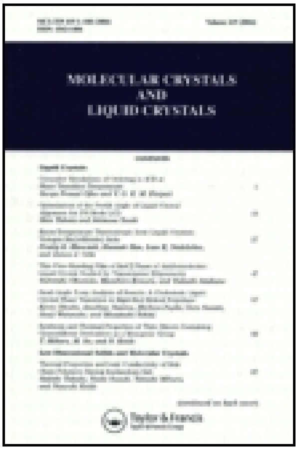

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Ordering of Chiral Smectics in Freely Suspended Film

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The method to study phase transitions of thin systems on the basis of a bulk phase diagram is applied to a freely suspended film of ferroelectric smectics showing a first-order phase transition in the bulk, where an ordering effect resulting from surface layers is replaced by an effective field that is conjugate to the order parameter. In the framework of a phenomenological free energy whose coefficients are determined form the experimental evidence about C7, the behavior of the transition is being clarified, which coincides with experimental findings, and especially the small shift of transition temperature from the bulk one is elucidated. The mechanism of the continuous change occurring in the system of thickness just below a critical thickness is clarified, where an unstable state that is never realized in the bulk appears at the interior layers. The behavior of this continuous change discloses the difference between the ordering effects resulting from the boundaries and the external fields.

Keywords: bulk phase diagram; chiral smectics; effective symmetry-breaking field; first-order transition; freely suspended film; unstable state

INTRODUCTION

A freely suspended film of chiral smectics is a very interesting and useful system to elucidate not only the film ordering itself but the property of a bulk phase [1–10]. By a study of such system, the phase structure free from an anchoring effect because of boundary walls can be observed [9,10]. On the other hand, surface layers of the film are known to order at a temperature higher than the bulk critical temperature for both ferroelectric [1–5] and antiferroelectric [6,7] smectics.

Now, a ferroelectric material 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxy-biphenyl (C7) shows a first-order phase transition from a

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smectic A phase (SmA) to a smectic C phase (SmC*) [11], whereas most of ferroelectric smectics exhibit a second-order phase transition. A freely suspended film of C7 has been observed, in which no transition occurs in the system with a thickness lower than a critical thickness whereas in a thick system the transition is of the first order [3]. In antiferroelectric smectics, some materials undergo the first-order transition in cases where the transition from SmA to an antiferroelectric smectic C phase (SmC^*_A) occurs directly [12,13]. However, so far, no experimental evidence has been found from the freely suspended film of such antiferroelectric smectics showing the first-order transition.

An ordering effect resulting from boundary surfaces is normally considered to be similar to the one by an external field [13,14–22]. The present author has tried to explain the behavior of the thin systems under the boundary condition, in which the effective field is introduced for describing the boundary effect, and by analyzing a locus of the field on a field-temperature phase diagram of the bulk, phase transitions in smectics [23,24], and nematics [25,26]. The effective field is defined in a self-consistent equation for the order parameter, and a singular behavior of the thin system is expected to occur only in a singular region of the bulk systerm [24–26]. However, in a system modeling a freely suspended smectic film showing the first-order transition in the bulk, a continuous change is shown to occur in the singular region, and this change is proved to be accompanied by an unstable state which never occurs in the bulk [27]. It is quite interesting how such a continuous change would appear in a realistic system.

In the present article, the transition of the freely suspended film of C7[3] is studied on the basis of the theory previously mentioned in the framework of a phenomenological free energy [1,27]. An experimental finding [3] about a small change of transition temperature from the bulk one is explained and a mechanism for a continuous change in the system of thickness lower than the critical one is studied in detail.

PHASE DIAGRAM OF BULK SYSTEM IN THE FIELD

In phenomenological theory [1], the free energy of the freely suspended film is expressed as

$$f(\{\theta_n\}) = \sum_{n=2}^{N-1}\left(a\theta_n^2 - b\theta_n^4 + c\theta_n^6 + d\theta_n^8\right) + \sum_{n=1,N}\left(a'\theta_n^2 - b'\theta_n^4 + c'\theta_n^6 + d'\theta_n^8\right) + G\sum_{n=1}^{N-1}(\theta_n - \theta_{n+1})^2, \quad (1)$$

where θ_n is the order parameter of the nth layer indicating the tilt angle of director from the smectic layer normal; the first terms of Eq. (1) represent contributions from the inner layers, the second ones the free energies of the surface ones, third ones a coupling between adjacent layers with coupling constant, or equalizing parameter, G. N denotes the number of layers. Except for positive constants b, c, d, b', c', and d', a and a' are temperature-dependent as $a = a_0\ (T - T_0)$ and $a' = a'_0\ (T - T'_0)$ with the absolute temperature T together with positive constants a_0, a'_0, T_0, and T'_0. The eighth terms, θ_n^8, in the free energy are taken into account for better fitting to experimental results.

First, the phase diagram of bulk system in the field is studied. Corresponding to Eq. (1), the free energy for the bulk is given by

$$f(\theta) = t\theta^2 - b\theta^4 + c\theta^6 + d\theta^8 - h\theta, \tag{2}$$

where $t = T - T_0$ and a_0 is taken to be unity (that is, f, b, c, d, and h are scaled in the unit a_0). The field h, which. is conjugate to the order parameter θ, is fictitious because of the helical structure of chiral smectics, and it is defined to be positive although it can be extended to a negative value at an ordered phase in which the phase is metastable.

The parameters b, c, and d are determined from three sets of experimental evidences: 1) A width of the coexistence region observed during a cooling process is about 0.05 K [11], which is equal to $t_c - t_0$ with t_c the transition temperature (corresponding to the experimental estimate 55°C) and t_0 the temperature at which a disordered phase (a high temperature phase) becomes unstable. Here, $t_0 = 0$ in Eq. (2), and so we have $t_c = 0.05$. 2) The value of θ at t_c, θ_c, is estimated to be 16° (= 16/180) [11]. 3) As a value of θ at a certain temperature, we use $\theta = 32^\circ$ (= 32/180) at $t = -5$ taken from Fig. 5 of Ref. 3. Though we have another choice, e.g., $\theta = 19^\circ$ at $t = -1$ [11], this value is very small and the expansion form of f of Eq. (2) is inadequate to describe such saturated behavior of θ in the low temperature region.

From Eq. (2) the equilibrium condition is written as

$$2\theta(t - 2b\theta^2 + 3c\theta^4 + 4d\theta^6) - h = 0, \tag{3}$$

which is equivalent to the self-consistency equation. In the absence of h, conditions of the transition point are given by $f(\theta_c) = f'(\theta_c) = 0$, that is,

$$b - 2c\,\theta_c^2 - 3d\,\theta_c^4 = 0, \tag{4}$$

$$c\theta_c^4 + 2d\,\theta_c^6 - t_c = 0. \tag{5}$$

We have estimates, from, Eqs. (3)–(5) together with the above experimental data, $b = 13.2858$, $c = 715.898$, and $d = 23104.96$.

In this investigation, the set of values, $b = 13.29$, $c = 715.9$ and $d = 23105$, is chosen. The value t_c is determined to be 0.050029 with the jump $\theta_c = 15.002°$. The critical point, $t = t^*$ and $h = h^*$ with $\theta = \theta^*$, is determined from conditions $f'(\theta^*) = f''(\theta^*) = f'''(\theta^*) = 0$, which gives $t^* = 0.12518$, $h^* = 0.0073681$ and $\theta^* = 0.054172$. By the numerical analysis of Eq. (3) together with Eq. (2), we obtain the phase diagram on the h versus t plane as shown in Fig. 1, where Λ_α is the coexisting curve ending at C the critical point. The curves Λ_β and Λ_γ correspond to spinodal curves, that is, on the curve Λ_β (Λ_γ), the high-temperature phase (low-temperature phase) becomes unstable. For the field $h < h^*$, the first-order transition occurs inevitably in the area surrounded by Λ_β and Λ_γ even though a metastable state participates to the transition, while no transition occurs outside this region.

PHASE TRANSITION IN FREELY SUSPENDED FILM

Here, we discuss the phase transition of the film-system whose free energy is given by Eq. (1). Coefficients b', c', and d' in the second terms

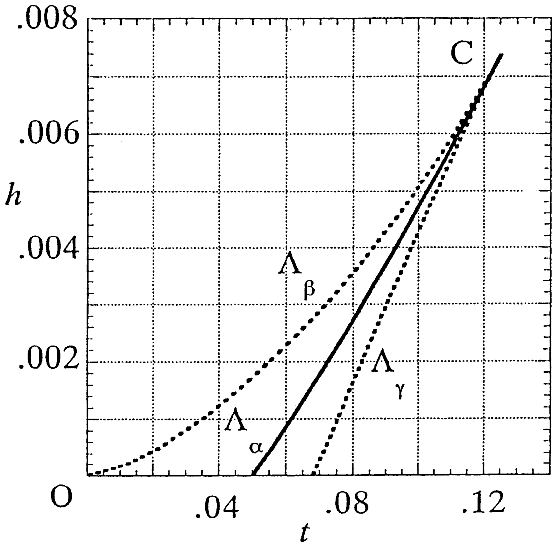

FIGURE 1 The phase diagram on h-T plane at the bulk.

may differ from the corresponding ones in the first terms. However, the effect of the surface layers on the behavior of the inner portion is mainly an enhancement of ordering, and so we choose the same parameters b, c, and d for the surface layers, and also we assume $a'_0 = a_0$, for simplicity. As the order parameter of the freely suspended film with two layers takes experimentally a large value about 26° even at the temperature higher by 5°C than the bulk transition temperature [3], the value $t - t'$ $(= T'_0 - T_0) = 7$ is taken for the present model. Equilibrium conditions for θ_n are written as

$$\theta_1\left(t' - 2b\theta_1^2 + 3c\theta_1^4 + 4d\theta_1^6\right) + G(\theta_1 - \theta_2) = 0, \tag{6}$$

$$\theta_n\left(t - 2b\theta_n^2 + 3c\theta_n^4 + 4d\theta_n^6\right) + G(2\theta_n - \theta_{n+1} - \theta_{n-1}) = 0, \quad (n = 2,\ 3,\ \ldots,\ N-1) \tag{7}$$

where the condition for θ_N is omitted. The simultaneous equations (6) and (7) are solved numerically under the condition, $\theta_{N/2+1} = \theta_{N/2}$ for even N and $\theta_{(N+3)/2} = \theta_{(N-1)/2}$ for odd N because of the symmetry. In practical calculations, mainly the cases of even number of N are studied. For a given thickness of the film, transition behavior depends on the value of G; for G larger than a certain G_c, no transition occurs and on the contrary for $G < G_c$ the system exhibits the discontinuous transition. In Fig. 2, the critical value G_c is plotted by a filled circle • for several value of N, together with the critical temperature t_g^* at $G = G_c$, shown by a filled diamond ◆. In the system of thickness N, the value t_g^* gives the maximum limit of the transition temperature.

Because of the experimental findings in C7, the critical thickness is about 16 layers [3], we choose here the value $G = 0.5$ $(> G_c)$, for which the discontinuous transition occurs at the system with $N = 17$ whereas the system undergoes the continuous change at $N = 16$.

Now, the system with $N = 16$ is studied in detail. Temperature dependences of θ_n for $n =$ 3–6 and 8 are shown in Fig. 3, where thin dotted curves are the $\theta - t$ relations at the constant field strength, $h = 0$, 0.001, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, and 0.008 from left to right, and the broken curve SP denotes the spinodal line. Although the continuous change occurs, the drastic increase of θ_n with inflexion point near $t = 0.08$ is observed because the layer number $N = 16$ is very close to the critical thickness. It is noted that the curves θ_n with $n = 4 - 8$ cross with the curve SP, even though in the area surrounded by SP the state is unstable in the bulk. To see what happens clearly, we rewrite Eqs. (6) and (7) in the form

$$2\theta_n\left(t - 2b\theta_n^2 + 3c\theta_n^4 + 4d\theta_n^6\right) - h_n = 0, \qquad (n = 1,\ 2,\ \ldots,\ N) \tag{8}$$

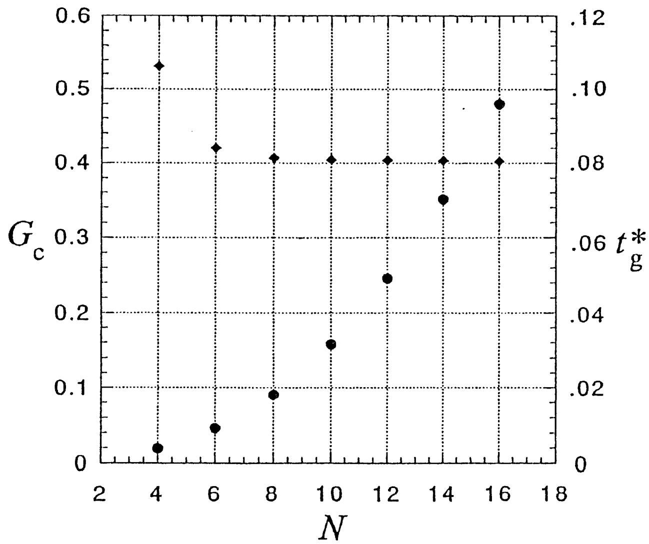

FIGURE 2 The critical value of the coupling constant $G_c(\bullet)$ and the critical temperature t_g^* at the critical value ($\blacklozenge$) for various value of N.

where the effective field h_n is given by

$$h_1 = 2G(\theta_2 - \theta_1), \quad h_N = 2G(\theta_{N-1} - \theta_N),$$
$$h_n = 2G(\theta_{n+1} + \theta_{n-1} - 2\theta_n), \quad (n = 2,\ 3,\ \ldots,\ N-1) \tag{9}$$

The free energy is expressed as

$$f(\{\theta_n\}) = \sum_{n=2}^{N-1}\left(t\theta_n^2 - b\theta_n^4 + c\theta_n^6 + d\theta_n^8\right) + \sum_{n=1,N}\left(t'\theta_n^2 - b\theta_n^4 + c\theta_n^6 + d\theta_n^8\right) - \frac{1}{2}\sum_{n=1}^{N} h_n\theta_n. \tag{10}$$

Because the origin of the fields is the interaction, the factor 1/2 appears in the field terms of Eq. (10). Equation (8) is nothing but the equilibrium condition, Eq. (3), for θ_n under the field h_n. It is stressed that even in the present film system any phase transition never occurs outside the area surrounded by Λ_β and Λ_γ in the $h-t$ plane of Fig. 1, because Eq. (8) [i.e., Eq. (3)] is the necessary condition for θ_n and the transition can occur only in this area as proved in the previous section.

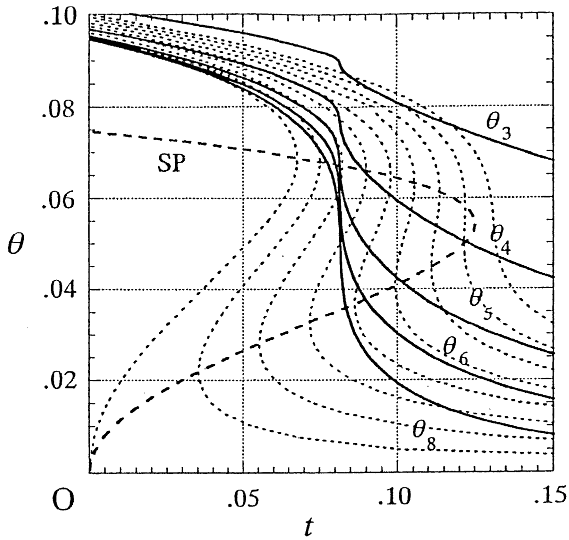

FIGURE 3 Temperature dependence of θ_n at the film of $N = 16$ ($n = 3$–6 and 8), in which $\theta - t$ curves at constant field strength are shown by dotted curves (see text) and the curve SP denotes the spinodal line.

For the system of 16 layers, curves of h_3, h_5, and h_7 are depicted in Fig. 4, where h_5 and h_7 contact tangentially with Λ_β at b and b′, respectively, and with Λ_γ at c and c′ whereas h_3 does not enter the singular region. The behavior of h_2 is similar to h_3, and h_4, h_6, and h_8 contact to Λ_β and Λ_γ as h_5 and h_7 do. In the interval between b and b′ (c and c′), the phase is unstable, which never appears in the bulk. Thus, the continuous change is realized in such a mechanism that the high-temperature branch ab (a′b′) is connected continuously to the low-temperature one cd (c′d′) by an insertion of the unstable branch bc (b′c′). In the course of the change, the field varies throughout, which enables the continuous change. This mechanism looks like surfing, where a surfer moves continuously keeping his footing on the top of a wave.

It is stressed that at the film system the unstable state in the area surrounded by the spinodal line SP is not unstable, because the free energy (1), or (10), takes minimum even in such unstable branch. To clarify this property, $f(\{\theta_n\})$ is shown as a function of θ_7 for various temperatures in Fig. 5, where other order parameters, θ_n, are fixed in the equilibrium values, respectively, at each temperature.

The first-order transition occurs in the system with thickness larger than 16. In Fig. 6 the field versus temperature relation is shown for

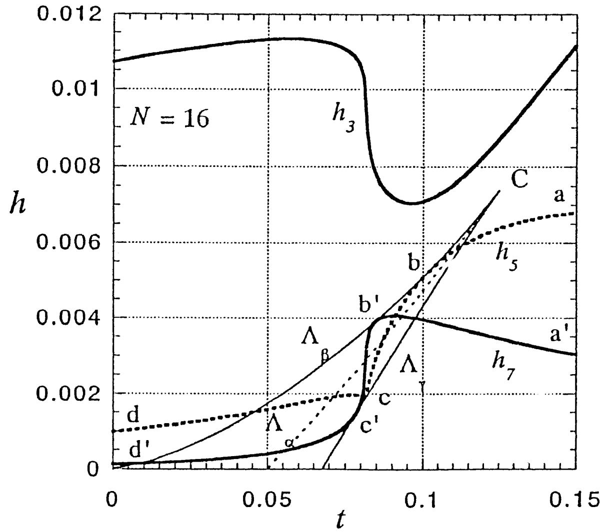

FIGURE 4 Temperature dependence of h_n of $N = 16$ ($n = 3,\ 5,$ and 7).

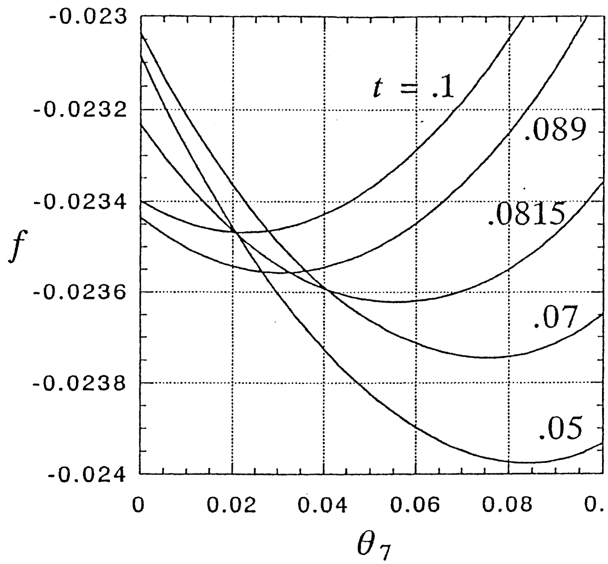

FIGURE 5 Behavior of $f(\{\theta_n\})$ as a function of θ_7 at $N = 16$, where other values of θ_n are fixed in the equilibrium values at each temperature.

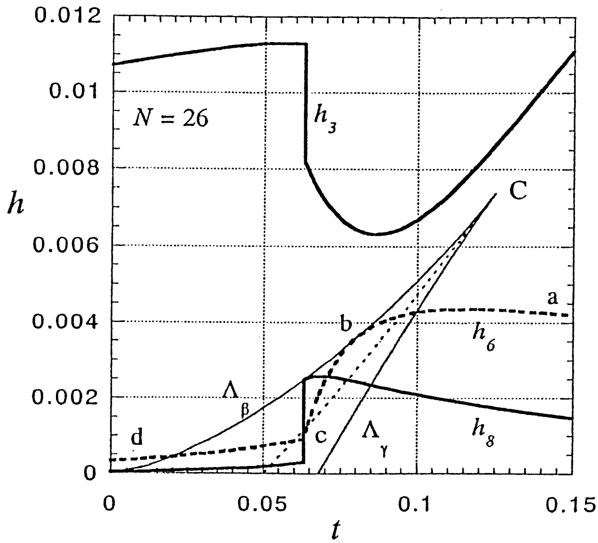

FIGURE 6 Temperature dependence of h_n of $N = 26$ ($n = 3,\ 6$, and 8), where the discontinuous transition occurs.

$N = 26$, where h_3, h_6, and h_8 are depicted. The curve h_8 shows that the eighth layer undergoes the transition from the metastable high-temperature phase to the metastable low-temperature one, which is common to h_8–h_{13}. On the other hand, h_6 shows that the unstable state is observed to appear at some layers near the surface, θ_4–θ_7, while no singular behavior except for the jump at the transition is observed at the layers just adjacent to the surface θ_2 and θ_3. These behaviors are common to the thicker system. On the other hand, at very thin system, the continuous change is not accompanied by any kind of singular behaviors. In Fig. 7, the changes of h_n in the system of $N = 10$ are shown, where all of h_n's are larger than h^* at $t = t^*$ and move in the analytic area in the field versus temperature plane.

As for the global feature of the present system (1), the temperature dependence of an average $\langle\theta\rangle = \Sigma_n\ \theta_n/N$ for various thickness is depicted in Fig. 8. These curves correspond to the experimental observation shown in Figure 5 of Ref. 3 where the shift of the transition temperature at the film system from the bulk one is quite small [3], at most 0.1–0.2°C. On the other hand, Eq. (8) indicates that the phase transition of the freely suspended film occurs only in the area of the singular region in Fig. 1, whose width is estimated as that $t^* - t_0 = 0.125$°C. In practice, the inflexion of the curves of θ_n occurs at the temperature $t = 0.08$ at $N = 16$, which means that the shift of

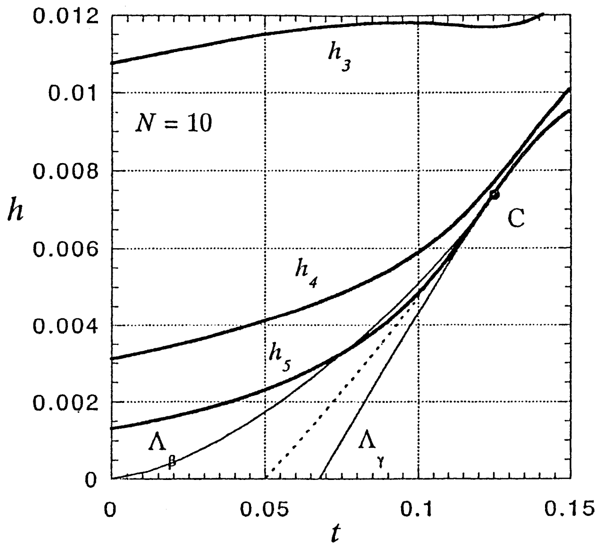

FIGURE 7 Temperature dependence of h_n of $N = 10$ ($n = 3$, 4, and 5), where $h_n > h^*$ for all value of n ($h_5 = 0.0073883 > h^*$).

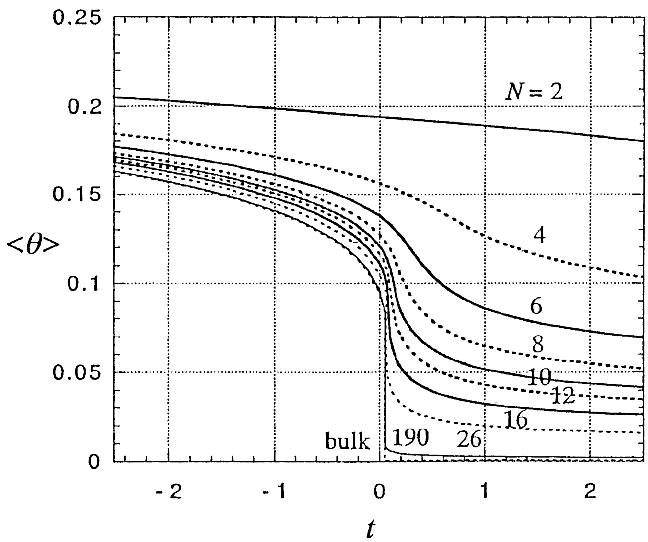

FIGURE 8 Temperature dependence of average tilt angle $< \theta >$ for various thickness ($N = 2$, 4, 6, 8, 10, 12, 16, 26, 190, and the bulk).

the transition temperature is estimated to be 0.03°C. Thus, the shift of the transition temperature is proved to be bounded to the value $t^* - t_0$, or $t^* - t_c$, on the phase diagram of the bulk.

SUMMARY AND DISCUSSION

Phase transitions of the freely suspended film of chiral smectics showing the first-order phase transition in the bulk are studied in the framework of the phenomenological theory. The coefficients appearing in the model are determined from the experimental data about the ferroelectric material C7 [11] where the critical thickness is about 16 layers [3]. The ordering effect resulting from the surface layers is expressed in terms of the effective field, which is defined in the equation of equilibrium condition for the order parameter. To study the behavior of the film system, the phase diagram of the bulk is obtained, in which not the coexisting line but the instability lines of the high-temperature and low-temperature phases play the leading part. By analyzing the variation of the effective field on the bulk phase diagram, the novel mechanism of the continuous change occurring in a thin system is clarified; at the system with thickness just below the critical thickness ($N = 16 - 12$), the stable high-temperature state changes to the low-temperature state by passing the metastable state, unstable state, and low-temperature metastable one successively at the inner layers ($n = 4, 5, \ldots, N - 4$), whereas for still thinner system ($N = 10 - 4$) every layer stays at the stable state at any temperature. However, the unstable state, which never appears in the bulk, is sustained by the boundary surfaces and the system is stable energetically as a whole. The shift in the transition temperature of the film system from the bulk one is proved to be bounded by the bulk critical point and is rather low, which is in agreement with the experimental finding [3].

In the present study, the Landau's free energy, that is, the expansion form, is used, by which it is difficult to describe such saturation phenomena of the order parameter observed in the low-temperature region [3]. In this respect the results obtained here are judged to be qualitative, or at most semi-quantitative, even though the parameters are determined as to fit the experimental data. However, the main parts of the present results are related in the singular region located at the transition temperature of the bulk, and accordingly those results are considered to be reasonable.

The mixture of C7 with 70PDOB is very attractive, because the jump of the order parameter at the transition point becomes small as the fraction of the latter is increased [11]. In the system of the freely suspended films of such mixture, the critical thickness is considered to become large as the latter fraction is increased. The critical point appearing in the film system, which is located in the singular area of the bulk phase diagram, is different from the bulk critical point, and the nature of the former is not yet clarified. It is interesting to clarify the nature together with the change of the critical point as the fraction is increased. In this respect, we suggest the experimental studies of such a film system together with the antiferroelectric smectic film system showing the first-order jump in the bulk.

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