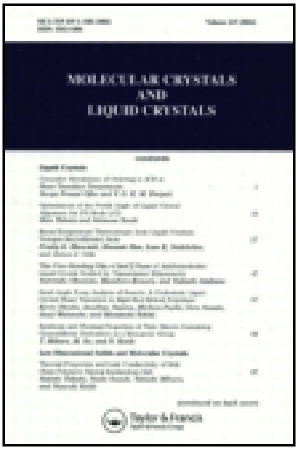

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The Specification of Steric Effects in The Flory Approach to Nematic Fluids

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The Specification of Steric Effects in The Flory Approach to Nematic Fluids

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A minor refinement of the steric influences in Flory's Statistical Mechanics of liquid crystals is presented. The results of Flory and Ronca and of Warner and Flory are recalculated, that is, the critical axial ratio of rods in the athermal limit, and, for thermotropic rods, the entropy and order at the transition, the transition temperature as a function of axial ratio and finally the phase equilibrium for mixtures of model nematogens. Comparison with experiments on such model systems shows that some improvement is obtained.

INTRODUCTION

There is, now, ample evidence that both[1-4] steric and anisotropic attractive interactions are necessary to describe the isotropic to nematic transition in a rod fluid. Thermotropic liquid crystals form the example of where both influences are in a fine balance. Such molecular rods are generally short enough that steric effects do not totally overwhelm the soft interactions. Axial ratios for these rods fall into the range 3 to 6.

We examine more closely the specification of steric hindrances for these interacting short rod systems within the classic theory of Flory,[5] recently refined[6] and extended to include angularly dependent soft interactions.[7] Flory's lattice theory should work best for the dense systems of rods of moderate length. Our aim is to look at the effect of a minor respecification of the steric obstruction (within mean field theory) one rod presents to another in the Flory approach. The restriction of configurational freedom resulting from the interference of misaligned rods controls the nematic to isotropic transition. In particular the effective hindrance presented by a rod when it is perceived by another from end-on is most critical for short rods, that is for rods where the cross-section has a lineal dimension a significant fraction of the rod length itself. For short rods the relative stability of the isotropic and ordered phases is found to be sensitive to the inclusion of such end effects. Important quantities such as the minimum axial ratio required to get an ordered phase in the absence of soft forces (the athermal limit), and the transition temperatures and latent entropies within an homologous family of nematogens will be presented. The critical axial ratio in the athermal limit turns out to be 8.75 in our calculation (to be compared with 6.4 of Flory and Ronca[6]). Experimental evidence on this point including the phase equilibria of rod mixtures is discussed.

Other lattice approaches (see Alben[8] and Cotter[9] for discussions of alternatives and more recently Dowell and Martire[10] and references therein) differ principally from the Flory theory in that they do not contain his prescription for allowing the transition to a continuum of rod orientations. The physical consequences of this restriction have been criticized and contrasted[6,11] with those of allowing fuller rod freedom. Since the above mentioned end effects relate to the transition to the continuum we limit our discussion to the Flory approach.

STERIC INTERACTIONS AND THE ANGULAR DISTRIBUTION OF RODS

Disorder in rod orientations with respect to the preferred axis (director) of the nematic is limited in a dense system by the requirement that overlap of molecules be avoided. Implications of this for the steric part of the partition function were calculated by Flory in his initial investigations of such fluids by means of a lattice. The crucial idea is then to represent a rod at a given inclination to the director by a *suitable* number y of sequences (each of x/y segments) parallel to the director, each sequence being laterally displaced one unit from the prior sequence. y relates to the projection of the molecule onto the plane perpendicular to the director and depends on a prescription for assigning continuous orientations to a lattice. The combinatorics of putting molecules into the lattice express the rod-like nature of the molecules and are at once solvable.

Clearly, perfectly aligned rods are represented by 1 sequence of length x (with $y = 1$). Such rods present the minimum hindrance to the deposition of other rods and contribute 1 to the mean field of disorder $\bar{y}$, the average value of y, appearing in the lattice calculation.

Although y takes discrete values in the lattice it is later allowed to vary continuously in accord with the actuality of such systems. The angle a rod makes with the director, ψ, is naively related to y by $y = x \sin \psi$. More exacting treatment[6] gives

$$y = 4/\pi \, x \sin \psi \qquad (1)$$

This suitable number of sequences required to represent the rod is constructed by Flory and Ronca[6] by projecting a *line* (representing the rod axis) at an angle ψ onto the perpendicular plane of the director and then assigning the projection to lattice squares ($4/\pi\, x \sin \psi$ on average). Small values of $\psi (\equiv y < 1$ in (1)) are assigned to $y = 1$ for the purposes of lattice combinatorics and subsequently revert to small angles ψ (with finite weight $\sin \psi d \psi$) for later analysis. What relation (1) neglects is that associated with the axis line is a finite cross-section which also has to be projected and will additionally contribute so that the number of lattice squares, and hence y, is always greater than 1 ($= 1$ at $\psi = 0$). For large x this neglect is irrelevant since the variation with ψ and x, that is $4/\pi\, x \sin \psi$, is what dominates physically.

Since the projection of the molecule onto the perpendicular plane is what determines the mapping of molecular configurations onto the lattice representation (y), we argue that projection of a spherocylinder gives a more realistic representation of a mesogenic molecule than projection of a line does. These commonly considered models would then give

$$y = 4/\pi\,(x - 1) \sin \psi + 1 \tag{2}$$

for the division of the molecule into y sequences. Equation (2) is consistent with the above observation that molecules with perfect orientational order ($\psi = 0$) present the minimum obstacle of $y = 1$ to the deposition of other molecules in the lattice. This state of perfect liquid crystalline order ($\psi = 0$ but disordered centers of mass) now has zero weight in the continuous representation ψ. Since we are simply describing rotations in 3-D there is no particular reason to preserve this state on the transition to a continuous description in contrast to the $k = 0$ state in the Bose fluid or the state of crystalline order for simple particles. That the state $y = 1$ is considered in the lattice calculation is due to the assignment in Eq. (2) of molecules with $\psi \gtrsim 0$ (so that $y \gtrsim 1$) to the value $y = 1$ just as molecules with ψ such that $y \sim 2$ (greater and less than) are assigned to $y = 2$ and so on. The precise assignment is not important since analysis is performed by reversion to the $\{\psi\}$ where the states with small but finite ψ recover a finite weight.

Prescription Eq. (1), in assigning states in the interval of ψ corresponding to $y = (0, 1)$ to the value $y = 1$ in the lattice (to account for the small ψ states in projecting a line) and thereafter giving them finite weight, implies a great importance to these states because of the exponential nature of the distribution function.[6] By contrast Eq. (5) below indicates that a minimum value of 1 for y in the projection of a spherocylinder puts more emphasis in the wings, that is, the states of relatively high alignment are less favored than suggested by Eq. (1) because even molecules with $\psi \sim 0$ have an appreciable steric effect. An immediate consequence of Eq. (3) is that for short rods (with x not very much greater than 1) the values of y in the anisotropic phase ($y \gtrsim 1$) are not very much less than the average $\bar{y} = x$ found in the isotropic phase. Thus the relative stability of the two phases is effected by the adoption of Eq. (3) instead of Eq. (2) and becomes apparent in, for instance, the values of x_{crit} and $\bar{y}_{\mathrm{crit}}$ presented below for the athermal transition. The present value of x_{crit} is greater than that of Ref. 6, reflecting the reduced stability of the nematic phase with respect to the disordered phase.

DERIVATIONS OF THE EQUILIBRIUM EQUATIONS

The lattice combinatorics are the same as Flory and Ronca,[6] as is the treatment of soft forces[7,12] and hence the resulting equations are quoted only where they differ as a result of adopting Eq. (2).

The n-1 sine moment of the distribution function are the $\{f_n\}$ which are now

$$f_n = \int d\psi \ \sin^n \psi \exp(-\alpha(x-1) \sin \psi - \tfrac{3}{2} x \, \theta^{-1} \, s \, v_x \sin^2 \psi) \qquad (3)$$

ν_x is the volume fraction of rods, s the order parameter $\langle P_2 \rangle$ and $\alpha\left(\equiv \frac{4}{\pi} a\right)$ is $-4/\pi \ln(1 - \nu_x(1 - \bar{y}/x)$. $P_2(\cos \psi)$ is $-\frac{3}{2} \sin^2 \psi$ to within constants. Soft interactions between rods are represented by a mean field proportional to s. θ is a reduced temperature[12] related to T of Ref. 7 by $\theta = \tilde{T} x$.

The mean field of disorder $\bar{y}$ is now given by:

$$\bar{y} = \frac{4}{\pi}(x-1) f_2/f_1 + 1 \qquad (4)$$

The distribution of orientations n_ψ, by analogy[7,12] is

$$\frac{n_\psi}{n_x} = f_1^{-1} \sin \psi \exp(-\alpha(x-1) \sin \psi - \tfrac{3}{2} x \, \theta^{-1} s \, v_x \sin^2 \psi) \qquad (5)$$

(all additional factors resultant on the adoption of (2) being absorbed into the normalisation).

The free energy G for the anisotropic phase now has the term $+an_x$ additional to that of Ref. 12 reflecting the now greater difficulty of inserting a rod when the others are highly ordered ($y \sim 1$). G for the isotropic phase is unchanged. The appropriate derivatives of the G give the 4 chemical potentials μ_s and μ_x (of solvent and rod respectively) for the anisotropic and isotropic phases. Only $\mu_{x_{\mathrm{aniso}}}$ is altered (by the additional term $+a$). Equilibrium conditions from equating free energies (neat fluid) or chemical potentials (mixtures) are similar to in Warner and Flory[12] and are solved in the same manner.

SOLUTION OF THE EQUILIBRIUM EQUATIONS

The Athermal Limit

We consider a neat rod fluid ($v_x = 1$) in the limit of zero soft interaction. Equating the isotropic and anisotropic values of G gives the condition for the critical axial ratio, x_{crit}:

$$a + \bar{y} - x - \ln f_1 = 0 \tag{6}$$

to be simultaneously satisfied along with Eq. (4) for $\bar{y}$ and (3) for f_n (with $\theta^{-1} = 0$). (Results in upper row of table below.)

The solution also gives the disorder $\bar{y}_{crit}$ and the order parameter s_{crit} for the critical system. In the following table the lower row represents the consequences of Eq. (1). Notice that now the value of $\bar{y}_{crit}$ is much larger than before as a result of $y_{min} = 1$. Even the scaled version is greater ($\bar{y}_{crit}/x_{crit}$). The significance of the increased value of x_{crit} is examined later.

x_{crit}	$\bar{y}_{crit}$	$\bar{y}_{crit}/x_{crit}$	s_{crit}
8.7536	2.8287	.32314	.9216
6.4166	1.2445	.19394	.9473

Thermotropic Rods

Finite values of the interaction and hence of θ^{-1} allow the possibility of nematic states for rods with $x < x_{crit}$. Equating the free energies of disordered and ordered phases now gives:

$$\theta = \frac{xs(1 - s/2)}{\bar{y} - x + a - \ln f_1} \tag{7}$$

(a condition for the reduced transition temperature). Equation (7) is solved simultaneously with the relations defining s, $\bar{y}$ and the f_n. The variation of reduced transition temperature (θ_{ni}), the order parameter at the transition (s_{crit}) and the reduced latent entropy (S_{ni}/k_B) as functions of the axial ratio are given in Figures 1, 2 and 3 respectively.

Thermotropic Rods in Dilution

We do not present results for thermotropic rods diluted with a simple solvent[12] ($x = 1$) but concentrate on mixtures of rods of axial ratio x_α with a homologue x_β. This is because the model system of thermotropic rods hitherto considered,[7,12] the polyphenyls, are only weakly soluble in simple solvents although homologues are miscible. The generalization of s, $\bar{y}$ (to $\bar{y}_p$, the number weighted disorder field), the f_n, the distributions, free energies and potentials is

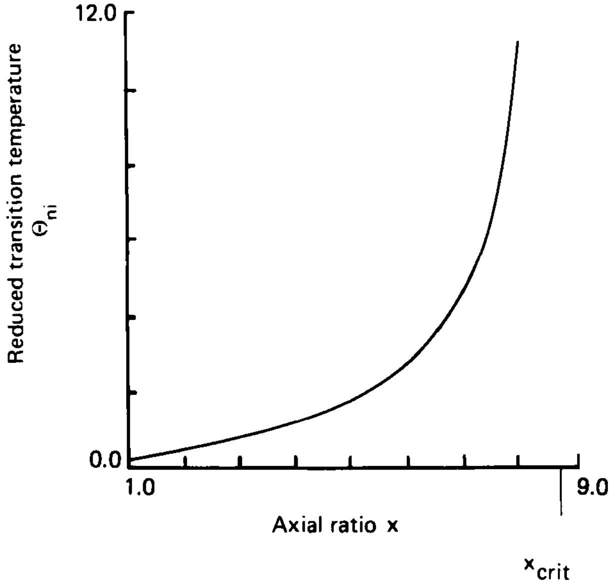

FIGURE 1 Reduced transition temperature θ_{ni} is plotted against axial ratio x. The athermal limit is shown as x_{crit} (= 8.75).

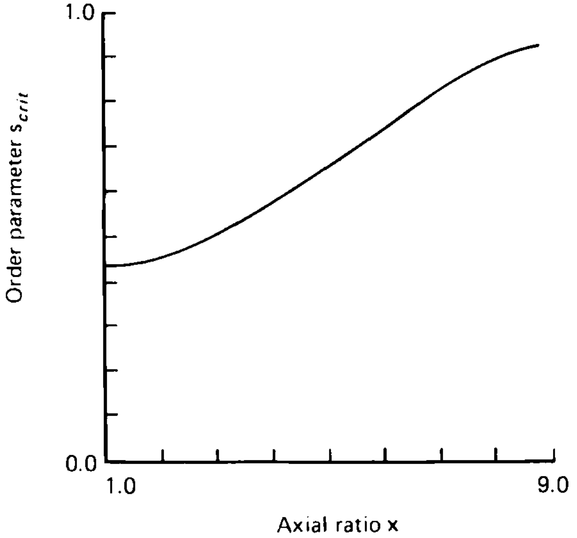

FIGURE 2 Order parameter at the transition s_{crit} is plotted against axial ratio.

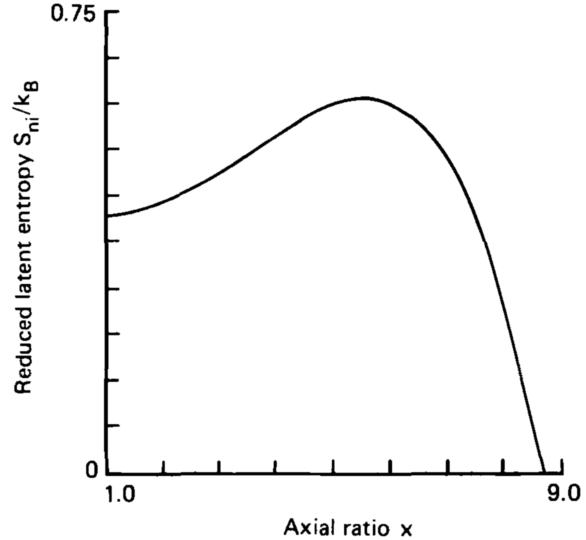

FIGURE 3 Reduced latent entropy S_{ni}/k_B is plotted against axial ratio.

analogous to that of Warner and Flory.[12] In anisotropic phases the free energy has the additional term $n_p a$ and the chemical potentials the term a. n_p is the total number of segments and a is now $-\ln(\bar{y}_p/\bar{x})$ with $\bar{x}$ the number weighted axial ratio.

The phase diagram for an $x = 5$, $x = 4$ mixture has been calculated by equating chemical potentials and using the appropriate self consistency conditions on s and $\bar{y}$. In Figure 4 reciprocal reduced temperature is plotted against volume fraction of the x_5 rods (as the composition variable). It is more appropriate to reduce temperatures by an experimental temperature, for instance the transition temperature of the x_5 species ($T_{ni(5)}$), and to use mole fraction as the composition variable (see Figure 5).

DISCUSSION OF THE RESULTS

The polyphenyls, which we shall take as model molecules, have been discussed by Flory and Ronca.[7] They argue that, although the phenyl group departs from cylindrical shape about the axis defined by the molecule as a whole, random staggering of the orientation of each group about this axis makes the molecule effectively cylindrical. Thus a mean diameter of 4.8 Å is taken for the cylinders representing these rodlike homologues.

Recent measurements of T_{ni} for quinquephenyl give 417°C[13] or 410°C.[14,15] This allows us to set the energy scale T^* by which all temperatures are reduced

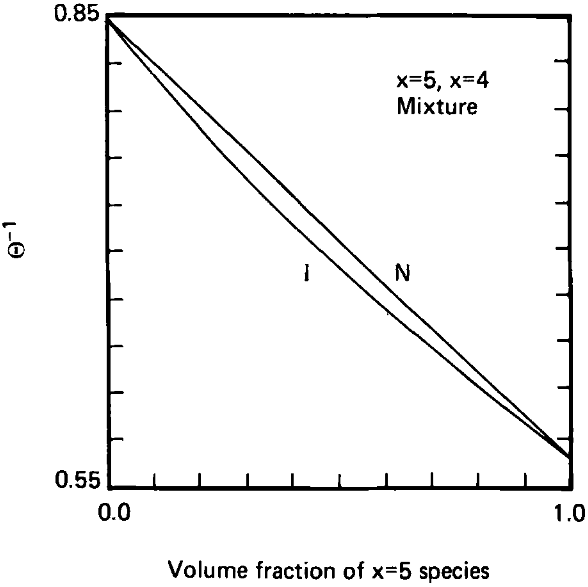

FIGURE 4 The phase diagram for a mixture of rods of $x = 5$ with $x = 4$. Reciprocal reduced temperature θ^{-1} is plotted against volume fraction of the $x = 5$ species as composition variable. These are the natural variables of the calculation.

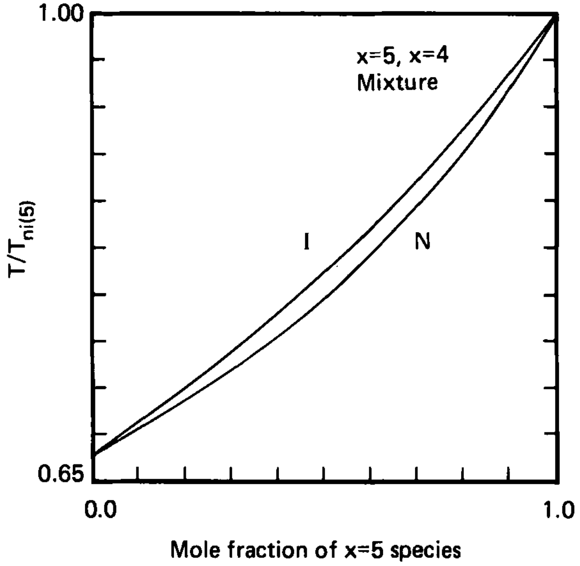

FIGURE 5 The phase diagram for a mixture of rods of $x = 5$ with $x = 4$. Temperature, reduced by the transition temperature $T_{ni(5)}$ (of the $x = 5$ species alone) is plotted against mole fraction of the $x = 5$ species. This diagram is proposed for mixtures of quinque- and quaterphenyl. The variables chosen here are more natural experimental variables than those of Figure 4.

($\theta = T/T^*$). Taking the result for $x = 5$ one gets for $T^*(= T_{ni,\,\mathrm{expt}}/\theta_{ni,\,\mathrm{calc}})$ 388°K. Our T^* is greater than that obtained by using relation Eq. (1) for the steric hindrance. The shift to larger values is reasonable since adoption of Eq. (2) (i.e. $y \geq 1$) makes the ordered phase less stable w.r.t. the disordered phase than formerly and a corresponding increase in the soft forces is required in compensation.

The energy scale now fixed, other transition temperatures are predicted, for instance $T_{ni(4.1)} = 202$°C and $T_{ni(5.9)} = 681$°C (the axial ratios taken to correspond[7] to quater- and sexiphenyl respectively). The former transition is masked by the crystallization of quaterphenyl at 320°C; the latter is difficult to observe since the stability of sexiphenyl at such elevated temperatures is questionable. The high temperature behavior of sexiphenyl has been investigated[16] and reveals first a smectic-A phase followed at higher temperatures by a nematic phase. Experiments suggest[17] a nematic to isotropic transition at 520°C.

In fact the experiment that most closely corresponds to the calculation being discussed is that performed at constant volume. McColl and Shih[4] discuss the effect of constancy of volume in elevating the transition temperature. Thus stability and volume considerations imply that $T_{ni(6),\,\mathrm{expt}}$ of 520°C is a lower limit.

A guide[7] to locating the athermal limit is this sequence of transition temperatures $T_{ni(x)}$ (Figure 1, the absolute scale is fixed by $T_{ni(5)}$). The proximity[17] of $T_{ni(5.9),\,\mathrm{expt}}$ with $T_{ni(5),\,\mathrm{expt}}$ (a difference of only 100–200 C°) indicates that $x = 5$ and $x = 5.9$ are not on a steep part of Figure 1, that is, the athermal limit is well above 6.4. By contrast (1) (which gives 6.4 for the athermal limit) predicts $T_{ni(5.9)} = 1900$°C upon fixing the scale with quinquephenyl.

The inaccessibility of $T_{ni(4)}$ and the difficulties associated with measuring $T_{ni(6)}$ suggest that one examines mixtures as a test of the theory. $T_{ni(5)}$ is still used to fix the energy scale. All other features should then be consequences of the theory. One can thus consider the slope of the phase diagram (Figure 5) as a crude measure of $T_{ni(4.1)}$. Thus experiments to determine this phase diagram would clarify the nature of Figure 1 (the variation of the transition with axial ratio) and ultimately x_{crit}. In Figure 5 we approximate quaterphenyl by $x = 4$. The initial slope of the nematic phase line is an observable quantity. Our value is approximately .56. The phase diagram has been measured[18] and suggests a smaller value than this for the slope. By contrast Warner and Flory[12] obtain a slope roughly twice the present result. Provisionally a lowering of the slope suggests that we have an improved estimate for x_{crit}.

The latent entropy S and the order parameter at the transition s_{ni} are related by

$$\frac{S}{k_B} = \tfrac{1}{2}\, xT^*\, s_{ni}^2/T_{ni} = \tfrac{1}{2}\, x\, \theta_{ni}^{-1}\, s_{ni}^2 \tag{8}$$

Thus a discussion of S is related to one of s and θ_{ni}, as indeed the failure of the mean field to differentiate between long and short range order demands.

Smith[13] gets a value of .1612 for the reduced latent entropy of quinquephenyl. The present theory predicts the much greater value:

$$\frac{S}{k_B} = .5988$$

The agreement is worse than these figures suggest since correction to constant volume (by use of $\gamma = (\partial P/\partial T)_v = (\partial S/\partial V)_p$) would further reduce the experimental value. Correspondingly the value of $\langle P_2 \rangle$ at the transition (i.e. s_{ni}) obtained here (.649) is higher than the values measured by Sherrell and Crellin[15] (.325) or Wallis and Roy[19] (.28).

These discrepancies point to the seriousness of neglecting short-range order and, consequently, underestimating the influence of soft interactions in rod fluids. In a discussion of the magnitudes of soft forces in nematogens Warner[3] suggests that rods in contact with another have angular freedom roughly that of rods rotating in 2-D. Thus in a dense disordered rod fluid, even in the absence of soft aligning forces and many-rod steric effects, the restriction of rotational freedom because of steric hindrance would provide a "local" value of s of $\frac{1}{4} (\int d^2\,\Omega P_2(\Omega) = \frac{1}{4})$. We refer here to the average of orientations of one rod with respect to a neighbor and not to a long-range order. A crude lower bound of the extent to which this local order effects the thermodynamics can be made: in a fluid with no long-range order the residual local order remaining from the hindered rotation is roughly (using Eq. (8) with $s_{\text{resid}} = \frac{1}{4}$)

$$\frac{\Delta S_{\text{resid}}}{k_B} \sim \frac{1}{2}\, x\, \theta_{ni}^{-1} \left(s_{\text{resid}} = \frac{1}{4} \right)^2 \tag{9}$$

With soft interactions the residual local value of s in the isotropic fluid (to be used in the above relation) is further enhanced—configurations of the rotating rod w.r.t. a fixed rod are weighted by the factor $\exp(-\frac{3}{2}\, x\, \theta^{-1} \sin^2 \psi)$. the interaction is no longer between a rod and the mean field, that is $-\langle P_2 \rangle P_2(\cos \psi)$ where ψ is the angle with respect to the director defining the long-range order, but is the form experienced between pairs of molecules—$P_2(\cos \psi)$ when ψ is now the angle between the pair of rods concerned (see for instance Zannoni[20] for an example of a non-mean field use of the potential, that is the absence of the s term in the potential). The absence of the sin prefactor expresses the local 2-D character of the rotations.

s_{resid} is then given by

$$s_{\text{resid}} = \frac{\displaystyle\int_0^{\pi} d\psi \,\{1 - \tfrac{3}{2} \sin^2 \psi\}\, e^{-3/2\, x\, \theta^{-1} \sin^2 \psi}}{\displaystyle\int_0^{\pi} d\psi\, e^{-3/2\, x\, \theta^{-1} \sin^2 \psi}}$$

$$= \frac{3}{2} I_1 \left(\frac{3x}{4\theta}\right) / I_0 \left(\frac{3x}{4\theta}\right) - \frac{1}{2}$$

where I_n is the nth order Bessel function of imaginary argument. Tables of standard functions give $s_{\text{resid}} = .473$ (for $x = 5$ and $\theta = \theta_{ni(5)} = 1.759$), a result much enhanced over the steric value of $\frac{1}{4}$. For a Maier-Saupe system on a lattice, that is where there is no steric inducement of local order, computer simulations[20] also record finite values of a "local" P_2. The correlation function is defined as it is here, that is, $\langle P_2(\Omega_{12})\rangle\ \Omega_{12} = \sigma(r_{12})$ where the average is over the relative orientations Ω_{12} of the rods 1 and 2. r_{12} is put equal to the nearest neighbor spacing.

Subtraction of the residual entropy (implied by Eq. (9) and the above-estimated residual order remaining in the isotropic fluid) from the latent entropy derived within mean field theory (which assumes the short-range order is the same as the long-range order) gives $S/k_B = .28$ for the latent entropy of quinquephenyl. The reduction in entropy due to pairwise restrictions on rotational freedom is of course a lower limit. Consideration of a rod and at least two of its nearest neighbors shows that collective hindrances will produce stronger local order than that derived above for pairs (even in a rod fluid well above its ordering temperature). Such local correlations enhance the depolarized light scattering from the isotropic phase. We refer here not to the enhancement due to incipient long-range order as the transition is approached,[21] but to the situation at higher temperatures where the effects are purely local.

CONCLUSIONS

Modification of the relation between orientation ψ and the hindrance field y used in the Flory calculation of the configurational partition function for rod fluids is shown to produce a higher axial ratio at the athermal limit. The rods are now "seen" even from end-on in the highly ordered state. The resulting reduction in the stability of the ordered state relative to the disordered is reflected in the increase in the transition temperatures of thermotropic rods of varying aspect. More importantly the present modification changes the slope of the temperature-composition phase diagram of quinque-quaterphenyl mixtures in the direction indicated by experiment.

The role of short-range order in the treatment of internal energy is discussed. It is proposed that the neglect of the considerable residual order in the isotropic fluid is partially responsible for the high value of the latent entropy implied by the mean field theory (which assumes no short-range order in the isotropic state). Subtraction of the contribution from ΔS_{resid} does not complete the agreement and it is clear by comparison with experiments[15,16] on the order parameter that further attention is required on this aspect of mean field lattice theories.

References

1. J. I. Kaplan and E. Drauglis, *Chem. Phys. Letts.*, **9,** 645 (1971).
2. A. Wulf, *J. Chem. Phys.*, **64,** 104 (1976).
3. M. Warner, *J. Chem. Phys.*, **73,** 5874 (1980).
4. J. R. McColl and C. S. Shih, *Phys. Rev. Letts.*, **29,** 85 (1972).
5. P. J. Flory, *Proc. Roy. Soc., Ser. A*, **234,** 73 (1956).
6. P. J. Flory and G. Ronca (I), *Mol. Cryst. Liq. Cryst.*, **54,** 289 (1979).
7. P. J. Flory and G. Ronca (II), *Mol. Cryst. Liq. Cryst.*, **54,** 311 (1979).
8. R. Alben, *Mol. Cryst. Liq. Cryst.*, **13,** 193 (1971).
9. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **35,** 33 (1976).
10. F. Dowell and D. E. Martire, *J. Chem. Phys.*, **68,** 1088 (1978), (are concerned with the effect of tail flexibility on the transition).
11. M. Warner, *Mol. Cryst. Liq. Cryst.*, **80,** 79 (1982).
12. M. Warner and P. J. Flory, *J. Chem. Phys.*, **73,** 6327 (1980).
13. G. W. Smith, *Mol. Cryst. Liq. Cryst.*, **49,** (letters), 207 (1979).
14. E. Clar, "Polycyclic Hydrocarbons" (2 vols), Academic Press, London (1964).
15. P. L. Sherrell and D. A. Crellin, *J. Phys. (Paris)*, **40,** C3-211 (1979).
16. I. C. Lewis and C. A. Kovac, *Mol. Cryst. Liq. Cryst.*, **51,** 173 (1979).
17. I. C. Lewis, private communication. The experiment was done over a short period of time in a quartz vessel under an atmosphere of N_2.
18. G. P. Wallis, Ph.D. Thesis, Cambridge University (1978).
19. G. P. Wallis and S. K. Roy, *J. Phys. (Paris)*, **41,** 1165 (1980).
20. C. Zannoni, Chapt. 9 of "The Molecular Physics of Liquid Crystals", ed. G. R. Luckhurst and G. W. Gray, Academic Press, London (1979).
21. G. R. Alms, T. D. Gierke and W. H. Flygare, *J. Chem. Phys.*, **61,** 4083 (1974).
22. C. Destrade, H. Gasparoux and F. Guillon, *Mol. Cryst. Liq. Cryst.*, **40,** 163 (1977).
23. Further experiments are in progress, P. J. Flory, private communication.