Isotropic, Nematic and Smectic A Phase Behaviour in a Fictitious Field

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Phase behaviours of liquid crystals under external fields, conjugate to the nematic order and smectic order, are studied within the framework of mean field approximation developed by McMillan. It is found that phase diagrams, of temperature vs interaction parameter of smectic A order, show several topologically different types caused by the external fields. The influences of the field conjugate to the smectic A phase, which is fictitious field, are precisely discussed.

KEYWORDS: nematic phase, smectic A phase, McMillan model, phase transition, external field

1. Introduction

Electric and magnetic fields may influence on the liquid crystalline ordering and thus on the phase behaviour of the liquid crystal systems. These fields directly couple to the nematic order and influence on the nematic ordering. Strong external fields may induce a nematic order even in the isotropic phase.1,2 The external fields also slightly raise the isotropic-nematic (I-N) transition temperature. As the external field is increased, the nematic order in the nematic phase at the transition temperature decreases; together with the increase of the nematic order in the isotropic phase at the transition temperature, the discontinuity at the I-N transition is reduced. Eventually the discrete I-N transition vanishes under a sufficiently strong field, as shown in ref. 1 theoretically and in ref. 2 experimentally.

The influences of the external fields show a richer variety and are much complex if we consider the smectic A order in addition to the nematic order. For example, a system which intrinsically shows direct isotrop-smectic A (I-A) transition under zero external field can exhibit the nematic phase between isotropic and smectic A phases under an external field. The existence of such a field-induced (non-spontaneous) nematic phase was predicted theoretically in ref. 3 and found experimentally in ref. 4. The appearance of this non-spontaneous nematic phase is a consequence of the direct coupling between the field and the nematic order. The external fields also couple to the smectic A order indirectly, through the direct coupling between nematic order and smectic A order. Thus the fields may influence the smectic order and may change the type of the nematic-smectic A (N-A) transition. Actually, it is shown that a system which shows a first order N-A transition under zero external fields may undergo a second order N-A transition under an external field.5,6

These studies have investigated the effects of the external field conjugate to the nematic order, since the (squares of) magnetic and electric fields are the fields conjugate to the nematic order.7 The external field conjugate to the smectic order, which should induce a one-dimensional periodic density modulation in addition to the orientational order of the molecules, is not experimentally available and not realistic field. (The electric field may play a role of the field conjugate to the smectic order by the effect of, so called, smectic electrostriction,8 which is the density change induced by the electric field. However, the effect of the electrostriction is negligibly weak except for the case where the coupling between nematic order and smectic order is weak.8)

The purpose of the present paper is to clarify the phase behaviour of the liquid crystals under the influence of not only the external field, \( h_s \) conjugate to the nematic order but also the external field, \( h_\sigma \) conjugate to the smectic order. The field \( h_\sigma \) is fictitious and arbitrary field; however, the application of such an external field is of interest from theoretical aspects since it completes the description of the phase diagram. In addition, a field conjugate to an order parameter naturally arises as an effective field, as a result of the spatial inhomogeneity of the order parameter. Such an effective field is helpful to understand the phase transitions in inhomogeneous systems. In fact, one of the authors has disclosed the mechanism of phase transition of the freely suspended smectic films, by utilising the effective field conjugate to the smectic order parameter.9

In the present paper, we investigate the McMillan’s liquid crystal model,10 which has a parameter \( \alpha \) showing a dimensionless interaction strength for the smectic A phase. By analysing order parameters and transition temperatures for a suitable range of \( \alpha \), we elucidate the phase behaviour of the system. The knowledge of the behaviour of the homogeneous systems under the fictitious field is useful to investigate the inhomogeneous systems; the relation between the fictitious field and the effective field due to the spatial inhomogeneity is discussed in §4.

2. McMillan Model

We use a mean field approximation of liquid crystalline model introduced by McMillan.10 Let \( s \) and \( \sigma \) be order parameters of nematic order and smectic order, respectively. Then, the McMillan’s one-body potential is expressed as

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

where we assume the director is parallel to \( z \)-axis, and \( \theta \) is the angle between the long axis of a molecule and...
z-axis; $P_2(x) = 3x^2 - 1)/2$ is the second order Legendre polynomial and $d$ denotes the thickness of a single smectic layer. The second term on right hand side of eq. (1) denotes the smectic order interaction and parameter $\alpha$ is the smectic order interaction strength. The order parameters are self-consistently determined from

$$s = \langle P_2(\cos \theta) \rangle_{\beta, s, \sigma},$$

$$\sigma = \cos \left( \frac{2\pi z}{d} P_2(\cos \theta) \right)_{\beta, s, \sigma},$$

where the angular brackets denote the canonical ensemble average for one-particle:

$$\langle A(\theta, z) \rangle_{\beta, s, \sigma} = \frac{1}{Z(\beta, \beta V_0 s, \beta V_0 \alpha \sigma)} \int_0^{\pi} d\theta \sin \theta \int_0^{d} dz A(\theta, z) \exp \left( \beta V_0 \left[ s + \alpha \sigma \cos \left( \frac{2\pi z}{d} \right) \right] P_2(\cos \theta) \right),$$

where $Z$ denotes the one-particle partition function

$$Z(\beta, \beta V_0 s, \beta V_0 \alpha \sigma) = \int_0^{\pi} d\theta \sin \theta \int_0^{d} dz Z(\beta, \beta V_0 s, \beta V_0 \alpha \sigma) \exp \left( \beta V_0 \left[ s + \alpha \sigma \cos \left( \frac{2\pi z}{d} \right) \right] P_2(\cos \theta) \right),$$

Under the external fields, the potential energy induced by the external fields is

$$V_{\text{ext}} = -\left[ h_s P_2(\cos \theta) + h_\sigma \cos \left( \frac{2\pi z}{d} \right) P_2(\cos \theta) \right],$$

where $h_s$ and $h_\sigma$ are the external fields conjugate to, respectively, $s$ and $\sigma$. The mean field one-particle partition function is then $Z(\beta, \beta h_s + \beta V_0 s, \beta h_\sigma + \beta V_0 \alpha \sigma)$. For later convenience to obtain the free energy, we introduce symmetry breaking fields $\eta$ and $\zeta$, which are conjugate to the nematic order and smectic order, respectively. The symmetry breaking fields should be zero at the thermal equilibrium. The one-particle partition function with symmetry breaking fields is $Z(\beta, \eta + \beta h_s + \beta V_0 s, \zeta + \beta h_\sigma + \beta V_0 \alpha \sigma)$. The self-consistent equations for order parameters are

$$s = I(\beta, \eta + \beta h_s + \beta V_0 s, \zeta + \beta h_\sigma + \beta V_0 \alpha \sigma),$$

$$\sigma = J(\beta, \eta + \beta h_s + \beta V_0 s, \zeta + \beta h_\sigma + \beta V_0 \alpha \sigma),$$

where $I(\beta, \eta, \zeta)$ and $J(\beta, \eta, \zeta)$ are defined as

$$I(\beta, \eta, \zeta) = \frac{\partial}{\partial \eta} \ln Z(\beta, \eta, \zeta),$$

$$J(\beta, \eta, \zeta) = \frac{\partial}{\partial \zeta} \ln Z(\beta, \eta, \zeta).$$

Among the sets of solutions of eqs.(7), the thermodynamically stable set gives a minimum of the following function (the work done by the symmetry breaking fields):

$$\beta \tilde{F}(\beta, h_s, h_\sigma; s, \sigma) = \int_0^s ds' \eta(h_s, h_\sigma; s', 0) + \int_0^\sigma d\sigma' \zeta(h_s, h_\sigma; s, \sigma'),$$

where $\eta(h_s, h_\sigma; s, \sigma)$ and $\zeta(h_s, h_\sigma; s, \sigma)$ are the inverse solutions $\eta$ and $\zeta$ of the self-consistent equations (7). The minimum of $\tilde{F}(\beta, h_s, h_\sigma; s, \sigma)$ for given $h_s$ and $h_\sigma$ is the thermodynamic free energy per molecule. We can rewrite eq.(9) by use of eqs.(7) as

$$\beta \left( \tilde{F}(\beta, h_s, h_\sigma; s, \sigma) - \tilde{F}(\beta, h_s, h_\sigma; 0, 0) \right) = \frac{\beta V_0 s^2 + \beta V_0 \alpha \sigma^2}{2} - \ln \frac{Z(\beta, \eta + \beta h_s + \beta V_0 s, \zeta + \beta h_\sigma + \beta V_0 \alpha \sigma)}{Z(\beta, 0, 0)},$$

where $s$ and $\sigma$ are the solutions of eqs.(7) for given $h_s$ and $h_\sigma$ with $\eta = \zeta = 0$.

3. Results

Here, we show our numerical results obtained from the above formulation. For convenience of the following observation, we first show the phase diagram of the systems without external fields, which is originally shown in ref. 10. The $\alpha-T$ phase diagram is shown in Fig.1(a). For a system with small $\alpha$, i.e., $\alpha < 0.986$, the system undergoes I-N transition at $T = T_{\text{IN}} = 0.22019$, and N-A transition at lower temperature $T_{\text{NA}}$. The transition temperature $T_{\text{NA}}$ is a monotonically increasing function of $\alpha$. For small $\alpha$, the N-A transition is a second order transition, i.e., $s$ and $\sigma$ are continuous but their differential coefficients have discontinuity at the N-A transition. If $\alpha$ and $T_{\text{NA}}$ are sufficiently large, i.e., $\alpha > \alpha_{\text{tc}}$.
and \( T_{NA} > T_{tc} \), the N-A transition turns to first order transition. The tricritical values of \( \alpha \) and \( T_{NA} \) as \( \alpha_{tc} = 0.703 \) and \( T_{tc} = 0.1910 \). The existence of the tricritical point on N-A coexisting line was also pointed out within the framework of the Landau-de Gennes theory. The N-A coexisting line meets I-N coexisting line at triple point \( \alpha_{triple} = 0.986 \), \( T_{triple} \approx 0.2202 \). A system with \( \alpha > \alpha_{triple} \) exhibits direct I-A transition.

We directly show that the independence of \( T_{IN} \) on using the analogue of the Clapeyron relation for coexisting lines of fluid phases. As done in the Clapeyron relation we can write the slope of a coexisting line at point \((\alpha, T_{IN}(\alpha))\) as

\[
\frac{dT_{IN}(\alpha)}{d\alpha} = -\frac{\Delta F_{\alpha}}{\Delta F_T},
\]

where \( F \) is the thermodynamic free energy per molecule given by minimizing \( \tilde{F}(\beta, h_s, h_{\sigma}; s, \sigma) \) with respect to \( s \) and \( \sigma \). The factors on the right hand side of eq.(11) are evaluated at the point \((\alpha, T_{IN}(\alpha))\) and at the phase indicated by the subscript. Then \( \Delta F_{\alpha} = -\Delta\{V_0\sigma^2/2\} = 0 \) since \( \sigma \) is zero in both isotropic and nematic phases; \( \Delta F_T \) is the entropy change at the transition and is nonzero. Therefore \( T_{IN} \) is independent of \( \alpha \).

In the following, we investigate the phase diagrams under the influence of external fields, \( h_s \) and \( h_{\sigma} \). We restrict our investigations to ranges \( 0 \leq h_s \leq 0.03 \) and \( 0 \leq h_{\sigma} \leq 0.06 \). We believe that the phase diagrams are qualitatively the same if the fields exceed the ranges, and that these upper bounds are sufficiently large to observe the influence of the fields. We also confirmed that, using our inhomogeneous model systems, the effective fields induced by the spatial inhomogeneity of the order parameter do not exceed the ranges indicated above. The inhomogeneous model systems we used are McMillan model systems sandwiched between strong homeotropic anchoring walls; we discuss these models and the effective fields in § 4.

The phase diagrams of systems in nonzero external fields are shown in Figs.1 (b), (c) and (d) for various \( h_s \) and \( h_{\sigma} \). These external fields change the phase diagram not only quantitatively but also qualitatively.

We first discuss the effect of \( h_s \). If \( h_s < h_s^{(c)} = 0.0104 \), the application of \( h_s \) does not induce a topological change on the phase diagram, and increases both \( T_{IN} \) and \( T_{NA} \) linearly. We note that the triple point goes to high-\( \alpha \) region by the application of \( h_s \). Thus, under the field \( h_s \), we have a parameter region in which the nematic phase appears, even if the systems do not exhibit the nematic phase under zero fields; i.e., the field induced non-spontaneous nematic phase \( c \) appears also in the McMillan model. For \( h_s > h_s^{(c)} \) and \( h_s = 0 \), the I-N coexisting line entirely vanishes and thus only N-A coexisting line remains (Fig. 1(b)). The fact that I-N transition vanishes under a strong external field \( h_s \) was shown in ref. 1 for \( \alpha = 0 \), i.e., for Maier-Saupe model.

The effect of \( h_{\sigma} \) is observed on the small \( \alpha \) region even if \( h_s \) is very small. The field \( h_{\sigma} \) removes the second order transition part on the N-A coexisting line (Fig. 1(c)). Thus the tricritical point turns to a critical point. As \( h_{\sigma} \) increases, N-A line moves to higher temperature region; I-N line is not sensitive to \( h_{\sigma} \). If \( h_{\sigma} \) is strong enough, even if \( h_s > h_s^{(c)} = 0.0104 \), a part of I-N line survives and it terminates at the I-N critical point (Fig. 1(d)). As \( h_{\sigma} \) increases, the temperature at I-N critical point \( T_{IN}^{(c)} \) decreases, and \( \alpha \) value at I-N critical point \( \alpha_{IN}^{(c)} \) decreases, so that I-N line is elongated. The application of \( h_{\sigma} \) also increases both of \( T_{IN}^{(c)} \) and \( \alpha_{IN}^{(c)} \), and thus shorten the I-N line. The \( \alpha_{IN}^{(c)} \) is sensitive to \( h_s \), so that the I-N line rapidly shrinks and vanishes for increasing \( h_s \). For \( h_s > h_s^{(c)} \), and finite \( h_s \), there are paths where phases may change from isotropic to nematic, and nematic to smectic, without discontinuous transitions. Furthermore, I-N line rapidly shrinks as \( h_s \) increases, and N-A line also rapidly shrinks as \( h_{\sigma} \) increases. Thus the bifurcated coexisting line becomes a single line which terminates at a critical point.

We estimate the effect of \( h_s \) on the N-A critical point more quantitatively. From our numerical calculations, the N-A critical temperature \( T_{NA}^{(c)} \) is obtained to depend on \( h_{\sigma} \) as

\[
\frac{T_{NA}^{(c)}(h_s, h_{\sigma}) - T_{NA}^{(c)}(h_s, 0)}{T_{NA}^{(c)}(h_s, 0)} = ah_{\sigma}^{2/5}, \tag{12}
\]

as shown in Fig.2(a). The \( h_{\sigma} \)-dependence of the coefficient \( a \) is weak; the coefficients \( a \) are 0.423, 0.431, 0.458 and 0.491 for \( h_s = 0, 0.011, 0.020 \) and 0.030, respectively. The \( h_{\sigma} \) dependence of N-A critical point is approximately linear, i.e., for \( h_s = 0 \),

\[
\frac{T_{NA}^{(c)}(h_s, 0) - T_{NA}^{(c)}(0, 0)}{T_{NA}^{(c)}(0, 0)} = bh_{\sigma}, \tag{13}
\]
the N-A transition turns to be continuous under high 
I-N line thus the system again undergoes I-N transition 
thus N-A critical point appears (Fig. 3(c)). If 
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Fig. 3. The temperature-field (T-h_s) phase diagrams for (a)α = 
0.975, b = 0.01 < h_s(c), (b) α = 0.975, b = 0.0106 > h_s(c), 
(c) α = 0.93, b = 0.01, and (d) α = 0.93, b = 0.0106. The labels 
I, N and A in (a) denote the isotropic, nematic and smectic A 
phases, respectively.

where b = 1.88. Thus h_s and h_σ dependence of T_{NA(c)} is 
completed as

\[ T_{NA(c)}(h_s, h_σ) - T_{NA(c)}(0, 0) = bh_s + a(1 + bh_s)h_s^{2/5}. \]  

If h_s increases, the T_{NA(c)} increases up to I-N transition 
temperature, then N-A line vanishes. The h_σ-dependence of 
N-A critical value of α, \( \alpha_{NA(c)} \), seems to be scalable 
for several h_s as shown in Fig. 2(b). However, in the present 
stage, it is difficult to obtain a simple function form of 
scalled \( \alpha_{NA(c)} \).

In order to show clearly the effect of h_σ on the phase 
behaviour, we show h_σ-T phase diagrams in Fig. 3. In the 
system with \( \alpha = 0.975 \), if the external field h_s is weak, 
three phases are divided by first order transition lines 
(Fig. 3(a)). The transition temperature T_{NA} increases 
almost linearly to h_σ. On the other hand, h_σ-dependence of 
T_{IN} is weak. In fact, in the vicinity of h_s = 0, T_{IN} 
does not depend on h_σ. In analogy to the Clapeyron equation, we 
obtain

\[ \frac{dT_{IN}}{dh_σ} = \frac{\Delta(\partial F/\partial h_σ)}{\Delta F_T} = \frac{\Delta \sigma}{\Delta S}, \]  

where \( \Delta \sigma \) and \( \Delta S \) are the changes of, respectively, \( \sigma \) 
and entropy per molecule at the I-N transition. Thus, 
\( dT_{IN}/dh_σ \) is zero since \( \sigma \) is zero in both isotropic 
and nematic phases at h_s = 0. By the application of h_σ, the 
smectic order is induced in isotropic and nematic phases, 
so that the change in \( \sigma \) is finite and T_{IN} becomes 
dependent on h_σ. If the field h_s exceeds h_s(c), in the system 
with \( \alpha = 0.975 \), the I-N transition turns to be continuous 
at h_σ ~ 0. But the application of h_σ recovers the 
I-N line thus the system again undergoes I-N transition 
(Fig. 3(b)). For h_s < h_s(c) and small \( \alpha \), e.g. \( \alpha = 0.93 \), 
the N-A transition turns to be continuous under high h_s; 
thus N-A critical point appears (Fig. 3(c)). If h_s exceeds 
h_s(c) in \( \alpha = 0.93 \) system, I-N transition at low h_s 
becomes a continuous change without transition. Then the 
system has paths from isotropic phase to smectic phase

without discontinuous transition (Fig. 3(d)).

4. Summary and Discussions

We have studied the phase diagram of the McMillan 
model system under external fields h_s, and h_σ. By the 
application of h_σ, second order transition line on N-A 
line at low \( \alpha \) region vanishes and N-A transition turns to 
be smooth. The I-N line vanishes under an external field 
h_s higher than h_s(c), however h_σ recovers the nematic 
order and I-N coexisting line.

The fictitious field h_σ, which we mainly discussed in 
the present paper, is resulted from the spatial inhomogeneity 
of the order parameter \( \sigma \). As an concrete example, 
let us consider a thin system sandwiched by two 
parallel walls and assume that the walls force liquid crystal 
talline moleculeres at wall surfaces to stick perpendicular 
to the walls(homeotropic anchoring). In the following, 
we discretise the system into N layers parallel to the 
walls, and assume the nth layer has order parameters \( s(n) \) 
and \( \sigma(n) \). In the mean field theory, the inhomogeneity due to walls changes the mean field contributions in the arguments of eqs.(7): e.g., \( V_0s \) turns to \( V_0's(n) + V_0''s(n+1) \) with constants \( V_0 ' \) and \( V_0'' \) 
denoting intralayer and interlayer interactions, respectively. 
Then we may write the self-consistent equation as

\[ s(n) = I(\beta, \beta'h_s^{(n)} + \beta'V_0s(n), \beta'h_σ^{(n)} + \beta'V_0\alpha\sigma(n)), \]  

\[ \sigma(n) = J(\beta, \beta'h_s^{(n)} + \beta'V_0s(n), \beta'h_σ^{(n)} + \beta'V_0\alpha\sigma(n)), \]  

where the \( h_s^{(n)} \) and \( h_σ^{(n)} \) are defined by

\[ h_s^{(n)} = V_0'('s(n-1) - 2s(n) + s(n+1)), \]  

\[ h_σ^{(n)} = V_0''('s(n-1) - 2\sigma(n) + \sigma(n+1)), \]  

and the boundary conditions are \( s(1) = s(N) = 1 \) and 
\( \sigma(1) = \sigma(N) = 1 \). In eqs.(16) and (17) we redefined 
\( V_0 \) = \( V_0 ' + 2V_0'' \) in order to emphasise the equivalence 
of eqs.(7) and (16) in the homogeneous limit. We summarised 
the effect of inhomogeneity of the order parameters 
into \( h_s^{(n)} \) and \( h_σ^{(n)} \). From the similarity between 
eqs.(7) and (16), we may call the variables \( h_s^{(n)} \) and 
\( h_σ^{(n)} \) the effective fields corresponding to h_s and h_σ, 
respectively. The stability condition for the inhomogeneous 
system is minimizing the work done by the symmetry 
breaking fields on the whole system, not the work on 
the each layer. Except for the difference in the stability 
conditions, each layer of the inhomogeneous thin system 
under effective fields may be viewed as a homogeneous 
bulk system under external fields which depend on 
position and on temperature. From this point of view, we 
may analyse the thermal behaviour of the thin system by 
observing the locus of the fields on the bulk phase 
diagram of the field versus temperature plane. In fact, such 
an analysis is shown to be useful in order to uncover 
the mechanism of smectic A-C^* phase transition,9 and I-
N phase transition of Maier-Saupe model.13,14 For thin 
system version of the model we analysed in the present 
paper, we have investigated the phase transitions and 
thermal behaviour of physical quantities by utilising the
phase diagram obtained in the present paper, which will be reported in a near future.\textsuperscript{15}

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