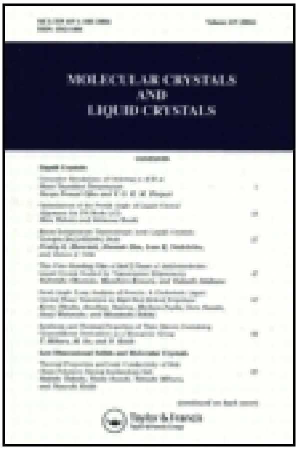

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On the Molecular Requirements for the Stabilisation of Thermotropic Biaxial Ordering in Rod-Plate Nematics

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A nematic consisting of rod-like and plate-like molecular species is expected to exhibit phase biaxiality over a range of concentrations. Phase separation, however, prevents the achievement of such concentrations in mixtures of conventional, low molar mass, thermotropic calamitic and discotic mesogens. We present a theoretical study of the molecular requirements for phase biaxiality in three types of rod-plate nematics, namely in (i) binary mixtures of hard rods and discs, (ii) mixtures of rods and discs exhibiting molecular association, either by direct rod-disc interaction or through selective interactions with a third molecular species and (iii) single component systems with interconverting rod-like and plate-like conformations.

Keywords: Biaxial nematics; calamitic; discotic; interconverting conformations

INTRODUCTION

The creation and experimental identification of thermotropic biaxial nematic phases has been posing a challenge since the appearance of the first theoretical predictions[1–4] for the possibility of phase transitions from a uniaxial nematic phase to a biaxial one as well as of transitions from the isotropic directly to the biaxial nematic phase. Although phase biaxiality has been conclusively identified in lyotropic systems[5] and there were subsequent reports[6–9] on side-chain polymer compounds exhibiting biaxial order in the nematic phase, none of the numerous efforts[10–14] was to date successful in producing a low molar mass thermotropic nematic of unequivocal phase biaxiality.

On the molecular design level, the pursuit of low molar mass thermotropic biaxial nematics is mainly based either on the optimisation of molecular biaxiality[1,2,4,15–21] or on the mixing of two uniaxial phases[3,22–34] with noncoincident

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directors. The second approach appears to offer a number of options. In the simplest realisation it involves the mixing of rod-like (calamitic) and plate-like (discotic) nematogens. In this way one in principle gets rid of some of the difficulties encountered in the single component strategy. In particular, molecular biaxiality is no longer a critical factor, in fact the calamitic and discotic components need not be biaxial at all. In addition, the formation of smectic or columnar phases, which could compete with the biaxial nematic phase in single component systems, is strongly inhibited in rod-plate binary mixtures. Furthermore, in the rod-plate mixture approach the relative concentration of the two components offers an additional, easily adjustable, external parameter for tuning the biaxiality of the phase. The main difficulty with this approach is that the concentrations that are necessary for the appearance of the biaxial phase usually lead to phase separation.

The molecular requirements for the stabilisation of the biaxial mixture against demixing have been investigated theoretically[33,34] for the case of hard rods and discs with additional, site specific, interactions. Whilst dipolar and quadrupolar interactions turned out to have marginal effects on the stability[33], it was found that interactions of the hydrogen-bond or donor-acceptor type operating selectively between rods and discs could be very efficient in stabilising phase biaxiality in the mixture[34]. In the present work we extend the study to schemes based on rod-plate associating interactions but entailing more complex mechanisms of self-assembly. We also study the conditions under which a single component system exhibiting interconverting rod and plate conformations could self-organise into a biaxial nematic. The relative advantages of the various schemes are discussed in relation to the molecular design possibilities they suggest.

ROD-PLATE MIXTURES

The theoretical results to be discussed here are obtained in the context of the generalised Onsager approach[33,34] wherein the free energy F for a positionally disordered mixture of N rods and plates is approximated by the expression

$$
\begin{aligned}
F/NkT \approx{}& \ln\rho - 1 - \sum_{s} x_s \ln(\zeta_s/x_s) \\
&- (\rho^*/2) \sum_{s,s'} x_s x_{s'} \int d\omega\, d\omega' q_{s,s'}(\omega,\omega') f_s(\omega) f_{s'}(\omega'), \qquad (1)
\end{aligned}
$$

Here the subscripts denote the type of molecular species (rod or plate), x_s denotes the respective concentration and $f_s(\omega)$ is the orientational distribution function for a molecule of species s with orientation ω. The distribution is determined self-consistently by functional minimisation of the free energy. The overall number density is denoted by $\rho = N/V$ and ρ^* is an effective density[35] that coincides with ρ at low densities and diverges as the maximal packing density is approached. The molecular structure enters through $q_{s,s'}(\omega,\omega')$ which is obtained from the positional averaging of the intermolecular interaction potential $u_{s,s}(\mathbf{r},\omega,\omega')$ according to

$$q_{s,s'}(\omega,\omega') = \int d\mathbf{r}\{1 - \exp[-u_{s,s'}(\mathbf{r},\omega,\omega')/kT]\}, \tag{2}$$

where $\mathbf{r}$ denotes the intermolecular vector for a pair of molecules of species s,s' and orientations ω,ω' respectively. The single-molecule pseudopartition function ζ_s for species s is given by

$$\zeta_s = \int d\omega e^{-\rho^* \sum_{s'} x_{s'} \int d\omega' q_{s,s'}(\omega,\omega') f_{s'}(\omega')} . \tag{3}$$

The general form of the pressure-concentration phase diagram obtained from the free energy of Eq. (1) is shown in Fig. 1 for the most symmetric case where a pair of rods has identical $q_{s,s'}(\omega,\omega')$ with a pair of discs. The low-pressure part of the phase diagram is isotropic throughout the entire concentration range. A first-order phase transition line separates the isotropic region from the two uniaxial nematic phases N_r and N_d in which the ordering results from the alignment of the rods and discs respectively. A biaxial nematic island N_{BX}, separated by second-order phase transition lines from either N_r or N_d, appears at intermediate concentrations. The high-pressure border of the biaxial island separates it from a biphasic region of coexisting N_r and N_d nematics. The possibility of phases with positional ordering, such as smectic or columnar, is not considered on the phase diagram of Fig. 1.

The biaxial island could or could not appear (equivalently, could shrink into a point at the intersection of the I, N_r, N_d, N_r+N_d transition lines) depending on the details of the molecular interaction. In what follows we consider the conditions under which the biaxial island appears for certain cases of intermolecular interactions.

Hard body interactions

In this case, aside from the molecular volumes, the only other molecular parameters are the aspect ratios of the rods (length/diameter) and of the discs (diameter/thickness). Typical aspect ratio values for low molar mass thermotropic nematogens are around 5. The calculations produce no stable biaxial phase for such aspect ratios[33]. Stabilisation is predicted[23,33], however, at much higher

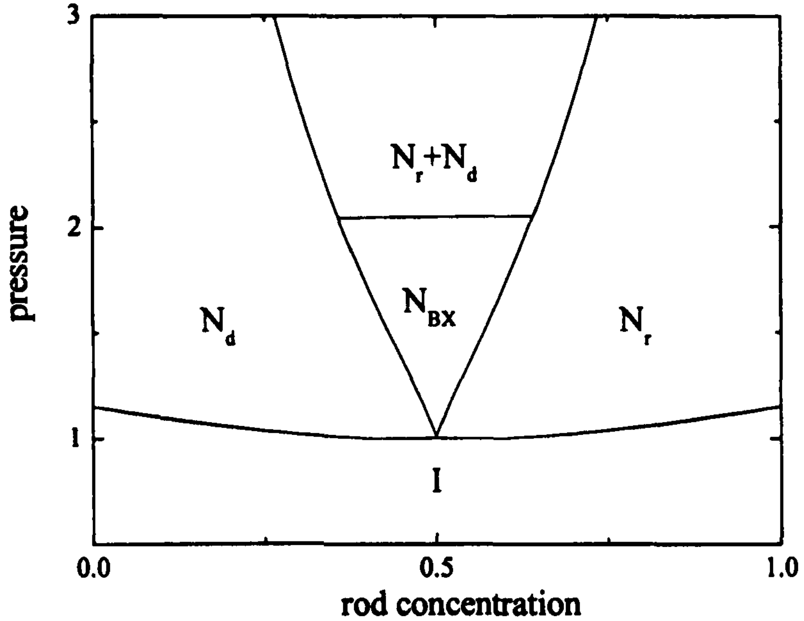

FIGURE 1 Pressure *vs.* rod concentration phase diagrams for rod-disc mixtures with symmetric interactions. The pressure is in arbitrary units

aspect rations (30 or higher) which are well above the conventional thermotropic regime. It was shown in a recent study of colloidal rod-plate mixtures that aspect rations in the range 10–15 did not produce a stable biaxial nematic mixture[36].

The inhibition of phase separation at high aspect ratios can be rationalised by considering the competition between the mixing and the configurational contributions to the entropy. The former is independent of the aspect ratio. The configurational part decreases in the mixed state because of the additional configurational restrictions imposed on a rod molecule by the presence of disc molecules (and *vice versa*). Increasing the aspect ratio, however, enhances the configurational restrictions in the pure rod (or disc) state as well. Accordingly, as the aspect ratio is increased the configurational entropy drop in the mixed state becomes relatively smaller compared to the entropy of the demixed state and is eventually compensated by the gain in mixing entropy.

Rod-plate association

If, in addition to the hard-body interactions of the previous paragraph, an interaction mimicking hydrogen bonding between a rod and a disc molecule is included,

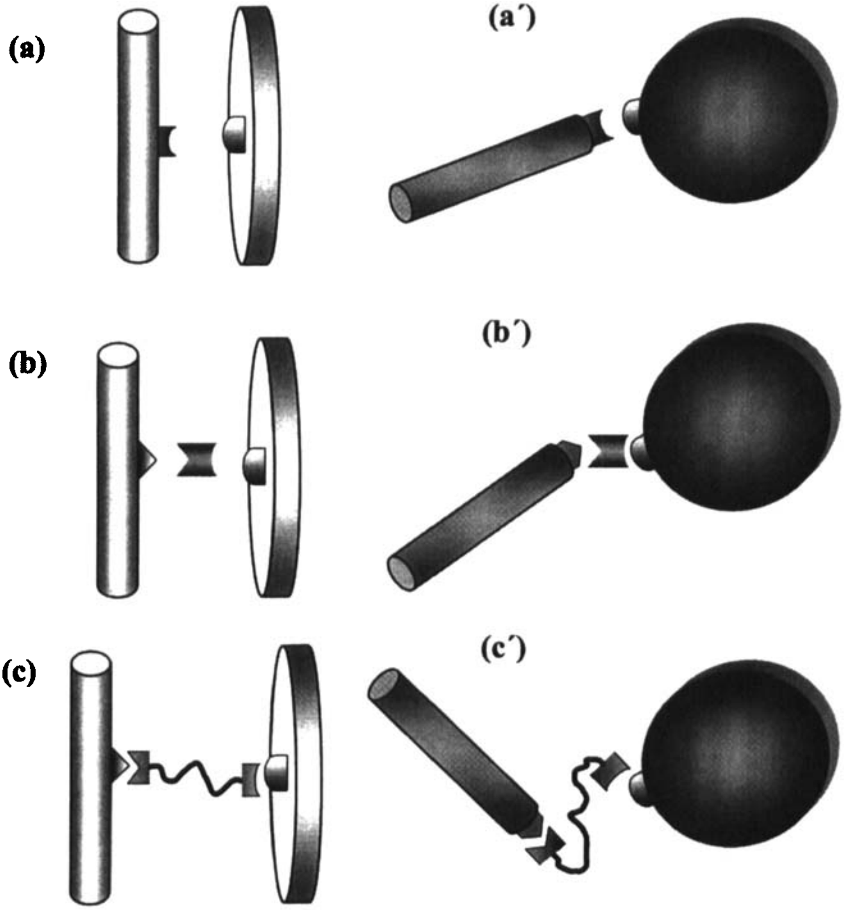

FIGURE 2 Schemes of selective attractive interactions leading to rod-plate association. The interactions could be either direct as in (a), (a') or mediated by a third molecular species. The mediator molecules could be either rigid as in (b), (b') or flexible as in (c), (c')

then the biaxial phase can be stabilised for aspect ratios typical of common thermotropic nematogens[34]. The strength of the rod-disc association interaction required to stabilise biaxiality for given aspect ratios of the molecules depends on the positioning of the interaction centres within the molecular frame and on the spatial range over which the interaction is effective. For example, calculations[34] performed with the interaction sites positioned as in Fig. 2(a) and represented by hemispheres whose overlapping entails an energy drop by ε, show that for rod aspect ratio of 5 the biaxial island first appears at $\varepsilon \approx 9kT$ and expands very rapidly as ε is increased above this threshold. The diameter of the hemispheres, representing the effective range of the associating interaction, was in this case set equal to one fifth of the rod diameter.

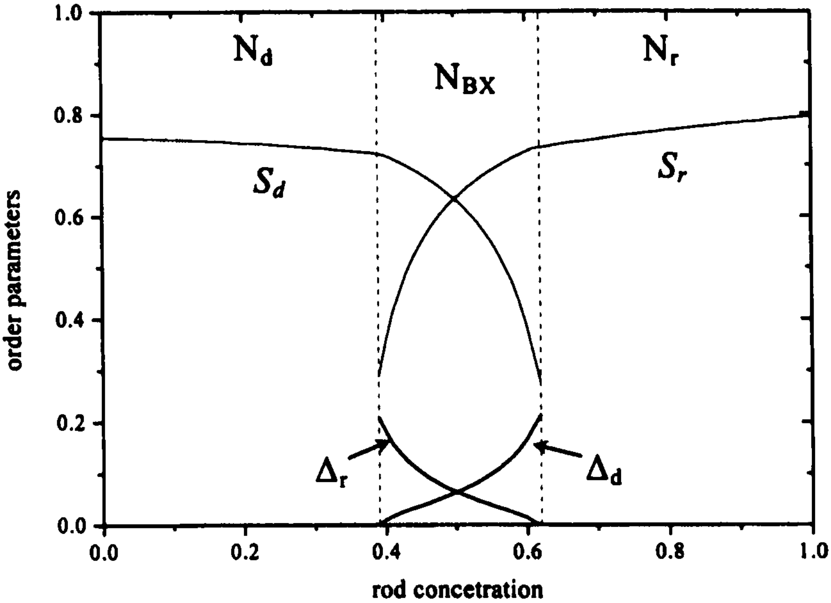

FIGURE 3 Order parameters *vs.* rod concentration at constant pressure $P = 1.8P_C$ for a mixture of rods and discs with the interaction sites as in Fig. 2(a)

The orientational order parameters that are of direct relevance to phase biaxiality and to biaxial molecular ordering are shown in Fig. 3, as a function of rod concentration, for $\varepsilon = 9.5kT$ at constant presssure $P = 1.8P_C$, where P_C is the four-phase (I, N_r, N_d, N_{BX}) coexistence pressure in the phase diagram of Fig. 1. The order parameters for the rods are defined as

$$S_r = \langle P_2(\cos(\theta_r))\rangle \text{ and } \Delta_r = (\sqrt{6}/4)\langle \sin^2(\theta_r)\cos(2\phi_r)\rangle. \qquad (4)$$

Here θ_r is the polar angle of the rod symmetry axis relative to the primary director of rod alignment and ϕ_r, is the azimuthal angle of the same rod axis with respect to the second (biaxial) director of rod ordering (which in this case coinsides with the primary director of disc alignment). The disc order parameters S_d, Δ_d are defined similarly in terms of the angles θ_d, ϕ_d of the disc symmetry axis relative to the primary and second director of disc ordering.

In general, the stabilisation of biaxiality is rather sensitive to the strength ε of the interaction and to its range. If the interaction is not strong enough it will not inhibit demixing. If it is too strong, the rod and disc will be practically bonded into a single structure and this could lead to destabilisation of the nematic ordering altogether. On the other hand, the range of the association interaction in a real system has a fixed effective value. The suitability of such value for the stabilisation of biaxiality depends on the positioning of the interaction sites and on the size of the molecules. For example, it is obvious from Fig. 2(a) that keeping the range of the interaction fixed and increasing the dimensions of the rod and disc molecules makes it increasingly more difficult for the interaction sites to overlap except when the rod axis is parallel to the flat surface of the disc. By contrast, if the interaction sites are positioned as in Fig. 2(a′), i.e on one end of the rod and on the rim of the disc, then the overlapping of the sites is not affected as strongly by the size of the molecules. In this respect, the site configuration in 2(a′) is preferable to the central site configuration of 2(a). The latter configuration, however, is advantageous in another respect: whereas the rod-disc coupling in 2(a′) could lead to lamellar or columnar stacking, the coupling in 2(a) does not (except in the case of accidental matching of the rod and plate dimensions).

As the strength and range of the associating interactions are in general difficult to adjust synthetically, it may be useful to look for schemes where these parameters can in effect be adjusted continuously without altering the chemical structure of the mesogens. Possible schemes for this purpose are shown in Figs. 2(b),(b′),(c) and (c′). They are based on self-assembly schemes where the rods and discs cannot associate directly but they both have associative interactions (of different type) with a third molecular species. In that case the rod-disc association is mediated through the third species. Accordingly, by varying the concentration of the latter, one can adjust the degree of rod-disc association. In this sense, the variation of the concentration of the third component mimics the effect of varying the interaction strength in the two component mixture. The third species, which need not be mesogenic, could be either a small rigid molecule, as shown in Figs 2(b) and 2(b′), or a molecule with two interaction sites connected by a spacer. In the latter case, variation of the length of the spacer has a range-adjusting effect on the rod-disc association interaction mediated by the flexible third species.

Phase separation is of course precluded if the rods and discs are chemically bonded into a dimesogen by means of a flexible spacer. It would appear, therefore, that if the linkage to the spacer gives rise to a favourable configuration (such as shown in Fig. 2 (c) and (c′)) of the rod part relative to the disc part of the dimesogen then the nematic ordering of such a system would be biaxial. It should be pointed out, however, that in this case demixing of the phase is avoided at the expense of strongly coupling the transitional motion of the rod and disc components and thus restricting translational freedom which is essential for the stabilisation of nematic ordering. The degree to which translational freedom, and therefore nematic stability, is affected depends primarily on the length and flexibility of the spacer. Furthermore, the permanent bonding of rods and plates restricts the concentration to 50% for each species. Such concentrations, however, are favourable for biaxiality only in the case of nearly equal rod-rod and plate-plate interactions since only then does the biaxial region extend nearly symmetrically around the 50% concentration.

INTERCONVERTING ROD AND PLATE CONFORMATIONS

Another case in which phase separation is precluded could be provided by single component systems where the rods and plates appear as different conformations of the same molecular species. Such interconversions between rod-like and plate-like molecular shapes are not commonly exhibited by low molar mass thermotropics but they are expected to be possible for dendromesogens[37–40] of certain architectures. In such systems, aside from the rod-like and plate-like conformations, the molecules can exist in a number of other, intermediate, conformations. To study the possibility of obtaining a biaxial nematic from interconverting rod-plate shapes we ignore the complications arising from such intermediate conformations and restrict our considerations to idealised systems exhibiting just a rod-like and a plate-like conformation. These are assumed to interconvert on the same time scale with the translational and reorientational motion of the molecules. However, as will be shown below, even under such conditions, the stabilisation of biaxiality is very unlikely. The difficulty is now due to packing-induced shifting of the conformation probabilities. Such shifting causes one of the two competing conformations to practically dissapear in the bulk phase.

The free energy for a system of N molecules exhibiting rapidly interconverting rod and plate conformations is given, under the same approximations leading to Eq. (1), by the expression[41]

$$
\begin{aligned}
F/NkT &= \ln\rho - 1 - \ln\zeta \\
&\quad - (\rho^*/2)\sum_{n,n'} e^{-(E_n+E_{n'})/kT}\int d\omega\, d\omega' q_{n,n'}(\omega,\omega') f_n(\omega) f_{n'}(\omega'), \qquad (5)
\end{aligned}
$$

where now the subscript n denotes molecular conformation instead of molecular species and E_n is the respective conformation energy. The interaction function $q_{n,n'}(\omega, \omega')$ is given by the expression in Eq. (2) with the species index s replaced by the conformation index n. The pseudopartition function ζ is simply the weighted sum of the single conformation pseudopartition functions ζ_n,

$$\zeta = \sum_{n} e^{-E_n/kT} \zeta_n . \tag{6}$$

The latter are obtained from the expression in Eq. (3) by replacing *s* with *n* and by using the respective conformation weight $\exp(-E_n / kT)$ in place of the concentration x_s.

The probability for the isolated molecule to be found in conformation *n* will be referred to as the intrinsic probability of the n^{th} conformation and is given by

$$p_n^0 = e^{-E_n/kT} / \sum_{n'} e^{-E_{n'}/kT} . \tag{7}$$

Due to the intermolecular interactions, the probability p_n for finding the n^{th} conformation in the bulk phase differs from the intrinsic probability, and is given by

$$p_n = \zeta_n e^{-E_n/kT} / \sum_{n'} \zeta_{n'} e^{-E_{n'}/kT} . \tag{8}$$

Phase stability was studied as a function of density and intrinsic probability for a system of such interconverting rod-plate conformations that interact as hard objects. The respective phase diagram has an isotropic region at low densities and two uniaxial nematic regions, N_r and N_d, at higher densities. In each of the nematic regions, the probability of the respective dominant conformation is very large, irrespectively of its intrinsic probability. These calculations show that hard body packing constraints do not allow the two conformations to coexist in comparable probabilities in order to produce biaxial ordering.

To investigate the possibility of modifying the intermolecular interaction in such a way as to allow for biaxial ordering, the interaction function $q_{n,n'}(\omega, \omega')$ is put in the form of a tensor expansion for uniaxial objects in terms of Legendres polynomials $P_l(\cos\theta)$,

$$q_{n,n'}(\omega, \omega') = q_{n,n'}(\theta) = \sum_{l} q^{l}_{n,n'} P_l(\cos\theta) . \tag{9}$$

The expansion is then truncated above the second rank contributions and the retained tensor coefficients are scanned for combinations that could yield a stable biaxial nematic phase. The phase diagram for such a combination, where the rod and disc tensor coefficients are treated symmetrically, is shown in Fig. 4.

The respective diagram for the variation of the probability of the disc conformation on increasing the density at constant intrinsic probability is shown in Fig. 5. It is apparent on this diagram that the probability of the disc conformation increases on increasing the density in each of the ordered phases until the saturation value of 1 is reached.

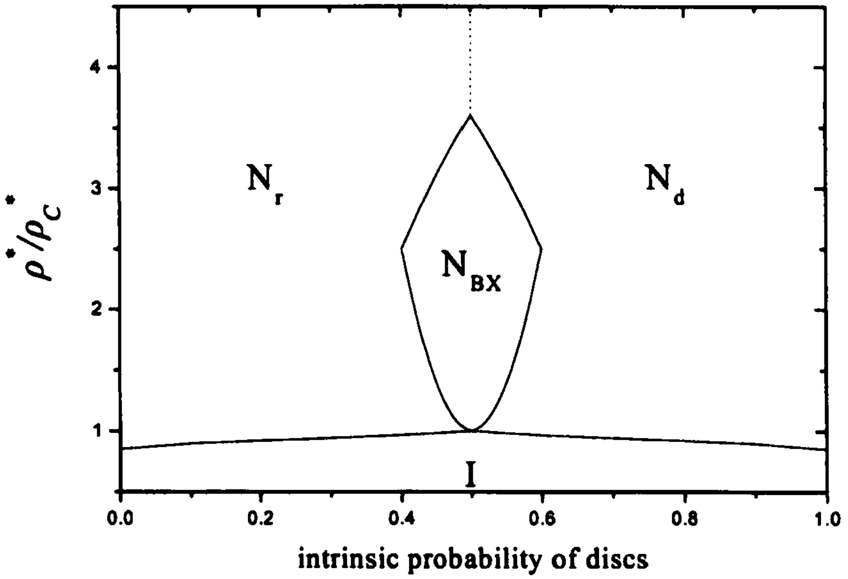

FIGURE 4 Phase diagram of reduced effective density, ρ^*/ρ_C^*, *vs.* the intrinsic probability (p_{disc}^0) of the disc-like conformation in a system with interconverting rod-like and disk-like conformations. ρ_C^* denotes to the effective density at the four phase coexistence point direct transition from the isotopic phase to the biaxial nematic. The diagram is obtained with the following values (in units of ρ_C^*) for the tensor coefficients of Eq. (9): $q_{rr}^0 = q_{dd}^0 = 1.80$, $q_{rd}^0 = 0.20$ and $q_{rr}^2 = q_{dd}^2 = -q_{rd}^2 = -5.14$. Coefficients with $l>2$ are ignored

What is of interest from the molecular design point of view is to ascribe the combination of values of the tensor coefficients in Fig. 4 to specific structural and intermolecular interaction features. However, neither for this combination nor for other similar combinations resulting in phase biaxiality was it possible to identify corresponding structures and interactions among those commonly encountered in thermotropic mesogens.

CONCLUSIONS

Our theoretical study suggests that the thermodynamic stabilisation of phase biaxiality in nematic mixtures of rod-like and plate-like molecules is promoted by (i) high aspect ratios of the molecules (long and thin rods, large and thin plates) and (ii) selective interactions, such as hydrogen bonding, that give rise to

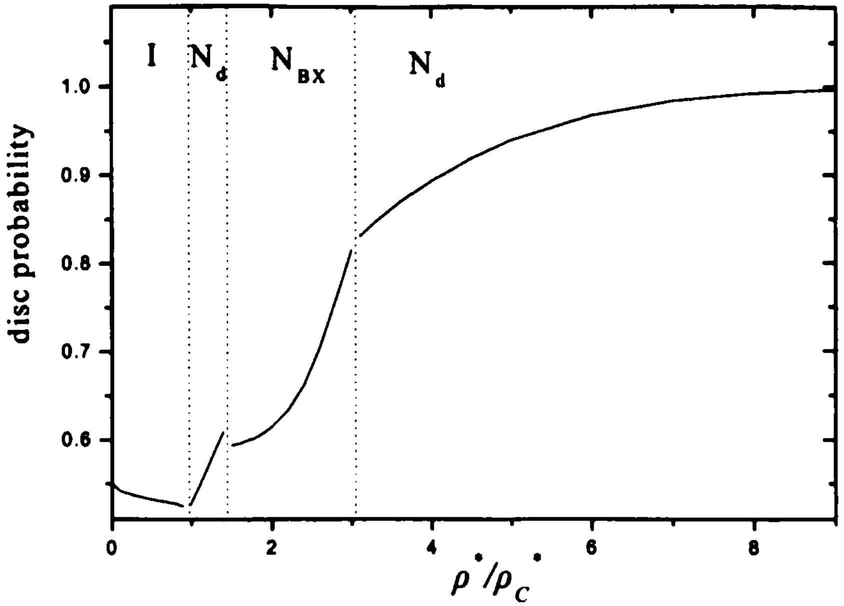

FIGURE 5 The dependence of the probability of interacting disc-shaped conformations of the phase diagram in Fig. 4 on the reduced density ρ^*/ρ_c^* at fixed intrinsic probability $p^0_{disc} = 0.55$

rod-plate association. The range and strength of such interactions are to be chosen judiciously in relation to the sizes of the molecules and the positioning of the interaction sites on the molecules. A possibility of adjusting indirectly the range and strength of the interactions by introducing a third molecular species into the rod-plate mixture is proposed.

In systems where the rods and plates are different conformational states of a single molecular species, packing restrictions do not favour the coexistence of both states in the proportions required for biaxial nematic ordering. The conditions for the stabilisation of biaxiality in such systems stipulate molecular structures and interactions that are hard to relate to real thermotropic mesogens.

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