transition. $P(r=0)$, $P(r=d/2)$, and P are polarizations at the center, on the surface, and the average value, respectively. The parameters are those of $BaTiO_3$ in Table I.

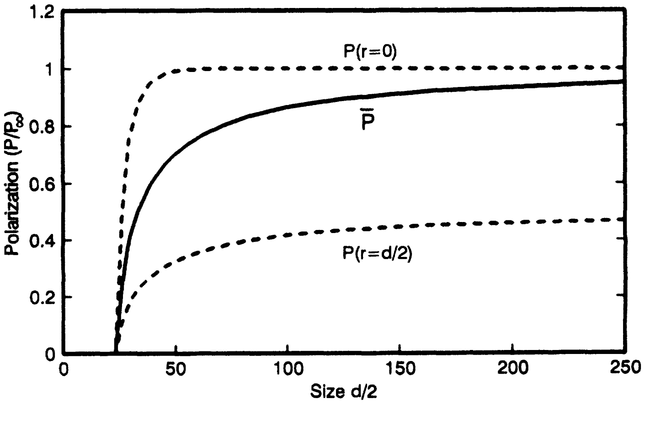

FIG. 5. Size dependence of the polarization of a ferroelectric particle with a second-order phase transition. $P(r=0)$, $P(r=d/2)$, and P are polarizations at the center, on the surface, and the average value, respectively. $A=1$, $B=1$, $D=100$, $\delta_\infty=10$.

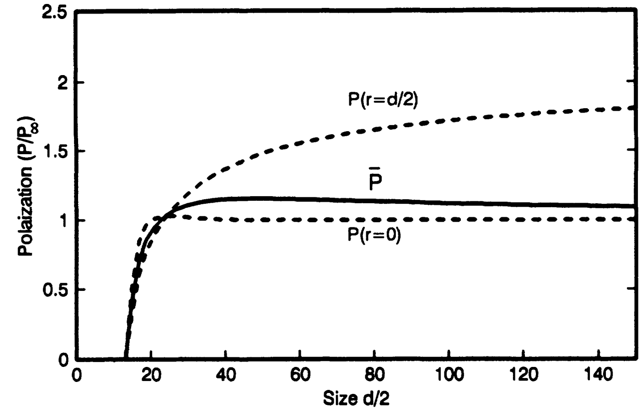

FIG. 6. Same as Fig. 5, but $\delta_\infty = -10$.

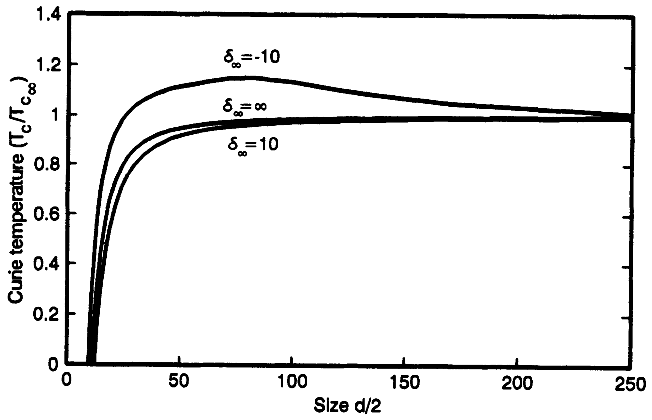

FIG. 8. T_C as a function of size for ferroelectrics with a first-order phase transition. $A = 1$, $B = 0.12$, $C = 0.09$, $D = 25$, $T_{C\infty} = 1$, $T_{0\infty} = 0.97$.

eter values adequate to $BaTiO_3$ (see Table I in Sec. IV). It gives a ferroelectric critical size of 44 nm.

For ferroelectrics with a second-order phase transition, Figs. 5 and 6 show the size dependence of the polarization when $\delta_\infty > 0$ and $\delta_\infty < 0$, respectively. In this case, a size-driven phase transition is also demonstrated. It is interesting to note the behavior of the polarization near the critical size. In Figs. 3 and 4, the polarization jumps down to zero, while in Figs. 5 and 6, the polarization reaches zero continuously. The former is a characteristic of a first-order phase transition; the latter is that of a second-order phase transition. Thus the size-driven phase transitions have the same order as the temperature-driven phase transitions.

IV. SIZE DEPENDENCE OF THE CURIE TEMPERATURE

Having obtained the polarization distribution in the particle, the total free energy F [Eq. (1) or (6)] can be calculated. By equalizing the free energy of the ferroelectric and paraelectric phases, the Curie temperature T_C is obtained.

For ferroelectrics with a second-order phase transition, Fig. 7 shows the reduced Curie temperature $T_C/T_{C\infty}$ as a function of d at different δ_∞. Parallel results for ferroelectrics with a first-order phase transition are shown in Fig. 8. $\delta_\infty = \infty$ means that there is no difference between the surface and bulk. It is seen that when $\delta_\infty > 0$, T_C is always lower than that for $\delta_\infty = \infty$. When $\delta_\infty < 0$, T_C can be higher than $T_{C\infty}$. These are similar to those in ferroelectric films.[8,27] In any case, T_C reaches zero provided that the particle is small enough.

There is an interesting difference between films and particles. For ferroelectric films with $\delta < 0$, T_C increases with decreasing thickness and will never become zero.[8,27] For ferroelectric particles with $\delta_\infty < 0$, T_C becomes zero at a small enough diameter. This is another result of the size dependence of δ. When $d < 5|\delta_\infty| + a_0$, δ will be positive even if $\delta_\infty < 0$. Therefore ferroelectricity disappears eventually.

Although T_C becomes zero when the size is small enough no matter $\delta_\infty > 0$ or $\delta_\infty < 0$, the T_C versus d curve is not monotonic when $\delta_\infty < 0$. T_C increases with decreasing particle size when d is large and decreases when d is small. The explanation is similar to that of the size dependence of the polarization. At larger values of d, the effective extrapolation length δ changes very little, but

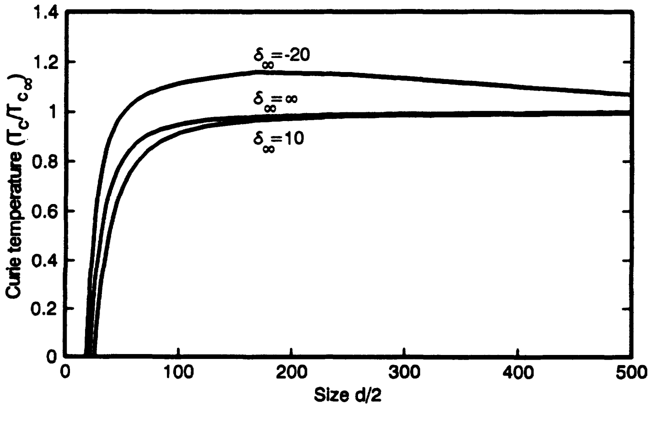

FIG. 7. T_C as a function of size for ferroelectrics with a second-order phase transition. $A = 1$, $B = 1$, $D = 100$, $T_C = 1$.

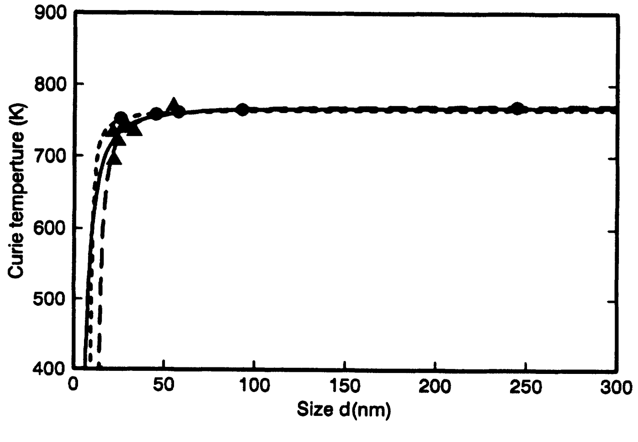

FIG. 9. Size dependence of the T_C of $PbTiO_3$ particles.

TABLE I. Parameter values for $PbTiO_3$ and $BaTiO_3$ (cgs units).

	$T_{C\infty}$ (K)	$T_{0\infty}$ (K)	Curie constant (10^5 K)	A (10^{-5})	B (10^{-12})	C (10^{-21})	D (10^{-16})	δ_∞ (nm)
$PbTiO_3$	765[a]	722[a]	4.1[a]	3.1	−2.0	5.8	5	3
$BaTiO_3$	403[b]	391[b]	1.7[b]	7.4[b]	−4.4[b]	3.7[b]	1263	43

[a] Reference 34.

[b] Reference 35.

the volume fraction of the surface layer increases, leading to an increase in T_C. At smaller values of d, δ will become positive, and so T_C behaves like that for $\delta_\infty > 0$.

The size at which $T_C = 0$ K is the ferroelectric critical size. Obviously, if $\delta_\infty < 0$, ferroelectricity can persist at smaller sizes. As shown in Figs. 7 and 8, the critical size for $\delta_\infty < 0$ is indeed smaller than that for $\delta_\infty > 0$.

To validate the theory, experimental data in the literature are used. The size dependence of T_C for $PbTiO_3$ has been obtained in Refs. 14 and 15 and that for $BaTiO_3$ in Ref. 18. Both are ferroelectrics with a first-order phase transition. For the theoretical calculation, the parameters A, B, and C are determined from the reported data of the bulk.[34,35] Since there has not yet been data to determine D and δ, we take them as adjustable. The relevant data are listed in Table I.

Figure 9 shows the size dependence of the T_C of $PbTiO_3$ particles, where the solid line is our calculation, solid triangles with the long-dashed line are Raman results and an empirical fitting from Ref. 14, and solid circles with the dashed line are specific heat measurements and an empirical fitting from Ref. 15. Figure 10 is the same for $BaTiO_3$, in which the solid line is our calculation and solid circles with the dashed line are the crystal axis ratio measurements and an empirical fitting from Ref. 18.

It can be seen from the two figures that the agreement between the experimental data and our theoretical calculation is good. A noticeable difference is that the critical size predicted by the theory is smaller than that by the empirical fitting. For $PbTiO_3$, the theoretically predicted critical size is 4.2 nm, while that from the empirical fitting is 13.8 nm (Ref. 14) or 9.1 nm.[15] For $BaTiO_3$, the corresponding two values are 44 and 115 nm,[18] respectively. The mechanism leading to the difference may be the polarization gradient, the noncrystalline surface layer, and depolarization effect. To clarify this, we can derive the size dependence of T_C by omitting the gradient term in Eq. (6):

$$T_C = T_{C\infty} - \frac{6D}{\delta A d} . \tag{13}$$

It has a similar form to the empirical formula in Refs. 14, 15, and 18. In addition, if there exists a noncrystalline layer, it will make the experimental size larger.

The neglect of the depolarization is another factor that makes the predicted critical size smaller. The depolarization effect in a film between two metal electrodes has been investigated in detail.[28,32,33] In particular, numerical estimates for the critical thickness have been given[33] for films in this configuration. However, it is difficult to compare them with the critical size in particles discussed in this paper since there are no electrodes.

As stated in Sec. III, the critical size can also be defined as the size at which the size-driven ferroelectric-paraelectric phase transition takes place. It provided an alternative way to determine the critical size. Figure 3 gives a critical size of 44 nm, which equals that from Fig. 10, as expected.

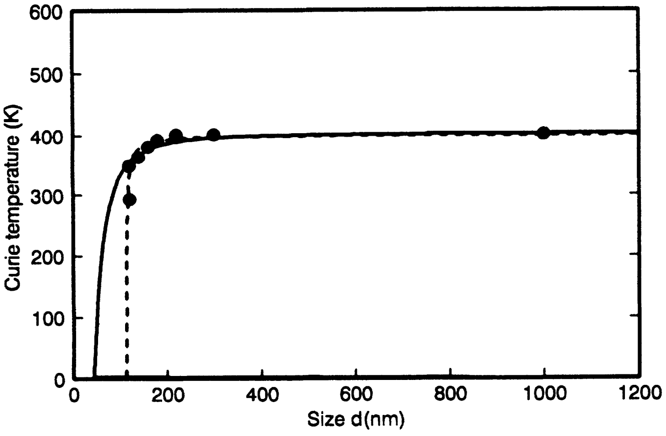

FIG. 10. Size dependence of the T_C of $BaTiO_3$ particles.

V. CONCLUSION

The Landau phenomenological theory is extended to spherical ferroelectric particles. Contrary to the situation in ferroelectric films, the extrapolation length δ in the particle is size dependent. An expression of δ is derived. Even if δ_∞ is negative, δ will become positive when d is small. The polarization decreases with decreasing particle size and eventually disappears; i.e., a size-driven phase transition takes place. The size-driven phase transitions have the same order as the temperature-driven phase transitions. The Curie temperature decreases with decreasing particle size and reaches zero at the critical size. The calculated size dependence of T_C for $PbTiO_3$ and $BaTiO_3$ is in agreement with the experimental results in the literature.

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