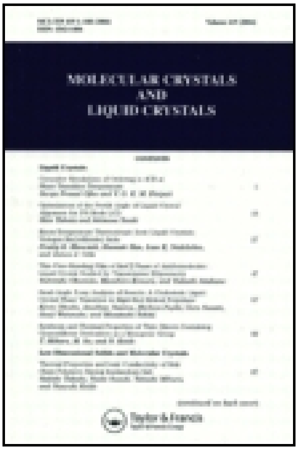

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A New Theory of the Equilibrium Properties of Nematic Liquid Crystals

M. Warner [a]

[a] Rutherford and Appleton Laboratories, Chilton, Didcot, Oxon OX11 OOX

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A New Theory of the Equilibrium Properties of Nematic Liquid Crystals

M. WARNER
Rutherford and Appleton Laboratories, Chilton, Didcot, Oxon OX11 OOX

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A new theory of nematics applicable to dense systems of rodlike particles is presented. The formulation endeavors to avoid the use of a lattice, steric effects involved in the dense packing of mesogenic molecules being treated in a manner consistent with this advance. The theory has many similarities with the well-known Flory approach and shares the same analytic simplicity.

The results of the theory give improved estimates of the athermal limit, the order parameter at the transition and the latent entropy for nematics.

INTRODUCTION

It is generally considered[1] that molecular shape and hardness of rodlike systems are the major factors determining fluid properties, a viewpoint in the equilibrium theory of simple liquids going back to van der Waals. Soft, attractive interactions merely provide the background sustaining the liquid density; the detailed atomic packing relates to shape alone. Thus the major problem facing a theory of nematics is to describe the dense packing of rods. Early theories[2] based on virial expansion are suited to dilute solutions of rods in solvents of no inherent mesogenic tendency. For shorter rod systems (axial ratio $x \lesssim 40$), tending to order under denser conditions, the packing problem is met head on and no resort to virial techniques may be made.[1,3]

Pioneering work on the dense packing problem was made by Flory[4] who formulated the problem on a lattice. He developed a technique wherein the rod is assigned to the lattice and yet retains the essential notion of partial rotational freedom for a rod in a fluid. The basic Flory method was extended and refined by Flory and Ronca[5] who made the specification of lattice properties more precise and answered certain physical objections.[3] This approach was the stimulus for the present theory. Work[6,7] subsequent to Flory's 1956 paper avoided his technique of representing rotational freedom, rods being restricted to lie in one of 3 or 5 principal lattice directions. It has been argued[5] that this gross restriction of rotational entropy has a severe effect on the physical results obtained. The present work, which allows continuous rotational freedom for the rods, confirms the assertion and we shall return to this in comparing our new theory with earlier work. As shall emerge however, this is only one of the difficulties in the lattice theories that is overcome by our investigation.

An attractive feature of all lattice theories of dense packing is their analytic tractibility (we retain that simplicity in what follows). However, instead of implementing the van der Waals picture via a lattice it is appealing to use the methods of classical liquid theory, for example those used for purely repulsive spherocylindrical model systems.[1] The results are encouraging but there still remains a degree of disparity, as in the lattice theories, between prediction and experiment. The order parameters and the latent entropy at the nematic to isotropic transition are both too high in each of the approaches mentioned above, and a strong motivation for what is to follow was to try to reduce these estimates.

Woo and coworkers[8] have made powerful application of conventional liquids formalism to systems where there is orientational order resulting from hard and soft forces. They obtain estimates of latent volume change unobtainable from the present work.

Although there exists clear physical grounds why the present theory predicts an ordered fluid with lower orientational order than hitherto predicted by "steric" theories, there however remains a most important element unaccounted for, namely, it is strongly suspected that a degree of responsibility for the discrepancy between theory and experiment lies in the neglect of short range order. In particular, previous estimates of the latent entropy of transition are 5 to 10 times too large indicating the neglect of short range order in the isotropic phase especially. Evidence for short range order appears in the great similarity between the x-ray diffraction patterns above and below the transition, indicating that the local structure is relatively unchanged. The extremely low values of $\Delta V/V$ (the fractional volume change on transition), typically a few parts in a thousand for nematics, adds further weight to the argument. (The low values of $\Delta V/V$ and a knowledge of the thermodynamic coefficient $(\partial E/\partial V)$ show further that volume changes cannot be the driving force of the transition.) Alben[9] has argued convincingly about the importance of considering short-range order in any estimation of the configurational entropy involved in rod packing.

Theories of the transition based purely on the soft forces (in the original form by Maier and Saupe[10]—referred to as M-S), which neglect shape effects, give good quantitative agreement with the order parameter at the transition. However, the fitted value of the coupling constant turns out to be much too large and its volume dependence unphysical; the temperature dependence of the order parameter is also incorrect. To account for some, or all, of these failings still more parameters can be introduced[11,12] as the coefficients of higher terms in the expansion of the potential in even order Legendre polynomials. This is somewhat phenomenological. The use of several terms in the expansion of the potential *and* the use of clusters to enhance the mean field nature of the calculation has also been attempted.[13] On the other hand, computer simulation[14] confirms that it is not the use of mean-field approximation that alone can account for the short-comings listed above. It is rather the underlying neglect of steric forces. Short range order stemming from the spatial requirements of the dense packing of rods has been invoked[15] in an attempt to go beyond the empirical nature of the above mentioned soft force theories (for instance to provide an explanation of the large value of the coupling constant required). This was implicitly the motivation of Ref. 13 but it is the author's belief that the basis of nematic theory must be explicitly steric as in Refs. 1, 2, 4–9.

In what follows we present a new theory of nematics and the transition to the isotropic state. The theory, in calculating the number of ways of placing hard rods into a limited volume, derives much from the Flory approach. What is new is that the steric constraints of the other rods are handled in a way that is consistent for both the component of rods lying parallel and transverse to the director. The same requirement of consistency is what had prompted the theories[6,7] allowing the rods to adopt only a limited number of (principal) directions. Further, we argue in Appendix A that it is possible to avoid the use of a lattice in calculating the configurational freedom of the rod assembly. The appearance of a continuum of rotational states is thus immediate and is exploited throughout the paper—in particular the form of the above-mentioned steric constraints is a natural consequence of the method.

The most striking result of our theory is that the isotropic state is more stable than estimated by previous theories which therefore alters the balance between the ordered and disordered states. Consequently the predicted limiting athermal axial ratio, x_{crit}, is greater (8.99), and the order parameter and latent entropy at transition less, than hitherto. The achievement of these three goals and the related effect on phase diagrams was the principal motivation for the theory.

2 A NEW THEORY OF ROD-LIKE SYSTEMS

The configurational and orientational partition functions for an assembly of rods will be calculated in both the athermal and then the thermotropic limit (the absence and presence of soft, angularly-dependent forces). That the former function (representing the positional freedom) is inextricably coupled via shape effects to the latter (orientational freedom) is the essence of the liquid crystal problem. With the resulting expression for the free energy the distribution function of rod orientations will be derived and thus the actual free energy and order of both the nematic and isotropic states determined.

In the athermal limit the total number of ways of inserting n_x rods of axial ratio x and n_s solvent molecules into a limited volume will give the configurational partition function. The assumptions, also made in lattice theories of simple and polymeric mixtures and in lattice theories of liquid crystals, that free volumes before and after mixing remain the same and that the size and structure of the basic unit of solvent and solute are identical means that the total volume (n_o) is given by

$$n_o = xn_x + n_s$$

(where volume is measured in terms of the volume of a basic unit, i.e. a solvent molecule).

The justification for extending the class of results obtained by Flory and others from a lattice to the case of a continuum of allowed orientations is given in Appendix A. In essence, what is calculated below is the number of ways ν_{j+1} of putting the $(j+1)^{\text{th}}$ rod into the volume n_o, j rods already having been inserted. This is the probability of finding x contiguous, collinear segmental spaces for the test rod $(j+1)$ and thus the method has similarity with the scaled particle method[1] (which finds the free energy of such a cavity in the fluid) and a method touched on by Alben[9] in a collection of several lattice-theoretical approaches.

Let each of the rods (j) be characterized by the solid angle Ω_j occupied by its axis (with respect to a fixed reference direction in space). We then employ a mean field approach: the first segment finds a vacancy with a probability given by the mean fraction of vacancies in the volume n_o, i.e.

$$\left(\frac{n_o - x_j}{n_o}\right)$$

Each of the $x-1$ successive segments then finds a vacancy with a probability given by the mean fraction of vacancies in the mixture of vacancies and rods "seen" in projection by the rod $(j+1)$. Let the projection of a rod i onto the plane defined by the axis of rod $j+1$ be p_i^{j+1}. Then this mean fraction is

$$\left(\frac{n_o - xj}{n_o - xj + \sum_{i=l}^{j} p_i^{j+1}}\right)$$

and the resulting probability of putting the rod $(j+1)$ into the volume n_o is

$$\frac{\nu_{j+1}}{n_o} = \left(\frac{n_o - xj}{n_o}\right)\cdot\left(\frac{n_o - xj}{n_o - xj + \sum_{i=1}^{j} p_i^{j+1}}\right)^{x-1} \tag{1}$$

The probability factor used for the remaining $(x - 1)$ segments has a similarity to the factor $(n_o - xj)/(n_o - xj + \sum_{i=1}^{j} y_i)$ used by Flory[4,5] for segments (other than the first) of the sequences he uses to represent rods subtending finite angles with the director. The motivation is the same, that is, such segments enter with an enhanced probability since not the entire volume of the other rods can compete for this volume element, the preceding volume element already being occupied. The arguments are close for rods of high alignment. For high disorientation or for the isotropic state there is an important difference—the component of the rod transverse to the reference direction of the calculation (the initial segments of the y sequences in Flory's picture) should only "see" a projection and not the entire length of the other rods (which they do if one uses the factor $(n_o - xj)/n_o$ for them. In the case of great disorder an appreciable fraction of the other rods will have large transverse components and the use of the volume fraction for the initial segments will introduce substantial error (to be discussed after Eq. (23) for the free energy of the isotropic state).

In the present case the actual projection is taken, avoiding the need for the division into sequences or the restriction to principal directions only. The penalty is in the complication of two labels on p (rather than one on the sequence label y) with the consequence that the resulting equation will be an integral rather than transcendental equation.

The configurational part of the partition function, Z_{config}, for placing the n_x identical rods is

$$Z_{\text{config}} = \frac{1}{n_x!}\prod_{j+1=1}^{n_x} \nu_{j+1}$$

$$= \frac{1}{n_x!}\prod_{j+1=1}^{n_x} \frac{(n_o - xj)!}{(n_o - x(j+1))!}\,\frac{\left(n_o - x(j+1) + \sum_{i=1}^{j} p_i^{j+1}\right)!}{\left(n_o - xj - 1 + \sum_{i=1}^{j} p_i^{j+1}\right)!} \tag{2}$$

where, for greater accuracy, we have replaced the power expressions in (1) by factorials. Cancellations which normally reduce expressions such as (2) to a trivial form are now longer possible because of the second label on p. Further reduction is delicate and done in Appendix B.

To achieve this reduction the mean-field of disorder $\bar{p}$ which acts as a steric constraint on the rods is introduced and is defined by the *double* average, firstly over the "other" rods i:

$$\overline{p^{j+1}} = \langle p_i^{j+1} \rangle_i \tag{3}$$

which is a function of Ω_{j+1} and then over the rods $j + 1$ to give $\bar{p}$

$$\bar{p} = \langle \overline{p^{j+1}} \rangle_{j+1} \tag{4}$$

The use of a mean field $\bar{p}$ (or $\bar{y}$[4,5]) is of course entirely consistent with the use of the mean field probabilities $(n_o - xj)/n_o$ and $(n_o - xj)/[n_o - xj + \Sigma\,(p \text{ or } y)]$ themselves, that is, a given rod sees a mean occupancy or mean disorder characteristic of the entire fluid and not of its local environment. Thus the fact that in the calculation with the y's one can cancel certain consecutive terms in Z does not mean that one has any accuracy greater than that implied by the use of a mean field. Indeed one concludes with an expression for Z purely in terms of $\bar{y}$ obtained by the mean field assumption that the last rod n_x sees a disorder field $\bar{y}$ representing the fluid average. The mean field $\bar{p}$ is quite different from $\bar{y}$ since the molecular distribution function appears twice in it (see remarks before Eq. (2) and after (12)) indicating that *both* a test molecule *and* those other molecules comprising the steric field are governed by the distribution.

In terms of this mean-field it is shown in Appendix B that

$$\ln(Z_{\text{config}}) = \left(\frac{x-1}{x-\bar{p}}\right)(n_s + \bar{p}\, n_x) \ln(1 - v_x(1 - \bar{p}/x)) - n_x \ln\left(\frac{n_x}{n_o}\right) - n_s \ln\left(\frac{n_s}{n_o}\right) \tag{5}$$

v_x is the volume fraction of rod (xn_x/n_o). The ideal mixing result for 1 dimensional binary solutions is apparent at $\bar{p} = 1$.

For the disordered state the result of allowing Ω_i and Ω_{j+1} to range freely over 4π in (3) and (4) is that $\bar{p} = x\pi/4$. Care will subsequently be taken to check that this is a stationary value of $\bar{p}$ and does in fact correspond to a minimal value of the free energy.

The orientational partition function, Z_{orient}, measures the rotational disorder implied by the distribution of rods and is

$$Z_{\text{orient}} = \prod_{\theta} \left(\sigma\, \omega_\theta \frac{n_x}{n_\theta}\right)^{n_\theta} \tag{6}$$

n_θ is the number of rods with angle θ to the preferred direction—a cylindrically symmetric distribution function normalized such that

$$\sum_{\theta} \frac{n_\theta}{n_x} = 1$$

σ is an arbitrary constant relating to the cell size in orientational phase space and can be neglected in classical statistical mechanics. ω_θ is sin θ in three dimensions, any other constants being arbitrary in the same way σ is.

The Gibbs free energy G can now be written down as:

$$G/k_B\mathrm{T} = n_x \ln (n_x/n_o) + n_s \ln (n_s/n_o) - \sum_{\theta} n_\theta \ln \left(\frac{\omega_\theta n_x}{n_\theta} \right) - \left(\frac{x-1}{x-\bar{p}} \right) (\bar{p} n_x + n_s) \ln [1 - v_x (1 - \bar{p}/x)] \tag{7}$$

Thus G involves (the as yet unknown) distribution function n_θ directly and indirectly through p which we now examine more closely. Moreover $\bar{p}$, the mean-field of disorder, contains all the $\{p_i^j\}$, which will now be expressed in terms of angles characterizing the rods.

Elementary geometry[2] shows that

$$p_i^j \sim \sin |\Omega_i - \Omega_j| \tag{8}$$

where Ω_i and Ω_j are the orientations of rods i and j. Because of cylindrical symmetry n_θ contains only one angle and hence in order to use a mean-field one must express the projection in terms of the two polar angles θ_i and θ_j corresponding to i and j. Then $\bar{p}$ is

$$\bar{p} = (x-1) \sum_{\theta_i, \theta_j} \frac{n_{\theta_i}}{n_x} \frac{n_{\theta_j}}{n_x} p_i^j + 1 \tag{9}$$

(See Appendix C for details). The form of (9) corresponds to that adopted by Warner[16] and gives a projection of $p = 1$ for rods with parallel axes. Results will also be presented for the case where $\bar{p}$ is defined by the relation

$$\bar{p} = x \sum_{\theta_i, \theta_j} \frac{n_{\theta_i}}{n_x} \frac{n_{\theta_j}}{n_x} p_i^j \tag{10}$$

corresponding to Flory and Ronca[5,17] and Warner and Flory.[18]

It remains to determine the actual rod distribution which is done by minimizing G with respect to the distribution function n_θ, that is

$$\delta G/\delta n_\theta = 0 \tag{11}$$

To explore this condition we require the functional derivative $\delta\bar{p}/\delta n_\theta$

$$\delta\bar{p}/\delta n_\theta = 2(x-1) \left[\sum_{\theta'} \frac{n_{\theta'}}{n_x^2} p_\theta^{\theta'} \right] \equiv 2(x-1) q(\theta)/n_x \tag{12}$$

where the symmetry of θ and θ' has been employed in $p_{\theta'}^{\theta}$. The factor of 2 results from the two degrees of freedom implicit in (3) and (4) defining $\bar{p}$, and would be unity if we were to consider simply projections onto a single fixed plane in space.

The function $q(\theta)$, defined by relation (12), is a measure of the steric field, a rod with orientation θ experiences from the projection of all other rods at angles θ' and will be shown to govern the rod distribution. (13) defines q:

$$q(\theta) = \sum_{\theta'} \frac{n_{\theta'}}{n_x} p_{\theta}^{\theta'} \tag{13}$$

Functional differentiation of G then yields

$$(1/k_BT)\ \delta G/\delta n_\theta = q(\theta)\ 2\left(\frac{x-1}{x-\bar{p}}\right)^2 \left\{\frac{ax}{v_x} - (x-\bar{p})\right\} - \ln\left(\frac{\omega_\theta n_x}{n_\theta}\right) + 1 \tag{14}$$

where a is defined as

$$a = -\ln\left(1 - v_x(1 - \bar{p}/x)\right) \tag{15}$$

Equating the derivative (14) of G to zero the relation for n_θ emerges

$$\frac{n_\theta}{n_x} \sim \omega_\theta \exp(-\, b(x-1)q(\theta)) \tag{16}$$

where b is

$$b = \frac{2(x-1)x}{(x-\bar{p})^2}\left\{\frac{a}{v_x} - 1 + \bar{p}/x\right\} \tag{17}$$

In (16) both b and the unknown function $q(\theta)$ on the right hand side are functionals of n_θ. Closure is achieved by insertion of (16) into (13) and yields the integral equation

$$q(\theta) = \frac{\int d\theta' \sin\theta'\, p_\theta^{\theta'} \exp(-\, b[q(\theta)]\ (x-1)\ q(\theta'))}{\int d\theta' \sin\theta' \exp(-\, b[q(\theta)]\ (x-1)\ q(\theta'))} \tag{18}$$

to be solved simultaneously with relation (17) for b and (10) for $\bar{p}$. Equation (10) can be used to effect in the form

$$\bar{p} = (x-1)\bar{q} + 1 \tag{19}$$

The denominator in (18) is the normalization of n_θ/n_x required in (16). We denote it by f_1 and will have occasion to use f_n generally

$$f_n = \int d\theta \sin^n\theta \exp(-\, b(x-1)\ q(\theta)) \tag{20}$$

(no longer explicitly displaying the functional dependence of b on $q(\theta)$).

Solutions of (18) for $q(\theta)$ and b then yield the distribution function and thence $\bar{p}$ and b, and ultimately the free energy G (substituting the normalized version of (16) into (7)).

$$\frac{G_{\text{aniso}}}{n_x k_B T} = -\ln (x f_1) + 2\left(\frac{\bar{p}-1}{x-\bar{p}}\right)(x-1) - \left(\frac{x-1}{x-\bar{p}}\right)\left\{\bar{p} - 2x\frac{\bar{p}-1}{x-\bar{p}}\right\} \ln (\bar{p}/x) \quad (21)$$

We have now limited discussion to neat rod systems with no solvent ($v_x = 1$). In terms of the variable q (21) can be rearranged to

$$\frac{G_{\text{aniso}}}{n_x k_B T} = -\ln (x f_1) + \frac{2\bar{q}}{1-\bar{q}}(x-1) - \frac{1}{1-\bar{q}}\left\{\bar{q}(x-1) + 1 - \frac{2x\bar{q}}{1-\bar{q}}\right\} \ln\left(\frac{(x-1)\bar{q}+1}{x}\right) \quad (22)$$

For the isotropic phase we have $\bar{q} = \pi/4$ and an isotropic value of a (a_i) of

$$a_i = -\ln\left(\frac{x-1}{x}\pi/4 + \frac{1}{x}\right)$$

The Gibbs free energy is then

$$\frac{G_{\text{iso}}}{n_x k_B T} = -\ln x - \left(\frac{(x-1)\pi/4+1}{1-\pi/4}\right) \ln\left(\frac{x-1}{x}\frac{\pi}{4} + \frac{1}{x}\right) \quad (23)$$

The corresponding result obtained[5] by setting $\bar{y} = x$ is

$$\frac{G_{\text{iso}}}{n_x k_B T} = -\ln x + (x-1)$$

which for a test rod $j+1$ with $y_j + 1 \sim x$ derives from basic probabilities like

$$\frac{v_{j+1}}{n_o} \sim \left(\frac{n_o - xj}{n_o}\right)^x$$

(each segment corresponds to a whole sequence). $G_{\text{iso}}/n_x k_B T$ is greater than that in (23) by an amount $\sim .1.(x-1)$ for $x > 1$ (say around x_{crit}) reflecting the fact that the entropy of disordering rods is greater than the volume fraction result above which is the limiting value obtained for stiff *polymers.* That is, the present calculation, in allowing for rods in states of high disorder to "see" the rest of the rod fluid in an appropriate projection, produces a lower estimate of the isotropic state free energy than that given by volume fractions (with a consequence for relative phase stabilities to be discussed in the next section).

All of the above calculations were for a system of purely hard rods, that is, in the athermal limit where soft interactions play no role (or, equivalently, temperature $T = \infty$). Results will be presented in the next section for athermal rods and we proceed to the question of soft interactions (thermotropic liquid crystals).

For a uniaxial system the simplest form possible within mean-field theory for angularly dependent soft interactions between molecules is

$$U(\theta) = -x\, k_B T^*\, v_x\, s P_2 (\cos \theta) \tag{24}$$

Here $k_B T^*$ is the energy characterizing the interaction (the coupling constant), s is the simplest order parameter

$$s = \langle P_2 (\cos \theta) \rangle \tag{25}$$

and P_2 is the second Legendre polynomial. Such anisotropic van der Waals interactions derive from the often highly polarizable and anisotropic constituents of liquid crystal molecules. The forces form the basis of the M-S theory[10] and are discussed in detail by them. Within the present (segment) picture dispersion forces have been discussed by Flory and Ronca[17] and by Warner.[19] The size of T^* and its applicability to M-S theory has been discussed by many authors.[19–21]

The potential $U(\theta)$ is inserted as a Boltzmann factor into the expression (16) for n_θ:

$$\frac{n_\theta}{n_x} = f_1^{-1} \sin \theta \exp\left(- b(x-1)\, q(\theta) - \frac{3}{2}\, x\, s\Theta^{-1} \sin^2 \theta \right) \tag{26}$$

where $\Theta = T/T^*$ is the reduced temperature and $-3/2 \sin^2 \theta$ is P_2 to within constants which cancel in the normalization. f_n is now

$$f_n = \int d\,\theta \sin^n\theta \exp(- b(x-1)\, q(\theta) - \tfrac{3}{2}\, x\, s\Theta^{-1} \sin^2 \theta) \tag{27}$$

(we continue setting $v_x = 1$).

There are now two self consistency conditions to be satisfied simultaneously with the integral equation representing closure on $q(\theta)$. They are the previous condition on b and the consistency of s which appears in n_θ, and is defined by

$$s = 1 - (\tfrac{3}{2})\, f_3/f_1 \tag{28}$$

Thus relations (28) and (17) are to be satisfied with the integral equation

$$q(\theta) = \frac{\int d\theta' \sin \theta'\, p_\theta^{\theta'} \exp(-b(x-1)\, q(\theta') - \tfrac{3}{2}\, x\, s\Theta^{-1} \sin^2 \theta')}{\int d\theta' \sin \theta' \exp(-b(x-1)\, q(\theta') - \tfrac{3}{2}\, x\, s\Theta^{-1} \sin^2 \theta')} \tag{29}$$

The internal energy, E, is

$$\frac{E}{n_x k_B T} = \frac{1}{2} x \Theta^{-1} s^2 \tag{30}$$

Adding this to G and substituting in the new n_θ from (26) the result is:

$$\frac{G_{\text{aniso}}}{n_x k_B T} =$$

$$\frac{2\bar{q}}{1-\bar{q}}(x-1) - \frac{1}{1-\bar{q}}\left\{\bar{q}(x-1) + 1 - \frac{2x\bar{q}}{1-\bar{q}}\right\} \cdot \ln\left(\frac{x-1}{x}\bar{q} + \frac{1}{x}\right)$$

$$- \ln(x f_1) - x\Theta^{-1} s(1 - s/2) \tag{31}$$

In the isotropic phase $s = 0$ and Eq. (23) for G_{iso} remains unchanged.

Variation of temperature can now influence the order in the rod fluid. For a system of rods with axial ratio x less than a certain critical value x_{crit} there exists an ordering temperature T_{ni} at which point the order parameter abruptly takes a finite value and a latent entropy is observed. This is the isotropic-to-nematic transition for thermotropic rods. Rods with $x > x_{\text{crit}}$ are always ordered.

The solution of (29) and its implications for the phase transitions of thermotropic rods (x) are discussed in the next section.

3 CALCULATION OF THE PROPERTIES OF SYSTEMS OF ROD LIKE PARTICLES

The equations for $q(\theta)$ and the rod distribution function n_θ set up in the previous section will be solved in the athermal and thermotropic cases to yield the physical quantities of interest.

Minimizing G determines n_θ and the solution of the ensuing integral equation under the subsidiary conditions completes the closure. It is important to confirm that the isotropic state ($q(\theta) = \pi/4$) is in fact a solution (i.e. a stationary point of the functional G). If not, the ordered solution would be the stable solution under all conditions which would clearly be unphysical.[3] We demonstrate that $q(\theta) =$ constant is indeed a solution (see Appendix D). The integral equation encountered in either (18) or (29) is trivial to solve numerically (see Appendix D) and is discussed no further.

Athermal Rods

In the athermal limit of our theory it is found that for x above a certain value, x_{crit}, neat fluids composed of rod-like particles are always ordered and, below, always disordered. The axial ratio x_{crit} is determined by the equality of G in the ordered and disordered phases of athermal systems. Equating (21) and (23) one obtains an equation satisfied by rods with $x = x_{\text{crit}}$:

$$\frac{2\bar{q}}{1-\bar{q}}(x-1) - \frac{1}{1-\bar{q}}\left\{\bar{q}(x-1) + 1 - \frac{2x\bar{q}}{1-\bar{q}}\right\}\ln\left(\frac{x-1}{x}\bar{q} + \frac{1}{x}\right) + \frac{\pi/4\,(x-1)+1}{1-\pi/4}\ln\left(\frac{x-1}{x}\frac{\pi}{4} + \frac{1}{x}\right) - \ln f_1 = 0 \qquad (32)$$

We tabulate the solution along with the values of $\bar{q}$ and s in the ordered phase at the athermal limit. The second row of Table I gives the equivalent results when the projection (10) is taken instead. To make contact with the other theories to which the present theory has the closest relation the first and second rows should be compared with Refs. 16 and 5, respectively, where the results were (8.7536, .9216, .3231) and (6.42, .9473, .1939) for x_{crit}, s_{crit} and $\bar{y}/x_{\text{crit}}$ (the latter quantity being the most closely related to $\bar{q}$). By comparison a theory in which the orientations of rods are restricted to lie in three principal lattice directions[9] (an extreme form of the restriction of orientational phase space) produces a value of x_{crit} of 3.652 (compare with 8.983).

The large spread in the theoretical predictions relates to two factors. Firstly the latter approaches[6,7,9] severely under-estimate the rotational entropy of the molecules, more pronouncedly for the disordered state than in the nematic where rods are biased toward the director (a principal direction) anyhow. Thus the disordered state is unphysically penalized with respect to the ordered state with the consequence that the system orders at lower axial ratios. The present work and that of Flory and Ronca,[5] in allowing for continuous rotation, inevitably produce a larger estimate of x_{crit}.

Secondly, but less dramatically, the provision in the present theory that a rod experiences not the full length of the other rods but only that projection of the other rods in a perpendicular plane means that rods in the nematic phase with an appreciable degree of disorientation do not pay such a high entropy penalty, a conclusion reinforced by arguments after (23) where the isotropic phase is seen to have a greater stability. (The comparison is between $x_{\text{crit}} = 7.72$ stemming from Eq. (10) and 6.4, the latter being the result[5] of only considering projections of rods on a plane transverse to the director.)

TABLE I

Projection	x_{crit}	s_{crit}	$\bar{q}$
Eq. (9)	8.9832	0.8314	.4018
Eq. (10)	7.7213	0.8847	.3351

This second factor, in allowing greater disorientation to be tolerated in the ordered state produces values of s smaller than in other such steric theories (a most encouraging fact when considering experimental data on the order in thermotropic nematics). Related is the flatter nature of the distribution function in the nematic phase. A comparison is presented in Appendix D between $q(\theta)$ and the previous functional form, sin θ.

However, that the Flory approach does not seriously over-estimate the transverse steric hinderance is illustrated by the following argument: Warner[16] argues that for a phase with high degree of alignment it is important, since a given test molecule sees the other molecules mostly in an end-on position, to accurately specify the steric hinderance in that relative orientation. The connection between the projection y and the orientation θ was then taken as

$$y = 4/\pi(x - 1)\sin\theta + 1 \tag{33}$$

For larger angles θ the distinction between the above connection and that employed by Flory and Ronca[5] becomes unimportant. The remainder of Ref. 16 is in the spirit of Flory and Ronca and results in $x_{\text{crit}} = 8.75$. With the same motivation as (33) (that is (9) instead of (10)) x_{crit} is 8.98, a rather small shift indicating that the omission of the "transverse" effect in Flory's approach is not very serious. (See however the discussion of s values in the experimental section.)

Thermotropic Rods

The compouding of the aligning influence of the soft forces with that of the steric forces considered above means that rods with axial ratio $x < x_{\text{crit}}$ now find it possible to order below a certain transition temperature $\Theta_{ni}(x)$. Associated with the transition is a reduced latent entropy of

$$S/k_B = \tfrac{1}{2}\, x\, s_{ni}^2/\Theta_{ni}$$

where s_{ni} is the value of the order parameter in the ordered phase at the transition.

We plot in Figures 1–3 the variation of reciprocal reduced transition temperature Θ_{ni}^{-1}, order parameter at the transition s_{ni} and the reduced latent entropy S/k_B as functions of rod axial ratio.

We turn now to a confrontation of theory and experiment.

4 EXPERIMENTAL

Our comparison of theoretical prediction with experimental data divides into two parts—that of the so-called athermal limit and that of the thermal proper-

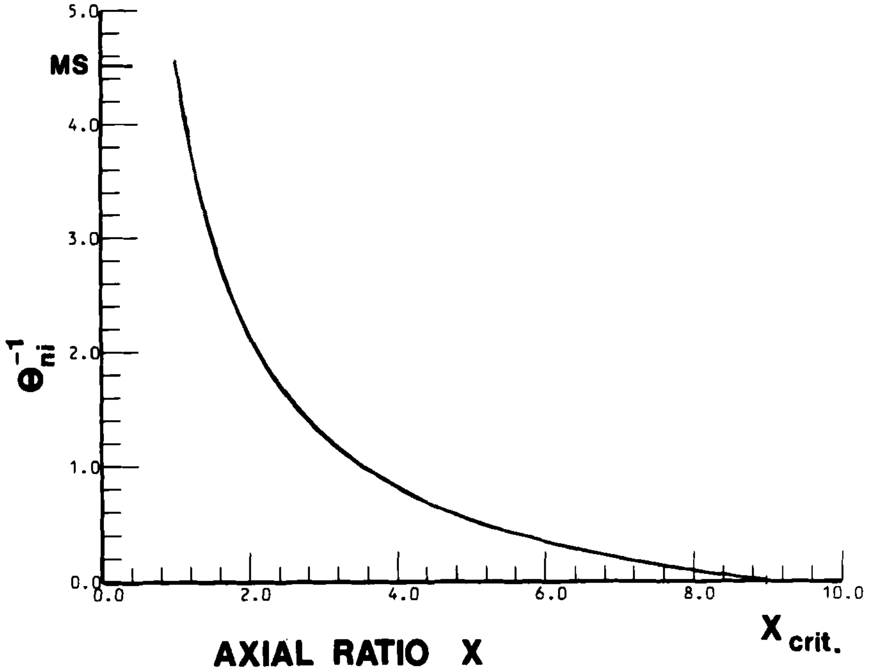

FIGURE 1 Reciprocal reduced transition temperature $\Theta_{ni}^{-1}(x)$ is plotted against axial ratio x. The value $x = 1$ is the Maier Saupe limit of no steric effects (denoted by MS). The limit at $\Theta_{ni}^{-1} = 0$ is the athermal limit. Rods of axial ratio x greater than x_{crit} are always ordered in the neat fluid.

ties of rods where, because of soft forces, temperature plays a significant role (thermotropic nematics).

The athermal limit can of course only be discussed in terms of the limiting behavior of Figure 1, that is, the values of x where the transition temperature increases dramatically. Thus one requires a homologous sequence of nematogenic molecules with varying x but similar soft coupling T^* per segment so that the sequence of transition temperatures hopefully has the same structure as in the theory above. We take (following Flory and Ronca[17]) the polyphenyls. It should be noted that these are stiff molecules where the transition temperature appears to increase markedly with axial ratio. In contrast, Cotter[6] considered homologous families where increasing the length of the flexible alkyl tail causes the opposite phenomenon, namely a decrease in T_{ni} with increasing x.

Quinquephenyl is a nematic liquid crystal with an elevated transition temperature. We use the measured T_{ni} to estimate T^* via the predicted transition temperature Θ_{ni}

$$T^* = T_{ni}/\Theta_{ni}$$

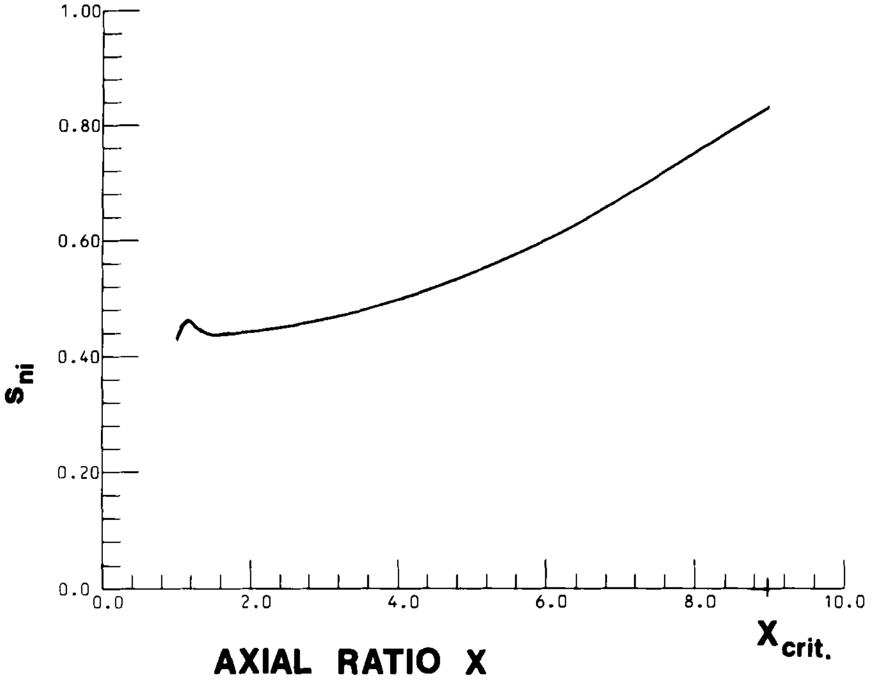

FIGURE 2 Order parameter at the transition s_{ni} is plotted against axial ratio x.

and find $T^* = 362$ K°. Thus fixed, T^* enables us to predict the properties of other homologues which are presented below in Table II which is analogous to Table I of Flory and Ronca.[17]

Given that the single parameter T^* in the theory must be fixed from the above transition it remains to investigate x_{crit} and otherwise test the theory by locating further points on the $T_{ni}(x)$ curve. In the case of quaterphenyl, crystallization masks the nematic-isotropic transition and $T_{ni}^{expt}(4.1)$ may only be estimated by an examination of two component systems exhibiting a nematic phase over a finite range of the $n = 4$ species. Warner and Flory[18] and Warner[16] considered $n = 4, n = 5$ mixtures which have had preliminary measurements made on them.[22] Thus one can extrapolate on the phase diagram in order to estimate $T_{ni}^{expt}(4.1)$.

(A more rigorous test of the theory is to look at the detailed shape of the phase diagram[16,18]). Calculations of the two component aspects of the present model will be given elsewhere and we simply predict a crude measure of the slope of the phase diagram, namely

$$\left(\frac{T_{ni}(5) - T_{ni}(4.1)}{T_{ni}(5)}\right)_{\text{calc}} = .3160$$

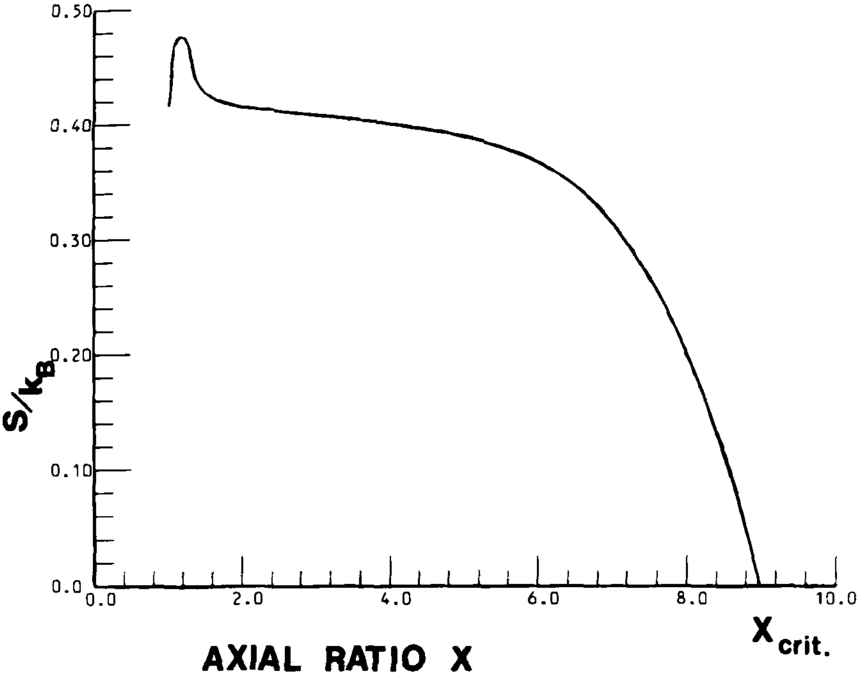

FIGURE 3 Reduced latent entropy of transition S/k_B is plotted against axial ratio x.

Sexiphenyl exhibits a clearing temperature[23,24] so elevated that it is difficult to attribute much certainty to the results. Vorlander[23] finds a clearing temperature (T_{ni}^{expt} (5.9)) certainly above 620°C, Lewis[24] at 520°C. Partial decomposition produces fragments tending to depress the transition and hence although the figures presented are in rough agreement with our prediction we feel the question of the athermal limit will only be settled via mixtures.

TABLE II

x†	n	T_{ni}°C	θ_{ni}^{-1}	Theory T_{ni}°C‡	s_{ni}	S/k_B
4.1	4	*	.7749	194	.5019	.4001
5.0	5	410	.5300	($T^* = 362$K°)	.5427	.3902
5.9	6	*	.3562	743	.5937	.3704

† Calculated[17] from van der Waals radii.
* Not known directly (see above).
‡ Estimated from $T^* = 362$K° deduced from quinquephenyl.

Thermotropic Rods

Our model predicts that rods of axial ratio less than x_{crit} (=8.98) require soft forces, in addition to shape effects, to get a transition to the ordered state. Indeed, quinquephenyl, employed in our discussion of the athermal limit, is such a thermotropic nematic.

We present in Table III, in addition to predictions and data on quinquephenyl (ϕ_5), results for a limited number of other nematics. They are P.A.A. (one of the canonical compounds studied) and two diphenyldiacetylenes reported by Grant[25] and discussed in the present context by Flory and Ronca.[17] The latter systems were chosen because of their rigidity, relative simplicity and rod-like structure, diminutive dipole moment and the existence of thermodynamic data.[26] The compounds are *p,p'*-di-3-alkyldiphenyldiacetylene and *p,p'*-di-2-alkoxydiphenyldiacetylene denoted by I and II here (compounds 4 and 5 of Ref. 17).

The values of s_{ni} predicted for ϕ_5 and PAA are too large and there is a corresponding discrepancy in the values of S/R. Flory and Ronca,[17] in the case of PAA, suggest that this discrepancy could be due in part to the large dipole moment in PAA causing local association which could invalidate the T^* assumption (see also Ref. 15). The (then unknown) result for ϕ_5 now suggests that this is not the entire explanation for the discrepancy (which in this case is larger even though the polar character is less).

TABLE III

Predicted and Experimental Properties of four thermotropic liquid crystals

	Compound			
Property*	ϕ_5	PAA	I	II
x[17]	5.0	3.6	4.7	5.0
T_{ni}^{expt} °C	410[27]	135[28]	132[25]	210[25]
Θ_{ni}	1.887	1.041	1.662	1.887
T^* K°	362	392	244	256
s_{ni}^{calc}	.5427	.4830	.5280	.5427
s_{ni}^{expt}	.325[27]	.40[28]		
$(S/R)_{calc}$	.390	.404	.394	.390
S/R	.1612[29]	.22[30] (.07)†	.41[26]	.61[26]

* The properties tabulated are, respectively, the axial ratio (x), the observed transition temperature (T_{ni}^{expt}), the calculated reduced transition temperature (Θ_{ni}), the temperature characterizing interactions (T^*), the calculated and observed order parameters at the transition (s_{ni}^{calc}, s_{ni}^{expt}) and the calculated and observed reduced latent entropies ($(S/R)_{calc}$, S/R).

† The result of correcting[17] the experiment to constant volume. Other quantities should ideally, also be corrected.

Compounds I and II show a better agreement, which would be even better if the (unknown) corrections to constancy of volume were to be made.

It is possible to make further comments about the role of volume in our model:

T^* is absent from the equations determining the state of the fluid. Therefore, a change in volume, and thus in T^*, shifts the actual transition temperature $T_{ni}(=\Theta_{ni}T^*)$ but leaves Θ_{ni}, s_{ni}, S/R etc all unchanged. This remark relates also to the experiments of Deloche *et al.*[28] where the transition temperature T_{ni} for PAA was followed to 3kbar. They found that changes of 15% in specific volume and 17% in absolute temperature of transition produced no change in the order parameter at the transition, in accordance with our model. Interpreted in terms of our calculation it would seem apparent that there is a minimal change in the configurational part of the free energy with changing density, since changes in T^* can provide no nugatory effect in this theory.

One can perhaps draw the conclusion that the configurational part of the theory is well-given in a consideration of the packing of similar molecular cores and that this feature, once one is at liquid-like densities, will not vary with minor adjustments to the local density of particles, the *relative positions* remaining unchanged (the thesis of Appendix A). Certainly the viewpoint that volume changes are the driving force of the nematic-to-isotropic transition is not borne out. (Further arguments based on the comparison of S/R and $(\partial E/\partial V)\cdot \Delta V/RT_{ni}$ are also compelling to the insensitivity of the transition to volume changes.)

Finally, we present in Figure 4 the variation of order parameter with temperature for the cases of quinquephenyl and PAA. The order parameter and temperature are both reduced by their values at the transition, s_{ni} and T_{ni} respectively; that is, we plot s/s_{ni} against T/T_{ni}^{calc} $(\equiv \Theta/\Theta_{ni})$. The dotted section of each curve is the region of metastability (super-heated nematic) terminating at a temperature quite close to the transition temperature.

5 SUMMARY

We have presented a theory of the nematic-to-isotropic transition and a description of the nematic state for dense phases of rod-like molecules. Our approach assumes the dominance of steric (i.e. packing) effects associated with the molecular asymmetry found in mesogenic compounds. Soft forces are included in the spirit of van der Waals. The treatment and results have much similarity with the approach of Flory[4,5,17] and Alben.[9] In fact, a conclusion we can draw is that Flory's estimate of steric hinderances is good, and that the artificialities of the lattice formulation are rendered less severe by his adoption

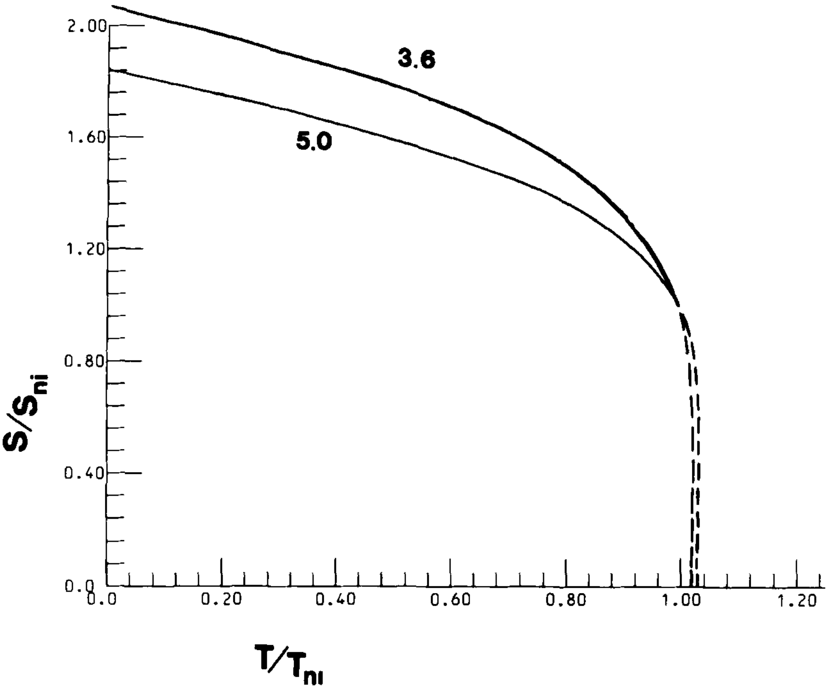

FIGURE 4 Order parameter normalized by the order parameter at the transition (s/s_{ni}) is plotted against temperature normalized by the transition temperature (T/T_{ni}) for rods of axial ratio $x = 5$ and $x = 3.6$ corresponding to quinquephenyl and PAA respectively. The dotted section ($T/T_{ni} > 1$) represents metastable nematic states.

of the "random freeway driver" model for the various orientation rods may adopt. On the other hand, lattice models with orientations restricted to principal lattice directions vastly under-estimate the orientational entropy of rods, especially in the isotropic fluid.

Two principal conceptual advantages of our theory are the continuous rotational freedom allowed the rods from the outset and the consequently consistent treatment of steric interaction (in effect considered in directions both perpendicular and parallel to the director). It is found, however, that analytic tractibility is not sacrificed by the adoption of the above two requirements.

Born out of the enhanced rotational freedom and consistency in the steric constraints are (i) larger estimates of the limiting athermal axial ratio and (ii) lower estimates of the order parameter and latent entropy at the nematic-to-isotropic transition. Both these estimates give improved agreement with experiment.

Despite the formal similarity of our theory with the Onsager theory[2] (the occurrence of an integral equation), the two works are really quite different. The Onsager theory is in terms of the interaction of two rods alone and in their entirety and thus relates to dilute solution. Here we examine the packing of a rod in a dense field of other rods where each segment of the test rod interacts with many other segments of other rods. Two separated segments on one rod, although interacting each with many segments, are not necessarily each interacting with segments of the same other rod. Another way of saying this is that we are at densities such that the combined covolume of the rods is much greater than the volume of the system and a virial approach is inappropriate. Certainly, nematic liquid crystals are usually encountered with low enough axial ratios and at sufficiently high densities that the present approach is preferable to that of Onsager (see also the conclusion of Ref. 5).

Further improvement could undoubtedly be obtained by an effective model of the short-range order imposed by the molecular shape of nematogens.

References

1. M. A. Cotter, Chapter 7 of "The Molecular Physics of Liquid Crystals", Ed: G. R. Luckhurst and G. W. Gray, Academic Press, London (1979).
2. L. Onsager, *Ann. NY Acad. Sci.*, **51,** 627 (1949).
3. J. P. Straley, *Mol. Cryst. Liq. Cryst.*, **22,** 333 (1973).
4. P. J. Flory, *Proc. Roy. Soc., Ser. A,* **234,** 73 (1956).
5. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54,** 289 (1979).
6. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **35,** 33 (1976).
7. M. A. Cotter and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, **7,** 295 (1969).
8. See L. Feijoo, V. T. Rajan and C-W Woo, *PR,* **A19** 1263 (1979) and the references contained therein.
9. R. Alben, *Mol. Cryst. Liq. Cryst.*, **13,** 193 (1971).
10. W. Maier and A. Saupe, *Z Natf,* **14a** 882 (1959).
11. S. Chandrasekhar and N. V. Madhusudana, *Acta. Cryst.*, **27,** 303 (1971).
12. R. L. Humphries, P. G. James and G. R. Luckhurst, *J. Chem. Soc. Faraday. Trans. II,* **68,** 1031 (1972).
13. P. Sheng and P. J. Wojtowicz, *PR,* **A14,** 1883 (1976).
14. C. Zannoni, Chapter 9, ref. 1.
15. G. R. Luckhurst and C. Zannoni, *Nature,* **267,** 412 (1977).
16. M. Warner, *Mol. Cryst. Liq. Cryst.*, **80,** 67 (1982).
17. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54,** 311 (1979).
18. M. Warner and P. J. Flory, "The Phase Equilibria in Thermotropic Liquid Crystalline Systems", *J. Chem. Phys.*, **73,** (12) 6327 (1980).
19. M. Warner, "Interaction Energies in Nematogens", *J. Chem. Phys.*, **73,** (11), 5874 (1980).
20. J. I. Kaplan and E. Draughlis, *Chem. Phys. Letts.*, **9,** 645 (1971).
21. A. Wulf, *J. Chem. Phys.*, **64,** 104 (1976).
22. G. P. Wallis, Ph.D. Thesis, Cambridge University (1978).
23. D. Vorlander, *Z. Phys. Chem.*, **A126,** 449 (1927).
24. I. C. Lewis, private communication.
25. B. Grant, *Mol. Cryst. Liq. Cryst.*, **48,** 175 (1978).
26. E. M. Barrall, B. Grant and A. R. Gregges, pp. 19–39 in "Liquid Crystals and Ordered Fluids", vol. 3, Ed: J. F. Johnson and R. S. Porter, Plenum (1978).
27. P. L. Sherrell and D. A. Crellin, *J. de Phys.* (*Paris*) *Colloq.*, **C3,** suppl. au 4, **40,** C3–211 (1979).

28. The value for T_{NI} taken at 1 bar, B. Deloche, B. Cabane and D. Jerome, *Mol. Cryst. Liq. Cryst.*, **15**, 197 (1971).
29. G. W. Smith, *Mol. Cryst. Liq. Cryst.*, **49**, 207 (1979).
30. E. M. Barrall, R. S. Porter and J. F. Johnson, *J. Phys. Chem.*, **71**, 895 (1967).
31. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York (1953).

APPENDIX A

The philosophy behind the basic mixing result of the text is presented in the context of the mixing of simple liquids and of simple liquid and polymer in order to make contact with the usual method and assumptions made in calculating mixing entropy.

Two fluids of identical structure have an entropy of mixing (S_{mix}) given exactly and without a lattice by

$$\frac{S_{\text{mix}}}{k_B} = \ln\left(\Omega_{\text{mix}}\right) = \ln\left(\frac{n_o!}{n_1!\, n_2!}\right) = -\, n_1 \ln \nu_1 - n_2 \ln \nu_2 \tag{A1}$$

where

$$n_o = n_1 + n_2$$

and ν_i and n_i denote the volume fraction and number of molecules of the i^{th} species. (A1) derives from the number of ways of assigning sites in a particular realization of the fluid (Figure A1) to the type 1 or 2. "Sites" here are molecules in the fluid which are as yet unlabelled, the fluid structure, as a result of the molecular similarity, being common to both species. Thus the entropy of positional randomness in the fluid (the "communal entropy", S_{com}) decouples from S_{mix} since for each realization in the ensemble of states making up S_{com} the same number of assignments (Ω_{mix}) are still possible. The result is the same as on a lattice since the combinatorics are identical and the violence done to the communal entropy in limiting the molecules to lattice sites is considered to decouple (as above) and physically plays no role in mixing. It is thus evident that the two approaches implicitly have the same basic assumption—that the underlying structures of the two fluids to be mixed are sufficiently similar that changes in the communal entropy can be ignored with respect to S_{mix}.

Likewise the entropy of mixing of a polymer with simple solvent can be considered on Figure A1 by connecting together successive sites in the realization shown to form a path (polymer) through the structure (equivalent to the sitewise insertion of a polymer molecule into the mixture). Let the local coordination in the fluid be z. Then the $(j + 1)^{\text{th}}$ polymer can be put in with probability

$$\frac{\nu_{j+1}}{n_o} = \left(\frac{n_o - jx}{n_o}\right) z \left(\frac{n_o - jx}{n_o}\right)\left[(z - 1)\left(\frac{n_o - xj}{n_o}\right)\right]^{x-2} \tag{A2}$$