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Mean-field theory of binary mixtures of nematic liquid crystals consisting of biaxial molecules

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Binary mixtures of liquid crystals whose constituent molecules are not cylindrically symmetric are considered. For a mixture consisting of biaxial molecules with D_{2h} symmetry, two tensor order parameters are required to specify the orientational order of each component. Using mean-field theory, expressions for the free energy of the mixture and the orientational order parameters are obtained as functions of temperature. In the geometric-mean approximation, the parameters of the theory are ratios of anisotropic interaction strengths, which can be determined from measurements on the pure components. The theoretical predictions are compared with recent experimental results of ^{2}H-NMR measurements on the binary mixture of the liquid-crystal 2-fluorenyl-4′-tetradecyloxy-benzoate-d_9 (FLOC$_{14}$) and p-xylene-d_{10} (p-Xy).

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INTRODUCTION

Although most nematic-liquid-crystal phases are uniaxial, the constituent molecules do not usually possess cylindrical symmetry. Recently, considerable theoretical [1–5] and experimental [6–8] work has been performed on pure materials to investigate the role of molecular biaxiality in determining the characteristic physical properties of bulk samples. However, most efforts directed towards understanding the behavior of liquid crystalline mixtures [9–15] have ignored the biaxiality of the constituent molecules.

Information on orientational order and molecular dynamics of liquid crystals [16] is frequently obtained from results of measurements on dissolved probe molecules. Such measurements include fluorescence depolarization [16], UV [17], IR [18], and Raman [16] spectroscopy, electron spin resonance (ESR) [16], NMR [19–27], and neutron scattering [16]. A satisfactory theoretical framework has yet to be established for mixtures of biaxial molecules on the basis of which the behavior of the liquid crystal can be inferred from that of the probe.

In this paper a mean-field theory is proposed to describe binary mixtures of liquid crystals consisting of biaxial molecules which form isotropic, uniaxial, or biaxial nematic phases. A general pseudopotential consistent with the symmetry of the constituent particles is constructed, and thermodynamic information is obtained by minimizing the resulting free energy. If the particles are cylindrically symmetric, the model of binary nematic mixtures [13,15] which has been successful in describing component order parameters [19–22] and the phase behavior of mixtures of rod- and disklike molecules [28] is recovered. If only one component is present, the formalism reduces to a model of biaxial particles interacting via dispersion forces [5], which is formally equivalent to the biaxial hard particle model of Straley [2]. The first unambigous determination of the biaxial orientation (of the rigid segment) of a liquid-crystal molocule in a pure nematic phase was reported by Wu, Ziemnicka, and Doane [8]; their observations are consistent with the predictions of this model.

A complete theoretical description of orientational order in binary mixtures of biaxial particles must include the effects of molecular asymmetry. Emsley, Luckhurst, and Sachdev [24] have recently proposed a model of orientational order of a biaxial solute in a uniaxial nematic phase in the infinite dilution limit. The approach presented here is more complete in that it enables the determination of the order parameters of both species for the entire range of compositions and allows the evaluation of the free energy and calculation of the phase diagram.

In this formalism, the orientation of each species is characterized by two orientational order parameter tensors. Since these tensors are traceless, four scalar order parameters are associated with each component of the mixture; two of these are zero if the phase is uniaxial. These order parameters are measurable by techniques, such as NMR, which are capable of distinguishing the orientational order of each species [29]. The parameters of the theory are coupling constants which provide a measure of the strength of the interaction between individual molecules and the effective nematic field. In order to reduce the number of parameters, the geometric-mean assumption is made. In this approximation, all particles couple to the same mean field and the coupling constants may be determined from measurable properties of the pure constituents. In order to demonstrate the applicability of this approach, connection is made with recent experimental results of ^{2}H-NMR measurements [29] on a binary mixture of the liquid-crystal 2-fluorenyl-4′-

tetradecyloxy-benzoate-d_9 (FLOC_{14}) and p-xylene-d_{10} (p-Xy).

THEORY

Order parameters

The definition of suitable order parameters may be obtained by considering the polarizability of a biaxial particle. It is assumed that the particle has D_{2h} symmetry and principal polarizabilities κ_1, κ_2, and κ_3 along the orthogonal molecular axes $\hat{\mathbf{n}}_1$, $\hat{\mathbf{n}}_2$, and $\hat{\mathbf{n}}_3$. The polarizability tensor $\kappa_{\alpha\beta}$ of the particle is

$$\kappa_{\alpha\beta}=\kappa_1 n_{1\alpha} n_{1\beta}+\kappa_2 n_{2\alpha} n_{2\beta}+\kappa_3 n_{3\alpha} n_{3\beta} \tag{1}$$

where $n_{1\alpha}$ is the α component of the unit vector $\hat{\mathbf{n}}_1$ in a laboratory fixed frame. Choosing $\hat{\mathbf{n}}_3$ arbitrarily as the distinguished axis, the polarizability may be written as

$$\begin{aligned}\kappa_{\alpha\beta}=&\bar{\kappa}\delta_{\alpha\beta}+(\kappa_3-\bar{\kappa})\tfrac{1}{2}(3n_{3\alpha}n_{3\beta}-\delta_{\alpha\beta})\\&+\tfrac{1}{3}(\kappa_1-\kappa_2)\tfrac{3}{2}(n_{1\alpha}n_{1\beta}-n_{2\alpha}n_{2\beta})\end{aligned} \tag{2}$$

where the isotropic average is $\bar{\kappa}=\frac{1}{3}(\kappa_1+\kappa_2+\kappa_3)$. Thus the orientation of the particle enters the polarizability only through the quantities

$$\sigma_{\alpha\beta}=\tfrac{1}{2}(3n_{3\alpha}n_{3\beta}-\delta_{\alpha\beta}) \tag{3}$$

and

$$\tau_{\alpha\beta}=\tfrac{3}{2}(n_{1\alpha}n_{1\beta}-n_{2\alpha}n_{2\beta}) \ . \tag{4}$$

It is expected that the nematic interaction is primarily determined by second rank tensor properties of the particles. Therefore for a system of biaxial particles the orientational order parameters can be defined as

$$S_{\alpha\beta}=\langle\sigma_{\alpha\beta}\rangle=\langle\tfrac{1}{2}(3n_{3\alpha}n_{3\beta}-\delta_{\alpha\beta})\rangle \tag{5}$$

and

$$T_{\alpha\beta}=\langle\tau_{\alpha\beta}\rangle=\langle\tfrac{3}{2}(n_{1\alpha}n_{1\beta}-n_{2\alpha}n_{2\beta})\rangle \tag{6}$$

where $\langle\ \rangle$ denotes the ensemble average. If $S_{\alpha\beta}$ and $T_{\alpha\beta}$ are codiagonal, as may be expected for reasons of symmetry [30], then, in the principal axis frame

$$S_{\alpha\beta}=\begin{bmatrix}-\frac{1}{2}(Q-P) & 0 & 0\\ 0 & -\frac{1}{2}(Q+P) & 0\\ 0 & 0 & Q\end{bmatrix} \tag{7}$$

and

$$T_{\alpha\beta}=\begin{bmatrix}-\frac{1}{2}(D-C) & 0 & 0\\ 0 & -\frac{1}{2}(D+C) & 0\\ 0 & 0 & D\end{bmatrix} \ . \tag{8}$$

The matrix elements are given, in terms of the usual [31] Euler angles (θ,ϕ,ψ), by

$$q=\tfrac{1}{2}(3n_{3z}n_{3z}-1)=\tfrac{1}{2}(3\cos^2\theta-1) \ , \tag{9a}$$

$$Q=\langle q\rangle \ , \tag{9b}$$

$$p=\tfrac{3}{2}(n_{3x}n_{3x}-n_{3y}n_{3y})=-\tfrac{3}{2}\sin^2\theta\cos2\phi \ , \tag{10a}$$

$$P=\langle p\rangle \ , \tag{10b}$$

$$d=\tfrac{3}{2}(n_{1z}n_{1z}-n_{2z}n_{2z})=-\tfrac{3}{2}\sin^2\theta\cos2\psi \ , \tag{11a}$$

$$D=\langle d\rangle \ , \tag{11b}$$

$$\begin{aligned}c&=\tfrac{3}{2}(n_{1x}n_{1x}-n_{2x}n_{2x}-n_{1y}n_{1y}+n_{2y}n_{2y})\\&=\tfrac{3}{2}[(1+\cos^2\theta)\cos2\phi\cos2\psi-2\cos\theta\sin2\phi\sin2\psi] \ ,\end{aligned} \tag{12a}$$

$$C=\langle c\rangle \ . \tag{12b}$$

For a pure material these order parameters are identical to those obtained by considering explicit dispersion interactions between particles with D_{2h} symmetry [5], and are equivalent to those of Straley [2]. It is worth noting that even in the case of the cylindrically symmetric uniaxial nematic phase ($P=C=0$), two order parameters (Q and D) are necessary to describe the orientational order of biaxial particles. The physical significance of a nonzero value of D (often denoted [6–8] by $S_{xx}-S_{yy}$) is that there is a preference of one of the two minor molecular axes to align parallel to the nematic director of the uniaxial phase.

The single-particle pseudopotential

In general, to describe orientational order in a binary mixture, four order parameter tensors, $S_{1\alpha\beta}$, $T_{1\alpha\beta}$, $S_{2\alpha\beta}$, and $T_{2\alpha\beta}$, are required; the subscripts 1 and 2 refer to components of the mixture. The orientational part of the single-particle pseudopotential consists of a linear combination of scalar invariants formed from the orientation-dependent terms $\sigma_{\alpha\beta}$ and $\tau_{\alpha\beta}$, and the order parameters $S_{\alpha\beta}$ and $T_{\alpha\beta}$. To lowest order, the single-particle pseudopotential for a particle of species 1 is

$$\begin{aligned}\varepsilon_1(\Omega_1)=-\tfrac{1}{2}\rho_1\gamma_{11}-\tfrac{1}{2}\rho_2\gamma_{12}-\tfrac{2}{3}(&\rho_1 U_{11}S_{1\alpha\beta}\sigma_{1\alpha\beta}+\rho_2 U_{12}S_{2\alpha\beta}\sigma_{1\alpha\beta}+\rho_1\tilde{U}_{11}S_{1\alpha\beta}S_{1\alpha\beta}+\rho_2\tilde{U}_{12}S_{2\alpha\beta}S_{1\alpha\beta}\\&+\rho_1 V_{11}S_{1\alpha\beta}\tau_{1\alpha\beta}+\rho_2 V_{12}S_{2\alpha\beta}\tau_{1\alpha\beta}+\rho_1\tilde{V}_{11}S_{1\alpha\beta}T_{1\alpha\beta}+\rho_2\tilde{V}_{12}S_{2\alpha\beta}T_{1\alpha\beta}\\&+\rho_1\Pi_{11}T_{1\alpha\beta}\sigma_{1\alpha\beta}+\rho_2\Pi_{12}T_{2\alpha\beta}\sigma_{1\alpha\beta}\\&+\rho_1 W_{11}T_{1\alpha\beta}\tau_{1\alpha\beta}+\rho_2 W_{12}T_{2\alpha\beta}\tau_{1\alpha\beta}+\rho_1\tilde{W}_{11}T_{1\alpha\beta}T_{1\alpha\beta}+\rho_2\tilde{W}_{12}T_{2\alpha\beta}T_{1\alpha\beta})\end{aligned} \tag{13}$$

where Ω_i is the generalized orientational coordinate of the particle, ρ_i is the number density of species i, γ_{ij}, U_{ij}, $\tilde{U}_{ij}$,

V_{ij}, $\tilde{V}_{ij}$, Π_{ij}, W_{ij}, and $\tilde{W}_{ij}$ are coupling constants, and summation is implied over repeated Greek indices. The pseudopotential of a particle of species 2 is obtained by interchanging the indices 1 and 2 in Eq. (13). Even though the isotropic terms, such as $\frac{1}{2}\rho_1\gamma_{11}$, and the anisotropic terms, such as $\rho_2\tilde{U}_{22}S_{2\alpha\beta}S_{2\alpha\beta}$, do not contain the orientational coordinates of the particle (and hence do not give rise to torques), they are included in the pseudopotential to allow calculation of the free energy and the subsequent determination of the phase behavior of the system.

The configurational free energy density of the system is given by [15]

$$\mathcal{F}=-\rho_1 kT\ln\frac{1}{\rho_1}\int e^{-\varepsilon_1(\Omega_1)/kT}d\Omega_1-\rho_2 kT\ln\frac{1}{\rho_2}\int e^{-\varepsilon_2(\Omega_2)/kT}d\Omega_2 \tag{14}$$

where k is Boltzmann's constant and $d\Omega=\sin\theta d\theta d\phi d\psi$. Since at equilibrium the free energy density $\mathcal{F}$ is a minimum, its derivative with respect to the order parameters must vanish. Therefore

$$\rho_1\left\langle\frac{\partial\varepsilon_1(\Omega_1)}{\partial S_{i\alpha\beta}}\right\rangle+\rho_2\left\langle\frac{\partial\varepsilon_2(\Omega_2)}{\partial S_{i\alpha\beta}}\right\rangle=0 \tag{15}$$

and

$$\rho_1\left\langle\frac{\partial\varepsilon_1(\Omega_1)}{\partial T_{i\alpha\beta}}\right\rangle+\rho_2\left\langle\frac{\partial\varepsilon_2(\Omega_2)}{\partial T_{i1\alpha\beta}}\right\rangle=0 \tag{16}$$

where $i=1,2$. These equations yield relations between the coupling constants (e.g., $\tilde{U}_{11}=-\frac{1}{2}U_{11}$, $\Pi_{11}=V_{11}$, etc.) which simplify the expressions for the pseudopotentials to give

$$\begin{aligned}\varepsilon_1(\Omega_1)=&-\tfrac{1}{2}\rho_1\gamma_{11}-\tfrac{1}{2}\rho_2\gamma_{12}-\tfrac{2}{3}(\rho_1U_{11}S_{1\alpha\beta}+\rho_2U_{12}S_{2\alpha\beta}+\rho_1V_{11}T_{1\alpha\beta}+\rho_2V_{21}T_{2\alpha\beta})(\sigma_{1\alpha\beta}-\tfrac{1}{2}S_{1\alpha\beta})\\&-\tfrac{2}{3}(\rho_1V_{11}S_{1\alpha\beta}+\rho_2V_{12}S_{2\alpha\beta}+\rho_1W_{11}T_{1\alpha\beta}+\rho_2W_{12}T_{2\alpha\beta})(\tau_{1\alpha\beta}-\tfrac{1}{2}T_{1\alpha\beta})-\tfrac{1}{3}\rho_2V_{21}T_{2\alpha\beta}S_{1\alpha\beta}+\tfrac{1}{3}\rho_2V_{12}S_{2\alpha\beta}T_{1\alpha\beta}\end{aligned} \tag{17}$$

and similarly for $\varepsilon_2(\Omega_2)$.

The coupling constant U_{ij} gives a measure of the strength of the interaction coupling the orientations of the distinguished (major) axes of particles of species i with those of j. From Eqs. (15) and (16) it is found that $U_{21}=U_{12}$. Similarly, since W_{ij} gives a measure of the strength of the interaction coupling the orientations of minor axes of particles of species i with those of j, from Eqs. (15) and (16) it follows that $W_{21}=W_{12}$. V_{ij} gives a measure of the strength of the interaction coupling the orientation of the minor axes of particles of species i with the orientation of the major axes of particles of species j. In this case, there is no such reciprocal relation, and thus, in general $V_{21}\neq V_{12}$. It is interesting to note that, on substitution of the above pseudopotentials into the expression for the free energy, the last two terms of $\varepsilon_1(\Omega_1)$, in Eq. (17), cancel with the corresponding ones in $\varepsilon_2(\Omega_2)$. Henceforth these terms will be ignored.

The self-consistent equations for the order parameters are

$$S_{i\alpha\beta}=\langle\sigma_{i\alpha\beta}\rangle=\frac{\int\sigma_{i\alpha\beta}e^{-\varepsilon_i(\Omega_i)/kT}d\Omega_i}{\int e^{-\varepsilon_i(\Omega_i)/kT}d\Omega_i} \tag{18}$$

and

$$T_{i\alpha\beta}=\langle\tau_{i\alpha\beta}\rangle=\frac{\int\tau_{i\alpha\beta}e^{-\varepsilon_i(\Omega_i)/kT}d\Omega_i}{\int e^{-\varepsilon_i(\Omega_i)/kT}d\Omega_i} \tag{19}$$

where $i=1,2$. At a given temperature and composition, these coupled self-consistent equations for the order parameters must be solved simultaneously. Since the system is nonlinear, a number of distinct solutions may exist. (For example, the isotropic phase with all order parameters equal to zero is always a solution.) Once the order parameters are known, the free energy corresponding to each solution can be evaluated and this enables the phase diagram to be determined.

The geometric-mean assumption

In the general case of a binary system, there are 13 independent coupling constants ($\gamma_{11},\gamma_{22},\gamma_{12}=\gamma_{21}$, $U_{11},U_{22},U_{12}=U_{21}$, $V_{11},V_{22},V_{12},V_{21},W_{11},W_{22},W_{12}=W_{21}$). In order to reduce the number of parameters in the problem, the geometric-mean assumption is made. In this assumption, the coupling constant for the interaction between particles of different species is taken to be the geometric mean of the coupling constants for the corresponding interaction between particles of the same species. Specifically, $U_{12}=U_{21}=(U_{11}U_{22})^{1/2}$ $W_{12}=W_{21}=(W_{11}W_{22})^{1/2}$, $V_{11}=(W_{11}U_{11})^{1/2}$, $V_{22}=(W_{22}U_{22})^{1/2}$, $V_{12}=(W_{11}U_{22})^{1/2}$, and $V_{21}=(W_{22}U_{11})^{1/2}$. This assumption can be justified for dispersion interactions [32], and has been shown to give a good description of nematics where the molecules are assumed to have cylindrical symmetry [19–21]. Making use of these relations, the pseudopotentials become

$$\begin{aligned}\varepsilon_1(\Omega_1)=&-\tfrac{1}{2}(\gamma_{11})^{1/2}\Gamma-(U_{11})^{1/2}\Lambda_{\alpha\beta}(\sigma_{1\alpha\beta}-\tfrac{1}{2}S_{1\alpha\beta})\\&-(W_{11})^{1/2}\Lambda_{\alpha\beta}(\tau_{1\alpha\beta}-\tfrac{1}{2}T_{1\alpha\beta})\end{aligned} \tag{20}$$

and similarly for $\varepsilon_2(\Omega_2)$, where

$$\Gamma=\rho_1(\gamma_{11})^{1/2}+\rho_2(\gamma_{22})^{1/2} \tag{21}$$

and

$$\Lambda_{\alpha\beta}=\tfrac{2}{3}[\rho_1(U_{11})^{1/2}S_{1\alpha\beta}+\rho_2(U_{22})^{1/2}S_{2\alpha\beta}+\rho_1(W_{11})^{1/2}T_{1\alpha\beta}+\rho_2(W_{22})^{1/2}T_{2\alpha\beta}]\ . \tag{22}$$

In the geometric-mean approximation, therefore, all particles are affected by the same nematic field, $\Lambda_{\alpha\beta}$, and they couple to it via the appropriate coupling constants, as given in Eq. (20). The free energy in this case is a function of $\Lambda_{\alpha\beta}$ only. Each species is characterized by the isotropic (γ_{ii}) and anisotropic (U_{ii} and W_{ii}) interaction strengths; if the four anisotropic coupling constants are known, the temperature dependence of the order parameters may be readily calculated from the self-consistent equations, Eqs. (18) and (19), and the phase behavior of the system may be obtained by examining the corresponding free energy.

RESULTS AND DISCUSSION

Parameters of the theory are the ratios of the coupling constants, and it is therefore useful to define $r_1=(U_{22}/U_{11})^{1/2}$, $r_2=(W_{11}/U_{11})^{1/2}$ and $r_3=(W_{22}/U_{11})^{1/2}$. In terms of these, the pseudopotentials become

$$\varepsilon_1(\Omega_1)=-\tfrac{1}{2}(\gamma_{11})^{1/2}\Gamma-(U_{11})^{1/2}[\Lambda_{\alpha\beta}(\sigma_{1\alpha\beta}-\tfrac{1}{2}S_{1\alpha\beta})-r_2\Lambda_{\alpha\beta}(\tau_{1\alpha\beta}-\tfrac{1}{2}T_{1\alpha\beta})] \tag{23a}$$

and

$$\varepsilon_2(\Omega_2)=-\tfrac{1}{2}(\gamma_{22})^{1/2}\Gamma-(U_{11})^{1/2}[r_1\Lambda_{\alpha\beta}(\sigma_{2\alpha\beta}-\tfrac{1}{2}S_{2\alpha\beta})-r_3\Lambda_{\alpha\beta}(\tau_{2\alpha\beta}-\tfrac{1}{2}T_{2\alpha\beta})]\ . \tag{23b}$$

For pure materials consisting of uniaxial molecules $r_1=r_2=r_3=0$, and the theory reduces to the usual Maier-Saupe theory [33]. For mixtures of uniaxial particles, $r_2=r_3=0$, and the model is identical to that of Ref. [15]; where

$$r_1=\left[\frac{T_{\mathrm{NI}2}\rho_1}{T_{\mathrm{NI}1}\rho_2}\right]^{1/2} \tag{24}$$

and $T_{\mathrm{NI}i}$ and ρ_i are the nematic-isotropic transition temperature and the number density of the ith component, respectively. For pure materials consisting of biaxial molecules, the formalism reduces to that of Ref. [5].

To illustrate the usefulness of the proposed formalism, order parameters are calculated for a binary nematic mixture from Eqs. (18) and (19). These self-consistent equations are solved simultaneously for given values of r_i; results for the uniaxial nematic phase are shown in Figs. 1–3. As can be seen from Eq. (23), the degree of orientational order is essentially determined by the nematic field $\Lambda_{\alpha\beta}$. If the quantity $[(U_{11})^{1/2}/kT]\Lambda_{\alpha\beta}$ is known, the corresponding order parameters can be calculated. Each point on these order parameter curves corresponds to an extremum of the free energy; whether this is a minimum or a maximum depends on both temperature and composition. Consequently, not all values of order parameters are realized in any one system. The significance of the curves in Figs. 1–3 is that if any one order parameter is known for a system with given values of r_i, the remaining order parameters are determined regardless of temperature or composition.

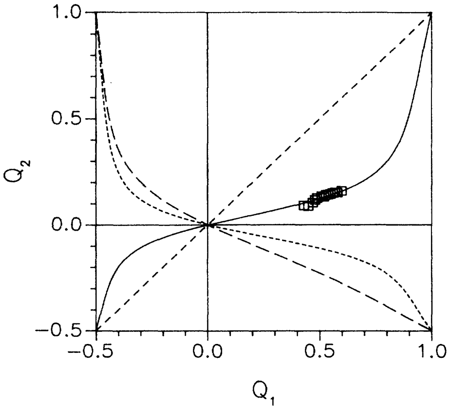

FIG. 1. Order parameters Q_1 and Q_2 of the two biaxial components of a uniaxial nematic binary mixture. The curves correspond to various values of the ratios of the anisotropic interaction strengths as follows: ——, $r_1=0.251$, $r_2=0.160$, and $r_3=0.084$; — — —, $r_1=1.000$, $r_2=0.400$, and $r_3=0.400$; ---, $r_1=-0.251$, $r_2=-0.160$, and $r_3=-0.084$; — —, $r_1=-0.500$, $r_2=0.300$, and $r_3=0.300$. The open squares are the ^{2}H-NMR experimental results from the binary mixture of FLOC$_{14}$ and p-Xy [29].

Superposed on the theoretical curves are experimental-

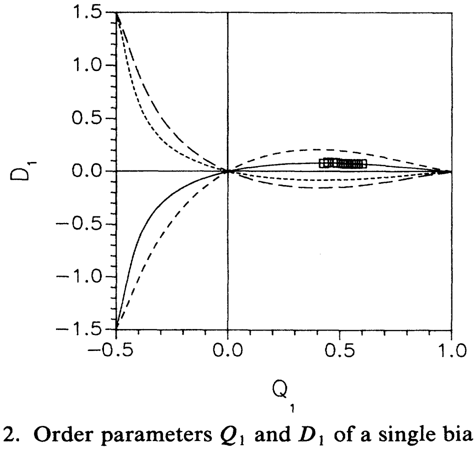

FIG. 2. Order parameters Q_1 and D_1 of a single biaxial component of a uniaxial nematic binary mixture. The curves correspond to various values of the ratios of the anisotropic interaction strengths as follows: ——, $r_1=0.251$, $r_2=0.160$, and $r_3=0.084$; — — —, $r_1=1.000$, $r_2=0.400$, and $r_3=0.400$; ---, $r_1=-0.251$, $r_2=-0.160$, and $r_3=-0.084$; — —, $r_1=-0.500$, $r_2=-0.300$, and $r_3=0.300$. The open squares are the ^{2}H-NMR experimental results from the binary mixture of FLOC$_{14}$ and p-Xy [29].

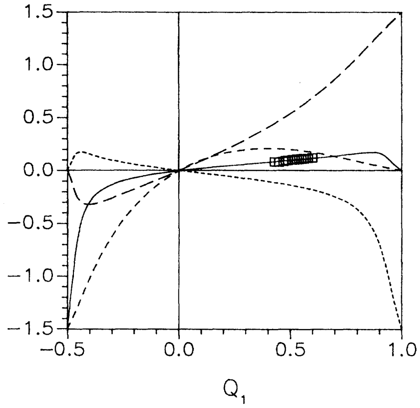

FIG. 3. Order parameters Q_1 and D_2 of the two biaxial components of a uniaxial nematic binary mixture. The curves correspond to various values of the ratios of the anisotropic interaction strengths as follows: ——, $r_1=0.251$, $r_2=0.160$, and $r_3=0.084$; — — —, $r_1=1.000$, $r_2=0.400$, and $r_3=0.400$; ---, $r_1=-0.251$, $r_2=-0.160$, and $r_3=-0.084$; — —, $r_1=-0.500$, $r_2=-0.300$, and $r_3=0.300$. The open squares are the ^{2}H-NMR experimental results from the binary mixture of FLOC$_{14}$ and p-Xy [29].

ly determined values [29] of the order parameters for the binary mixture of the liquid-crystal FLOC$_{14}$ and p-Xy. The solid curves were obtained for least-squares fit of the theoretical expressions to the data [29], and correspond to $r_1=0.251$, $r_2=0.16$, and $r_3=0.084$. FLOC$_{14}$-d_9 is a liquid crystal with an isotropic nematic transition temperature $T_{\mathrm{NI}}=409$ K, while p-xylene-d_{10} is nonmesogenic and an isotropic liquid at room temperature. If it is assumed that Eq. (24) is approximately valid, the virtual transition temperature [21] obtained for p-xylene is $T^*_{\mathrm{NI}}=26$ K; well below its crystallization temperature. The value of r_2 can be calculated from the order parameters of the pure material; fitting the theoretical curve to measurements [8] on the pure compound gives [29] $r_2=0.13$, in reasonable agreement with the mixture results. While the parameter $r_3=0.084$ is small, the ratio $r_3/r_1=(W_{22}/U_{22})^{1/2}=0.33$ gives a measure of the biaxiality of the p-xylene. Thus it would appear that the nonmesogenic p-xylene is more biaxial than the liquid-crystal FLOC$_{14}$. It is likely that the effect of conformational averaging of the alkyl chain is to reduce the observed biaxiality of the FLOC$_{14}$ molecule [29].

The relations between the experimentally determined order parameters appear to be in good agreement with predictions of the theory, and the three parameters r_i are physically reasonable and are consistent with behavior of the pure components. Although the experimental results are shown for a single mixture (11 mol % p-xylene) over a range of temperatures (7 K) in the nematic phase, order parameter values for other compositions (including pure FLOC) and temperatures are predicted to fall on the same solid curves. Although the calculation of the order parameters is straightforward in principle, in general it requires the solution of eight coupled nonlinear equations with multiple solutions. Calculation of the free energy and the phase diagrams will be reported elsewhere.

The above formalism has the usual limitations of the Maier-Saupe theory of pure nematics. These may be overcome by using a Landau–de Gennes form for the free energy instead; we anticipate that the expansion coefficients for the mixture in the geometric-mean approximation are simply related to those of the pure material. In this model the Maier-Saupe formalism has been chosen in order to minimize the number of adjustable parameters.

CONCLUSIONS

The simple mean-field theory of binary mixtures proposed in this paper allows the calculation of orientational order parameters of the constituent biaxial particles over the entire range of temperature and composition. It describes both uniaxial and biaxial nematic phases, and makes possible the determination of phase diagrams. In the geometric-mean approximation, the behavior of the mixture is determined by the ratios of anisotropic interaction strengths of the pure constituents; these may be independently determined from measurements on the pure materials. The theory thus allows the calculation of the behavior of any mixture once these coupling constants for the constituents are known.

Predictions of this model for the relation between the component order parameters are in good agreement with results of ^{2}H-NMR measurements [29] on a binary mixture of FLOC$_{14}$ and p-xylene. Such a model may be useful in understanding mixtures of liquid crystals, and in interpreting results from spectroscopic techniques which employ probe molecules.

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