Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Improved analysis of the Landau theory of the uniaxial-biaxial nematic phase transition

Prabir K. Mukherjee

Online publication date: 06 August 2010

To cite this Article Mukherjee, Prabir K.(1998) 'Improved analysis of the Landau theory of the uniaxial-biaxial nematic phase transition', Liquid Crystals, 24: 4, 519 — 523
To link to this Article: DOI: 10.1080/026782998206966
URL: http://dx.doi.org/10.1080/026782998206966

LIQUID CRYSTALS, 1998, VOL. 24, NO. 4, 519–523

Improved analysis of the Landau theory of the uniaxial–biaxial nematic phase transition

by PRABIR K. MUKHERJEE
Saha Institute of Nuclear Physics, LTP Division, 1/AF Bidhannagar, Calcutta-700 064, India

(*Received 12 August 1997; accepted 14 August 1997*)

A phenomenological theory is developed for uniaxial and biaxial nematic phases, based on a two component tensor order parameter. Phase diagrams are plotted and investigated in the plane of two thermodynamic parameters. Anomalies in thermal properties are studied in the vicinity of an isolated four-phase critical point. The temperature dependences of the order parameter and the thermodynamic quantities are also calculated theoretically for the first time.

1. Introduction

More than twenty years ago it was shown by Freiser [1, 2] that with decreasing temperature a nematic liquid crystal consisting of biaxial molecules will have two successive transitions according to the scheme: isotropic→ uniaxial order→biaxial order. The main purpose of the present paper is to re-establish this prediction in an improved way and to calculate the temperature dependences of the order parameter and thermodynamic quantities which are still lacking.

Interest in the theory of the nematic liquid crystal phase was stimulated by the experimental discovery of the long-predicted biaxial nematic phase by Saupe and coworkers [3–5]. They studied the phase diagram and critical properties of the ternary system potassium laurate–1-decanol–D_2O over concentration ranges where nematic phases were likely to occur. They showed that in these limited concentration ranges the following phase sequence may be observed on heating and on cooling: isotropic–uniaxial nematic (N_U^+) (positive optical anisotropy)–biaxial nematic (N_B)–uniaxial nematic (N_U^-) (negative optical anisotropy). They observed that an intermediate N_B phase is formed for a certain concentration range while in other ranges a direct first order N_U^+–N_U^- transition is seen. The N_U^+–N_B or N_U^-–N_B transitions appear to be second order.

Experimentally, transitions have been observed that seem to land directly from N_U^+ to N_U^- via a first order transition. A few miceller nematic liquid crystals are known where the phase diagrams suggest the existence of a Landau point on the nematic–isotropic (N–I) transition line. The nematic phases formed can be positive or negative uniaxial and even biaxial, depending on the shape of the micelles. The phase diagram of the mixture of rod-like and plate-like molecules of comparable size and in comparable amounts also indicates the approach of the Landau point. Evidence has been found that the mixture undergoes a transition to two coexisting uniaxial phases, rather than to a single biaxial phase.

Again, the important study by Alben of binary mixtures [6] included only the hardcore repulsion of rod-like and plate-like molecules, and obtained a number of interesting results. For example, the introduction of plate-like molecules increases the N–I transition temperature of rod-like molecules. Another result was that, at a lower temperature, the uniaxial nematic phase can undergo a second order transition to a more highly ordered biaxial nematic phase. Between the two regions N_U^+ and N_U^-, Alben's calculation showed that the two second order lines between the uniaxial nematic and biaxial nematic phases form a sharp cusp separating the rod-like nematic phase N_U^+ and plate-like nematic phase N_U^-, and that the cusp touches the first order isotropic–uniaxial nematic transition line. The intersection of the two second order lines and the first order transition line forms a special critical point. However, because the phase diagram which Alben presented in his paper was the result of a numerical calculation, it is difficult to examine the detailed thermodynamic and critical behaviour in the region between the N_U^+ and N_U^- transitions.

Further theoretical investigations [7–10] have predicted that a biaxial nematic phase is likely to form as an intermediate phase between two uniaxial nematic phases. These theoretical investigations show that an isolated critical point is obtained in the phase diagram, where the N_B–N_U^+ and N_B–N_U^- phase boundaries meet a first order N_U^+–N_U^- line. At this isolated critical point the cubic coefficient of the order parameter in the effective Hamiltonian becomes zero. In the present paper the character of the order is discussed, together with the various thermal properties in the different phases.

The molecules which comprise a typical nematic liquid crystal (NLC) do not have an axis of rotational symmetry. This raises the question of whether any vestige of the lower molecular symmetry is present in ordinary nematic liquid crystals, and the possibility of biaxial liquid crystals in which the molecular asymmetry becomes manifest [11, 12]. These problems have been discussed previously in the literature [7–10]. Freiser [1] has discussed a generalization of the Maier–Saupe [13] theory involving an order to biaxial character; Alben [9] has discussed the corresponding Landau theory. The present work proposes a generalization of the Landau theory which contains this order parameter. Phase transitions from NLC to isotropic liquids (IL) are generally weakly first order. It is shown that, in a broad region of pressures, the nematic phase should possess axial symmetry and be described by a uniaxial ellipsoid of revolution. Near the isolated critical point a narrow region without axial symmetry (biaxial phase) can exist. Between these phases a second order transition is possible. Baskakov *et al.* [14], by extrapolating the experimental dependence of the specific volume discontinuity on the temperature and pressure, conclude that an isolated point exists.

In this work a generalized Landau theory is given. The main results of this work are: (1) the possibility of a re-entrant uniaxial phase with decreasing temperature, below the biaxial phase; (2) the characterization of the order of the different transitions; (3) the characterization of thermal properties near the critical point.

2. Landau theory

The basis of the Landau theory is the assumption that there is a free energy F which can be regarded as an analytic function of an appropriate order parameter whose value is determined by minimizing F. We choose the order parameter [1]

$$Q_{lm} = \sum_{m'} D^{l}_{m'm} \bar{Q}_{lm} \tag{1}$$

where the $D^{l}_{m'm}$ are the elements of the transformation matrices of the spherical harmonics, Y_{lm}, under rotation. The Q_{lm} are molecular parameters which transform under rotation as the Y_{lm}. The ground state of a system with pairwise interaction is one in which all the molecules have the same orientation. This is easily seen if one uses for the Q_{lm} a Cartesian representation in which this effective 'quadrupole' is a real symmetric matrix of zero trace. The isotropic state with $\bar{Q}_{lm}=0$ for all m, is always an extremum of free energy F. For $l=2$ and with symmetric molecules such that $\bar{Q}_{22}$ is zero unless $m=0$, equation (1) reduces to the P_2 interaction of Maier and Saupe.

From the molecular shape of any biaxial object, we can always choose the frame of reference so that $\bar{Q}_{2,+1}=0$; $\bar{Q}_{2,0}\neq 0$ and real; $Q_{2,2}=\bar{Q}_{2,-2}\neq 0$ and real. The last term is zero for axially symmetric molecules. Without the loss of generality, we may use the following polar coordinates in the order parameter space by defining

$$\bar{Q}_{2,0} = r\cos\theta; \qquad \bar{Q}_{2,2} = 2^{-1/2} r \sin\theta$$

so that

$$S_1 = r^2 = \bar{Q}^2_{2,0} + 2\bar{Q}^2_{2,2} \tag{2 a}$$

$$S_2 = r^3 \cos 3\theta = \bar{Q}_{2,0}(\bar{Q}^2_{2,0} - 6\bar{Q}^2_{2,2}) \tag{2 b}$$

To construct the free energy F, it can be shown that since F must be invariant under rotations its expansion must be polynomial in the two invariants $r^3\cos 3\theta = S_1$ and $r^2 = S_2$. For our model the expansion of the free energy F by considering sixth degree expansion is well approximated by

$$F = \frac{A}{2}S_1 + \frac{B}{4}S_1^2 + \frac{C}{6}S_1^3 + \frac{D}{3}S_2 + \frac{E}{6}S_2^2 + \frac{G}{5}S_1 S_2 \tag{3}$$

In this free energy expansion odd terms of order three and higher are allowed. There are two independent sixth order terms.

As we shall see, the presence of E term introduces the possibility of a biaxial phase. The parameters A, B, C, D, E and G are phenomenological parameters. As is usual for the Landau theory, we assume that A is linear in temperature. Instead of considering only A (temperature) as the controllable variable, we will now construct the phase diagrams as functions of A and D. The physical meaning of D will be discussed elsewhere. It is readily verified that the structure of equation (3) implies all of the major features of the phase diagram.

The minimization of F leads to three possible stable phases:

(1) Phases II (N_U^+) and III (N_U^-) corresponding to $\bar{Q}_{2,0}=Q$ and $\bar{Q}_{2,2}=0$, associated with the extremum condition

$$A + D\bar{Q}_{2,0} + B\bar{Q}^2_{2,0} + G\bar{Q}^3_{2,0} + C\bar{Q}^4_{2,0} = 0 \tag{4}$$

(2) Phase IV (N_B), with $\bar{Q}_{2,0}\neq 0$, $\bar{Q}_{2,2}\neq 0$, associated with the conditions

$$\left.\begin{aligned} A + \frac{B}{2}S_1 + \frac{C}{2}S_1^2 + \frac{G}{5}S_2 = 0 \\ \frac{D}{3} + \frac{E}{3}S_2 + \frac{G}{5}S_1 = 0 \end{aligned}\right\} \tag{5}$$

Phases II and III differ only in the sign of the order parameter $\bar{Q}_{2,0}$. Their symmetry is characterized by rotational elements which are three times smaller than in the case of a symmetric phase. The symmetry group of phase IV is a subgroup of index 2 of the symmetry group of phases II and III. As shown in the figure they result from a first order transition I–II or I–III.

In the limit $Q \to 0$, the stability conditions of phases of type II reduce to the contradictory inequalities $F_2 \geqslant 0$, $F_2 \leqslant 0$ indicating that the transition from a symmetric phase I to phases II and III is possible only at an isolated critical point $A = 0$, $D = 0$ (Landau condition [15]). The transitions I–II and I–III are second order only at the Landau critical point defined by

$$A = F_1(Q = 0) = 0 \quad \text{and} \quad D = F_2(Q = 0) = 0 \qquad (6)$$

where

$$\left.\begin{aligned} F_1 = \partial F/\partial S_1 = \frac{A}{2} + \frac{B}{2} S_1 + \frac{C}{2} S_1^2 + \frac{G}{5} S_2 = 0 \\ F_2 = \partial F/\partial S_2 = \frac{D}{3} + \frac{E}{3} S_2 + \frac{G}{5} S_1 = 0 \end{aligned}\right\} \qquad (7)$$

Now from expressions (5) it is clear that in the case of phase IV the likelihood of the second order transition from a symmetric phase is no higher than at an isolated point in the phase diagram. The coordinates of this point in the diagram are also given by the intersection of the lines $A = 0$, $D = 0$.

The stability conditions for phase IV are

$$F_{11} F_{22} - F_{12} F_{21} \geqslant 0, \qquad F_{11} \geqslant 0 \qquad (8)$$

where,

$$F_{11} = \frac{B}{2} + C S_1, \qquad F_{22} = \frac{E}{3}, \qquad F_{12} = F_{21} = \frac{G}{5}$$

In the vicinity of the critical point, they reduce to the inequalities

$$\Delta = (25BE - 6G^2) > 0, \qquad B > 0 \qquad (9)$$

Near the boundary between the isotropic and uniaxial phases we find from equation (4) that

$$Q = \frac{1}{2B} [-D \pm (D^2 - 4AB)^{1/2}] \qquad (10)$$

The condition of 'proximity' in an isotropic phase, deduced from equation (4), means that $A \sim D^2$. The stability condition $\mathrm{d}^2 F/\mathrm{d}\bar{Q}_{2,2}^2 > 0$ shows that at the boundary with the isotropic phase we have $Q > 0$ for $D < 0$ and $Q < 0$ for $D > 0$. The stability boundary of phases II and III is provided by the inequality $\mathrm{d}^2 F/\bar{Q}_{2,0}^2 > 0$ which is explicited by

$$-D^2 - 4AB = 0 \qquad (11)$$

represented by line 2 in the figure.

To construct the phase diagram (1) the fifth order term F in the free energy is retained and A and D are both linear functions of temperature. To bring the biaxial nematic phase into reach, the uniaxial nematic temperature range should be reduced, possibly by lowering the value of $|D|$. The above condition is identical with the requirement that Q be real. The equation for the phase transition line is

$$2D^2 - 9AB = 0 \qquad (12)$$

represented by the solid line 1 in the figure.

The experimental re-entry phase behaviour [3, 16] is quite different from the phase diagram shown in the figure. In a system of the type considered above and shown in the figure, the ground state is an ordered nematic phase. In contrast, for the re-entry transition system, the ground state is an isotropic phase. Additionally, in figure 1, the biaxial nematic phase forms an open area, but in the re-entry system the biaxial region becomes narrow at lower temperatures and one can expect it to close somewhere.

This comparison indicates that the underlying interaction is different for the two cases. Since the equilibrium state is determined by the competition between entropy and energy, the re-entry phase diagram reflects a more complex dependence of the entry on orientation. The model considered here may be modified to include the possibility of re-entrant behaviour.

The phase transition from uniaxial nematic to biaxial nematic is determined from our calculations to be a second order transition. In the figure the two second order lines form a sharp cusp which separates the N_U^+ and N_U^- phases and forms a special critical point. These results support experimental observation [3–5, 16, 17].

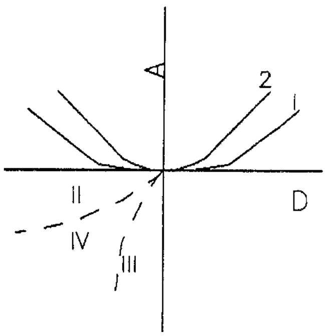

Figure 1. Phase diagram of biaxial–uniaxial transitions near an isolated four phase critical point ($A = D = 0$). The dashed lines represent second order phase transitions between biaxial phase IV (N_B) and the uniaxial phases II (N_U^+) and III (N_U^-). The continuous line 1 represents first order phase transitions between isotropic and uniaxial phases. The continuous line 2 represents the stability of phases II and III.

Now the solution of the system (5) can be obtained near the Landau critical point by the approximate expressions

$$S_1 = \frac{1}{P}(2GD - 5EA) \qquad S_2 = \frac{1}{P}(3GA - 5BD) \quad (13)$$

where,

$$P = \frac{1}{5}(25BE - 6G^2)$$

Since S_1 and S_2 are linear with respect to A and D, but are of different order with respect to Q, phase IV may exist only inside the part of the phase diagram bounded by the dotted lines in the figure, whose equations are

$$5BD - 3GA \pm 30P(-A/B)^{3/2} = 0 \quad (14)$$

and, consequently, the width of the region of existence of phase IV in the (A, D) diagram is of the order of $\tau^{3/2}$, where τ is the distance from the critical point in the diagram (when the width of the biaxial region has shrunk to zero, leaving a first order N_U^+–N_U^- transition). The lines defined by equation (14) are the boundaries of the region where S_1 and S_2 are real for a biaxial phase and represent the loss of stability of uniaxial phases. Consequently, second order phase transitions occur on these lines. Finally, we can give the approximate expression for the order parameter components in phases II and III, which is given by equation (10), and in phase III:

$$Q = \pm\left[(-A/B)^{1/2} + \frac{1}{2B}(D + 5\Delta(-A/B)\right] \quad (15)$$

Let us note that the symmetry of phase IV is always lower than the symmetries of phases II and III.

Near the boundary with the biaxial phase, where $A \sim D$, the expression for the order parameter of uniaxial phases is

$$Q = y_1 + y_2 + y_3 + \ldots \quad (16)$$

with

$$\left.\begin{aligned} y_1 &= \pm(-A/B)^{1/2} \\ y_2 &= \frac{1}{2B}(D + 5\Delta y_1^2) \\ y_3 &= (1/8B^2 y_1) \\ &\quad \times [D^2 + 30\Delta D y_1^2 + 125\Delta^2 y_1^4 - 4B(C+E)y_1^4] \end{aligned}\right\} \quad (17)$$

When the biaxial phase is absent, a first order transition between the two uniaxial phases occurs along the line

$$A = (5BD/3G) \pm (10/9)^{1/2}(D/G)^{1/2} \quad (18)$$

with a liberation of the latent heat

$$q = -(5D/6G)T(\partial A/\partial T) + [-(5A/6G) + (25/18)(BD/G^2)]T(\partial D/\partial T) \quad (19)$$

The thermal properties near the critical point can be investigated using expansion (3). At the critical point itself the heat of transition vanishes and it rises, away from this point, along the first order phase transition described by $\sim A$. If the transition at the critical point is a uniaxial phase, the specific heat C_P increases abruptly by an amount

$$\Delta C_P = \frac{T}{2B}\left(\frac{\partial A}{\partial T}\right)^2 \quad (20)$$

If the transition is from isotropic to biaxial phase the change is

$$\Delta C_P = C_P^{biaxial} - C_P^{isotropic} = \frac{T}{180\Delta}[15E(\partial A/\partial T)^2 - 12G(\partial A/\partial T)(\partial D/\partial T) + 10B(\partial D/\partial T)^2] \quad (21)$$

The positive definite nature of the quadratic form of equation (21) follows from the conditions of stability (9) of the biaxial phase. Near the point $A = D = 0$, the abrupt change in the specific heat at the boundary between the biaxial and uniaxial phases is

$$\Delta C_P = C_P^{biaxial} - C_P^{uniaxial} = \frac{T}{5B\Delta}\left[3G(\partial A/\partial T) - 5B\left(\frac{\partial D}{\partial T}\right)\right]^2 \quad (22)$$

3. Conclusion

Experimental indications for the existence in nematic liquid crystals of a phase transition from a uniaxial to a biaxial phase have been previously reported. Accurate measurements of all order parameters and of the specific heat in the neighbourhood of the transition temperature are still lacking; the theories proposed previously were still undeveloped. The present work provides theoretical calculations for both the order parameters and the specific heat for the first time.

It is useful to make a comparison between the Landau theory of nematic liquid crystals presented here and the earlier theories of Freiser [1, 2], Alben [9] and Straley [10]. The work of Freiser and Alben assumed a second rank tensor as the order parameter and this was allowed for in our theory. But the phase diagram of the figure is slightly different from the phase diagram of earlier works. In the present diagram we have indicated the actual stability limit of all the phases. The temperature dependencies of the order parameters have been calculated in all the phases; this was absent in Alben's work. The behaviour of the physical quantities in the vicinity of an isolated critical point is also calculated theoretically for the first time. It is also interesting to calculate the specific heat experimentally at the boundary of the different phases. The generalization of the present analysis might be of significance in three respects: (1) it would afford a more nearly quantitative description of a real liquid crystal; (2) it could be useful in describing biaxial phases of lower symmetry; (3) it might lead to an alternation of Alben's critical point.

As an illustration of the application of Landau theory to the biaxial nematic phase one can also consider the behaviour of the magnetically induced birefringence near the critical point. Stinson *et al.* [17] have shown that there is a divergence of magnetically induced birefringence near the isotropic to nematic phase transition.

Ideally, experimental observation should resolve whether transitions such as positive uniaxial nematic (N_U^+), negative uniaxial nematic (N_U^-) and isotropic to biaxial, etc. actually occur, or whether in fact the proper order parameter is indeed a second rank tensor. At the present time it appears that all known uniaxial phases are of type N_U^+, while the only observed biaxial nematic phase occurs in the lyotropic mixtures pioneered by Saupe and coworkers [3–5, 17]. Thus insufficient data are yet available to resolve these important questions.

References

[1] Freiser, M. J., 1970, *Phys. Rev. Lett.*, **24,** 1041.
[2] Freiser, M. J., 1971, *Mol. Cryst. liq. Cryst.*, **14,** 165.
[3] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45,** 1000.
[4] Saupe, A., Boonbrahm, P., and Yu, L. J., 1983, *J. chem Phys.*, **80,** 7.
[5] Boonbrahm, P., and Saupe, A., 1984, *J. chem. Phys.*, **81,** 2076.
[6] Alben, R., 1973, *J. chem. Phys.*, **59,** 4299.
[7] Freiser, M. J., 1970, *Phys. Rev. Lett.*, **24,** 1041; Vigman, P. B., Larkin, L., and Filev, V. M., 1977, *Sov. Phys. JETP*, **42,** 944.
[8] Shih, C. S., and Alben, R., 1971, *J. chem. Phys.*, **57,** 3055.
[9] Alben, R., 1973, *Phys. Rev. Lett.*, **30,** 778.
[10] Stralay, J. P., 1974, *Phys. Rev. A*, **10,** 1881.
[11] Taylor, T. R., Fergason, J. L., and Arora, S. L., 1970, *Phys. Rev. Lett.*, **24,** 389.
[12] Alben, R., McColl, J. R., and Shih, C. S., 1972, *Solid State Commun.*, **11,** 1081.
[13] Maier, W., and Saupe, A., 1958, *Z. Naturforsch A*, **13,** 564; Maier, W., and Saupe, A., 1959, *Z. Natukrforsch A*, **14,** 882.
[14] Baskakov, V. Ya., Semenchenko, V. K., and Byankin, V. M., 1974, *Sov. Phys. JETP*, **39,** 383.
[15] Landau, L. D., 1965, *Collected Papers* (Oxford: Pergamon Press).
[16] Bartolino, R., Chiaramza, T., Meuti, M., and Campagnoni, R., 1982, *Phys. Rev. A*, **26,** 116.
[17] Stinson, T. W., Litster, J. D., and Clark, N. A., 1972, *Suppl. J. Phys. (Paris)*, **69,** C1; Saupe, A., 1989, *Phys. Rev. A*, **39,** 1597.