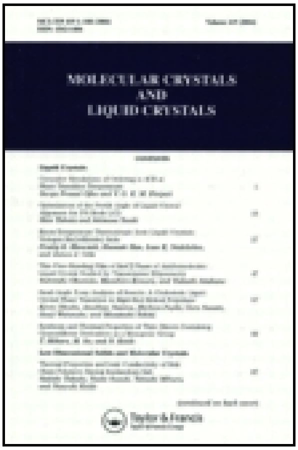

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Phase Diagram Behaviors for Rod/Plate Liquid Crystal Mixtures †

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We present a simple theory of rod/plate liquid-crystal mixtures in which the angle-dependent pair interactions are assumed to be of second-rank form. Calculations are reported for varying relative anisotropies of the "rods" and "plates". Temperature vs. mole-fraction phase diagrams show successive isotropic (I) → uniaxial (U) and U → biaxial (B) transitions which are first- and second-order, respectively. For each pair of species there exists a special composition (x_{rod}^*) for which cooling of the isotropic phase leads directly (and continuously) to a biaxial liquid. As x_{rod} approaches x_{rod}^* from either side, the first-orderness of the I → U transition (i.e. discontinuities in volume, order parameter, etc.) becomes vanishingly small. Furthermore the transition temperature of the rod-(plate-) solvent is found to be depressed when "doped" by not-too-anisotropic plates (rods) and *elevated* when doped by sufficiently anisotropic plates (rods). These behaviors are explained in terms of simple excluded volume considerations and compared with recent experimental data on rod/plate mixtures.

I. INTRODUCTION

The nematic phases of all thermotropic liquid crystals are observed to be *uniaxial*. (If the constituent molecules are rod-like, their long axes align; if they are plate-like, their short axes order. In both cases the liquid is rotationally invariant about the preferred direction.) This fact is somewhat surprising, since virtually all liquid-crystal-forming molecules are themselves *biaxial*. The classic PAA, MBBA and cyanobiphenyl homologues, for example, all involve a conjugated (and hence

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rigid, planar) pair of benzene rings; they are characterized simultaneously by both cylindrical and lathlike symmetry elements. In principle, then, it should be possible for a biaxial state to appear as the uniaxial phase is cooled—in addition to the alignment of long axes, say, the short axes (and hence the molecular planes) can order as well.[1] But, it turns out, the nematic liquid freezes instead.

In earlier work[1] we considered the effects of molecular biaxiality on the stability of uniaxial nematics. In particular we treated the dependence of isotropic-nematic transition temperatures, and volume and entropy changes, on small deviations of molecular symmetry from cylindrical. The magnitude of the first-order phase change was found to decrease dramatically upon inclusion of molecular biaxiality. (Correspondingly, there is a significant rise in transition temperature.) This behavior follows from a competition between the orientational ordering tendencies of the long and short axes. If the molecules are sufficiently rod-like (plate-like) the free energy is minimized by strong alignment of the long (short) axes *alone*; only at still lower temperatures do the short (long) axes align in addition. But with increasing particle biaxiality the difference between ordering tendencies becomes small, eventually vanishing for a special intermediate shape. At this point *both* long *and* short axes align simultaneously and *infinitesimally*—the isotropic liquid undergoes a direct (*second*-order) transition to a biaxial phase.

In the present paper we consider a binary mixture of uniaxial particles, one a rod and the other a plate. This system is essentially equivalent to the one-component liquid of biaxial molecules mentioned above. In the neat-liquid case, biaxiality arises because the middle molecular axis is different from the short and long ones. In the binary mixture, on the other hand, biaxiality enters via the rod-plate interaction (even though each species is itself cylindrically symmetric). Experimental data on these systems is now available, since many thermotropic nematics composed of "plates" have recently been reported.[2] By doping these liquids with "rods",[3] phase diagrams are obtained which can be compared against theoretical calculations. Conversely, conventional nematics can be doped with "plates" in an effort to understand transition temperature depressions and decreases in the relative stability of the liquid crystal.[4]

Section II outlines the simple theory behind our treatment of binary mixtures of rod-like and plate-like molecules. Numerical results—in particular, the isotropic/uniaxial/biaxial phase diagrams—are presented in III and discussed in IV, where they are compared with related experiments and theories.

II. ORDER-PARAMETER THEORY

Let x_r and x_p denote the fixed mole fractions of rods and plates: $x_r + x_p = 1$. Let $f_r(\theta_r\varphi_r)$ denote the fraction of rods whose long axis makes the spherical polar angles $\theta_r\varphi_r$ with respect to the space-fixed coordinate system. Similarly, $f_p(\theta_p\varphi_p)$ is the one-particle distribution function for the plates; $\theta_p\varphi_p$ are the spherical polar angles of a plate's *short* axis with respect to the space-fixed frame. Now suppose we treat the rods and plates as *hard* particles, i.e. they interact with each other only via their excluded volumes. Then it is easy to show that the dimensionless Helmholtz free energy per molecule is given by[5]

$$\frac{A}{NkT} = \ln y - y + x_r\int d\Omega_r f_r(\Omega_r)\ln f_r(\Omega_r) + x_p\int d\Omega_p f_p(\Omega_p)\ln f_p(\Omega_p)$$
$$+\frac{y}{2}x_r^2\int d\Omega_r\int d\Omega_{r'} f_r(\Omega_r)f_r(\Omega_{r'})V_{rr}(\theta_{rr'})/v$$
$$+\frac{y}{2}x_p^2\int d\Omega_p\int d\Omega_{p'} f_p(\Omega_p)f_p(\Omega_{p'})V_{pp}(\theta_{pp'})/v$$
$$+\,yx_rx_p\int d\Omega_r\int d\Omega_p f_r(\Omega_r)f_p(\Omega_p)V_{rp}(\theta_{rp})/v$$
$$+\text{ terms independent of } y \text{ and } f + \theta(y^2). \quad (1)$$

Here $y = \nu\rho/1 - \nu\rho$, where ν is the hard core volume of the particles (for convenience we take $\nu_r = \nu_p = \nu$) and $\rho = N/V$ is the total number density. $V_{ij}(\theta_{ij})$ is the excluded volume associated with a pair of particles whose symmetry axes make an angle θ_{ij} with respect to one another. Thus the last three lines of (1) represent the "translational" (or "packing") entropy contributions, whereas the first line describes the ("ideal gas") "entropy of mixing". Note that (1) is *not* a virial series but contains powers of the density *to all orders*; as discussed elsewhere[5,6] this "y-expansion" is quickly convergent, even at liquid densities.

The pair excluded volume $V_{ij}(\theta_{ij})$, for right-circular cylinders of arbitrary dimensions, has been evaluated explicitly by Onsager.[7] For present purposes, however, it is convenient to approximate it by the leading terms in a Lengendre polynomial expansion:

$$\frac{V_{ij}(\theta_{ij})}{2} \rightarrow \frac{\tilde{V}_{ij}(\theta_{ij})}{\nu} \equiv A_{ij} + B_{ij}P_2(\cos\theta_{ij}) \quad (2)$$

where $P_2(\cos\theta) = \frac{3}{2}\cos^2\theta - \frac{1}{2}$ is the second Legendre polynomial. Using the addition theorem for spherical harmonics[8]—$P_2(\cos\theta) \propto$

$Y_{20}(\theta\varphi)$—and invoking the appropriate symmetry properties of the one-particle distribution functions,[9] it is straightforward to show that

$$\frac{A}{NkT} \rightarrow \ln y - y + x_r \int d\Omega_r f_r \ln f_r + x_p \int d\Omega_p f_p \ln f_p$$
$$+ \frac{y}{2}(x_r^2 A_{rr} + 2x_r x_p A_{rp} + x_p^2 A_{pp})$$
$$+ \frac{y}{2}\left(x_r^2 B_{rr}\left[\eta_r^2 + \frac{3}{4}\beta_r^2 \right] + x_p^2 B_{pp}\left[\eta_p^2 + \frac{3}{4}\beta_p^2 \right] \right)$$
$$+ y x_r x_p B_{rp}\left(\eta_r \eta_p + \frac{3}{4}\beta_r \beta_p \right) + \ldots \quad (3)$$

Here

$$\eta_r \equiv \int_{-1}^{+1} d(\cos\theta_r) \int_0^{2\pi} d\varphi_r P_2(\cos\theta_r) f_r(\theta_r\varphi_r) \quad (4)$$

and

$$\beta_r \equiv \int_{-1}^{+1} d(\cos\theta_r) \int_0^{2\pi} d\varphi_r \sin^2\theta_r \cos 2\varphi_r f_r(\theta_r\varphi_r)$$

are the uniaxial and biaxial order parameters[10] describing the rods, and similarly for η_p, β_p of the plates ($r \rightarrow p$). From (3), equations for the dimensionless pressure (Pv/kT) and Gibbs free energy (G/NkT) are obtained in the usual way, i.e. $P = -\partial A/\partial V$, $G/N = A/N + P/\rho$. Minimizing A/NkT with respect to normalized f's ($\int d\Omega f = 1$) leads to

$$f_r(\theta_r\varphi_r) = \frac{\tilde{f}_r(\theta_r\varphi_r)}{\int_{-1}^{+1} d(\cos\theta_r) \int_0^{2\pi} d\varphi_r \tilde{f}_r(\theta_r\varphi_r)} \quad (5a)$$

where

$$\tilde{f}_r(\theta_r\varphi_r) = \exp\{-y[x_r B_{rr}\eta_r + x_p B_{rp}\eta_p] P_2(\cos\theta_r)$$
$$- \tfrac{3}{4} y[x_r B_{rr}\beta_r + x_p B_{rp}\beta_p] \sin^2\theta_r \cos 2\varphi_r\} \quad (5b)$$

and similarly for $f_p(\theta_p\varphi_p)$ of the plates (just switch r and p subscripts again).

Eqs. (4) and (5) constitute a set of self consistency relations for the four order parameters η_r, η_p, β_r and β_p. These are solved in the following section for various choices of rod and plate anisotropies, i.e. for different A_{ij}'s and B_{ij}'s.

III. NUMERICAL RESULTS: PHASE DIAGRAMS

We treat first the case of "equal" anisotropies. More explicitly, consider right-circular-cylindrical rods and plates whose lengths and diameters are L_r, L_p and D_r, D_p respectively. A_{ij} and B_{ij} in Eq. (2) can be written as explicit functions of these four dimensions by requiring that $V_{\text{Onsager}}(\theta_{ij})/v = A_{ij} + B_{ij} + P_2(\cos\theta_{ij})$ for $\theta_{ij} = 0$ and $\pi/2$. (Here $V_{\text{Onsager}}(\theta_{ij})$ is the exact excluded volume associated with a pair of particles whose symmetry axes make the angle θ_{ij} with respect to each other.) Equating A_{rr} with A_{pp} and B_{rr} with B_{pp} then gives L_r/D_r in terms of L_p/D_p. Requiring further that $v_r = \pi D_r^2 L_r/4 = \pi D_p^2 L_p/4 = v_p$ and choosing (arbitrarily) $D_r = 1.0$, we have the remaining two conditions necessary to determine L_r, D_r, L_p and D_p (and hence the A_{ij}'s and B_{ij}'s) in the "equal" anisotropy case.

For each value of $x_r(= 1 - x_p)$ we calculate the values of the dimensionless pressure, Pv/kT, at which occur phase transitions from isotropic (I) to uniaxial (U) and from U to biaxial (B) phases. For $I \rightarrow U$, we do so by solving four simultaneous equations for y_I, y_U and η_r^U and η_p^U ($\beta_r \equiv 0 \equiv \beta_p$ in both phases):

$$\left(\frac{Pv}{kT}\right)_I = g(y_I, \eta_r = \eta_p = 0) = \left(\frac{Pv}{kT}\right)_U = g(y_U, \eta_r^U, \eta_p^U)$$

$$\left(\frac{G}{NkT}\right)_I = h(y_I, \eta_r = \eta_p = 0) = \left(\frac{G}{NkT}\right)_U = h(y_U, \eta_r^U, \eta_p^U)$$

plus, as in Eq. (4),

$$\eta_r^U = \langle P_2(\cos\theta_r)\rangle$$

$$\eta_p^U = \langle P_2(\cos\theta_p)\rangle.$$

This transition is found to be first order, characterized by the order parameters η_r^U and η_p^U and the fractional volume changes $\Delta\rho/\bar{\rho} = (\rho_U - \rho_I)/\frac{1}{2}(\rho_U + \rho_I)$.

In the case $L_r = 10$, $D_r = 1$ and $L_p = 0.395$, $D_p = 5$ (corresponding to $A_{rr} = A_{pp} = 26.0$, $B_{rr} = B_{pp} = -10.3$ and $A_{rp} = 23.4$, $B_{rp} = 16.5$), we obtain the results given in Table I. Note that the discontinuities $\Delta\eta_r = \eta_r^U$, $\Delta\eta_p = \eta_p^U$ and $\Delta\rho$ all go to zero at $x_r = \frac{1}{2}$ i.e. the first orderness becomes vanishingly small as the mixture approaches equal mole fraction. This is the special point where the rods and plates have equal tendencies to order. (It is analogous to the special intermediate particle

TABLE I

$I \to U$ transition for "equal" rods and plates

x_r	η_r^U	η_p^U	$\Delta\rho/\bar{\rho}$	$T^* \equiv kT/P\nu$
.50	0.000	0.000	0.000	.511
.51	0.011	−0.011	2×10^{-5}	.511
.60	0.064	−0.064	7×10^{-4}	.504
.70	0.144	−0.141	3×10^{-3}	.485
.80	0.249	−0.229	0.010	.454
.85	0.317	−0.276	0.016	.435
.95	0.461	−0.350	0.031	.395
1.00	0.531	—	0.041	.374

$L_r = 10.0$, $D_r = 1.0$; $L_p = 0.395$, $D_p = 5.03$
$A_{rr} = A_{pp} = 26.1$
$B_{rr} = B_{pp} = -12.5$
$A_{rp} = 27.5$
$B_{rp} = 13.3$

biaxiality for which the earlier mentioned one-component liquid undergoes a direct second-order transition from isotropic to biaxial.)

For $x_r > \frac{1}{2}(x_p < \frac{1}{2})$ the rods are *effectively* more anisotropic than the plates for the simple reason that they are more numerous—recall that each ν_{ii} term in the free energy is weighted by x_i^2 ($i = r, p$). Accordingly, it is the rods which order first ($\eta_r > 0$), their long axes aligning along the space fixed z-axis ($\theta_r = 0$). Then, because the rod-plate excluded volume is a maximum when the symmetry axes are parallel $[V_{rp}(0) > V_{rp}(\pi/2)]$, the plates are forced to keep out of the rods' way by "slipping" in between them with their short axes *perpendicular* ($\theta_{rp} = \pi/2$) to z. Thus, $\eta_p < 0$ because of the excluded volume interaction of the plates with the rods rather than with other plates. Conversely, for $x_r < \frac{1}{2}$, the *rods* become "outnumbered" and are constrained ($\eta_r < 0$) by the *plate* ($\eta_p > 0$) alignment.

The $U \to B$ transition turns out to be second order. More explicitly, solving Eqs. (4) for η_r, η_p, β_r and β_p we find that only $\beta_r = 0 = \beta_p$ solutions exist for y less than some "critical" value $y^t(x_r)$. For $y = y^t + 0^+$ a new solution appears, with β_r and β_p nonzero but infinitesimal, which provides the new minimum for A/NkT. y^t—and hence $(P\nu/kT)_{\text{transition}}$—is found to increase dramatically as we depart from $x_r = \frac{1}{2}$.

Figure 1a shows, then, the phase diagram obtained for the "equal anisotropy" case outlined above. The solid and dotted lines refer to first and second order coexistence curves respectively. For any mole fraction $x_r \neq \frac{1}{2}$, cooling of the mixture at constant P leads to the series of transitions $I \to U \to B$. For $x_r = \frac{1}{2}$, the system passes directly (and continuously) from an isotropic into a biaxial state where the rods and

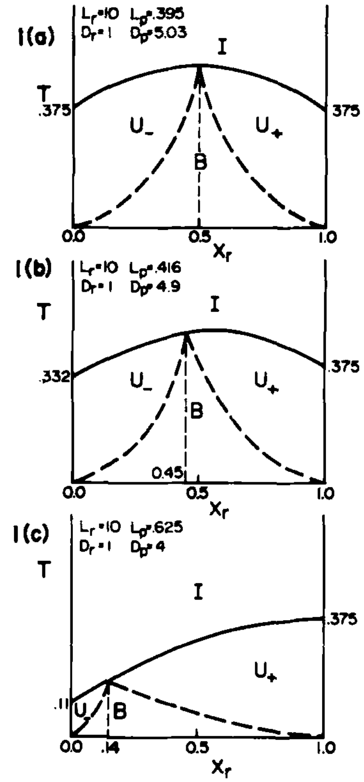

FIGURE 1 T vs. x_r phase diagrams for different cases of plate anisotropy. In (a) the rod and plate have "equal" anisotropy, i.e. the pure ($x_r = 1.0$ and $x_r = 0.0$) liquids have the same $T_{I\text{-}U}$ and $x_r^* = 0.5$. In (b) and (c) the plates are progressively less anisotropic, the "special" point moving to the left ($x_r^* = 0.5 \to 0.45 \to 0.14$) and the maximum in $T_{I\text{-}U}$ disappearing to the right. (The particle volume is held constant at $\nu = 7.85$.) The + and − subscripts on U refer to rod ($\eta_r > 0$) and plate ($\eta_p > 0$) ordering, respectively. T is a dimensionless temperature, defined by $P\nu/k$.

plates are ordered to equal extents. Finally we again stress that the strength of the first-order $I \to U$ transition decreases as $x_r \to \frac{1}{2}$ from either side, vanishing identically at $x_r = \frac{1}{2}$.

Now suppose we keep the hard core volumes equal ($\nu = 7.85$ as before) but make the plates less anisotropic than the rods. For $L_r = 10.0$, $D_r = 1.0$ (as before) and $L_p = 0.625$, $D_p = 4.0$ ($A_{rr} = 26.0$ $A_{pp} = 18.7$, $B_{rr} = -10.$, $B_{pp} = -9.86$ and $A_{rp} = 16.2$, $B_{rp} = -4.16$), for example, we obtain the phase diagram shown in Figure 1c. In this case $T_{I\text{-}U}$ *decreases* as a liquid of rods ($x_r = 1$) is doped with plates, as opposed to the situation in Figure 1a; these behaviors are discussed further in IV. Also, the special value of x_r for which the first-order $I \to U$ transition gives way to second order $I \rightarrow B$ has moved from $x_r = 0.5$ to $x_r = 0.143$. That is, we need relatively fewer rods to have equal tendencies for rod and plate ordering—the difference in numbers is offset by the greater anisotropy of the rods. (Figure 1b shows the T vs. x_r phase diagram for a mixture in which the plate anisotropy is intermediate between those of Figures 1a and 1c. The special value x_r^* of the rod mole fraction is intermediate between those of Figures 1a and 1c, and the maximum has not yet disappeared—doping of *either* pure solvent leads to an *increase* in transition temperature.)

IV. DISCUSSION

It is interesting to go back to Eq. (1) and consider what happens when we allow only for discrete orientations, i.e. we constrain the principle axes of each particle to lie along the space-fixed x-, y- and z-directions. In this case

$$\int d\Omega_r f_r(\Omega_r) \rightarrow \sum_k x_r^{(k)}$$

where $x_r^{(k)}$ is the fraction of rods whose long axes point along the $k(x,y,$ or $z)$ spaced-fixed direction, and so on. Using the *exact* pair excluded volumes appropriate to such a situation—i.e. avoiding the P_2 approximation of Eq. (2)—a preliminary numerical calculation[11] shows that $I \rightarrow U$ coexistence properties are similar to those discussed above but that the $U \rightarrow B$ phase transition is everywhere *first* order! (Only $I \rightarrow B$ at $x_r = x_r^*$ is second order, as can be shown analytically.[11]) This is in marked contrast to the theory just outlined which involves continuous (rather than discrete) orientations and P_2 (cos θ_{ij}), vs. nonanalytic, forms for V_{ij} (θ_{ij}). Alben[12] has presented a discrete-orientation lattice model whose analysis indicated phase diagram behaviors similar to those obtained in Section III. His conclusion that the $U \rightarrow B$ transitions are second order was based on an application of Landau theory[13] in which—following earlier work by Freiser[14]—the free energy is expanded in powers of the invariants appropriate to a second rank (e.g. P_2) form for the pair interactions.

It is now possible to compare our theoretical predictions against recently obtained experimental data. Consider again our Figure 1c. In Figure 1c we see that addition of a slightly disc-like solute depresses the $I \rightarrow U$ transition temperature in the way which is characteristic of spherical dopants.[15] For a solute which is a little more anisotropic, our calculations show that this decrease becomes smaller. Furthermore, the special point x_r^* moves to the right (toward smaller plate mole fractions); accordingly the $I \rightarrow U$ transition becomes more nearly second-order. This is precisely the behavior reported recently by Goozner and Labes[3] who dope a uniaxial phase of *plate*-like molecules (actually a 1:1 mixture of two benzene-hexa-n-alkanoates) with successively more anisotropic *rods*.

When the solute is still more anisotropic, doping leads instead to an *increase* in transition temperature—see Figures 1b and 1a. This is because, say, the plates are so anisotropic that they can only go into solution if their host is orientationally ordered. That is, by aligning the long axes of the rods, the plates can more easily be accommodated than if the rods were disordered—recall that $V_{rp}(\pi/2) < V_{rp}(0)$. Elevation of the $I \rightarrow U$ transition temperature has in fact been reported by Sigaud *et al.*[16] who doped various nematic solvents with small amounts of the highly anisotropic plate chrysene. Further data of this kind will be of great help in elucidating the enhanced stabilities of liquid crystal mixtures.

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