Biaxial nematic phase, multiphase critical point, and reentry transition in binary liquid crystal mixtures[a]

Zhong-Ying Chen
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
J. M. Deutch
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 22 July 1983; accepted 18 November 1983)

A model considering both short-range and long-range interactions for liquid crystals mixtures of rod-like and plate-like molecules is presented in this paper. The model is treated in the framework of a mean field, van der Waals-type theory. The relationship of the model to a Landau-type treatment is discussed in an Appendix. It can be shown for this model that a multiphase critical point exists between the isotropic, rod nematic, plate nematic, and biaxial nematic phases. This point can be located from a set of analytic equations. The fluctuations and the magnetically induced birefringence around this point are calculated. The model predicts the phase diagrams of binary liquid crystal mixtures both with and without reentry transition. The reentrant phase transitions from the biaxial to the uniaxial nematic phase and from the uniaxial nematic to the isotropic phase have not received prior theoretical attention but have been demonstrated in recent experiments.

I. INTRODUCTION

Liquid crystals have richer phase diagrams than simple liquid systems and exhibit novel phase transitions.[1] However, the underlying mechanism of these transitions is not difficult to understand qualitatively. For example, simple theoretical models where only the hard core repulsion of rod-like molecules is considered, exhibit the isotropic to nematic phase transitions.[2–8]

There are several methods available to study phase transitions of this type. One method relies upon the introduction of an impurity molecule. For each type of impurity molecule introduced, the effect of the interaction with the molecules of the other species is analogous to the effect of an external field. The magnitude of the interaction between different molecules is normally of the same order as the interaction between molecules of the same species. Therefore, the addition of another kind of molecule will alter the phase transition of a pure system. Of course the distribution of two different kinds of molecules are dependent upon each other, so the interaction is nonlinear.

An example of this method is Alben's important study of binary mixtures[9] by use of a method similar to that employed by Flory.[10] Alben includes only the hard core repulsion of rod-like and plate-like molecules, and obtains a number of interesting results. For example, the introduction of plate-like molecules increases the isotropic–nematic transition temperature of rod-like molecules, because the addition of plate-like molecules makes it more difficult for the rods to distribute randomly. Another result is that, at a lower temperature, the uniaxial nematic phase can undergo a second order transition to a more highly ordered biaxial nematic phase. In this biaxial nematic phase there is a second favorable axis for the rod and plate molecules in addition to the most favorable axis. This problem has also been studied by Gelbart[11] and by Rabin, McMullen, and Gelbart.[12]

It is easy to understand that at low concentrations of plate-like molecules, the system will pass from the isotropic phase to the rod-nematic phase $N(+)$ as the temperature decreases. This is because the interaction energy between the rods is the dominant contribution to the total energy. Similarly, at a high concentration of plate-like molecules, there will be a transition from the isotropic to the plate-nematic phase $N(-)$, in which most plates stack in one direction. In this phase most rod-like molecules will line up in the plane where most plates are stacked, while in the rod-nematic phase most rods line up in one direction instead of one plane.

Between the two regions $N(+)$ and $N(-)$, Alben's calculation shows that the two second order lines between the uniaxial nematic and biaxial nematic phases form a sharp cusp separating the rod-nematic phase $N(+)$ and plate-nematic phase $N(-)$, and that the cusp touches the first order isotropic-uniaxial nematic transition line. The intersection of 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 is the result of a numerical calculation, it is difficult to examine the detailed behavior in the region between rod-nematic and plate-nematic phase.

In order to study this interesting phase behavior and its associated special critical point, we have formulated a model which contains *both* long-range and short-range interactions. Thus, the present model includes more phenomena than Alben's model. In particular when the long-range and short-range interactions tend to align the molecules in opposite ways, we expect a reentry phase transition from the biaxial nematic phase to the uniaxial nematic phase and from the uniaxial nematic phase to the isotropic phase. It is interesting to point out that the recent experimental result[13] shows the existence of this kind of reentry transitions.

---

[a] Supported in part by the National Science Foundation Grant No. CHE 81-16613.

This paper consists of seven sections. In Secs. II and III we present the theoretical model and the calculated phase diagram. In Sec. IV we derive the conditions for determining the critical point, and the correlation function for the order parameter is calculated in Sec. V. In Sec. VI the reentry phase transition is described and qualitatively compared with the experimental results. In Sec. VII we summarize the results of this work. Finally, in the Appendix we briefly discuss the relationship of our model to Landau theory and calculate the magnetically induced birefringence near the critical point.

II. THEORETICAL MODEL

The model we employ to describe the two component liquid crystal mixture is adapted from the work of Zwanzig,[4] further developed by Cotter[6] and by Wulf and De Rocco[8] for pure rods. In this model, the system is divided into n cells of volume Δ and the molecules in each cell can only adopt three discrete orientations in the x, y, and z direction. The molecules interact by a short-range repulsion which acts only within each cell and a long-range interaction which acts between cells. The long-range attraction is taken to be very weak and the size of the cell $\Delta^{1/3}$ is large compared to the range of intermolecular repulsion. This approximation permits the long-range attraction to be assumed constant over any particular cell so that the attractive interaction energy may be expressed in terms of the occupancy of each pair of cells.

The partition function for this van der Waals type model is evaluated by a maximum term method as described by van Kampen[14] and later employed by Mountain and Zwanzig,[15] Deutch and Zwanzig,[16] and Cohen and Deutch.[17] This mean field type analysis reveals much of the important physics of this complex system while permitting simple calculations.

We assume the system is composed of N^R rod shaped molecules of volume $v = d^2 l$ and N^P plate shaped molecules of volume $v = w^2 h$. The long-range interaction between each pair of molecules in cell i and cell j is denoted $\omega_{ij}^{\alpha\beta}$ where $\alpha(\beta)$ refers to the orientation and species in cell $i(j)$. We define the number of rod molecules N_i^R in cell i, in orientation x, y, and z as $N_i^{(1)}$, $N_i^{(2)}$, and $N_i^{(3)}$, respectively, and the number of plate molecules N_i^P in cell i, in orientation x, y, and z as $N_i^{(4)}$, $N_i^{(5)}$, $N_i^{(6)}$, respectively. Thus we have the conditions:

$$N_i^R = N_i^{(1)} + N_i^{(2)} + N_i^{(3)} \quad \text{and} \quad N_i^P = N_i^{(4)} + N_i^{(5)} + N_i^{(6)} \tag{2.1}$$

with

$$N_i = N_i^R + N_i^P \quad \text{and} \quad \sum_i N_i = N. \tag{2.2}$$

The configurational partition function for this system may be expressed as

$$Q = \sum_{\substack{\{N_i(\alpha)\} \\ \alpha = 1\ldots 6}} C(R)C(P) \prod_{i=1}^{n} \frac{N_i^R!}{N_i^{(1)}!N_i^{(2)}!N_i^{(3)}!} \frac{N_i^P!}{N_i^{(4)}!N_i^{(5)}!N_i^{(6)}!} \int \prod_{l=1}^{N} d\mathbf{R}_l \exp\left[-\frac{(H_S + H_L)}{kT} \right], \tag{2.3}$$

where

$$C(X) = \frac{1}{3N^x} \frac{1}{\prod_{i=1}^{n} N_i^x!}, \quad x = R, P. \tag{2.4}$$

The integral in Eq. (2.3) is evaluated for a fixed distribution of the molecules among the various cells.

We approximate the long-range contribution to the Boltzmann factor as

$$\exp\left[-\frac{H_L}{kT} \right] = \exp\left\{ \frac{1}{2kT} \sum_{\substack{i,j \\ \alpha,\beta}} [N_i^{(\alpha)} \omega_{ij}^{\alpha,\beta} N_j^{(\beta)}] \right\}. \tag{2.5}$$

The short-ranged contribution is approximated by a product of configurational integrals for N_i molecules in each cell.

$$\int \prod_{l=1}^{N} d\mathbf{R}_l \exp\left[-\frac{H_S}{kT} \right] = \prod_{i=1}^{n} \int \sum_{l=1}^{N_i} d\mathbf{R}_l \exp\left[-\frac{H_i}{kT} \right], \tag{2.6}$$

where H_i denotes the configurational Hamiltonian of the N_i particles interacting within cell i. Accordingly, each integral can be associated with the configurational free energy for the N_i molecules

$$\Delta^{N_i} e^{-\phi_s(N_i)/kT} = \int \prod_{l=1}^{N_i} d\mathbf{R}_l \exp[-H_i/kT]. \tag{2.7}$$

Following Onsager[2] and Zwanzig[4] we evaluate this free energy in the limit of low density, which yields

$$\exp[-\phi_s(N_i)/kT] = \exp\left[\sum_{\alpha,\beta} N_i^{(\alpha)} B^{\alpha\beta} N_i^{(\beta)} \right], \tag{2.8}$$

where $B^{\alpha\beta}$ is related to the two particle cluster integral

$$B^{\alpha\beta} = \frac{1}{\Delta^2} \frac{1}{2} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \left[\exp\left(-\frac{u_{\alpha\beta}}{kT} \right) - 1 \right]. \tag{2.9}$$

We shall assume that the short-range intermolecular repulsion is exclusively hard-core exclusion.

Truncation of the virial expansion is an approximation first introduced by Onsager for the limiting case of rods with an infinite aspect ratio (l/d). Several authors[18-20] have studied the isotropic to nematic phase transition for one component rod systems at smaller aspect ratios (l/d). These results suggest that for $(l/d) \geqslant 10$ qualitatively correct transitions are predicted by truncation of the expansion at the second virial coefficient.

Evaluation of $B^{\alpha\beta}$ requires calculation of the overlap volume between the molecules in given orientation. For example, $B^{11} = -4ld^2/\Delta$ and $B^{14} = -[(w+d)^2(l+h)/2\Delta]$. The resulting matrix B is symmetric and of the form

$$\mathrm{B} = \begin{pmatrix} a & b & b & e & f & f \\ b & a & b & f & e & f \\ b & b & a & f & f & e \\ e & f & f & c & d & d \\ f & e & f & d & c & d \\ f & f & e & d & d & c \end{pmatrix}. \tag{2.10}$$

Collecting the above results leads to the following expression for the configurational free energy after use of

Sterling's approximation for the factorials:

$$-\frac{A}{kT} = N - N\ln 3 + N\ln\Delta - \sum_{i,\alpha} N_i^{(\alpha)}\ln N_i^{(\alpha)} + \sum_{\substack{i,j\\ \alpha,\beta}} N_i^{(\alpha)} V_{ij}^{\alpha\beta} N_j^{(\beta)}, \tag{2.11}$$

where

$$V_{ij}^{\alpha\beta} = B^{\alpha\beta}\delta_{ij} + \omega_{ij}^{\alpha\beta}/2kT. \tag{2.12}$$

We shall restrict our attention to a spatially homogeneous equilibrium state and deviations from the state. In this case the $N_i^{(\alpha)}$ and the mole fractions $X_\alpha = (N_i^{(\alpha)}/\Delta\rho)$ are constant in each cell. Thus,

$$-\frac{A}{NkT} = 1 - \ln 3 - \ln\rho - \sum_\alpha X_\alpha \ln X_\alpha + \rho\sum_{\alpha,\beta} X_\alpha V_0^{\alpha\beta} X_\beta, \tag{2.13}$$

where $\rho = N/V$ and

$$V_0^{\alpha\beta} = B^{\alpha\beta}\Delta + \omega_0^{\alpha\beta}/2kT, \tag{2.14}$$

with

$$\omega_0^{\alpha\beta} = \lim_{n\to\infty}\sum_{j=1}^{n}\omega_{ij}^{\alpha\beta}\Delta = n\,\infty\int_0^\infty \omega^{\alpha\beta}(\mathbf{r})d\mathbf{r}. \tag{2.15}$$

The free energy Eq. (2.13) can formally be expressed in terms of a local mean field ψ_α[6]:

$$-\frac{A}{NkT} = 1 - \ln 3 - \ln\rho - \sum_\alpha X_\alpha \ln X_\alpha + \sum_\alpha X_\alpha\psi_\alpha,$$

where

$$\psi_\alpha = \rho\sum_\beta X_\beta V_0^{\alpha\beta}.$$

For simplicity we assume that the symmetry of the matrix $\omega_0^{\alpha\beta}$ is the same as $B^{\alpha\beta}$ so that V_0 retains the same form exhibited in Eq. (2.10).

The fraction of plate molecules denoted f is

$$f = X_4 + X_5 + X_6 \tag{2.16}$$

and the fraction of rod-like molecules is therefore

$$1 - f = X_1 + X_2 + X_3. \tag{2.17}$$

The equilibrium conditions require us to minimize the free energy (2.13) with respect to X_1, X_2, and X_4, X_5 for fixed f. This leads to the following four equations:

$$-\ln\left[\frac{X_1}{1-f-X_1-X_2}\right] - \rho p_1(1-f-2X_1-X_2) + \rho p_2(f-2X_4-X_5) = 0, \tag{2.18}$$

$$-\ln\left[\frac{X_2}{1-f-X_1-X_2}\right] - \rho p_1(1-f-X_1-2X_2) + \rho p_2(f-X_4-2X_5) = 0, \tag{2.19}$$

$$-\ln\left[\frac{X_4}{f-X_4-X_5}\right] - \rho p_3(f-2X_4-X_5) + \rho p_2(1-f-2X_1-X_2) = 0, \tag{2.20}$$

$$-\ln\left[\frac{X_5}{f-X_4-X_5}\right] - \rho p_3(f-X_4-2X_5) + \rho p_2(1-f-X_1-2X_2) = 0, \tag{2.21}$$

where

$$p_1 = \frac{1}{kT}(\omega_0^{11}-\omega_0^{12}) + 2\Delta(B^{11}-B^{12}), \tag{2.22}$$

$$p_2 = \frac{1}{kT}(\omega_0^{15}-\omega_0^{14}) + 2\Delta(B^{15}-B^{14}), \tag{2.23}$$

$$p_3 = \frac{1}{kT}(\omega_0^{44}-\omega_0^{45}) + 2\Delta(B^{44}-B^{45}). \tag{2.24}$$

It is interesting to note that p_1 corresponds to the difference in interaction energy of parallel and perpendicular rods; p_3 corresponds to the difference between parallel and perpendicular plates; and p_2 corresponds to the difference between the configuration where the rod and plate are parallel and the configuration where the rod and plate are perpendicular.

The pressure of the system may be calculated according to the formula

$$\frac{p}{kT} = -\frac{1}{kT}\left(\frac{\partial A}{\partial V}\right)_{T,N} = \rho - \rho^2\sum_{\alpha,\beta} X_\alpha V_0^{\alpha\beta} X_\beta, \tag{2.25}$$

which may, in turn, be solved to determine $\rho = \rho(T,p)$.

Solving Eqs. (2.18)–(2.21) in combination with Eq. (2.25) permits us to determine the minimum Gibbs free energy per particle $(G/N) = (A/N) + (p/\rho)$ for fixed T and p and consequently the phase diagram for the system.

III. PHASE DIAGRAM

In order to calculate the phase diagram we must adopt a form of the long-range attraction $\omega_0^{\alpha\beta}$. If we assume the long-range interaction can be expressed in terms of short-range interaction parameters, the problem is greatly simplified. For example we may write $\omega_0^{\alpha\beta}$ as

$$\omega_0^{\alpha\beta} = b + cB^{\alpha\beta}\Delta \quad\text{with}\quad \omega_0^{\alpha}\geqslant 0. \tag{3.1}$$

It is easy to see that the choice of $c > 0$ corresponds to the case where the long-range attraction tends to align the molecules in the same way as hard core interaction, i.e., to align the molecules parallel to each other. Therefore $c > 0$ favors the nematic phase.

In the case $c < 0$, the long-range force tends to favor perpendicular configurations of molecular pairs. In this case the long-range force is favorable to the isotropic phase and the short-range, hard-core interaction tends to favor the nematic phase. Thus the choice of $c < 0$ will result in the interesting circumstance of competition between long-range and short-range interactions.

If $b = c = 0$, the system contains only hard-core interaction, which corresponds to the situation considered by Alben.[9]

In the case considered here, Eq. (3.1), the p_α defined in Eqs. (2.22)–(2.24) take the form

$$p_\alpha = l^3\left(\frac{c}{2kT}+1\right)p'_\alpha, \quad \alpha = 1,2,3, \tag{3.2}$$

where

$$p'_1 = \frac{2\Delta}{l^3}(B^{11}-B^{12}), \tag{3.3}$$

$$p'_2 = \frac{2\Delta}{l^3}(B^{15}-B^{14}), \tag{3.4}$$

$$p'_3 = \frac{2\Delta}{l^3}(B^{44}-B^{45}). \tag{3.5}$$

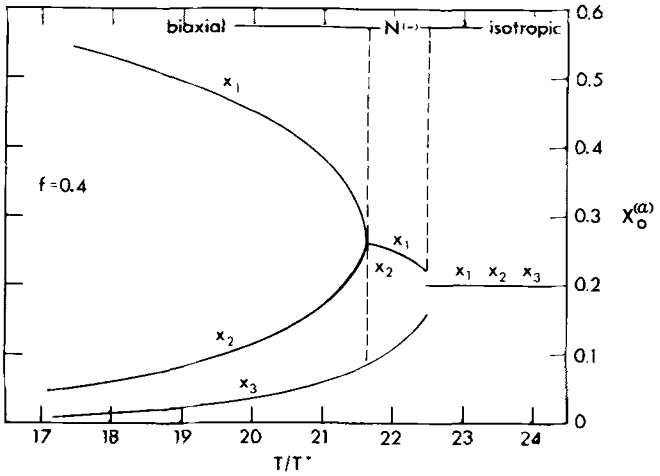

FIG. 1. Rod distribution as function of temperature for $f = 0.4$, $b = 0.2$, $c = 1.0$, $p/p^* = 50$.

With the selection, the solutions $\{X_\alpha\}$ of Eqs. (2.18)–(2.21) depend on the dimensionless parameter $R = l^3\rho[c/2kT) + 1]$ and f, p, T. When there are multiple solutions only the solution which gives a global minimum in the Gibbs free energy is retained.

As an example we assume rod dimensions $l = 1$, $d = 0.1$ and plate dimensions $w = 0.5$ and $h = 0.04$ which yields equal molecular volumes for the rods and plates. We write b, c in units of energy ϵ and define the reduced temperature $T^* = 0.1\epsilon/k$ and reduced pressure $p^* = 0.1\epsilon/l^3$, where l is the length of the rod.

The result of the calculations for the phase diagram are displayed in Figs. 1 to 4 which give the rod and plate distribution as functions of tempertaure T for fixed composition and pressure with $c > 0$. Figures 1 and 2 represent the cases where the plate contribution to the free energy is more important than the corresponding contribution of rod, while Figs. 3 and 4 represent the cases where the rod contribution to the free energy is more important.

In all these figures, both rods and plates are in the isotropic phase at high temperature. This is because at high temperature the entropy is the dominant contribution to the free energy.

At lower temperatures, the contribution of the interaction energy to the free energy is comparable with that from the entropy. So the system will undergo transitions from the isotropic phase to the nematic phase. Since the system consists of two kinds of molecules, the free energy depends also on the mixture ratio. When the concentration of plate molecules is higher than a certain value, the system undergoes a first order phase change to the plate nematic phase $N(-)$ (see Figs. 1 and 2). In this phase most of the plates are oriented in one direction $X_6 > X_4 = X_5$ [see the $N(-)$ region in Fig. 2], and most rods align in the x, y plane to accommodate the plates in the z direction $X_1 = X_2 > X_3$ [see $N(-)$ region in Fig. 1].

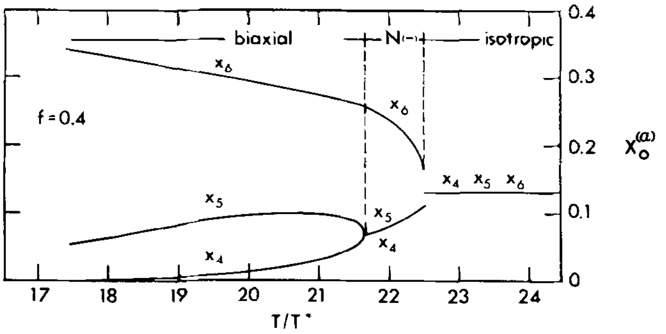

FIG. 2. Plate distribution as function of temperature for $f = 0.4$, $b = 0.2$, $c = 1.0$, $p/p^* = 50$.

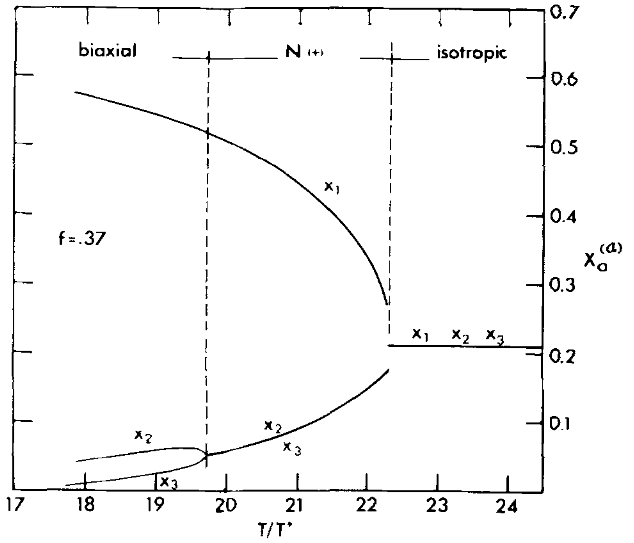

FIG. 3. Rod distribution as function of temperature for $f = 0.37$, $b = 0.2$, $c = 1.0$, $p/p^* = 50$.

When the concentration of plate molecules is lower than a certain value, the isotropic phase makes a first order transition to the rod nematic phase $N(+)$ (see Figs. 3 and 4). In this nematic phase $N(+)$, most rods align in one direction, while in the plate nematic phase, $N(-)$, most rods go to one plane rather than a single axis.

In the uniaxial nematic phases [$N(+)$ and $N(-)$], most rods (or plates) are aligned in one direction; the rest of the rods (or plates) are aligned equally in the other two directions. At even lower temperatures, the interaction between the rods (or plates) in two equivalent directions competes with the entropy, and the symmetry between these two di-

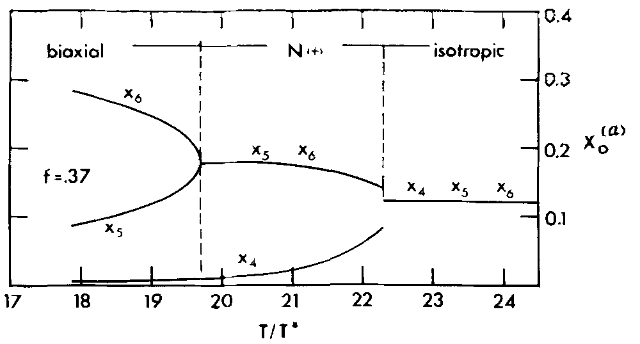

FIG. 4. Plate distribution as function of temperature for $f = 0.37$, $b = 0.2$, $c = 1.0$, $p/p^* = 50$.

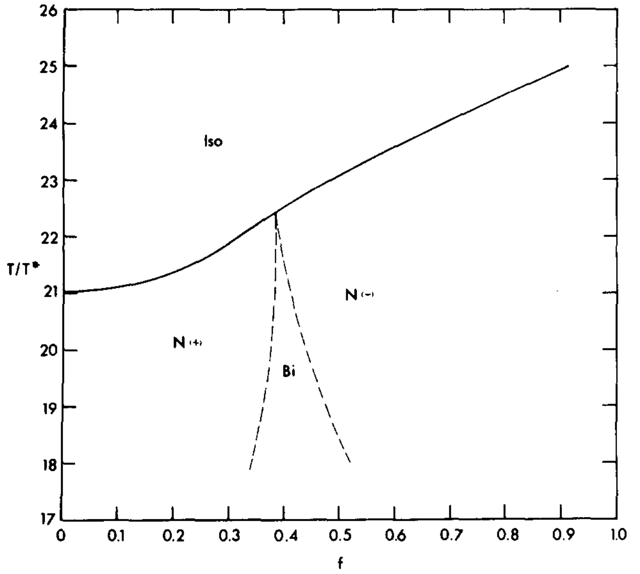

FIG. 5. Calculated phase diagram for $c > 0$, $p/p^* = 50$, $b = 0.2$, $c = 1.0$.

rections is broken. In this case a secondary favorable axis is formed and the phase forms a biaxial nematic ordering (see the biaxial region in Figs. 1 to 4).

The phase diagram in the T-f plane (with constant pressure) is given in Fig. 5. We add a note of caution concerning the first order isotropic to nematic transition in Fig. 5 (and Fig. 6 in Sec. VI). Our numerical calculations which involve relatively coarse interval of f ($\Delta f \sim 0.05$) may not reveal a narrow coexistence region between the isotropic and nematic phases. This possibility is discussed in Ref. 9. This phase diagram is qualitatively correct if the long-range interactions which are present also tend to align the molecules parallel to each other or are negligible compared with the short-range interaction ($c > 0$ and $c = 0$, $b = 0$, respectively).

For $c < 0$, the phase diagram is more complicated, as we shall discuss in Sec. VI.

The phase transition from the uniaxial nematic to the biaxial nematic is determined from our calculations to be a second order transition. This second order transition is also analyzed in Ref. 21. In the Appendix we relate the results of this model to a Landau-type treatment of the free energy and we show why the transition from isotropic to nematic phase is first order in general and the nematic to biaxial transition is second order. In Fig. 5 the two second order lines form a sharp cusp which separates the rod nematic phase and the plate nematic phase and forms a special critical point. We analyze the nature of this point in the next section.

IV. THE CRITICAL POINT

In order to investigate the critical point (T_c, f_c) within mean field theory, the free energy is expanded in terms of the order parameters δX_α from the presumed critical point $\{X_\alpha^c\}$. The dimensionless free energy per particle $F = (A/NkT)$ is expressed as

$$F(\{X_\alpha^c + \delta X_\alpha\}) = F(\{X_\alpha^c\}) + \tfrac{1}{2}\delta \mathrm{X}^T \cdot \mathrm{A} \cdot \delta \mathrm{X} + \cdots, \quad (4.1)$$

where we have introduced vector notation with the matrix A defined by

$$A_{\alpha\beta} = \left.\frac{\partial^2 F}{\partial X_\alpha \partial X_\beta}\right|_c .$$

At the critical point we expect the first and third order contributions to the free energy to vanish and the fourth order contribution to be positive for all variations $\{\delta X_\alpha\}$. Without loss of generality we may use the constraints Eqs. (2.16) and (2.17) to eliminate δX_3 and δX_6.

At the critical point at least one of the positive eigenvalues of A vanishes and the eigenvector corresponding to this eigenvalue (a particular combination of the δX_α) gives the direction of the second order phase transition. The location of the critical point is determined from the condition $\mathrm{A} \cdot \delta \mathrm{X} = 0$ by searching for appropriate values of T and f. In general this will require numerical solution of four nonlinear equations. However, in our case the critical point touches the isotropic phase for which we have the simple conditions:

$$X_1^c = X_2^c = X_3^c = \frac{1-f_c}{3} \text{ and } X_4^c = X_5^c = X_6^c = \frac{f_c}{3}. \quad (4.2)$$

Thus, we may express the $\{X_\alpha^c\}$ in terms of f_c and determine the matrix A:

$$\mathrm{A} = \begin{bmatrix} \frac{6}{1-f_c} - 2a_0 p_1' & \frac{3}{1-f_c} - a_c p_1' & 2a_c p_2' & a_c p_2' \\ \frac{3}{1-f_c} - a_c p_1' & \frac{6}{1-f_c} - 2a_c p_1' & a_c p_2' & 2a_c p_2' \\ 2a_c p_2' & a_c p_2' & \frac{6}{f_c} - 2a_c p_3' & \frac{3}{f_c} - a_c p_3' \\ a_c p_2' & 2a_c p_2' & \frac{3}{f_c} - a_c p_3' & \frac{6}{f_c} - 2a_c p_3' \end{bmatrix}, \quad (4.3)$$

where $a_c = \rho l^3(c/2kT_c + 1)$ and p_i' is given by Eqs. (3.3) to (3.5).

After rearranging this equation we obtain

$$a_c p_2' - \frac{(3/f_c - p_3' a_c)(3/(1-f_c) - p_1' a_c)}{p_2' a_c} = 0, \quad (4.4)$$

which corresponds to det(A) = 0, and find that a_c can be expressed in terms of f_c according to

$$a_c = \frac{-\left(\frac{3}{f_c}p_1' + \frac{3}{1-f_c}p_3'\right) + \sqrt{\left(\frac{3}{f_c}p_1' + \frac{3}{1-f_c}p_3'\right)^2 + 4\left(\frac{3}{1-f_c}\right)\left(\frac{3}{f_c}\right)[(p_2')^2 - p_1'p_3']}}{2[(p_2')^2 - p_1'p_3']}. \tag{4.5}$$

Here, the positive solution is chosen because the ordered phase is only possible for positive a_c.

Examination of the matrix equation $\mathsf{A}\cdot\delta\,\mathbf{X} = 0$ leads to the solutions

$$\delta X_4 = -\frac{1}{a_c p_2'}\left(\frac{3}{1-f_c} - p_1' a_c\right)\delta X_1, \tag{4.6}$$

$$\delta X_5 = -\frac{1}{a_c p_2'}\left(\frac{3}{1-f_c} - p_1' a_c\right)\delta X_2, \tag{4.7}$$

where use is made of Eq. (4.4). These equations show the relation, close to the critical point, between the change in rod and plate distributions.

We next compute the third order contribution to F. Direct calculation, with use of Eqs. (4.6) and (4.7), leads to

$$\sum_{\alpha,\beta,\gamma} \frac{\partial^3 F}{\partial X_\alpha \partial X_\beta \partial X_\gamma}\bigg|_c \delta X_\alpha \delta X_\beta \delta X_\gamma$$

$$= 3\left[\left(\frac{3}{1-f_c}\right)^2 - \left(\frac{3}{f_c}\right) \times \left(\frac{1}{a_c p_2'}\right)^3 \left(\frac{3}{1-f_c} - a_c p_1'\right)^3\right]$$

$$\times [\delta X_1^2 \delta X_2 + \delta X_1 \delta X_2^2]. \tag{4.8}$$

This third order contribution to the free energy must vanish at the critical point for all variations δX_1 and δX_2. For this to be true, the first bracketed term must vanish which can be further simplified to

$$a_c = 3\left[(1-f_c)p_1' + p_2'\sqrt[3]{f_c^2(1-f_c)}\right]^{-1}. \tag{4.9}$$

This equation together with Eq. (4.5) predicts the location of the critical point f_c and T_C. Finally, the fourth order contribution to F may be calculated in order to confirm that it is positive definite for all nontrivial δX_α. Since this critical point is shared by four phases, we call it a multiphase critical point.

For the simple mixture model described in the previous section one determines the critical point $f_c = 0.3815$ and $T_c/T^* = 2.245$ at $p/p^* = 50$ [see Fig. 5] where we have employed the equation of state Eq. (2.25). At the critical point $vp = 0.116$, where v is the volume of a rod or plate.

The existence of a critical point is not always guaranteed. For example, in the case of a mixture of rods and cubes $[p_2' = p_3' = 0]$ which has been described by Alben[9] does not possess a biaxial phase because the cubes cannot orient the rods in a particular direction.

We have considered the case of a simple interaction defined by Eq. (3.1). For a system where the long-range interaction is more complicated, we may arrive at a condition for the critical point equivalent to Eqs. (4.5) and (4.9) with $a_c p_1'$, $a_c p_2'$, $a_c p_3'$ replaced by ρp_1, ρp_2, ρp_3 with the definitions Eqs. (2.22)–(2.24).

V. FLUCTUATIONS AT THE CRITICAL POINT

In this section we study the fluctuations that occur at the critical point within the mean field theory which has been developed. We apply the methods developed previously for treating pure[14,15] and binary fluids.[16,17] The isotropic to nematic transition is known to be weakly first order and turns to be second order at the critical point, so considerable fluctuations may be observed at this transition.[22–25] Our model sheds some light on the character of these fluctuations.

We proceed by writing the free energy per particle as

$$F = F^0 + \frac{1}{2}\sum_{i,j}^{n} \delta\mathbf{X}^T(i)\cdot\mathsf{A}_{ij}\cdot\delta\,\mathbf{X}(j), \tag{5.1}$$

where $\delta X_\alpha(i)$ denotes the deviation of species α from its equilibrium value in the ith cell. The matrix A_{ij} depends only upon the distance between cells

$$A_{ij}^{\alpha\beta} = \frac{1}{NkT}\frac{\partial^2 A}{\partial X_\alpha(i)\partial X_\beta(j)} = A^{\alpha\beta}(|\mathbf{R}_i - \mathbf{R}_j|), \tag{5.2}$$

where $\mathbf{R}_i$ is the position of the center of cell i.

In terms of the Fourier transformation

$$\delta X_\alpha(i) = \frac{1}{\sqrt{n}}\sum_{k\neq 0} \delta\hat{X}_\alpha(\mathbf{k})\exp[i\mathbf{k}\cdot\mathbf{R}_i], \tag{5.3}$$

$$\delta\hat{X}_\alpha(\mathbf{k}) = \frac{1}{\sqrt{n}}\sum_{\mathbf{R}_i} \delta X_\alpha(i)\exp[-i\mathbf{k}\cdot\mathbf{R}_i], \tag{5.4}$$

we may write

$$\delta F = \frac{1}{2}\sum_{k\neq 0} \delta\hat{\mathbf{X}}^T(-\mathbf{k})\cdot\mathsf{A}(\mathbf{k})\cdot\delta\hat{\mathbf{X}}(\mathbf{k}). \tag{5.6}$$

The matrix $A_{ij}^{\alpha\beta}$ has the following structure, when X_3 and X_6 are eliminated according to Eqs. (2.16) and (2.17):

$$\mathsf{A}_{ij} = \begin{pmatrix} J & W & 2Q & Q \\ W & K & Q & 2Q \\ 2Q & Q & M & P \\ Q & 2Q & P & N \end{pmatrix}, \tag{5.7}$$

where

$$J = \delta_{ij}\left(\frac{1}{X_1^0} + \frac{1}{1-f-X_1^0-X_2^0}\right) - 2\rho\left(V^{(1)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(1)}\right),$$

$$K = \delta_{ij}\left(\frac{1}{X_2^0} + \frac{1}{1-f-X_1^0-X_2^0}\right) - 2\rho\left(V^{(1)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(1)}\right),$$

$$M = \delta_{ij}\left(\frac{1}{X_3^0} + \frac{1}{f-X_3^0-X_4^0}\right) - 2\rho\left(V^{(3)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(3)}\right),$$

$$N = \delta_{ij}\left(\frac{1}{X_4^0} + \frac{1}{f - X_3^0 - X_4^0}\right) - 2\rho\left(V^{(3)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(3)}\right),$$

$$W = \delta_{ij}\left(\frac{1}{1 - f - X_1^0 - X_2^0}\right) - \rho\left(V^{(1)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(1)}\right),$$

$$P = \delta_{ij}\left(\frac{1}{f - X_3^0 - X_4^0}\right) - \rho\left(V^{(3)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(3)}\right),$$

$$Q = \rho\left(V^{(2)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(2)}\right). \tag{5.8}$$

The quantities $V^{(\nu)}\delta_{ij} + \omega_{ij}^{(\nu)}/kT$ ($\nu = 1,2,3$) are defined as follows:

$$V^{(1)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(1)} = 2\Delta\,(B^{11} - B^{12})\delta_{ij} + \frac{1}{kT}(\omega_{ij}^{11} - \omega_{ij}^{12}), \tag{5.9}$$

$$V^{(2)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(2)} = 2\Delta\,(B^{15} - B^{14})\delta_{ij} + \frac{1}{kT}(\omega_{ij}^{15} - \omega_{ij}^{14}), \tag{5.10}$$

$$V^{(3)}\delta_{ij} + \frac{1}{kT}\omega_{ij}^{(3)} = 2\Delta\,(B^{44} - B^{45})\delta_{ij} + \frac{1}{kT}(\omega_{ij}^{44} - \omega_{ij}^{45}). \tag{5.11}$$

The matrix $\hat{\mathsf{A}}(\mathbf{k})$ has the same form as Eq. (5.7) with

$$\hat{J} = \frac{1}{X_1^0} + \frac{1}{1 - f - X_1^0 - X_2^0} - 2\rho V^{(1)} - \frac{2\rho}{kT}\frac{\hat{\omega}^{(1)}(k)}{\Delta},$$

$$\hat{K} = \frac{1}{X_2^0} + \frac{1}{1 - f - X_1^0 - X_2^0} - 2\rho V^{(1)} - \frac{2\rho}{kT}\frac{\hat{\omega}^{(1)}(k)}{\Delta},$$

$$\hat{M} = \frac{1}{X_3^0} + \frac{1}{f - X_3^0 - X_4^0} - 2\rho V^{(3)} - \frac{2\rho}{kT}\frac{\hat{\omega}^{(3)}(k)}{\Delta},$$

$$\hat{N} = \frac{1}{X_4^0} + \frac{1}{f - X_3^0 - X_4^0} - 2\rho V^{(3)} - \frac{2\rho}{kT}\frac{\hat{\omega}^{(3)}(k)}{\Delta},$$

$$\hat{W} = \frac{1}{1 - f - X_1^0 - X_2^0} - \rho V^{(1)} - \frac{\rho}{kT}\frac{\hat{\omega}^{(1)}(k)}{\Delta},$$

$$\hat{p} = \frac{1}{f - X_3^0 - X_4^0} - \rho V^{(3)} - \frac{\rho}{kT}\frac{\hat{\omega}^{(3)}(k)}{\Delta},$$

$$\hat{Q} = \rho V^{(2)} - \frac{\rho}{kT}\frac{\hat{\omega}^{(2)}(k)}{\Delta}. \tag{5.12}$$

Since we know that $\{X_\alpha^0\}$ is an implicit function of T and f in the ordered phase, it is easier to study the fluctuation from the isotropic side. For the isotropic phase, a relation between X_α^0 and f similar to Eq. (4.2) holds and $\hat{\mathsf{A}}(\mathbf{k})$ has the following simple form:

$$\hat{\mathsf{A}}(\mathbf{k}) = \begin{vmatrix} 2(B-\Delta B) & B-\Delta B & 2(C-\Delta C) & C-\Delta C \\ B-\Delta B & 2(B-\Delta B) & C-\Delta C & 2(C-\Delta C) \\ 2(C-\Delta C) & C-\Delta C & 2(D-\Delta D) & D-\Delta D \\ C-\Delta C & 2(C-\Delta C) & D-\Delta D & 2(D-\Delta D) \end{vmatrix}, \tag{5.13}$$

where

$$B = \frac{3}{1-f} - \rho\left(V^{(1)} + \frac{\hat{\omega}^{(1)}(0)}{kT\Delta}\right),$$

$$D = \frac{3}{f} - \rho\left(V^{(3)} + \frac{\hat{\omega}^{(3)}(0)}{kT\Delta}\right),$$

$$C = \rho\left(V^{(2)} + \frac{\hat{\omega}^{(2)}(0)}{kT\Delta}\right),$$

$$\Delta B = \frac{\rho}{kT}\left(\frac{\hat{\omega}^{(1)}(k)}{\Delta} - \frac{\hat{\omega}^{(1)}(0)}{\Delta}\right),$$

$$\Delta D = \frac{\rho}{kT}\left(\frac{\hat{\omega}^{(3)}(k)}{\Delta} - \frac{\hat{\omega}^{(3)}(0)}{\Delta}\right),$$

$$\Delta C = \frac{\rho}{kT}\left(\frac{\hat{\omega}^{(2)}(k)}{\Delta} - \frac{\hat{\omega}^{(2)}(0)}{\Delta}\right).$$

The probability of a fluctuation in the system is assumed to be Gaussian[26] according to

$$P_r[\delta\hat{\mathbf{X}}(\mathbf{k})] \propto \exp[-N\delta F]. \tag{5.14}$$

Thus the mean square fluctuation is given by

$$\langle\delta\hat{X}_\alpha(-\mathbf{k})\delta\hat{X}_\beta(\mathbf{k}')\rangle = [\hat{\mathsf{A}}(\mathbf{k})^{-1}]_{\alpha\beta}\delta_{\mathbf{k}\mathbf{k}'} = \frac{\tilde{A}_{\beta\alpha}}{|\mathsf{A}(\mathbf{k})|}\delta_{\mathbf{k}\mathbf{k}'}, \tag{5.15}$$

where $\tilde{A}_{\beta\alpha}$ is the cofactor of the matrix element $\hat{A}_{\alpha\beta}(\mathbf{k})$. In coordinate space we have

$$C_{\alpha\beta}(|\mathbf{R}_{ij}|) = \langle\delta X_\alpha(\mathbf{R}_i)\delta X_\beta(\mathbf{R}_j)\rangle = \frac{1}{8\pi^3}\int d\mathbf{k}\,\tilde{A}_{\beta\alpha}\exp[i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)]\,[|\hat{\mathsf{A}}|]^{-1} - \frac{1}{V}\left[\frac{\tilde{A}_{\beta\alpha}}{|\hat{\mathsf{A}}|}\right]_{k=0}\delta(\mathbf{R}_i - \mathbf{R}_j). \tag{5.16}$$

To calculate this integral we must know the long-range interaction function $\omega(|\mathbf{R}_i - \mathbf{R}_j|)$. However, since $\omega(r)$ is a slow varying function of r, we can expand $\omega(k)$ in terms of k, and retain only the lowest order term.

$$\omega(k) = \omega_0 - \omega_2 k^2 + o(k^4): \tag{5.17}$$

Then

$$\Delta B = -\frac{\rho}{KT}\left(\frac{\hat{\omega}_2^{(1)}k^2}{\Delta}\right),$$

$$\Delta D = -\frac{\rho}{KT}\left(\frac{\hat{\omega}_2^{(3)}k^2}{\Delta}\right),$$

$$\Delta C = -\frac{\rho}{KT}\left(\frac{\hat{\omega}_2^{(2)}k^2}{\Delta}\right). \tag{5.18}$$

Substituting Eq. (5.18) into (5.13), we obtain

$$|\hat{\mathsf{A}}(\mathbf{k})| = A_0 + Uk^2 + o(k^4) \tag{5.19}$$

with

$$A_0 = 9(BD - C^2)^2, \tag{5.20}$$

$$U = 18(BD - C^2)(D\omega_2^{(1)} - 2C\omega_2^{(2)} + B\omega_2^{(3)})\frac{\rho}{\Delta KT}. \tag{5.21}$$

Similarly we find

$$\tilde{A}_{11} = G + Hk^2 + o(k^4) \tag{5.22}$$

with

$$G = 6D(BD - C^2), \tag{5.23}$$

$$H = \frac{6\rho}{\Delta KT}\,[D^2\omega_2^{(1)} + (2BD - C^2)\omega_2^{(3)} - 2DC\omega_2^{(2)}]. \tag{5.24}$$

We proceed to compute an explicit expression, valid for large distance, for the fluctuation matrix (5.16). For example,

$$\begin{aligned} C_{11}(|\mathbf{R}_{ij}|) = {} & \frac{(G - HI^2)}{4\pi|\mathbf{R}_i - \mathbf{R}_j|}\, e^{-|\mathbf{R}_i - \mathbf{R}_j|/\xi} \\ & - \frac{1}{V}\left(\frac{G}{A_0}\right)\delta(\mathbf{R}_i - \mathbf{R}_j), \end{aligned} \tag{5.25}$$

where

$$\xi = \frac{1}{I} = \sqrt{\frac{2(D\omega_2^{(1)} - 2C\omega_2^{(2)} + B\omega_2^{(3)})\rho/\Delta kT}{(BD - C^2)}}. \tag{5.26}$$

We see that the correlation length ξ is proportional to $\sqrt{1/(BD - C^2)}$. At the critical point $(BD - C^2) \to 0$, so the correlation length will diverge.

It is possible to calculate the manner in which the correlation length diverges as the critical point is approached. We approach the critical point from the isotropic side along $f = f_c$ and express B, D, and C in terms of their values at the critical point and the deviation $\delta T = T - T_c$. A lengthy calculation yields

$$BD - C^2 = [BD - C^2]_c + \delta T \cdot \text{const} = \delta T \cdot \text{const}. \tag{5.27}$$

Therefore, as we expect, from a mean field treatment

$$\xi \sim (T - T_c)^{-\nu} \text{ with } \nu = 1/2 \tag{5.28}$$

and the correlation of the order parameter behaves as $e^{-r/\xi}/r^{d-2+\eta}$ with $\eta = 0$. Measurements of the critical exponent for liquid crystal mixtures will determine the applicability of mean field theory to this type of system.

VI. THE REENTRY TRANSITION

It is interesting to point out, that although the existence of a biaxial nematic phase was predicted in the early 1970's,[9,21] it was not until 1980 that this phase was first observed by Yu and Saupe.[13] More recent experiments have been carried out by Bartolino *et al.*[27] The experiment of Yu and Saupe[13] was carried out on a three-component mixture of potassium laurate, 1-decanol, and water. This system can form both plate- and rod-like micelles so it is quite plausible to characterize this real system in terms of the model presented here. However, it is possible that the biaxial phase in the real system is composed of a third type of ellipsoidal micelle with three different axial lengths in the biaxial phase. Also, the experimental result shows that at a lower temperature, the system reenters from the biaxial nematic phase to the uniaxial nematic phase and from the uniaxial nematic phase to the isotropic phase. The biaxial region in the phase diagram becomes narrow at lower temperatures.

This reentry phase behavior is quite different from the phase diagram shown in Fig. 5. In a system of the type considered above and shown in Fig. 5, the ground state is an ordered nematic phase. In contrast, for the reentry transition system, the ground state is an isotropic phase. Additionally, in Fig. 5, the biaxial nematic phase forms an open area, but in the reentry 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 reentry phase diagram reflects a more complex dependence of the energy on orientation.

The model considered here may be modified to include the possibility of reentrant behavior. In our model we consider both long- and short-range interactions, and the relation between these two interactions is simply determined by the parameter c in Eq. (3.1). For $c > 0$ the long-range interaction tends to align the molecules in the same way as the short-range force so the energy is always lower for the ordered phase. This is the case presented in Fig. 5.

For $c < 0$, the long-range force tends to align the molecules in the opposite way from the short-range interaction. Moreover, in this model the short-range interaction is a hard-core type repulsion: $u_{\alpha\beta} = 0$ when two molecules do not overlap, and $u_{\alpha\beta} = \infty$ when two molecules intersect. Obviously, $u_{\alpha\beta}/kT$ is independent of temperature.

At high temperature the entropy dominates the free energy and the system is in the disordered phase (isotropic).

At intermediate temperature the short-range, hard-core interaction makes the major contribution to the total configurational energy and the system is determined by the competition between the short-range interaction and the entropy. In this case the system becomes more ordered when the temperature decreases.

At low temperatures the long-range interaction dominates the configuration energy. For $c < 0$, the molecules tend to align in a disordered way, so the system reenters from the biaxial nematic phase to uniaxial nematic phase and from the nematic phase to the isotropic phase. This is the reentry transition.

A sample calculation is given in Fig. 6 for $c = -0.8$,

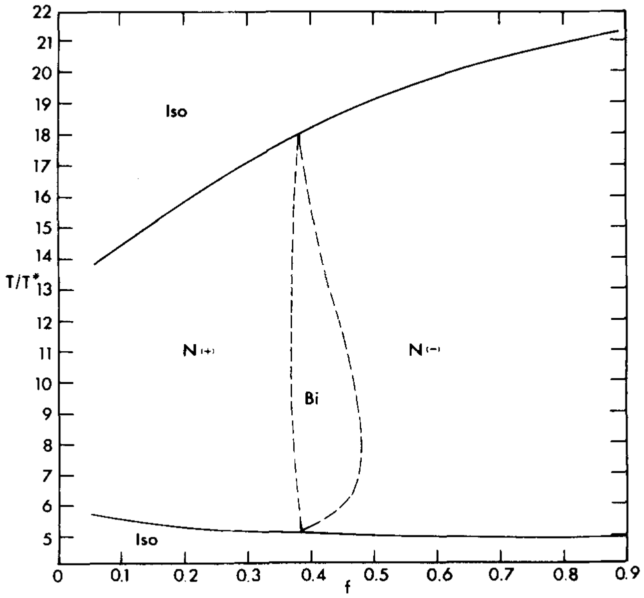

FIG. 6. Calculated phase diagram with reentry transition $p/p^* = 80$, $b = 0.1 \times 10^{-6}$, $c = -0.8$.

$b = 0.1 \times 10^{-6}$, while the molecules have the same geometric shape as in Fig. 5. The phase diagram shows reentry transitions similar to the experimental result and the biaxial phase forms a closed region.

It is interesting to note that the biaxial regions has an asymmetric shape. The shape of the biaxial region depends on the extent to which the molecules are anisotropic. For example, if the plate molecules get flatter, the biaxial region will tilt towards $N(+)$ region near $f = f_c$. The sample calculation for plates having size $[1 \times 1 \times 0.01]$ shows stronger tilt than the plates with size of $[0.5 \times 0.5 \times 0.04]$. The similar tendency can also be seen in Ref. 9. Figure 6 exhibits the sequence of phase transitions Iso→$N(-)$→Bi→$N(-)$→Iso at certain concentrations upon cooling. This is experimentally observed.[13] It is possible that with greater assumed molecular asymmetry when the cusp tilts further to $N(+)$ the more complicated sequence of phases which is also observed[13] upon cooling at constant concentration Iso→$N(-)$→Bi→$N(+)$→Bi→$N(-)$→Iso may also be predicted by our model.

There is another critical point at the reentry transition and both critical points occur at the same composition of the mixture f_c. This occurs because our model simplifies the relation between the long-range and the short-range interaction through the single parameter c which introduces a proportionality between these two interactions. For real systems the relation between the long-range and the short-range interaction can be expected to be more complicated, so the reentry critical point will, in general, occur at a different concentration ratio.

A reentry critical point is not evident in the experimental phase diagram shown in Ref. 13. But in this experiment, the biaxial region in that phase diagram becomes narrower at low temperatures in the phase diagram, and it may be expected that two second order lines surrounding the biaxial region will form a second critical point. A multiphase critical point where the $N(+)$, $N(-)$, and biaxial phase all meet at a single point on the isotropic phase boundary is plausible from extrapolation of existing experiments.[13] In Ref. 28 Saupe *et al.* present additional experiment results to support this possibility. An alternative possibility is that the nematic-biaxial phase boundaries meet at a point below the isotropic phase line and that a direct $N(+)/N(-)$ transition occurs from this point to the isotropic phase boundary.

Although a hard-core potential approximation is used for the short-range repulsion in our model, it will in general be true that the temperature dependences of the long-range and the short-range interactions behave differently. Therefore, the competition between these two general interactions can credibly result in a similar picture as shown in Fig. 6.

VII. SUMMARY DISCUSSION

The model of liquid crystal mixtures developed here calculates interactions between molecules on a special lattice basis. The model also approximates the interaction by separation into short-range repulsions and long-range, van der Waals-like attractions. Competition between energy and entropy gives rise to a phase diagram which exhibits a variety of subtle phenomena that have recently been observed in liquid crystal mixtures.[13] These include the existence of a biaxial nematic phase for binary liquid crystal mixtures and the existence of a reentrant phase transition. Our method also permits calculation of the effect of fluctuations at the critical point albeit in the restricted framework of a mean field theory.

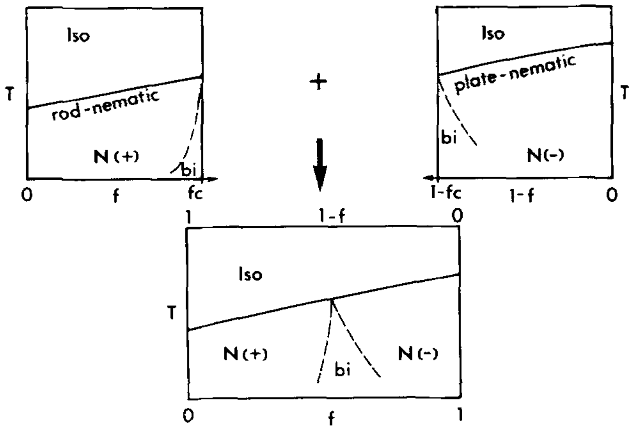

FIG. 7. Heuristic explanation of these phase diagram.

The principal virtue of the model we propose is its simplicity and, we believe, its clarity in relating observed phase behavior to molecular interactions. It differs from Alben's model[9] in several respects; most importantly we include the effect of attractive forces and we adopt a simpler approximate method for evaluation of the partition function. Using a simple form of free energy in conjunction with the Landau theory we show (see the Appendix) that the transition from the isotropic phase to the nematic phase is first order in general and the nematic to biaxial transition is second order. We also show that the isotropic to nematic transition becomes second order only when two transitions (isotropic→nematic and nematic→biaxial) occurs simultaneously.

The most novel feature of the plate-rod nematic system is the existence of a special critical point which is shared by four phases in apparent violation of the "phase rule". But notice that the two nematic phases are separated from the biaxial phase by a second order phase transition as described in the Appendix.

The formation of this multiphase critical point can be understood by comparing the effect of introducing another kind of molecule with the effect of an external field. For each kind of molecule introduced the interaction is similar to applying a nonlinear external field. This impurity field will adjust the discontinuity of the order parameter over the isotropic to nematic transition (which is reflected in the cubic term in the free energy expansion), and at a certain mixture ratio the isotropic to nematic transition becomes a second order transition. The influence of one species over the other is mutual, so we may view the phase diagram as the addition of two phase diagrams as heuristically displayed in Fig. 7.

ACKNOWLEDGMENT

The authors thank J. D. Litster and A. N. Berker for their valuable comments and suggestions.

APPENDIX: RELATIONSHIP TO LANDAU-TYPE THEORY

In this section we relate the formalism developed to a Landau-type theory[1] where the free energy is expanded in a power series in relevant order parameters. For a liquid crystal the order parameter can be taken as a real, symmetric, and traceless tensor.

In a system consisting of two species, generally two order tensor parameters are needed to describe the system. The free energy per particle then can be written in the following form:

$$\begin{aligned}\frac{A}{NkT} = \frac{A^0}{NkT} &+ \frac{B_1}{2}\operatorname{Tr} Q^r_{\alpha\beta}Q^r_{\beta\alpha}\\
&+ \frac{B_2}{2}\operatorname{Tr} Q^p_{\alpha\beta}Q^p_{\beta\alpha} + B_3\operatorname{Tr} Q^r_{\alpha\beta}Q^p_{\beta\alpha}\\
&+ \frac{C_1}{6}\operatorname{Tr} Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^r_{\gamma\alpha} + \frac{C_2}{6}\operatorname{Tr} Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^p_{\gamma\alpha}\\
&+ \frac{C_3}{2}\operatorname{Tr} Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^p_{\gamma\alpha} + \frac{C_4}{2}\operatorname{Tr} Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^r_{\gamma\alpha}\\
&+ \frac{D_1}{24}\operatorname{Tr} Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^r_{\gamma\delta}Q^r_{\delta\alpha}\\
&+ \frac{D_2}{24}\operatorname{Tr} Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^p_{\gamma\delta}Q^p_{\delta\alpha}\\
&+ \frac{D_3}{6}\operatorname{Tr} Q^p_{\alpha\beta}Q^r_{\beta\gamma}Q^r_{\gamma\delta}Q^r_{\delta\alpha}\\
&+ \frac{D_4}{6}\operatorname{Tr} Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^p_{\gamma\delta}Q^r_{\delta\alpha}\\
&+ \frac{D_5}{6}\operatorname{Tr} Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^p_{\gamma\delta}Q^p_{\delta\alpha}\\
&+ \frac{D_6}{12}\operatorname{Tr} Q^r_{\alpha\beta}Q^p_{\beta\gamma}Q^r_{\gamma\delta}Q^p_{\delta\alpha},\end{aligned}\tag{A1}$$

where $Q^r_{\alpha\beta}$ and $Q^p_{\alpha\beta}$ are the tensor order parameters for rods and plates, respectively, and the coefficients of the terms $B_1, B_2, \ldots$ are functions of temperature T, the fraction of plates f, and the pressure.

In order to apply Landau theory to our model, we must identify the relevant order parameter. Although our model has a cubic symmetry, we understand that all the properties calculated through this model are equivalent to a system described by second-rank tensors with rotational symmetry.

In some representation the tensor order parameter for rods and plates will be diagonal and can be written as

$$Q^r_{\alpha\beta} = \begin{pmatrix} 2p_1 & 0 & 0\\ 0 & -p_1+q_1 & 0\\ 0 & 0 & -p_1-q_1\end{pmatrix},\tag{A2}$$

$$Q^p_{\alpha\beta} = \begin{pmatrix} 2p_2 & 0 & 0\\ 0 & -p_2+q_2 & 0\\ 0 & 0 & -p_2-q_2\end{pmatrix},\tag{A3}$$

where p_1 and p_2 are the nematic order parameters, q_1 and q_2 are the biaxial nematic order parameters. The case $p_i = 0$, $q_i = 0$ $(i = 1,2)$ corresponds to the isotropic phase. The case $p_i \neq 0, q_i = 0$, or $q_i = 3p_i$ $(i = 1,2)$ corresponds to the uniaxial nematic phase and the case $p_i \neq 0$, $q_i \neq 0$, and $q_i \neq 3p_i$ $(i = 1,2)$ corresponds to the biaxial nematic phase.

In this representation the coordinates x,y,z are exactly the principal coordinates for the tensors $Q^r_{\alpha\beta}$ and $Q^p_{\alpha\beta}$.

We choose the following definitions for the rods:

$$\begin{aligned}&3\delta X_1/(1-f) = 2p_1,\\ &3\delta X_2/(1-f) = -p_1+q_1,\\ &-3(\delta X_1+\delta X_2)/(1-f) = -p_1-q_1\end{aligned}\tag{A4}$$

and for the plates

$$\begin{aligned}&3\delta X_4/f = 2p_2,\\ &3\delta X_5/f = -p_2+q_2,\\ &-3(\delta X_4+\delta X_5)/f = -p_2-q_2.\end{aligned}\tag{A5}$$

This selection of the order tensor parameters is not unique and the different definitions of the order parameters will result in different coefficients in the free energy expansion, but the thermodynamic quantities calculated will not be affected by the definition of the order parameters.

Employing the results of Sec. IV where the free energy was expanded in terms of $\{\delta X_i\}$, we find to fourth order:

$$\begin{aligned}\frac{A}{NkT} = \frac{A^0}{NkT} &+ \frac{B_1}{2}\left(\frac{3}{1-f}\right)^2(\delta X_1^2+\delta X_2^2+\delta X_1\delta X_2)\\
&+ \frac{B_2}{2}\left(\frac{3}{f}\right)^2(\delta X_4^2+\delta X_5^2+\delta X_4\delta X_5)\\
&+ B_3\left(\frac{3}{1-f}\right)\left(\frac{3}{f}\right)\\
&\times(2\delta X_1\delta X_4+2\delta X_2\delta X_5+\delta X_1\delta X_5+\delta X_2\delta X_4)\\
&+ \frac{C_1}{6}\left(\frac{3}{1-f}\right)^3(3\delta X_1^2\delta X_2+3\delta x_1\delta X_2^2)\\
&+ \frac{C_2}{6}\left(\frac{3}{f}\right)^3(3\delta X_4^2\delta X_5+3\delta X_4\delta X_5^2)\\
&+ \frac{D_1}{24}\left(\frac{3}{1-f}\right)^4[\delta X_1^4+\delta X_2^4+(\delta X_1+\delta X_2)^4]\\
&+ \frac{D_2}{24}\left(\frac{3}{f}\right)^4[\delta X_4^4+\delta X_5^4+(\delta X_4+\delta X_5)^4],\end{aligned}\tag{A6}$$

where the coefficients $B_1, \ldots, D_2$ are given by

$$\begin{aligned}&B_1 = \left(\frac{3}{1-f} - ap_1'\right)\left(\frac{1-f}{3}\right)^2,\\
&B_2 = \left(\frac{3}{f} - ap_3'\right)\left(\frac{f}{3}\right)^2,\\
&B_3 = ap_2'\left(\frac{1-f}{3}\right)\left(\frac{f}{3}\right),\\
&C_1 = -\left(\frac{1-f}{3}\right),\\
&C_2 = -f/3,\\
&D_1 = 2\left(\frac{1-f}{3}\right),\\
&D_2 = 2f/3.\end{aligned}\tag{A7}$$

Employing the definition for $Q^r_{\alpha\beta}$ and $Q^p_{\alpha\beta}$ given in Eqs. (A2) to (A5) one finds that the free energy can be written as

$$\frac{A}{NkT} = \frac{A^0}{NkT} + \frac{B_1}{2}\operatorname{Tr} Q^r_{\alpha\beta} Q^r_{\beta\alpha} + \frac{B_2}{2}\operatorname{Tr} Q^p_{\alpha\beta}\, Q^p_{\beta\alpha} + B_3 \operatorname{Tr} Q^r_{\alpha\beta}\, Q^p_{\beta\alpha} + \frac{C_1}{6}\operatorname{Tr} Q^r_{\alpha\beta} Q^r_{\beta\gamma} Q^r_{\gamma\alpha} + \frac{C_2}{6}\operatorname{Tr} Q^p_{\alpha\beta} Q^p_{\beta\gamma} Q^p_{\gamma\alpha} + \frac{D_1}{24}\operatorname{Tr} Q^r_{\alpha\beta} Q^r_{\beta\gamma} Q^r_{\gamma\delta} Q^r_{\delta\alpha} + \frac{D_2}{24}\operatorname{Tr} Q^p_{\alpha\beta} Q^p_{\beta\gamma} Q^p_{\gamma\delta} Q^p_{\delta\alpha}, \tag{A8}$$

where the coefficients are defined in Eq. (A7).

Thus we see that our model may be cast in the form of Landau theory. However, since our approach is based on a molecular model, it is possible to identify the coefficients which appear in the free energy expansion of the order parameters with molecular parameters.

Furthermore, for our work we find that the free energy functional can be written in terms of scaler order parameters p_1, q_1 and p_2, q_2:

$$\frac{A}{NkT} = \frac{A_0}{NkT} + (3B_1 p_1^2 + C_1 p_1^3 + \tfrac{3}{4} D_1 p_1^4) + (3B_2 p_2^2 + C_2 p_2^3 + \tfrac{3}{4} D_2 p_2^4) + 6B_3 p_1 p_2 + \left(B_1 - C_1 p_1 + \frac{D_1}{2} p_1^2\right) q_1^2 + \left(B_2 - C_2 p_2 + \frac{D_2}{2} p_2^2\right) q_2^2 + 2B_3 q_1 q_2 + \frac{D_1}{12} q_1^4 + \frac{D_2}{12} q_2{}^4. \tag{A9}$$

From the structure of this free energy functional the following conclusion can be drawn:

(i) The phase transition from the isotropic phase to the nematic phase must occur before, or simultaneously with, the transition from the nematic phase to the biaxial phase. This is because there is a pq^2 term in the free energy. The transition from the isotropic phase ($p = 0$) to the nematic phase ($p \neq 0$) is only possible where there is no linear term of p. (ii) The transition from the isotropic to the nematic phase is a first-order transition except at the multiphase critical point, becuase generally the third order terms in the free energy do not vanish. (iii) The transition from the nematic to the biaxial phase is second order, because there is no third-order term in q in the free energy expansion. This is a consequence of the symmetry of the tensor order parameters. The free energy has an even symmetry for the order parameter q.

The conditions for the transition from the nematic to the biaxial phase are

$$\left|\frac{\partial(A/NkT)}{\partial q_1 q_2}\right|_{q_i=0} = 0, \quad \left.\frac{\partial(A/NkT)}{\partial p_1}\right|_{q_i=0} = 0, \quad \left.\frac{\partial(A/NkT)}{\partial p_2}\right|_{q_i=0} = 0. \tag{A10}$$

This yields

$$\left(B_1 - C_1 p_1 + \frac{D_1}{2} p_1^2\right)\left(B_2 - C_2 p_2 + \frac{D_2}{2} p_2^2\right) - B_3^2 = 0, \tag{A11}$$

$$2B_1 p_1 + C_1 p_1^2 + D_1 p_1^3 + 2B_3 p_2 = 0, \tag{A12}$$

$$2B_2 p_2 + C_2 p_2^2 + D_2 p_2^3 + 2B_3 p_1 = 0. \tag{A13}$$

All the coefficients $B_1, C_1, D_1, \ldots$ are functions of T and f with pressure fixed. Solving Eqs. (A11)–(A13) simultaneously will determine the two second-order transition lines from the nematic phases [$N(+)$ and $N(-)$] to the biaxial phase in the T-f plane.

At the first order transition line (isotropic–nematic), the free energies are equal for the isotropic phase ($p_i = 0$) and the nematic phase ($p_i \neq 0$); therefore

$$3B_1 p_1^2 + C_1 p_1^3 + \tfrac{3}{4} D_1 p_1^4 + 3B_2 p_2^2 + C_2 p_2^3 + \tfrac{3}{4} D_2 p_2^4 + 6B_3 p_1 p_2 = 0. \tag{A14}$$

Equations (A12)–(A14) determine the location of the first-order transition in the $T - f$ plane. See Fig. 8 for a qualitative display of the various phase boundaries.

When approaching the multiphase critical point along with the two transition lines from the nematic phase to the biaxial phase, we can simplify Eqs. (A11)–(A13) by keeping the leading terms. Equations (A12) and (A13) are reduced to

$$2B_1 p_1 + 2B_3 p_2 = 0, \tag{A15}$$

$$2B_2 p_2 + 2B_3 p_1 = 0, \tag{A16}$$

which in turn yields

$$B_1 B_2 - B_3^2 = 0, \tag{A17}$$

$$p_2 = -(B_1/B_3) p_1 = -(B_3/B_2) p_1. \tag{A18}$$

Equation (A11) is reduced to

$$B_1 B_2 - B_3^2 - C_1 B_2 p_1 - C_2 B_1 p_2 = 0, \tag{A19}$$

which becomes with the aid of Eqs. (A17) and (A18):

$$C_1 - C_2 (B_3/B_1)^3 = 0. \tag{A20}$$

Equations (A17) and (A20) are exactly the second and third order conditions determined in Sec. IV, Eqs. (4.4) and (4.9), respectively.

As an illustration of the application of Landau theory in biaxial nematic phase we consider the behavior of the magnetically induced birefringence near the critical point. Stinson and Litster[29] have shown that there is a divergence of magnetically induced birefringence near the isotropic to nematic phase transition. For a binary mixture system described by this model, there is also a similar divergence of the birefringence.

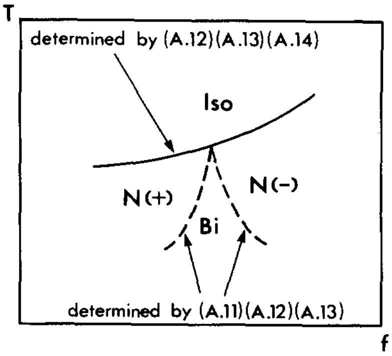

FIG. 8. Determination of transition lines in the vicinity of critical point by using Landau theory.

For a binary mixture of rods and plates, the diamagnetic susceptibility $\chi_{\alpha\beta}$ and dielectric constant tensors $\epsilon_{\alpha\beta}$ may be written as follows:

$$\chi_{\alpha\beta} = [(1-f)\bar{\chi}_r + f\bar{\chi}_p]\delta_{\alpha\beta} + \tfrac{2}{3}[(1-f)\Delta\chi_r Q^r_{\alpha\beta} + f\Delta\chi_p Q^p_{\alpha\beta}], \tag{A21}$$

$$\epsilon_{\alpha\beta} = [(1-f)\bar{\epsilon}_r + f\bar{\epsilon}_p]\delta_{\alpha\beta} + \tfrac{2}{3}[(1-f)\Delta\epsilon_r Q^r_{\alpha\beta} + f\Delta\epsilon_p Q^p_{\alpha\beta}], \tag{A22}$$

where $\Delta\chi_r, \Delta\epsilon_r$ and $\Delta\chi_p, \Delta\epsilon_p$ are the anisotropies in $\chi_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$ for a completely ordered rods and plates, respectively.

In a magnetic field the free energy functional becomes

$$\begin{aligned}\frac{A}{NkT} = \frac{A^0}{NkT} &+ \frac{B_1}{2}\mathrm{Tr}\, Q^r_{\alpha\beta}Q^r_{\beta\alpha} \\ &+ \frac{B_2}{2}\mathrm{Tr}\, Q^p_{\alpha\beta}Q^p_{\beta\alpha} + B_3\,\mathrm{Tr}\, Q^r_{\alpha\beta}Q^p_{\beta\alpha} \\ &+ \frac{C_1}{6}\mathrm{Tr}\, Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^r_{\gamma\alpha} \\ &+ \frac{C_2}{6}\mathrm{Tr}\, Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^p_{\gamma\alpha} \\ &+ \frac{D_1}{24}\mathrm{Tr}\, Q^r_{\alpha\beta}Q^r_{\beta\gamma}Q^r_{\gamma\delta}Q^r_{\delta\alpha} \\ &+ \frac{D_2}{24}\mathrm{Tr}\, Q^p_{\alpha\beta}Q^p_{\beta\gamma}Q^p_{\gamma\delta}Q^p_{\delta\alpha} \\ &- \frac{1}{2}\chi_{\alpha\beta}H_\alpha H_\beta.\end{aligned} \tag{A23}$$

Minimizing the free energy Eq. (A23) with the condition $\mathrm{Tr}\, Q^r_{\alpha\beta} = 0$ and $\mathrm{Tr}\, Q^p_{\alpha\beta} = 0$, and keeping the lowest order terms leads to

$$Q^r_{\alpha\beta} = \frac{[(1-f)B_2\Delta\chi_r - fB_3\Delta\chi_p](3H_\alpha H_\beta - H^2\delta_{\alpha\beta})}{9(B_2B_1 - B_3^2)}, \tag{A24}$$

$$Q^p_{\alpha\beta} = \frac{[fB_1\Delta\chi_p - (1-f)B_3\Delta\chi_r](3H_\alpha H_\beta - H^2\delta_{\alpha\beta})}{9(B_2B_1 - B_3^2)}. \tag{A25}$$

When $f = 0$, or $f = 1$, Eqs. (A24) and (A25) reduced to

$$Q^r_{\alpha\beta} = \frac{\Delta\chi_r}{9B_1}(3H_\alpha H_\beta - H^2\delta_{\alpha\beta}), \tag{A26}$$

$$Q^p_{\alpha\beta} = \frac{\Delta\chi_p}{9B_2}(3H_\alpha H_\beta - H^2\delta_{\alpha\beta}). \tag{A27}$$

These are identical to the formula in Ref. 29 for pure liquid crystals.

If we take the H to lie along the z axis, the resulting birefringence will be

$$\begin{aligned}\Delta n = \epsilon_{zz}^{1/2} - \epsilon_{xx}^{1/2} = {}& \frac{1}{9\sqrt{(1-f)\epsilon_r + f\epsilon_p}}\frac{H^2}{(B_1B_2 - B_3^2)} \\ &\times[(1-f)^2B_2\Delta\epsilon_r\Delta\chi_r - f(1-f)B_3(\Delta\epsilon_r\Delta\chi_p \\ &+ \Delta\epsilon_p\Delta\chi_r) + f^2B_1\Delta\epsilon_p\Delta\chi_p].\end{aligned} \tag{A28}$$

Here $B_1B_2 - B_3^2$ is proportional to $|\partial^2(A/NkT)/\partial X_i\partial X_j|$. For reasons similar to those discussed in Ref. 29, for a phase transition to occur it is necessary that the determinant $|\partial^2(A/NkT)/\partial X_i\partial X_j|$ go through zero. Therefore, we will observe a similar divergence of birefringence near the isotropic to the nematic transition. In Ref. 29 the transition from the isotropic to the nematic phase is first order, so the experiment does not exhibit complete divergence. But for the case of biaxial phase there will be a divergence at the critical point which should be experimentally observable.

[1] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
[2] L. Onsager, Phys. Rev. **62**, 558 (1942); Ann. N.Y. Acad. Sci. **51**, 627 (1949). Also see S. Isihara, J. Chem. Phys. **19**, 1142 (1951).
[3] P. J. Flory, Proc. R. Soc. London Ser. A **234**, 73 (1956).
[4] R. Zwanzig, J. Chem. Phys. **39**, 1714 (1963).
[5] L. K. Runnels and C. Colvin, J. Chem. Phys. **53**, 4219 (1970).
[6] M. A. Cotter, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979).
[7] B. Barboy and W. M. Gelbart, J. Chem. Phys. **71**, 3053 (1979); J. Stat. Phys. **22**, 709 (1980).
[8] A. Wulf and A. G. DeRocco, J. Chem. Phys. **55**, 12 (1971).
[9] R. Alben, J. Chem. Phys. **59**, 4299 (1973).
[10] P. J. Flory, J. Chem. Phys. **12**, 425 (1944); Proc. R. Soc. London Ser. A **234**, 60, 73 (1956).
[11] W. M. Gelbart, J. Phys. Chem. **86**, 4298 (1982).
[12] Y. Rabin, W. E. McMullen, and W. M. Gelbart, Mol. Cryst. Liq. Cryst. **89**, 67 (1982).
[13] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[14] N. G. van Kampen, Phys. Rev. A **135**, 362 (1964).
[15] R. D. Mountain and R. Zwanzig, J. Chem. Phys. **48**, 1451 (1968).
[16] J. M. Deutch and R. Zwanzig, J. Chem. Phys. **46**, 1612 (1967).
[17] C. Cohen and J. M. Deutch, J. Chem. Phys. **54**, 4965 (1971).
[18] J. P. Straley, Mol. Cryst. Liq. Cryst. **24**, 7 (1973).
[19] M. A. Cotter and D. E. Martire, J. Chem. Phys. **53**, 4500 (1970).
[20] G. Lasher, J. Chem. Phys. **53**, 4141 (1970).
[21] M. J. Frieser, Phys. Rev. Lett. **24**, 1041 (1970).
[22] T. W. Stinson III and J. D. Litster, Phys. Rev. Lett. **25**, 503 (1970).
[23] B. Chu, C. S. Bak, and F. L. Lin, Phys. Rev. Lett. **28**, 1111 (1972).
[24] C. P. Fan and M. J. Stephen, Phys. Rev. Lett. **25**, 500 (1970).
[25] R Alben, Mol. Cryst. Liq. Cryst. **10**, 21 (1970); **13**, 193 (1971).
[26] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, english translation (Pergamon, New York, 1970).
[27] R. Bartolino, T. Chiaranza, M. Meuti, and R. Compagnoni, Phys. Rev. A **26**, 1116 (1982).
[28] A. Saupe, P. Boonbrahm, and L. J. Yu, J. Chim. Phys. **80**, 7 (1983).
[29] T. W. Stinson, J. D. Litster, and N. A. Clark, Suppl. J. Phys. (Paris) **33**, C1-69 (1972).