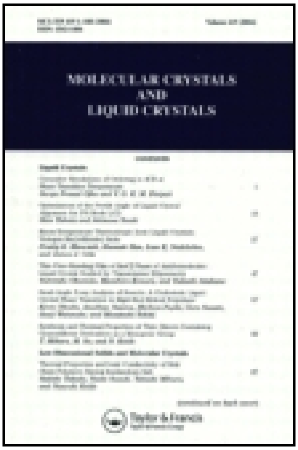

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Molecular-Field Theory of the Switching Transition in Mixtures of Liquid Crystals of Opposite Diamagnetic Anisotropies

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Molecular-Field Theory of the Switching Transition in Mixtures of Liquid Crystals of Opposite Diamagnetic Anisotropies

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The molecular field theory of mixtures of nematic liquid crystals developed by Humphries, James and Luckhurst is applied to the description of the switching transition for a mixture of nematic liquid crystals of opposite diamagnetic anisotropy in a homogeneous external magnetic field. A phase diagram is constructed, which shows the transition from parallel to perpendicular alignment as a function of both temperature and concentration.

Keywords: molecular field theory, switching transition, diamagnetic anisotropy

I. INTRODUCTION

Mixtures of liquid crystals with opposite diamagnetic anisotropies have been observed to exhibit a switching transition from a parallel to a perpendicular orientation of the director relative to an externally applied homogeneous magnetic field.[1–5] A Landau-type mean-field theory of the switching transition has been presented by Sinha, Subburam and Khetrapal.[6,7] In order to obtain the temperature dependence of the order parameters, the above authors introduced an approximate molecular field treatment based on a truncated Landau expansion and an *ad-hoc* decoupling of the order parameters corresponding to the two components of the mixture.

A molecular-field theory of mixtures of nematic liquid crystals has been developed by Humphries; James and Luckhurst (HJL).[8,9] Its subsequent development was reviewed by Martire.[10] Our purpose is to show that the approximations made in Refs. 6, 7 can be avoided, since the switching transition develops naturally from the HJL picture of nematic liquid crystal mixtures.

As pointed out by Martire,[10] the HJL model does not predict the two-phase region over a (narrow) temperature range close to the nematic-isotropic transition. Although this effect can be explained using an appropriately refined theory,[9,11–13] we shall ignore it in the present paper, restricting our attention to temperatures well below T_{NI} (but a complete calculation must, of course, take it into account).

II. THE MODEL

The model we use to describe the thermodynamic properties of the liquid crystal mixture was originally proposed by Humphries, James and Luckhurst.[8] It can be written in terms of the mean-field Hamiltonian

$$\mathcal{H} = -Nu\left\{X_a^2 \cdot \frac{\alpha}{2} S_a^2 + X_b^2 \cdot \frac{\alpha^{-1}}{2} S_b^2 + X_a X_b S_a S_b\right\} \tag{1}$$

where S_a and S_b are the orientational order parameters for molecules of type a and b, respectively, N_a, N_b are the number of molecules of each type, and $N = N_a + N_b$, $X_i = N_i/N$ $(i = a, b)$.

One obvious requirement, satisfied by this Hamiltonian, is that when the two components become identical, i.e. $\alpha = 1$, it reduces into the form $-NuS^2/2$ where $S = S_a = S_b$.

The mean-field equations obtain the form

$$S_i = W_2(\gamma_i);\ i = a, b \tag{2}$$

where

$$\gamma_a = -(X_a \alpha S_a + X_b S_b)/\tau;\ \gamma_b = \gamma_a/\alpha$$

$$\tau = kT/u,$$

and $W_2(x)$ is the Maier-Saupe function[14]

$$W_2(x) = \frac{1}{2x}\left[1 - \frac{2}{\sqrt{\pi}}\frac{y \cdot e^{-y^2}}{\mathrm{erf}(y)}\bigg|_{y=\sqrt{\frac{3x}{2}}}\right] - \frac{1}{2}. \tag{3}$$

The free-energy per particle, which is needed in order to determine the (first order) phase transition temperatures, is given (in units of u) as

$$F_{\mathrm{NI}} = X_a f_a + X_b f_b \tag{4}$$

where

$$f_i = \left(1 - \frac{S_i}{2}\right)\gamma_i + \tau \ln\left[1 - \gamma_i(1 + 2S_i)\right]$$

The anisotropic part of the interaction energy between the nematic mixture and an external magnetic field can be written in the form

$$-\frac{\delta}{2}(\hat{n} \cdot \vec{H})^2 \tag{5}$$

where

$$\delta = C_a\,\Delta_a(\text{index})\,S_a + C_b\Delta_b S_b. \tag{6}$$

C_a, C_b are the number densities of the two components, $\hat{n}$ is a unit vector along the director and $\vec{H}$ is the external magnetic field. In writing Eq. (5) we have taken into consideration the fact that the energy of interaction with an external magnetic field is much smaller than the nematic interaction,[15] so that the two components remain ordered along a common director in the presence of the field. The director is parallel or perpendicular to the external magnetic field, depending on the sign of δ.

In principle, one could easily incorporate the magnetic contribution in the mean-field equations. As a consequence of the smallness of this contribution the values of the order parameters are virtually unaffected by it.

In view of the fact that δ depends on both the concentrations of the two nematogens and on the temperature, *via* the order parameters, one may expect that if the magnetic anisotropies Δ_a and Δ_b are of opposite signs, a switching transition, corresponding to a sign reversal of δ, can occur with change of either temperature or concentration. Thus, in the temperature-concentration plane the phase boundary between the parallel and perpendicular alignments of the nematic mixture is determined by the condition

$$\delta(x_A, \mathrm{T}) = 0. \tag{7}$$

III. RESULTS AND DISCUSSION

The two coupled mean-field equations, Eqs. (2), were solved for the order parameters as functions of the temperature, for various concentrations, as discussed in the appendix, Figure 1 illustrates the general nature of the results. Using these results, the phase diagram representing the possible states of the system studied, in the temperature-concentration plane, was constructed. It is presented in Figure 2. The curve separating the parallel and perpendicular nematic phases is calculated using Eq. (7). As T → 0 we have $S_a = S_b = 1$

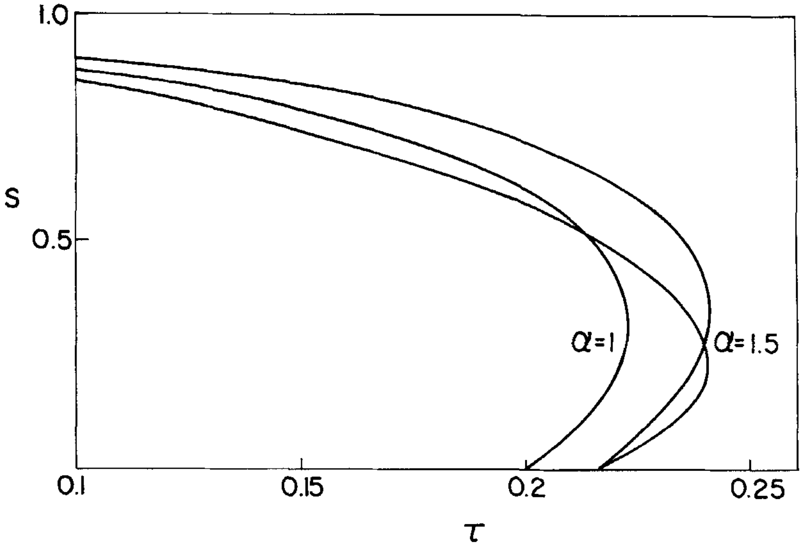

FIGURE 1 The order parameters for a mixture of nematic liquid crystals. The curve labeled α = 1 corresponds to the Maier-Saupe model. The two curves labeled α = 1.5 correspond to the order parameters for the two components of a mixture with $X_a = X_b = 0.5$.

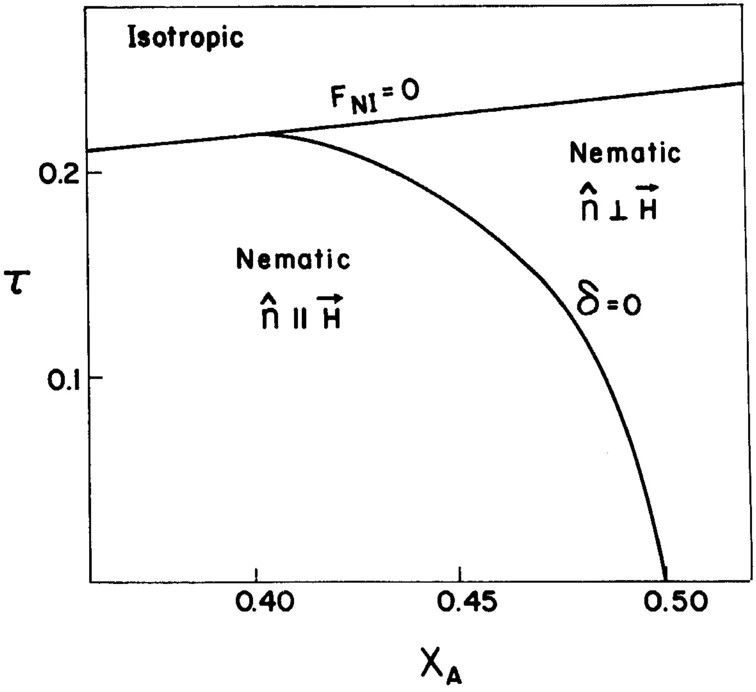

FIGURE 2 The temperature-concentration phase diagram for a mixture of liquid crystals of opposite diamagnetic anisotropies ($\Delta_a = -\Delta_b$, $\alpha = 1.5$). The switching transition occurs upon crossing the $\delta = 0$ curve. The nematic to isotropic transition occurs upon crossing the $F_{NI} = 0$ curve.

so that the $\delta = 0$ curve crosses the $T = 0$ line at $X_a = \Delta_b/(\Delta_b - \Delta_a)$. The line separating the nematic and isotropic phases corresponds to F_{NI} $(X_a, T) = 0$. This line turns out to be extremely close to the straight line discussed by Humphries, James and Luckhurst.[8,9]

$$T_{NI} = X_a T_a + X_b T_b.$$

An exact linear relation can easily be derived for the lowest supercooling temperature, which is the temperature at which the mean-field equations have solutions S_a, $S_b \rightarrow 0$.

The results shown in Figure 2 indicate that, within a certain range of concentrations, a switching transition can take place as a function of the temperature. Similarly, within a certain range of temperatures, this same transition can take place as a function of the concentration.

We note that for samples with a restricted geometry, the phase boundary may be shifted slightly due to the ordering effect of the walls. For example, assuming strong anchoring (parallel or perpendicular to the wall) it is clear from the theory of the Frederiks transition[16] that the switching transition will take place at some finite value of δ, depending on the magnetic field, H, and thickness of the specimen, d. Following de Gennes,[16] the phase boundary will be determined by

$$\delta(X_a, \mathrm{T}) = \mathrm{K}_i\left(\frac{\pi}{d\,H}\right)^2 \tag{8}$$

where K_i is the appropriate elastic constant of the mixture. This is some concentration-weighted average of the elastic constants of the pure components whose value depends on the order parameter, and therefore is temperature dependent. For sufficiently large values of H and d, Eq. (8) reduces to Eq. (7), for which the actual computations discussed in the previous section are made.

Novel features of the switching transition can arise at strong magnetic fields. In principle, a strong enough field could cause phase separation. This is not likely to happen with realistic fields except in the vicinity of the nematic-isotropic transition. Since, as we have already pointed out, a consistent treatment of this region of the phase diagram requires a certain refinement of the model, we postpone its detailed examination to a later occasion.

APPENDIX

We shall now present two aspects of the computational procedure. Both are relevant to a wider class of mean-field problems than those discussed in the present letter.

a. Evaluation of $W_2(x)$

Using the continued fraction form of the error function[17] we have

$$W_2(x) = -\left[2\left(\frac{3}{Z_2} + 1\right)\right]^{-1} \tag{A1}$$

where

$$Z_2 = \cfrac{6X}{5 - \cfrac{9X}{7 + \cfrac{12X}{9 - \ldots}}} \tag{A2}$$

This continued fraction is generated by the recurrence relation:

$$Z_n = \frac{(-1)^n \cdot n \cdot 3X}{2n + 1 + Z_{n+1}} \tag{A3}$$

Starting from, say $Z_{20} = 0$, and iterating backwards, we easily obtain W_2 to nine significant figures for $-5 < x < 0$, which is the relevant range.

b. Solution of the mean-field equations

Eqs. (5) and (9) can be written in the form

$$S_a = W_2(-V) \tag{A4}$$

$$S_b = W_2(-V/\alpha) \tag{A5}$$

where

$$V = (\alpha X_a S_a + X_b S_b)/\tau. \tag{A6}$$

Given α and X_a we choose an arbitrary (positive) value for V, and obtain S_a and S_b using Eqs. (A4) and (A5). Eq. (A6) can now be used to evaluate the temperature $\tau = (\alpha X_a S_a + X_b S_b)/V$ at which the above values of S_a and S_b solve the mean-field equations. A plot of S_a and S_b vs. τ is easily constructed. Note that no iteration was involved.

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