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# Theory of nematic backbone polymer phases and conformations

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**Abstract.** The nematic–isotropic phase transition of long flexible polymers using mean-field theory with the Maier–Saupe expression of the van der Waals interaction are described. The order parameter of nematic polymers is calculated as a function of reduced temperature,  $k_B T / (a\epsilon)^{1/2}$ , where  $a$  is the quadrupolar mean-field strength per unit length of the molecules and  $\epsilon$  is the bend elasticity of the polymers. The reduction factor  $(a\epsilon)^{1/2}$  is in contrast to the factor in the Maier–Saupe theory of conventional nematics,  $a$ , indicating via  $\epsilon$  the polymer aspect to the problem.

The transition temperature, critical-order parameter and latent heat are given. For very long chains the transition between the nematic and isotropic phases occurs when  $T = 0.38775 (a\epsilon)^{1/2} / k_B$  where the order parameter is equal to 0.35642. We predict the temperature dependence of the order parameter and transition behaviour for different lengths of the polymer chain.

A detailed procedure is suggested for comparison with experiment involving order parameters, latent entropy and configurational properties as revealed by small-angle neutron and x-ray scattering.

## 1. Introduction

At present there is much interest in polymer liquid crystals (for reviews see Ciferri *et al* (1982), Blumstein (1985) and Chapoy (1985)). Among the questions addressed, especially among the emergent theories of such polymers, are those of the nature of the nematic–isotropic transition and the character of the order and molecular configuration in the nematic phase. ten Bosch *et al* (1983a, b, c) employ as a model the worm-like chain. The same model and similar techniques were used by Warner *et al* (1985). Ronca and Yoon (1982) took a model for their chains which was only globally inextensible. de Gennes (1984) had addressed the problem arising if the chain interacts with its surroundings as an elastic continuum. Odijk (1985) has taken a scaling approach to chain configurations and obtains a second characteristic length, longer than the effective step of the worm, as a result of the nematic field. A closely related problem is that of molecular behaviour in lipid membranes (Jähnig 1979, 1981).

Many polymers can exist in two different liquid phases—ordered (nematic) or disordered (isotropic)—with a transition between them induced by changing temperature. The nematic phase shows long range orientational order. Previous work (Warner *et al* 1985, hereafter referred to as wGB) pursued a worm-like chain model and mapped it onto a quantum problem that allowed a description of chain configurations. This paper will develop mean-field theory with the Maier–Saupe (MS) expression for interactions of the quadrupolar type, to describe the dependence of the

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order parameter on temperature, and to relate the bend elasticity and the quadrupolar mean field to the transition of thermotropic polymers. Thus within the spirit of MS, steric (shape-dependent) forces between molecules are neglected.

We shall accordingly review conventional MS theory, the model of worm polymers, WGB and the self-consistency requirements on the polymer order parameter. As we are interested in transitions we will evaluate the free energy of the nematic and isotropic phases. Our results show the phase behaviour and order of chains as functions of their length and temperature. Results for the latent entropy complete our description of the phase transition.

## 2. A Maier-Saupe theory of polymers

According to the Maier-Saupe theory (Maier and Saupe 1959, 1960) of small molecule liquid crystals, the interaction mean field is orientation dependent, i.e.

$$V = -aS(\frac{3}{2}\cos^2\theta - \frac{1}{2}) \quad (1)$$

$a$  being the strength of the quadrupolar mean field and varying from one substance to another, and  $S$  the order parameter, defined as the average  $\langle \rangle$  below

$$S = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle \equiv \langle P_2(\cos\theta) \rangle \quad (2)$$

where  $\theta$  is the angle between the molecule long axis and the preferred axis, i.e. the director  $\hat{n}$ . Expression (1) considers only the soft, dispersion interaction taking no account of steric effects.

The order parameter is calculated self-consistently since the distribution of orientations required in (2) is just the Boltzmann factor deriving from (1) and itself involves  $S$ . Thus (2) becomes a self-consistency equation for  $S$ . When the temperature is higher than  $T^* = 0.22284 a/k_B$  then  $S = 0$  is the only solution, representing isotropic fluid. Below  $T^*$  two more non-zero solutions appear but it is not until a lower temperature  $T_c = 0.22019 a/k_B$  that one of these, the nematic phase, has a free energy lower than that of the isotropic phase. There is a first-order transition but with a weak latent heat and the order parameter  $S$  jumps from zero to 0.4289 at the transition temperature  $T_c$ . The MS theory describes semi-quantitatively the nematic-isotropic transition and explains the dependence of order parameter on the temperature and the pre-transition behaviours. WGB was concerned with asymptotic questions of chain conformation. Limiting estimates of  $T^*$  were made when considering self-consistency. By considering the free energy, we shall find  $T_c$  and the character of the transition.

The model polymers are considered as long, worm-like, continuous elastic chains. Intramolecular and intermolecular interactions are represented solely by the bend elasticity,  $\epsilon$ , of the chain and the anisotropic part of the attractive van der Waals force,  $a$ , respectively, neglecting all other interactions of the polymers. Monomers, subsumed into the worm model, would be small-molecule nematics. The tangent is equivalent to the molecule long axis of the small-weight liquid crystal. Obviously, different parts of the chain have different tangents, but the tangent can change continuously along the chain contour. What our model neglects is inhomogeneity in the chemical sequence of the chain. For long range universal properties of polymers such questions are not usually of any significance (de Gennes 1979). However, there is an alternation of properties of nematic polymers according to whether there is an even or odd number of elements comprising the spacer units between stiff elements of the backbone. This is equivalent to an anisotropy of the bend constant  $\epsilon$  employed here (Luckhurst 1985).

We suppose the mean energy per unit length of the chain again has the MS form (1) where  $a$  is now an energy per unit length,  $\theta$  is the angle between the tangent of the local chain and the preferred axis, e.g.  $z$  axis, and the order parameter is expressed by (2) taken along the chain

$$S = \frac{1}{L} \left\langle \int_0^L ds P_2(\cos \theta(s)) \right\rangle \quad (3)$$

$L$  being the total chain length and  $s$  the arc length along the chain from one end.

Denoting the *unit* tangent vector by  $\hat{u}(s)$ , the total bending energy is given in terms of the total curvature along the chain and a bend elasticity  $\varepsilon$ , i.e.

$$\frac{1}{2}\varepsilon \int_0^L ds \left| \frac{d\hat{u}(s)}{ds} \right|^2. \quad (4)$$

We may now write the complete partition function for a polymer chain, including both the bending energy of the worm and the effect of the nematic mean field on the chain energy, by summing over all configurations  $\hat{u}(s)$ , where  $u_z \equiv \cos \theta$ , namely

$$Z = \int \delta\hat{u}(s) \exp\left(-\frac{1}{2}\beta\varepsilon \int_0^L \left| \frac{d\hat{u}(s)}{ds} \right|^2 ds + \beta a S \int_0^L ds \left(\frac{3}{2}u_z^2 - \frac{1}{2}\right)\right). \quad (5)$$

Various authors (see WGB) have recognised that the path integral is the same as that for diffusion over the surface of a sphere with a diffusion constant  $D = 1/(2\beta\varepsilon)$  and a potential  $-aSP_2(\cos \theta)$ . The integral with initial and final directions constrained to given values represents the total weight associated with the transition in 'time'  $s$  from the initial to the final condition. This is simply the propagator,  $G$ , for the diffusional process that the tangent vector undergoes and can be expressed (WGB) more conventionally as a diffusion equation, albeit of the Schrödinger type:

$$[\partial/\partial s - D\nabla_{\hat{a}}^2 - \beta a S(\frac{3}{2}\cos^2 \theta - \frac{1}{2})]G(\hat{u}, \hat{u}'; s - s') = \delta(\hat{u}, \hat{u}')\delta(s - s') \quad (6)$$

where  $\nabla_{\hat{a}}^2$  is written explicitly with the unit vector  $\hat{u}$  to indicate that it is the angular part of the Laplace operator. The Green function  $G(\hat{u}, \hat{u}', s, s')$  is the propagator taking the tangent vector  $\hat{u}$  along the chain from initial direction  $\hat{u}'$  at the point  $s'$  to the final  $\hat{u}$  at the other point  $s$ . This is extensively discussed by WGB who show that the most interesting properties of nematic polymers arise from a non-perturbative solution of (6). In particular, transitions of the tangent vector between the poles of the unit sphere through the equatorial nematic potential are the hairpins first introduced by de Gennes (1982). Models not conserving chain length locally (Ronca and Yoon 1982) presumably have difficulty in describing such defects in chain conformation. de Gennes (1982) and WGB show that hairpins can have a profound effect on chain dimensions.

Measuring  $s$  in units of  $D^{-1}$ , the step length for the worm chain (4) without the nematic field, setting  $\Delta^2 \equiv -\frac{3}{2}Sa\beta/D = -3Sa\beta^2\varepsilon$ , assuming the  $s$  dependence  $e^{-\lambda_n s}$ , and supposing azimuthal symmetry we get the standard form of the spheroidal wave equation of zero order of Meixner and Schäfke (1954) (see Jähnić 1979)

$$\left[ \Lambda_n + \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) + \Delta^2(1 - \cos^2 \theta) \right] S p_n(\theta) = 0 \quad (7)$$

with  $\Lambda_n = \lambda_n - \frac{2}{3}\Delta^2$ . Denoting the eigensolutions of (7) by  $S p_n(\theta)$ , the spheroidal

wavefunctions of zero order, the Green function of (6) is

$$G(z, z'; L) = \sum_{n=0}^{\infty} \frac{2n+1}{2} Sp_n(z)Sp_n(z') e^{-\lambda_n L} \tag{8}$$

the weight of a chain configuration with initial and final directions  $z, z'$  (with  $z \equiv \cos \theta$ ).

Having written an explicit expression for the propagator  $G$ , we can use it to evaluate the partition function, the contribution of the chain's internal degrees of freedom to the total free energy of the system and then we can discuss the order parameter  $S$  and the nematic-isotropic transition of the polymers.

Accordingly the partition function  $Z$  is obtained by summing  $G$  over  $z$  and  $z'$ , having removed the aximuthal variation and the  $2\pi$  normalisation:

$$Z = \int dz dz' G(z, z'; L, 0) = \sum_{n=0}^{\infty} \frac{2n+1}{2} \left( \int dz Sp_n(z) \right)^2 \exp(-\lambda_n L). \tag{9}$$

For a free chain, i.e. in the isotropic liquid phase,  $\Delta^2 \rightarrow 0$ , so  $Sp_n \rightarrow P_n$ , the Legendre polynomials, and  $Z = 2$ .

In the nematic phase the order parameter is

$$S = \int_0^L \frac{ds}{L} \frac{\int dz dz' dz'' G(z', z; L, s)G(z, z''; s, 0)P_2(z)}{\int dz dz' dz'' G(z', z; L, s)G(z, z''; s, 0)}. \tag{10}$$

The  $Sp_n$  and  $\Lambda_n$  appearing in  $Z$  and  $S$  depend on  $\Delta^2$ , and hence the nematic order  $S$  and  $T$ ; therefore the resulting order parameter  $S$  must be made self-consistent.

The eigenfunctions  $Sp_n$  are expanded in terms of the  $P_n$ , the Legendre polynomials, which is useful for the evaluation of matrix elements of  $P_0, P_1$  and  $P_2$  necessary for the calculation of the order parameter and chain dimensions:

$$Sp_n(z) = \sum'_{2r \geq -n} a_{n,2r} P_{n+2r}(z) \tag{11}$$

where  $\Sigma'$  indicates that  $2r$  starts at  $-n$  or  $-n+1$  depending on  $n$  even or odd, respectively, i.e.  $Sp_n$  depends only on  $P_{n+2r}$  which has the same parity.

Substituting (11) into equation (7), we finally obtain a matrix equation with eigenvalues  $\Lambda_n$  and eigenvectors  $a_{n,2r}$  which have been numerically obtained to high accuracy. For  $\Delta^2 \rightarrow 0$ ,  $\Lambda_n$  takes the value  $n(n+1)$ , but for  $\Delta^2 \rightarrow -\infty$  the  $\Lambda_n$  coalesce in pairs for consecutive  $n$ ; the difference of  $\Lambda_2$  and  $\Lambda_0$  becomes greater as  $|\Delta|^2$  becomes larger. This is explained in wGB in terms of an analogy with quantum mechanical barrier penetration.

### 2.1. Very long chains

Substituting (8) into (10), only the  $Sp_n$  with  $n$  even survive because they are composed of the even  $P_n$ . For chains very long with respect to  $D^{-1}$  only the lowest eigenstate contributes because of the exponentials and

$$S = \frac{1}{2} \int_{-1}^1 dz [Sp_0(z)]^2 P_2(z). \tag{12}$$

Finally, we can obtain the expression for  $S$  using  $a_{0,2r}$  as follows:

$$S = \sum_{r=1}^{\infty} \frac{2r}{(4r+1)(4r-1)} \left( \frac{2r+1}{4r+3} a_{0,2r}^2 + \frac{3(2r-1)}{4r-3} a_{0,2r} a_{0,2r-2} \right). \tag{13}$$

This is a self-consistency equation since the  $a$  depend on  $\Delta^2$ , itself dependent on  $S$ .

The numerical results are depicted in figure 1.  $S = 0$  is a solution at all temperatures. This is the disordered phase, i.e. isotropic liquid phase. For temperatures  $T$  below  $0.39066 (a\epsilon)^{1/2}/k_B$ , two non-zero solutions to equation (13) appear. The upper branch tends to unity at absolute zero temperature and represents the nematic phase which means all the parts of the chains tend to align with a preferred axis, the director. The lower branch approaches  $-\frac{1}{2}$  at absolute zero temperature, implying that in this phase all parts of the chains would attempt to line up perpendicular to the preferred direction without azimuthal order. It is easy to prove from the free energy that at low temperatures this phase and the disordered phase are unstable with respect to the parallel-aligned nematic phase.

The free energy per chain for the mean-field problem follows from the partition function  $Z$  as

$$F_N = -k_B T \ln Z + \frac{1}{2} a S^2 L D^{-1} = -k_B T (-\lambda_0 L + \ln 2 + 2 \ln a_{0,0}) + \frac{1}{2} a S^2 L D^{-1}. \quad (14)$$

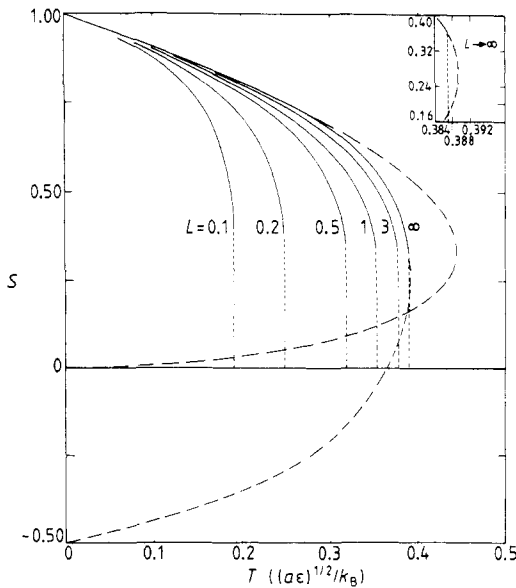
The second term seems unusual, the reason for its appearance in the free energy being the mean-field replacement of pair interactions by temperature-dependent potentials of a single monomer.

The free energy per chain of the isotropic phase of polymers is

$$F_I = -k_B T \ln 2. \quad (15)$$

The phase transition occurs when the free energies  $F_N$  and  $F_I$  of the nematic and the isotropic phases are equal. Typically,  $a_{0,0}$  is close to unity. For long chains,  $L \rightarrow \infty$ , equating free energies yields

$$\lambda_0 + \frac{aS^2}{2k_B T D} \equiv \lambda_0 + \frac{S^2}{T^2} = 0 \quad (16)$$



**Figure 1.** Order parameter  $S$  as a function of  $T$  (in units of  $(a\epsilon)^{1/2}/k_B$ ) for different chain lengths  $L$  (in units of  $D^{-1}$ ). The chain curve is the asymptotic result of wGB, given here in equation (29). The inset shows the transition region for very long chains in more detail.

where  $\tilde{T} \equiv k_B T / (a\epsilon)^{1/2}$  is the reduced temperature. The reduction by  $(a\epsilon)^{1/2}$ , in contrast to MS after (2), shows the interplay between polymer bend and the nematic field.

Numerical solution of (16) shows that  $F_I = F_N$  when  $T_c = 0.38775 (a\epsilon)^{1/2} / k_B$ . For  $T$  greater than the critical temperature  $T_c$ , the part of the upper branch of solutions shown in figure 1 has  $F_N$  greater than  $F_I$ , whence the polymers are in the isotropic liquid phase. When  $T$  is less than  $T_c$ , then  $F_N < F_I$ , thus the stable nematic liquid crystal phase appears. The order parameter  $S$  jumps from zero to 0.35642 at the transition temperature  $T_c$ .

The definition of  $\tilde{T}$  was recognised as appropriate by Jähmig who first introduced the worm model in this context, solved it perturbatively and exploited the quantum mechanical map. The results for  $T_c$  and  $S_c$  are the same as his though the aims here differ, particularly concerning the roles of finite length, chain dimension and latent entropy.

## 2.2. Finite chains

**2.2.1. The dependence of chain properties on length  $L$ .** If the chain is not long compared with the step length,  $D^{-1}$ , the Green functions (8) appearing in (10) for  $S$  are no longer dominated by their smallest eigenvalues,  $\lambda_0$ , as in (12), and  $S$  becomes, on performing  $L^{-1} \int ds$

$$S = \sum_{n,m=0}^{\text{even}} \left[ (2n+1)(2m+1) a_{n,0} a_{m,0} \frac{\exp(-\lambda_m L) - \exp(-\lambda_n L)}{L(\lambda_n - \lambda_m)} \right. \\ \left. \times \sum_{r=1}^{\infty} \frac{4r a_{m,2r}}{(4r+1)(4r-1)} \left( a_{n,2r} \frac{2r+1}{4r+3} + a_{n,2r-2} \frac{3(2r-1)}{4r-3} \right) \right] Z^{-1} \tag{17}$$

where  $Z$ , the partition function, is given below in equation (18).

The dependence of the order parameter on the temperature  $T$  for different chain lengths  $L$  is depicted in figure 1. At a given temperature,  $S$  decreases slowly with  $L$  until  $L \sim 1$  whereupon it decreases more rapidly. The corresponding variation of the transition temperature with  $L$  derives from the partition function (9) where, now, there are many contributors because  $L$  is not large:

$$Z = \sum_{n=0}^{\text{even}} 2(2n+1) a_{n,-n}^2 \exp(-\lambda_n L). \tag{18}$$

The free energy per chain of the nematic phase is

$$F_N = -k_B T \ln \left( \sum_{n=0}^{\text{even}} 2(2n+1) a_{n,-n}^2 \exp(-\lambda_n L) \right) + \frac{1}{2} a S^2 \frac{L}{D}. \tag{19}$$

Thus, from the equality of  $F_N$  and  $F_I$ , the equilibrium condition is

$$\frac{S^2}{T^2} L - \ln \left( \sum_{n=0}^{\text{even}} (2n+1) a_{n,-n}^2 \exp(-\lambda_n L) \right) = 0. \tag{20}$$

The results of the equation are shown in figure 2. The transition temperature is sharply increasing as the length is increasing and saturates rapidly as the length  $L$  is greater than  $D^{-1}$ , but the order parameter  $S$  is approximately constant.

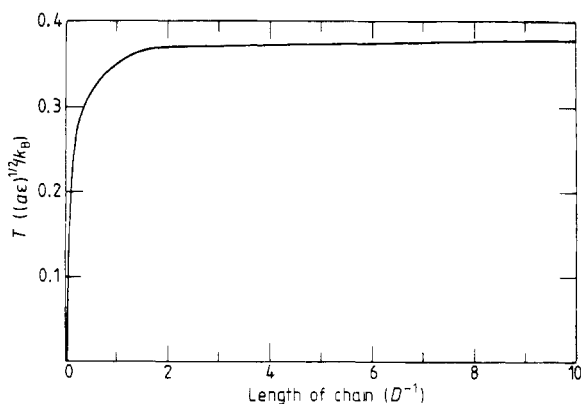


Figure 2. The variation of transition temperature on chain length, units being  $(a\varepsilon)^{1/2}/k_B$  and  $D^{-1}$  respectively.

We now pause to make contact with the MS theory of low molecular weight nematics. As  $L$  decreases rods become effectively stiffer (more rod-like) and, as the internal degrees of freedom become less significant, one would expect the surviving molecular field to dominate and thus Maier-Saupe behaviour to result since this is the sole ingredient of MS. At  $L = 1$  (in units of  $D^{-1}$ ) for an isotropic worm (no nematic field acting) we have for the ratio of the mean square  $z$  dimensions (wGB equation (2.6)),  $\langle r_z^2 \rangle / L^2 = 0.56 \times \frac{1}{3}$ , about half of the rod value of  $\frac{1}{3}$ , indicating the effect of internal flex modes coiling and hence shortening the 'rod'. When  $L = \frac{1}{8}$  the ratio of dimension to length is  $0.94 \times \frac{1}{3}$ , close to a rod. Indeed we see from figure 1 that for  $L \sim 0.15$  the dependence of  $S$  on temperature is similar to the MS theory which has  $S_{NI} = 0.441$  and  $T_{NI} = 0.22 a/k_B$ . It must be remembered though that this theory has two parameters  $a$  and  $\varepsilon$  when  $L$  is finite (only one, namely  $(a\varepsilon)^{1/2}$ , when  $L \rightarrow \infty$ ) and is different from MS which only has one parameter. This reflects the two aspects, polymeric and nematic, to this problem.

2.2.2. Entropy and latent heat. The entropy per chain of the nematic phase is given by

$$S_N = -k_B \langle \ln f \rangle \equiv k_B \ln Z + \frac{1}{T} \int ds \langle \frac{1}{2} \varepsilon \dot{u}^2(s) - a S P_2(u_z(s)) \rangle \quad (21)$$

where  $f$  is the distribution function for a configuration  $\mathbf{u}(s)$  and is the integrand in (5) divided by  $Z$ . The average  $\langle \dots \rangle$  is the usual  $\int \delta \mathbf{u}(s) f[\mathbf{u}(s)] \dots$ . The second part above is the mean energy. On transition not only the nematic mean field contributes to the latent entropy, but also the energy recovered from unbending the chain. The expression for  $S_N$  reduces in fact to the conventional

$$S_N = k_B \ln Z - k_B \beta (\partial / \partial \beta) \ln Z \quad (22)$$

despite the extra term in (14) for  $F_N$  and hence

$$S_N / k_B = [-\lambda_0 + \beta \partial \lambda_0 / \partial \beta + \lambda_0 \beta (\partial D / \partial \beta) / D] L + O(L^0). \quad (23)$$

We recall that the  $\lambda_0 L$  term of  $\ln Z$  has an additional temperature dependence in that the dimensionless length  $L$  has been reduced by  $D^{-1}$ , thus explaining the additional term  $\partial D / \partial \beta$  in (23). The terms non-extensive with  $L$  are as in (14) and arise from the prefactors in  $Z$ . From the definition of  $D$  we find that  $D^{-1} \partial D / \partial \beta = -1/\beta$ ,



ignoring the temperature dependence of  $\epsilon$ , as justified here by Jähnig (1979). To evaluate the derivative of  $\lambda_0$  we note that  $\lambda_0 = 2\Delta^2/3 + \Lambda_0$  and that  $\partial\lambda_0/\partial\beta \equiv (2\Delta^2/\partial\beta)(\partial\lambda_0/\partial\Delta^2)$  is readily accessible from (7) by applying the Pauli trick of deriving (7) with respect to  $\Delta^2$ , multiplying by  $S\rho_0$  and integrating. The result, noting that the normalisation of the wavefunctions is constant as  $\Delta^2$  varies, is

$$\partial\Lambda_0/\partial\Delta^2 = -2(1-S)/3$$

whence we obtain

$$\partial\lambda_0/\partial\beta = (2/\beta)\Delta^2 2S/3 \quad (24)$$

and for  $S_N$

$$S_N/k_B = -2\lambda_0 L + 4S\Delta^2 L/3. \quad (25)$$

The entropy of the isotropic phase is

$$S_I/k_B = \ln 2. \quad (26)$$

For long chains, the entropy change  $\Delta S$  at the transition is, from (16) which gives  $\lambda_0$  at the transition,

$$\Delta S/k_B = (S_I - S_N)/k_B = (2\lambda_0 + 4S_c^2/\tilde{T}_c^2)L = 2S_c^2 L/\tilde{T}_c^2. \quad (27)$$

The latent heat at the transition  $\Delta Q$  is  $T_c\Delta S$ . These both scale, in this limit, with the reduced molecular length  $L$ ; dividing through by  $L$  we accordingly obtain the latent entropy and latent heat per step length  $D^{-1}$  of the worm-like chain, the latent entropy being

$$\Delta S/(Lk_B) = 1.69. \quad (28)$$

This result is difficult to compare with the MS results because that theory does not have a length scale associated with the interaction energy scale (our  $a$  is an energy per unit length). Our length scale in addition depends on the flexibility  $\epsilon$ , a concept also absent in Maier-Saupe. What is clear here is that extra entropy is involved in the internal degrees of freedom of a chain becoming accessible above the nematic-isotropic transition, when chains can adopt the full range of worm conformations.

### 3. Discussion of theoretical results

The results of this paper are in broad agreement with those of Jähnig, albeit for a different class of systems. The present results differ however in that they derive from a theory (WGB) which treats the limit of strong nematic fields exactly, a limit shown to be inaccessible to perturbation approaches. Asymptotically the order parameter  $S$  (equation (5.21) of WGB) can be shown to be, from the solution of the cubical self-consistency equation,

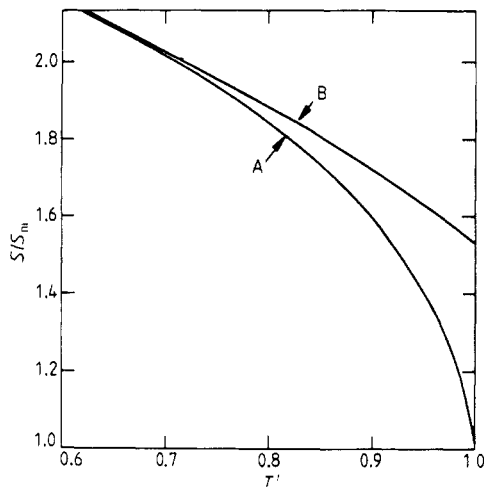
$$S = \frac{4}{3} \cos^2\left(\frac{1}{3}\{2\pi \pm \cos^{-1}[\frac{2}{3}k_B T/(a\epsilon)^{1/2}]\}\right). \quad (29)$$

The numerical analysis presented here from equations (12) or (13) for the upper branch of  $S$  is shown to be given accurately by (29), taking the upper sign, if  $T$  is below about  $0.3(a\epsilon)^{1/2}/k_B$ .

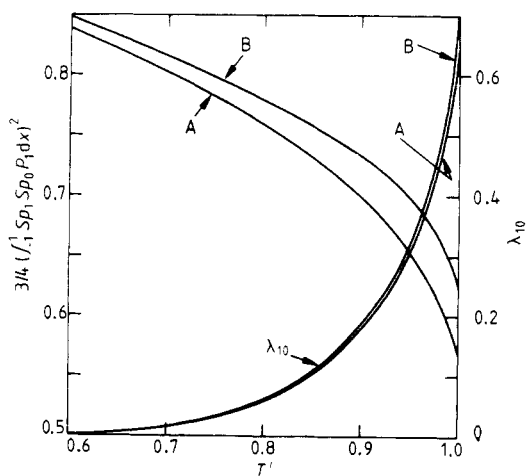
As the phase transition is first order with a jump in  $S$  to a finite value it is not guaranteed that perturbation theory, which requires a small potential and hence a small  $S$ , can ever work. Our numerical analysis in fact shows that the description of

the transition from asymptotic analysis is much better and that a perturbation analysis to third order (wGB) is never valid. Fourth-order theory can be shown to be adequate around the transition, but must fail at lower temperatures where  $\Delta^2$  become larger. Figures 3 and 4 illustrate how good the asymptotic analysis is.

Results are presented here also for chains of finite length. Inspection of the figures showed that (a) as chain length increases one rapidly approaches asymptotia, transition temperatures rapidly reach a limit, transition order parameters depend weakly on  $L$ ;



**Figure 3.** The variation of reduced order parameter  $S'$  with reduced temperature  $T' = T/T_{n1}$ . The exact numerical (A) and asymptotic (B) results are given. They are close below  $T' \sim 0.85$ . The reduced order parameter allows, via (32) and (33), the calculation of the nematic coupling  $\Delta^2$ , in turn determining chain dimensions.



**Figure 4.** The difference in eigenvalues,  $\lambda_{1,0}$ , and the matrix element expression, determining chain dimension in (34), as functions of reduced temperature  $T'$ . In each case exact numerical (A) and asymptotic expressions (B) are given, the latter for  $\lambda_{1,0}$  being highly accurate (36) right up to the transition. The eigenvalue difference or tunnelling rate from one orientation to another determines chain dimensions, particularly random walk to rod transitions (35).

(b) the transition does not become second order as previous authors have suggested. Indeed the additional collective aspects to the problem, the internal degrees of freedom coupled to the nematic field, make the transition more strongly first order than the corresponding MS description of conventional nematics (see note added in proof).

#### 4. Comparison with experiment

Experiment can be confronted in two ways, either (i) by estimating the parameters  $a$  and  $\varepsilon$  or (ii) by using reduced quantities to predict further properties.

(i) Jähmig (1979) discusses the evidence for  $a$  and  $\varepsilon$  in lipids. The lipid system has a potential with dipolar symmetry in addition to our quadrupolar potential. In its limiting form there are similarities. Taking the product  $(a\varepsilon)^{1/2}$  which avoids the complications in scaling out lengths, Jähmig gives the value 1.3 kcal mol<sup>-1</sup>. Then  $T_c$  is 253 K from his result of  $\tilde{T}_c = 0.388$ , a value in the range encountered in lipids.

(ii) Our theory produces an order parameter,  $S_{ni}$ , and latent entropy at the nematic isotropic transition which are universal to all polymers. The *reduced* transition temperature is also given. The transition order parameter  $S_{ni} = 0.356$  is of the order of that reported by many authors (see, for instance, Sigaud *et al* 1983). Other authors report higher values, perhaps as a consequence of the difficulty in locating  $T_c$  for viscous polymeric systems. As yet there appears to be little consensus of values. The question of the universal latent entropy is addressed below.

Because the comparison of theory and experiment merely at the transition offers so little scope we suggest below a detailed scheme for comparison and prediction involving order parameter, entropy and chain dimension. It is sensible to reduce experimental quantities by  $S_{ni}$  and  $T_c$ :

$$S' = S/S_{ni} \quad (30)$$

$$T' = T/T_c \equiv \tilde{T}/\tilde{T}_c = \tilde{T}/0.388. \quad (31)$$

The all-important nematic coupling is then

$$|\Delta|^2 = 3Sa\varepsilon/(k_B T)^2 = |\Delta_{ni}|^2 S'/T'^2 \quad (32)$$

where the value at the transition is

$$|\Delta_{ni}|^2 = 3S_{ni}/\tilde{T}_c^2 = 7.094. \quad (33)$$

Thus, given a plot of  $S'(T')$  in figure 3,  $|\Delta|^2$  can be found as a function of  $T'$  from (32). It can be seen that the asymptotic expression (29) is good below  $T' \sim 0.8$ .

Aside from the order parameter, the main quantity of interest is the chain dimension in the ordering direction,  $\langle R_z^2 \rangle$ , and perpendicular,  $\langle R_\perp^2 \rangle$ . These are discussed in WGB and are, correcting (5.14) of WGB for  $\langle R_\perp^2 \rangle$ ,

$$\langle R_z^2 \rangle = \frac{2LD^{-1}}{\lambda_{1,0}} \left\{ 1 + \frac{\exp(-\lambda_{1,0}L/D^{-1}) - 1}{(\lambda_{1,0}L/D^{-1})} \right\} \frac{3}{4} \left( \int dx Sp_0 P_1 Sp_1 \right)^2$$

$$\rightarrow L^2(1 - 1/|\Delta|) \quad \text{for } L/D^{-1} \gg \lambda_{1,0}^{-1} \quad \text{and large } |\Delta|^2 \quad (34)$$

$$\langle R_\perp^2 \rangle \rightarrow LD^{-1}/|\Delta|^2 \quad \text{for large } |\Delta|^2. \quad (35)$$

These can be found by small-angle neutron and x-ray scattering and have, we predict, important variation with temperature.

At low temperature such that the nematic field  $|\Delta|^2$  becomes large and  $\lambda_{1,0}$  small,  $\langle R_z^2 \rangle$  tends to a rod and the perpendicular extent  $\langle R_\perp^2 \rangle$  becomes a random walk of a small extent. What was found in wGB was that the former tends to a rod in a dramatic way when  $L/D^{-1} \sim \lambda_{1,0}^{-1}$ , the dominance of hairpins, the latter shrinks in a more uniform manner. Thus, with a knowledge of  $\lambda_{1,0}(T')$  and the matrix element,  $M$ , in (34) the chain extent can be calculated as a function of  $T'$  for a fixed  $L/D^{-1}$  and compared with experiment. The eigenvalue and matrix element are accordingly given in figure 4. Alternatively, a knowledge of  $\lambda_{1,0}(T')$  can be used to determine what length chains are required for experiment. Consideration of some numbers is illuminating: for the isotropic state  $\lambda_{1,0} = 2$  and  $L/D^{-1} \gg \frac{1}{2}$  is sufficient to give a random walk. At the transition  $|\Delta|^2 = 7$  and  $\lambda_{1,0} = 0.6$  whereupon the chain must be of a length such that  $L/D^{-1} \gg \frac{3}{2}$  that we essentially still have a random walk. If we want a transition to a rod to occur at the low temperature  $T' = 0.8$  we require there  $L/D^{-1} \sim \lambda_{1,0}^{-1}$ . We can estimate crudely in this example by guessing  $S' \sim 2$  from figure 3 and using (32) obtain  $|\Delta|^2 \sim 22$ . The asymptotic form for  $\lambda_{1,0}$  can be taken from wGB, equation (5.6):

$$\lambda_{1,0} = 32|\Delta|^2 \exp(-2|\Delta|)(1 - 1/|\Delta| + \dots) \quad (36)$$

which is shown in figure 4 and can safely be used here. It yields  $\lambda_{1,0} \sim 0.058$  whereupon  $L/D^{-1} \sim 17$ . This illustrates the prediction of wGB that the transition to the nematic phase does not, for reasonably long chains, mean an immediate adoption of the rod state, but that for a given  $L/D^{-1}$  this state will be found at a lower temperature. If the system is not already glassy at this  $T'$  we would expect a concomitant drop in viscosity. In this example a choice of  $L/D^{-1}$  intermediate to the limits  $\frac{3}{2}$  and 17 would hopefully reveal an interesting variation of behaviour in  $\langle R_z^2 \rangle$  as observed by scattering. Figure 5 illustrates the deviation from rod dimensions by dividing the mean square  $z$  dimension by  $L^2$  and plotting against reduced temperature. Polymers of various reduced lengths  $L/D^{-1}$  are shown. However since  $D^{-1}$  is a function of temperature,  $2\varepsilon/k_B T$ , this is not a good basis for comparison with experiment. Jähni $\ddot{g}$  (1979) shows that for  $(\text{CH}_2)$  entities that  $\varepsilon$  is a weak function of temperature and for the present illustration we assume that this additional temperature variation can be ignored. It is practical to proceed by taking out the temperature variation of  $D^{-1}$  by normalising to the value  $D_{ni}^{-1}$  and the relevant variable becomes  $\lambda_{1,0} T'$ . The difference is seen not to be very great.

It remains to discuss the effective step length  $D^{-1}$  itself. In the absence of knowledge of  $\varepsilon$  it can be measured via  $\langle R_z^2 \rangle$  and a scattering experiment in the isotropic phase for simplicity. However the theory puts an additional constraint on  $D^{-1}$  at the transition, i.e. on  $D_{ni}^{-1}$ , via the latent entropy (28), since putting back the  $D^{-1}$  into  $L$  we have

$$\Delta S_{\text{calc}} = 1.69 k_B L / D_{ni}^{-1} \quad (28')$$

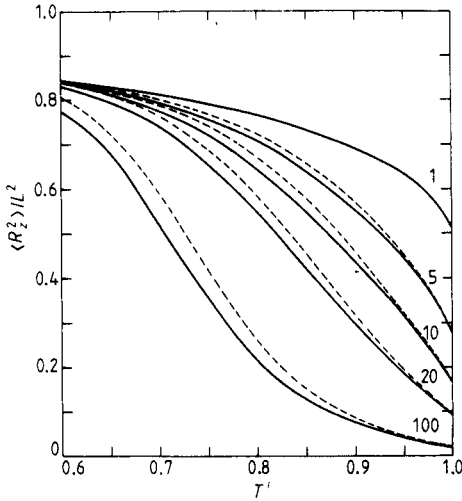
and  $1.69 k_B$  is the entropy per effective step length. Experiments are normalised to the latent entropy per monomer,  $\Delta s$  (Luckhurst (1985) quotes experiments)

$$\Delta S = \Delta s L / l \quad (37)$$

where  $l$  is the length of a monomer. Equating (37) with (28') we obtain, changing to molar values,

$$\frac{D_{ni}^{-1}}{l} = \frac{1.69}{\Delta s / R} \quad (38)$$

This relation scales in the correct manner: a more flexible chain, where  $D_{ni}^{-1}$  is diminished with respect to  $l$ , exhibits a larger latent entropy because the loss of freedom



**Figure 5.** Mean-square dimension of a chain along the nematic ordering direction reduced by the rod value,  $\langle R_z^2 \rangle / L^2$ , as a function of reduced transition temperature  $T'$ . Plots are given for several values of the chain length reduced by the effective step length,  $L/D^{-1}$ , as indicated. Note that short polymers transform quickly to rods (a reduced dimension  $\sim 1$ ) whereas longer polymers are only a small fraction of their rod dimension until much lower temperatures where the nematic field causes a rapid expansion, more rapid for longer chains. The reduction by  $D^{-1}$  appropriate to theory contains an additional temperature variation. This is taken out, as described in the text, and the dotted lines show the variation of dimensions of chains with temperature where chain lengths are reduced by the effective step length at the transition,  $D_{ni}^{-1}$ . The curves are taken from the expression (34) for long chains and the result for  $L/D^{-1} = 1$  is accordingly approximate.

of the chain in becoming nematic is greater. Typical values of  $\Delta s/R$  are in the region of 0.8–2.0 when  $D_{ni}^{-1} \geq l$ . Reported values of  $D_{ni}^{-1} \sim 6l$  would seem to have to be accompanied by low latent entropies, in our model around  $0.3R$ . Returning to our numerical example above, for the transition to a rod phase around  $T' \sim 0.8$  estimates of the degree of polymerisation would typically be in the region 1–3 to 15–45 depending on (38). We would like to see the comparison between thermodynamics and scattering afforded by (38).

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*Note added in proof.* Since the completion of this work, Rusakov and Shliomis (1985) have also solved the Jähniig model solved here, obtaining  $T_c$  and  $S_c$ . Although mainly interested in the relevant Landau theory they also notice, as we do in (b) at the end of § 3, that ten Bosch *et al* (1983c) wrongly obtain a second-order transition for very long chains. For finite chains their figure 1 is not directly comparable to our figure 2 since the reduction in length is different. Equally the variation of transition temperature with chain length in Jähniig's figure 7 cannot be compared with that in our figures 1 and 2 because of constraints acting in his case.

## References

- Blumstein A (ed) 1985 *Polymer Liquid Crystals* (New York: Plenum)
- Chapoy L L (ed) 1985 *Recent Advances in Liquid Crystalline Polymers* (London: Elsevier)
- Ciferri A, Krigbaum W R and Meyer R B (ed) 1982 *Polymer Liquid Crystals* (New York: Academic)
- de Gennes P-G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- 1982 *Polymer Liquid Crystals* ed A Ciferri, W R Krigbaum and R B Meyer (New York: Academic) p 124
- 1984 *Mol. Cryst. Liquid Cryst.* **102** L95-104
- Jähnig F 1979 *J. Chem. Phys.* **70** 3279
- 1981 *Mol. Cryst. Liquid Cryst.* **63** 157
- Luckhurst G R 1985 *Recent Advances in Liquid Crystalline Polymers* ed L L Chapoy (London: Elsevier) p 105
- Maier W and Saupe A 1959 *Z. Naturf.* **14a** 882
- 1960 *Z. Naturf.* **15a** 287
- Meixner J and Schäfke F M 1954 *Mathieu'sche Funktionen und Sphäroidfunktionen* (Berlin: Springer)
- Odiijk T 1985 *Polymer Commun.* **26** 197
- Ronca G and Yoon D Y 1982 *J. Chem. Phys.* **76** 3295
- Rusakov V V and Shliomis M I 1985 *J. Physique Lett.* **46** L935
- Sigaud G, Yoon D Y and Griffin A 1983 *Macromol.* **16** 875
- ten Bosch A, Maissa P and Sixou P 1983a *Phys. Lett.* **94A** 298
- 1983b *J. Chem. Phys.* **79** 3462
- 1983c *J. Physique Lett.* **44** L105
- Warner M, Gunn J M F and Baumgärtner A B 1985 *J. Phys. A: Math. Gen.* **18** 3007