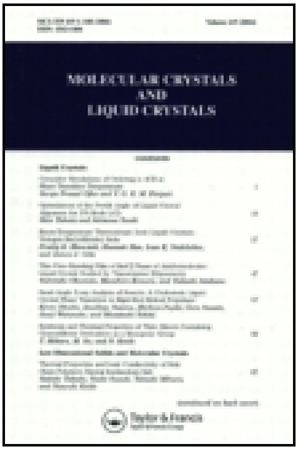

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A New Theory of Nematic Liquid Crystal Mixtures

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A New Theory of Nematic Liquid Crystal Mixtures

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A recent theory of hard rod packing allowing a continuum of rod orientations and a specification of steric constraints rotationally invariant and correct in the isotropic limit is generalized to the multicomponent case. The additional effect of temperature on packing, used in a description of one component thermotropic nematics, is employed here in describing the effects of temperature on lyotropic nematics, that is, where the second component is simple solvent. Complicated phase diagrams characteristic of nematic mixtures are given for the examples of rods of axial ratio $x = 5$ and $x = 50$ diluted by solvent. Mixtures of two rod components are solved, the phase diagrams of models of quater-quinque-phenyl and quater-sexiphenyl mixtures being presented as more demanding tests of theory than the one component properties previously calculated.

1. INTRODUCTION

Broadly speaking molecular theories of nematic liquid crystals rely either on the dominance of soft, anisotropic dispersion forces or on hard steric forces deriving from molecular shape. We are going to describe a theory where the constraint of non-overlap of hard molecules when they are densely packed is the over-riding driving force for the orientational order characterizing nematic fluids. Soft forces will

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†At Rutherford Appleton Laboratory during the period of this work.

be incorporated within the description of rod mixtures of concern here. Their effect is to introduce temperature which, along with composition, will play an important part in the complex phase behaviour of multi-component nematics.

The dense packing of hard rods is an old problem, pioneered by Flory[1] and subsequently refined[2] and has been comprehensively reviewed.[3] A new approach[4] derives much from the lattice approach of Flory[1,2] but has two major differences concerned with the specification of how one molecule sterically interferes with another and with the problem of allowing a rod-like molecule continuous orientational freedom. We shall only outline the method below and refer the reader to a description of the approach.[4]

Mixtures of mesogens, typically rod-like molecules, with either other mesogens or with non-mesogenic solvents are on the one hand the most common technological and biological context of nematics and on the other hand a severe test of theory. Indeed we show below that aspects of nematic behaviour, inaccessible because crystallization or prohibitively high temperatures intercede, are revealed in the properties of mixtures. Complex behaviour resulting from the interplay of soft forces and the dilution of the effect of hard forces by compositional variation is also seen. This behaviour was proposed by Flory[1] and calculated for anisotropic dispersion forces by Warner and Flory.[5] In this paper we therefore extend the new approach to the description of multi-component phase equilibrium.

In section 2 we outline the method and its application to many components. In section 3 we present the results of our calculations and in section 4 summarize and point the way to future improvements.

2. THEORY OF NEMATIC MIXTURES

To calculate the configurational part of the partition function, Z_c, (and hence the free energy) one must know how many ways there are of putting a general rod, the $j + 1$th say, into the fluid given that j are already so placed. Instead of using a lattice it was argued[4] in the present approach that an ensemble of realizations of a hard sphere liquid should be taken. The neat fluid or rod mixture is then realized by attempting to insert the many contiguous collinear series of segments comprising the rods into each particular realization of the fluid. This can evidently be done with the same degree of accuracy as in a lattice approach. The advantages are that one has no a priori preferred direction(s) imposed by the lattice, rods have a continuum of allowed orientations (ultimately allowed in Flory theory, but not in the more extreme versions of lattice theory restricting rods to three principal directions only[3]) and that projections of other rods onto a test rod preserves their integrity as rods, even in the case of an isotropic rod fluid. The latter point is not so in earlier lattice approaches. In the isotropic limit their partition functions reduce to those of flexible polymer fluids. Hereafter we use the term lattice to encompass the ensemble of sites alluded to above.

Our model of a rod with axial ratio x is that of a collinear sequence of x spheres of the fluid mentioned above which are taken to have unit diameter.

We can therefore take the rod i as presenting a projection $P^{\underline{\theta}_j}_{\underline{\theta}_i}$ onto the plane perpendicular to the rod j that is characteristic of a sphero-

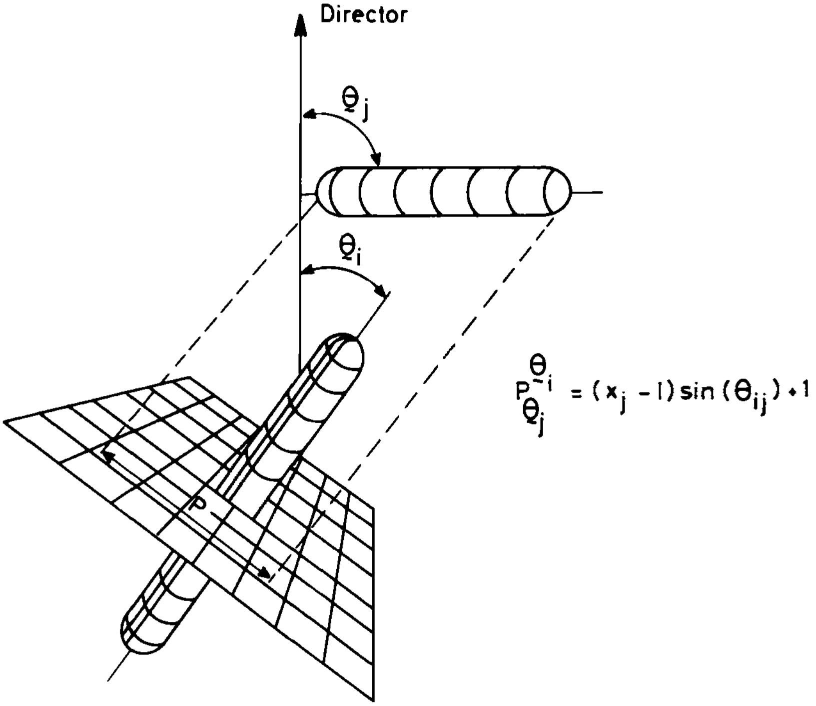

FIGURE 1 Illustration of the projection of the molecule j onto the plane perpendicular to molecule i. The orientations $\underline{\theta}$ of the rods are expressed with respect to an axis, in this case the director. An essential advantage of this theory is that the projection p, which determines the steric hindrance to laying down i in the fluid, is independent of which axis is chosen as a reference of angle. The angle $\underline{\theta}_{ij}$ between the rods, is expressible in terms of the two angles $\underline{\theta}_i$ and $\underline{\theta}_j$. A concomitant advantage of this theory over others is that the rod-character is preserved by the representation of the isotropic state.

cylinder of axial ratio x_i, that is

$$P^{\theta_j}_{\theta_i} = (x_i - 1)\sin\theta_{ij} + 1 \tag{2.1}$$

where θ_{ij} is the angle between the rods i and j. The projection P is the vital element in calculating the configurational partition function and is illustrated in Figure 1.

Derivation of the partition functions

Let $\underline{\theta}$ represent the two Euler angels (θ, ϕ) of a rod with respect to the director, and n_0 denote the total number of sites in the fluid. Consider that j molecules have already been placed. There are $(n_0 - \Sigma_{i=1}^{j} x_i)$ sites into which the first segment of molecule $j + 1$ can be placed. Having placed the first segment the probability of placing the second segment such that the molecule $j + 1$ makes an angle θ_{j+1} to the director is

$$\frac{\left(n_0 - \sum_{i=1}^{j} x_i - 1\right)}{\left(n_0 - \sum_{i=1}^{j} x_i - 1 + \sum_{i=1}^{j} P^{\underline{\theta}_{j+1}}_{\underline{\theta}_i}\right)} \tag{2.2}$$

This probability reflects the fact that although molecule i occupies x_i lattice sites only $P^{\underline{\theta}_{j+1}}_{\underline{\theta}_i}$ of them are competing with the segments of molecule $j + 1$ for lattice sites. If we now continue to place in the remaining segments we find that the number of ways of placing the $j + 1$th molecule is

$$\nu_{j+1} = \frac{\left(n_0 - \sum_{i=1}^{j} x_i\right)!\left(n_0 - \sum_{i=1}^{j+1} x_i + \sum_{i=1}^{j} P^{\underline{\theta}_{j+1}}_{\underline{\theta}_i}\right)!}{\left(n_0 - \sum_{i=1}^{j+1} x_i\right)!\left(n_0 - \sum_{i=1}^{j} x_i - 1 + \sum_{i=1}^{j} P^{\underline{\theta}_{j+1}}_{\underline{\theta}_i}\right)!} \tag{2.3}$$

The configurational partition function, being the number of distinct ways of placing all of the molecules in the lattice, is therefore

$$Z_c = \prod_{j+1=1}^{n_p} \nu_{j+1} \prod_{\alpha} \frac{1}{n_\alpha!} \tag{2.4}$$

where n_α is the number of rods of species α (having an axial ratio x_α), and n_p is the total number of rods $= \Sigma_\alpha n_\alpha$.

We proceed by following the analysis of reference 4 but replace the x_i by the average axial ratio, $\bar{x} = \Sigma_i x_i / n_p = \Sigma_\alpha n_\alpha x_\alpha / n_p$, and the $P_{\theta_i}^{\theta_j}$ by the average, $\bar{p}$. The average, the approximations it engenders and an alternative scheme are described below. It amounts to replacing specific interactions between two rods by a mean interaction between one rod and the others in the sample. It will be seen in (2.13) that the other rods feel the Onsager reaction field. The average projection, $\bar{p}$, is a functional of their distributions. The result for the configurational partition function is, with n_s $(= n_0 - n_p)$, the number of solvent molecules,

$$Z_c = \prod_\alpha (1/n_\alpha !) \frac{n_0 !}{n_s !(n_0 - 1)!}$$
$$\times \left(n_0 - n_p \bar{x} + (n_p - 1)\bar{p}\right)! \left(n_0 - (n_p - 1)(\bar{x} - \bar{p})\right)^{-n_p(\bar{p}-1)}$$
$$\times \exp\left[\left(\frac{\bar{p} - 1}{\bar{x} - \bar{p}}\right) n_0 \left\{\frac{n_p}{n_0}(\bar{x} - \bar{p}) + \ln\left[1 - \frac{n_p}{n_0}(\bar{x} - \bar{p})\right]\right\}\right] \quad (2.5)$$

We turn now to the calculation of the orientational partition function. The relative number of different orientations that a molecule at an angle θ to the director can lie in is $\sigma\omega(\theta)$. The constant, σ arbitrary in classical statistical mechanics, depends on the mesh size in phase space and will be shown to be irrelevant. The factor $\omega(\theta) = \sin\theta$ from considering rotations in three-dimensional space. If the number of molecules of species α at an angle θ to the director is $n_\alpha(\theta)$ then the number of configurations of all the α-type molecules is:

$$\prod_\theta (\sigma \sin\theta)^{n_\alpha(\theta)} n_\alpha ! / n_\alpha(\theta)! \quad (2.6)$$

the factor $n_\alpha ! / n_\alpha(\theta)!$ avoids over-counting identical configurations.

We shall be concerned with a continuum of orientations θ. To avoid a discussion of continuous products one can take at this stage a discrete set of allowed orientations θ_ν and variables $n_\alpha(\theta_\nu)$ to assign meaning to Π_θ in (2.6)–(2.8). Subsequently upon taking logarithms we take this set $\{\theta_\nu\}$ to tend to a continuum, replacing at the same time sums by integrals. The minimization of the free energy with respect to the functions $n_\alpha(\theta)$ is a functional problem, as indicated in (2.14) f.f. Readers unfamiliar with such functional analysis should retain the idea of a discrete set of variables along with sums in what follows and take ordinary derivatives in (2.14) f.f. with respect to the $n_\alpha(\theta_\nu)$ instead of functional derivatives.

The orientational partition function is then simply

$$Z_0 = \prod_\alpha n_\alpha ! \prod_\theta (\sigma \sin\theta)^{n_\alpha(\theta)} / n_\alpha(\theta)! \tag{2.7}$$

The total partition function, $Z = Z_c Z_0$ can then be written in the convenient form

$$\begin{aligned} Z = \prod_\alpha \frac{1}{n_\alpha !} & \frac{(n_0 - n_p(\bar{x} - \bar{p}))!}{n_s !} (n_0 - n_p(\bar{x} - \bar{p}))^{-n_p(\bar{p}-1)} \\ & \times \exp\left[\frac{(\bar{p} - 1)}{(\bar{x} - \bar{p})} n_0 \left\{ \frac{n_p}{n_0}(\bar{x} - \bar{p}) + \ln\left[1 - \frac{n_p}{n_0}(\bar{x} - \bar{p}) \right] \right\} \right] \\ & \cdot \prod_{\alpha, \theta} \frac{(\sigma \sin\theta)^{n_\alpha(\theta)} n_\alpha !}{n_\alpha(\theta)!} \end{aligned} \tag{2.8}$$

(We have replaced the $(n_0 - 1)$ and $(n_p - 1)$ by n_0 and n_p)

The Helmholtz Free Energy (F) is obtained from the partition function by $-F = kT \ln Z$ which for our hard rods yields, after rearranging terms and using Stirling's approximation,

$$\begin{aligned} -F/kT = & -n_s \ln(n_s/n_0) - \sum_\alpha n_\alpha \ln(n_\alpha/n_0) \\ & + \left(\frac{\bar{x} - 1}{\bar{x} - \bar{p}} \right) (n_s + n_p \bar{p}) \ln\left[1 - n_p(\bar{x} - \bar{p})/n_0 \right] \\ & + \sum_\alpha \int d\theta \, n_\alpha(\theta) \ln(\sigma \sin\theta \, n_\alpha / n_\alpha(\theta)) \end{aligned} \tag{2.9}$$

The free energy above is a functional of the orientational distribution functions, $n_\alpha(\theta)/n_\alpha$, of the molecules, as yet unknown. These distribution functions appear explicitly in the expression for the free energy in the last term and also implicitly, as we shall see, in all terms involving $\bar{p}$.

The average projection, $\bar{p}$

The projection of a sphero-cylinder, i, onto the plane perpendicular to a sphero-cylinder, j, is $(x_i - 1)\sin\theta_{ij} + 1$. The angle θ_{ij} between rods i

and j is given, in terms of the angles between the rods and the director, by $\cos\theta_{ij} = \sin\theta_i \sin\theta_j \cos\phi_i + \cos\theta_i \cos\theta_j$. With no loss of generality one can take $\phi_j = 0$. In the nematic phase we can average freely over ϕ_i to give

$$P_{\theta_i}^{\theta_j} = (x_i - 1) q_{\theta_i}^{\theta_j} + 1 \tag{2.10}$$

$$q_{\theta_i}^{\theta_j} = \frac{1}{\pi}\int_0^{\pi} \sqrt{1 - (\sin\theta_i \sin\theta_j \cos\phi_i + \cos\theta_i \cos\theta_j)^2}\, d\phi_i \tag{2.11}$$

We then use the distribution functions to average over θ_i

$$\sum_\alpha (n_\alpha/n_p) q_\alpha(\theta_j) = \sum_\alpha (n_\alpha/n_p) \int d\theta (n_\alpha(\theta)/n_\alpha) q_\theta^{\theta_j} \tag{2.12}$$

and finally average over θ_j to get the mean projection onto the mean molecule:

$$\bar{p} = \sum_{\alpha\alpha'} \int d\theta\, d\theta' \frac{(x_{\alpha'} - 1) n_\alpha(\theta) n_{\alpha'}(\theta')}{n_p^2} q_\theta^{\theta'} + 1 \tag{2.13}$$

This device of averaging the steric field twice when proceeding from (2.3) and (2.4) to (2.5) derives from reference 4. The distribution function $n(\theta)$ appears twice in $\bar{p}$, once from the sterically hindering molecule and once from the molecule under consideration, a fact essential in (2.14). It is necessary to put both in if one wants to avoid the assumption implicit in Flory theory that components of a rod in different directions see a different type of steric field. Double averaging as we have done is an additional approximation even though the second average is self-consistent with the first. A suggested alternative would be to generalize to a continuum of directions as in the philosophy of the approaches where the steric field is calculated in each principal direction of a lattice.[3] Instead of using a double average to simplify the product (2.4) of terms ν_{j+1} (2.3) one takes the geometric mean $\bar{\nu}_{j+1}$ of the ν factors and the term $\Sigma_{i=1}^{j} P_{\theta_i}^{\theta_{j+1}}$ is replaced by the single average over angles θ_i, i.e. $j(\Sigma_\alpha n_\alpha x_\alpha q_\alpha(\theta_j)/n_p)$. Let the average over rod species α of $x_\alpha q_\alpha(\theta)$ be denoted by $\overline{p(\theta)}$, then the equivalent of (2.3) becomes

$$\overline{\nu_{j+1}} = \frac{(n_0 - j\bar{x})^{\bar{x}}}{\prod_\alpha \prod_\theta \left[n_0 - j\bar{x} + j\overline{p(\theta)}\right]^{n_\alpha(\theta)(x_\alpha - 1)/n_p}}$$

which arguably retains more structure. We do not pursue this possible improvement here but proceed, according to the approach of reference (4), to the question of the distribution functions.

Calculating the distribution functions

The distribution functions minimize the free energy. To determine them we therefore functionally differentiate F with respect to these functions and equate the result to zero. We firstly differentiate $\bar{p}$.

$$\delta\bar{p}/\delta n_\lambda(\psi) = \sum_{\alpha'}\int d\theta \frac{(x_{\alpha'}-1)n_{\alpha'}(\theta)}{n_p^2} q_\theta^\psi + (x_\lambda - 1)\sum_\alpha \int d\theta \frac{n_\alpha(\theta)}{n_p^2} q_\psi^\theta$$
$$= \sum_\alpha \frac{n_\alpha}{n_p^2}(x_\alpha + x_\lambda - 2)q_\alpha(\psi) \tag{2.14}$$

where (2.12) or (2.14) define $q_\alpha(\psi)$ and we use the fact that $q_\theta^\psi = q_\psi^\theta$.

We then differentiate F itself to give

$$-\delta F/\delta n_\lambda(\psi) = \frac{\bar{x}-1}{(\bar{x}-\bar{p})^2}\left[(\bar{x}-\bar{p}) + \frac{n_0}{n_p}\ln\bigl(1 - n_p(\bar{x}-\bar{p})/n_0\bigr)\right]$$
$$\cdot \sum_\alpha \frac{n_\alpha}{n_p}(x_\alpha + x_\lambda - 2)q_\alpha(\psi)$$
$$-\ln\left[\frac{n_\lambda(\psi)}{\sigma n_\lambda \sin\psi}\right] + \text{const} = 0 \tag{2.15}$$

which yields finally the distribution for the species λ

$$\frac{n_\lambda(\psi)}{n_\lambda} = \frac{\sin\psi}{f_\lambda^1}\exp\left\{-b\sum_\alpha \frac{n_\alpha}{n_p}(x_\alpha + x_\lambda - 2)q_\alpha(\psi)\right\} \tag{2.16}$$

where

$$b = -\frac{(\bar{x}-1)}{(\bar{x}-\bar{p})^2}\left[(\bar{x}-\bar{p}) + \frac{n_0}{n_p}\ln\left(1 - \frac{n_p}{n_0}(\bar{x}-\bar{p})\right)\right] \tag{2.17}$$

and

$$f_\lambda^1 = \int d\psi \sin\psi \exp\left\{-b\sum_\alpha \frac{n_\alpha}{n_p}(x_\alpha + x_\lambda - 2)q_\alpha(\psi)\right\} \tag{2.18}$$

The arbitrary constant σ has been discarded in (2.18) since it appears equally in the normalisation constant, f_λ^1, thus demonstrating the earlier assertion of its irrelevance.

Combining equation (2.16) with (2.12) and (2.18) we obtain a non linear integral equation which must be solved for $q_\lambda(\theta)$

$$q_\lambda(\theta) = \int_0^{\pi/2} \sin\psi\, q_\psi^\theta \exp\left\{-b\sum_\alpha \frac{n_\alpha}{n_p}(x_\alpha + x_\lambda - 2)q_\alpha(\psi)\right\} d\psi \tag{2.19}$$

This equation can be solved by a simple iterative procedure. From initial guesses of the constant b and the functions $q_\alpha(\psi)$ better estimates of $q_\alpha(\psi)$ are calculated and used to generate still better estimates of b. The iterative process is then repeated until successive interactions agree within a specified accuracy.

When the functions $q_\alpha(\theta)$ and the distribution functions have been calculated they can be substituted into equation (2.13) to find $\bar{p}$ which is put into equation (2.9) for the free energy.

In the isotropic phase $q_\alpha(\theta) = \pi/4$, independent of θ. We then have for $\bar{p}$

$$\bar{p} = (\bar{x} - 1)\pi/4 + 1 \tag{2.20}$$

The theory of reference 4 has now been generalized for many rod components plus simple solvent. We now proceed to:

The chemical potential

For a system consisting only of rods of one species the transition between the isotropic and anisotropic phases is found simply by equating the free energies of the respective phases. In the above theory, in the case of one component, all that can be varied to effect the transition is the axial ratio of the rods. Warner[4] found that using this theory a neat system of rods having axial ratios greater than 8.98 would always be anisotropic. To see more varied phase behaviour we thus turn to mixtures of rods and spheres or rods and rods. In the present athermal limit we shall have a model of lyotropic liquid crystals.

We need to calculate the chemical potentials, or partial molar free energies, of species α

$$\mu_\alpha = \partial F/\partial n_\alpha \tag{2.21}$$

Care must be taken that partial differentiation is done without varying the distribution functions or the amounts of any other component.

Most of the terms in equation (2.9) involve n_α implicitly. After much tedious calculation we find:

$$-\mu_s/kT = \frac{(\bar{x}-1)}{(\bar{x}-\bar{p})}\ln\bigl(1 - v_p(\bar{x}-\bar{p})/\bar{x}\bigr) - \ln v_s \tag{2.22}$$

$$\begin{aligned}-\mu_\alpha/kT = \frac{(\bar{x}-1)}{(\bar{x}-\bar{p})}\Biggl\{\Biggl[\bar{p} - \frac{\bar{x}(\bar{p}-1)(\bar{x}+x_\alpha-2)}{v_p(\bar{x}-1)(\bar{x}-\bar{p})}\\ + \frac{(\bar{p}-1)(x_\alpha-\bar{x})}{\bar{x}-1}\Biggr]\\ \cdot\ln\bigl(1 - v_p(\bar{x}-\bar{p})/\bar{x}\bigr) - \frac{(\bar{p}-1)(\bar{x}+x_\alpha-2)}{(\bar{x}-1)}\Biggr\}\\ -\ln(v_\alpha/x_\alpha) + \ln f_\alpha^1\end{aligned} \tag{2.23}$$

where v_α $(= x_\alpha n_\alpha/n_0)$ is the volume fraction of species α. The total volume fraction of the rods is v_p $(= \Sigma v_\alpha)$ and v_s $(= 1 - v_p)$ is the volume fraction of the spheres. We have used the fact that $\Sigma_\alpha \Sigma_\theta n_\alpha(\theta)\ln(n_\alpha(\theta)/\sin\theta) = -2b(\bar{p}-1) - n_p \ln f_\lambda^1$. In the isotropic phase the chemical potentials are

$$-\mu_s^{\text{iso}}/kT = \frac{1}{(1-\pi/4)}\ln\left(1 - \frac{v_p(\bar{x}-1)(1-\pi/4)}{\bar{x}}\right) - \ln v_s \tag{2.24}$$

$$\begin{aligned}-\mu_\alpha^{\text{iso}}/kT = \frac{1}{1-\pi/4}(1 + \pi/4(x_\alpha - 1))\\ \times\ln\left(1 - v_p\frac{(\bar{x}-1)(1-\pi/4)}{\bar{x}}\right) - \ln(v_\alpha/x_\alpha)\end{aligned} \tag{2.25}$$

The transition from the isotropic to the anisotropic phase of a mixture can now be driven by changing the composition of the mixture and is found by solving the following simultaneous equations for the chemical potentials.

$$\mu_s^{\text{iso}}(\text{composition } 1) = \mu_s^{\text{aniso}}(\text{composition } 2)$$

$$\mu_\alpha^{\text{iso}}(\text{composition } 1) = \mu_\alpha^{\text{ansio}}(\text{composition } 2) \tag{2.26}$$

where μ^{aniso} denotes the chemical potentials (2.22) or (2.23) evaluated in the nematic phase.

If we look specifically at a binary system of rods and solvent from the solutions of the simultaneous equations we can calculate a phase diagram of composition against axial ratio at nematic-isotropic coexistence (Figure (2)). This diagram above is similar to one produced by Flory.[1] His lower limit for the existence of an anisotropic phase was 6.42, in contrast to the value 8.98 obtained[4] in the present method. As is usual for very long rods, the rod volume fractions for the coexisting isotropic and nematic phases both become very small. Consequently the phase gap becomes very narrow.

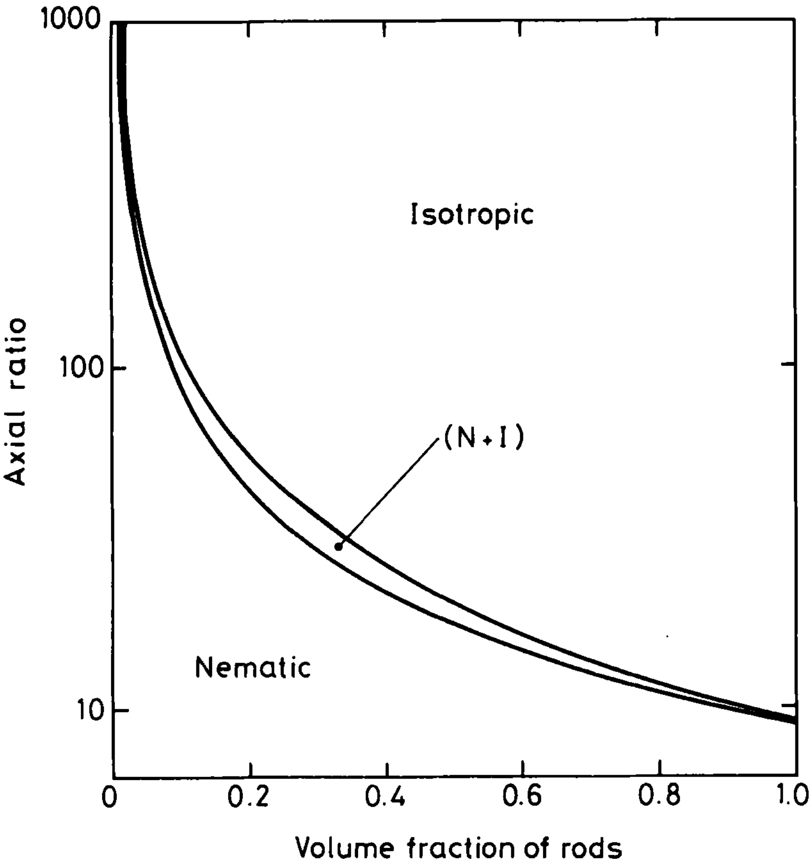

FIGURE 2 Biphasic equilibrium of athermal rods and solvent as a function of rod axial ratio. The right curve is the locus of nematic volume fractions of rods, the left curve is the locus of the isotropic fractions.

Thermotropic systems

So far we have neglected the role of soft forces between molecules. Composition has been the sole factor determining ordering and phase equilibrium. We have thus described lyotropic systems and, for reasons outlined with the theory, only molecules with an axial ratio $x \geq 9$. Short rods require the additional influence of soft forces before ordering can occur. Temperature now enters the expression for the free energy in a non trivial way. We now proceed to a discussion of thermotropic mixtures, that is mixtures of rods with other rods or with solvent where temperature plays a role.

The angularly dependent interaction energy between two segments of relative orientation χ with respect to each other is, on general grounds[6] (we let the relevant rod axis define a direction in each segment):

$$U(\chi) = -kT^*P_2(\cos\chi) \tag{2.27}$$

where kT^* expresses the energy of interaction in terms of a temperature T^*, and where P_2 is the 2nd Legendre polynomial.

The interaction U between one rod of species α and a *mean field* of the other rods is then

$$U(\theta)/kT = -\Theta^{-1}x_\alpha v_p P_2(\cos\theta)S \tag{2.28}$$

where the order parameter S, the average of P_2 for the rods comprising the mean field, is given by:

$$S = \sum_\beta \frac{n_\beta x_\beta}{n_p\bar{x}} \int \frac{n_\beta(\psi)}{n_\beta} P_2(\cos\psi)\, d\psi \tag{2.29}$$

and the reduced temperature Θ is:

$$\Theta = T/T^* \tag{2.30}$$

This term is added as a Boltzmann factor to the expression for the distribution functions, thus

$$\frac{n_\lambda(\psi)}{n_\lambda} = \frac{\sin\psi}{f_\lambda^1}\exp\left\{-b\sum_\alpha \frac{n_x}{n_p}(x_\alpha + x_\lambda - 2)q_\alpha(\psi)\right.$$
$$\left. + \Theta^{-1}x_\lambda v_p S P_2(\cos\psi)\right\} \tag{2.31}$$

with

$$f_\lambda^1 = \int d\psi \sin\psi \exp\left\{ -b \sum_\alpha \frac{n_\alpha}{n_p} (x_\alpha + x_\lambda - 2) q_\alpha(\psi) \right. \\ \left. + \Theta^{-1} x_\lambda v_p S P_2(\cos\psi) \right\} \tag{2.32}$$

The distribution functions are found as self-consistent solutions of equations (2.31), (2.32), (2.29), (2.27) and (2.12) using a process similar to the athermal case. Averaging the potential energy gives the energetic contribution to the free energy,

$$E/kT = -n_p \bar{x} v_p S^2 \Theta^{-1}/2 \tag{2.33}$$

which combined with equation (2.31) for the distribution function gives the thermodynamic free energy:

$$\begin{aligned} -F/kT = {} & -n_s \ln(n_s/n_0) - \sum_\alpha n_\alpha \ln(n_\alpha/n_0) + n_p \ln f_\lambda^1 \\ & - \Theta^{-1} v_p \bar{x} n_p S^2/2 \\ & + \frac{(\bar{x}-1)}{(\bar{x}-\bar{p})} \left[n_0 + n_p(\bar{p}-\bar{x}) - n_0 \frac{2(\bar{p}-1)}{\bar{x}-\bar{p}} \right] \\ & \times \ln\left(1 - n_p/n_0(\bar{x}-\bar{p})\right) - 2\frac{(\bar{x}-1)(\bar{p}-1)}{(\bar{x}-\bar{p})} n_p \end{aligned} \tag{2.34}$$

The chemical potentials in the nematic phase composed of solvent and rods of species α, are

$$-\mu_s/kT = \left(\frac{\bar{x}-1}{\bar{x}-\bar{p}}\right) \ln\left(1 - v_p(\bar{x}-\bar{p})/\bar{x}\right) - \ln v_s - v_p^2 S^2/2\Theta \tag{2.35}$$

$$\begin{aligned} -\mu_\alpha/kT = {} & \left(\frac{\bar{x}-1}{\bar{x}-\bar{p}}\right) \\ & \times \left\{ \left[\bar{p} - \frac{\bar{x}(\bar{p}-1)(\bar{x}+x_\alpha-2)}{v_p(\bar{x}-1)(\bar{x}-\bar{p})} + \frac{(\bar{p}-1)(x_\alpha-\bar{x})}{\bar{x}-1} \right] \right. \\ & \left. \times \ln\left(1 - v_p(\bar{x}-\bar{p})/\bar{x}\right) - \left(\frac{\bar{p}-1}{\bar{x}-1}\right)(\bar{x}+x_\alpha-2) \right\} \\ & - \ln v_\alpha/x_\alpha - S^2 x_\alpha v_p^2/2\Theta + \ln f_\alpha^1 \end{aligned} \tag{2.36}$$

In the isotropic phase $S = 0$ and the chemical potentials are still given by equations (2.24) and (2.25) for the athermal limit. Using the chemical potentials derived above allows us to proceed to a discussion of phase equilibria in rod mixtures.

3. NUMERICAL RESULTS

The solution of simultaneous conditions for equality of chemical potential for each component in the various phases has been referred to already for the athermal limit. The variation of the biphasic region with axial ratio was shown in Figure 2. When soft forces between molecules are considered, temperature and composition can both be varied. For a given rod species with axial ratio x we can study the

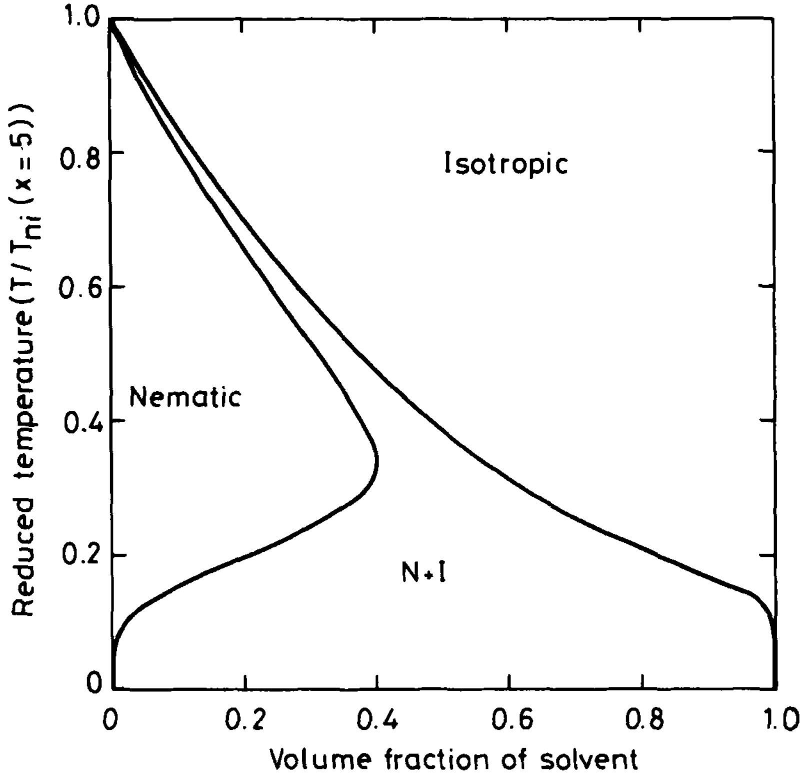

FIGURE 3 Equilibrium of rods of axial ratio $x = 5$ with simple solvent. Temperature is scaled by the nematic-to-isotropic transition temperature for a neat fluid of these rods. The phase diagram opens in an extreme manner on cooling.

effect for instance of dilution with simple solvent ($x = 1$) and of variation of temperature. This is shown in Figure 3 for rods with $x = 5$. Temperature is scaled in the theory by T^*, the strength of the interaction (T and T^* appear in all expressions of section 2 as T/T^*). Estimates of T^* exist in the literature[7] but we circumvent the need to know T^* by reducing all temperatures by a known temperature $T_{ni}(x = 5)$, the transition temperature for the pure $x = 5$ system to go from the nematic to isotropic state. In Figure 3 we see the typical opening out of the phase diagram found for instance by Warner and Flory.[5] The effect appears heightened here since we are not plotting

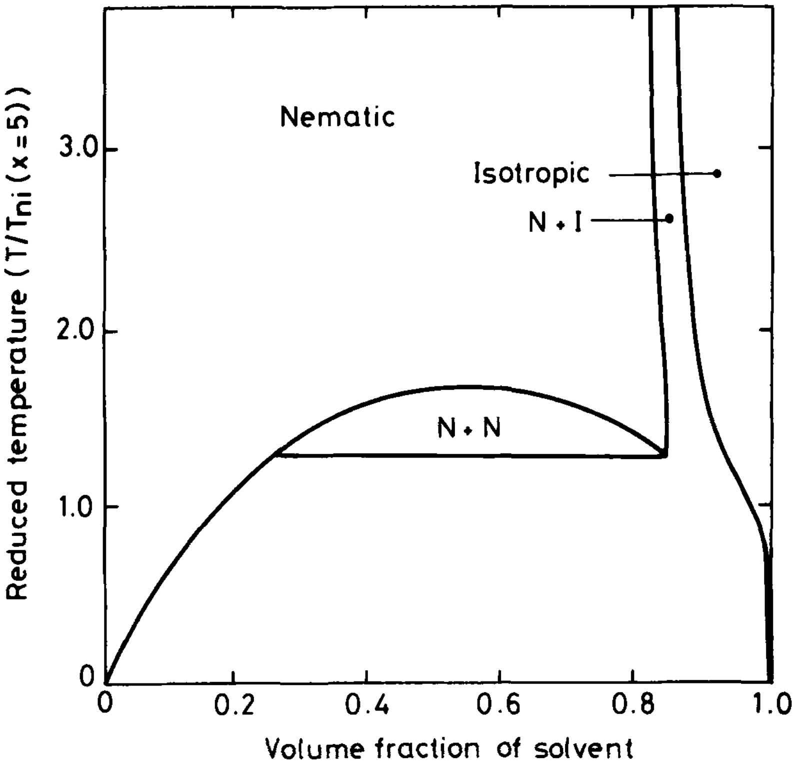

FIGURE 4 Equilibrium of rods of $x = 50$ with simple solvent. For comparison temperature is scaled in the same way as in figure 3, that is, by the transition temperature of the neat $x = 5$ system. The narrow biphasic region opens on cooling to give two possible pairs of phases. The first (labeled N + I) is highly fractionated, rods being almost completely expelled by the solvent in the isotropic phase, solvent being expelled by rods in the nematic phase. The second (N + N) consists of two nematic phases coexisting. Both are highly ordered since these are long rods, for example at a reduced temperature of 1.41 the phase richer in rods has an order parameter of $S = 0.995$, the poorer, $S = 0.943$. The richer phase is essentially aligned.

reciprocal temperature and, as temperature is lowered, rods are strongly expelled from the isotropic phase (the solvent volume fraction tends to 1). Thus at a rod volume fraction of 70%, for instance, lowering temperature from an initially isotropic single phase state will lead firstly to nematic–isotropic biphasic equilibrium, then to a single nematic phase and finally again to biphasic equilibrium with large degrees of fractionation.

Mixtures of rods with $x = 50$ and a solvent ($x = 1$) produce the phase diagram of Figure 4. Temperature is again reduced, for comparison with the above mixture, by the transition temperature $T_{ni}(x = 5)$. In practice it is not possible to progress in a homologous series of rigid rods over a factor of 10 and so $T_{ni}(x = 5)$ would not provide a specially significant scaling factor. Again the nature of the plot emphasises the strong fractionation at low temperatures. The remarkable features of nematic–nematic equilibrium, a triple point and a critical point reported earlier[5] are also found here. The experiments of Miller *et al.*[8] show that phase diagrams of this character are indeed found for long rod systems.

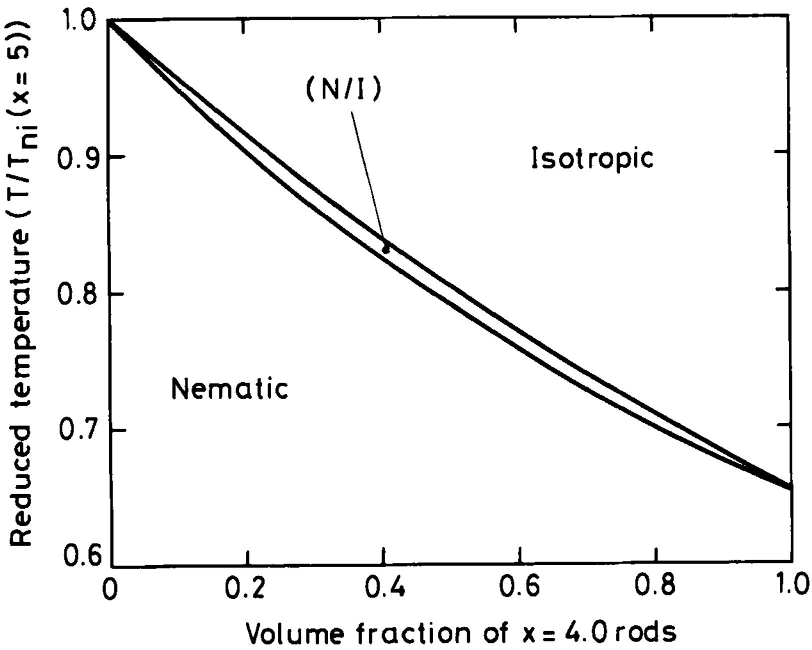

FIGURE 5 Equilibrium of rods of $x = 4$ with rods of $x = 5$. Temperature is reduced by the quinquephenyl transition temperature. This pair of components is approximately a model of quater-quinquephenyl mixtures. Composition is measured by the volume fraction of quaterphenyl.

Mixtures of rods with axial ratio x_α with rods x_β can also be described by the expressions in section 2 for μ, the chemical potentials. We consider here rods of the same homologous series so that their structural elements, the segments, can be considered to interact via anisotropic dispersion forces characterized by one interaction strength T^*. An example is given in Figure 5 of rods of $x = 5$ mixed with rods of $x = 4$. The temperature plotted is reduced by the transition temperature of the $x = 5$ neat phase, $T_{ni}(x = 5)$. The phase diagram is a thin lense of biphasic equilibrium separating nematic and isotropic single phase regions. As an example of mixing two members

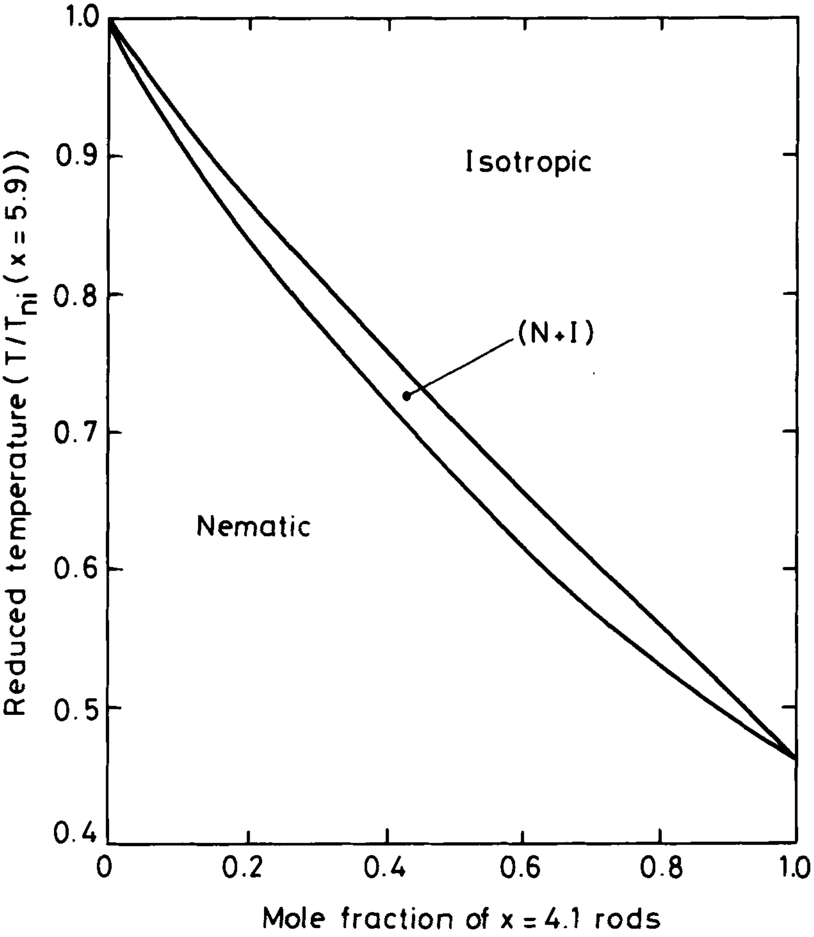

FIGURE 6 Equilibrium of rods $x = 4.1$ with rods $x = 5.9$. Temperature is reduced by the transition temperature for the $x = 5.9$ species. These rods are a model of quater-sexiphenyl mixtures. Composition is measured by mole fraction of quaterphenyl.

of a homologous series we turn in Figure 6 to mixtures of $x = 5.9$ with $x = 4.1$. These two systems are models of sexiphenyl and quaterphenyl, chosen before[2,4,5] because the family of homologues are relatively stiff and differ one from the other substantially only in their lengths. The structural units are, roughly speaking, the phenyl groups. Temperature is now reduced by $T_{ni}(x = 5.9)$ and composition is mole fraction of quaterphenyl. Again a lense-like figure is obtained. Such phase diagrams are of considerable importance since in the pure systems $T_{ni}(5.9)$ is obscured by the effects of decomposition[9] and $T_{ni}(4.1)$ by the prior transition to the crystal by the isotropic liquid. Thus Figure 6 would represent a stringent test of theory if it were to be measured. If the assumptions of uniformity of T^* throughout the series are correct,

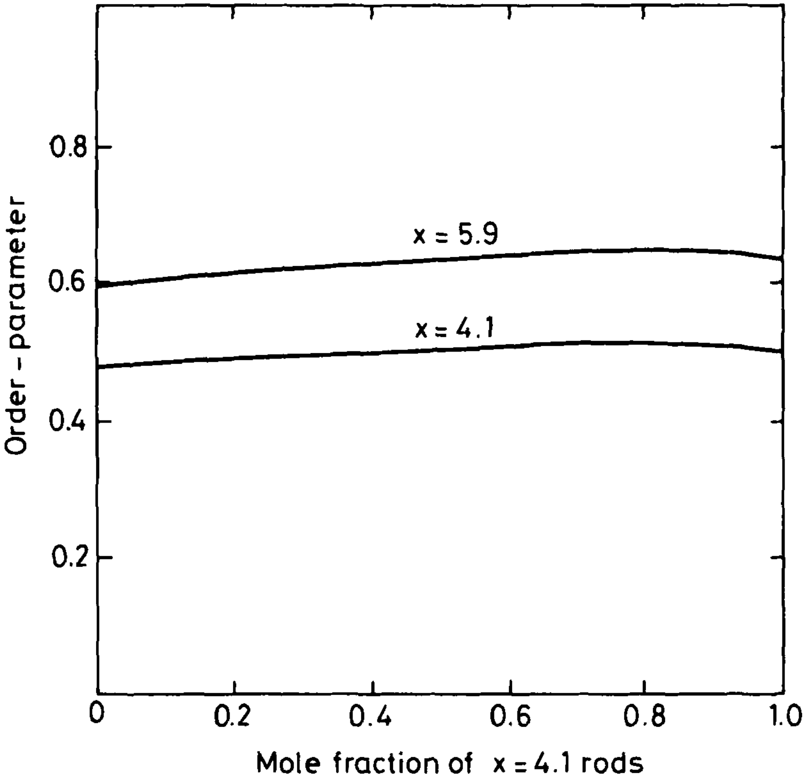

FIGURE 7 Order-parameters of the $x = 4.1$ and $x = 5.9$ rods in the nematic phase of their biphasic equilibrium. The state of order of the rod components is almost constant as we pass across Figure 6. The measured order-parameter is the average of these two values, weighted by their mole fraction. Therefore, as we go through a factor of two in temperature we would predict an almost constant order-parameter in the mixture of Figure 6.

then one could instead reduce the temperature scale by T_{ni} for quinquephenyl in which case there are no surviving parameters within the description of sexi-quaterphenyl mixtures. Preliminary investigations have been carried out[10] on quinque-quaterphenyl mixtures. The results suggest that the slopes of Figure 5 at the quinquephenyl end are too great but uncertainties in the measurement and the narrowness of the accessible temperature region preclude any accurate comparison.

To conclude we plot in Figure 7 the values of the order-parameters for the sexiphenyl and quaterphenyl rods in their mixtures at the biphasic equilibrium points of Figure 6. As one would expect, in the nematic phase, the longer rods have a higher characteristic degree of order than the shorter rods. The measured order-parameter will be an average of the two values weighted according to the mole fraction and will therefore change little over the temperature range of Figure 6. This is in contrast to one component variations shown in Figure (4) of reference 4.

Summary

We have generalized a new theory of the dense packing of rods to a description of the phase equilibrium of rod mixtures. Free energies and chemical potentials for many components in either nematic or isotropic fluids were obtained. They were used to solve the two component problems of rods mixed with simple solvent or of rods of one species mixed with rods of another species with different axial ratio. The motivation was partly to examine the influence of temperature on lyotropic systems and partly to look at equilibria in mixtures within a homologous series of rods as a more stringent test of theory than a one component system can offer. As a preliminary the variation of biphasic equilibrium with axial ratio in the athermal limit was also calculated.

Our results show that temperature has a rich influence on lyotropic liquid crystal phase diagrams. Rods of moderate length diluted by simple solvent exhibit a re-entrance of nematic-isotropic biphasic equilibrium on cooling. Long rods show a triple and critical point and the three types of biphasic equilibrium anticipated in earlier work.[1,5]

Thermotropic rods diluted by other rods, both species being shorter than the critical axial ratio x_{crit}, display lense-shaped phase diagrams. We present results for models of mixtures of various polyphenyl homologues. These compounds have previously been chosen as models[2,4] for their molecular symmetry and stiffness and for the simplicity of their soft interactions. Clear predictions are made for the phase diagrams of quater-, quinque- and sexiphenyl mixtures.

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