



Reentrant nematic and tricritical behavior of the nematic to smectic-A phase transition in liquid crystal mixture



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ABSTRACT

We present an improved analysis of the reentrant nematic and tricritical behavior of the nematic to smectic A phase transition in liquid crystal mixture within phenomenological theory. To describe the nematic–smectic A–reentrant nematic phase sequence in binary mixture, nematic and smectic order parameters have been coupled with the concentration. We show that reentrant nematic and the tricritical point on the N–SmA phase transition line can be achieved in the same phase diagram under certain conditions. We predict two tricritical points. One corresponds to nematic to smectic A phase transition and other corresponds to reentrant nematic to smectic A phase transition. A comparison of the results with experimental phase diagrams is described in great details. The predictions of the theory are in good agreement with available experimental data.

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1. Introduction

Since its discovery by Cladis [1], the reentrant phase transition remains one of the interesting topic in the physics of liquid crystals. Over the past forty years or so, a large number of experimental [2–25] works have been carried out to describe the reentrant nematic behavior of the nematic to smectic-A (N–SmA) phase transition. This concerns the physical properties of reentrant phenomena using X-ray diffraction techniques [6–8], specific heat measurements [9,10], optical experiments [6,11–14], NMR dynamic determinations [15–17], dielectric spectroscopy [18–20], viscosity measurements [21,22] and volumetric determinations [23,24]. Thus, the reentrant nematic (RN) phenomenon in liquid crystals has resulted an extensive experimental studies. Cladis et al. [1–4] showed experimentally that the reentrant nematic behavior is readily induced either by the application of modest pressure or by forming mixtures with a second species. The observation with decreasing temperature was: nematic, then smectic A, then nematic again. The nematic phase reentered at a lower temperature than the more ordered smectic A state. As the concentration of a shorter isomeric compound increased, the nematic range became broader.

Cusmin et al. [25] studied the monotropic reentrant nematic behavior for the two component system heptyloxycyanobiphenyl (7OCB) + nonyloxycyanobiphenyl (9OCB) using modulated

differential scanning calorimetry (MDSC) and optical microscopy measurements. Their experimental results confirm that for the pure compound 9OCB, the N–SmA phase transition is first order in nature. Other experimental results [26–28] also confirm the first order nature of the N–SmA phase transition for the pure compound 9OCB. For the pure compound 9OCB, the temperature stability limit for the N phase for the N–SmA phase transition was determined to be almost an order of magnitude higher from dielectric spectroscopy than from specific heat or density measurements, which in addition differ by a factor two [27,29]. In their two component system 7OCB + 9OCB study, Cusmin et al. [25] predicted two tricritical points, one for the nematic to smectic-A_d (N–SmA_d) phase transition and the other for the RN to SmA_d (RN–SmA_d) phase transition. Experimental evidence for the N–SmA_d tricritical point were obtained from latent heat determination as well as from specific heat critical exponents ($\alpha = 0.5$). The existence of the RN–SmA_d tricritical point was not experimentally attained. However, their thermodynamic analysis (Oonk's equal-Gibbs energy analysis) indicated the possibility of the existence of the N–SmA_d tricritical point from which they obtained the possible melting phase diagram.

Theoretical studies on the reentrant nematic phase have been carried out by several authors [30,4,5,31–39]. These include are phenomenological [30,4,5,31,32,37] and microscopic [33–39] theories. The first theoretical attempt to understand the reentrant nematic phase was performed by Cladis et al. [4,5]. In her work [5], Cladis was successful in predicting the onset of the reentrant phase transition as a result of temperature dependent coupling

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between nematic and smectic order parameters. Vaz and Doane [37] showed that reentrant phase transition can also be explained by temperature independent coupling between nematic and smectic order parameters. Pershan and Prost [30] showed that the reentrant nematic to smectic A (SmA) phase transition can be described from the Landau theory if one assumes the existence of an optimum density for smectic ordering. Using their microscopic theories, Longa and de Jeu [36] showed that reentrant behavior in nematic liquid crystals can be described by the treatment of the system as a mixture of monomers and dimers interacting through attractive induced soft interactions as well as hard-core repulsions. Other theories [31–35,38,39] were also quite successful for explaining the reentrant phase transition.

In spite of these microscopic and phenomenological theories, the understanding of the reentrancy behavior in liquid crystals still be far from being definitive. On the other hand there is no detailed theoretical works to explain the both the reentrancy behavior and tricritical behavior of the N–SmA phase transition in a binary mixture. The character of the N–SmA phase transition is still a puzzle. The first order N–SmA phase transition have been observed only when the nematic range is extremely narrow. The experimental studies [40–43] showed that the N–SmA phase transition can indeed be continuous when measured to the dimensionless temperature $(T_{IN} - T_{NA})/T_{IN} \approx 0.10$, with T_{NA} the N–SmA transition temperature and T_{IN} the isotropic to nematic (I–N) transition temperature. In their adiabatic-scanning calorimetry experiment, Thoen et al. [44] suggest continuous N–SmA phase transition for all $T_{NA}/T_{IN} < 0.99$. Thus, for $T_{NA}/T_{IN} \approx 0.99$ a TCP is suggested. McMillan [45] and de Gennes [46] suggested that the N–SmA transition could be first or second order. Owing to a coupling between nematic and smectic order parameters, strongly influenced by the extension in temperature of the nematic range, a crossover behavior from the strict second-order transition up to the tricritical point ($\alpha = 0.5$), beyond which the N–SmA phase transition becomes first-order in nature, is observed. Alben [47] predicted a $^3\text{He}/^4\text{He}$ -like TCP in a binary liquid crystal mixture. Other theoretical studies [48–50] also predicted the tricritical behavior of the N–SmA phase transition.

The purpose of the present work is to investigate the reentrant nematic behavior and tricritical behavior of the N–SmA phase transition in a binary mixture as observed experimentally [25]. First we discuss the reentrant behavior. Then we explain briefly the tricritical behavior of the N–SmA phase transition. This is followed by plotting and discussing the topologies in the possible phase diagrams. Following the approaches [4,5,37], we developed a Landau model to investigate the reentrant nematic and tricritical behavior of the N–SmA phase transition.

2. Theory

We consider the binary mixture of two liquid crystalline compounds (say 7OCB + 9OCB). Pure forms of 9OCB shows the first order N–SmA phase transition. When mixing with nematic 7OCB liquid crystal, the experiments confirm the existence of monotropic reentrant nematic phase and the N–SmA tricritical point (TCP). In the case of mixture, the free energy must be expressed in terms of the symmetry-breaking order parameters and the concentration (mole fraction) of the solute $x = n_{sol}/(n_{sol} + n_{lc})$, where n 's are the number densities of the solute and liquid crystal. Let x be the concentration (mole fraction) of the second compound 9OCB in a mixture with 7OCB + 9OCB. The layering in the SmA phase is characterized [46] by the order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-i\Psi)$, which is a complex scalar quantity whose modulus ψ_0 is defined as the amplitude of a one dimensional density wave characterized by the phase Ψ . The nematic order parameter proposed by de

Gennes [51] is a symmetric, traceless tensor described by $Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij})$. The quantity S defines the strength of the nematic ordering.

Keeping homogeneous terms up to the quartic order, the excess free energy density for binary mixture can be written as

$$F = F_0 + \frac{1}{3}aQ_{ij}Q_{ij} - \frac{4}{9}bQ_{ij}Q_{jk}Q_{ki} + \frac{1}{9}c_1(Q_{ij}Q_{ij})^2 + \frac{1}{9}c_2Q_{ij}Q_{jk}Q_{kl}Q_{li} + \frac{1}{2}\alpha_1|\psi|^2 + \frac{1}{4}\beta_1|\psi|^4 + \frac{1}{3}\delta Q_{ij}Q_{ij}|\psi|^2 + \frac{4}{9}\omega Q_{ij}Q_{jk}Q_{ki}x \quad (2.1)$$

F_0 is the free energy density of the isotropic phase. The material parameters a and α_1 can be assumed as $a = a_0(T - T_{NI}^*(x))$ and $\alpha_1 = \alpha_0(T - T_{NA}^*(x))$. $T_{NI}^*(x)$ and $T_{NA}^*(x)$ are virtual transition temperatures. a_0 and α_0 are positive constants. b , c_1 , c_2 and β_1 are material parameters. The coefficients b , c_1 , c_2 , and β_1 are assumed to be positive. δ and ω are coupling constants. The negative values of δ favor the SmA phase over the nematic phase.

From the experimental phase diagrams [25] one observe that concentration vs. temperature curves for the N–SmA and I–N phase transitions are not straight lines. We therefore assume the quadratic form of T_1^* and T_2^* ,

$$T_{NI}^*(x) = T_1 + u_1x + v_1x^2 \quad (2.2)$$

$$T_{NA}^*(x) = T_2 + u_2x + v_2x^2 \quad (2.3)$$

where u_1 , u_2 , v_1 and v_2 are constants. We assume that the temperature and concentration regions are not small so that the nonlinear dependence of phase transitions on concentration is justified.

The substitution of Q_{ij} and ψ into Eq. (2.1) leads to the free energy density expansion

$$F = F_0 + \frac{1}{2}aS^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + \frac{1}{2}\alpha_1\psi_0^2 + \frac{1}{4}\beta_1\psi_0^4 + \frac{1}{2}\delta\psi_0^2S^2x + \frac{1}{3}\omega S^3x \quad (2.4)$$

where $c = c_1 + c_2/2$.

The value of the smectic ordering in the SmA phase can be expressed as

$$\psi_0^2 = -\frac{1}{\beta_1}(\alpha_1 + \delta S^2x) \quad (2.5)$$

Eq. (2.5) shows that a nonzero real value of ψ_0 exists only when $(\alpha_1 + \delta S^2x) < 0$. Since there is a small temperature range where $\alpha_1 > 0$ and $\delta < 0$ in this region. As the positional order ψ_0 increases in the SmA phase, the orientational order S also increases if $\delta < 0$. The smectic phase disappears for $\delta > 0$.

By the substitution of ψ_0 from Eq. (2.5) into Eq. (2.4), we obtain

$$F = F_0 + \frac{1}{2}a_1S^2 - \frac{1}{3}b_1S^3 + \frac{1}{4}c_1S^4 \quad (2.6)$$

with the renormalized coefficients

$$F_0 = F_0 - \frac{\alpha_1^2}{4\beta_1} \quad (2.7)$$

$$a_1 = a - \frac{\delta\alpha_1}{\beta_1}x \quad (2.8)$$

$$b_1 = b - \omega x \quad (2.9)$$

$$c_1 = c - \frac{\delta^2}{\beta_1}x^2 \quad (2.10)$$

There is a region of coexistence of nematic and SmA phases which is bounded by the loss of stability line of the SmA phase

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