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Landau Theory of Nematic-Smectic-A Transition in a Liquid Crystal Mixture

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Binary mixtures of HBAB [*p*-[(*p*-hexyloxy-benzylidene)-amino] benzonitrile} and CBOOA [*N*-*p*-cyanibenzylidene-*p*-*n*-octyloxyaniline] exhibit a two phase region where both smectic-A and nematic phase coexists. The reason for this two phase region is discussed by means of Landau formalism. The problem of the first or second order nature of the nematic-smectic-A phase transition is explored. General Landau theory for coupled orientational, translational order parameters and concentration is developed.

Keywords: Nematic phase; smectic phase; phase transition

PACS number(s): 64.70. Md; 42.70. Df

INTRODUCTION

Liquid Crystals (LC) are among the most interesting condensed states of matter, they are interesting in their own right and we also expect that insights into their properties will help to understand other condensed phases that exists in nature. In spite of considerable research activity over the past twenty years the nematic-smectic-A (NA) phase transition remains one of the principal unsolved problem in equilibrium Statistical Physics of condensed matter. The nematic (N) phase is an orientationally ordered but translationally disordered phase with rod like molecules aligned with their long axes parallel to the director \hat{n} . The smectic-A (SmA) phase is usually described as being composed of equidistant planes of molecules, each molecule being on the average perpendicular to the planes (i.e., the

system is uniaxial). The N phase occurs at a higher temperature than the smectic (s) phase.

The original theories due to McMillan [1] and de Gennes [2] suggested that this transition could be first or second order. De Gennes using a Landau expansion of the S free energy, emphasized the coupling between the S or density order parameter, ψ and the N or orientational order parameter Q . When large fluctuations in Q are permitted, this can cause the phase transition to be first order. A N phase of large extent, however, would result in Q being saturated, thereby reducing the importance of the coupling term, so the transition becomes second order. McMillan used a molecular-field theory to obtain a similar conclusion. These theories thus imply the existence of a tricritical point (TCP) at the crossover from second to first order behavior. Again Alben [3] predicted a $^3\text{He}/^4\text{He}$ -like TCP in binary LC mixtures. However, the theoretical story is more complex and Halperin, Lubensky and Ma [4] argued that the NA transition can never be truly second order, which of course rules out the possibility of a TCP. During the past twenty years, many high resolution heat capacity and X-ray studies have been devoted to the NA transition [5–14].

Again Cladis [15] obtained a new type LC phase diagram in which the S phase may be formed which reverts to the N phase at still lower temperature. She showed that NA transition temperature of mixtures of HBAB { p -[(p -hexyloxy-benzylidene)-amino]benzonitrile} and CBOOA [N - p -cyanibenzylidene- p - n -octyloxyaniline] becomes multivated with increasing concentration of HBAB. She also observed that some materials (CBOOA) that have a SmA to N phase transition which is not reentrant, reentrant behavior can be induced by mixing it with a second kind LC (HBAB) that only has a N phase [15] (Fig. 1). In the Figure 1 there is a two phase region where both SmA and N phase coexist. The purpose of the present article is to investigate the reason of this new type of phase diagram within the framework of Landau theory. The primary interest will be to investigate as generally as possible those factors which determine this two phase region and whether the transition is first or second order.

LANDAU THEORY

We start by defining an order parameter for the S phase. The order parameter ψ , is defined as the amplitude of a one dimensional density wave where wave vector, q_0 , is parallel to the N director (the z -axis):

$$\rho(\vec{r}) = \rho_0 \{1 + \text{Re}[\psi \exp(iq_0 z)]\} \quad (1)$$

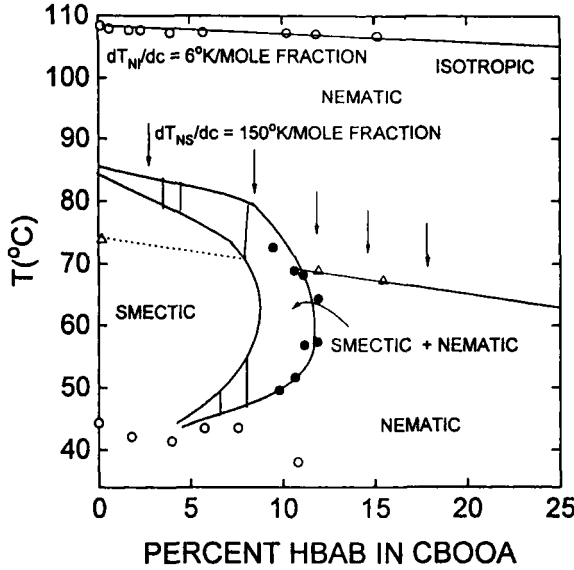


FIGURE 1 The phase diagram (T, c) for mixtures of CBOOA and HBAB. T is the degree centigrade and c the weight percent (approximately the mole fraction). (Reproduced from Ref. [15]).

where $a = 2\pi/q_0$ is the layer spacing and $\psi(\vec{r}) = |\psi| \exp(iq_0 u)$. Here u is the displacement of the layers in the z direction away from their equilibrium position ($u = u(x, y, z)$). It is natural to consider the complex function $\psi(\vec{r})$ as the order parameter for a SmA phase. It is analogous to the two component vector order parameters found in both the superconducting transition in a metal and the superfluid transition in liquid helium.

Expanding of the free energy in powers of the SmA order parameter modulus has the form

$$F - F_0 = \frac{1}{2} A |\psi|^2 + \frac{1}{4} B |\psi|^4 + \frac{1}{6} C |\psi|^6 \quad (2)$$

with $A = a(T - T_{NA})$. If $B > 0$, the NA transition is second order and occurs at $T = T_{NA}$; if $B < 0$ a first order transition occurs at $T = T^* + (3B^2/16ac)$. The NA transition can become first order owing to coupling between the S and N ordering [2, 4, 16]. Then the free energy expansion is

$$F - F_0 = \frac{1}{2} A |\psi|^2 + \frac{1}{4} B |\psi|^4 + \frac{1}{6} C |\psi|^6 + \frac{1}{2} \alpha Q^2 + \frac{1}{3} \beta Q^3 + \frac{1}{4} \gamma Q^4 + \lambda |\psi|^2 Q \quad (3)$$

with $\alpha = \alpha_0(T - T^*)$; Q is the N order parameter and λ is the coupling constant. Let us now consider the binary mixture of HBAB and CBOOA. Since the sample HBAB contain only N phase. So we consider x is the concentration (mole fraction) of HBAB. The sample CBOOA has both N and S phase. Then the free energy density of HBAB-CBOOA mixture may be represented in the form

$$F^*(\psi, Q, x) = F_0 + \frac{1}{2}A^*|\psi|^2 + \frac{1}{4}B^*|\psi|^4 + \frac{1}{6}C^*|\psi|^6 + \frac{1}{2}\alpha^*Q^2 + \frac{1}{3}\beta^*Q^3 + \frac{1}{4}\gamma^*Q^4 + \lambda^*|\psi|^2Q + \frac{1}{2}Ex^2 + \delta|\psi|^2x + \eta Q^2x \quad (4)$$

with $A^* = a'(T - T_{NA}^*)$ and $\alpha^* = \alpha'(T - T^*)$.

Where T_{NA}^* is the NA transition temperature in the absence of coupling between ψ , Q and x . The term Ex^2 is the free energy of HBAB and the lowest order coupling between ψ , Q and x are considered.

From the condition

$$\partial F^*/\partial x = Ex + \delta|\psi|^2 + \eta Q^2 = M \quad (5)$$

where M is the field thermodynamically conjugate to x , the HBAB concentration.

From Eq. (5) we have

$$x = (M - \delta|\psi|^2 - \eta Q^2)/E \quad (6)$$

Again

$$E = (\partial^2 F^*/\partial x^2) = (\partial M/\partial x) \quad (7)$$

Hence from Eq. (6), we have

$$\begin{aligned} x &= M(\partial x/\partial M) - (\delta|\psi|^2 + \eta Q^2)(\partial x/\partial M) \\ &= x_{NA} + \Delta x_1 + \Delta x_2 \end{aligned} \quad (8)$$

with $x_{NA} = M(\partial x/\partial M)$; $\Delta x_1 = -\delta|\psi|^2(\partial x/\partial M)$ and $\Delta x_2 = -\eta Q^2(\partial x/\partial M)$. On transforming $F^*(\psi, Q, x)$ to the free energy depending on the field variable M

$$\begin{aligned} F(\psi, Q, M) &= F^*(\psi, Q, x) - Mx \\ &= F_0 + \frac{1}{2}\left(A^* + \frac{2M\delta}{E}\right)|\psi|^2 + \frac{1}{4}\left(B^* - \frac{2\delta^2}{E}\right)|\psi|^4 + \frac{1}{6}C^*|\psi|^6 \\ &\quad + \frac{1}{2}\left(\alpha^* + \frac{2M\eta}{E}\right)Q^2 + \frac{1}{3}\beta^*Q^3 + \frac{1}{4}\left(\gamma^* - \frac{2\eta^2}{E}\right)Q^4 + \lambda^*|\psi|^2Q \end{aligned} \quad (9)$$

and comparing (9) with (3), one finds the renormalized coefficients

$$A = A^* + \frac{2M\delta}{E} \quad (10a)$$

$$B = B^* - \frac{2\delta^2}{E} \quad (10b)$$

$$C = C^* \quad (10c)$$

$$\alpha = \alpha^* + \frac{2M\eta}{E} \quad (10d)$$

$$\beta = \beta^* \quad (10e)$$

$$\gamma = \gamma^* - \frac{2\eta^2}{E} \quad (10f)$$

$$\lambda = \lambda^* \quad (10g)$$

It can be seen from (10a)–(10g) that taking into account of coupling of ψ and Q with concentration x leads to the renormalization of the constant A , B , α and γ .

From the conditions $A=0$, $\alpha=0$ and $|\psi|=0$, $Q=0$ one finds from (10a) and (10d) at the second order NA and NI transition line

$$T_{NA}(x) = T_{NA}^* - 2(a')^{-1}\delta x \quad (11)$$

$$T_{NI}(x) = T^* - 2(\alpha')^{-1}\eta x \quad (12)$$

The coupling constants δ and η determine the shift of the NA and NI transition temperature and can be easily found from experiment

$$\delta = -(a'/2)(dT_{NA}(x)/dx) \quad (13)$$

$$\eta = -(\alpha'/2)(dT_{NI}(x)/dx) \quad (14)$$

From Eqs. (13) and (14) we find

$$dT_{NA}/dT_{NI} = \delta\alpha'/\eta a' \quad (15)$$

RESULTS AND DISCUSSION

From the relation (8) it is clear that the additional terms Δx_1 and Δx_2 in the concentration x is related to the S and N order parameter. In the case

of second order NA transition, $\psi=0$ and $\Delta x_1=0$. Hence only the N phase appears i.e., no two phase region exist. But in the case of first order NA transition the term Δx_1 is proportional to $|\psi|$. Then both SmA and N phase can coexist i.e., a two phase region appears. Then there is first order NA transition occur within this two phase region. Thus this two phase region indicates the first order character of the NA transition. When the terms $\Delta x_1=0$; $\Delta x_2=0$ i.e., when $|\psi|=0$ and $Q=0$, then only the isotropic phase appears above the N phase (Fig. 1). Thus as long as $\Delta x_1 \neq 0$ and $\Delta x_2 \neq 0$ there is a possibility of two phase region as in Figure 1. The variation of NA and NI transition with concentration x are also calculated in Eqs. (13) and (14).

Now minimization (4) with respect to Q (neglecting the terms like $(\beta^*$ and $\gamma^*)$

$$\partial F^*/\partial Q = \alpha^* Q + \lambda^* |\psi|^2 + 2\eta Q x = 0 \quad (16)$$

$$\text{i.e.,} \quad Q = -\lambda^* |\psi|^2 / (\alpha^* + 2\eta x) \quad (17)$$

Substituting this in Eq. (4), one obtains

$$F^* = F_0 + \frac{1}{2} A^* |\psi|^2 + \frac{1}{4} B_1^* |\psi|^4 + \frac{1}{6} C^* |\psi|^6 + \frac{1}{2} E x^2 + \delta |\psi|^2 x \quad (18)$$

with

$$B_1^* = B^* - 2\lambda^{*2} / (\alpha^* + 2\eta x) \quad (19)$$

Now from Eq. (18) we have

$$\partial F^*/\partial |\psi| = A^* |\psi| + B_1^* |\psi|^3 + c^* |\psi|^5 + 2\delta |\psi| x \quad (20)$$

with A^* linear in $T - T_{NA}^*$ this represents a second order phase transition at $T = T_{NA}^*$ if $B_1^* > 0$ with $A^* \propto (T_{NA}^* - T)^{1/2}$ and therefore $Q \approx (T^* - T)$ in the low temperature phase. If $B_1^* < 0$ the transition occurs at $T > T_{NA}^*$ and is of first order. We therefore have two non-zero order parameters appearing in the two phase region when $B_1^* < 0$ i.e., a two phase region occurs where both SmA and N phase are present.

Now considering the field variable N_1 and N_2 corresponding to the order parameters ψ and Q . They are defined by

$$N_1 = \partial F^*/\partial |\psi|_{Q,T} = A^* |\psi| + B^* |\psi|^3 + C^* |\psi|^5 + 2\lambda^* |\psi| Q + 2\delta |\psi| x \quad (21a)$$

$$N_2 = \partial F^* / \partial Q|_{|\psi|, T} = \alpha^* Q + \beta^* Q^2 + \gamma^* Q^3 + \lambda^* |\psi|^2 + 2\eta Qx \quad (21b)$$

The associated reciprocal responses follows as

$$\partial N_1 / \partial |\psi| |_{Q, T} = A^* + 3B^* |\psi|^2 + 5C^* |\psi|^4 + 2\lambda^* Q + 2\delta x \quad (22a)$$

$$\partial N_2 / \partial Q |_{|\psi|, T} = \alpha^* + 2\beta^* Q + 3\gamma^* Q^2 + 2\eta x \quad (22b)$$

It is now clear that, whereas the parameter ψ responses $(\partial N_1 / \partial |\psi|)^{-1}$ diverges as $T \rightarrow T_{NA}$ ($|\psi| \rightarrow 0$, $Q \rightarrow 0$) by virtue of the proportionality of α^* to $(T - T^*)$, the Q response remains quite finite.

Since HBAB-CBOOA mixtures are nonideal and therefore in principle there should exist values of the temperature ($T = T_{NA}^C$) and concentration ($x = x_{NA}$) at which $(\partial M / \partial x)_{T, P} = 0$.

From the relations (10a) and (10b), we see that with the increase of the concentration, the temperature decreases, the quantity $(\partial M / \partial x)$ decreases and the constants B tends to zero i.e., a tricritical point appears. On further variation of the temperature and concentration the coefficient B changes sign and the transition becomes first order. Further since the coupling between $|\psi|^2$ and x contribute a negative contribution to B , it indicates the tendency of first order behavior of NA transition. Thus the two phase region of Figure 1 appears. Also since for dilute solutions the quantity $(\partial M / \partial x)^{-1} \propto x$ one can reasonably expect that the effect of adding a second order NA transition may be induce a tricritical point at some finite x . Thus when tricritical point appears i.e., when $B = 0$, the width of the two phase region is given by

$$\Delta x \propto x^2 \quad (23)$$

Otherwise in the ordinary case

$$\Delta x \propto x \quad (24)$$

From the relation (11), the NA transition temperature decreases with the increase of the concentration. The depression of the NA transition temperature is connected with the width of the two phase region and the entropy of the transition

$$T_{NA} - T_{NA}^* = \Delta x / \Delta S_{NA} \quad (25)$$

where T_{NA} is the temperature of the NA transition in a pure specimen. This relation is valid for only the first order transition at low solute concentration i.e., NA equilibria. Eq. (25) clearly shows that if $\Delta S_{NA} \neq 0$, a two phase region must exist at fixed T_{NA}^* and that the size of this region depends only on the magnitude of ΔS_{NA} . This is same analogy of binary mixture of LC and non-mesogenic substance [17]. Thus the present analysis indicates the first order character of the NA transition and also possibility of TCP.

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