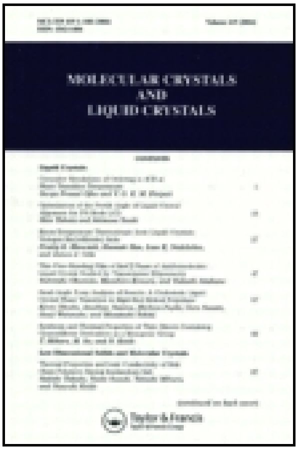

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Biaxial Field and Crossover between Homeotropic and Homogeneous Structures in the System Anchored by Biaxial Walls

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Landau free energy with both of uniaxial and biaxial order parameters is derived in the framework of Maier-Saupe model, based on which a phase diagram in two types of external fields is obtained. The free energy is generalised to be applied to the thin system sandwiched by parallel boundary walls of biaxial anchoring, and nematic ordering occurring therein is studied, where the biaxiality is introduced by the fixed orientation of molecules on the boundary walls. The first order phase transition becomes critical behaviour at a critical thickness, and the system thinner than this has no transition as the case of homeotropic structure, and biaxiality dependence of the critical thickness is evaluated. A crossover between homeotropic and homogeneous structures is shown to occur at a certain biaxial condition, where the first order transition changes to the second order one as the thickness decreases.

Keywords: biaxiality; bulk phase diagram; effective field; homeotropic structure; homogeneous structure; nematic phase

INTRODUCTION

An order of liquid crystals is generally soft, and boundary effect reaches deeply into the interior region of bulk liquid crystals unlike the case of solids [1]. In the thin system, the nematic phase transition is changed even qualitatively; at a certain thickness of the system, a jump at the nematic-isotropic transition disappears and for the system with thickness smaller than the critical thickness no transition occurs

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[2–6]. This behaviour caused by boundary walls is similar in part to the one by an external field, where at the critical field strength the critical point appears and phase changes continuously for high field [7,8]. Practically, a competition between both effects due to walls and the external field is applied to the liquid crystal display technology [9]. On the other hand, the wall acts only on molecules adjacent to the wall surfaces, while the field is applied to the whole bulk system. Thus, a difference between those effects is also of interest.

To clarify the similarity and dissimilarity between the effects due to walls and field, one of the present authors has introduced an effective field in the self-consistency equation for order parameter in order to describe nonuniformity caused by walls [10], and it is shown that near the critical thickness of nematic system a peculiar state corresponding to an unstable state which never appears in the bulk is found to occur which plays an important role in the mechanism of continuous change [11]. Similarly in a freely suspended film of ferroelectric smectics, such unstable state is also shown to appear [12]. In these investigations, a phase diagram of the bulk in the external field has given a precious information about the phase transitions occurring in thin systems [10–12].

In the present paper we study the ordering in the thin nematic system sandwiched by parallel walls with biaxial anchoring condition from a microscopic view. As a concrete Hamiltonian, the Maier-Saupe model [13] is utilised and by statistical mechanical calculation the Landau free energy is derived as a function of uniaxial and biaxial order parameters [10,14,15] in the mean field approximation. By analysing the Landau free energy the phase diagram in a couple of fields, uniaxial and biaxial fields, is obtained. The free energy is generalised to the thin system, in which nonuniformity is described in the discretised fashion and the boundary condition is given by a set of molecules on the walls whose orientations are restricted to have a fixed angle so as to give rise to the biaxial condition. The dependence of the critical thickness on the angle is studied. Especially, at the angle, $\pi/4$, a crossover from the homeotropic structure to the homogeneous one is shown to occur and both structures coexist at a temperature lower than the transition temperature. Then, the critical point changes to a tricritical point. Finally, discussions in relation to the bulk phase diagram and summary are given.

BULK SYSTEM WITH UNIAXIAL AND BIAXIAL ORDERS

The nematic phase transition of biaxial order has been studied [10,14–16], in which a uniaxial order parameter s and a biaxial order one σ are defined, respectively, as

$$s = \frac{1}{N_t} \sum_{i=1} \langle P_2(\cos\theta_i) \rangle, \tag{1}$$

$$\sigma = \frac{1}{N_t} \sum_{i=1} \left\langle \sin^2\theta_i \cos 2\varphi_i \right\rangle, \tag{2}$$

where θ_i and φ_i denote the polar and azimuthal angles, respectively, of i-th molecular long axis in the Cartesian coordinate system with the principal axis in z-axis, $N_{\rm t}$ the total number of molecules and $\langle \cdots \rangle$ the thermal average. Then, the field energy is expressed with conjugate fields, h_z and h, as

$$H_{ext} = -\sum_i \left\{ h_z P_2(\cos\theta_i) + h \sin^2\theta_i \cos 2\varphi_i \right\}. \tag{3}$$

Landau Free Energy

The nematic ordering is well-described by the Maier-Saupe model [13]. In the mean field theory, the orientational freedoms do not couple with translational ones, and eventually the effective Hamiltonian is given by

$$H_0 = -V \sum_{(i,j)} P_2(\cos\theta_{ij}), \tag{4}$$

in which θ_{ij} denotes an angle between two long axes of i-th and j-th molecules.

We derive here the free energy as a function of s and σ, the Landau's thermodynamical potential, in a concrete form. The partition function of the system with symmetry breaking fields, η and ς, is expressed as

$$Z(\eta,\varsigma) = \prod_i \left[\int_0^{2\pi} d\varphi_i \int_0^{\pi} d\theta_i \sin\theta_i \exp\left\{ \eta P_2(\cos\theta_i) + \varsigma \sin^2\theta_i \cos 2\varphi_i \right\} \right] e^{-\beta H_0}, \tag{5}$$

where β is the inverse temperature $1/k_{\rm B}T$ with the Boltzmann constant $k_{\rm B}$. In the presence of the fields, h_z and h, η and ς are given by $\eta = \eta' + \beta h_z$ and $\varsigma = \varsigma' + \beta h$. By expanding the Boltzmann factor $\exp(-\beta H_0)$ in Eq. (5) up to the first order of β, we write

$$Z(\eta,\varsigma) = \prod_i \left[\int_0^{2\pi} d\varphi_i \int_0^{\pi} d\theta_i \sin\theta_i \exp\left\{ \eta P_2(\cos\theta_i) + \varsigma \sin^2\theta_i \cos 2\varphi_i \right\} \right] \times (1 - \beta H_0) + 0(\beta^2), \tag{6}$$

which leads to the mean field theory [10,11,17]. Here, a partition function for one particle is introduced as

$$z_0(\eta,\varsigma) = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \exp\{\eta P_2(\cos\theta) + \varsigma \sin^2\theta \cos 2\varphi\}. \tag{7}$$

Then, using an addition theorem for $P_2(\cos\,\theta_{ij})$ given by

$$P_2(\cos\theta_{ij}) = P_2(\cos\theta_i)P_2(\cos\theta_j) + 2\sum_{l=1}^{2}\frac{(2-l)!}{(2+l)!} \times P_2^l(\cos\theta_i)P_2^l(\cos\theta_j)\cos l(\varphi_i - \varphi_j), \tag{8}$$

the partition function $Z(\eta,\,\varsigma)$ is reduced to

$$Z(\eta,\varsigma) = \exp\left[N_t\left\{\ln z_0 + \frac{\beta V z}{2}\left(I^2 + \frac{3}{4}J^2\right)\right\}\right], \tag{9}$$

where z denotes a mean of the neighbouring molecular numbers, and functions $I(\eta,\varsigma)$ and $J(\eta,\varsigma)$ are defined by

$$I(\eta,\varsigma) = \frac{\partial \ln z_0(\eta,\varsigma)}{\partial\eta}, \tag{10}$$

$$J(\eta,\varsigma) = \frac{\partial \ln z_0(\eta,\varsigma)}{\partial\varsigma}, \tag{11}$$

respectively. It is noticed that the term with $l = 1$ in Eq. (8) vanishes in Eq. (9) and has no contribution to the partition function in the mean field theory.

The order parameters, s and σ, are derived as

$$\begin{aligned} s &= \frac{1}{N_t}\frac{\partial \ln Z(\eta,\varsigma)}{\partial\eta} \\ &= I(\eta,\varsigma) + \beta V z\left\{I(\eta,\varsigma)\frac{\partial I(\eta,\varsigma)}{\partial\eta} + \frac{3}{4}J(\eta,\varsigma)\frac{\partial J(\eta,\varsigma)}{\partial\eta}\right\}, \end{aligned} \tag{12}$$

$$\begin{aligned} \sigma &= \frac{1}{N_t}\frac{\partial \ln Z(\eta,\varsigma)}{\partial\varsigma} \\ &= J(\eta,\varsigma) + \beta V z\left\{I(\eta,\varsigma)\frac{\partial I(\eta,\varsigma)}{\partial\varsigma} + \frac{3}{4}J(\eta,\varsigma)\frac{\partial J(\eta,\varsigma)}{\partial\varsigma}\right\}, \end{aligned} \tag{13}$$

respectively. By using the relation $I_\varsigma = J_\eta = (\ln z_0)_{\varsigma\eta}$ with the notation that subscripts show the partial derivatives of functions, Eqs. (12) and

(13) are rewritten in the framework up to the order of β as

$$s = I\left(\eta + \beta Vzs, \varsigma + \frac{3}{4}\beta Vz\sigma\right), \quad (14)$$

$$\sigma = J\left(\eta + \beta Vzs, \varsigma + \frac{3}{4}\beta Vz\sigma\right), \quad (15)$$

which are nothing but the self-consistency equations in the mean field theory. From Eqs. (14) and (15) the fields η' and ς' are determined as functions of s and σ, $\eta'(s, \sigma)$ and $\varsigma'(s, \sigma)$. Then, the thermodynamical potential $F(s, \sigma)$, or free energy, is derived as

$$\beta(F(s,\sigma) - F(0,0)) = \int_0^s \eta'(s',0)ds' + \int_0^\sigma \varsigma'(s,\sigma')d\sigma'. \quad (16)$$

In the analysis of Eqs. (14)–(16), double integrals are required for each values of parameters. Here, we obtain the free energy in the expansions form of s and σ, that is the Landau free energy. The fields $\eta'(s, \sigma)$ and $\varsigma'(s, \sigma)$ are calculated from Eqs. (14) and (15) as

$$\eta'(s,\sigma) = (5 - \beta Vz)s - \frac{25}{7}s^2 + \frac{425}{49}s^3 + \frac{75}{28}\sigma^2 + \frac{1275}{196}s\sigma^2 - \beta h_z, \quad (17)$$

$$\varsigma'(s,\sigma) = \frac{3}{4}(5 - \beta Vz)\sigma + \frac{3825}{784}\sigma^3 + \frac{75}{14}s\sigma + \frac{1275}{196}s^2\sigma - \beta h. \quad (18)$$

Then, the integrals in Eq. (16) are carried out straightforwardly and $F(s, \sigma)$ is obtained as

$$\begin{aligned}\beta(F(s,\sigma) - F(0,0)) = {} & \frac{1}{2}(5 - \beta Vz)s^2 - \frac{25}{21}s^3 + \frac{425}{196}s^4 + \frac{3}{8}(5 - \beta Vz)\sigma^2 \\ & + \frac{3825}{3136}\sigma^4 + \frac{75}{28}s\sigma^2 + \frac{1275}{392}s^2\sigma^2 - \beta(h_z s + h\sigma),\end{aligned} \quad (19)$$

which is the concrete form of Landau free energy for Maier-Saupe model in the mean field theory, as contrasted with the phenomenological theory [14,15].

Bulk Phase Diagram

The thermal equilibrium is obtained under the conditions $\eta'(s, \sigma) = 0$ and $\varsigma'(s, \sigma) = 0$ in Eqs. (17) and (18) together with minimum condition of $F(s, \sigma)$ of (19). The phase diagram on h_z versus h plane (the projection of the phase diagram in h_z-h-T space) is shown in Figure 1, in which the bold points, TC, indicate tricritical point and full curves the critical line. In the area enclosed by the critical lines, the first order phase transition occurs, and the segments of thin lines ($h = 0$ (l_z), $h_z = -2/3\,h$ (l_x) and $h_z = 2/3\,h$ (l_y)), between the origin O and tricritical points, respectively, are the triple lines. To show a temperature dependence of the phase diagram, a session at $h = 0$ is shown in Figure 2 in which TC and C denote the tricritical point and the critical one, corresponding to same symbols in Figure 1. Critical values of h_z and T are $h_{zc} = 35/7038$ $(=0.004973)$ Vz and $T_c = 51/230$ $(=0.2217)$ Vz/k_B, and the tricritical values are $h_{ztc} = -35/1343$ $(= -0.02606)$ Vz and $T_{tc} = 272/1185$ $(=0.2295)$ Vz/k_B. These results are compared with values free from the expansion, $h_{zc} = 0.01045$ Vz, $T_c = 0.2309$ Vz/k_B, $h_{ztc} = -0.05383$ Vz and $T_{tc} = 0.2415$ Vz/k_B [10], and the phase diagram of Figure 2 agrees qualitatively with the one in [11] which is also derived without Landau expansion. For vanishing h_z, the transition temperature is obtained as $153/715$ $(=0.2140)$ Vz/k_B with the jump of s $14/51$ $(=0.2745)$, while the transition temperature and the jump

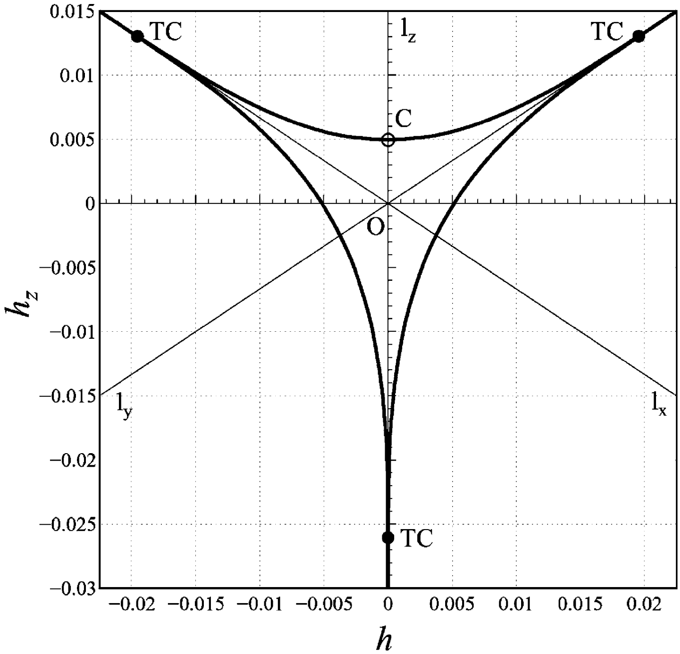

FIGURE 1 The critical curves on h_z-h plane.

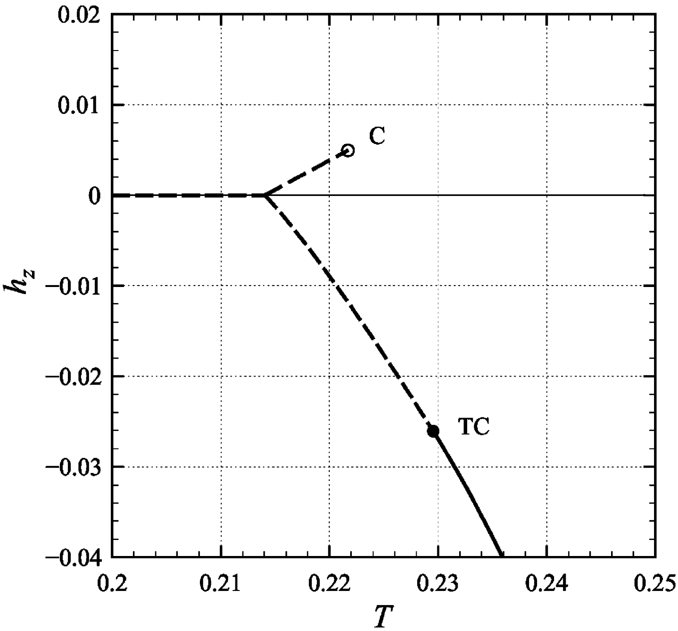

FIGURE 2 The phase diagram on h_z-T plane ($h = 0$).

are 0.2202 Vz/k_B and 0.4290 in the calculation free from the expansion [11]. From this comparison we comprehend a degree of reliability of the results based on the Landau expansion.

TRANSITION BEHAVIOUR IN BIAXIALLY ANCHORED SYSTEM

Model and Landau Free Energy

In the thin system sandwiched by boundary walls, the order parameters depend on the position, that is, a distance from the wall. We describe the nonuniformity of the system in discretised form, where the system is decomposed into N sheets with order parameters, s_n and σ_n, for the n-th sheet ($n = 1, 2, \ldots, N$). Assume that a certain molecule is surrounded by each one molecule in the neighbouring sheets in addition to $(z-2)$ molecules in the same sheet. Then, the self-consistency Eqs. (14) and (15) are generalised for s_n and σ_n as

$$s_n = I\Big(\eta_n + \beta V\{(z-2)s_n + s_{n+1} + s_{n-1}\}, \\ \varsigma_n + \frac{3}{4}\beta V\{(z-2)\sigma_n + \sigma_{n+1} + \sigma_{n-1}\}\Big), \quad (20)$$

$$\sigma_n = J(\eta_n + \beta V\{(z-2)s_n + s_{n+1} + s_{n-1}\}, \varsigma_n + \frac{3}{4}\beta V\{(z-2)\sigma_n + \sigma_{n+1} + \sigma_{n-1}\}), \tag{21}$$

in which the interaction parameter between molecule and wall is taken to be $V'(=\alpha V)$ because the molecules consisting boundary walls are different from the molecules of the system concerned. Values at the walls, s_0, σ_0, s_{N+1} and σ_{N+1}, are assumed to be given with a parameter θ_0 by

$$s_0 = s_{N+1} = P_2(\cos\theta_0), \quad \sigma_0 = \sigma_{N+1} = \sin^2\theta_0, \tag{22}$$

by which the biaxial character of walls is described. This assumption means that a molecule in the wall is in the fixed orientation with a polar angle θ_0 and an azimuthal one φ_0 (=0 and π with distribution of equal probabilities). Then, in the absence of the fields, the symmetry breaking fields are given in the expansion forms by

$$\eta_n(\{s_n\},\{\sigma_n\}) = (5-\beta Vz)s_n - \frac{25}{7}s_n^2 + \frac{425}{49}s_n^3 + \frac{75}{28}\sigma_n^2 + \frac{1275}{196}s_n\sigma_n^2 - \beta V(s_{n+1} + s_{n-1} - 2s_n), \tag{23}$$

$$\varsigma_n(\{s_n\},\{\sigma_n\}) = \frac{3}{4}(5-\beta Vz)\sigma_n + \frac{3825}{784}\sigma_n^3 + \frac{75}{14}s_n\sigma_n + \frac{1275}{196}s_n^2\sigma_n - \frac{3}{4}\beta V(\sigma_{n+1} + \sigma_{n-1} - 2\sigma_n), \tag{24}$$

and the free energy $F(\{s_n\}, \{\sigma_n\})$ is obtained as

$$\begin{aligned}\beta(F(\{s_n\},\{\sigma_n\}) - F(\{0\},\{0\})) &= \sum_{n=1}^{N}\Bigg[\frac{5}{2}s_n^2 - \frac{25}{21}s_n^3 + \frac{425}{196}s_n^4 + \frac{15}{8}\sigma_n^2 + \frac{3825}{3136}\sigma_n^4 + \frac{75}{28}s_n\sigma_n^2 + \frac{1275}{392}s_n^2\sigma_n^2 \\ &\quad - \frac{1}{2}\beta V\Bigg\{(z-2)s_n^2 + s_{n+1}s_n + s_{n-1}s_n \\ &\quad + \frac{3}{4}\left((z-2)\sigma_n^2 + \sigma_{n+1}\sigma_n + \sigma_{n-1}\sigma_n\right)\Bigg\}\Bigg] \\ &\quad - \frac{1}{2}\beta V\left(s_0s_1 + \frac{3}{4}\sigma_0\sigma_1 + s_Ns_{N+1} + \frac{3}{4}\sigma_N\sigma_{N+1}\right).\end{aligned} \tag{25}$$

Numerical Results

From the symmetry of the boundary condition (22), we assume the symmetry of the ordering, where the simultaneous equations (23) and (24) are solved under the conditions

$$s_{N/2+1} = s_{N/2} \quad \sigma_{N/2+1} = \sigma_{N/2}, \quad (N : \text{even}) \tag{26}$$

$$s_{(N+1)/2+1} = s_{(N+1)/2-1}, \quad \sigma_{(N+1)/2+1} = \sigma_{(N+1)/2-1}, \quad (N : \text{odd}) \tag{27}$$

We choose here $\alpha = 1$, exclusively.

First, a case of homeotropic walls ($\theta_0 = 0$) is studied, where the phase is of course the homeotropic structure with vanishing σ_n. In Figure 3, an average of s_n, $\bar{s}$, is shown for various value of N, from which we obtain an estimate of critical thickness N_c approximately 12. These results are compared with those obtained previously [11], which correspond to solutions to Eqs. (20) and (21) free from the Landau expansion; profiles of ordering are quite similar to each other while N_c is 9 in [11].

For nonvanishing θ_0, biaxiality appears, and at θ_0 near $\pi/4$ solutions describing homogeneous structure with negative values of $s_n$are obtained. In Figure 4, free energies are shown at $\theta_0 = 44^\circ$, in which marks L(homeo) and L(hg) denote homeotropic structure and homogeneous one, respectively, and H the high temperature phase. Under this condition, the homogeneous structure is metastable while the homeotropic structure is stable. At $\theta_0 = \pi/4$ ($= 45^\circ$), both structures coexist as shown in Figure 5, where the free energies agree completely to each other. The temperature dependence of averaged order parameters, $\bar{s}$ and $\bar{\sigma}$, is shown in Figure 6. The stable state exchanges bordering at $\theta_0 = \pi/4$ as shown in Figure 7, in which $\theta_0 = 46^\circ$ and the transition temperature agrees with the one for $\theta_0 = 44^\circ$ in Figure 4. The changes of free energies of Figure 7 also coincide to those in Figure 4, where the stable phase is exchanged. Thus, a crossover aspect from homeotropic structure to the homogeneous one is observed at $\theta_0 = \pi/4$.

For the angle θ_0 near 0 or $\pi/2$, the conditions of walls (22) enhance the homeotropic or homogeneous order, respectively, while for the angle near $\pi/4$ the walls suppress both order. In Figure 8 profiles of homeotropic ordering at the system $N = 14$ with $\theta_0 = \pi/4$ are shown, where we can see the suppressed order near the wall at the ordered phase. In practice, $s_0 = 0.25$ at $\theta_0 = \pi/4$ which is smaller than the value 0.27 at the first order transition point of bulk system, and the ordering of ordered phase is suppressed. By neglecting the coupling between s_n and σ_n, rough estimate of the limit of θ_0 for ordering wall

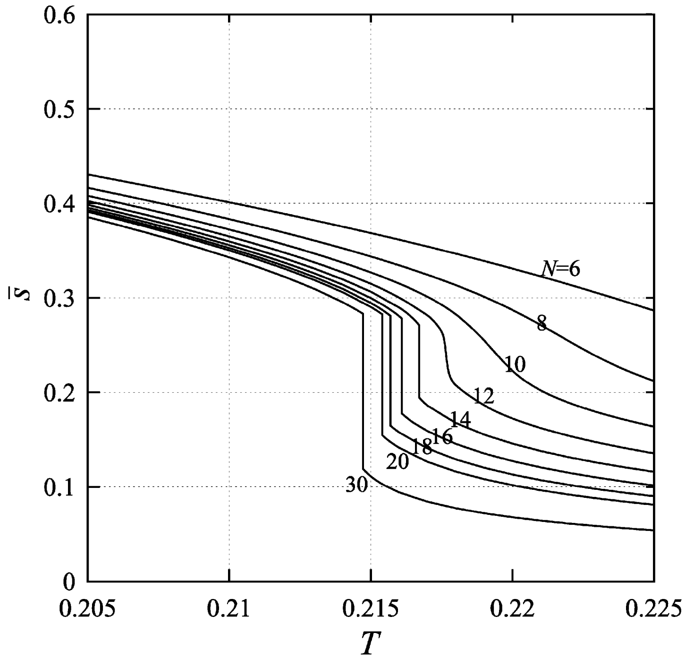

FIGURE 3 Temperature dependence of an average of order parameters s_n ($\theta_0 = 0$).

is given by $P_2(\cos\theta_0) = 14/51$, which leads to $\theta_0 = 44.1^\circ$. This angle depends on the value of α. If the transition is of second order, even this wall with $\theta_0 = \pi/4$ works as the ordering wall irrespective of positive value of α. This situation is common to the homogeneous structure, because $P_2(\sin\theta_0\cos\varphi_0) = 0.25$ at $\theta_0 = \pi/4$.

Finally the dependence of the critical thickness N_c on θ_0 is studied as shown in Figure 9. The value N_c is evaluated as the extrapolation of zero of $(\bar{s}_L - \bar{s}_H)^2$ with Decreasing N, where $\bar{s}_L$ and $\bar{s}_H$ are the values of $\bar{s}$ of the low temperature phase and of high temperature one, respectively, at the transition point. The decrease of N_c becomes remarkable near the value $\theta_0 = 40^\circ$, which is considered to come from the decrease of ordering effect of walls near the angle 44.1° in addition to the increase of σ_0.

Correspondence between Thin System with Walls and the Bulk

Let cos ν_x, cos ν_y and cos ν_z be direction cosines ($\theta_i = \nu_{iz}$). Then, using the identity, $P_2(\cos\,\nu_{ix}) + P_2(\cos\,\nu_{iy}) + P_2(\cos\,\nu_{iz}) = 0$, the field energy

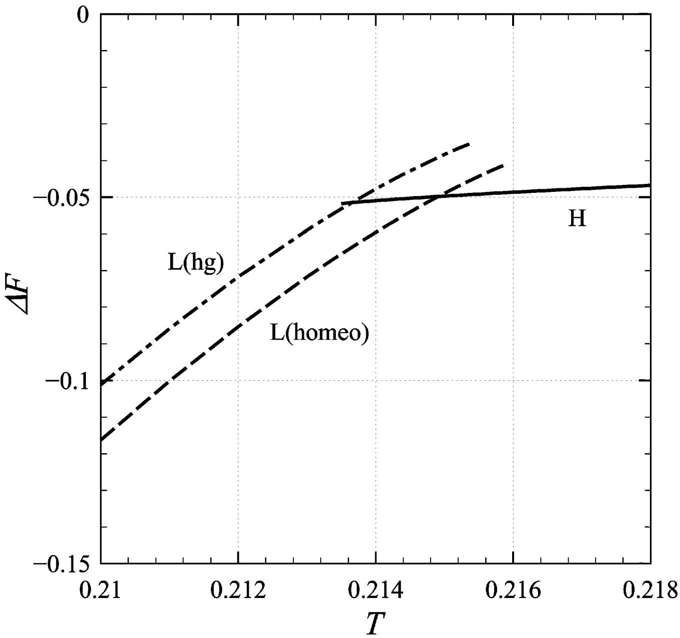

FIGURE 4 Temperature dependence of the free energy ($N = 14$, $\theta_0 = 44^\circ$).

(3) is rewritten as

$$H_{ext} = -\left(h_z + \frac{2}{3}h\right)\sum_i P_2(\cos\nu_{iz}) - \frac{4}{3}h\sum_i P_2(\cos\nu_{ix}). \qquad (28)$$

In case $h_z = -2/3\,h$, which is the thin line l_x in Figure 1, the system is uniaxial with principal axis in x-axis. In practice, from Eqs. (17) and (18) we obtain $s = -1/2\sigma$, and by inserting this relation to the free energy (19) the uniaxial free energy is obtained, which coincides strictly with $F(\sigma, 0)$ in eq. (19). It is noticed that on the line l_y in Figure 1, the fields for $P_2(\cos\nu_{iz})$ and $P_2(\cos\nu_{ix})$ are identical and this case will be discussed in the below.

Here, we rewrite Eqs. (20) and (21) in the forms,

$$s_n = I\left(\beta V z s_n + \beta h_{zn}, \frac{3}{4}\beta V z \sigma_n + \beta h_n\right), \qquad (29)$$

$$\sigma_n = J\left(\beta V z s_n + \beta h_{zn}, \frac{3}{4}\beta V z \sigma_n + \beta h_n\right), \qquad (30)$$

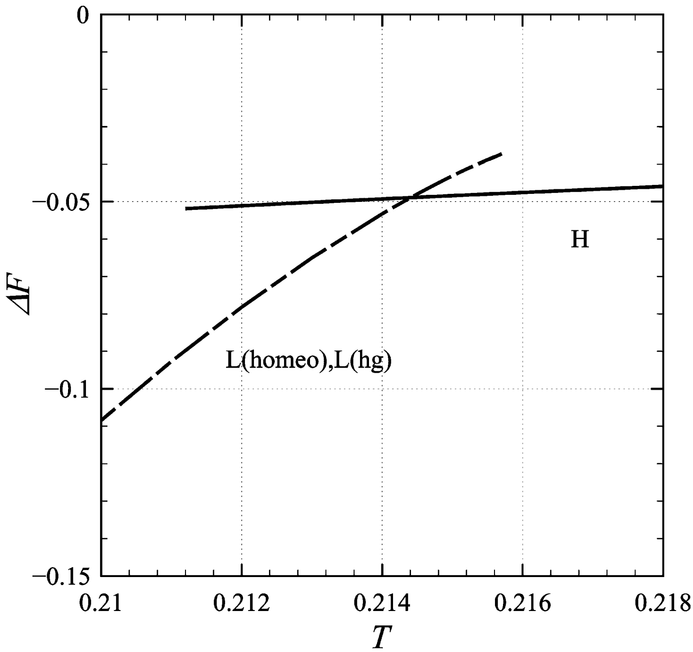

FIGURE 5 Temperature dependence of the free energy ($N = 14$, $\theta_0 = 45°$).

in which effective fields, h_{zn} and h_n are given by,

$$h_{zn} = V(s_{n+1} + s_{n-1} - 2s_n), \tag{31}$$

$$h_n = \frac{3}{4}V(\sigma_{n+1} + \sigma_{n-1} - 2\sigma_n). \tag{32}$$

The forms (29) and (30) are the same to the self-consistency equations of the bulk (14) and (15) in the, h_{zn} and h_n. Though the effective fields are not completely equivalent to real fields, these forms are useful to study the transition phenomena. In the case of homeotropic anchoring, $\theta_0 = 0$, we obtain $\sigma_n = 0$ and $h_n = 0$ from Eq. (32). Then, the system is on the thin line $h = 0$ (l_z in Figure 1), and phase transitions are already studied in detail [11]. The homogeneous structure with uniaxiality is achieved at $\theta_0 = \pi/2$. As mentioned in the above, this structure is equivalent to homeotropic one because the both boundary conditions are also equivalent to each other.

In the case $h_z = 2/3\ h$, the fields for $P_2(\cos\ \nu_{iz})$ and $P_2(\cos\ \nu_{ix})$ in Eq. (28) are same, where the system is equivalent to the one in the

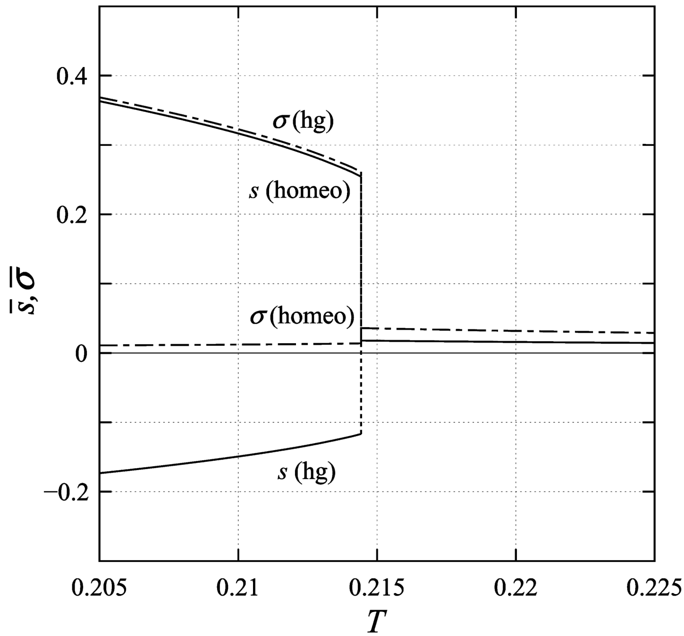

FIGURE 6 Temperature dependence of averages of order parameters s_n and σ_n ($N = 14,\ \theta_0 = 45°$).

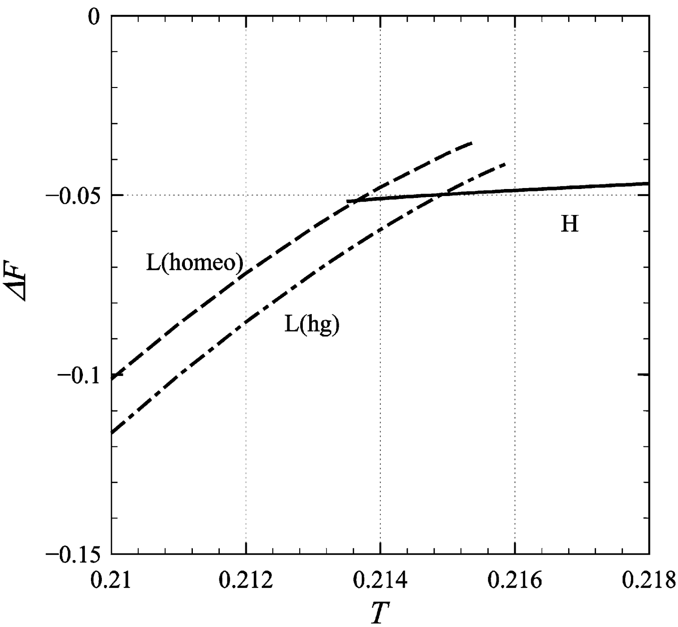

FIGURE 7 Temperature dependence of the free energy ($N = 14,\ \theta_0 = 46°$).

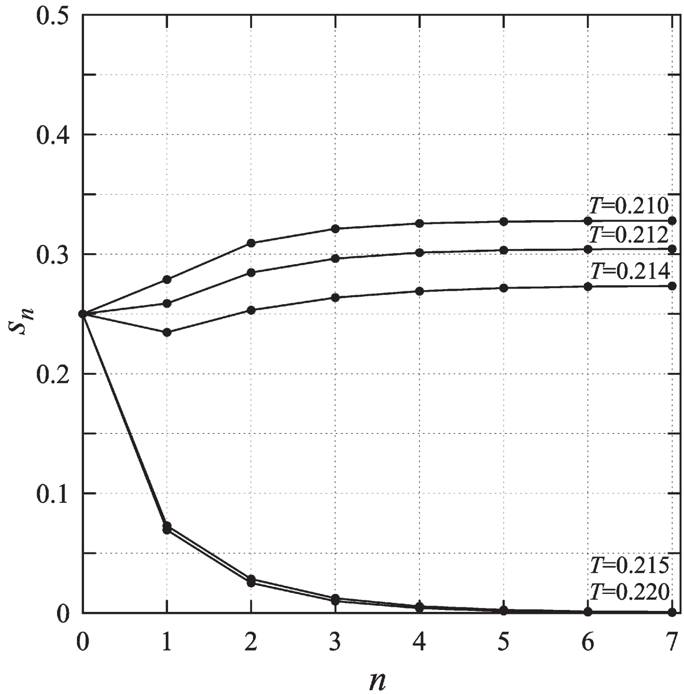

FIGURE 8 Change of profile of ordering at the homeotropic structure ($N = 14$, $\theta_0 = 45°$).

field $-4/3\ h$ in y-axis. From Eqs. (17) and (18), we obtain a relation $s = 1/2\sigma$. At the positive value of h, the symmetry in x-z plane is broken at low temperature phase, where the order parameter is $2/3 < P_2$ (cos ν_{iz}) $-P_2(\cos\nu_{ix}) >$ ($=s$–$1/2\sigma$) while the relation is satisfied at the disordered phase. This case is applied to the thin system with $\theta_0 = \pi/4$. We obtain a set of solutions to simultaneous Eqs. (29)–(32) with the relations, $s_n = 1/2\sigma_n$ and $h_{zn} = h_n$, which corresponds to the high temperature phase. At low temperature the symmetry is broken and two phases coexist as shown in Figure 5. In this respect, the critical thickness N_c becomes a special one for the tricritical point, which corresponds to the one in the bulk, TC on l_y in Figure 1. Except for the uniaxial case with negative field, the phase transition is the same qualitatively to the uniaxial one even though biaxiality appears because of h. Accordingly the thickness dependence of transition behaviour is similar to the homeotropic one for the angle of general value.

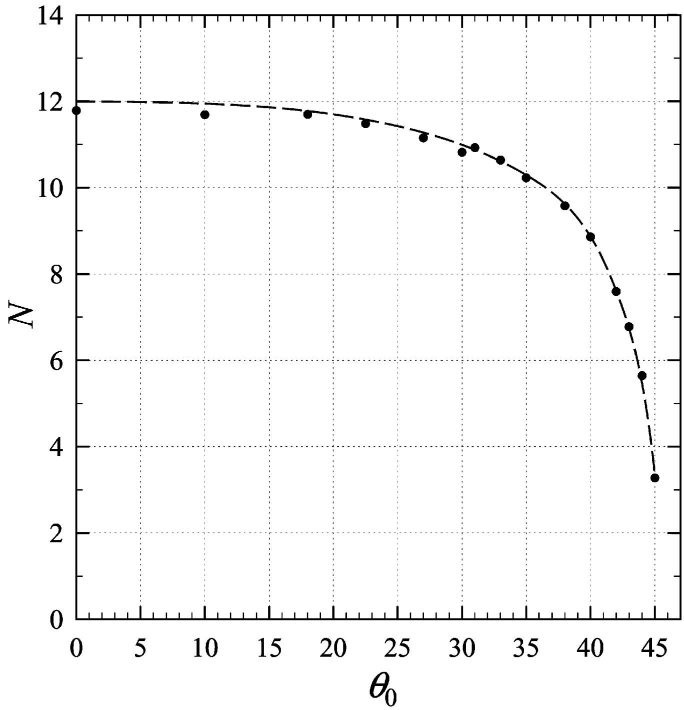

FIGURE 9 θ_0 dependence of the critical thickness.

SUMMARY

The Landau free energy as a function of a couple of order parameters, uniaxial and biaxial ones, is calculated practically for the Maier-Saupe model in the framework of the mean field theory, based on which phase diagram in the field space is obtained. By generalising the free energy to be applicable to the thin system sandwiched by biaxial walls, phase transition occurring therein is studied. The results for bulk and homeotropic anchoring case are equivalent qualitatively to those studied already without order parameter expansion [11,16]. In comparison with these, we can realise the meaning of those derived from Landau expansion in various situations such as the thin system. The biaxial anchoring condition of walls is prepared by introducing a set of fixed molecular orientations on the walls, where the strength of biaxiality is parametrised by the angle of molecules. For the system with angle $\pi/2$, the homogeneous structure occurs, which is the same to the homeotropic structure at the Marie-Saupe model because the positional freedoms are decoupled completely to the orientational ones. Dependence of the critical thickness at which the first order transition changes to the critical one is evaluated. For general value of angle the behaviour of the system is essentially the same to the homeotropic one except for the angle $\pi/4$, at which the crossover between homeotropic structure and homogeneous ones occurs. Below the transition temperature both phases coexist showing that at the critical thickness the tricritical behaviour occurs. This change corresponds to the appearance of the tricritical point in the bulk system. In a narrow range of angle near the angle $\pi/4$, the anchoring is shown to work as the disordering walls.

In the present study, the molecules on the walls are assumed to take only two directions, θ_0 and φ_0 $(= 0$ and $\pi)$, and the coupling strength α is chosen to be 1, where the disordering effect due to walls barely appears only in a narrow range of angle. In the real system the distribution of molecular orientation on the walls are assumed to be widely distributed and the nematic order near the walls is disturbed considerably even though the distribution remains biaxial. For small value of α, nematic ordering is apparently suppressed near the wall. By taking account of these circumstances, the disordering wall will be achieved in more wide range of wall conditions.

At the crossover point between homeotropic and homogeneous structures, the system is uniaxial and as the thickness decreases the molecules tend to lie in a plane perpendicular to the principal axis (x-z plane in the present coordinate system). Then, system approaches to the one described by two-dimensional XY model, and a crossover from the ordered phase with long range order to a Kosterlizt-Thouless phase may occur [15]. In the Maier-Saupe model studied here, homeotropic phase and homogeneous one are described equally, while in a real system the homogeneous structure is not uniaxial and continuous symmetry of rotation in the plane is not retained. In this respect, more realistic model is required to study the details of the crossover phenomena.

To study the phase transitions occurring in the thin system, the phase diagram of the bulk system is referred, where the similarity between the effect due to walls and external fields is stressed here. However, dissimilarity among them is also interesting, especially the appearance of curious state which is unstable in the bulk is related to the mechanism of continuous change at thin system [11,12]. An investigation of the mechanism of the crossover is required from this point of view as a next question.

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