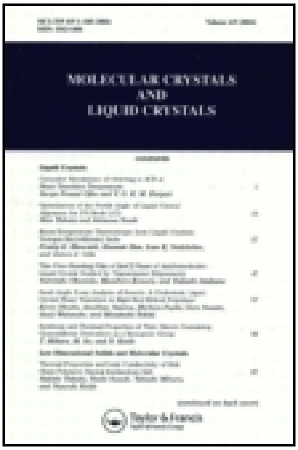

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Similarity and Dissimilarity between Influences of Anchoring Walls and of External Fields on Nematic and Smectic A Phases

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To cite this article: M. Torikai & M. Yamashita (2005): Similarity and Dissimilarity between Influences of Anchoring Walls and of External Fields on Nematic and Smectic A Phases, Molecular Crystals and Liquid Crystals, 441:1, 59-67

To link to this article: http://dx.doi.org/10.1080/154214091009545

Mol. Cryst. Liq. Cryst., Vol. 441, pp. 59–67, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214091009545

Similarity and Dissimilarity between Influences of Anchoring Walls and of External Fields on Nematic and Smectic A Phases

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The McMillan liquid crystalline models under the influence of homeotropic anchoring walls and of external fields are investigated. For thin systems, the existence of the critical thickness, below which the system does not undergo a discrete phase transition, is confirmed. Apparent differences between the influence of the anchoring walls and of external fields are elucidated by investigating the order parameters and a temperature vs external field phase diagram for the bulk systems.

Keywords: external field; homeotropic anchoring; nematic phase; smectic A phase

1. INTRODUCTION

The anchoring conditions at the boundary walls strongly influence the behavior of the liquid crystals. The effects of the anchoring is remarkable at isotropic(I)–nematic(N) phase transition, since the discontinuity of extensive variables at I–N transition is rather small. For instance, in a thin liquid crystal system bounded by two parallel walls at which the liquid crystal molecules are anchored homeotropically, the I–N transition occurs at higher temperature than the transition temperature of the bulk system [1–4]. Furthermore if the homeotropic anchoring is strong and the system is thin enough, the I–N transition disappears and the system undergoes a continuous change between

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high- and low-temperature phases. It is found that there is a critical thickness below which the system has no transition [1,2].

The effects of the anchoring at boundaries are similar to the effects of a uniform external field, as indicated in the early study by Sheng [1]. Under the external field which aligns liquid crystal molecules, the I–N transition temperature shifts higher, as under the influence of homeotropic anchoring at boundaries. Corresponding to the existence of the critical thickness for I–N transition in thin systems, there is a critical strength of the external field; i.e., the I–N transition vanishes and becomes a continuous change under the external field stronger than the critical external field [5,6]. The similarities between the influence of the external field and of the anchoring boundary condition were discussed by Poniewierski and Sluckin [4]. In Ref. [4], they investigated the boundary effects by considering a boundary ordering potential at the walls; they compared the effects of external field and the effects of anchoring walls by relating the external field and averaged anchoring potential over the bulk. The predictions of the averaged anchoring potential approximation are well satisfied if the anchoring potential is weak.

In the present paper, we study the influence of anchoring walls and of external fields upon the N and smectic A (A) phases. Then we discuss the differences between the influence of the anchoring conditions and of external fields. We use so-called McMillan's liquid crystal model, which exhibits I, N, and A phases [7]. We consider the situation in which the liquid crystal system is sandwiched between two parallel walls and the liquid crystal molecules are strongly anchored homeotropically at the walls. Changing the temperature and the thickness of the system, we investigate the temperature dependence of the order parameters and transition behaviors. In addition we introduce effective fields due to the inhomogeneity of the order parameters, and compare the behaviors of the system under the effective fields and of the system under the external fields.

2. FORMULATION

In this paper, we use the formulation given in Ref. [8] for McMillan's liquid crystal model under the external fields and under the strong anchoring boundary condition, which is carried out in the framework of the molecular field approximation.

First we introduce the self-consistent equations for a bulk system under uniform external fields conjugate to the order parameters. We denote the N and A order parameters by s and σ, respectively. These order parameters are defined, as was done in McMillan's original work, as $s = \langle P_2(\cos\theta)\rangle$ and $\sigma = \langle \cos(2\pi z/d) P_2(\cos\theta)\rangle$ where z and θ are, respectively, the z-coordinate (z-axis is taken to be parallel to the director) and polar angle of a molecule. Here we assume that the smectic layer thickness is d. Within the mean field approximation, the one-body potential for McMillan model is

$$V(z, \cos\theta) = -V_0\left[s + \alpha\sigma\cos\left(\frac{2\pi z}{d}\right)\right]P_2(\cos\theta), \tag{1}$$

where the function P_2 is the second order Legendre function $P_2(x) = (3x^2 - 1)/2$, and the parameter α is a dimensionless interaction strength for A phase relative to N phase. Now we introduce two external fields h_s and h_σ corresponding to the order parameters s and σ, respectively. Then the self-consistent equations for order parameters are

$$s = I(\beta(h_s + V_0 s), \beta(h_\sigma + V_0\alpha\sigma)), \tag{2a}$$

$$\sigma = J(\beta(h_s + V_0 s), \beta(h_\sigma + V_0\alpha\sigma)), \tag{2b}$$

where β denotes the inverse temperature. The functions $I(\eta, \zeta)$ and $J(\eta, \zeta)$ are defined as

$$I(\eta, \zeta) = \frac{\partial}{\partial\eta}\ln Z(\eta, \zeta), \tag{3a}$$

$$J(\eta, \zeta) = \frac{\partial}{\partial\zeta}\ln Z(\eta, \zeta), \tag{3b}$$

where Z is

$$Z(\eta, \zeta) = \int_0^\pi d\theta \sin\theta \int_0^d dz \exp\left\{\left[\eta + \zeta\cos\left(\frac{2\pi z}{d}\right)\right]P_2(\cos\theta)\right\}. \tag{4}$$

For a given set of external fields, the self-consistent Eqs. (2) have some sets of solutions corresponding to I, N, and A phases. Among these sets of solutions, the thermodynamically stable set gives the smallest value of a function

$$\beta F(\beta, h_s, h_\sigma; s, \sigma) = \frac{\beta V_0}{2}s^2 + \frac{\beta V_0}{2}\alpha\sigma^2 - \ln\frac{Z(\beta(h_s + V_0 s), \beta(h_\sigma + V_0\alpha\sigma))}{Z(0,0)}, \tag{5}$$

and the smallest value of F is the thermodynamic free energy. The other sets of solutions correspond to the metastable and unstable states.

In order to treat the inhomogeneous systems, we use a discrete McMillan model in which the systems are divided into layers by planes parallel to the boundary walls. We choose the layer thickness thin enough to neglect the spacial variance of order parameters inside the layer; then we can assume the nth layer has its own N and A order parameters s_n and σ_n, respectively. We assume that this layer thickness and the smectic layer thickness d are of the same order. In the following we restrict ourselves to the systems which have thickness $D = (N+2)d$ with integer N (0th and $N+1$th layers are in contact with walls). Under these assumptions, the molecular field contributions appearing in the right-hand side of Eqs. (2), $V_0 s$ and $V_0 \alpha\sigma$, are divided into the intralayer and interlayer molecular field contributions. Then the self-consistent equations of homogeneous systems is generalized to the self-consistent equations of inhomogeneous systems as

$$s_n = I\big(\beta\big(\tilde{h}_s^{(n)} + V_0 s_n\big), \beta\big(\tilde{h}_\sigma^{(n)} + V_0 \alpha\sigma_n\big)\big), \tag{6a}$$

$$\sigma_n = J\big(\beta\big(\tilde{h}_s^{(n)} + V_0 s_n\big), \beta\big(\tilde{h}_\sigma^{(n)} + V_0 \alpha\sigma_n\big)\big), \tag{6b}$$

where $V_0 = V_0' + 2V_0''$; the parameters V_0' and V_0'' are the intralayer and interlayer interaction potentials, respectively. The quantities $\tilde{h}_s^{(n)}$ and $\tilde{h}_\sigma^{(n)}$ are defined as

$$\tilde{h}_s^{(n)} = V_0''(s_{n-1} - 2s_n + s_{n+1}), \tag{7a}$$

$$\tilde{h}_\sigma^{(n)} = V_0''(\sigma_{n-1} - 2\sigma_n + \sigma_{n+1}), \tag{7b}$$

and these quantities vanish if the system is homogeneous. We shall call $\tilde{h}_s^{(n)}$ and $\tilde{h}_\sigma^{(n)}$ the *effective fields* because of the similarity between (2) and (6). Corresponding to the Eq. (5), the thermodynamically stable set of solutions of Eq. (6) gives the smallest value of a function

$$\begin{aligned}\beta F(\beta, \{s_n\}, \{\sigma_n\}) = \sum_{n=1}^{N} \Bigg\{ & \frac{\beta V_0}{2} s_n^2 + \frac{\beta V_0}{2} \alpha\sigma_n^2 \\ & - \ln \frac{Z\big(\beta\big(\tilde{h}_s^{(n)} + V_0 s_n\big), \beta\big(\tilde{h}_\sigma^{(n)} + V_0 \alpha\sigma_n\big)\big)}{Z(0,0)} \Bigg\} \\ & + \sum_{n=1}^{N-1} \{V_0'' s_n s_{n+1} + \alpha V_0'' \sigma_n \sigma_{n+1}\},\end{aligned} \tag{8}$$

where the sets $\{s_n\}$ and $\{\sigma_n\}$ are the solutions to Eqs. (6).

We impose strong homeotropic anchoring condition, i.e., the perfect nematic order is induced by the walls and thus $s_0 = s_{N+1} = 1$. Furthermore we assume that the boundary walls are smooth planes and thus the smectic order parameter is also unity at each wall, i.e., $\sigma_0 = \sigma_{N+1} = 1$.

3. RESULTS AND DISCUSSIONS

The McMillan model exhibits qualitatively different phase behavior depending on the value of parameter α. The bulk system undergoes a first-order transition directly from I phase to A phase for $\alpha \gtrsim 0.98$. For $\alpha \lesssim 0.98$, N phase appears as an intermediate phase between the I phase and A phase. Both the I–N and N–A transitions are first-order in $0.70 \lesssim \alpha \lesssim 0.98$. The N–A transition becomes a second-order transition for $\alpha \lesssim 0.70$ while I–N transition remains a first-order transition. Although it is important to investigate systems of several α, we restrict ourselves here to the system which has three (I, N and A) phases and the two transitions between them are both first-order. We choose the parameter $\alpha = 0.88$. The results for the other α values have been published [9].

We show in Figure 1 the order parameter profiles for systems with different thickness. These profiles are calculated at temperatures near the bulk transition temperature. Since Figure 1(b) exhibits the first order transition and Figure 1(a) does not, the critical thickness for $\alpha = 0.88$ is $N = 13$. The transition temperatures of the thin system is slightly higher than the bulk transition temperature. The thickness dependence of the transition temperature are shown in Figure 2. The change in transition temperature $\Delta T = T(N) - T(\infty)$ behaves as $\Delta T \sim N^{-2}$ for small N. We note that the thickness dependence of ΔT seems inconsistent with the prediction of Kelvin equation: $\Delta T \sim N^{-1}$ [2,3]. However, since the Kelvin equation is obtained by neglecting the thickness dependence of latent heat and of the surface tension [4], the inconsistency only indicates that our studies are restricted to the very thin systems where the Kelvin equation is not valid. Since the difference between influence of external fields and of the anchoring walls is mainly focused in the present study, the discussion on relation between our results and Kelvin equation will be published elsewhere.

We can see the difference between the influence of external fields and of boundary conditions by investigating the order parameters quantitatively. The order parameter σ_n for $n = 6$ of thin ($N = 12$) system and order parameter σ of bulk system under some external fields are shown in Figure 3. There is a region, as shown in Figure 3, where the bulk system is metastable or unstable no matter how the external fields are. However an order parameter of a single layer in a thin system pass through the region where the bulk system is not stable. In other words, even if we apply the uniform external fields at any

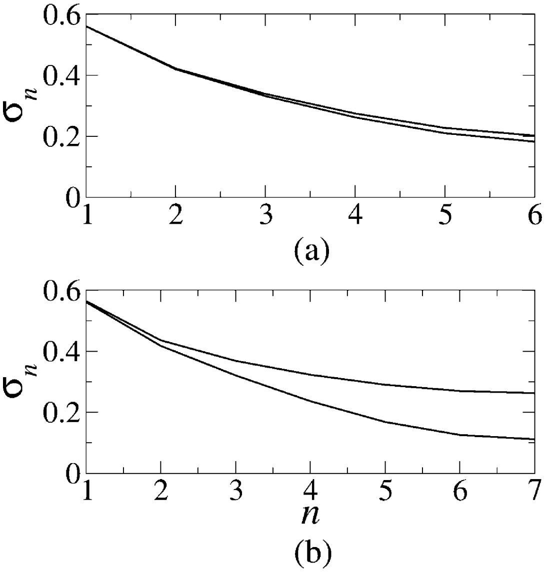

FIGURE 1 Smectic A order parameter profile σ_n for the systems with thickness (a) $N = 12$ and (b) $N = 13$. In both figures, curves are calculated at temperatures where the order parameter difference $\sigma_n(T + \Delta T) - \sigma_n(T)$ is maximum ($\Delta T = 10^{-6}$); (a) $T = 0.212192$ and $T = 0.212193$; (b) $T = 0.211898$ and $T = 0.211899$.

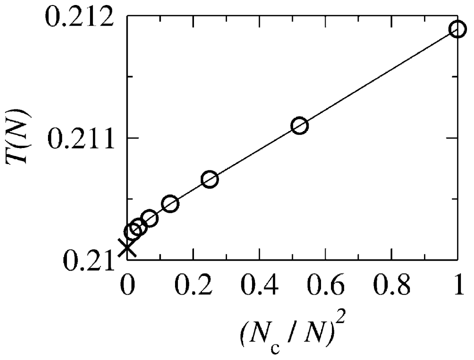

FIGURE 2 The thickness dependence of the transition temperature $T(N)$ (circles) for the system with parameter $\alpha = 0.88$. The horizontal axis represents the square of inverse thickness normalized by the critical thickness $N_c = 13$. The transition temperature for the bulk system is indicated with a symbol “x”.

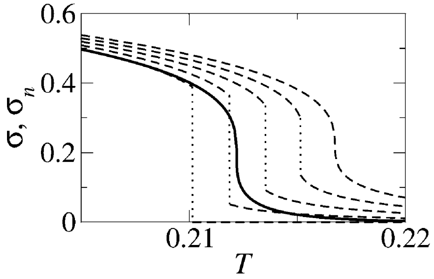

FIGURE 3 Dashed curves are the order parameters $\sigma(T)$ for bulk systems under several external fields: $h_s = h_\sigma = 0$, 2.5×10^{-3}, 5.0×10^{-3}, 7.5×10^{-3}, and 1.0×10^{-2}, from right to left. Vertical dotted lines indicate jumps of the $\sigma(T)$. The region where the dotted lines appear cannot be reached by thermodynamically stable bulk systems. Solid curve is the order parameter $\sigma_6(T)$ for thin ($N = 12$) system.

strength, we cannot obtain the same order parameter values of a single layer. This fact clearly shows the difference in the influence of the external fields and of the effective fields.

In the following, we directly compare a system under uniform external fields with a single layer under effective fields due to the inhomogeneity of order parameters, using a procedure originally introduced in Ref. [10]. We focus on the system whose thickness is less than the critical thickness, i.e., the system does not have phase transition. In order for the direct comparison of external fields with effective fields, it is better to draw a path of a point $(\tilde{h}_s^{(n)}(T), \tilde{h}_\sigma^{(n)}(T))$ on T-h_s-h_σ phase diagram of bulk system. However, since the three-dimensional phase diagram is too complicated, we consider the h_σ-T phase diagram, not for fixed h_s but for $h_s = \tilde{h}_s^{(n)}(T)$; i.e., we consider the phase diagram not on the three-dimensional T-h_s-h_σ space but on its two-dimensional subspace defined by the equation $h_s = \tilde{h}_s^{(n)}(T)$.

The h_σ-T phase diagram is shown in Figure 4. In this figure we show, in addition to the coexisting line, the superheating line and supercooling line. The N phase is metastable between the coexisting line and supercooling line, and the A phase is metastable between the coexisting line and superheating line. If a bulk system crosses the coexisting line of Figure 4 from high temperature to low temperature, the system undergoes a phase transition from N phase to A phase. The bulk system can change from N phase to A phase without any discrete transition only if the external field h_σ is stronger than the critical value, where the N–A coexisting line terminates.

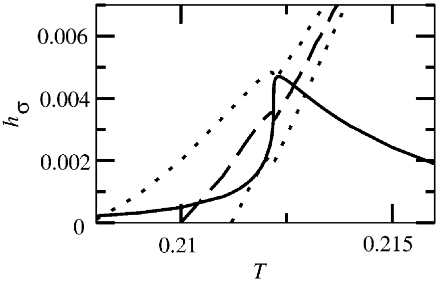

FIGURE 4 The temperature dependence of effective field $h_\sigma^{(n)}(T)$ ($n = 6$ in the system with thickness $N = 12$) and the bulk phase diagram. Solid curve and dashed curve are the effective field and the coexisting curve between N and A phases, respectively. Right and left dotted curves are superheating and supercooling curves, respectively.

On this phase diagram, we drawn the effective field $\tilde{h}_\sigma(T)$. As the temperature decreases, the $\tilde{h}_\sigma(T)$ crosses the coexisting line, touches the supercooling line and the superheating line, and again crosses the coexisting line. During this process, the thin system does not undergo any discrete transition, although the system crosses the coexisting line. This fact shows that a simple analogy between the effective field and external field is not valid on discussing the phase transitions. Although the thin system is always in stable states, the system seems to have undergone metastable and unstable states during the process from high temperature to low temperature. This is because the stable states of the bulk system and a layer of the thin system are determined by different functions (5) and (8), respectively, though these systems obey the equivalent equations (2) and (6), respectively.

In summary, we have studied the influence of anchoring walls and of external fields on N–A phase transition, using a McMillan model. We have confirmed that the systems sandwiched between homeotropic anchoring walls exhibit the transition temperature increase and, in extremely thin systems, disappearance of the phase transition; these effects of anchoring walls are similar to the effects of external fields. However, by investigating the order parameter of a layer and the effective field, we have found that the influence of the anchoring walls cannot be understood with a simple analogy of the influence of the external field.

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