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Effective Landau–Devonshire-Type Theory of Phase Transitions

in Ferroelectric Thin Films Based on the Tilley–Zeks Model

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A generalized thermodynamic theory (effective Landau–Devonshire-type theory) for ferroelectric thin films undergoing second order phase transition is developed within the framework of the Landau–Ginzburg theory via the concept of extrapolation length � in the Tilley–Zeks model. The free energy of the Tilley–Zeks model for ferroelectric thin films is cast into a clearer and simpler form from the usual integral expression form using suitable order parameters. The target coefficients A and B for the second order and fourth order terms, respectively, of the free energy are expressed as a function of temperature, film thickness, extrapolation length and other physical parameters. The intrinsic effects of surface on the order of phase transitions are discussed analytically with an emphasis on asymmetric films.

KEYWORDS: ferroelectricity, thin films, phase transitions   
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| 1. | Introduction | effective LD-type theory. By examining the quantity A from |
| the second order term of the free energy, the exact |

Ferroelectric thin films are intensively studied because of their promising applications in memories devices.1)In thin films, a surface modified layer may develop at the surface and has a crucial influence on phase transitions in ferro-electric films. Many studies have found that the physical properties of ferroelectric thin films are quite different from that of bulk materials and significantly depend on the surface conditions of films.2,3)With an increasing trend towards greater miniaturization, surface and interface become an increasingly important factor in functioning of devices. Thus, from the applications point of view, understanding of the intrinsic effects of surface is crucial as they control the characteristics of the films, e.g. polarization reversal and dielectric properties.

Since the Landau–Devonshire (LD) theory gives a very good account for much of the data on bulk ferroelectrics, it is natural that extensions to films should be sought. One approach has been to apply the Landau–Ginzburg (LG) free energy to account for the intrinsic surface effect by the

expressions for determining the critical thickness of a ferroelectric thin film has been discussed as a function of temperature, film thickness and other physical parameters for symmetric and asymmetric surface conditions.

In this article, we extend the previous study11)by deriving the effective LD-type free energy up to fourth order terms. By the introduction of suitable order parameters, a complete TZ free energy for second order ferroelectric thin films is cast into a simpler and clearer form without the necessity of integrating over thickness. The intrinsic effect of surface on the order of phase transitions for ferroelectric films is studied by examining the target coefficients A and B for the second order and fourth order terms.

The present article is organized as follows. The basic thermodynamic relations for the model are formulated and presented in §2. In §3, a complete derivation for ferroelectric films undergoing second order transition is discussed with emphasis on asymmetric films. General discussion and conclusion are presented in §4.

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| concept of extrapolation length � as well as the ‘‘gradient’’ | 2. | Theory |
| energy.4–10)The framework was firstly applied to semi- |

infinite medium with depolarization effects by Krestchmer and Binder.4)Tilley and Zeks5)extended the semi-infinite model4)to the second order ferroelectric thin films by ignoring the depolarization (the Tilley–Zeks model). The Tilley–Zeks (TZ) model5)was then theoretically analysed by Ishibashi et al.6)and reconsidered by Ong et al.7)recently. Scott et al.8)and Tan et al.9)analysed numerically a first order ferroelectric film by extending the Landau–Devonshire free energy up to sixth order term. The claim by Scott et al.8) that there are two phase transitions, one by the surface polarization and the other by the bulk polarization, has been discussed in detail recently by Ishibashi and Iwata.10)   
 Recently, Ishibashi et al.11)analytically derived the LD free energy for ferroelectric thin films on the basis of the TZ model. The free energy for the second order ferroelectric thin films is expressed in a simpler and clearer form, identical to the original LD expression but with a redefined order parameter. This theory is here referred to as an

We consider a one-dimensional model with the order parameter and related physical quantities varying with coordinate z without including the depolarization effect. The LG free energy per unit area for a ferroelectric film of thickness L with a second-order phase transition is

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| F ¼1 | �Z L=2�L=2 | | | f p;dp� dz | �dz þ1 2� p2��þ  þ | þp2��� | | � | � | ð1Þ |
| with | | | | | | | | | | |
| f p;dp� dz | | � | ¼1 2�p2 þ 1 4�p4 þ 1 2� dp� | | | | �2 | ð2Þ | | |
| where � ¼ aðT � T0Þ. Since � is directly related to temper-ature, it is often referred below to as a ‘‘temperature | | | | | | | | | | |

parameter’’ or loosely as ‘‘temperature’’. a, � and � are temperature-independent positive coefficients. T and T0 represent the temperature and transition temperature of the ferroelectric. � is the ‘‘gradient’’ coefficient determining the

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energy cost owing to the inhomogeneity of polarization pðzÞ. The final surface term in eq. (1), where the so-called

extrapolation length �� is used, is physically and mathemati-

cally closely related to the ‘‘gradient’’ term as it comprises

the surface field contribution in the formation of the possible

variation of polarization pðzÞ. The interrelation of the two terms is reflected by the use of the same coefficient �. The

surface term in eq. (1) leads to the boundary conditions for

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| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Z | � | dp | �2 | dz | Z | � | dp | �dp: |
|  | � | dz | � | ¼ | Z | � | dz |  |

By adopting pm as the new order parameter, eq. (7) can be

rewritten in terms of pm as

F ¼1 2Ap2 mþ 1 4Bp4 m; ð8Þ

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| pðzÞ | dp p | 0 | at | zL | 3a | where A and B are the target coefficients which now depend |
| on temperature, film thickness, extrapolation length and |
| other related physical parameters. |
| and | dzþ�þ | ¼ |  | ¼ | ðÞ |  |
| The free energy of eq. (8) is an effective LD-type free |
| energy which is in a simpler and clearer form compared to |

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| dp  dzþ p�� | ¼ 0 | at | z ¼ �L 2: | ð3bÞ |

The intrinsic effects of the film surfaces on polarization are

described by the extrapolation length ��. pþ and �þ represent the surface polarization and extrapolation length

at z ¼ L=2, respectively, whereas p� and �� at z ¼ �L=2. Vendik and Zubko suggested that the boundary conditions as

the free energy of the TZ model as expressed in eq. (1) with the usual integral form. Exact expressions for the physical properties of thin films can now be obtained from eq. (8). In the present study, the nature of transition below the film critical temperature is examined by looking into the sign of coefficient B. The sign of coefficient B when A ¼ 0 gives the order of transition at the film critical temperature.

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| described in eq. (3) were realized in the case of SrTiO3 film capacitor with superconducting electrodes.12) | 3. | Derivation of Target Coefficients for Asymmetric |
| Ferroelectric Films |

In the present model there are four length scales characterizing the thin film and its transitions, i.e., L, ��and �. The final one � is determined by � and � as � ¼ ð��=�Þ1=2for � < 0, and as � ¼ ð�=�Þ1=2for � > 0. Physical properties of the system such as the transition temperature, critical thickness, average polarization, etc., are governed by the interplay of these scales.

For �� > 0, the polarization is suppressed at the film surfaces. The degradation of polarization at film surface is commonly observed in most perovskite ferroelectrics.13,14) On the other hand, it was reported that the polarization is enhanced near the surface of 4-nm-thick PbTiO3 and 12-nm-thick BaTiO3 ultrathin films.15,16)The enhancement of polarization at the film surface is represented by �� < 0. In equilibrium, minimization of F gives the Euler–

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| Lagrange equation for pðzÞ  �d2p   dz2 ¼ �p þ �p3 | ð4Þ |

with boundary conditions eq. (3). From eq. (4), integrate once gives

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| 2� dp� | �2 | þ I ¼1 2�p2 þ 1 4�p4; | ð5Þ |

where I is the constant of integration.

The integration constant I of eq. (5) is independent of z and thus may be evaluated at a convenient point, e.g., at the extremum of polarization pðzÞ. Let dp=dz ¼ 0 at z ¼ zm and pðz ¼ zmÞ ¼ pm, then   
 I ¼1 2�p2 mþ 1 4�p4 m: ð6Þ

Manipulations of eq. (1) together with eq. (5) give

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| F� | Z | � | dp | �dp I1 | � | � | p2   þ | p2  � | � | 7 |
| ¼ | Z | � | dz | þ þ | L | � | �þ | þ�� |  | ðÞ |

where use is made of the equality

The derivation of the target coefficients A and B as in eq. (8) for symmetric and asymmetric cases is discussed in this section. Symmetric films correspond to the films with the same surface conditions at both boundary surfaces. As modern electronic devices consist of films on substrate, films are generally constrained by asymmetric boundary condi-tions. For instance, one surface is placed on substrate and the other is a free surface, not counting the electrodes. Experimentally,17)the asymmetric behavior of thin films is reflected in, e.g., a shift of p–E (p: polarization; E: electric field) loop with respect to the E-axis. While extensive theoretical studies have been made for thin film,5–11)most theories have treated the symmetric surface conditions, except the recent work by Ishibashi et al.11)Under this circumstance we put the emphases on the asymmetric cases, since the symmetric film can be regarded as a special case of the asymmetric film.

For polarization suppressed or enhanced at both film surfaces, the asymmetrical properties of films are described by extrapolation lengths of the same sign albeit with different magnitudes: the ‘‘positive–positive’’ or ‘‘nega-tive–negative’’ surface conditions. More interesting asym-metrical surface conditions are described by extrapolation lengths with different signs: the ‘‘positive–negative’’ surface conditions.

3.1 Positive–positive surface conditions   
 For the ‘‘positive–positive’’ case, the extrapolation lengths are set as

�þ 6¼ �� > 0: ð9Þ The extremum of polarization,11)where dp=dz ¼ 0, is located at some point within the film thickness determined by the values of �þ and ��. By taking the extremum of polarization pm as the transition parameter, the free energy of eq. (8) for the ‘‘positive–positive’’ case can be expressed in terms of pm. The surface polarizations pþ and p� at z ¼ L=2 and z ¼ �L=2, respectively, are smaller than the bulk

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value and are expressible (up to order p4) as

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| p2�� | � | p2 bþ p2   p2 b  ���p2 m� 1�p2 bþ p2 1  ��  " 1 ��p2 bþ p2 p2 b  ���2 # p4 m | � | ð10Þ |
| � |
| where the bulk polarization pb is given by p2 b¼  ��=�ð� < 0Þ, and p2 The free energy as a function of the new order parameter��denotes �=��2�. | | | | |

pm is obtained by substituting eq. (10) into eq. (7). After a

tedious mathematical manipulation (see Appendix A), the

coefficients in the free energy function of eq. (8) are found as

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| --- | --- | --- | --- |
| A ¼ � þ | ffiffiffiffiffiffiffiffiffi p | ð�0� þ �0þÞ | ð11Þ |
| and  B ¼ � þ �5 8L r ffiffiffiffiffiffiffiffi ð�0� þ �0þÞ  þ �1 4L r ffiffiffiffiffiffiffiffi�ðsin 2�0� þ sin 2�0þÞ ð12Þ  þ1 8ðsin 4�0� þ sin 4�0þÞ�;  where �0� ¼ cos�1 ness L dependence of A and B for given constants �, �, � and p ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi . These show the thick-  the surface parameters ��. Equation (12) clearly shows that  below the film critical temperature A < 0, the coefficient B is | | | |

always a positive value for given L and �� implying the film is of second order transition.

Let us examine A and B for special cases of �þ and ��. For free boundary conditions with both �þ and �� being infinite, eqs. (11) and (12) are reduced to A ¼ � and B ¼ �, respectively, irrespective of L, as they should. Thus, there

is no effect of thickness. When both �þ and �� are zero, eqs. (11) and (12) are reduced to

and A ¼ � þ�p ffiffiffiffiffiffiffiffiffi ð13Þ

B ¼ � þ �5�r ffiffiffiffiffi~~ffi~~ffiffi : ð14Þ

Thus, if L is infinite, we see that A ¼ � and B ¼ �, again as they should.

The transition point is given by A ¼ 0, from which the relationship between the critical thickness Lc and ‘‘critical

temperature parameter’’ �c is determined. By using these �c

and Lc, the B at the critical point, Bc, is given. If Bc is

positive, the transition will be likely of the second order. As

can be seen from the above, for infinite �þ and ��, the transition is characterized by �c ¼ 0 and Bc ¼ �, which is positive, thus implying the transition is of the second order.

On the other hand, for zero �þ and ��, the relation between the critical temperature parameter �c and the critical

thickness Lc is given as Lc ¼ �3�=8. p ffiffiffiffiffiffiffiffiffiffiffiffiffi , leading to Bc ¼

For general �þ and ��, the relation between the critical temperature parameter �c and the critical thickness Lc given

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| --- | --- | --- | --- | --- |
| Lc ¼ | r | ffiffiffiffiffi~~ffiff~~iffiffiffi | ð�0� þ �0þÞ | ð15Þ |

while the B at the critical point is given as

|  |  |
| --- | --- |
| Bc ¼3 8� þ � 1 4L r ffiffiffiffiffiffiffiffi�ðsin 2�0� þ sin 2�0þÞ  þ1 8ðsin 4�0� þ sin 4�0þÞ�: | ð16Þ |

The order of transition at the film critical temperature can be examined from eq. (16), and is found to be the second order.

conditions at the two film surfaces are identical: p2 p2 symmetric films can be easily obtained from eqs. (11) and sand p2   
For symmetric films with �þ ¼ �� ¼ �, the boundary

�þ¼ p2��¼ p2�. Thus, the coefficients A and B for þ¼ p2�¼

(12).

3.2 Negative–negative surface conditions   
 For the ‘‘negative–negative’’ case, the extrapolation lengths are set as

�þ 6¼ �� < 0: ð17Þ Similar to the previous case, the extremum of polarization11) pm is located within the film thickness and we adopt the minimum value of polarization pm as the new order

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| parameter. The surface polarization p� is related to pm, pb  and p�� as  p2���p2 b� p2 p2 b  ���p2 mþ 1�p2 b� p2   1  ���  �" 1 ��p2 b� p2 p2 b  ���2 # p4 m ð18Þ  where the bulk polarization pb is given by p2 b¼ �=�  ð� > 0Þ. p2 The thickness L dependence of the coefficients A and B for��denotes as before �=��2�. |

given material constants �, �, � and the surface parameters

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| �� are (Appendix B) | L ffiffiffiffiffiffi p | ð�0� þ �0þÞ | ð19Þ |
| A ¼ � � |
| and |
| B ¼ � � �5 8L r ffiffiffiffi�ð�0� þ �0þÞ  þ �1 4L r �ðsin 2�0� þ sin 2�0þÞ ð20Þ  þ1 8ðsin 4�0� þ sin 4�0þÞ�;  where �0� ¼ tanh�1 second order, irrespective of thickness L and surface p ffiffiffiffiffiffiffiffiffiffiffiffiffi . The nature of transition is of  parameters ��.  For films with no thickness effect, both �þ and �� are  infinite. Equations (19) and (20) automatically reduced to | | | |

A ¼ � and B ¼ � without dependence on film thickness L, as expected. For both �þ and �� approaching zero from the negative side, the hyperbolic functions in eqs. (19) and (20) become complex values, implying that the transition temper-

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| by A ¼ 0 is | ature increases in proportion to the inverse sequare of ��. But this limit is of academic interest because the shift of the |

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transition temperature to infinity is not physically plausible. For general boundary conditions (non-zero �þ and ��), the nature of transitions for the film at the critical region can be

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| examined by setting A ¼ 0. Thus   Bc ¼3 8� þ � 1 4L r �ðsin 2�0� þ sin 2�0þÞ  þ1 8ðsin 4�0� þ sin 4�0þÞ� | | | | | ð21Þ  ð22Þ |
| with | Lc ¼ | r | ffiffiffiffiffiffi� | ð�0� þ �0þÞ: |

Equation (21) clearly indicates that the order of transition is

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| critical temperature for non-zero �þ and �� can be examined  similarly as in the previous cases. By letting A ¼ 0, we have  Bc ¼3 8� þ � 1 4L r ffiffiffiffiffiffiffiffi�ðsin 2�0� � sin 2�0þÞ  þ1 8ðsin 4�0� � sin 4�0þÞ�: ð25Þ | | | |
| with | Lc ¼ | r ffiffiffiffiffi~~ffi~~ffiffi ð�0� � �0þÞ: | ð26Þ |
| Equation (25) showed that the transition is also of second | | | |

order at the film critical temperature.

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| of second order at the film critical temperature. | 3.3.2 | � > 0 |

3.3 Positive–negative surface conditions   
 For the mixed-sign11)case (one extrapolation length is positive, the other negative), no extremum of pðzÞ is found within the film thickness. The extremum of polarization ph (hypothetical polarization) is located at z ¼ zh (outside the film). For generalization, we denote h ¼ m, thus, ph ¼ pm and zh ¼ zm. Two possibilities of polarization profile exist for the ‘‘positive–negative’’ surface condition case:11)(i)� > 0 and (ii) � < 0. Without loss of generality we take that the surface polarization pþ at z ¼ L=2 is described in terms of the positive extrapolation length �þ and p� at z ¼ �L=2 the negative extrapolation length ��.

3.3.1 � < 0   
 For � < 0, the extremum of pðzÞ where dp=dz ¼ 0 is located at z ¼ zm < �L=2 with j�þj < j��j. By adopting pm as the transition order parameter, the free energy of eq. (8) is now expressed in term of pm. The surface polarization p� is related to pm, pb and p�� by eq. (10).

The free energy as a function of the new order parameter pm is obtained by substituting eq. (11) into eq. (7). The thickness L dependence of coefficients A and B are given as (Appendix C.1)

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| --- | --- | --- | --- |
| A ¼ � þ | ffiffiffiffiffiffiffiffiffi p | ð�0� � �0þÞ | ð23Þ |
| and  B ¼ � þ �5 8L r ffiffiffiffiffiffiffiffi ð�0� � �0þÞ  þ �1 4L r ffiffiffiffiffiffiffiffi�ðsin 2�0� � sin 2�0þÞ ð24Þ  þ1 8ðsin 4�0� � sin 4�0þÞ�;  where �0� ¼ cos�1  easily found that B > 0 for given L and �� (�� < 0 and p ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi   . From eq. (24), it is  �þ > 0 with j�þj < j��j) indicating the film is of second order transition.  Analytical studies of eqs. (23) and (24) for both �þ and ��  infinite leads to A ¼ � and B ¼ �, which is consistent with physical phenomena for no surface effect. For the case of | | | |

both �þ and �� zero, we found that eqs. (23) and (24) reduce to eqs. (13) and (14), respectively, as expected.

The effect of surface on the nature of transition at the film

For � > 0, the extremum of pðzÞ where dp=dz ¼ 0 is at z ¼ zm > L=2 with j�þj > j��j. The surface polarization p�is related to pm, pb and p�� as in eq. (15). The coefficients in the free energy are given as (Appendix C.2)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| and | A ¼ � � | | L ffiffiffiffiffiffi p | ð�0� � �0þÞ | ð27Þ |
| B ¼ � � �5 8L r ffiffiffiffi�ð�0� � �0þÞ  þ �1 4L r �ðsin 2�0� � sin 2�0þÞ ð28Þ  þ1 8ðsin 4�0� � sin 4�0þÞ�;  where �0� ¼ tanh�1 second order transition regardless of L and ��. p ffiffiffiffiffiffiffiffiffiffiffiffiffi . It is seen that the film is of  From eqs. (27) and (28), the analytical study for �þ ¼�� ¼ 0 and �þ ¼ �� ! 1 leads to similar results as discussed in the ‘‘negative–negative’’ case. For general �þ  and ��, the nature of transition at the film critical temper-  ature can be examined by the usual method by setting A ¼ 0, thus | | | | | |
| Bc ¼3 8� þ � 1 4L r �ðsin 2�0� � sin 2�0þÞ  þ1 8ðsin 4�0� � sin 4�0þÞ�; | | | | | ð29Þ |
| with | Lc ¼ | r ffiffiffiffiffiffi�ð�0� � �0þÞ | | | ð30Þ |

which is of second order transition.

4. Discussions

In this article, a generalized thermodynamics theory for ferroelectric thin films undergoing second order phase transition is developed within the framework of the TZ model. The free energy for ferroelectric thin films is cast from the usual integral form into a simpler and clearer LD form which can be more readily applied to realistic situations. A comprehensive study on the intrinsic effects of surface on the order of transition for films with symmetric and asymmetric boundary conditions has been performed by looking into the coefficients A and B, which are expressed in

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terms of temperature, film thickness, surface conditions and other related physical parameters.

Compared to the previous works on the influence of surface and thickness on ferroelectrics thin film undergoing second order transition, the present model (the effective LD-type theory) together with Ong et al.5)support the TZ model that for the case of symmetric case where the extrapolation length �þ and �� are equal, the added surface energy is expected not to affect the order of transition of the films. However, the most important results in the present study are concerned with films constrained with asymmetric boundary conditions, which are less emphasized in most literatures in spite that they correspond to more realistic situations. For asymmetric films with equal sign in extrapolation lengths, as well as mixed signs case, it is found that the order of transition is still of second order for given L and ��.

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Appendix A: Positive–Positive Surface Conditions

From eqs. (5) and (6), we find

|  |  |  |
| --- | --- | --- |
| dp  dz¼ | r ffiffiffiffiffiffiffiffi s ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi~~ffiffif~~fiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi  r ffiffiffiffiffi~~ffi~~ffiffi ðp2 m� p2Þ1=2 1 � 1� 4p2 b ðp2 mþ p2Þ� | ðA:1Þ |
| � |
| where p2 b¼ ��=� and � < 0. By using dp=dz � p=�� ¼ 0  (at z ¼ �L=2) and setting the surface polarization p ¼ p�, eqs. (5) and (6) give | | |
| p2�¼ ðp2  ��p2   bþ p2  bþ p2   p2 b  ��Þ �  ���p2   q  m� 1   ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi  �p2 bþ p2   1  ���  �" 1 ��p2 bþ p2 p2 b  ���2 # p4 m | | ðA:2Þ |

which is the eq. (10) and p2��is �=��2�. In eq. (A·2) or (10), the power series expansion in term of pm is truncated at the order p4 mwhich is appropriate for the free energy of ferroelectrics with second order transition.

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| (A·2). We find Putting p� ¼ pm cos �� and �� ¼ �0� þ ��0� into eq. | | | | |
| and thus | cos �0� ¼ | |  |  | | --- | --- | | p | pb  ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi  p�� | | ; | ðA:3Þ |
| A:4 |
| sin � |
| with | 0� ¼ | p ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi |  | ðÞ |

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| --- |
| p ¼ pm cos � gives  F ¼ ffiffiffiffiffiffiffiffiffi�p2 m�Z ��sin2�d� þ Z �þ sin2�d�� p  �p4 4p2  m  b�Z ��ð1 � cos4�Þd� þ Z �þ ð1 � cos4�Þd���  þ   p  ffiffiffiffiffiffiffiffiffi� 1 2 sin �0� cos �0� p2� m� p4 2p2  m  b ð1 � cos4�0�Þ�  þ1 2 sin �0þ cos �0þ p2� m� p4 2p2  m  b ð1 � cos4�0þÞ��  þ�2p2 mþ �2p4 m�; ðA:7Þ � |

with the integrals

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Z �� | sin2�d� ¼ | � | 2� � 1 4 sin 2� | ��� |
| ¼1 2ð�0� þ ��0�Þ  �1 4ðsin 2�0� þ 2 cos 2�0���0�Þ | | | |

and

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Z �� | ð1 � cos4�Þd� ¼ | � | 8� � 1 4 sin 2� � 1 32 sin 4� | ��� |
| ¼5 8ð�0� þ ��0�Þ | | |

�1 4ðsin 2�0� þ 2 cos 2�0���0�Þ

|  |
| --- |
| �1 32ðsin 4�0� þ 4 cos 4�0���0�Þ: |

Thus, eq. (A·7) is reduced to

|  |  |  |
| --- | --- | --- |
| F ¼ | p ffiffiffiffiffiffiffiffiffi p2 m��0�2þ �0þ�  þ�4L r ffiffiffiffiffiffiffiffi p4 m�8ð�0� þ �0þÞ� 5  þ�4L r ffiffiffiffiffiffiffiffi p4 m� 1 4ðsin 2�0� þ sin 2�0þÞ  þ1 32ðsin 4�0� þ sin 4�0þÞ�  þ�2p2 mþ �2p4 m�:  � | ðA:8Þ |

Comparison of eq. (A·8) with eq. (8) gives the target

coefficients A and B as expressed in eqs. (11) and (12),

respectively.

Appendix B: Negative–Negative Surface Conditions

From eqs. (5) and (6), we find

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| and | ��0� ¼ c0�p2 m | | | ðA:5Þ | dp  dz¼ | |  |  | | --- | --- | | r ffiffiffiffi�s ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi~~ffiffif~~fiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi | | | � | 1 | | ðB:1Þ |
| c0� ¼ | | 1 | ½1 � cos4�0��: | ðA:6Þ |
| 4pbp�� | � | |  |  | | --- | --- | | r ffff ðp2� p2 mÞ1=2 1 þ 1� 4p2 b | ðp2 mþ p2Þ� | |  |
| Substitution of eqs. (A·1) and (6) into (7) together with | | | | |

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|  |
| --- |
| where p2 b¼ �=� and � > 0. By using dp=dz � p=�� ¼ 0 (at z ¼ �L=2) and setting the surface polarization p ¼ p�, eqs. (5) and (6) give  p2�¼ �ðp2  ��p2 b� p2   b� p2  p2 b  ����Þ � �p2 mþ 1 q ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi �p2 b� p2   1  ���  �" 1 ��p2 b� p2 p2 b  ���2 # p4 m ðB:2Þ |

which is the eq. (18) and p2��is �=��2�. In eq. (A·2) or (18), the power series expansion in terms of pm is truncated at the order p4 mwhich is appropriate for the free energy of ferroelectrics with second order transition.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| (B·2). We find Putting p� ¼ pm cosh �� and �� ¼ �0� þ ��0� into eq. | | | | | |
| and thus | pb  cosh �0� ¼ p ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi  pe�  sinh �0� ¼ �p ffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffiffi | | | ; | ðB:3Þ |
| ðB:4Þ |
| with |
| and | ��0� ¼ c0�p2 m | | | | ðB:5Þ |
| c0� ¼ � | | 1 | ½1 � cosh4�0��: | | B:6 |
| 4pbp�� | ðÞ |

then eq. (A·3) may be written in the form of eq. (A·4).

Substitution of eqs. (B·1) and (6) into (7) together with

|  |
| --- |
| p ¼ pm cosh � gives  F ¼ L ffiffiffiffiffiffi�p2 m�Z ��sinh2�d� þ Z �þ sinh2�d�� p  þp4 4p2  m  b�Z ��ðcosh4� � 1Þd� þ Z �þ ðcos4� � 1Þd���  �  p  L ffiffiffiffiffiffi� 1 2 sinh �0� cosh �0� p2� m� p4 m  b ðcosh4�0� � 1Þ�  þ1 2 sinh �0þ cosh �0þ p2� m� p4 m  b ðcosh4�0þ � 1Þ��  þ�2p2 mþ �2p4 m�; ðB:7Þ � |

with integrals

|  |  |  |  |
| --- | --- | --- | --- |
| Z �� | sinh2�d� ¼ | ��1 2� þ 1 4 sinh 2� | ��� |
| ¼ �1 2ð�0� þ ��0�Þ  þ1 4ðsinh 2�0� þ 2 cosh 2�0���0�Þ | | |

and

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Z �� | ðcosh4� � 1Þd� ¼ | � | �5 8� þ 1 4 sinh 2� þ 1 32 sinh 4� | ��� |

¼ �5 8ð�0� þ ��0�Þ   
 þ1 4ðsinh 2�0� þ 2 cosh 2�0���0�Þ

|  |
| --- |
| þ1 32ðsinh 4�0� þ 4 cosh 4�0���0�Þ |

Thus, we obtain

|  |
| --- |
| F ¼ �  p  L ffiffiffiffiffiffi p2 m��0�2þ �0þ���4L r ffiffiffiffi�p4 m�5  8ð�0� þ �0þÞ�  þ�4L r ffiffiffiffi�p4 m� 1 4ðsinh 2�0� þ 2 sinh 2�0þÞ  þ1 32ðsinh 4�0� þ sinh 4�0þÞ�  þ�2p2 mþ �2p4 m� ðB:8Þ  � |

Comparison of eq. (B·8) with eq. (8) gives the target coefficients A and B as expressed in eqs. (11) and (12), respectively.

Appendix C: Positive–Negative Surface Conditions

C.1 � < 0   
 Manipulations are the same as in eqs. (A·1) to (A·8) in the‘‘positive–positive’’ case. However, integration of the free energy throughout the film thickness is different because from the extremum of polarization pm is located outside the film. Thus, substitutions of eqs. (A·1) and (6) into (7)

|  |
| --- |
| together with p� ¼ pm cos �� as in Appendix A gives  F ¼ ffiffiffiffiffiffiffiffiffi�p2 m�Z ��sin2�d� �Z �þ sin2�d�� p  �p4 4p2  m  b�Z ��ð1 � cos4�Þd� �Z �þ ð1 � cos4�Þd���  þ   p  ffiffiffiffiffiffiffiffiffi� 1 2 sin �0� cos �0� p2� m� p4 m  b ð1 � cos4�0�Þ�  �1 2 sin �0þ cos �0þ p2� m� p4 m  b ð1 � cos4�0þÞ��  þ�2p2 mþ �2p4 m�; ðC.1.1Þ � |

Simplifying, we obtain

|  |  |  |
| --- | --- | --- |
| F ¼ | p  ffiffiffiffiffiffiffiffiffi p2 m��0�2� �0þ�  þ�4L r ffiffiffiffiffiffiffiffi p4 m�8ð�0� þ �0þÞ� 5  þ�4L r ffiffiffiffiffiffiffiffi p4 m� 1 4ðsin 2�0� � sin 2�0þÞ  þ1 32ðsin 4�0� � sin 4�0þÞ�  þ�2p2 mþ �2p4 m�  � | ðC.1.2Þ |

Comparison of eq. (C.1.2) with eq. (8) gives the target coefficients A and B as expressed in eqs. (23) and (24),

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respectively.

C.2 � > 0   
 Manipulations are the same as in eqs. (B·1) to (B·8) in the‘‘negative–negative’’ case. However, integration of the free energy throughout the film thickness is different because the extremum of polarization pm is located outside the film. Thus, substitution of eqs. (B·1) and (6) into (7) together with

|  |
| --- |
| p� ¼ pm cosh �� as in Appendix B gives  F ¼ ffiffiffiffiffiffiffiffiffi�p2 m�Z ��sinh2�d� �Z �þ sinh2�d�� p  þp4 4p2  m  b�Z ��ðcosh4� � 1Þd� �Z �þ ðcos4� � 1Þd���  � ffiffiffiffiffiffiffiffiffi� 1 2 sinh �0� cosh �0�  p  � p2� mþ p4 m  b ð1 � cosh4�0�Þ�  �1 2 sinh �0þ cosh �0þ p2� mþ p4 m  b ð1 � cosh4�0þÞ��  þ�2p2 mþ �2p4 m�; ðC.2.1Þ  � |

Simplifying, we obtain

|  |
| --- |
| F ¼ �  p  L ffiffiffiffiffiffi p2 m��0�2� �0þ���4L r ffiffiffiffi�p4 m�5  8ð�0� þ �0þÞ�  þ�4L r ffiffiffiffi�p4 m� 1 4ðsinh 2�0� � sinh 2�0þÞ |

|  |  |
| --- | --- |
| þ1 32ðsinh 4�0� þ sinh 4�0þÞ�  þ�2p2 mþ �2p4 m�  � | ðC.2.2Þ |

Comparison of eq. (C.2.2) with eq. (8) gives the target coefficients A and B as expressed in eqs. (27) and (28), respectively.

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