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Landau theory of second-order phase transitions in ferroelectric films

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A detailed discussion is given of the predictions of the Landau-Devonshire theory for the behavior of thin ferroelectric films. It is assumed that the phase transition in the bulk is second order, and the theory is extended by the inclusion in the free-energy density of a term proportional to $|\nabla P|^2$ together with a boundary condition involving an extrapolation length δ. Expressions for the polarization profile $P(z)$ are given in terms of Jacobi elliptic functions; some of these are in a clearer and simpler form than has been available previously. Interesting analytic results for the entropy in terms of elliptic integrals and elliptic functions are also presented. Graphical illustrations of the main results are included. Careful consideration is given to the nature of the phase transition, and it is concluded that it is second order in all cases.

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I. INTRODUCTION

The way in which ferroelectric phase transitions may be modified by the presence of surfaces and interfaces has been studied for many years and has recently become of greater urgency because of the application of ferroelectric films in memory devices.[1–3] The most important early study was that due to the IBM group.[4–7] They considered a thin film between semiconductor electrodes so that the electric field was transverse to the film and produced a depolarizating field. They emphasized the point that the electrodes must be included as part of the thermodynamic system and their key result was that depolarization always tends to reduce the critical temperature of the film.

An alternative approach was initiated by the work of Lubensky and Rubin[8] on mean-field theory for phase transitions in semi-infinite media. Their idea was that for various reasons the order parameter, for example, polarization P in a ferroelectric, might be a function of distance from the surface. To include this, a term proportional to $|\nabla P|^2$ is added to the Landau-Devonshire (LD) free-energy density. The inclusion of this leads to a term in $\nabla^2 P$ in the Euler-Lagrange equation and this in turn means that a boundary condition on P at the surface is required. Clearly if $\mathbf{P}$ is parallel to the surface there is no depolarizing field and papers using purely the LD model often stipulate this restriction. A similar method[9] makes use of the Ising model in a transverse field (IMTF). The chain of reasoning used for the LD approach was already familiar in the continuum model of magnetism[10] where it is found that the term in $|\nabla M|^2$ arises from the bulk exchange interaction and the boundary condition reflects first a lower coordination number at the surface and second the fact that the surface exchange constants may be different from the bulk values. Similar results hold for the IMTF and the relationships between the IMTF and LD parameters have been established for both second-order[9] and first-order[11] phase transitions.

Many subsequent theoretical developments have pursued one or more of these basic models and because the ideas are, in a way, inescapable, the formalism has been reinvented more than once. Kretschmer and Binder[12,13] discussed the LD model for a semi-infinite medium and included depolarization effects for the special case of a perfectly conducting electrode. The implications of the LD model, without depolarization, for a film, were studied by Tilley and Zeks[14] for the case of materials in which the bulk transition is second order. The extension to first-order materials has been given by Scott *et al.*[15] and by Tan *et al.*[16] In Ref. 14 it is shown that the polarization profile $P(z)$, i.e., the variation of the polarization across the film, can be given explicitly in terms of Jacobi elliptic functions. Various important results, however, and in particular the expression for the critical temperature, can be given in terms of elementary functions. For first-order materials the differential equation for P is more complicated and in practice numerical methods are required.[15,16] The expression for the critical temperature derived in Ref. 14 shows a dependence on the film thickness L and this possible size dependence continues to attract attention.[17] The formalism of Ref. 14 has recently been presented anew[18] and some of the simpler results rederived. Qu *et al.*[19] have numerically evaluated the LD free energy and claim that even if the bulk transition is second order in some circumstances the film transition can be first order. We are not convinced by their argument, and we return to the point in Sec. II A. The LD free-energy functional for first-order materials[15,16] has been used by Ishikawa and Uemori[20] in their analysis of surface relaxation in $PbTiO_3$ and $BaTiO_3$ nanocrystals as determined by x-ray diffraction. Jiang and Burskill[21] use a variant of the LD method in which the expansion coefficients are given an assumed thickness dependence and they applied this formalism in a discussion of size effects in $PbTiO_3$ nanoparticles.

Similar calculations to those described for films have been presented for cylinders[22] and spheres,[23–25] with the size effect on the critical temperature again the main focus of interest. Some attention has also been given to calculation of the dielectric susceptibility within the LD model.[26,27]

A general framework for ferroelectric thin films with electric field normal to the interfaces should include both depolarization effects and the possible intrinsic variation of P. An expression for the free energy of a film with metal electrodes combining the LD free energy with the depolarization energy has been given[28,29] but so far little has been done to explore the implications. It should be mentioned also that Vendik

TABLE I. Size ranges in some recent work on ferroelectric nanoparticles. The first paper is concerned with application of a modified Landau-Devonshire (LD) theory to published data, and the remainder all report experimental work. Where LD theory is applied in the analysis, this is noted.

Ref. (date)	Materials/analysis	Size range
21 (1999)	Theory (modified LD)	applied to <50 nm
34 (1994)	$BaTiO_3$ crystallites/LD	10 nm–1 μm
35 (1997)	$BaTiO_3$ crystallite films	1–8 μm film, 8–35-nm crystals
36 (1997)	$(Ba, Sr)TiO_3$ films/LD	24–160 nm
37 (1999)	$(Ba, Sr)TiO_3$ ceramics	grains >100 nm
38 (1988)	$PbTiO_3$ particles	20–50 nm
39 (1993)	$PbTiO_3$ particles	20–200 nm
40 (1996)	$PbTiO_3$ films	>70 nm
41–43 (1999–2000)	$SrTiO_3$ films	0.3–2 μm
44 (1998)	SBT-BTN films	80–500 nm
45 (1999)	SBT films	~200 nm
46 (1999)	SBT films	170 nm
47 (1999)	$Pb(Zr, Ti)O_3$ films	100 nm–1 μm
49 (2000)	LB polymers/LD	0.5–20 nm

and coworkers[30,31] have used a formalism similar to the LD one with inclusion of a boundary condition on P in discussing the dielectric properties of $SrTiO_3$ and $Ba_xSr_{1-x}TiO_3$ films sandwiched between various electrodes. The work discussed so far is all based on a phenomenological treatment of the ferroelectric. Mention should also be made of the more fundamental approach taken by Zhou and Newns[32] and later by Sheshadri *et al.*[33] In both of these papers, the starting point is a Hamiltonian for the anisotropic lattice dynamics that ultimately leads to the phase transition.

Since the aim of this paper is theoretical, we do not give a critical review of the rapidly increasing body of experimental work on size effects in ferroelectric nanostructures. However, we believe it is worthwhile to list some recent papers, with no pretense at completeness, in the hope that these may give a way into the literature. Studies of $BaTiO_3$ and $Ba_xSr_{1-x}TiO_3$ nanocrystals,[34] films,[35,36] and ceramics[37] have been reported. Work on $PbTiO_3$ particles[38,39] and films[40] has appeared. Measurements on the low-temperature phonon spectra of films of the near-ferroelectric $SrTiO_3$ have been reported by Sirenko and co-workers[41–43] and these bear directly on the microscopic theories.[32,33] Raman measurements[41,43] are interpreted in terms of microstructural inhomogeneities in the film. The combination of far-infrared ellipsometry,[42] low-frequency dielectric measurements,[42] and Raman spectroscopy[43] shows that the soft-mode frequency is increased in these films relative to the bulk value and in agreement with the Lyddane-Sachs-Teller relation the static dielectric constant $\varepsilon(0)$ is reduced. Application of a static electric field further hardens the soft mode and reduces $\varepsilon(0)$.[43] A number of studies on various ferroelectric thin-film structures may also be cited[44–47] and a general review of the whole topic is given in a recent monograph.[48]

In view of the growing interest in the properties of ferroelectric thin films, we believe it is worthwhile to reconsider the results that can be derived from the basic LD model. It might be said that with the trend to lower thicknesses the LD model has outlived its usefulness but in our view this is not so and in fact it is timely to extend the known body of results. In support of this, we present in Table I a summary of thickness and size scales in a representative selection of recent work on ferroelectric nanoparticles. It is seen that in almost all cases the size is upwards of 20 nm. The LD model would generally be regarded as applicable for sizes above about 20–50 nm and it is noteworthy that it is used in the analysis of the experimental results for the thinnest films[49] in the table. As far as applications go, Auciello *et al.*[2] mention thicknesses of less than 200 nm as necessary for future nonvolatile ferroelectric random-access memory (NVFRAM's), while Scott[50] discusses the possibility of thicknesses as low as 30 nm. The purpose of this paper is to clarify the general analytic solution for a film of a second-order material, to give it in the most convenient form for subsequent generalization to multiple layers, and to give a much fuller account of the basic thermodynamic functions than has been done previously. We include a careful analysis of the order of the phase transition.

II. FORMALISM AND POLARIZATION PROFILES

The free energy is written in the form[14]

$$\frac{F}{S}=\int_{-L/2}^{L/2}dz\left[\frac{A}{2\varepsilon_0}P^2+\frac{B}{4\varepsilon_0^2}P^4+\frac{D}{2\varepsilon_0}\left(\frac{dP}{dz}\right)^2\right]+\frac{D}{2\varepsilon_0\delta}(P_-^2+P_+^2), \tag{1}$$

where S is the area of the film with plane surfaces at $z=\pm L/2$ and $P_\pm=P(\pm L/2)$. The constants B and D are positive and A is taken in the form $A=a(t-1)$ where $t=T/T_{C0}$ with T_{C0} the critical temperature of the bulk material. The D term inside the integral in Eq. (1), which represents the additional free energy due to spatial variation of P, may be regarded as well established since it is necessary in the theory of incommensurate structures[51,52] and in models of domain walls.[53] The final term involving δ is symmetry allowed and leads to a necessary boundary condition. It can also be derived from the continuum limit of the IMTF.[9] Variation of Eq. (1) about the equilibrium form $P(z)$ shows that this satisfies the Euler-Lagrange equation

$$D\frac{d^2P}{dz^2}-AP-\frac{B}{\varepsilon_0}P^3=0 \tag{2}$$

with boundary conditions

$$\frac{dP}{dz}\pm\delta^{-1}P=0 \quad \text{at } z=\pm L/2. \tag{3}$$

It follows from Eq. (3) that if the extrapolation length δ is positive, $P(z)$ turns down near the surface, and if it is negative, $P(z)$ turns up. In consequence, the critical temperature T_C of the film is reduced below T_{C0} for positive δ and increased for negative δ. A detailed study of the size dependence of T_C in a film has been given recently.[17]

Equation (2) has a first integral (energy integral) which leads to

$$\frac{dP}{dz}=\pm\left(\frac{B}{2D}\right)^{1/2}\left(\frac{P^4}{\varepsilon_0^2}+\frac{2A}{B\varepsilon_0}P^2+\frac{4G}{B}\right)^{1/2}, \tag{4}$$

where G is the constant of integration. The extremum of $P(z)$ is at $z=0$ so that the central value $P(0)$ is a solution of the quadratic equation corresponding to $dP/dz=0$:

$$P^4+\frac{2\varepsilon_0 A}{B}P^2+\frac{4\varepsilon_0^2 G}{B}=(P^2-P_1^2)(P^2-P_2^2)=0, \tag{5}$$

where the roots P_1^2 and P_2^2 have been introduced for later use; we order the roots as $P_2^2>P_1^2$. It follows from Eq. (5) that the product $P_1^2P_2^2$ has the same sign as G and it will be seen that while P_2^2 is always positive for both signs of δ, in the case of $\delta<0$ there is a temperature interval in which G and therefore P_1^2 are negative.

The P integral resulting from Eq. (4) can be expressed by inverse elliptic functions[54–56] so that ultimately $P(z)$ is expressed in terms of an elliptic function. The detailed forms depend on the sign of δ.

A. $\delta>0$

In this case it can be shown that $0\leqslant G\leqslant A^2/4B$ so that, P_1^2 and P_2^2 are both positive. Since positive δ leads to a decrease of $P(z)$ at the surface of the film we have the inequalities $0\leqslant P(z)\leqslant P_1\leqslant P_2$. The central value $P(0)$ is the maximum value of $P(z)$ and is in fact equal to P_1. The expression for $P(z)$ is

$$P(z)=P_1\,\mathrm{sn}(K-z/\xi,\lambda) \tag{6}$$

in standard notation for elliptic functions.[54] The modulus λ is given by

$$\lambda=P_1/P_2, \tag{7}$$

$K\equiv K(\lambda)$ is the complete elliptic integral, and the scale length ξ is

$$\xi=(2\varepsilon_0^2D)^{1/2}/(B^{1/2}P_2). \tag{8}$$

Equation (6) is an alternative form of the much more cumbersome expression given previously,[14] to which it is related by linear transformation into Legendre's standard form.[54]

The expressions in Eqs. (5)–(7) depend on the one temperature-dependent parameter G, which is found from the boundary condition (3). Substituting from Eq. (6) we find that this takes the form

$$\frac{\xi}{\delta}\mathrm{sn}\left(K-\frac{L}{2\xi}\right)-\mathrm{cn}\left(K-\frac{L}{2\xi}\right)\mathrm{dn}\left(K-\frac{L}{2\xi}\right)=0. \tag{9}$$

Examples of polarization profiles $P(z)$ calculated from Eqs. (6) and (9) have been published previously[14] and will not be emphasized here. In this study we concentrate on the temperature dependence of the parameters G, $P(L/2)$, and P_1, and related thermodynamic functions.

It is in the present case of positive δ that Qu *et al.*[19] suggest that the phase transition may be of first order and we now explore this possibility. We start by finding from Eq. (9) the temperature T_{CF} for which $P_1\to 0$ and therefore $P(z)$ for all z tends to zero. If the transition is first order, then T_{CF} has the significance of a critical superheating temperature for the ferroelectric phase. When $P_1\to 0$ then also $G\to 0$, $\lambda\to 0$, and $K\to\pi/2$. The elliptic functions then reduce to trigonometric functions and Eq. (9) gives for T_{CF}, which is less than the bulk critical temperature T_{C0}:

$$\tan(L/2\xi_1)=\xi_1/\delta, \tag{10}$$

where

$$\xi_1=(D/|A|)^{1/2} \tag{11}$$

is the usual temperature-dependent coherence length. Now the point about Eq. (10) is that it is *identical* to the expression for the critical supercooling temperature for the paraelectric phase. This was shown previously[14] but it may be helpful to review the argument. To find the supercooling temperature we imagine that the temperature is lowered from above T_{C0}; the supercooling temperature is the one at which the solution $P=0$ of Eq. (2) becomes unstable for infinitesimal perturbations. This can be found by solving the linearized form of Eq. (2) subject to the boundary conditions. The solution is

$$P(z)=P_0\cos(z/\xi_1) \tag{12}$$

with ξ_1 given by Eq. (11) and P_0 arbitrary. Substitution into the boundary conditions gives the equation for the supercooling temperature, which is easily seen to be the same as Eq. (10). Now the issue seems clear: for a first-order transition the thermodynamic critical temperature lies between the supercooling and superheating temperatures. When these are equal, as here, then there cannot be any hysteresis and the transition must be second order.

The above argument may be seen as quite satisfactory. However, the claim for a first-order transition[19] is based on a

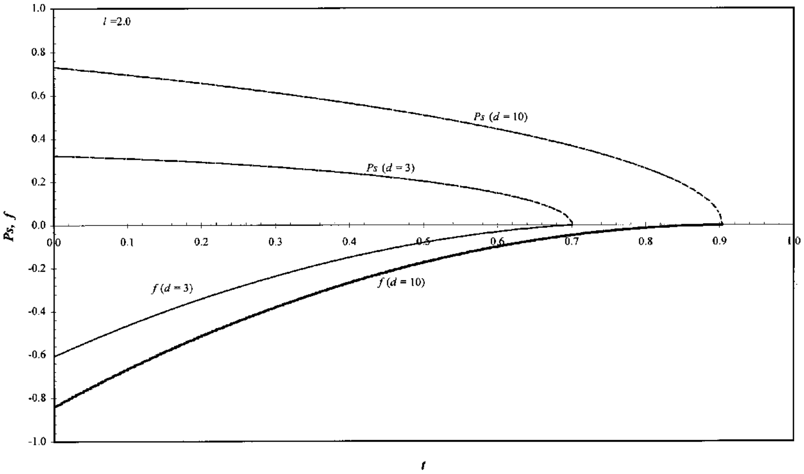

FIG. 1. Temperature dependence of the surface polarization p_s found from Eq. (6) and of the free energy $f = FB/a^2S$ calculated by substitution of Eq. (6) in Eq. (1) for $\delta = 3$ and 10.

statement that the free energy, given by the variational minimum of Eq. (1), is positive in some temperature interval below T_{CF}. For the sake of completeness therefore we discuss this possibility. First, it is not difficult to show that when the solution (12) is substituted into Eq. (1) the quadratic part of *F*, including the surface term, vanishes because of the boundary condition (10); the corresponding result for negative δ was pointed out previously.[14] Now we consider some temperature *T* below T_{CF} and apply a variational argument. We use Eq. (12) as the variational function with the value of ξ_1 given by Eq. (11) with *A* as the value for T_{CF}: $\xi_1 = (D/|A_{CF}|)^{1/2}$ with $A_{CF} = a(T_{CF} - T_{C0})/T_{C0}$, which is negative because $T_{CF} < T_{C0}$. In view of Eq. (10) this function satisfies the boundary conditions. Note that $A_D = A(T_{CF}) - A(T)$ is positive because $T < T_{CF}$. Substitution of Eq. (12) into Eq. (1) produces a number of elementary integrals which can be evaluated to yield

$$\frac{F}{S} = -\frac{1}{2}A_D P_0^2\left[\frac{L}{2} + \frac{\xi_1}{2}\sin\left(\frac{L}{\xi_1}\right)\right] + \frac{1}{4}BP_0^4\left[\frac{3L}{8} + \frac{\xi_1}{4}\sin\left(\frac{L}{\xi_1}\right) + \frac{\xi_1}{32}\sin\left(\frac{2L}{\xi_1}\right)\right]. \tag{13}$$

Since the coefficient of P_0^2 is negative and the coefficient of P_0^4 is positive, the minimum value of *F* found within this approximation is negative, and therefore the exact value must also be negative. We have verified this proof that *F* is negative for $T < T_{CF}$ by numerical evaluation using the exact solution (6) for a selection of values of the parameters and an example is shown in Fig. 1. The forms of the graphs are consistent with the functional dependences $F \propto (T_{CF} - T)^2$ and $P_s \propto (T_{CF} - T)^{1/2}$ that might be expected from Eq. (13). We now simplify the notation by identifying $T_{CF} \equiv T_C$.

B. $\delta < 0$

In this case the analytic work is more complicated because there is a temperature interval $T_0 \leqslant T \leqslant T_C$ in which $G < 0$ and $P_1^2 \leqslant 0 \leqslant P_2^2 \leqslant P^2(z)$. In the interval where *G* is negative, $P(z)$ takes the form, as previously derived,[14]

$$P(z) = \frac{P_2}{\mathrm{cn}(z/\zeta, \lambda_1)}, \tag{14}$$

where the modulus is given by

$$\lambda_1^2 = -P_1^2/(P_2^2 - P_1^2) \tag{15}$$

and the scaling length by

$$\zeta^2 = \frac{2\varepsilon_0^2 D}{B(P_2^2 - P_1^2)}. \tag{16}$$

The temperature dependence of *G*, and therefore of all the parameters in Eq. (14), are derived from the boundary condition (3), which gives

$$\mathrm{sn}\left(\frac{L}{2\zeta}\right)\mathrm{dn}\left(\frac{L}{2\zeta}\right) + \frac{\zeta}{\delta}\mathrm{cn}\left(\frac{L}{2\zeta}\right) = 0. \tag{17}$$

At lower temperatures, $T < T_0$, the parameters satisfy the inequalities $G > 0$, $0 < P_1^2 < P_2^2 < P^2(z)$ and the polarization profile is found to be

$$P(z) = \frac{P_2}{\mathrm{sn}(K - z/\xi, \lambda)}, \tag{18}$$

where λ and ξ are given by the previous expressions (7) and (8) and $K \equiv K(\lambda)$ as before. Equation (18) is an improvement on the previous expression,[14] and is related to it by linear transformation into Legendre's standard form. Application of the boundary condition (3)–(15) gives the equation for the temperature dependence of *G*, etc.:

$$\mathrm{cn}\left(K - \frac{L}{2\xi}\right)\mathrm{dn}\left(K - \frac{L}{2\xi}\right) + \frac{\xi}{\delta}\mathrm{sn}\left(K - \frac{L}{2\xi}\right) = 0. \tag{19}$$

At the temperature T_0 which divides the regions where Eqs. (14) and (18) apply, $G = 0$. The *P* integral in Eq. (4) is elementary at this particular temperature and insertion of the solution into the boundary condition (3) gives the equation for T_0:[14]

$$\tan(L/2\xi_1) = -\xi_1/\delta. \tag{20}$$

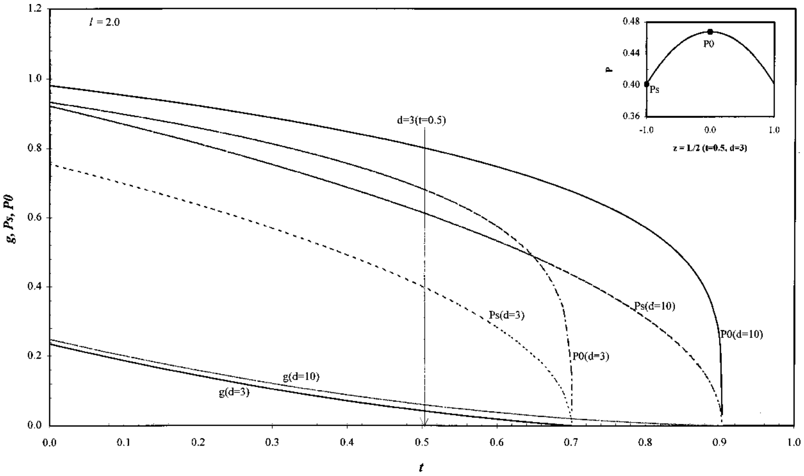

FIG. 2. Temperature dependence of g, p_0, and p_s for the two positive values $d=3$ and 10. The inset shows the polarization profile $P(z)$, calculated from Eq. (6), for $d=3$ and $t=0.5$ (section marked).

The film critical temperature T_C is found from Eqs. (14) and (17). As $T\rightarrow T_C$, $\lambda_1\rightarrow 1$ so that the elliptic functions become hyperbolic and Eq. (17) simplifies to

$$\tanh(L/2\xi_1) = -\xi_1/\delta. \tag{21}$$

It is accepted that for negative δ the film phase transition is second order. For the sake of completeness, we point out that Eq. (21), which in principle gives the critical superheating temperature of the ferroelectric phase, is identical to the expression previously derived[14] for the critical supercooling temperature of the paraelectric phase. This confirms that the phase transition is second order.

III. THERMODYNAMIC FUNCTIONS

We now turn to a more explicit discussion of the entropy and specific heat than has been given before. The expression for the entropy Σ is derived from Eq. (1) by means of $\Sigma = -(\partial F/\partial T)_P$, and this leads to[14]

$$\frac{\Sigma}{S} = \frac{1}{2}\frac{dA}{dT}\int_{-L/2}^{L/2} P^2 dz. \tag{22}$$

The integral in Eq. (22) can be evaluated explicitly for all three expressions in Eqs. (6), (14), and (18). First, for positive δ substitution of Eq. (6) gives

$$\frac{\Sigma}{S} = -\frac{a\xi P_2^2}{\varepsilon_0 T_{C0}}\left[\frac{L}{2\xi} - E(L/2\xi) + \frac{\lambda^2\,\mathrm{sn}(L/2\xi)\,\mathrm{cn}(L/2\xi)}{\mathrm{dn}(L/2\xi)}\right], \tag{23}$$

where $E(L/2\xi)$ is the incomplete elliptic integral of the second kind, the modulus of the elliptic functions is λ, given by Eq. (7), and ξ is given by Eq. (8). For negative δ the results are

$$\frac{\Sigma}{S} = -\frac{a\xi P_2^2}{\varepsilon_0 \lambda T_{C0}}\left[\frac{L}{2\xi} - E(L/2\xi) + \frac{\mathrm{dn}(L/2\xi)\,\mathrm{sn}(L/2\xi)}{\mathrm{cn}(L/2\xi)}\right] \quad \text{for } 0<T<T_0 \tag{24}$$

and

$$\frac{\Sigma}{S} = -\frac{a\zeta P_2^2}{\varepsilon_0 T_{C0}(1-\lambda_1^2)}\left[\frac{L}{2\zeta} - E(L/2\zeta) + \frac{(1-\lambda_1^2)\,\mathrm{sn}(L/2\zeta)\,\mathrm{cn}(L/2\zeta)}{\mathrm{dn}(L/2\zeta)}\right] \quad \text{for } T_0<T<T_C. \tag{25}$$

The heat capacity is

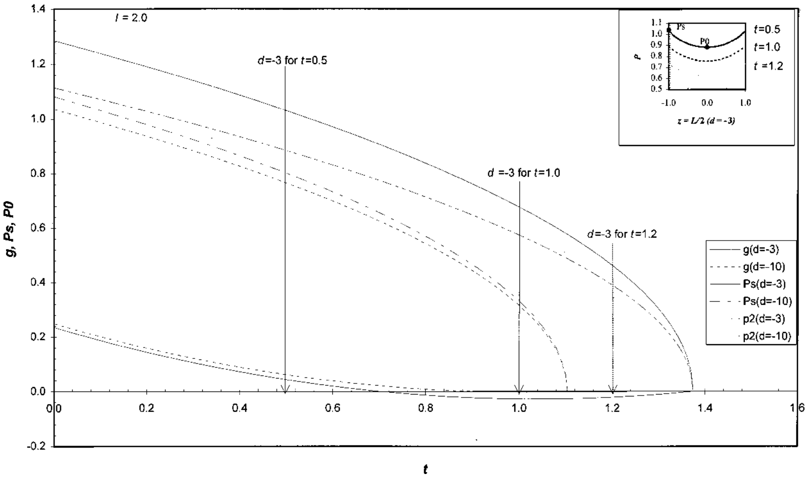

FIG. 3. Temperature dependence of g, p_0, and p_s for the two negative values $d=-3$ and -10. The inset shows profiles $P(z)$ for $d=-3$. These are calculated from Eq. (14) for $t=0.5$ and from Eq. (18) for $t=1.0$ and 1.2.

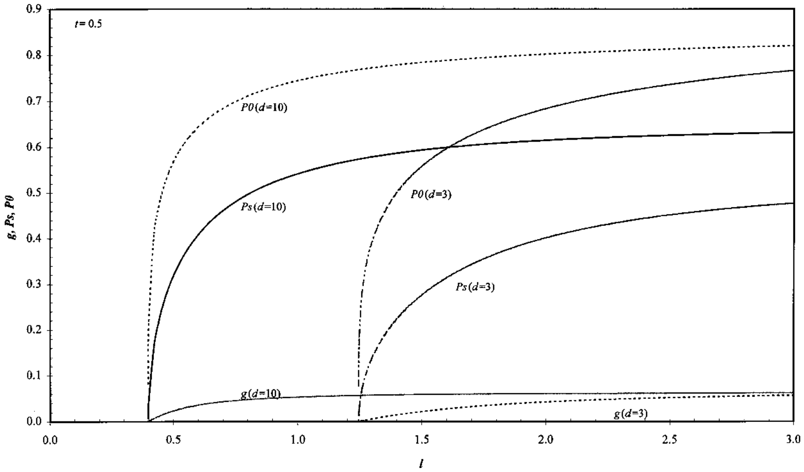

FIG. 4. Dependence on dimensionless thickness l of g, p_0, and p_s at temperature $t=0.5$ for surface parameters $d=3$ and 10.

$$C=T\frac{d\Sigma}{dT}. \tag{26}$$

The temperature dependence in Eqs. (23)–(26) is partly explicit, through the arguments of the elliptic functions, but in addition there is an implicit part arising from the temperature dependence of the parameter G as shown subsequently in Figs. 2 and 3. For the illustrations in the next section we have therefore evaluated Eq. (26) by numerical differentiation of the entropy curves.

IV. NUMERICAL RESULTS

We present here a range of graphical results based on the formulas that have been derived. The graphs use a number of dimensionless variables, defined as follows:

$$t=T/T_{C0}, \tag{27}$$

where T_{C0}, as in Eq. (1), is the bulk critical temperature.

$$l=L/\xi_0, \tag{28}$$

where L is the film thickness and ξ_0 is the zero-temperature value of the length ξ_1 that is defined in Eq. (11), namely $\xi_0=(D/a)^{1/2}$;

$$g=GB/a^2, \tag{29}$$

$$P_0=P(0)/P_{0\infty}, \tag{30}$$

where $P(0)$ is the central $(z=0)$ value of $P(z)$ and $P_{0\infty}$ is the zero-temperature value for a bulk material, i.e., $P_{0\infty}=(\varepsilon_0 a/B)^{1/2}$;

$$P_s=P(L/2)/P_{0\infty}, \tag{31}$$

where $P(L/2)$ is the surface value; and finally

$$d=\delta/\xi_0, \tag{32}$$

where δ is the surface extrapolation length of Eqs. (1) and (3).

Figures 2 and 3 show the temperature dependence of parameters g, p_0, and p_s for two positive and two negative values of δ. The variation with temperature of the energy integral g is obtained from Eq. (9) for positive δ and from Eqs. (17) and (19) for negative δ. For positive δ, g decreases from a positive value at $T=0$ to zero at the critical temperature T_C. For negative δ there are two régimes: $g>0$ for $T<T_0$ and $g<0$ for $T_0<T<T_C$ where T_0 is given by Eq. (20). It follows from the formulas of Sec. II that the temperature dependence of p_0 comes partly from its dependence on g. Because of Eqs. (6), (14), and (18), $P(0)$ at all temperatures is equal to P_1 (positive δ) or P_2 (negative δ), the quantities defined in Eq. (5). The surface polarization, $P(L/2)$

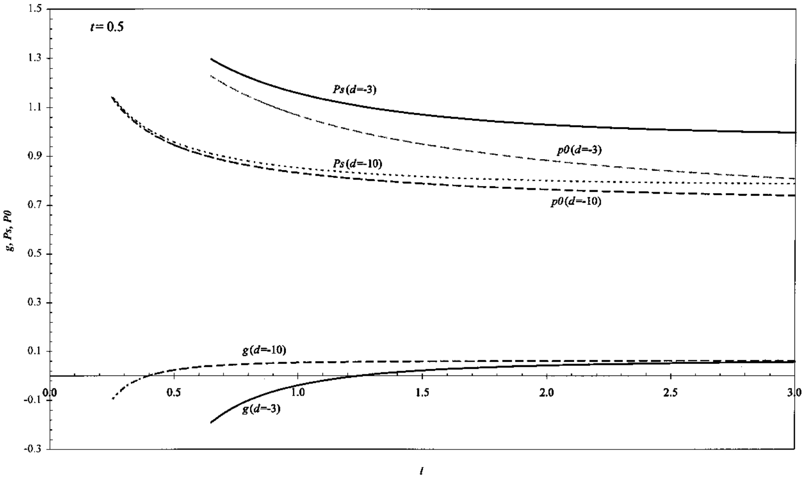

FIG. 5. Dependence on dimensionless thickness l of g, p_0, and p_s at temperature $t=0.5$ for surface parameters $d=-3$ and -10. For all negative d, the values diverge for $l\rightarrow 0$ as $p_0\rightarrow\infty$, $p_s\rightarrow\infty$, and $g\rightarrow-\infty$; the graphs shown are truncated at convenient points.

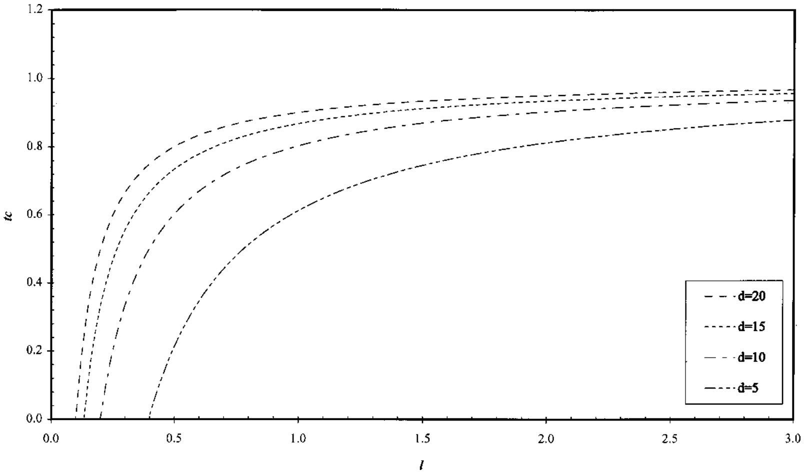

FIG. 6. Dependence on dimensionless thickness l of the critical temperature $t_C = T_C / T_{C0}$ for $d = 5$ (lowest curve), 10, 15, and 20 (highest curve).

$= P(-L/2)$ is calculated from the same equations. For both positive and negative δ, a continuous change of p_0 and p_s with temperature is consistent with the fact that the phase transition in this model is second order.

There continues to be considerable interest in the study of the size effect on the phase transition properties of ferroelectric particles and films.[17] We show in Figs. 4 and 5 some results for the thickness dependence of g, p_0, and p_s. The limiting behavior of p_0 and p_s when δ is positive, Fig. 4, can be deduced analytically from Eq. (6). First, suppose that the temperature t is fixed. When the thickness approaches the critical value L_C at which p_0 and p_s vanish for this t then $G \to 0$ and $T \to T_C (< T_{C0})$. Hence $P(0) \to 0$ [in this case $P(0)$ is P_1] and in addition $P(\pm L/2) = P_1 \,\mathrm{sn}(K - L/2\xi) \to 0$. With this condition, from Eq. (10) we have $\tan(L_C/2\xi_C) = \xi_C / \delta$, where $\xi_C = \xi_0 / \sqrt{\Delta T}$ and $\Delta T = T_{C0} - T_C$. Thus the critical thickness of the film is

$$L_C(t) = 2\xi_C \tan^{-1}\left(\frac{\xi_C}{\delta}\right). \tag{33}$$

As stated in the caption, in the case of negative δ p_0 and p_s do not show a similar size effect; in fact, g becomes more negative as L decreases with the consequence that p_0 and p_s ultimately diverge.

For positive δ it is also of interest to define a critical thickness L_{1C} as the value for which the film critical temperature T_C given by Eq. (10) vanishes. When $T_C \to 0$, it follows from Eq. (11) that $\xi_1 \to \xi_0 / \sqrt{T_{C0}}$ so that Eq. (10) gives

$$L_{1C} = \frac{2\xi_0}{\sqrt{T_{C0}}} \tan^{-1}\left(\frac{\xi_0}{\delta\sqrt{T_{C0}}}\right) \tag{34}$$

which shows the dependence on δ of the critical thickness for which $T_C \to 0$. As $\delta \to \infty$, $L_{1C} \to 0$. Some results are shown in Fig. 6.

In the case of negative δ, the size dependence of t_C is found from Eq. (20) and some results are plotted in Fig. 7. As seen there, t_C increases with decreasing l and the effect becomes more marked as $\delta \to 0$.

The analytic expressions for the thermodynamic functions presented in Sec. III are new, as far as we know, and we now give some illustrations of the results. The analytic expressions for the entropy in Eqs. (23)–(25) are plotted in Figs. 8 and 9 for typical positive and negative δ values. For both positive and negative δ the entropy is continuous for the whole range of temperature with $\Sigma \to 0$ (the paraelectric-phase value) at T_C. Exactly the same graphs for the entropy are obtained by numerical integration of Eq. (22). As men-

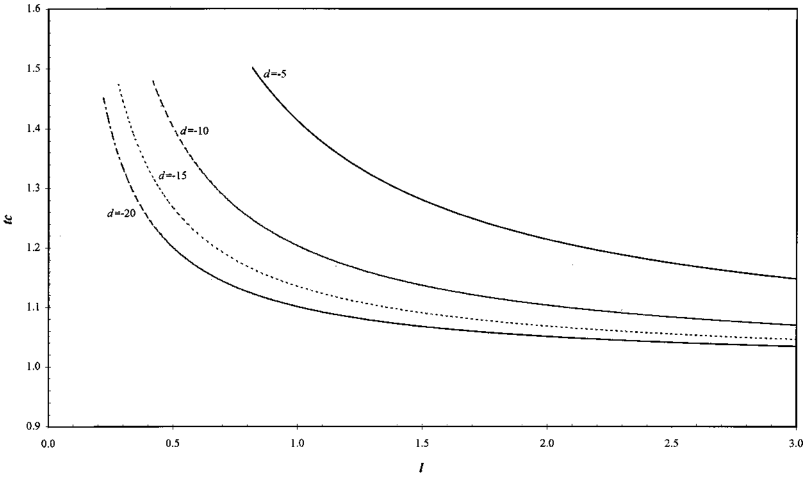

FIG. 7. Dependence on dimensionless thickness l of the critical temperature $t_C = T_C / T_{C0}$ for $d = -5$ (highest curve), -10, -15, and -20 (lowest curve).

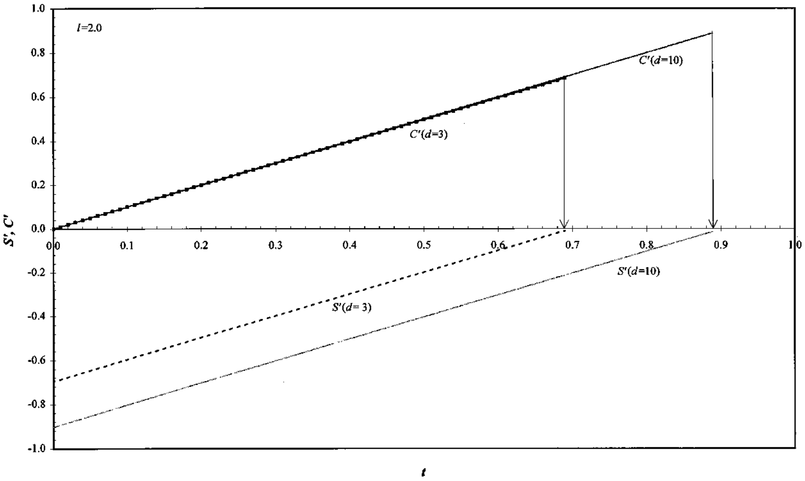

FIG. 8. Temperature dependence of the entropy $S' = \Sigma/(a^2\xi_0/T_{C0}B)$ and heat capacity $C' = C/(a^2\xi_0/T_{C0}B)$, where $C = T d\Sigma/dT$ for $l=2$ and $d=3$ (dashed curves), $d=10$ (continuous curves).

tioned previously, the heat capacity is found from Eq. (26) by means of numerical differentiation. As is to be expected for these second-order phase transitions, for both positive and negative δ there is a finite discontinuity in the heat capacity at the film critical temperature T_C.

We draw attention to the fact that on the curves for negative δ, Fig. 9, both Σ and C are continuous through the bulk critical temperature T_{C0} $(t=1)$. This is of some interest. For a semi-infinite medium with $\delta<0$, it is a well-known result[8,12,13] that two phase transitions should be seen, the higher-temperature one at $T_{CS}>T_{C0}$ for which the surface orders, and the second at $T_{CB}\equiv T_{C0}$ for which the bulk orders. By analogy, we speculated earlier[14] that as L becomes large, in addition to the phase transition at $T_C>T_{C0}$ an ''incipient bulk transition,'' marked by some specific-heat anomaly, should appear at T_{C0}. Our numerical work now shows that this is not so. The reason appears to be that the coherence length ξ_1 of Eq. (11) diverges as $T\rightarrow T_{C0}$. Thus the ''surface phase'' penetrates deep into the bulk for temperatures near to T_{C0} and the limit $L/\xi_1\rightarrow\infty$ is unattainable.

V. DISCUSSION

We have given a detailed account of a range of analytic results that can be derived from the model summarized in Eq. (1). For the sake of illustration in Sec. IV we have used the simple temperature dependences $A=a(T/T_{C0}-1)$ and $B=\text{const}$. These cannot be expected to hold over the whole temperature range in a real material but the analytic results of the paper in Secs. II and III hold for any temperature dependence of these parameters. In view of the increasing interest in ferroelectric films we think it is worthwhile to present our results on this well studied model. First, we have corrected some misconceptions in the literature. Second, the results give a basis for a number of possible extensions. Discussion of ferroelectric superlattices is growing[57–62] and it should be possible to extend the present work to find polarization profiles and thermodynamic functions for superlattices. In devices the electric field is transverse to the film so inclusion of the depolarization field is an important matter. Since a rather general free-energy expression including the effects of depolarization is available[27,28] and other approaches have appeared in the literature[63] it should be possible to extend the present results to include depolarization. Likewise the extension to first-order materials could be taken beyond what is known at present.[15,16] Both of these generalizations would have to be primarily numerical and we believe that our analytic results would be useful in guiding numerical work.

We have assumed that the LD parameters in Eq. (1) are independent of the film thickness L. This is the conventional view[64] and it is based on the fact that in the derivation of Eq.

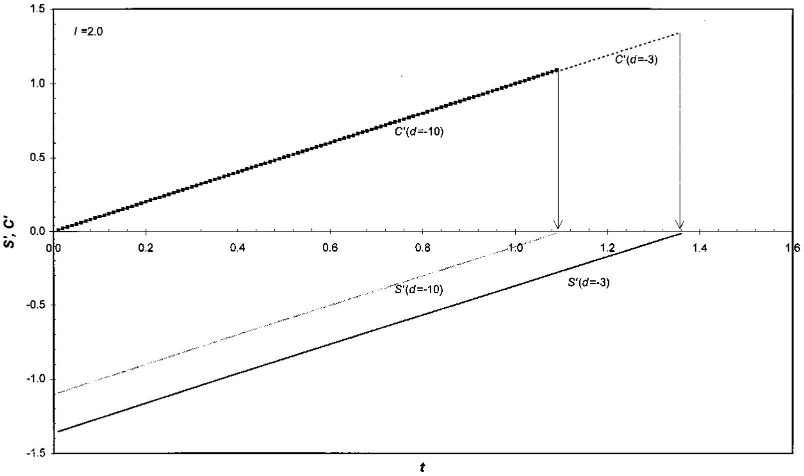

FIG. 9. Temperature dependence of the entropy $S' = \Sigma/(a^2\xi_0/T_{C0}B)$ and heat capacity $C' = C/(a^2\xi_0/T_{C0}B)$, where $C = T d\Sigma/dT$ for $l=2$ and $d=-3$ (dashed curves), $d=-10$ (continuous curves).

(1) as the continuum limit of the IMTF (Refs. 9, 11, and 64) it is found that the coefficients are indeed independent of L. The derivation given in Ref. 9 and later[11,64] is for a semi-infinite medium, but the proof goes through for a film provided the integral for the free energy runs from $-L/2$ to $L/2$ rather than 0 to ∞. The basic condition for the derivation to hold is that the film is sufficiently thick for a continuum variable $\langle S_z \rangle$ to be defined as an average over a volume some lattice constants across. It is not necessary, for example, that L should be large on the scale of the coherence length defined in Eq. (11). It is the requirement for L to be relatively large on the atomic scale that underlies the view, mentioned in Sec. I, that a thickness of somewhat greater than 20 nm is required for applicability of the LD theory. We mentioned in Sec. I that Jiang and Burskill[21] have proposed a model for ferroelectric thin films in which the parameters A and B are thickness as well as temperature dependent. This may be a very useful approach for analyzing experimental results but one may ask where the thickness dependence comes from. One approach would be to take the present formalism and introduce the spatial average of the polarization $\overline{P} = \int_{-L/2}^{L/2} P(z)\,dz$. An expansion of the free energy in terms of $\overline{P}$ could be constructed with use of our expressions for $P(z)$ and the parameters $\overline{A}$ and $\overline{B}$ in that expansion would automatically depend on L.

The most uncertain parameter in this formulation is the ‘‘extrapolation length’’ δ that appears in the free energy (1) and therefore in the boundary condition (3). Since the Euler-Lagrange Eq. (2) is a second-order differential equation some boundary condition is necessary and is usually invoked.[20,30,31] A similar question arises in formulations using the IMTF where the different surface coordination number and possible different surface exchange constant lead to a spatial variation $P(z)$; as mentioned in Sec. I expressions for δ in terms of the IMTF constants have been derived.[9,11] Some discussion of the physical origin of the boundary condition for perovskites is given by Ishikawa and Uemori[20] and they suggest that the relaxation of the c/a ration near surface may play a major part. Vendik and Zubko[30] analyze capacitance measurements on films of the ‘‘incipient ferroelectric’’ $SrTiO_3$ ($T_C \approx 0$ K) with gold and high-T_C superconductor (YBCO) electrodes with the tentative conclusion that $\delta \approx 0$ for the Au electrodes and $\delta \approx \infty$ for YBCO. The first result, however, does not apply for $Ba_xSr_{1-x}TiO_3$ in contact with a Pt electrode.[31] Finally in this context, we should like to draw attention to our own proposal[65] that far-infrared spectroscopy, as a dynamic probe, may be much more sensitive for ferroelectric size effects than quasistatic measurements like capacitance.

The implications of the free energy (1) for a bulk material, that is, Eq. (1) without the final surface-related term, have been extensively discussed in the literature on statistical physics, but since the emphasis here is specifically on ferroelectric films it is not relevant to discuss this literature in detail. It is worth pointing out that for the bulk material a soliton contribution to the specific heat has been discussed,[66,67] although as far as we are aware there is no experimental evidence for this contribution in bulk ferroelectrics, for which the LD result applies quite accurately. Our expressions derived in Sec. III and illustrated in Sec. IV are the generalization of the bulk LD result and could therefore serve as a starting point in the analysis of thin-film specific heats. It is possible that a soliton contribution should appear as a correction to the results derived in Sec. III. However, in order to estimate the magnitude of this term it would be necessary to extend the soliton calculations to the finite geometry described by Eq. (1) with the final term included. This would be likely to lead to a lengthy analysis, partly because of the asymmetry in Eq. (1) between the z axis and the other axes. This analysis has not yet been attempted and since there is no compelling experimental evidence to show that it is necessary we regard it as lying beyond the scope of the present paper.

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