

## Thickness dependence of the dielectric susceptibility of ferroelectric thin films

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From the phenomenological theory, the size effects on dielectric properties of ferroelectric thin films were calculated. When the spontaneous polarization is reduced in the surface layer, the mean susceptibility of the film increases with the decrease in film thickness and a size-driven phase transition will take place at a critical thickness. If the temperature-driven phase transition of the bulk is a second-order one, the size-driven transition will be accompanied by a dielectric divergence; if it is a first-order transition, a finite dielectric peak will appear. When the spontaneous polarization is enhanced in the surface layer, the mean susceptibility of the film decreases with the decrease in film thickness. No size-driven phase transition and hence no dielectric anomaly will occur in this case.

### I. INTRODUCTION

With development in the field of ferroelectric thin films and composites, surface and size effects on ferroelectricity have aroused great interest in the past decade.<sup>1-12</sup> Based on the continuum mean-field theory, a form of free energy of ferroelectric thin films has been developed and a so called "extrapolation length"  $\delta$ , which measures the strength of coupling in the surface layer, was introduced to describe the changes of the local spontaneous polarization near a free surface of a ferroelectric thin film. Much work has been done on the phase transition temperature and polarization of ferroelectric thin films.<sup>3-7</sup> The dielectric susceptibility, a parameter of both theoretical and practical importance, has not received a thorough treatment in theoretical work. Experimentally, the dependence of the dielectric constant on the film thickness was mostly investigated on samples of the size around  $\mu\text{m}$ ,<sup>11,13-15</sup> which is much larger than the correlation length  $\xi$ . The results always suggest a low  $\epsilon_r$  region in the surface layer which may result from the interface between the electrodes and the films. For small particles, we noticed that the room-temperature dielectric constant of  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  is not a monotonic function of particle size, but has a maximum value at the size  $\sim 400$  (Ref. 16) and 100 nm (Ref. 17), respectively.

In the present paper, we will discuss the thickness dependence of dielectric susceptibility in ferroelectric thin films from the phenomenological free energy. Both cases where the bulk phase transition is second order and first order are treated, respectively, in Sec. II and Sec. III. Finally in Sec. IV, we summarize the main points of the present work.

### II. SIZE EFFECTS ON DIELECTRIC SUSCEPTIBILITY, SECOND-ORDER PHASE TRANSITION

We consider a monodomain ferroelectric thin film between two metallic electrodes in short circuit condition; the film thickness is  $L$  and the spontaneous polarization  $P$  is perpendicular to the film surface. This is the most important configuration for many applications of ferroelec-

tric thin films. The free energy  $F$  has an expansion of the form<sup>4,6</sup>

$$F/S = \int_{-L/2}^{L/2} dz \left[ \frac{1}{2} AP^2 + \frac{1}{4} BP^4 + C \left( \frac{dP}{dz} \right)^2 - \frac{1}{2} E_d \cdot P - E_{\text{ext}} \cdot P \right] + \frac{1}{2} C\delta^{-1}(P_-^2 + P_+^2), \quad (1)$$

where  $S$  is the surface area of the film with plane surface at  $z = \pm L/2$ .  $P_+$  and  $P_-$  is the spontaneous polarization at  $z = \pm L/2$ ,  $\delta$  is the extrapolation length, and  $E_{\text{ext}}$  is the external electric field. It is assumed that  $B > 0$ ,  $C > 0$ , and  $A = a(T - T_{0C})$ .  $T_{0C}$  is the bulk Curie temperature.  $E_d$  is the depolarizing field due to the change in local polarization, which is given by<sup>3</sup>

$$E_d(z) = -4\pi \left[ P(z) - \frac{1}{L} \int_{-L/2}^{L/2} P(z) dz \right]. \quad (2)$$

In the following calculation, in order to get a clear picture of the depolarizing field effects, we first omit  $E_d$  in Eq. (1), and then discuss the modification caused by it.

When  $E_d$  is omitted, the Euler-Lagrange equation resulting from Eq. (1) is

$$C \frac{d^2 P}{dz^2} - AP - BP^3 = -E_{\text{ext}} \quad (3)$$

with the boundary conditions

$$\frac{dP}{dz} = \pm \delta^{-1} P(z) \quad z = \mp L/2. \quad (4)$$

Suppose that the configuration is symmetric, i.e.,  $P_+ = P_- = P_1$ ; the polarization reaches its extreme value  $P(0)$  at the center of the film, and  $dP/dz = 0$  at  $z = 0$ . The first integration of Eq. (3) is

$$\frac{C}{2} \left[ \frac{dP}{dz} \right]^2 = \frac{1}{2} A [P^2 - P^2(0)] + \frac{1}{4} B [P^4 - P^4(0)] - E_{\text{ext}} [P - P(0)] . \quad (5)$$

Inserting Eq. (4) into (5), we have the relation between

$$z = \pm \int_{P(0)}^{P(z)} \left[ \frac{2C}{2A [P^2 - P^2(0)] + B [P^4 - P^4(0)] - E_{\text{ext}} [P - P(0)]} \right]^{1/2} dP . \quad (7)$$

The signs before the integration depend on the signs of  $\delta$ . Therefore, the polarization profiles can be obtained numerically from Eqs. (6) and (7). Calculating the polarization profiles for  $E_{\text{ext}} = 0$  and  $E_{\text{ext}} \neq 0$ , respectively, then we have the susceptibility profile

$$\chi_s(z) = \Delta P(z) / E_{\text{ext}} \quad (8)$$

and the mean susceptibility of the film

$$\chi_f = \frac{L}{2 \int_0^{L/2} \{1 / [\chi(z) + 1]\} dz} - 1 . \quad (9)$$

#### A. The case of $\delta > 0$

When  $\delta > 0$ , the polarization profiles for different film thickness are shown in Fig. 1, where the abscissa is reduced by the bulk correlation length  $\xi = (C/|A|)^{1/2}$  and the ordinate is reduced by the bulk spontaneous polarization  $P_b = (-A/B)^{1/2}$ . The polarization is lowered in the surface layer and decreases with the decrease in film thickness. The susceptibility profiles are shown in Fig. 2. Unexpectedly, near the surface the  $\chi_s$  is not monotonic, but has a maximum for  $L/\xi \gg 1$ . The same behavior was also found in the analytic solution of the susceptibility in the semi-infinite system.<sup>18</sup> As the film thickness decreases the susceptibility of the inner film increases and goes down fast near the surface.

The thickness dependence of the mean susceptibility  $\chi_f$  and the spontaneous polarization  $P(0)$  is shown in Fig. 3. With decreasing  $L/\xi$ ,  $P(0)$  decreases and reaches

$P(0)$  and  $P_1$ :

$$\delta^2 B P_1^4 + (2\delta^2 A - 2C) P_1^2 - 4\delta^2 E_{\text{ext}} P_1 - \delta^2 P(0) [B P^3(0) + 2A P(0) - 4E_{\text{ext}}] = 0 . \quad (6)$$

The polarization profiles are given by

zero at a critical thickness implying the vanishing of ferroelectricity; while the mean susceptibility increases and goes up rapidly near the critical thickness. The results indicate a size-driven phase transition from ferroelectric to paraelectric and it is accompanied by a dielectric divergence. We believe that this behavior is a manifestation of superparaelectricity as discussed by Cross.<sup>19</sup> The phenomenon is analogous to superparamagnetism in ferromagnetic fine particles. As the size decreases, ferromagnetism vanishes at a critical size, whereas the particle shows very high susceptibility under weak magnetic field.<sup>20</sup> For ferroelectric thin films, when the thickness is smaller than a critical value, the polarization cannot line up under thermoequilibrium because of the weakened long-range interaction by the sample size, but when a weak electric field is applied, they line up easily and show a large dielectric susceptibility.

#### B. The case of $\delta < 0$

It was found in triglycine sulfate<sup>11</sup> and potassium nitrate<sup>7</sup> that the Curie temperature increases with the decrease in film thickness. The phenomenon can be explained by supposing that the spontaneous polarization in the surface layer is enhanced ( $\delta < 0$ ). The polarization and susceptibility profiles for different film thickness are shown in Figs. 4 and 5. As the film thickness decreases,  $P(z)$  increases while  $\chi_s(z)$  decreases. Contrary to the case of  $\delta > 0$ ,  $\chi_s$  has a minimum near the surface. The thickness dependence of  $P(0)$  and  $\chi_f$  is shown in Fig. 6, no size-driven phase transition was found in this case.

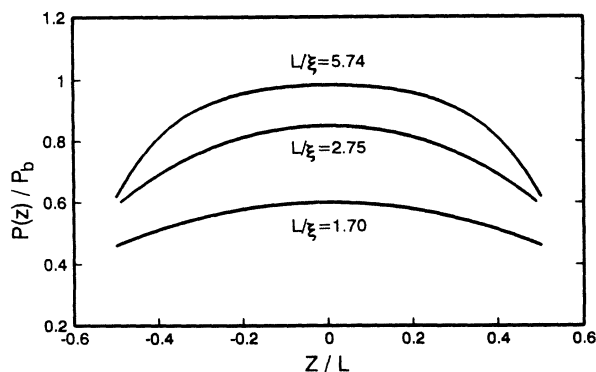


FIG. 1. The spontaneous polarization profiles in the films of different thickness for  $\delta/\xi = 1.41$ .

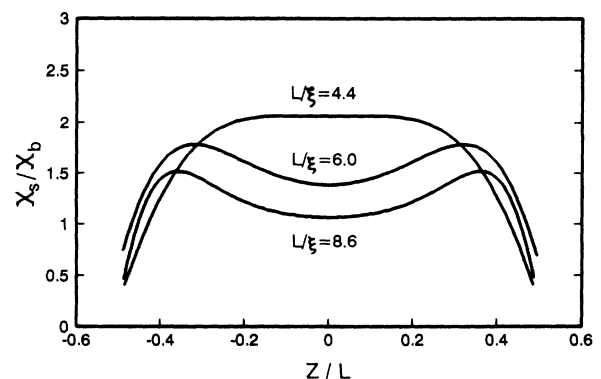


FIG. 2. The susceptibility profiles in the films of different thickness for  $\delta > 0$ .

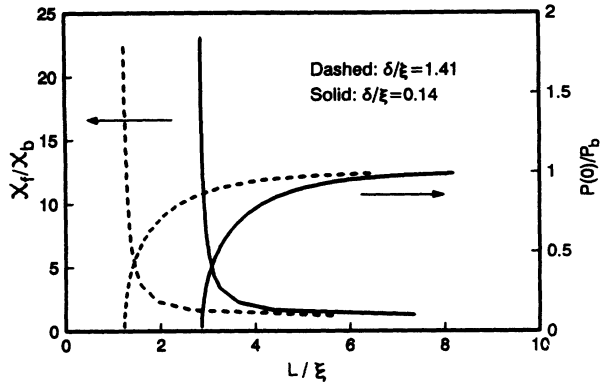


FIG. 3. The dependence of the mean susceptibility  $\chi_f$  and the spontaneous polarization  $P(0)$  on the film thickness for  $\delta > 0$ .

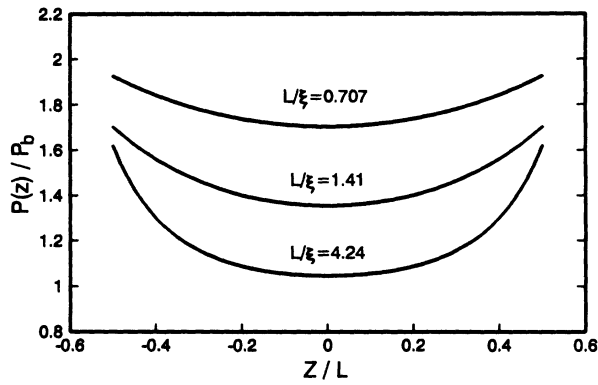


FIG. 4. The spontaneous polarization profiles in the films of different thickness for  $\delta/\xi = -1.41$ .

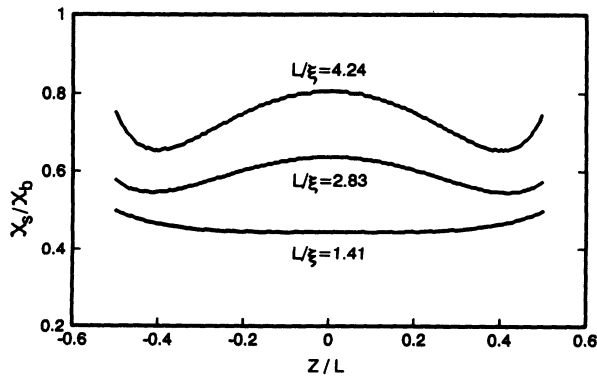


FIG. 5. The susceptibility profiles in the films of different thickness for  $\delta < 0$ .

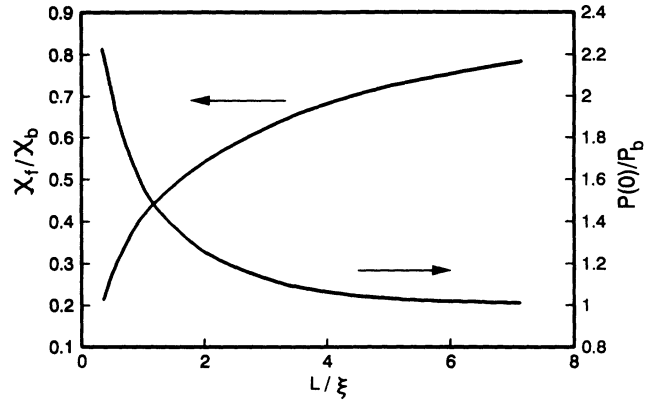


FIG. 6. The dependence of the mean susceptibility  $\chi_f$  and the spontaneous polarization  $P(0)$  on the film thickness for  $\delta/\xi = -1.41$ .

### C. The depolarizing field modification

Now take the depolarizing field into consideration. The Euler-Lagrange equation resulting from Eq. (1) is

$$C \frac{d^2 P}{dz^2} = AP(z) + BP^3(z) + 4\pi P(z) - E_{\text{ext}} - \frac{4\pi}{L} \int_{-L/2}^{L/2} P(z) dz ; \quad (10)$$

the boundary conditions are the same as Eq. (4).

Under the symmetry condition  $P_+ = P_- = P_1$ , the first integration of Eq. (10) is

$$\frac{C}{2} \left( \frac{dP}{dz} \right)^2 = \frac{1}{2} (A + 4\pi) [P^2 - P^2(0)] + \frac{1}{4} B [P^4 - P^4(0)] - (E_{\text{ext}} + 4\pi R) [P - P(0)] , \quad (11)$$

where

$$R = \frac{1}{L} \int_{-L/2}^{L/2} P(z) dz \quad (12)$$

is the mean polarization of the film. From Eqs. (11) and (4), the polarization profiles can be calculated numerically, and then we get the susceptibility profile and the mean

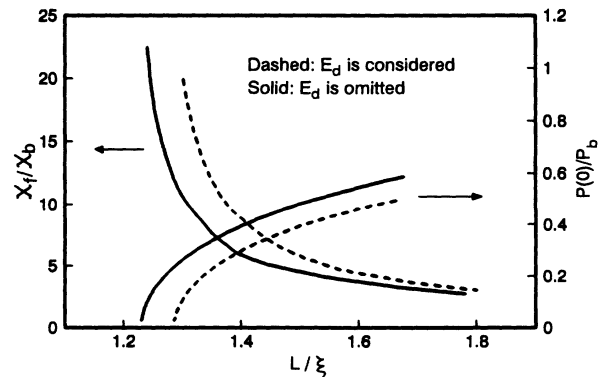


FIG. 7. The depolarizing field modification on the polarization  $P(0)$  and the mean susceptibility for  $\delta > 0$ .

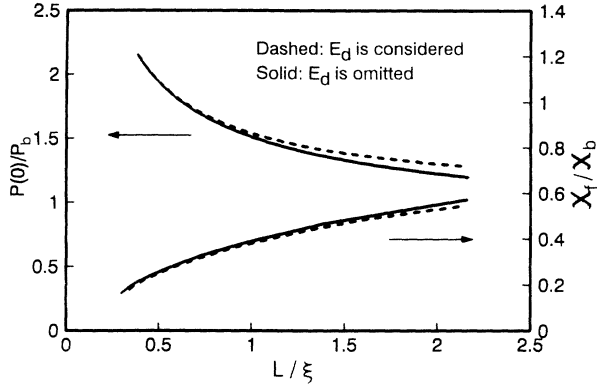


FIG. 8. The depolarizing field modification on the polarization  $P(0)$  and the mean susceptibility for  $\delta < 0$ .

susceptibility from Eqs. (8) and (9). The depolarizing field was determined by the iterative method.

When  $\delta > 0$ , Fig. 7 shows the thickness dependence of spontaneous polarization and mean susceptibility at the film thicknesses near the critical length. Compared with the case when the depolarizing field is omitted, the spontaneous polarization is depressed, while the mean susceptibility is increased. The critical length at which size-driven phase transition occurs shifts to a larger value.

It should be noticed that the depolarizing field discussed in this configuration is due to the change of local polarization, which is somewhat different from that discussed by Batra, Wurfel, and Siverman in ferroelectric-semiconductor systems.<sup>21</sup> The depolarizing field in that case is due to the lack of charge compensation, and a second-order phase transition in bulk is transformed to a first-order one in thin films. In the present case, however, the compensation is supposed to be ideal, our calculations for spontaneous polarization and the film free energy did not prove that the depolarizing field leads to the change of phase transition order.

When  $\delta < 0$ , the thickness dependence of  $P(0)$  and  $\chi_f$  is shown in Fig. 8. Compared with the case when  $E_d$  is omitted, the spontaneous polarization is enhanced, while the mean susceptibility of the film is reduced. But as the film thickness decreases, the depolarizing field effects are smeared. This is understandable because the polarization profile is smoother for  $L \ll \xi$  than that for thicker ones.

### III. SIZE EFFECTS ON DIELECTRIC SUSCEPTIBILITY, FIRST-ORDER PHASE TRANSITION

Most of the ferroelectric materials, such as  $\text{PbTiO}_3$ , and  $\text{BaTiO}_3$ , have a first-order phase transition. Therefore, in this section, we tackle the size effects on dielectric susceptibility when the bulk transition is first order. First-order phase transitions are modeled by taking the coefficient of the term in  $P^4$  in Eq. (2) to be negative and adding a term in  $P^6$  with a positive coefficient. The free energy of the film has the form

$$F/S = \int_{-L/2}^{L/2} \left[ \frac{A}{2} P^2 - \frac{B}{4} P^4 + \frac{C}{6} P^6 + \frac{D}{2} \left( \frac{dP}{dz} \right)^2 - \frac{1}{2} E_d P - E_{\text{ext}} P \right] dz + \frac{D}{2\delta} (P_-^2 + P_+^2), \quad (13)$$

where  $B, C, D > 0$  and  $A = a(T - T_0)$ ,  $T_0$  is the bulk Curie-Weiss temperature.

The Euler-Lagrange equation resulting from Eq. (13) is

$$D \frac{d^2 P}{dz^2} = AP(z) - BP^3(z) + CP^5(z) + 4\pi P(z) - E_{\text{ext}} - \frac{4\pi}{L} \int_{-L/2}^{L/2} P(z) dz \quad (14)$$

with boundary conditions

$$\frac{dP}{dz} \pm \delta^{-1} P(z) = 0 \quad z = \pm L/2. \quad (15)$$

Under the symmetry condition, the first integration of Eq. (14) is

$$\frac{D}{2} \left( \frac{dP}{dz} \right)^2 = \frac{(A + 4\pi)}{2} [P^2 - P^2(0)] - \frac{B}{4} [P^4 - P^4(0)] + \frac{C}{6} [P^6 - P^6(0)] - (E_{\text{ext}} + 4\pi R) [P - P(0)]. \quad (16)$$

As done in the above section, the polarization profiles and then the susceptibility profiles and the mean susceptibility can be calculated numerically from Eqs. (15) and (16). To show the depolarizing effects clearly, calculations for both the cases when  $E_d$  is omitted and considered are carried out separately.

#### A. The case of $\delta > 0$

When  $E_{\text{ext}} = 0$ , the thickness dependence of spontaneous polarization  $P(0)$  is shown in Fig. 9. For a definite film thickness, the spontaneous polarization may have two branches of solution. The solution corresponding to

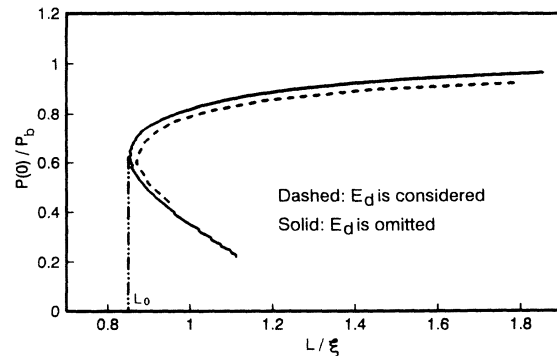


FIG. 9. The thickness dependence of spontaneous polarization  $P(0)$  when the bulk phase transition is first order.  $\delta/\xi = 1.41$ .

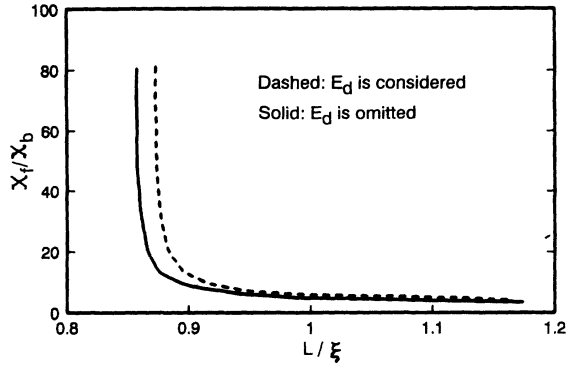


FIG. 10. The thickness dependence of the mean susceptibility when the bulk phase transition is first order.  $\delta/\xi = 1.41$ .

the lower value of polarization is not stable, therefore we are only interested in the branch of larger polarization. The spontaneous polarization decreases with the decrease in film thickness and vanishes abruptly at a critical thickness  $L_0$ , implying the vanishing of minimum film free energy. When the depolarizing field is considered, the critical thickness shifts towards a larger value.

The susceptibility profile in the film has a behavior similar to the case of the second-order phase transition, but the depolarizing field makes the profile smoother than the case when  $E_d$  is omitted. The thickness dependence of the mean susceptibility is shown in Fig. 10. The mean susceptibility increases with the decrease in film thickness and goes up anomalously near the critical thickness. Here again, when the depolarizing field is taken into consideration, the critical thickness is shifted to a larger value.

For the first-order phase transition, the Euler-Lagrange equation only guarantees the extreme value of the free energy. If the ferroelectric phase is stable, the free energy of it must be lower than the paraelectric phase, that is  $F < 0$ . Inserting  $P(z)$  into Eq. (9), the thickness dependence of free energy can be obtained as shown in Fig. 11 (the abscissa is actually the mean free energy per unit volume and has been reduced by the bulk one).

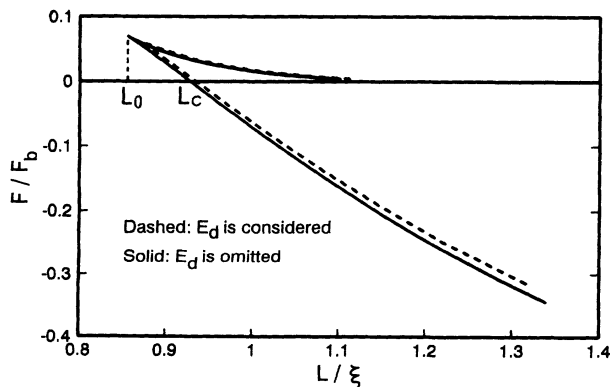


FIG. 11. The thickness dependence of film free energy for  $\delta > 0$ .

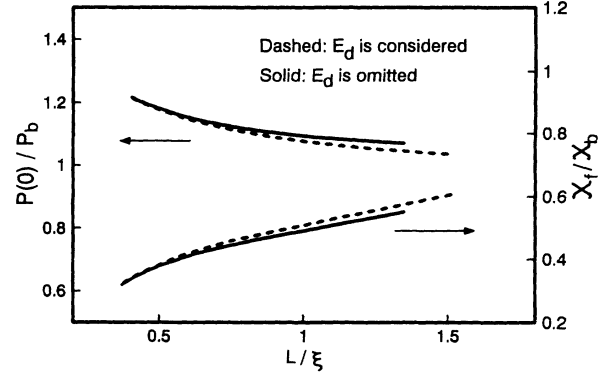


FIG. 12. The dependence of the mean susceptibility  $\chi_f$  and the spontaneous polarization  $P(0)$  on the film thickness for  $\delta/\xi = -1.41$ .

Corresponding to the two branches of polarization, the total free energy also has two branches. But the free energy corresponding to the lower value of polarization is always positive. Therefore we are only interested in the branch of large polarization. The free energy increases with decreasing film thickness and reaches zero at a critical thickness  $L_c$  ( $L_c > L_0$ ). For  $L_0 < L < L_c$ , the free energy of the film is positive. The stable ferroelectric phase in the film can only be maintained up to  $L_c$ , though the existence of the minimum of free energy can be maintained up to  $L_0$ . The results suggest that a size-driven phase transition also occurs in this case, but related to the disappearance of ferroelectricity, the susceptibility peak has a finite value. The phenomenon is very similar to the temperature-driven first-order phase transition.<sup>22</sup>

#### B. The case of $\delta < 0$

When  $\delta < 0$ , the spontaneous polarization is enhanced near the surface and increases with the decrease in film thickness. The susceptibility profile has a minimum near the surface, and decreases with the decrease in film thickness. The thickness dependence of the spontaneous polarization  $P(0)$  and the mean susceptibility  $\chi_f$  is shown in Fig. 12. As the film thickness decreases,  $P(0)$  increases while  $\chi_f$  decreases; no size-driven phase transition was found in this case.

#### IV. CONCLUSION

The susceptibility profile and its mean value as a function of the film thickness is calculated numerically for both second-order and first-order phase transitions. When the spontaneous polarization is reduced in the surface layer, the susceptibility profile has a maximum value near the surface; the mean susceptibility increases with the decrease in film thickness and a size-driven phase transition accompanied by a dielectric anomaly occurs at a critical thickness. When the spontaneous polarization is enhanced in the surface layer, the susceptibility profile has a minimum near the surface; the mean susceptibility decreases with the decrease in film thickness, no size-driven phase transition was found in this case.

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