Chemical Physics 423 (2013) 178–181

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Isotropic to biaxial nematic phase transition in an external magnetic field

Prabir K. Mukherjee [a,*], Muklesur Rahman [b]

[a] Department of Physics, Government College of Engineering and Textile Technology, 12 William Carey Road, Serampore, Hooghly 712201, India
[b] Department of Physics, Aliah University, Salt Lake Campus, Kolkata 700064, India

ARTICLE INFO

Article history:
Received 26 March 2013
In final form 24 July 2013
Available online 1 August 2013

Keywords:
Liquid crystals
Phase transition
Tricritical point

ABSTRACT

The first theoretical observation of the tricritical point for the isotropic to biaxial nematic phase transition of biaxial nematic liquid crystals in the presence of an external field is reported. The influence of an external magnetic field on the isotropic to biaxial nematic phase transition have been studied using Landau phenomenological theory. Topological classification of phase diagrams in the field – temperature coordinates is performed. It is shown that for a particular value of the magnetic field, the first order isotropic to biaxial nematic phase transition becomes second order phase transition at a tricritical point.

1. Introduction

During the last decade much progress has taken place in the field of biaxial nematic (N_B) liquid crystals both experimentally [1–15] and theoretically [16–41]. The first experimental discovery of the N_B phase in lyotropic mixture of potassium laurate, decanol and water was confirmed by Saupe and coworkers [1–3]. They showed that over a limited concentration range three distinct nematic phases are stable: two uniaxial (N_U^+ (prolate) and N_U^- (oblate)) and one biaxial (N_B), which merge at a four-phase "Landau" point with the high temperature isotropic phase. The N_U^+–N_B and N_U^-–N_B phase transitions appear to be second order followed by a first order isotropic (I)-uniaxial nematic (N_U) phase transition. Further experiments [5,6,9–13,15] on lyotropic systems also confirmed these observations. A few micellar systems are known for which the phase diagrams involving uniaxial and biaxial nematic phases suggest the existence of the "Landau" point on the I–N_U phase transition line. The nematic phases formed can be positive (prolate, rod-like) or negative (oblate, plate-like) uniaxial and even biaxial depending on the shape of the micelles. The optical and X-ray investigations on liquid crystalline side-on side-chain polymers by Leube and Finkelmann [7,8] indicate the existence of a N_B phase. They observed a direct phase transformation from isotropic to biaxial nematic (I-N_B) for a range of concentrations.

Theoretical descriptions of the biaxial state based on a Landau model were originally developed by Freiser [16] and Alben [17]. Their investigations predicted that a biaxial nematic phase is likely to form as an intermediate phase between two uniaxial nematic phases of oblate and prolate character, respectively. Theoretical studies [16–20,26] indicate that for systems with molecules with sufficiently low symmetry, a biaxial nematic state at lower temperature is expected, unless the system crystallizes before. There is another system in which a N_B phase could occur: a mixture of rod-like and plate-like molecules of comparable size and in comparable amounts [19,22,23,30]. The molecular mean-field approximation and computer simulation studies [31–33,36,39,40] also confirmed the formation of the biaxial nematic phase. Mukherjee and Sen [38] studied the I–N_B phase transition within a Landau theory. They also demonstrated that several biaxial phases and direct I–N_B phase transition are possible depending on the sign of the order parameter values. These results were experimentally verified by Souza et al. [13]. Mean field and computer simulation studies [34–36] also confirmed the I–N_B phase transition. Matteis and Virga [36] predict the possibility of a tricritical point along the line of the direct I–N_B phase transition.

It is worthwhile to point out that the mean-field and Landau theories mentioned above are able to reproduce the experimental observations of the direct I–N_B phase transition in the absence of an external field. It is interesting to study the I–N_B phase transition in the presence of an external magnetic field. Although Gramsbergen et al. [26] discussed the N_U–N_B phase transition in the presence of an external magnetic field, apparently no theoretical study has been undertaken on the I–N_B phase transition in the presence of an external magnetic field.

We present here an analysis for the I–N_B phase transition in the presence of an external magnetic field based on our previous analysis [38]. We find that the field induced tricritical point is indeed attainable in the I–N_B phase transition line. The structure of the

* Corresponding author. Fax: +91 3326621058.
E-mail address: pkmuk1966@gmail.com (P.K. Mukherjee).

0301-0104/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemphys.2013.07.012

phase diagrams in the vicinity of the tricritical points is investigated by Landau theory.

2. Theory

The starting point of our approach is the Landau free energy F used previously by several authors to study the behavior of I–N_U–N_B phase transitions. The nematic order parameter originally proposed by de Gennes [42,43] is a symmetric, traceless second rank tensor. The orientational order in a biaxial nematic liquid crystal can be described by the symmetric, traceless, second rank tensor order parameter Q_{ij}

$$Q_{ij}(\vec{r}) = S(\vec{r})\left[n_i(\vec{r})n_j(\vec{r}) - \frac{1}{3}\delta_{ij}\right] + \eta(\vec{r})[m_i(\vec{r})m_j(\vec{r}) - (\vec{n}(\vec{r}) \times \vec{m}(\vec{r}))_i(\vec{n}(\vec{r}) \times \vec{m}(\vec{r}))_j] \tag{2.1}$$

where $S(\vec{r})$ is the modulus of the uniaxial part of the order parameter and $\eta(\vec{r})$ represents the degree of biaxiality in Q_{ij}. $n_i(\vec{r})$ and $m_i(\vec{r})$ are orthogonal eigenvectors of Q_{ij} corresponding to eigenvalues $\frac{2}{3}S(\vec{r})$ and $-\frac{1}{3}S(\vec{r}) + \eta(\vec{r})$ respectively. The Landau free energy density in the presence of an external magnetic field for biaxial nematic phase can be obtained as up to sixth order in Q_{ij} and obtain

$$\begin{aligned} F = {} & F_0 + \frac{1}{2}AQ_{ij}Q_{ij} - \frac{1}{3}BQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}C_1(Q_{ij}Q_{ij})^2 \\ & + \frac{1}{4}C_2Q_{ij}Q_{jk}Q_{kl}Q_{li} + \frac{1}{5}D_1(Q_{ij}Q_{ij})(Q_{kl}Q_{lm}Q_{mk}) \\ & + \frac{1}{5}D_2Q_{ij}Q_{jk}Q_{kl}Q_{lm}Q_{mi} + \frac{1}{6}E_1(Q_{ij}Q_{ij})^3 + \frac{1}{6}E_2(Q_{ij}Q_{ij}) \\ & \times (Q_{kl}Q_{lm}Q_{mn}Q_{nk}) + \frac{1}{6}E_3(Q_{ij}Q_{jk}Q_{ki})^2 - \frac{1}{2}\Delta\chi_{max}H_iH_jQ_{ij} \end{aligned} \tag{2.2}$$

F_0 is the free energy density for the isotropic phase. $\Delta\chi_{max}$ is the anisotropy of the magnetic susceptibility. When $\Delta\chi_{max}$ is positive (negative), they then tend to align parallel (perpendicular) to the field. Here we assume both **H** and **n** are along the z-axis. As usual in Landau theory we assume A = a (T − T*). Instead of considering only A as control parameter, we will construct the phase diagrams as functions of both A and B. The main difference between this free energy density and that of Ref. [38] is the existence of the magnetic field term $-\frac{1}{2}\Delta\chi_{max}H_iH_jQ_{ij}$ in Eq. (2.2). The phase diagram and the nature of the various transition lines and the multicritical points are found to be strongly dependent on H. Substitution of Eq. (2.1) into Eq. (2.2) gives

$$F = F_0 + I(S) + \eta^2J(S) + \eta^4K(S) + \frac{4}{3}E\eta^6 \tag{2.3}$$

with

$$I(S) = \frac{1}{3}AS^2 - \frac{2}{27}BS^3 + \frac{1}{9}CS^4 + \frac{4}{135}DS^5 + \frac{4}{81}ES^6 + \frac{2}{243}E_3S^6 - H'S \tag{2.4}$$

$$J(S) = A + \frac{2}{3}BS + \frac{2}{3}CS^2 - \frac{8}{45}DS^3 + \frac{4}{9}ES^4 - \frac{4}{27}E_3S^4 \tag{2.5}$$

$$K(S) = C - \frac{4}{5}DS + \frac{4}{3}ES^2 + \frac{2}{3}E_3S^2 \tag{2.6}$$

where $C = C_1 + C_2/2, D = D_1 + 5D_2/6, E = E_1 + E_2/2$ and $H' = \frac{1}{2}\Delta\chi_{max}H^2$. Neglecting the η^6 term in Eq. (2.3) the biaxial solution gives

$$\eta^2 = -\frac{J(S)}{2K(S)} \tag{2.7}$$

Eq. (2.7) shows that a biaxial solution exists only when $J(S) < 0, K(S) > 0$. Uniaxial solutions can only be obtained when $J(S)$ becomes zero or positive. Thus the free energy of the uniaxial and biaxial phases takes the form

$$F_U(S) = I(S) \tag{2.8}$$

$$F_B(S) = I(S) - \frac{J^2(S)}{4K(S)} \tag{2.9}$$

Thus, whenever the biaxial solution is allowed, $F_U(S) > F_B(S)$. Depending on the magnitude of the external magnetic field, the free energy (2.3) describes various type of phase transition lines.

The conditions for the second order uniaxial–biaxial nematic phase transition can be obtained as

$$I'(S) = 0 \tag{2.10}$$

$$J(S) = 0 \tag{2.11}$$

$$F''_B(S) \geqslant 0 \tag{2.12}$$

The conditions for the first order uniaxial–biaxial nematic phase transition can be obtained as

$$I'(S) = 0 \tag{2.13}$$

$$J(S) = 0 \tag{2.14}$$

$$F''_B(S) \leqslant 0 \tag{2.15}$$

The conditions for the first order isotropic-biaxial nematic phase transition are given by

$$F_B(S) = 0 \tag{2.16}$$

$$F'_B(S) = 0 \tag{2.17}$$

$$F''_B(S) > 0 \tag{2.18}$$

The conditions for the second order isotropic-biaxial nematic phase transition are given by

$$F'_B(S) = 0 \tag{2.19}$$

$$F''_B(S) = 0 \tag{2.20}$$

$$F'''_B(S) > 0 \tag{2.21}$$

Finally the conditions for the first order uniaxial-isotropic phase transition read

$$I(S) = 0 \tag{2.22}$$

$$I'(S) = 0 \tag{2.23}$$

$$I''(S) > 0 \tag{2.24}$$

Solving Eqs. (2.10)–(2.24) simultaneously will determine the various phase transition lines in the A – B diagram.

3. Results and discussion

The various states which are realized in the Landau theory occupy different regions in the A–B phase diagrams. These regions are separated by phase transition lines of several types. The resulting phase diagram is predicted in Figs. 1 and 2. Figs. 1 and 2 summarize two new topologies of the phase diagrams associated with the free energy density (2.2), the conditions (2.10)–(2.24) and the different values of the phenomenological coefficients A, B, C, D, E and E_3 and magnetic field H'. Fig. 1 shows a novel phase diagram with the material parameters $C = 0.5, D = 0.5, E = 0.6$ and $E_3 = 3.2$ and field $H' = 0.0026$ using Eqs. (2.10)–(2.24). A–B phase