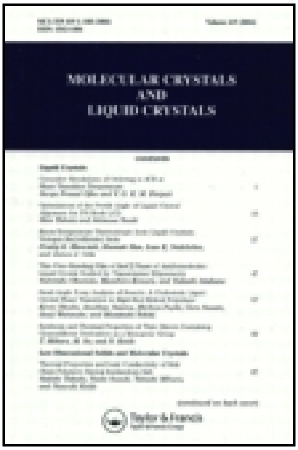

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David W. Allender [a] & Michael A. Lee [a]

[a] Department of Physics and Liquid Crystal, Institute Kent State University, Kent, Ohio, 44242

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LANDAU THEORY OF BIAXIAL NEMATIC LIQUID CRYSTALS

DAVID W. ALLENDER AND MICHAEL A. LEE
Department of Physics and Liquid Crystal Institute
Kent State University
Kent, Ohio 44242

The orientational order of molecules in a liquid crystal is traditionally described by spatial or temporal averages of functions that are quadratic in the direction cosines of molecular axes with respect to laboratory fixed axes. The free energy describing the nematic phase must be independent of the choice of coordinate systems and therefore rotationally invariant with respect to both laboratory and molecular frames. A Landau theory for biaxial and uniaxial nematics based on six fundamental invariants is developed which is properly rotationally invariant. Four possible nematic phases, two uniaxial and two biaxial, result. NMR experiments should be able to identify which of these actually occur in specific materials.

1. INTRODUCTION

Interest in the theory of the nematic liquid crystal phase has been stimulated by the recent experimental discovery of the long-predicted biaxial nematic phase by Saupe and co-workers.[1,2] Nearly ten years earlier, Freiser,[3,4] Alben[5] and Straley[6] had developed theories which suggested that such a phase should exist. The work of Alben involved a Landau theory which extended the

Landau theory of the uniaxial nematic phase[7,8] while the work of both Freiser and Straley generalized a microscopic statistical mechanical mean field theory first applied to the uniaxial nematic by Maier and Saupe.[9]

In this work a generalized Landau theory is given which shows that if the constituent molecules have biaxial symmetry, there may exist two microscopically distinct uniaxial nematic phases as well as two microscopically distinct biaxial nematic phases. This essential result of the theory is a consequence of the nature of the order parameter. To illustrate, a typical phase diagram is presented which is derived from the rotationally invariant Landau free energy. Comparison is made with the earlier theories mentioned above and similarities and differences are pointed out.

2. THE ORDER PARAMETER

The order parameter that we use to describe the orientational order of nematic phases was first discussed by Saupe[10] and has been presented in detail by de Gennes.[7] It is the tensor

$$S_{ij}^{\alpha\beta} = \tfrac{1}{2}\langle 3(\hat{M}_i\cdot\hat{L}_\alpha)(\hat{M}_j\cdot\hat{L}_\beta) - \delta_{ij}\delta_{\alpha\beta}\rangle$$

where $\hat{M}_i$ and $\hat{L}_\alpha$ are unit vectors defining arbitrary molecular and laboratory coordinate systems respectively, and the angular brackets denote a thermal average.

Although it is in general to be expected that a nematogenic molecule has a very low symmetry, we will assume that a molecule may be effectively treated as having either a D_{2h} point group symmetry or else a higher symmetry. Furthermore we may quite generally assume that the biaxial nematic phase being studied has D_{2h} symmetry while the uniaxial nematic has $D_{\infty h}$. Under these conditions the order parameter takes its simplest form when the rotation axis of the molecular point group is taken as $\hat{M}_z$ and the rotation axis of the laboratory point group is defined to be $\hat{L}_z$. Then $S^{\alpha\beta}_{ij}$ is non-zero only for $i=j$ and $\alpha=\beta$. In terms of Straley's[6] S,T,U, and V we have

$$S^{xx}_{xx} = \frac{1}{4}[S - \frac{3}{2}T - \frac{3}{2}U + 3V]$$

$$S^{xx}_{yy} = \frac{1}{4}[S - \frac{3}{2}T + \frac{3}{2}U - 3V]$$

$$S^{xx}_{zz} = \frac{1}{2}[-S + \frac{3}{2}T]$$

$$S^{yy}_{xx} = \frac{1}{4}[S + \frac{3}{2}T - \frac{3}{2}U - 3V]$$

$$S^{yy}_{yy} = \frac{1}{4}[S + \frac{3}{2}T + \frac{3}{2}U + 3V]$$

$$S^{yy}_{zz} = \frac{1}{2}[-S - \frac{3}{2}T]$$

$$S^{zz}_{xx} = \frac{1}{2}[-S + \frac{3U}{2}]$$

$$S^{zz}_{yy} = \frac{1}{2}[-S - \frac{3}{2}U]$$

$$S^{zz}_{zz} = S$$

where

$$S = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$$

$$T = \langle \sin^2\theta \cos 2\phi \rangle$$

$$U = \langle \sin^2\theta \cos 2\psi \rangle$$

$$V = \langle \frac{1}{2}(1+\cos^2\theta)\cos 2\phi \cos 2\psi - \cos\theta \sin 2\phi \sin 2\psi \rangle$$

and ϕ,θ,ψ are the Euler angles that rotate the laboratory coordinate system into being coincident with the molecular system.

The possible nematic phases are named as follows and are characterized by the given orientational order.

1) U_1: a uniaxial phase with only $S\neq 0$.
2) U_2: a uniaxial phase with only S and $U\neq 0$.
3) B: a biaxial phase having only S and $T\neq 0$.
4) B*: a biaxial phase with $S,T,U,V\neq 0$.

3. ROTATIONAL INVARIANTS AND THE LANDAU FREE ENERGY

The free energy is a scalar and therefore may be expanded as a power series in $S_{ij}^{\alpha\beta}$ where all possible contractions of the tensor indices must be considered. It is well known that for an order parameter which is a second rank tensor in a three-dimensional vector space, there are only three independent contractions, or so-called fundamental invariants. All other contractions can be expressed as simple polynomials in the three invariants. (If the tensor is traceless, there are only two non-zero invariants.) This is a powerful statement and its proof is based on the Fundamental Theorem of Symmetric Functions, as was pointed out by Freiser.[3] However, the order parameter under consideration is not a second rank tensor. We have been able to show that there are six independent invariants and the proof will be published elsewhere. The free energy is a polynomial in these invariants.

A transformation leads to a particularly useful parameterization of the invariants and the free energy.

$$S = r_1 \cos\alpha + r_2 \cos\beta$$

$$\frac{\sqrt{3}}{2} T = r_1 \sin\alpha + r_2 \sin\beta$$

$$\frac{\sqrt{3}}{2} U = -r_1 \sin\alpha + r_2 \sin\beta$$

$$V = r_1 \cos\alpha - r_2 \cos\beta$$

In terms of r_1, r_2, α, and β the invariants are

$$I_1 = 0$$

$$I_2 = r_1^2 + r_2^2$$

$$I_3 = r_1^3 \cos(3\alpha) + r_2^3 \cos(3\beta)$$

$$I_4 = r_1^2 - r_2^2$$

$$I_5 = r_1^3 \cos(3\alpha) - r_2^3 \cos(3\beta)$$

$$I_6 = r_1^3 r_2^3 \sin(3\alpha)\sin(3\beta)$$

Technically I_4 and I_5 are not totally invariant, but must appear only in combinations $I_4^{n_1} I_5^{n_2}$ such that n_1+n_2 is an even number.

The resulting free energy, to sixth order in $S^{ij}_{\alpha\beta}$, is

$$F = AI_2 + BI_3 + C_1 I_2^2 + C_2 I_4^2 + D_1 I_2 I_3 + D_2 I_4 I_5 + E_1 I_2^3 + E_2 I_2 I_4^2 + E_3 I_4^2 + E_3 I_3^2 + E_4 I_5^2 + E_5 I_6.$$

As is usual for a Landau theory, we assume that A is linear in temperature, namely $A = A_0(T-T_0)$, while the remaining coefficients are phenomenological material parameters.

Due to the large number of parameters we have only begun to examine the possible phase diagrams. By minimizing F with respect to r_1, r_2, α, and β, letting A and B vary while choosing $C_1 = -.6$, $C_2 = 1$, $D_1 = 2$, $D_2 = -1.5$, $E_1 = 2$, $E_2 = 1$, $E_2 = 3\sqrt{2}$, $E_4 = -\sqrt{2}$, and $E_5 = -4$ the phase diagram shown in Figure 1 was obtained.

The transition from the isotropic (I) phase to either U_2 or B* is first order, while the U_2 to B* transition is second order.

4. DISCUSSION

The phase diagram of Figure 1 is markedly different from those obtained by Freiser, Alben, and Straley. In particular we predict that a first order isotropic to biaxial transition can occur. It is not yet demonstrated whether our theory recovers Alben's phase diagram for suitable coefficients. Nonetheless our results have a close relationship to Straley's work. He did not obtain what we have called the U_1 phase, but instead had the U_2 phase. This occurred because of a particular term (coefficient γ) in his assumed form for the molecular interaction that forces a finite U if S is non-zero. However the Landau theory implies such a term is not fully rotationally invariant. The quadratic term in S,T,U, and V can only come from invariant I_2 which does not contain a term SU, in contradiction to Straley's result.

Alben's phase diagram has our U_1 phase but does not

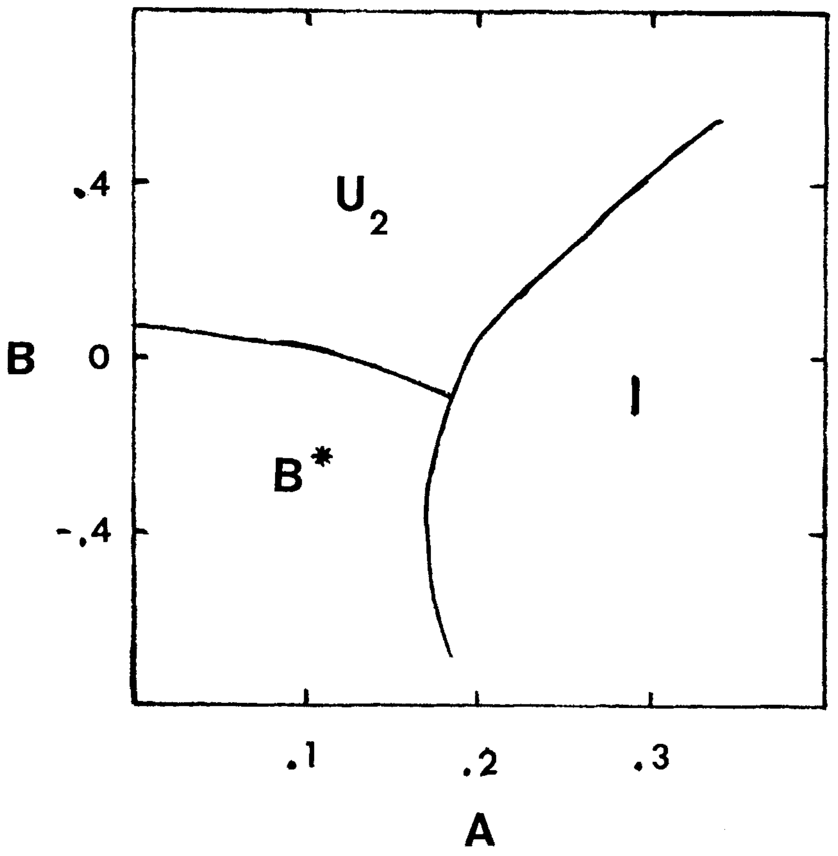

FIGURE 1. A typical phase diagram for a system of biaxial molecules. The choices of the phenomenological parameters are listed in the text.

have U_2 because he used a second rank tensor as the order parameter. That formulation does not permit a distinction between the U_1 and U_2 phases. (Similar statements apply regarding B and B*.)

Lastly we compare our results with experiment. NMR experiments are uniquely suited to measuring the parameters S,T,U, and V that distinguish the nematic phases. Evidence seems to indicate that no known uniaxial nematic is of type U_1 but in fact always seems to be of type U_2.[11] It is unknown whether the experimentally observed biaxial nematics in lyotropic systems[1] are of type B or B*. It may also be necessary to develop a theory dealing with mixtures of different shaped constituents in order to describe these systems.[12,13]

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