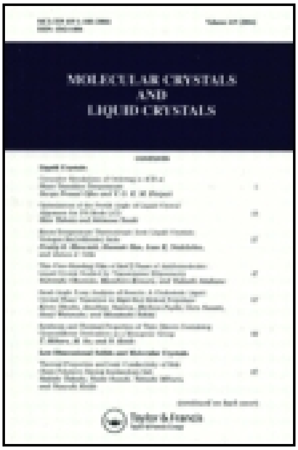

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Landau Theory of Biaxial and Uniaxial Nematic Liquid Crystals

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A Landau theory is developed for uniaxial and biaxial nematic phases, based on the order parameter $S_{ij}^{\alpha\beta}$. Four nematic phases, two uniaxial and two biaxial, are predicted and their symmetries are discussed. A typical phase diagram is presented and comparisons are made with earlier mean field theories and Landau theories based on a second rank tensor order parameter.

INTRODUCTION

The Landau theory of phase transitions is based on an order parameter which describes the change in symmetry of the substance when a phase transition occurs.[1] Usually the quantity which undergoes this change in symmetry is the atomic density function $\rho(1)$ where $\rho(1)dV_1$ is the probability of finding an atom in the volume element around point $\vec{r}_1$. (This function should not be confused with the molecular distribution function of mean field theory.) However, as pointed out by Landau and Lifshitz,[1] for anisotropic fluids like nematic liquid crystals, the function $\rho(1)$ is a constant and it is necessary to consider the atomic correlation functions which are the functions that undergo the requisite change in symmetry.

In developing our theory of nematic phases we will make the following simplifications. The fluid is assumed to consist of "biaxial" molecules in the sense that any second rank tensor property of the molecule, such as the moment of inertia or the magnetic susceptibility, yields three distinct principal values. Further, we assume that the molecules are not chiral and that no ordering of a vector nature occurs in any of the nematic phases.

The important atomic correlation functions are given by $\rho(1|2)$ and $\rho(1,2|3)$ where $\rho(1|2)dV_2$ is the probability of finding a particular type of atom at $\vec{r}_2$ given that there is another atom at $\vec{r}_1$, and $\rho(1,2|3)dV_3$ is the probability of finding an atom at $\vec{r}_3$ given that there are atoms at $\vec{r}_1$ and $\vec{r}_2$. Thus

$$\rho(1,2) = \rho(1)\,\rho(1|2)$$

and

$$\rho(1,2,3) = \rho(1)\,\rho(1|2)\,\rho(1,2|3)$$

where $\rho(1,2)dV_1dV_2$ is the probability of finding atoms at $\vec{r}_1$ and $\vec{r}_2$ and $\rho(1,2,3)dV_1dV_2dV_3$ is the probability of finding one at $\vec{r}_1$, one at $\vec{r}_2$, and one at $\vec{r}_3$.

The symmetry of the function $\rho(1|2)$ is restricted by the observation that all symmetry operations leave point $\vec{r}_1$ unchanged, i.e. the symmetry group will be a point group whose origin is $\vec{r}_1$. Due to our assumption of no vector ordering, the possible symmetry groups are K_h, D_{2h} and $D_{\infty h}$. (In principle D_{2nh} is possible, but for the simplest non-vector angular dependence, any rotation axis of order higher than two is equivalent to an axis of infinite order.) In contrast the function $\rho(1,2|3)$ must leave both $\vec{r}_1$ and $\vec{r}_2$ unchanged under a symmetry operation and therefore the only possible rotation axis is the axis defined by $\vec{r}_1$–$\vec{r}_2$. In general for arbitrary atoms at arbitrary points, the function $\rho(1,2|3)$ will have no symmetry at all. However for simplicity consider the particular function $\rho_o(1,2|3)$ such that the atoms at $\vec{r}_1$ and $\vec{r}_2$ are on the same molecule and $\vec{r}_1$–$\vec{r}_2$ is parallel to the long molecular axis. Under the assumptions mentioned previously, the possible symmetry groups of $\rho_o(1,2|3)$ are C_{2v} and $C_{\infty v}$.

The symmetry point groups of the atomic correlation functions $\rho(1|2)$ and $\rho_o(1,2|3)$ can now be categorized as in Table I. To our knowledge, only the symmetry of $\rho(1|2)$ has been previously considered explicitly in describing the nematic phases. At high temperature, $\rho(1|2)$ is invariant under both inversion and arbitrary rotations (the group K_h) while all functions $\rho(1,2|3)$ have $C_{\infty v}$ symmetry, and we logically associate this with the isotropic liquid. When the long molecular axes preferentially order along the nematic director, the correlation function $\rho(1|2)$ has a lower symmetry, $D_{\infty h}$. The function $\rho_o(1,2|3)$, because it has *two* atoms at given positions, is sensitive to rotations of a molecule about the long molecular axis; while $\rho(1|2)$ is only sensitive to the orientation of the long molecular axis relative

TABLE I

Catalog of possible point group symmetries of atomic correlation functions.

Case	Point group symmetry of $\rho(1\|2)$	Point group symmetry of $\rho_o(1,2\|3)$
1	K_h	$C_{\infty v}$
2	$D_{\infty h}$	$C_{\infty v}$
3	$D_{\infty h}$	C_{2v}
4	D_{2h}	$C_{\infty v}$
5	D_{2h}	C_{2v}

to the spatial coordinate axes. Four nematic phases are possible, listed as cases 2 through 5 in Table I. We will now show how these four phases may be described by a suitable order parameter.

THE ORDER PARAMETER AND ITS INVARIANTS

As presented in an earlier paper,[2] we take as the order parameter the tensor $S_{ij}^{\alpha\beta}$:

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

where $\hat{M}_i$ and $\hat{L}_\alpha$ are unit vectors defining molecular and laboratory coordinate systems respectively, and the angular brackets denote a thermal average. For a suitable choice of both sets of axes, the only finite elements are those such that $\alpha = \beta$ and $i = j$. The finite elements are linear combinations of Straley's four parameters[3] S, T, U, and V defined in terms of the Euler angles ϕ, θ and ψ which rotate the laboratory axes into coincidence with the molecular axes.

$$S \equiv \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle$$

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

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

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

A subsequent transformation to new variables r_1, r_2, α and β is later found to be useful.

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

$$\frac{1}{2}\sqrt{3}\, T = r_1 \sin\alpha + r_2 \sin\beta$$

$$\frac{1}{2}\sqrt{3}\, U = -r_1 \sin\alpha + r_2 \sin\beta$$

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

In order to construct the free energy, the rotational invariants of the order parameter must first be found. These invariants cannot depend on the choice of either the laboratory *or* molecular axes. There are five finite invariants (or pseudo-invariants) given by

$$I_2 = r_1^2 + r_2^2 = S^2 + \frac{3}{4} T^2 + \frac{3}{4} U^2 + V^2$$

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

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

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

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

I_2 and I_4 are second order in $S_{ij}^{\alpha\beta}$, I_3 and I_5 are third order, and I_6 is sixth order.

The proof that the free energy may be satisfactorily expanded as a polynomial in these five quantities is based on a generalization of Cauchy's proof of the Fundamental Theorem on Symmetric Functions.[4] Briefly the major points in the proof are outlined in the following way. As already mentioned, $S_{ij}^{\alpha\beta}$ reduces to the nine elements such that $\alpha = \beta$ and $i = j$ where α and i range over x, y, z for a special choice of both the molecular and laboratory axes. The nine elements are reduced to four independent ones by noting that $\sum_\alpha S_{ii}^{\alpha\alpha} = \sum_i S_{ii}^{\alpha\alpha} = 0$. However, the requirements of rotational invariance is expressed by the fact that invariant functions of the four independent elements must not change under any permutation of the molecular axes or any permutation of the laboratory axes. Quantities I_4 and I_5 change sign under some permutations and thus can occur only in combinations $I_4^{n_1} I_5^{n_2}$ such that the sum of the exponents $n_1 + n_2$ is an even number. By considering an arbitrary function of the four independent elements which satisfies invariance under permutations of axes and then substituting invariant I_2 for one of the four elements, the function can be written as a polynomial in the three elements and one invariant. Continuing to substitute, it is found that the function can always be written as a polynomial in the five quantities $I_2 - I_6$.

The free energy to sixth order is $S_{ij}^{\alpha\beta}$ is therefore found to be

$$F = AI_2 + BI_3 + C_1I_2^2 + C_2I_4^2 + D_1I_2I_3 + D_2I_4I_5$$
$$+ E_1I_2^3 + E_2I_2I_4^2 + E_3I_3^2 + E_4I_5^2 + E_5I_6.$$

The parameters A, B, C_1, C_2, D_1, D_2, E_1, E_2, E_3, E_4, and E_5 are phenomenological parameters and following the usual tenets of Landau theory we assume that A is linear in temperature. By minimizing the free energy with respect to r_1, r_2, α, and β the equilibrium state can be found for a given temperature and set of parameters. Table II lists the possible ordered nematic phases and their symmetry and identifies which of the order parameters S, T, U, and V are non-zero. U_1 and U_2 are uniaxial phases while B and B^* are biaxial.

TYPICAL PHASE DIAGRAMS

Because the free energy has so many phenomenological parameters, we have not yet carried out a systematic search to obtain all possible

TABLE II

List of nematic phases, their symmetry, and order parameters.

Name of phase	Symmetry of $\rho(1\|2)$	Symmetry of $\rho_o(1,2\|3)$	Finite parameters
Isotropic	K_h	$C_{\infty v}$	none
U_1	$D_{\infty h}$	$C_{\infty v}$	S
U_2	$D_{\infty h}$	C_{2v}	S, U
B	D_{2h}	$C_{\infty v}$	S, T
B^*	D_{2h}	C_{2v}	S, T, U, V

phase diagrams, although some interesting examples have been studied. In a previous paper[2] it was demonstrated that for a selected set of coefficients, treating A (i.e. temperature) and B as variables, a phase diagram is generated having isotropic to U_2, isotropic to B^*, and U_2 to B^* transitions. We will not repeat any further discussion here.

As a second interesting possibility, we have considered this set of parameters: $C_1 = 0$, $C_2 = 1$, $D_1 = 1$, $D_2 = 1$, $E_1 = 1$, $E_2 = 1$, $E_3 = 1$, $E_4 = 1$, $E_5 = -7$. The resulting phase diagram is shown in Figure 1. Three types of transitions are seen to be possible, namely

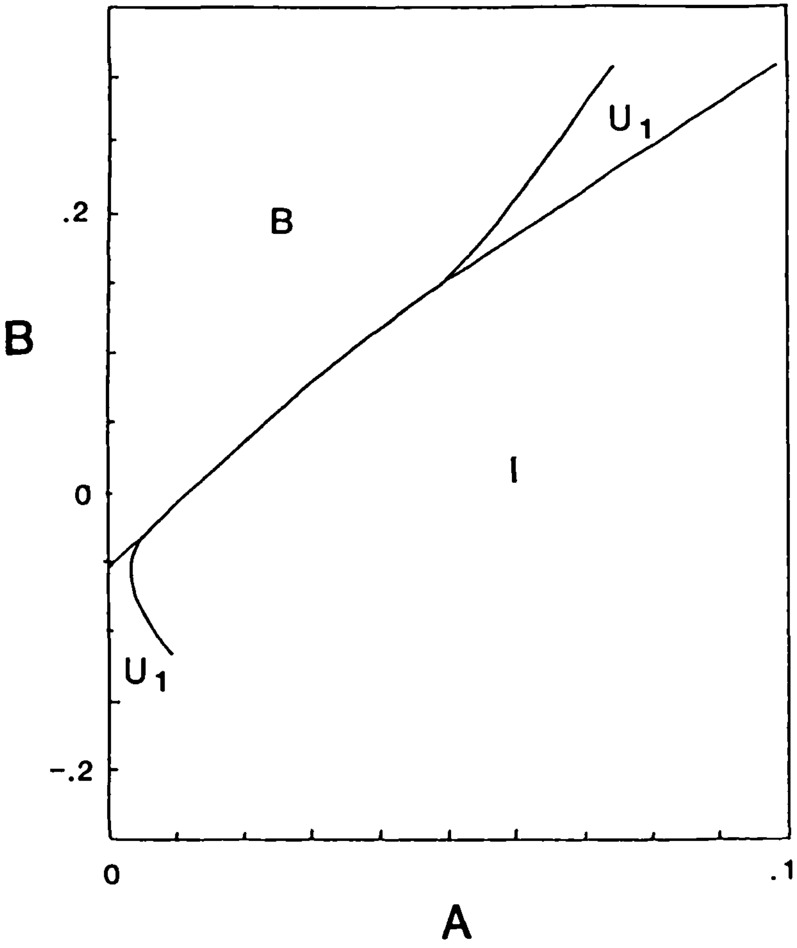

FIGURE 1 For the values of phenomenological parameters given in the text, this phase diagram results, having isotropic (I) to U_1, I to B and U_1 to B transitions.

isotropic to U_1, isotropic to B, and U_1 to B. For large absolute values of the parameter B, the U_1 to B transition is second order while all other transitions are first order. Of particular interest is the existence of the line of isotropic to B transitions. Furthermore, an examination of the expression for the free energy reveals that if the sign of the coefficient E_5 is reversed, the stability of the phase B is replaced with the U_2 phase, thus suggesting the possibility of having U_1 to U_2 transitions, as well as isotropic to U_2.

DISCUSSION

It is useful to make a comparison between the Landau theory of nematic liquid crystals presented here and the earlier theories of Freiser,[5,6] Alben,[7] Straley,[3] Luckhurst et al.,[8] and De Gennes.[9] The work of Freiser and Alben assumed a second rank tensor as the order parameter, and allowed, in our notation, only for the U_1 and B phases. The phase diagram published by Alben[7] has first order isotropic to U_1 transitions and second order U_1 to B transitions as well as a special point at which there is a transition from isotropic directly to the biaxial phase. It has been widely believed that such a diagram always results, regardless of the values of the parameters c, d, e, and f in Alben's free energy expression, Eq. (4) of reference 7. Guided by the results shown in Figure 1, we have re-examined Alben's free energy, and note that there are two regimes: for $4cf > d^2$, a phase diagram like Alben's occurs, but for $4cf < d^2$ a phase diagram like our Figure 1, having a line of isotropic to B transitions, occurs. We have also verified that a phase diagram like Alben's is obtained for an appropriate choice of parameters C_1 through E_5 so that the results of Freiser and Alben are contained within the present work.

De Gennes proposed that the second rank tensor order parameter for nematic phases could be taken to be $\chi^a_{\alpha\beta}$ which is related to $S^{\alpha\beta}_{ij}$ by the relation

$$\chi^a_{\alpha\beta} = \sum_{ij} A_{ij}\, S^{\alpha\beta}_{ij}$$

where $\chi^a_{\alpha\beta}$ is the anisotropic magnetic susceptibility and A_{ij} is the molecular magnetic susceptibility. Under this assumption it is straightforward to show that if the molecular susceptibility A_{ij} is biaxial, only the phases U_2 and B^* should occur while if A_{ij} is uniaxial the expected phases would be U_1 and B. This prediction is identical to the results of the mean field theories of Straley[3] and Luckhurst et al.[8] Each of these theories predict that a U_1 to U_2 transition should not occur (unless the molecular structure changes) which is in contradiction to the theory proposed here.

Ideally, experiment[10] should resolve whether transitions such as U_1 to U_2 and isotropic to B^* etc. actually occur, or whether in fact the proper order parameter is indeed a second rank tensor rather than $S_{ij}^{\alpha\beta}$. At the present time it appears that all known uniaxial nematic phases are of type U_2, while the only observed biaxial nematic phase occurs in the lyotropic mixtures pioneered by Saupe et al.[11,12] Thus not enough data are available yet to resolve the important questions.

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