Ordered phases of a liquid of biaxial particles

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A simple model for an interacting liquid of particles lacking an axis of rotational symmetry is proposed. The four order parameters necessary to describe an ordered phase are identified. An ensemble of such particles is described by a mean field theory. A phase diagram showing both uniaxial and biaxial phases results. The model predicts a phase diagram similar to that of the phenomenological model of Alben.

The molecules which compose typical nematic liquid crystals do not have an axis of rotational symmetry, nor are the interparticle forces between these molecules expected to have the high symmetry associated with rotationally symmetric particles. This raises the question of whether any vestige of the lower molecular symmetry is present in ordinary nematic liquid crystals and the possibility of biaxial liquid crystals in which the molecular asymmetry becomes manifest.[1] These problems have been discussed previously in the literature: Alben, McColl, and Shih[2] (AMS) have proposed a new subsidiary order parameter for uniaxial liquid crystals; Freiser[3] has discussed a generalization of the Maier-Saupe[4] theory involving an order parameter of biaxial character; Alben[5] has discussed the corresponding Landau theory; and Shih and Alben[6] have considered the discrete-orientation model (along the lines of the Zwanzig[7] model) corresponding to the Freiser model.

A Maier-Saupe treatment of the AMS ordering has not been given heretofore; the subsidiary order parameter seems to play no role in the work of Freiser[3] or Alben.[5] The present work proposes a generalization of the Maier-Saupe theory which contains this order parameter, as well as the phase transition discussed by Freiser and by Alben. As in the work of Shih and Alben, four independent order parameters appear. A form for the orientation-dependent part of the interparticle potential will be chosen which has the symmetry appropriate to the interaction between a pair of rectangular blocks. This potential will be treated in a mean-field approximation, leading to a set of coupled integral equations. These equations will be solved numerically, resulting in a phase diagram similar to that discussed by Alben, and in a prediction for the temperature and shape dependence of the AMS order parameter. Close attention will be paid to the role of molecular symmetry, and to the physical idea that the predictions of theory should be independent of the coordinate system used.

I. ORDER PARAMETERS

The Maier-Saupe theory introduces one order parameter,

$$S = \langle P_2(\theta) \rangle , \tag{1}$$

where θ is the angle between the ordering axis of the liquid crystal and the principal molecular axis, P_2 is the second Legendre polynomial, and the angular brackets indicate an ensemble average. The orientation-dependent potential of interacting particles is assumed to have the form

$$V(\theta_{ij}) = A P_2(\theta_{ij}) = \tfrac{1}{2} A[3(\vec{n}_i \cdot \vec{n}_i')^2 - 1] , \tag{2}$$

where θ_{ij} is the angle between the principal axis $\vec{n}_i$ of molecule i and the principal axis $\vec{n}_i'$ of molecule j, and A is a constant representing a configurational average of the radial dependence of the interaction.

The orientation of a general object can be specified by the three Euler angles[8] (ψ, θ, ϕ) referenced to an arbitrary laboratory frame. Likewise, the distribution of orientations in an ensemble can be described by a distribution function $f(\psi, \theta, \phi)$, which is proportional to the number of molecules having orientation within the solid angle $d\omega = \sin\theta \, d\theta \, d\psi \, d\phi$ of the orientation (ψ, θ, ϕ) and normalized to unity. All the required ensemble averages can be calculated from the distribution function

$$\langle F(\psi, \theta, \phi) \rangle = \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} f(\psi, \theta, \phi)$$
$$\times F(\psi, \theta, \phi) \sin\theta \, d\theta \, d\phi \, d\psi . \tag{3}$$

Note that by definition of f, $\langle 1 \rangle = 1$.

Rather than deal with an object of arbitrary shape, we will restrict our attention in what follows to molecules with the symmetry of a rectan-

gular parallelopiped: three mutually orthogonal mirror planes with inversion symmetry through their intersection. Then all distribution functions and functions entering into the definitions or order parameters must be invariant under the three transformations

$$\phi \rightarrow \phi + \pi,$$
$$\psi \rightarrow \psi + \pi,$$ (4)
$$\theta \rightarrow \pi - \theta, \quad \phi \rightarrow \pi - \phi, \quad \psi \rightarrow - \psi.$$

The smallest set of functions which contains P_2 and which is closed under arbitrary rotations through the three Euler angles contains no less than 25 functions[9] (as compared with just five spherical harmonics for $l = 2$); however, with this assumption of symmetry the set is reduced to nine, consisting of the four functions

$$F_1 = \tfrac{1}{2}(3\cos^2\theta - 1),$$
$$F_2 = \sin^2\theta \cos2\phi,$$
$$F_3 = \sin^2\theta \cos2\psi,$$ (5)
$$F_4 = \tfrac{1}{2}(1 + \cos^2\theta)\cos2\phi\cos2\psi - \cos\theta\sin2\phi\sin2\psi$$

and the functions which can be derived from these by making the replacement

$$\phi \rightarrow \phi + \tfrac{1}{2}\pi \quad \text{or} \quad \psi \rightarrow \psi + \tfrac{1}{2}\pi.$$

In what follows we shall assume that by appropriate choice of axes the latter five functions can be eliminated from consideration. This is not obvious but will be motivated below by reference to a model. Thus we shall attempt to write all interactions and distributions functions in terms of the four basis functions (5), and describe the ordered state by the four order parameters

$$S = \langle F_1 \rangle, \quad T = \langle F_2 \rangle,$$
$$U = \langle F_3 \rangle, \quad V = \langle F_4 \rangle.$$ (6)

The order parameter S is identical to Maier and Saupe's S; the order parameter T is that introduced by Freiser ($\overline{Q}_{22}$) and used by Alben; the order parameter U was called $\tfrac{2}{3}D$ in AMS; and V is new. The order parameters are bounded above by unity, and take on this value for certain perfectly ordered ensembles.

II. MODEL INTERACTION

A generalization of the interaction (1) appropriate to these biaxial objects is

$$V = \alpha + \tfrac{1}{2}\beta[3(\vec{n}_1 \cdot \vec{n}_1')^2 - 1] + 2\gamma[(\vec{n}_3 \cdot \vec{n}_3')^2 - (\vec{n}_2 \cdot \vec{n}_2')^2]$$
$$+ \tfrac{1}{2}\delta[(\vec{n}_2 \cdot \vec{n}_2')^2 + (\vec{n}_3 \cdot \vec{n}_3')^2 - (\vec{n}_2 \cdot \vec{n}_3')^2 - (\vec{n}_3 \cdot \vec{n}_2')^2].$$ (7)

This is the general form which is quadratic in the

relative direction cosines, invariant under axis reversal, and symmetric under interchange of the primed and unprimed coordinates. It is readily written in terms of the four basis functions as

$$V = \alpha + \beta F_1(\theta) + \gamma[F_2(\theta, \phi) + F_3(\theta, \psi)] + \delta F_4(\phi, \theta, \psi). \quad (8)$$

The functions F_2 and F_3 appear with the same coefficients as a consequence of the symmetry between primed and unprimed frames.

This interaction will be treated in the mean-field approximation in the present work. As a first step we shall perform an average of the interparticle potential over positions, while maintaining the orientations of the particles fixed. Then the coefficients α, β, γ, and δ, which are in principle dependent on interparticle distance and possibly also on the direction of the vector connecting particle centers, become constants and will be regarded as such in what follows. The potential V is then to be interpreted as the average potential a particular molecule of orientation (n_1', n_2', n_3') would see if all of its neighbors always had the orientation (n_1, n_2, n_3). The coefficients implicitly depend on the density of the liquid, which will be held constant.

As an aid to visualization of this interaction a parametrization of the coefficients α, β, γ, δ will be introduced. If we were to construct a theory for the gas of hard rectangular blocks (of dimension $L \times B \times W$) along the lines of Onsager's theory[10] for the gas of hard rods, in place of (8) would appear the mutually excluded volume of a pair of these rectangular blocks of differing orientations, such that the axes of one could be transformed into the axes of the other by the Euler angle transformation (ψ, θ, ϕ). Rather than considering this function in its full generality, consider just the values it takes on when the principal axes of the two blocks are coincident. As Shih and Alben have observed, there are six distinct ways of doing this. These are summarized in Table I, which also gives the mutually excluded volume and a description of these six orientations in terms of a particular choice of Euler angles, in which ϕ and ψ are rotations about the longest (L) axis, and θ is a rotation about the shortest (W) axis. Now we can parametrize the interaction V by choosing the coefficients α, β, γ, δ so that it fits the excluded volumes of a pair of blocks of a certain shape and size (L, B, W) for the six orientations of Table I. This gives

$$3\alpha = 2(L+W)(W+B)(B+L) + 8WLB,$$
$$3\beta = -2B(W^2 + L^2) - 2W(L^2 + B^2) + L(W^2 + B^2) + 8WBL,$$
$$\gamma = \tfrac{1}{2}(L^2 - BW)(B - W),$$ (9)
$$\delta = -L(W - B)^2.$$

TABLE I. Relative orientation of two blocks. Block 1 has the orientation $(W,B,L) = (x,y,z)$. The table gives the six special orientations of block 2 for which the principal axes are aligned with the coordinate axes.

				Euler angle description		
x	y	z	Mutually excluded volume	ψ	θ	ϕ
W	B	L	$8WBL$	0	0	0
B	W	L	$2L(W+B)^2$	α [a]	0	$(90° - \alpha$ [a]$)$
W	L	B	$2W(L+B)^2$	0	90°	0
L	W	B [b]	$(W+B)(B+L)(L+W)$	0	90°	90°
B	L	W [b]	$(W+B)(B+L)(L+W)$	90°	90°	0
L	B	W	$2B(L+W)^2$	90°	90°	90°

[a] The angle α is arbitrary.

[b] These two configurations are physically equivalent; this forces the coefficient of F_2 and F_3 in Eq. (8) to be the same.

This choice for V is not the most accurate fit (for all angles) to the excluded volume, but is a reasonable qualitative version of that function which in particular respects the symmetry of the blocks (i.e., if $B = W$, the blocks are effectively rods and the coefficients γ and δ vanish). It gives a parametrization to the coefficients of Eq. (8) which will hopefully guide the reader (as it did the author) to the physical significance of various choices. It is apparent, for example, that no better fit to the excluded volume could be obtained by introducing the additional five functions which were dropped from (4): for this case at least, there was a choice of principal axes which made the simple form (8) feasible.

Despite first appearances, the parametrization does not restrict us to a special subset of the $(\alpha, \beta, \gamma, \delta)$ space. For a given combination of values for β, γ, and δ, define $\tan(\mu + \nu) = -\frac{1}{2}\delta/\gamma$ and $\tan(\nu - \mu) = \frac{2}{3}\delta/\beta$. Then

$$L^3 = -\frac{3}{2}\beta[(\tan\mu + \tan\nu)(1 + \tan\mu \tan\nu)],$$

$$B = L\tan\mu, \quad W = L\tan\nu \tag{10}$$

is a set (L, B, W) which gives β, γ, and δ. Since α plays no role in the theory to be presented, this demonstrates that the parametrization is an adequate representation of the interaction (8). The parametrization also has the advantage of eliminating the arbitrariness of choice of axis for the Euler angles: there are six such choices for which all the rotations are made about the principal axes of the block, giving rise to six physically equivalent sets of parameters $(\alpha, \beta, \gamma, \delta)$. The six sets can be derived from Eq. (9) by letting L, B, and W be the six permutations of a set of three values.

This arbitrariness of axis choice has consequences for the order parameters also. A given uniaxial phase can be given several alternate and equivalent descriptions: a phase with the L axes

preferentially aligned along the z axis (of the external reference frame) with a slight tendency for the B axes to align along the x axis (S large and positive, U small and positive for the Euler angles used in Table I) can also be described as a phase with the B axes all nearly perpendicular to the z axis, and with a considerable tendency for the L axis to align along the z axis (which in terms of a different set of Euler angles for which θ is the angle between the B axis and z gives S large and negative and U large and positive). The transformation of the basis functions under change of axis choice is readily worked out, with the result that corresponding to the transformation $(L, B, W) \rightarrow (B, L, W)$ are

$$F_1 \rightarrow F_3 - \frac{1}{2}F_1 \text{ and } F_3 \rightarrow F_1 + \frac{1}{2}F_3; \tag{11}$$

and that $(L, B, W) \rightarrow (L, W, B)$ gives $F_1 \rightarrow F_1$ and $F_3 \rightarrow -F_3$. These imply similar transformations among the order parameters.

Both for the cases of flat plates ($L = B > W$) and long rods ($L > B = W$) an ordering of Maier-Saupe type is expected to occur; however, in the former case it is expected that all the "W" axes will be approximately parallel, whereas in the latter case it is an ordering of the "L" axes that is involved. Thus it is necessary to consider at least two distinct axis choices to discuss the general block and recover these two asymptotic limits in a straightforward way. Since Shih and Alben have shown that a competition between rodlike and platelike ordering is an important feature in the phase diagram, it is important that the transformations that the coefficients of (8) undergo in a change of axis choice be considered. Study of the dependence of $(\alpha, \beta, \gamma, \delta)$ on (L, B, W) as given by (9) shows that there is a "dual" relation such that if (L, B, W) gives $(\alpha, \beta, \gamma, \delta)$, then $(W, LW/B, L)$ gives $L^{-1}W^{-1}B^2 (\alpha, \beta, \gamma, \delta)$. This implies a relationship between the thermodynamic functions of

rods $(L > B \approx W)$ and plates $(L \approx B > W)$ which will enable us to limit our discussion in what follows to just one of the two cases. Furthermore, we can identify the "self-dual" class of blocks with dimensions $(L, (LW)^{1/2}, W)$: for this case the coefficients of the interaction are the same no matter whether ψ and ϕ represent rotations about the shortest or longest axis. Then if there is a competition between rodlike and platelike ordering, the dividing line between the two phases must be $B = (LW)^{1/2}$.

III. MEAN FIELD THEORY

A given particle will be subject to forces due to the orientations of its neighbors.[11] We will assume that these forces can be represented as an internal field, and that this internal field by proper choice of reference frame can be written in the form

$$W = wF_1(\theta) + xF_2(\theta, \phi) + yF_3(\theta, \psi) + zF_4(\psi, \theta, \phi),$$

$$(12)$$

where the angles are measured with respect to some fixed external reference frame. Given a field of this form, the orientation distribution function is found immediately to be

$$f(\psi, \theta, \phi) = C \exp[-W(\psi, \theta, \phi)/t],$$

$$(13)$$

where C is a constant which is determined by the condition that f be normalized to unity, and t is the absolute temperature measured in energy units.

The coefficients of W are determined by the self-consistency condition that the mean field be the ensemble average of the interaction (7) in which the neighboring molecules take up orientations with the probability given by the distribution function (1). In calculating these averages it is found that only the order parameters (6) enter. Explicitly,

$$w = \beta S + \gamma U, \qquad y = \gamma S + \tfrac{3}{4}\delta U,$$

$$x = \tfrac{3}{4}\beta T + \gamma V, \qquad z = \gamma T + \delta V.$$

$$(14)$$

The mean field theory thus leads to a set of four integral equations, namely the definitions (6) calculated with the distribution function (13), into which (11) and (14) have been substituted. In Secs. IV and V some numerical techniques for finding solutions to these equations will be discussed. It is evident at the outset that three distinct classes of solution are available: (i) all order parameters vanish; (ii) T and V vanish but S and U do not; and (iii) no order parameter vanishes. These are the isotropic, uniaxial, and biaxial phases, respectively. Because S and U are coupled in Eq.

(14), one must be nonzero when the other is.

We can obtain an indication of the location of the phase transition from the linear approximation to these equations. If all order parameters are small, the distribution function is approximately

$$f = (8\pi^2)^{-1}[1 - W(\phi, \theta, \psi)/t],$$

$$(15)$$

and the equations for the order parameters become $S = \tfrac{1}{5}w/t$, $T = \tfrac{4}{15}x/t$, $U = \tfrac{4}{15}y/t$, and $V = \tfrac{1}{5}z/t$. Reference to (14) shows that the variables S and U are not coupled to the variables T and V, so that the secular equation immediately factors into a pair of quadratic equations, which prove to be identically the same. The root of this quadratic corresponding to the higher temperature is

$$t^* = \tfrac{1}{10}[-\beta - \delta + (\beta^2 - 2\beta\delta + \delta^2 + \tfrac{16}{3}\gamma^2)^{1/2}].$$

$$(16)$$

This can be interpreted as the lowest temperature to which the isotropic phase can be supercooled: it is the limit of stability. Experience with the Maier-Saupe model leads us to expect that in general a reversible first-order phase transition will occur at a temperature somewhat above t^*. The ordered phase formed might be either uniaxial or biaxial, since the T, V part of the secular equation has the same stability limit as the S, U part. The nonlinearity of the integral equations couples the S, U part to the T, V part, and, as we shall see below, tends to suppress the biaxial phase.

If the expression for t^* is written in terms of the L, B, W parameters, it proves to be invariant under permutations of (L, B, W), thus confirming that the set of Euler angles chosen has no effect on the predictions of the model, which is a welcome result from the physical standpoint.

The free energy of an equilibrium phase may be calculated as

$$\frac{F}{N} = t \int f(\omega) \ln f(\omega)\, d\omega + \tfrac{1}{2}(wS + xT + yU + zV),$$

$$(17)$$

where ω is a shorthand for (ψ, θ, ϕ) and

$$d\omega = \sin\theta\, d\psi\, d\theta\, d\phi.$$

The most stable phase at a given temperature is that with the smallest free energy. This function can be extended to a function of w, x, y, and z alone (and defined for all values of these parameters) by substitution for f, S, T, U, and V from Eqs. (11)–(13); this function is extremal for the equilibrium phase (i.e., $\partial F/\partial w = 0$, etc.). However, this does not imply that the combination of (w, x, y, z) which gives the smallest free energy is necessarily the equilibrium combination; there are in fact nonphysical extrema for large values

of (w, x, y, z).

IV. UNIAXIAL PHASE

In this case where $x = z = T = V = 0$, there are three coupled integral equations to be solved for S and U as a function of t:

$$C^{-1} = \pi \int_0^{2\pi} d\psi \int_0^1 d(\cos\theta) \tilde{f}(\theta, \psi),$$

$$C^{-1}S = 4\pi \int_0^{2\pi} d\psi \int_0^1 d(\cos\theta) F_1(\theta) \tilde{f}(\theta, \psi), \quad (18)$$

$$C^{-1}U = 4\pi \int_0^{2\pi} d\psi \int_0^1 d(\cos\theta) F_3(\theta, \psi) \tilde{f}(\theta, \psi),$$

where $\tilde{f} = \exp[-(wF_1 + yF_3)/t]$ is the distribution function with another normalization, and w and y are related to S and U by Eq. (14). These equations were solved numerically by expanding $\tilde{f}$ in a powers series in yF_3/t (of which the first 16 terms were kept) and performing the integrals over ψ (analytically) and $\cos\theta$ (numerically) term by term. Since the dependence of C^{-1} on y is explicitly known, it is not necessary to consider the integral for U, which can be reconstructed from the identity

$$-\frac{t\partial C^{-1}}{\partial y} = UC^{-1}. \quad (19)$$

On performing the ψ integration in the other two integrals, half of the terms vanish (odd order in $\cos\psi$) and there results expressions for S and U in the form of a ratio of polynomials of eighth degree. A consistent combination of w, y, S, and U were found by iteration of this process.

The numerical integration was performed as a 200-point trapezoidal rule. A simple test is available to check the accuracy of this integration: a solution for (L, B, W) should generate a corresponding solution for (B, L, W) through the transformations (11), but discreteness errors will be specific to a certain axis choice and will not reproduce under change of axis choice. It is quite important that the calculations pass this test, for otherwise we would have to suspect that the numerical approximations were inadvertently breaking the symmetry of the interaction, which could lead to incorrect conclusions concerning relative stability of the various ordered phases. Several cases were checked, and it was found that the transformed solutions of the integral equations (18) were also solutions to good accuracy (1%).

Figure 1 shows the dependence of S and U on t for three special choices of particle shape (that is, three choices of the parameters L, B, W which

specify the interaction). We find that the auxiliary order parameter U is small but comparable in size to what AMS find for p-azoxyanisole.[2] The phase transition to the isotropic phase is first order in each case and located close to the high-temperature ends of the curves. The magnitude of the order parameter S at the phase transition decreases as B approaches the "self-dual" case $B = (WL)^{1/2}$.

Figure 2 is a phase diagram showing how the temperature at which the phase transition occurs depends on B for fixed $L = 10$, $W = 1$. The stability limit for the isotropic phase [t^* as given by (16)] as well as the results of the equations (18) are both shown; they are found to be closely similar. The tendency for the transition temperature to increase with B is due simply to the fact that the blocks are physically larger.

V. BIAXIAL PHASE

For this case where none of the order parameters vanish, we have five integrals equations. The distribution function no longer has a rotational symmetry; integrations must be performed over all three coordinates (ψ, θ, ϕ). It is desirable to do as many of these integrals analytically as possible. The strategy that was adopted was to expand the distribution function in powers of (x/t), (y/t), and (z/t) and do the integrals over both ψ and ϕ analytically. The strategy is similar to that used for the uniaxial phase. The algebra is
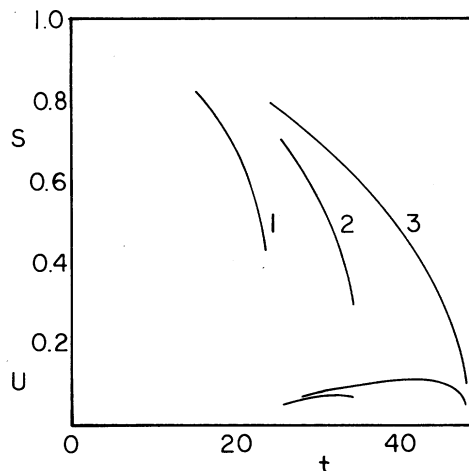

FIG. 1. t dependence of the order parameters in the uniaxial phase. The calculated values for S and U are given for $L = 10$, $W = 1$, and the three cases $B = 1$, 2, and 3. For $B = 1$, the molecules are rotationally symmetric and U vanishes. As B increases, so does U; and the discontinuity in S decreases as B approaches $(LW)^{1/2} = 3.162$.

considerably more complicated, however, for now the unnormalized distribution f $[=\exp(-W/t)]$ is

$$\tilde{f} = e^{-wF_1/t} \sum_{k,l,m,n} (xF_2)^k (yF_3)^l (zF_5)^m (zF_6)^n$$

$$\times \frac{(-t)^{-k-l-m-n}}{k!\,l!\,m!\,n!} , \qquad (20)$$

where the function F_4 has been subdivided into $F_5 = \frac{1}{2}(1 + \cos^2\theta)\cos2\psi\cos2\phi$ and $F_6 = -\cos\theta\sin2\psi$ $\times\sin2\phi$. As before T, U, and V can be found from the series for C^{-1}, so that only the integrals for C^{-1} and $C^{-1}S$ need be considered, and the analytic integrations over ϕ and ψ can be performed immediately

$$\Phi = \int\int_0^{2\pi} d\psi\, d\phi\, \tilde{f}$$

$$= e^{-wF_1/t} \sum_{k,l,m,n} (x\sin^2\theta)^k (y\sin^2\theta)^l$$

$$\times [\tfrac{1}{2}z(1+\cos^2\theta)]^m (z\cos\theta)^n C(k+m, n)$$

$$\times C(l+m, n)\frac{(-t)^{-k-l-m-n}}{k!\,l!\,m!\,n!} , \qquad (21)$$

where

$$C(p, q) = \int_0^{2\pi} d\phi\, \sin^q 2\phi\, \cos^p 2\phi . \qquad (22)$$

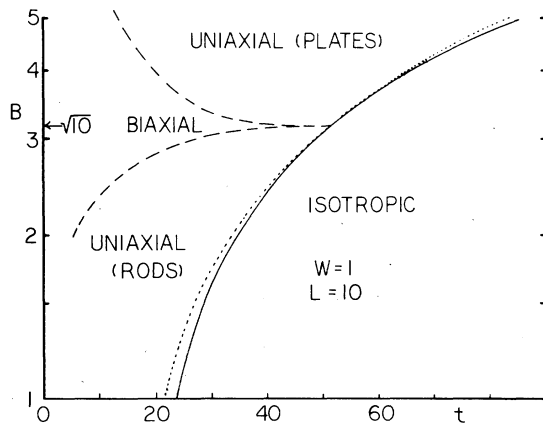All terms of (21) for which $k+m$, $l+m$, or n is

FIG. 2. Phase diagram for blocks of varying breadth. For the case $L=10$, $W=1$, and variable B, the locus of the first-order transitions between the isotropic and uniaxial phases is given as a solid line; and the loci of the second-order transitions between uniaxial and biaxial phases are given as dashed lines. Also shown is the stability limit of the isotropic phase (dotted line) as given by Eq. (16). The phases for $B > 10^{1/2}$ are related to the phases $B < 10^{1/2}$ by the "dual" transformation.

odd vanish. There are still many nonvanishing terms: e.g., there are 39 terms for which the exponent of t^{-1} is less than or equal to 6.

The interaction we have chosen is an idealization which we are treating in a mean-field approximation. Under these circumstances it may not be too important that the solutions be accurate, so long as the symmetry of the phase and the topology of the phase boundary is not seriously distorted. In particular, it might well be sufficient to truncate the series (21) at some low order in t^{-1}. Alben, in considering a similar expansion, observed[5] that it is necessary to keep terms through t^{-6} to develop the phenomenology of the phase diagram fully; therefore the 39 terms were kept.

Each term of (21) is a product of x, y, and z raised to various powers, a combinatorial coefficient, and a function of θ. For a given value of w, corresponding series

$$C^{-1} = \int_0^\pi \Phi\sin\theta\, d\theta ,$$

$$\qquad\qquad\qquad\qquad\qquad (23)$$

$$(C^{-1}S) = \int_0^\pi \Phi F_1(\theta)\sin\theta\, d\theta$$

were constructed by 50-point numerical integrations over the 78 integrands. Each is a 39-term series, each term of which is a product of x, y, and z raised to various powers and a coefficient which depends on w. From these series the quantities $S = (C^{-1}S)/C^{-1}$, $T = (dC^{-1}/dx)/C^{-1}$, $U = (dC^{-1}/dy)/C^{-1}$, and $V = (dC^{-1}/dz)/C^{-1}$ could be determined for any given x, y, z. A search for combinations of S, T, U, and V consistent with w, x, y, z [in the sense that Eq. (14) was satisfied] was then made by an iterative technique. Such solutions could be found for sufficiently low temperature for all non-uniaxial $(L > B > W)$ cases tried. The approximate location of the phase boundary is indicated in Fig. 2. The phase transition appeared to be second order. Just as Alben suggested, the biaxial phase separates the two uniaxial phases, and comes to meet the isotropic phase for blocks which meet the "self-dual" condition $B^2 = LW$.

Table II gives some examples of the behavior of the order parameters S, T, U, and V in a biaxial phase. It is seen that the order parameters T and U are small; the primary role in determining the coupling energies is played by S, which specifies the orientation of a molecular principal axis, and V, which is sensitive to the alignments of all the principal axes. Most of the cases given actually lie quite close to the phase boundary (as shown in Fig. 2); this is merely a consequence of the author's preoccupation with the location of the phase boundary and his disinclination to put too

TABLE II. Some typical biaxial phases. In each case $W = 1$.

L	B	t	t/t^*	S	T	U	V	F/Nt
100	10	0.00017	0.8772	0.188	0.228	0.144	0.100	−0.0233
4	2	0.0325	0.9030	0.172	0.221	0.139	0.100	−0.0163
10	1.7	0.0252	0.0856	0.967	0.002	0.004	0.100	−21.58
10	2.5	0.1238	0.3030	0.901	0.009	0.021	0.100	−3.070
10	3	0.2380	0.4896	0.779	0.043	0.063	0.150	−0.8996
		0.2670	0.5491	0.752	0.021	0.065	0.060	−0.6251
		0.2709	0.5572	0.748	0.015	0.066	0.040	−0.5928
		0.2726	0.5607	0.747	0.004	0.066	0.010	−0.5816
10	$10^{1/2}$	0.2381	0.4647	0.758	0.069	0.078	0.230	−1.007
		0.3226	0.6297	0.630	0.089	0.112	0.148	−0.3459
		0.419	0.8179	0.452	0.068	0.128	0.060	−0.0635
		0.4540	0.8862	0.363	0.029	0.122	0.020	−0.0226
		0.4733	0.9239	0.292	0.018	0.114	0.01	−0.0026

much effort into the description of a phase that may never be discovered.

VI. SUMMARY

A simple model for an interacting liquid of biaxial particles has been proposed. The approximate order parameters have been identified, and the equations resulting from a mean-field treatment have been solved. It has been shown that differing choice of axes in the definitions of the Euler angles can lead to differing descriptions of the ordered phases but that these are physically equivalent. A phase diagram showing both uniaxial and biaxial phases has been exhibited; and the temperature dependence of the order parameters for typical examples has been shown.

The model makes no claim to realism in regard to the details of angular dependence of the inter-particle potential; however, it does have symmetry less than uniaxial, and can claim to have a sort of generality; it has the lowest symmetry consistent with that of the rectangular block parti-

cles considered. Less symmetric particles would lead to a still more asymmetric interaction, more order parameters, and more integral equations. This generalization might be of interest in three respects: (i) it would afford a more nearly quantitative description of a real liquid crystal; (ii) it might be necessary in order to describe biaxial phases of lower or special symmetry (just as a generalization is required to describe enantiomorphic particles and their corresponding cholesteric phases); and (iii) it might lead to an alteration or obliteration of Alben's critical point. In each case an objection can be raised: (i) there is no real system for which we have a good model of the interparticle interaction, nor many for which the mean-field theory can be trusted[12]; (ii) it should be possible to judge the possible symmetries of a phase on general principles; detailed study of these can await the discovery of a biaxial liquid crystal; and (iii) it would surely be more fruitful to study the Alben critical point in terms of the competing modes of breaking the symmetry of the isotropic phase.

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[1]Smectic liquid crystals, in which the molecules have correlated positions as well as orientations, are known to exhibit biaxial phases [T. R. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Lett. 24, 359 (1970)]. This work will be restricted to phases in which only orientational symmetry is broken. There do not seem to be any known examples of such a phase.

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[4]W. Maier and A. Saupe, Z. Naturforsch. A 13, 564 (1958); 14, 882 (1959).

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[8]I will use the Euler angles as they are defined in H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, Mass., 1959), p. 107.

[9]These are the $\Lambda = 2$ eigenfunctions for the symmetric top molecule: see L. D. Landau and G. M. Lifshitz, Quantum Mechanics (Addison-Wesley, Reading, Mass., 1958), pp. 279–281; L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill, New York, 1935), p. 275.

[10]L. Onsager, Ann. N. Y. Acad. Sci. 51, 627 (1949).

[11]A particle is a neighbor of the given particle to the extent that it contributes to the average over positions mentioned after Eq. (8).

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