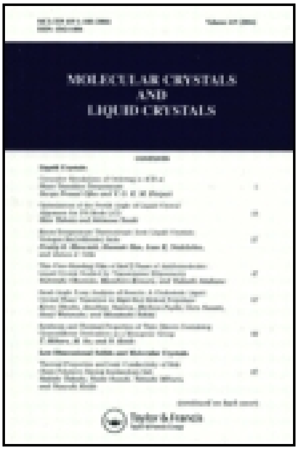

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On the Surface Stabilized Smectic Phase at Very Thin System

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The effect of the wall to the smectic layer ordering is studies at thin liquid crystalline system by generalizing the McMillan theory on smectics. Every order of smectic layers is proved not to vanish, and a crossover from a long range order to a surface sustained one is shown to occur near a bulk transition temperature. The dependence of transition temperature between smectic phase and nematic one at the parallel aligned case is obtained, where the transition temperature is determined from the global behaviour of the order averaged over the whole system.

Keywords: surface stabilized smectic phase; symmetry breaking field for smectic layer; MacMillan theory; homeotropic anchoring; XY model

INTRODUCTION

Ordering of liquid crystals near the wall surface is an interesting and important problem. The effect of walls has been studied exclusively, so far, how to control an orientational ordering of the molecular long axis. Lately, the wall was shown to induce the smectic layer ordering near the wall boundary at nematic phase,[1,2] and in a quite thin system the homeotropically anchored smectic phase was proved to appear in spite of the wall condition of homogeneous anchoring.[3,4] The wall works as the symmetry breaking field to the smectic layer, inducing a density wave in the vicinity of the wall.[5] Accordingly, at the very thin system this effect penetrates the whole system and eventually the surface stabilized smectic phase appears.[3,4] The stability of such surface stabilized smectic phase is certified by applying the transverse electric field as an analogue of the Freedericksz transition.[6,7]

These investigations are based on the molecular dynamics simulation of the Gay-Berne system,[8-10] where the transition from the usual smectic A phase of homogeneous structure to the surface stabilized smectic A phase of homeotropic one is also observed.[3] As a typical case to stabilize such surface stabilized smectic phase, the system with a homeotropic wall condition is also studied, where the smectic A phase with homogeneous structure never appears.[3,4] Here, the generalization of the McMillan theory5) on smectics to such inhomogeneous system is studied to find a clue of the theoretical basis of the surface stabilized smectic phase, which corresponds to the case of the homeotropic wall condition at the simulation.

In the framework of the mean field theory, the Hamiltonian of the system is introduced in the following section and typical case of parallel alignment of molecules is analyzed. It is proved that the smectic order never vanishes at finite temperature due to the wall effect. The transition temperature between smectic and nematic phases is determined from the behaviour of an average of the order parameters over the whole system for various values of system width.

GENERAL FORMULATION

Hamiltonian in the Mean Field Theory

McMillan theory[11] on the smectic-nematic-isotropic phase transition is a generalization of the Maier-Saupe theory[12-14] on the nematic-isotropic phase transition, where the ordering of smectic layer is taken into account. Though the Hamiltonian introduced by McMillan has a general feature, it is reduced to the following form in the framework of the mean field theory as

$$H = -V_0 \sum_{(i,j)} (1 + \alpha \cos\frac{2\pi z_i}{d} \cos\frac{2\pi z_j}{d}) P_2(\cos\theta_i) P_2(\cos\theta_j), \qquad (1)$$

where z_i denotes a z-coordinate of the i-th molecule, θ_i a tilt of the molecular long axis from the smectic layer normal with layer spacing d and $P_2(x)$ the second Legendre polynomial. The behaviour of the inhomogeneous system is analyzed in terms of two types of order parameters defined by

$$s_n = \langle P_2(\cos\theta_n) \rangle, \qquad (2)$$

$$\sigma_n = \langle \cos\frac{2\pi z_n}{d} P_2(\cos\theta_n) \rangle, \qquad (3)$$

where n denote the number of the layer and the angle brackets mean the thermal averages.

System of Parallel Molecules

In case the smectic-nematic transition temperature T_c is fairly separated from the nematic-isotropic line, the nematic order near T_c is sufficiently large and the fluctuation of molecular long axis is considered to be small.

Here, we introduce a typical model to discuss the smectic ordering, where all molecules are parallel to each other making an right angle to the walls of the system. Such parallel system has been utilized with fairy good success to elucidate the mechanism of phase transitions in liquid crystals.[15-18] Then, the Hamiltonian is given by

$$H_p = -V_1 \sum_{(i,j)} \cos\frac{2\pi z_i}{d} \cos\frac{2\pi z_j}{d}, \qquad (4)$$

where $V_1 = V_0\alpha$. We see that the Hamiltonian (4) is equivalent to the classical XY model in the mean field theory, and the critical temperature $T_c^{(0)}$ of the homogeneous system is easily determined (from the following eqs. (6) and (7)) with f_0 a half of the coordination number in the layer and k_B the Boltzmann constant as

$$T_c^{(0)} = (f_0 + 1) V_1 / k_B. \qquad (5)$$

In the inhomogeneous system with walls, the self-consistent condition for σ_n is expressed as

$$\sigma_n = J(\zeta_n), \tag{6}$$

where $J(x)$ is defined by $I_1(x)$ / $I_0(x)$ with the n-th modified Bessel function $I_n(x)$ and the molecular field ζ_n is given with temperature T by

$$\zeta_n = \frac{V_1}{k_B T}(2f_0\sigma_n + \sigma_{n+1} + \sigma_{n-1}). \tag{7}$$

The thermodynamical potential per particle $\Phi(\{\sigma_n\})$ is obtained as

$$\Phi(\{\sigma_n\}) = \Phi(\{0\}) + \frac{1}{2N}\sum_{n=1}^{N}[-V_1(2f_0\sigma_n + \sigma_{n-1}\sigma_n + \sigma_n\sigma_{n+1}) + 2k_B T(\zeta_n\sigma_n - \ln\frac{I_0(\zeta_n)}{I_0(0)})], \tag{8}$$

where N denotes the number of layers. We assume the following boundary condition, that is, the wall condition as

$$\sigma_0 = \sigma_{N+1} = 1. \tag{9}$$

RESULTS

Proof of the Non-vanishing Order Parameter

Prior to the numerical analysis, we prove that for any n σ_n never vanishes at finite temperature. Here it is mentioned that $J(\zeta_n)$ in eq. (6) is a single-valued odd function. Assume $\sigma_i = 0$ for i ($< N/2$). Then, we obtain $\sigma_{i+1} = -\sigma_{i-1}$ from eqs. (6) and (7), and the order parameters are determined successively with the antisymmetric alignment; $\sigma_i = 0$, $\sigma_{i+1} = -\sigma_{i-1}$, $\sigma_{i+2} = -\sigma_{i-2}$, ... At an end we obtain σ_{2i} ($= -\sigma_0$) $= -1$, which leads to $\zeta_{2i} = -\infty$ from eq. (6). This unbounded value of ζ_{2i} contradicts to the eq. (7) at finite temperature. Thus, it is proved that no order parameter vanishes except for the sites at the centre.

The order parameter at the centre is also proved not to vanish as follows. It is easily shown from eqs. (6) and (7) that all order parameters vanish in case any two succeeding order parameters vanish, $\sigma_i = \sigma_{i+1} = 0$. Apparently this result is applied to both of the wall sites, $i = 0$ and N+1, which contradicts to the condition given by eq. (9). Thus, two neighbouring order parameters are shown not to vanish simultaneously. In the case of even layer number, we can assume that $\sigma_{N/2} = \sigma_{N/2+1}$ because of the symmetry. So, $\sigma_{N/2}$ and $\sigma_{N/2+1}$ never vanish. Let assume $\sigma_{(N+1)/2} = 0$ for odd value of N. Because of the symmetry it is assumed that $\sigma_{(N-1)/2} = \sigma_{(N+3)/2}$. Then, it is derived from eq. (7) that $\sigma_{(N-1)/2}$ $(= \sigma_{(N+3)/2}) = 0$, and three succeeding order parameters vanish, which never occurs as shown just in the above.

We have shown that in the bounded system all order parameters never vanish at finite temperature only if the system couples to the boundary, given by eq. (9). To determine the transition temperature T_c, precise observations of the behaviour of the order parameter are required.

Numerical Analysis

Here, eq. (6) and (7) are analyzed numerically. The value, $f_0 = 3$, is used, which leads to $T_c^{(0)} = 4$ (the temperature is scaled in the unit V_1/k_B hereafter). Profiles of the order parameters in the system with $N = 20$ are shown in Fig. 1, where T = 3.5(○), 4.0(△), 4.52(•) and 5.0(×). Even at $T = 5.0$ in Fig. 1, all order parameters, σ_n, are finite. To see the global aspect of the system, the average of σ_n, $\bar{\sigma}$ $(= \Sigma_{n=1}^{N} \sigma_n / N)$, is appropriate. In Fig. 2, the behaviour of $\bar{\sigma}$ at N = 8(a), 20(b), 40(c) and

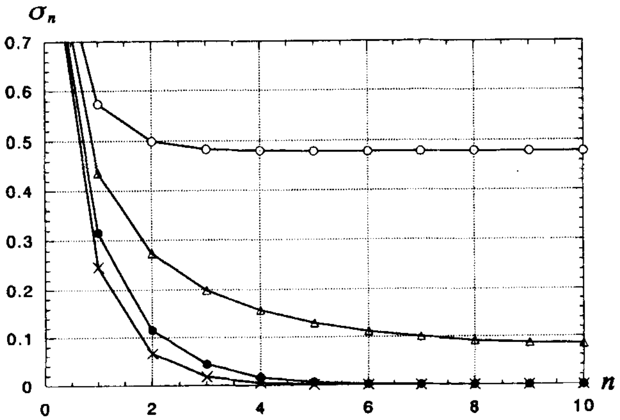

FIGURE 1 The profile of the ordering at $N = 20$

of σ_1 adjacent to the boundary for $N = 20$ are shown. All of these curves are convex for $T < T^*$ ($\simeq T_c^{(0)}$) and concave for $T > T^*$, demonstrating the crossover from the long range order to the surface sustained order to occur. Such crossover behaviour is observed for every order parameter σ_n. For the present, we define the transition tem-

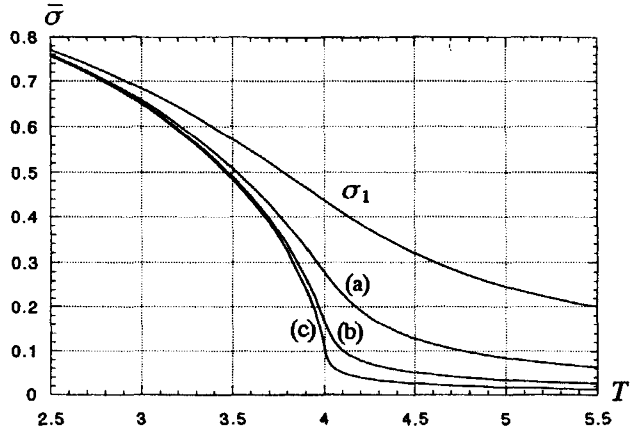

FIGURE 2 Temperature dependence of $\bar{\sigma}$ and σ_1

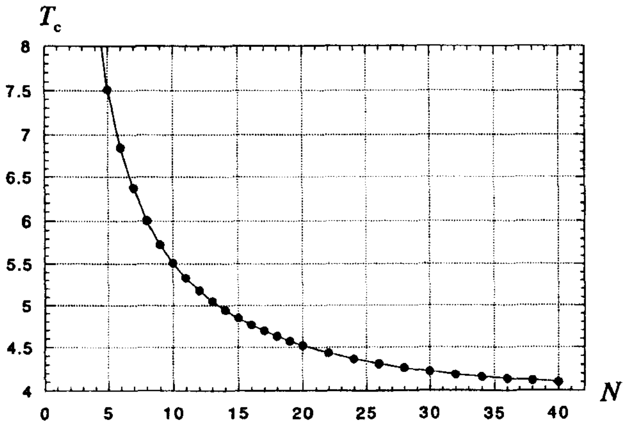

FIGURE 3 The size dependence of T_c.

perature T_c at which $\bar{\sigma}$ takes a small value, 0.05. Though the value 0.05 is not chosen as the logical consequence in nature, this value is proper for the concerning system. The value of the order parameter at the centre of the system is estimated at T_c as follows; 1×10^{-3} for $N = 8$, 4×10^{-5} for $N = 20$ and 9×10^{-5} for $N = 40$. It should be noted that for bulk system T_c does not coincide with $T_c^{(0)}$ but takes 3.995, which is derived from the following equation near T_c,

$$(f_0 + 1) - \frac{k_B T}{V_1} = \frac{(f_0 + 1)\,\sigma^2}{2}. \tag{10}$$

Under this definition the critical temperature is obtained for various value of N, as shown in Fig. 3. Thought the magnitude of T_c depends on the value of the criterion, 0.05, as a matter of course, the tendency of T_c in Fig. 3 is considered to be well described.

SUMMARY AND DISCUSSIONS

The phase transition of the surface stabilized smectic phase to the nematic one at thin system is studied as the generalization of the McMillan theory. The order of the smectic layer is proved not to vanish at finite temperature. The average of the order parameters over the whole system as well as each layer order is demonstrated to show the crossover from the long range order to the surface sustained order at the bulk transition temperature, and the transition temperature is determined here from the behaviour of the averaged order parameter. The dependence of the transition temperature on the width of the system is calculated.

The order of smectic layer at a temperature in the range, $T_c^{(0)} < T < T_c$, is not due to the cooperativity of the molecular interaction but due to the stabilization by the boundary wall, and in this respect the phase should be called really the surface stabilized phase. Even though the order is not the long range order in the meaning of cooperativity, the phase is nothing but the thermodynamically stable state. In practice, the surface stabilized smectic phase is observed at the low temperature side of the usual smectic

A phase at the molecular dynamics simulation.[3,4]

In the system practically analyzed here, the molecular directions are assumed to align parallel to each other. Such idealization is quite useful to study the mechanism of the concerning phenomenon. On the other hand, a realistic model is also required, since the results can be compared with the experimental ones and simulation. It is interesting in itself how the layer ordering is affected by the fluctuation of the molecular direction. Actually, the fluctuation at the transition between smectic and nematic phases is not small even in the thin system as observed at the molecular dynamics simulation.[3,4] In this respect, systematic molecular dynamics studies on the size dependence are required likewise.

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