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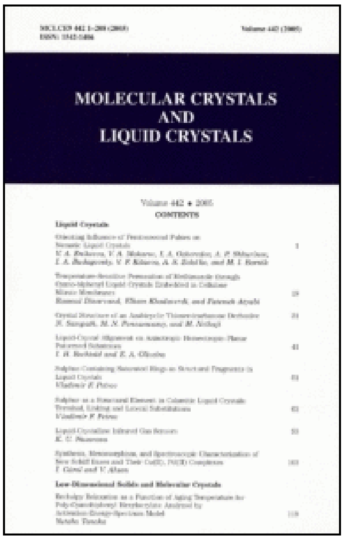

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Hydrogen-bonding and Phase Biaxiality in Nematic Rod–Plate Mixtures

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We study the possibility of using hydrogen-bonding interactions to promote the stabilisation of phase biaxiality in nematic binary mixtures of oblate and prolate thermotropic mesogens. We extend Onsager's theory of the isotropic–nematic transition to allow for such selective associations among unlike species and we use it to calculate the phase diagram of binary mixtures consisting of hard spherocylinders and cut spheres. The results show that directional, short-ranged attractions between rods and discs strongly stabilise the biaxial nematic mixture against demixing and suggest that interactions of hydrogen-bonding type may provide an efficient mechanism for sustaining phase biaxiality in binary mixtures of real thermotropic nematogens. Preliminary Monte Carlo simulations designed to test such predictions are discussed.

Keywords: Liquid crystals; biaxial nematics; Onsager theory; hydrogen bonding

1. INTRODUCTION

There are two basic strategies for designing thermotropic biaxial nematics, neither of which has, to date, led to the production of an actual thermotropic nematic compound of experimentally unquestionable biaxiality.

One strategy is based on promoting phase biaxiality by designing molecules which are sufficiently biaxial, in terms of their shape or, more generally, of their interactions. Support for this strategy comes from several theoretical models [1–4] and computer simulations [5–7] which show that certain idealised molecular models, when endowed with the "right"

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molecular biaxiality, give thermodynamically stable biaxial nematic phases. Perhaps the main difficulty of this approach is determining what the "right" biaxiality would be in the case of a real mesogenic molecule. Indeed, there is no unique way of defining molecular biaxiality in general, *i.e.*, for flexible molecules exhibiting several interactions of different symmetries, strengths and ranges. Thus there are instances of nematogens which are seemingly strongly biaxial (by virtue of their shape, for example) but fail to convey biaxiality to their nematic self-organisation. Furthermore, it is known theoretically [2–4] that increasing the biaxiality of molecular shape beyond a certain limit could lead to the removal of biaxial ordering in favour of uniaxial ordering in some other direction.

The other strategy is based on the idea of producing phase biaxiality simply be mixing two uniaxial phases with noncoincident directors. One way of modelling the realisation of this idea is to consider perfectly uniaxial rod-like and disc-like molecules. Mixtures of such molecules have been demonstrated, both by different theoretical models [8–16] and by computer simulation [15, 17, 18], to be capable of producing biaxial nematic mixtures under certain conditions. Conversely, however, it was shown [7, 19–21] that such biaxial mixtures may be unstable with respect to decomposition into two uniaxial phase (one rich in rods and the other rich in discs). The main difficulty of this strategy is associated with miscibility and phase decomposition. Accordingly, the determination of the molecular attributes that would promote the thermodynamic stability of the biaxial mixture against demixing is the central problem in this approach.

Some years ago, Stroobants and Lekkerkerker [10] used the Onsager theory to demonstrate that a mixture of very long rods and very thin discs of equal molecular volumes can give a stable biaxial nematic phase over a range of concentrations. Such aspect ratios could be expected in lyotropic systems but are clearly well above the range of aspect ratios encountered in thermotropics. There have also been several other theoretical [9, 11–14, 19, 20] and computer simulation studies [17] on the stability of the biaxial nematic mixture, in which, however, the conditions of stability involve certain mean-field or lattice site coupling constants that are not directly related to the parameters of molecular structure and interactions. Recently, Vanakaras and Photinos [16] examined the conditions of stability of the biaxial nematic rod–disc mixture directly in terms of molecular parameters. The results of their Onsager-type theoretical treatment suggest that a stable biaxial nematic mixture of prolate and oblate mesogens cannot be obtained for any molecular size, aspect ratio or molecular dipole interaction that could be reasonably identified with the molecular structures of common thermotropic mesogens. The results were analysed in terms of the competition between the interactions of like (rod–rod, disc–disc) and unlike (rod–disc) molecular species. The authors suggested that interactions of the hydrogen-bonding type could enhance the unlike interactions to the degree required for the stabilisation of biaxiality.

In the present work we study theoretically a specific example of a binary mixture of hard rods and discs exhibiting interactions which give rise to molecular association between unlike species. Experimental candidates for such interactions are primarily hydrogen-bonding and donor–acceptor interactions. We extend the Onsager formulation of the free energy to include such interactions and we use the extended theory to determine the phase diagram of all possible spatially uniform fluid phases of the binary mixture for different values of the binding energy between unlike species. The importance of hydrogen-bonding or donor–acceptor interactions in stabilising the biaxial nematic rod–plate mixtures is discussed in the light of these theoretical results together with the significance of the approximations involved and the consequent limitations on the predictions. We also give a preliminary account of Monte Carlo simulations designed to test the validity of the theoretical predictions at selected state points.

2. THEORY

In this section we present the Onsager-type free energy and self consistency conditions for a binary mixture of hard rods and discs with idealised hydrogen-bonding type interactions. We follow essentially the approach of Ref. [16], which is based on the variational cluster expansion [22]. The pertinent expression for the Helmholtz free energy in the two-site cluster approximation is as follows

$$\frac{\beta F^{(2)}}{N} = \ln\rho - 1 + \sum_s x_s \ln x_s - \sum_s x_s \ln\zeta_s - \frac{\rho}{2}\sum_{s,s'} x_s x_{s'} \langle q_{ss'}\rangle_{s,s'}. \tag{1}$$

The index s refers to the molecular species ($s = r$ for rods and $s = d$ for discs), x_s are the respective mole fractions, ζ_s are pseudo-partition functions associated with the single molecule orientational distribution functions $f_s(\omega)$ to be specified below, $\rho = N/V$ is the overall number density and $\langle q_{ss'}\rangle_{s,s'}$ denotes the average over the orientational distributions f_s and $f_{s'}$ of the quantity

$$q_{ss'}(\omega_{s,s'}) = \int dr\{1 - \exp[-\beta u_{ss'}(r, \omega_s, \omega_{s'})]\}. \tag{2}$$

Here, $u_{ss'}(r, \omega_s, \omega_{s'})$ represents the potential of interaction between the molecules of orientations ω_s and $\omega_{s'}$ of relative position r and of relative orientation $\omega_{ss'}$. For completely asymmetric molecules, $q_{ss}(\omega_{s,s'})$ can be expressed by means of a Wigner matrix $D^L_{m,m'}$ expansion [23] of the form

$$q_{ss'}(\omega_{s,s'}) = \sum_{L,m,m'} q^{ss'}_{L,m,m'} D^L_{m,m'}(\omega_{s,s'}). \tag{3}$$

This leads to the following expression for the orientational distribution functions,

$$f_s(\omega) = \frac{1}{\zeta_s} \exp\left[-\rho \sum_{s'} x_{s'} \sum q^{ss'}_{L,m,m'} \langle D^{L^*}_{m'',m'} \rangle_{s'} D^L_{m'',m}(\omega) \right], \tag{4}$$

where ζ_s is a normalisation factor such that $\int f_s(\omega) d\omega = 1$, and $\langle D^L_{m,m'} \rangle_s$ denote the orientational average (order parameters)

$$\langle D^L_{m,m'} \rangle_s = \int d\omega D^L_{m,m'}(\omega) f_s(\omega). \tag{5}$$

Equations (4) and (5) express the self consistency constraints of the theory. Given the expansion coefficients $q^{ss'}_{L,m,m'}$ these equations can be solved to yield the order parameters as a function of ρ and x_s, and from there to determine the free energy in Eq. (1) and to evaluate all the relevant thermodynamic quantities. In most cases of practical interest, a limited number of low rank coefficients $q^{ss'}_{L,m,m'}$ can adequately convey the essential features of the intermolecular potential $u_{ss'}$. It should be noted that the expressions of the free energy and of the distribution function in Eqs. (1) and (4) respectively, are similar to those used in the mean-field description of the rod–plate system. The novel feature of the present analysis is explicit inclusion of molecular strucutre through Eqs. (2) and (3).

The form in Eq. (1) is obtained under the assumption that the configurational energy is pairwise additive, with $u_{ss'}$ being the individual pair contributions. This additivity is valid for the hard-body potentials that prevents the molecular volumes from overlapping and is also valid for induction and electrostatic forces. However, interactions of the hydrogen-bonding type are saturable, *i.e.*, a given molecule cannot appear in more than one interacting pair, and therefore additivity is not valid. The corresponding expression of the free energy of Eq. (1) in the presence of such saturable interactions is in general rather complex. In the present work we shall consider a special case of such interactions which leads to simple expressions: representing the rod-like molecules by hard spherocylinders of cylindrical length L_r and diameter D_r and the disc-like molecules by hard cut spheres of diameter D_d and thickness L_d (see Fig. 1), we model the donor–acceptor interactions by introducing into the particles simple off-centre square-well sites of diameter D_w.

If the spheres associated with such sites are found to overlap for two molecules of the same species, no energetic contribution is considered. For unlike molecules, the overlapping of the spheres reduces the configurational energy of the system by an amount-ε. For the disc-like molecules the site is positioned at the centre of one of the circular faces. The molecule remains cylindrically symmetric. The site on the rod-like molecules is positioned on the surface of the cylinder, and equidistant from each end. The site destroys the cylindrical symmetry of the fully interacting molecule. We further make the crucial assumption that the diameter of the square-well is small enough to guarantee that the hard-body nature of the molecules prevents the simultaneous overlapping of the square-well site of any molecule with the site of more than one molecule of the other species. This geometrical condition is automatically satisfied provided that the diameter D_w is kept smaller than $(\sqrt{2}-1)D_r/2$. Under such circumstances the square-well interactions become effectively saturable and at the same time can be formally treated as being pariwise additive (although the hard-body constraints will preclude the participation of any molecule in more than a single interacting pair at a time). Within these restrictions, the intermole-

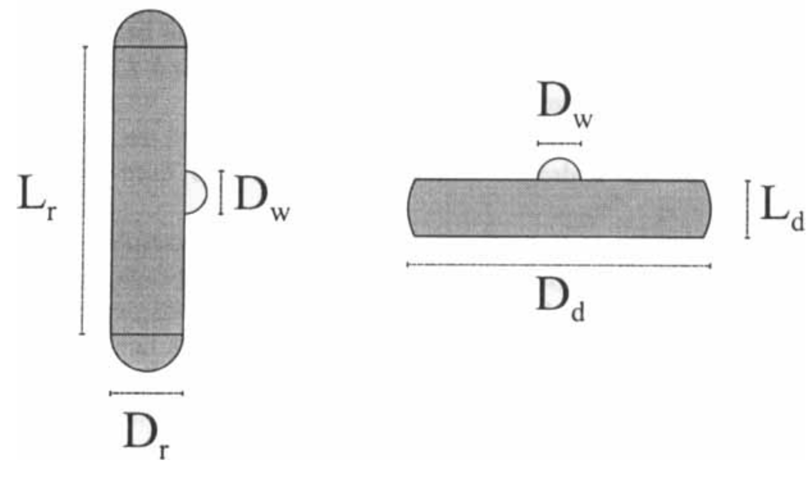

FIGURE 1 Geometrical parameters and interaction sties of the spherocylinder and cut-sphere molecules.

cular pair potential $u_{ss'}$ is such that exp $(u_{ss'}/kT)$ takes the values 0 (on overlap of the hard body volumes), exp (ε/kT) if only the sites of a rod – disc pair overlap and 1 in all other cases.

The truncation of the cluster expansion in Eq. (1) can be partly compensated for by using virial coefficients [24 – 26] of hard-sphere fluids in order to include higher-order density contributions. McGrother *et al.* [27] have recently shown that excellent qualitative agreement can be achieved between theory and simulation for associating systems by employing such resummation methods (see also references therein). Since in the present work we are primarily concerned with the relative stability of the various nematic phases and not with the absolute densities at the phase transitions, we shall not consider such higher-order contributions.

3. RESULTS

A. Onsager-type Theory with Hydrogen-bonding

To study the trends of the phase diagram in the presence of hydrogen-bonding interactions between rods and discs we have truncated the expansion in Eq. (3) above the second-rank contributions. The coefficients $q^{ss'}_{L,m,m'}$ on the truncated expansion were calculated for several values of the square-well "depth" ε in the range from $\varepsilon = 0$ (corresponding to purely hard-body interactions) to $\varepsilon/kT = 15$ (representing a reasonable upper bound estimate for hydrogen-bonding energies [28]). The aspect ratios were set to $L_r/D_r = 5$ (yielding a total length to breadth ratio of 6, which is somewhat larger than for typical calamitic mesogens) and $L_d/D_d = 0.13$. The relative molecular sizes were chosen by setting $D_d/D_r = 3.5$ which yields nearly equal molecular volumes for the spherocylinders and the cut spheres. The range of the hydrogen-bonding interaction was fixed by setting $D_w = 0.2D_r$.

All the solutions of the self-consistency equations correspond to non-polar phases, for which $\langle D^1_{m,m'}\rangle_s = 0$. Similarly, the second-rank parameters $\langle D^2_{m,m'}\rangle_s$ with m, $m' = \pm 1$ vanish. The non-trivial solutions pertain to the usual spatially uniform phases of rod – plate systems [8 – 10, 12 – 16], namely the isotropic (I) mixture, the nematic mixture with uniaxially aligned rods (N_r), the nematic mixture with uniaxially aligned discs (N_d), and the biaxial nematic mixture (N_{Bx}). The discrimination between these phases, according to the type of solutions for the second-rank order parameters, is shown in Table I. The order parameters $\langle D^2_{02}\rangle_r$ are non-vanishing in all the nematic

TABLE I Order parameter classification of the spatially uniform phases of rod-plate binary mixtures

	$\langle D^2_{0,0}\rangle_{r(d)}$	$\langle D^2_{2,0}\rangle_{r(d)}$	$\langle D^2_{0,2}\rangle_{r(d)}$	$\langle D^2_{2,2} + D^2_{2,-2}\rangle_{r(d)}$
Isotropic (I)	0(0)	0(0)	0(0)	0(0)
Rod Nematic N_r	$> 0(< 0)$	0(0)	$\neq 0(0)$	0(0)
Disc Nematic N_d	$< 0(> 0)$	0(0)	$\neq 0(0)$	0(0)
Biaxial N_{Bx}	$\neq 0(\neq 0)$	$\neq 0(\neq 0)$	$\neq 0(0)$	$\neq 0(0)$

phases due to the molecular biaxiality inflicted on the spherocylinders by the off-axis positioning of the hydrgen-bonding site. The order parameters $\langle D^2_{2,0}\rangle_s$ and $\langle D^2_{2,2} + D^2_{2,-2}\rangle_s$ are non-vanishing *only* in the presence of phase biaxiality.

At a given concentration there are in general, non-vanishing, solutions corresponding to more than one of the above phases. Phase coexistence and relative stability at constant pressure is then dictated by the requirement of global minimisation of the Gibbs free energy at that overall concentration. The phase diagram obtained according to this procedure for purely hard-body interactions ($\varepsilon = 0$) is shown in Figure 2(a). It shows the usual structure found in many previous studies [16, 19-21]. The biaxial phase is unstable with respect to spinodal decomposition into coexisting N_r and N_d phases which, as shown in Figure 2(a′), produce a total free energy which always lies below that of the biaxial phase. The phase diagram remains of the same type *i.e.*, without a stable biaxial phase, as ε is increased up to about $\varepsilon = 9kT$. On further increasing ε, second-order transitions to a stable biaxial nematic phase appear. The biaxial phase demixes into two coexisting uniaxial phases above a limiting pressure for values which increase very rapidly with ε. Figure 2(b) shows such a phase diagram for $\varepsilon = 10kT$. The biaxial region extends to very high pressures. The effects of ε on the free energy are depicted in Figrue 2(b′).

B. Monte Carlo Simulations

We have performed a preliminary Monte Carlo simulation study in the isothermal-isobaric (N_pT) ensemble for equal numbers ($N_r = N_d = 510$) of spherocylinders and cut spheres of the same geometrical and site bonding characteristics as in the previous section. In such simulations the reduced pressure $P^* = PD_r^3/\varepsilon$ and the reduced temperature $T^* = kT/\varepsilon$ are constant. The isotherm is commenced at low density (*i.e.*, the isotropic fluid) and the final configuration for each pressure is used as the starting point for subsequent higher-pressure runs. To monitor the degree or orientational

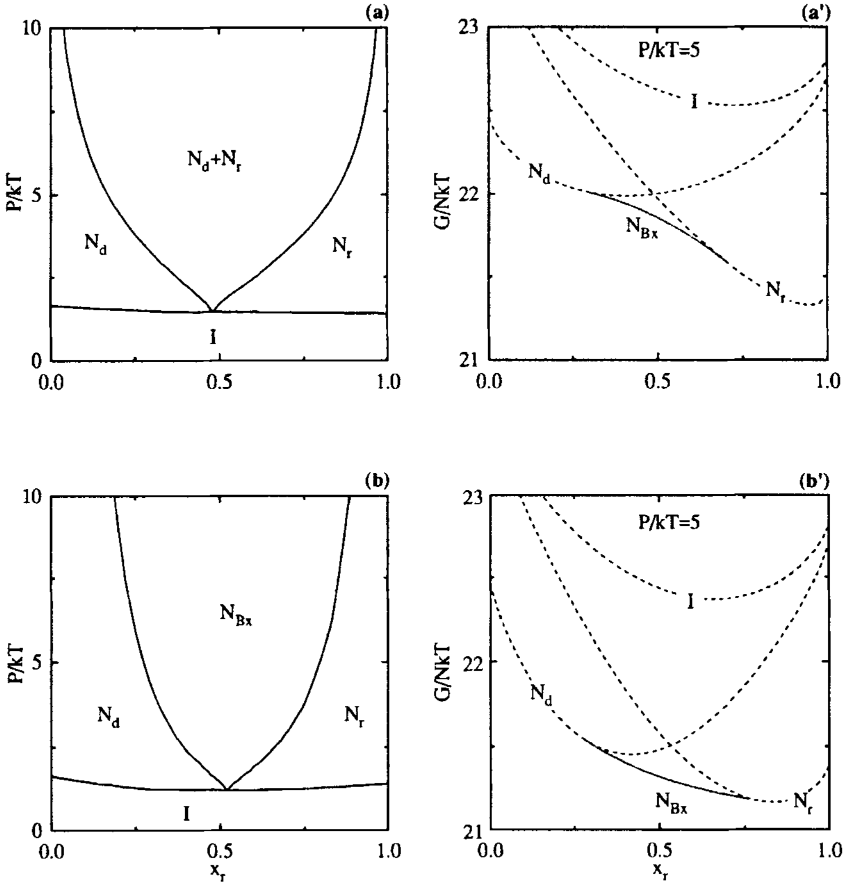

FIGURE 2 (a) Phase diagram of the binary mixture of spherocylinders with $L_r/D_r = 5$, $L_d/D_d = 0.13$ and $D_r/D_d = 3.5$ with purely hard body interactions ($\varepsilon = 0$). (a′) Free-energy diagram at constant pressure for the binary mixture in (a). (b) Phase diagram of the binary mixtures as in (a) with hard body interactions and hydrogen-bonding interactions with square-well energy $\varepsilon = 10kT$. (b′) Constant-pressure free-energy diagram for the system in (b).

order of each species, we calculate the nematic order parameter S of rods and discs separately. These calculations involve the diagonalisation of both full rotation matrices with the nematic order parameters being the largest eigenvalues, and the directors being the associated eigenvectors. For the uniaxial N_r phase the orientational distribution of the discs is expected to peak in an orthogonal direction to the rod director, but there is no preferred direction within that plane.

Preliminary simulations (at low pressure and high temperature) show that the system forms a mixed isotropic phase. Snapshots taken with the overall packing fraction $\eta = 0.18$, show no clustering of like particles, which would be indicative of demixing. The nematic order parameter S is less than 0.1 for both species at this density. As the pressure is increased the system begins to align, and presumably a biaxial nematic phase will be observed. In such isothermal-isobaric simulations, phase separation is prevented by the small system sizes, and so any biaxial phase which we observe may be merely an artefact of the techniques that we employ. Such simulations are at constant composition and thus are not the most appropriate to study phase separation in mixtures. A tendency for unlike molecules to cluster has been noted in previous studies and it has been suggested that this is evidence that the system would prefer to demix [15, 17]. Thus the stability of the observed biaxial phase (with respect to demixing) must be carefully examined.

Two Schemes Suggest Themselves

Gibbs ensemble Monte Carlo and a variation on a well-established method for studying vapour-liquid coexistence with interfaces. The Gibbs ensemble simulations are very costly, and so only state points clearly in the "biaxial" phase will be tested by such simulations. The Gibbs ensemble method has been used to examine demixing in rod-plate mixtures with large elongations [29]. Several problems are encountered in simulating our mixtures in the Gibbs ensemble: at the relatively high density of the nematic (or biaxial) phase, molecules are densely packed, and the probability of acceptance of the crucial particle transfer move is consequently very low. An alternative is a method similar to spinodal decomposition used to study vapour-liquid coexistence: with the densities obtained from the N_pT simulations, one performs NVT Monte Carlo simulations of the mixture commencing from a complately demixed configuration, *i.e.*, with rods in one half of the box and discs in the other. If the biaxial phase is stable, the system will again mix and show biaxial order. However if demixing is preferred, the system should remain essentially phase separated. In the latter case we have the opportunity to analyse some interesting interfacial effects.

4. DISCUSSION AND CONCLUSIONS

The extension of the usual hard-body Onsager-type theoretical description of the spatially uniform phases of rod-plate binary mixtures by the inclusion of site-specific and species-selective square-well intermolecular potentials, provides a relatively simple way to study the effects of hydrogen-bonding type interactions. In the context of this extended theory such interactions are found to induce dramatic changes on the phase diagram when their strength exceeds a certain threshold value. The quantitative results of the calculations suggest that binding energy values within the nominal range (20 – 30 kJ/mol) of hydrogen-bonding interactions [28] could be sufficient for the stabilisation of biaxial mixtures of oblate and prolate mesogens of sizes and aspect ratios within the thermotropic regime.

Due to the various limitations and approximations involved in the theory, the predictions are to be viewed in a comparative sense, *i.e.*, as indicative of the trends in the stabilisation of phase biaxiality in the presence or absence of a certain type of interaction. In particular, the present results show that hydrogen-bonding and donor – acceptor interactions could markedly promote the stabilisation of the biaxial phase against demixing. They do not, however, guarantee that the biaxial mixture will be thermodynamically stable in absolute terms since the theory does not consider transitions to spatially inhomogeneous fluid (smectic, columnar) or solid phases. Thus one cannot preclude that the conditions which favour biaxial nematic ordering could be even more favourable to complete or partial positional ordering. It is precisely this type of limitation that makes it necessary to test the theoretical predictions by molecular simulations at judiciously chosen state points. These difficulties in the theoretical description are more or less analogous to the difficulties posed by theories of single species biaxial nematics. Bearing this in mind, our results show that the realisation of nematic phase biaxiality in rod – plate mixtures is dependent on a wide variety of molecular factors, which can be be "tuned up" to stabilise the phase. This makes the rod – plate mixture a better candidate for biaxial phases that the optimisation of molecular biaxiality alone.

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