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THEORY OF BIAXIAL NEMATIC ORDERING IN ROD-DISC MIXTURES REVISITED

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Abstract We use the variational cluster approximation to study the relative thermodynamic stability of the spatially uniform phases of binary mixtures of hard rods and discs. The factors promoting the stability of the biaxial nematic phase are identified and discussed. The results suggest that a stable thermotropic nematic biaxial mixture cannot be obtained from molecules of the sizes and electric dipole interaction strengths commonly encountered in real calamitic and discotic thermotropic phases.

INTRODUCTION

The theoretical possibility of obtaining a nematic biaxial phase by mixing prolate and oblate mesogens was first demonstrated by Alben[1] many years ago. The mechanism giving rise to the biaxial ordering in such mixtures is rather simple: over a certain range of compositions there is combined preferential alignment of the prolate molecules along a "calamitic director" and of the oblate molecules along a perpendicular "discotic director". This possibility was subsequently investigated and confirmed by different theoretical methods[2-5]. However, no thermotropic biaxial mixture has been identified experimentally to date. According to the results of computer simulations[6] and of mean-field calculations[7], the difficulty in producing such a biaxial mixture is due to its instability with respect to decomposition into two uniaxial nematic phases (one of which is rich in rods and the other is rich in discs). It was later pointed out that the biaxial mixture may be stabilised if the interaction between the rod-like and disc-like molecules are made sufficiently strong[8,9]. Thus, on a more practical level, the following question is posed: can the intermolecular interactions of actual thermotropic mesogens (prolate and oblate) be assessed as to their role in promoting or suppressing the formation of biaxial mixtures? Stated differently, is it reasonable to expect that by molecular structure optimization it would be possible to stabilize a biaxial nematic mixture against decomposition? In the present work we attempt to answer this question for mesogens exhibiting steric repulsion as the dominant anisotropic interaction. The effects of the flexibility of the pendant chains and the effects of electric dipole-dipole interactions are considered as well. Accordingly, the results are applicable to a wide range of common thermotropic liquid crystals.

THEORY

The objective of our calculations is to construct the diagram of all the spatially uniform fluid phases of a rod-disc system with specified intermolecular interaction. To this end we formulate the free energy according to the variational cluster expansion method and obtain an approximate expression by retaining only the two-molecule cluster terms. Details on the implementation of this method in the case of single component phases can be found in ref[10]. The generalization to multicomponent phases is straightforward. The relevant expressions for the orientational distribution and for the free energy in the case of a binary mixture of axially symmetric rod-like and disc-like molecules are as follows.

With the indices r (for rods) and d (for discs) denoting the two components, we have for the orientational distribution of a rod molecule

$$f_r(\omega)=\frac{1}{\zeta_r}\exp\left[-\rho\sum_{L,m}\left(x_r q^L_{rr}\left\langle Y^L_m\right\rangle_r + x_d q^L_{rd}\left\langle Y^L_m\right\rangle_d\right)Y^L_m(\omega)\right] \tag{1}$$

Here ω describes the orientation of the symmetry axis of the rod molecule relative to the space-fixed (macroscopic) frame, $\rho=N/V$ is the molecular number density, x_r and $x_d(=1-x_r)$ are the molecular fractions of rods and discs, Y^L_m are the spherical harmonics, $<...>_{r(d)}$ denotes averaging with respect to the orientational distribution of the rods (discs) and ζ_r is the normalization factor of the distribution. The expression for the distribution function of a disc molecule is obtained from eq(1) simply by replacing everywhere the index r with d and conversely. The tensor coefficients q^L_{ij} are determined from the intermolecular potential $U_{i,j}(\mathbf{r}_{1,2},\omega_1,\omega_2)$ through the Legendre polynomial expansion of the irreducible cluster integral according to the relation:

$$q^L_{ij}=\int d\cos\theta_{1,2}\left(\int d\mathbf{r}_{1,2}\left(1-\exp[-\beta U_{ij}(\mathbf{r}_{1,2},\omega_1,\omega_2)]\right)\right)P_L(\cos\theta_{1,2}) \quad , \tag{2}$$

where the index i stands for either r or d and similarly for the index j. Here, $\theta_{1,2}$ denotes the relative orientation of molecules 1 (of type i) and 2 (of type j) and the respective intermolecular vector is denoted by $\mathbf{r}_{1,2}$.

The Helmholtz free energy is given by the expression:

$$\frac{\beta F^{(2)}}{N}=\ln\rho-1+x_r\ln x_r+x_d\ln x_d-x_r\ln\zeta_r-x_d\ln\zeta_d-(\rho/2)(x_r^2\bar{q}_{rr}+2x_rx_d\bar{q}_{rd}+x_d^2\bar{q}_{dd}) \quad , \tag{3}$$

where

$$\bar{q}_{ij}=\sum_{L,m}q^L_{ij}\left\langle Y^L_m\right\rangle_i\left\langle Y^L_m\right\rangle_j \, , \tag{4}$$

and the superscript in F is to indicate that contributions from higher than two-molecule clusters have been ignored in the right hand of eq(3). To within the same approximation, the expression for the pressure P of the mixture reads:

$$\beta P=\rho\left(1+\frac{\rho}{2}(x_r^2\bar{q}_{rr}+2x_rx_d\bar{q}_{rd}+x_d^2\bar{q}_{dd})\right) , \tag{5}$$

and the chemical potential of component i is given by

$$\beta\mu_i=\ln\rho+\ln x_i-\ln\zeta_i \quad , \tag{6}$$

from which the Gibbs free energy of the mixture may be directly obtained as

$$\frac{\beta G^{(2)}}{N} = x_r \mu_r + x_d \mu_d \ . \tag{7}$$

Given the intermolecular potentials $U_{i,j}(\mathbf{r}_{1,2},\omega_1,\omega_2)$, the procedure for determining the phase diagram is initiated by determining the tensor coefficients q^L_{ij} from eq(2). The order parameters $\langle Y^L_m \rangle$ are then determined self-consistently using the orientational distribution in eq(1) at fixed molecular fractions of the rods and discs. There are in general four types of solutions to the self consistency equations. All the solutions describe non-polar fluids, i.e. $\langle Y^L_m \rangle = 0$ for odd L or m, and correspond to one of the following phases:

(a) The isotropic (I) phase. Here $\langle Y^L_m \rangle_{r(d)} = 0$ for L>0.

(b) The uniaxial nematic phase (N_r) in which the rods are preferentially aligned along the macroscopic Z axis. Here $\langle Y^L_m \rangle_{r(d)} = 0$, except when $m=0$ and $\langle Y^2_0 \rangle_r > 0$, $\langle Y^2_0 \rangle_d < 0$.

(c) The uniaxial nematic phase (N_d) in which the discs are preferentially aligned along the macroscopic Z axis. Here $\langle Y^L_m \rangle_{r(d)} = 0$ except when $m=0$, and $\langle Y^2_0 \rangle_r < 0$, $\langle Y^2_0 \rangle_d > 0$.

(d) The biaxial nematic phase (N_{BX}) in which both, the discs and the rods, are aligned along mutually perpendicular directions. Here $\langle Y^L_m \rangle_{r(d)} \neq 0$.

The relative stability of each of these phases at given pressure is determined by comparing the corresponding Gibbs free energies.

RESULTS

Stroobants and Lekkerkerker[4] have studied the phase diagram of a mixture consisting of very long rods and very thin discs (a condition that could be realized in some lyotropic systems) and have found that a stable biaxial nematic phase can be obtained over the pressure-molecular fraction range shown in fig(1a). The nematic-isotropic phase transitions are, as usual, of first order and the transition from either of the uniaxial nematic phases to the biaxial one is of second order. In terms of the tensor coefficient of eq (2), this system corresponds to $q^0_{dd}/q^0_{rr} = q^0_{rd}/q^0_{rr} = 1$, $q^2_{dd}/q^2_{rr} = 1$, $q^2_{rd}/q^2_{rr} = -2$ and $q^L_{rd} = 0$ for L>2.

By changing just the value of the ratio q^2_{rd}/q^2_{rr} to -1 one obtains the system studied by Palffy-Mohoray *et al.*[7], which, as shown on the phase diagram of fig(1b), does not allow for a stable biaxial phase. It has instead a coexistence region of the two uniaxial phases N_r and N_d. The reason is readily seen on the diagram of fig(1b'): the biaxial phase corresponds to a local minimum of the Gibbs free energy around x_r=0.5 but the decomposition into two nematic phases yields a globally lower value of G.

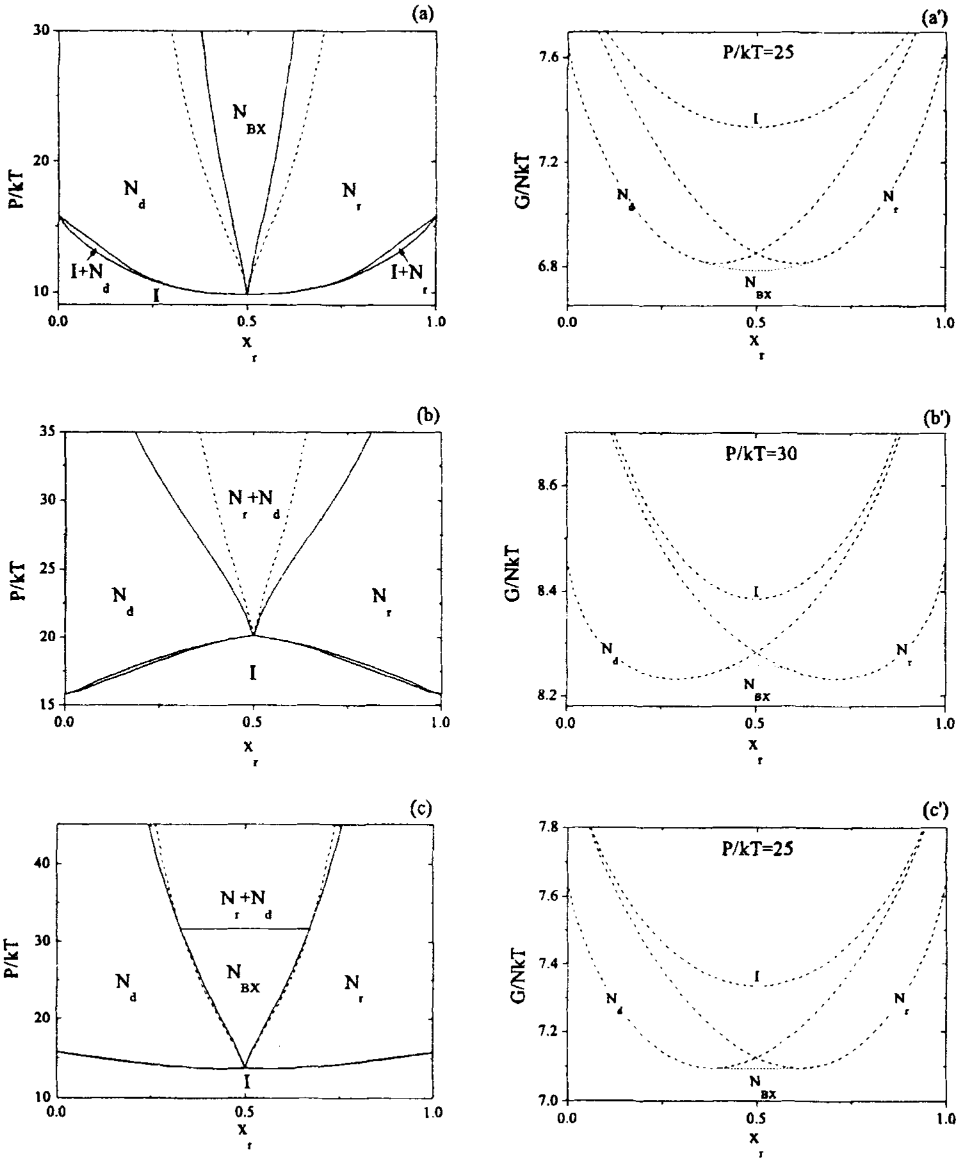

FIGURE 1 Pressure-composition phase diagrams (a, b, c) and Gibbs free energy plots at fixed pressure (a', b', c') for rod-disc mixtures with tensor coefficients $q^0_{dd}/q^0_{rr} = q^0_{rd}/q^0_{rr} = q^2_{dd}/q^2_{rr} = 1$ and neglecting coefficients for L>0. The figures differ in the values of the ratio q^2_{rd}/q^2_{rr} which is set at -2 in (a) and (a'), at -1 in (b) and (b') and at -1.48 in (c) and (c'). The dotted lines in (a), (b), (c) indicate the boundaries of the region where the self consistency equations yield biaxial solutions.

By contrasting these two examples it becomes apparent that the stability of the biaxial nematic phase is rather sensitive to the strength of the rod-disc interactions relative to the rod-rod and disc-disc interactions. This is further illustrated in fig(1c) which shows the phase diagram for the case of an intermediate value of the ratio $q^2_{rd}/q^2_{rr} = -1.48$. A stable biaxial phase is obtained at not too high pressures. As the absolute value of q^2_{rd}/q^2_{rr} is reduced, the upper pressure boundary of the biaxial phase moves to lower pressures until the biaxial region disappears completely from the phase diagram for $q^2_{rd}/q^2_{rr} > -1.4$.

In the three cases of the phase diagrams in fig(1) the tensor coefficients q^0_{ij} and q^2_{ij} are specified *ad hoc.* The variational cluster approach, however, makes it possible to determine these coefficients according to eq(2) for any given form of the intermolecular interaction. To construct phase diagrams that are more relevant to actual disc-rod mesogenic systems we have carried out such calculations for the following cases of binary mixtures.

Hard spherocylinders and cut-spheres.

These provide a crude approximation to mesogenic systems in which all other interactions are negligible compared to the steric repulsions. The determination of the tensor coefficients q^L_{ij} from eq(2) involves the evaluation of the excluded volumes for pairs of spherocylinders (of diameter D_r and length L_r for the cylindrical part) and/or cut-spheres (of diameter D_d and thickness L_d). The values of the leading coefficients are listed in Table I for a choice of relative geometrical parameter of the rods and discs that corresponds to sizes and aspect ratios of typical prolate and oblate thermotropic mesogens. It is apparent from this table that (i) the fourth and sixth rank coefficients are not negligible, (ii) the coefficients q^2_{rd} and q^4_{rd} are of opposite signs and therefore have opposite effects on the stability of N_{BX}, (iii) the coefficients q^0_{rd}, and q^2_{rd}, being of the same magnitude as the respective q^L_{rr} or q^L_{dd}, are not strong enough to suppress the decomposition of N_{BX} into two uniaxial mixtures. The phase diagram for this case is shown in fig(2). The biaxial mixture obtained from the solution of the self consistency conditions (keeping tensor coefficients up to 6th rank) is always unstable against decomposition into N_r and N_d.

Dipolar hard spherocylinders and cut-spheres.

To assess the effect of electric dipole interactions on the stability of the biaxial mixture we have repeated the calculations for spherocylinders and cut spheres which, in addition to their hard body interactions, exhibit dipolar interactions. These are taken to originate from dipole moments of strengths μ_r and μ_d which are positioned at the centres and directed along the symmetry axes of the spherocylinders and the cut spheres. The corresponding tensor expansion coefficients calculated from eq(2) are shown in table I in parentheses.

TABLE I Tensor expansion (in units of D_r^3) coefficients for a mixture of sperocylinders and cut-spheres of aspect ratios L_r/D_r=5 and L_d/D_d=0.2 respectively and D_d/D_r=3.5. The values in parentheses are for the case where the same molecules carry axial dipole moments of strength $\mu_r^2/kTD_r^3 = 3$ and $\mu_d^2/kTD_r^3 = 2$.

	disc-disc	rod-rod	rod-disc
q_{ij}^0	93.0 (92.3)	74.9 (73.1)	85.6 (84.4)
q_{ij}^2	-18.6 (-20.5)	-24.7 (-26.2)	28.0 (29.4)
q_{ij}^4	-10.4 (-12.6)	-5.5 (-6.0)	-11.3 (-12.6)
q_{ij}^6	-2.0 (-4.4)	-2.5 (-2.8)	4.5 (5.7)

Although these results are obtained for rather strong dipole moments (5~10Debye), the differences from the dipole-free tensor coefficients are marginal as far as the stabilization of the biaxial mixture is concerned. The respective phase diagram has only minor quantitative differences from the dipole-free diagram of fig(2a). The failure of the dipolar interactions to prevent decomposition is not surprising since these interactions cannot be restricted to rod-disc pairs (as it would be desirable for the prevention of phase decomposition). Other arrangements of the dipole moments were also considered, such as off-centre dipoles and radially directed dipoles. None of these arrangements leads to a substantial improvement of biaxial phase stability for any realistic dipole moment strengths.

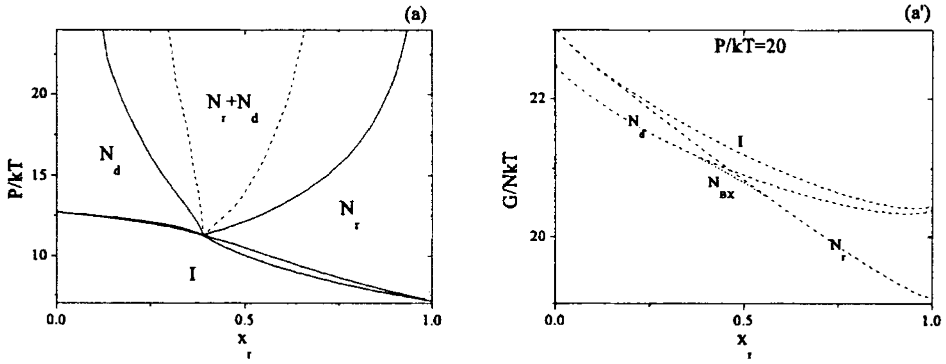

FIGURE 2 Pressure-composition phase diagram (a) and Gibbs free energy plots at fixed pressure (a') for a system of hard spherocylinders and cut spheres with L_r/D_r=5, L_d/D_d=0.2 and D_d/D_r=3.5.

DISCUSSION AND CONCLUSIONS

The results obtained in the previous section suggest that a stable biaxial nematic mixture of prolate and oblate mesogens cannot be obtained for any molecular size, aspect ratio and molecular dipole interaction that could reasonably be identified with the molecular structures of thermotropic nematogens. The results are of course approximate since they are based on a free energy in which higher than two-molecule clusters are ignored. Furthermore, they refer to rigid molecules and thus the effects of the flexible pendant chains, which are generally known to be important to the formation of mesophases, are not accounted for. The inclusion of flexible pendant chains would complicate the calculations enormously. However it can be argued that the resulting molecular flexibility would not improve the stability of the biaxial phase and, in fact, there are reasons to believe that it might constitute a further source of instability as a result of frustration effects in the ordering of the (radially attached) pendant chains of discotic molecules[11]. Such effects render the biaxial mixture (which exhibit more extensive frustration due to the high concentrations of both the rods and the discs) even more unstable towards decomposition into rod-rich and disc-rich nematics (in both of which the extent of frustration is smaller).

To promote the stability of the biaxial mixture it is necessary to enhance the rod-disc interaction relative to the rod-rod and disc-disc interactions but without substantially weakening the anisotropic part of either of the latter interactions, since then the nematic ordering may be lost altogether. Steric and electrostatic interactions (dipole or quadrupole) are not suitable for this purpose since they cannot be restricted to just the rod-disc pairs. Hydrogen bonding, on the other hand can provide such selective pair interactions and is therefore a possibility worth investigating in connection with the stabilization of biaxial mixtures of rods and discs. Such interactions, however, being pairwise saturated, entail certain essential modifications to the derivation of the free energy functional on which the present calculations were based.

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