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Discrete and continuum models of nematic polymers

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Abstract. Main chain polymer liquid crystals have been modelled as worms. In reality the stiffness is not distributed in this manner—rods are connected to each other by spacers. We examine the limits of this problem, that is worm and jointed-rod models, to see when each is applicable. Hairpins, found naturally in the worm problem, also exist for jointed systems but their scaling is quite different.

1. Introduction

Semi-flexible main chain polymer liquid crystals display isotropic, nematic and finally solid phases as temperature decreases. They consist of nematogenic rod elements connected by spacers of varying degrees of flexibility. Entering the nematic phase causes chains as a whole to become anisotropic (as seen by neutron scattering [1]), the degree of anisotropy of dimensions increasing more rapidly at temperatures lower than where the initial jump occurred (the nematic–isotropic transition). This behaviour is easy to describe using a worm model of a chain [2–6]. A worm has a *unit* tangent vector $\mathbf{u}(s)$ which means at each arc point s along its length the chain is inextensible. Changes in the tangent direction are penalized by an elastic bend energy $U_{el} = \int_0^L ds \frac{1}{2} \epsilon (\partial \mathbf{u} / \partial s)^2$ where ϵ is a bend constant, and the bend energy has been summed over all arc positions from 0 to the total length L of a chain. The possibility of bending has been attributed to all points of the chain not just localized at the spacers. We are concerned in this paper with (a) when is a continuum model a good representation of the underlying discrete polymer? and (b) can one obtain hairpins in the discrete model? Hairpins, introduced by de Gennes [2], are abrupt reversals of chain direction and prove to be significantly different in different models. The significance of the second question will emerge more fully when we discuss the first question. We shall also discuss another rather different, jointed model of nematic polymers due to Croxton [7–9] which also displays hairpins.

2. The continuum (worm) limit

Consider initially a set of discrete jointed rods to form a polymer (figure 1). The energy of such a polymer is

$$U = - \sum_i p Q P_2(\cos \theta_i) + \sum_i \frac{1}{2} q (\theta_{i+1} - \theta_i)^2. \quad (1)$$

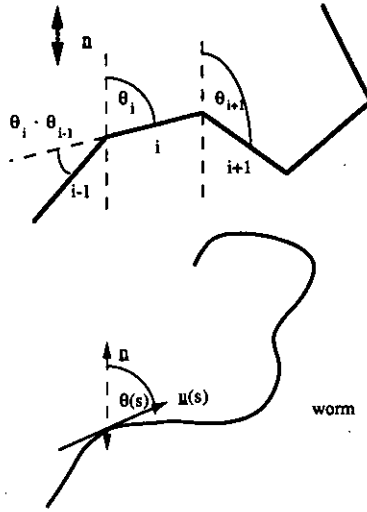


Figure 1. A section of jointed-rod chain with rods $i-1$, i , $i+1$ and their angles marked. The difference $\theta_i - \theta_{i-1}$ determines the bend energy. The worm limit is sketched with the tangent vector u at the arc point s having angle $\theta(s)$ with respect to the director n .

The first term is the nematic mean field energy, the order parameter is $Q = \langle P_2(\cos \theta) \rangle$ where $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$ is the second Legendre polynomial (appropriate to a quadrupolar system such as a nematic), p is a nematic coupling constant of a rod, and q is a bend elastic constant. In the elastic part we have taken a two-dimensional result for simplicity. There are no complications about the three-dimensional result [4]. If we take the limit of the rod length $l \rightarrow 0$ and the number N of rods $\rightarrow \infty$ such that $L = Nl = \text{constant}$, then we have $\sum_i l \rightarrow \int ds$ and the nematic part of U becomes

$$U_{\text{nem}} \rightarrow - \left(\sum_i l \right) \frac{p}{l} Q P_2 \rightarrow - \int ds v Q P_2 \quad (2)$$

with $v = p/l$ as $p \rightarrow 0$, $l \rightarrow 0$. The elastic part becomes

$$U_{\text{el}} \rightarrow \left(\sum_i l \right) \frac{1}{2} ql \left(\frac{\theta_{i+1} - \theta_i}{l} \right)^2 \rightarrow \frac{1}{2} \int ds \epsilon \left(\frac{\partial \theta}{\partial s} \right)^2 \quad (3)$$

with $\epsilon = ql$ as $l \rightarrow 0$, $q \rightarrow \infty$. Here v is a nematic energy per unit length and ϵ the bend elastic constant of the introduction. Natural scales of length and energy emerge from this. Let this length be λ , then scaling yields $x = s/\lambda$ whence

$$U \rightarrow \int_0^{L/\lambda} dx (\epsilon \dot{\theta}^2 / 2\lambda - \lambda v Q P_2) \quad (4)$$

where $\dot{\theta} \equiv \partial \theta / \partial x$. If λ is chosen so that the two terms enter with equal weight, $\epsilon/\lambda = \lambda v Q$, i.e. $\lambda = \sqrt{\epsilon/vQ}$ then $U \rightarrow \sqrt{\epsilon v Q} \int dx (\frac{1}{2} \dot{\theta}^2 - P_2)$. Hence and $\epsilon_h = \sqrt{\epsilon v Q}$ is the energy scale while $\lambda = \sqrt{\epsilon/vQ}$ is the length scale. The emergence of a length occurs physically because the nematic and bend processes in (2) and (3)

scale differently with the chain being divided into ever finer parts: $q = \epsilon/l \rightarrow \infty$ and $p = lv \rightarrow 0$ as $l \rightarrow 0$. If the physical length of rods is l_0 then the characteristic nematic length λ is, in terms of the parameters p and q of the discrete chain,

$$\lambda = \sqrt{\epsilon/vQ} \equiv \sqrt{ql_0/(pQ/l_0)} = l_0 \sqrt{q/pQ}. \quad (5)$$

Clearly a continuum picture of a nematic polymer is good if the characteristic length λ in the nematic problem is larger than the underlying length l_0 ; i.e. if $q > p$ in (5). Changes then take place over lengths long compared with l_0 , for instance a hairpin change in direction of a backbone of a liquid crystal polymer. The worm, with its continuum of allowed orientational states, successive sections of worm having nearby orientations, then accurately represents the angular entropy of the real polymer. This limit has been extensively examined at zero temperature [2] and at finite low temperatures [4, 6] where it is shown that ϵ_h becomes the energy of a hairpin, that is a change of chain direction from up to down (or the converse since there is quadrupolar symmetry) in the nematic field. In this limit $\epsilon_h \gg k_B T$ and, as is argued earlier, we must have $\lambda > l_0$. Worm models of nematic polymers have an energy scale ϵ_h derived from the product ϵv of bend and nematic potential. Our purpose is to see what the connection of this restricted form is to the results of discrete models of chains.

3. Discrete models of chains

In the limit where $\lambda \leq l_0$ the chain clearly behaves as a discrete object. For instance in the nematic field it might (in the low-temperature limit) make abrupt changes in direction (up to down), the bend being localized in one or two spacer units. Under those circumstances the continuum of allowed angular states of the spacer is clearly not the dominant feature. It is then interesting to model the chain by a jointed set of rods with discrete allowed orientational states. We adopt elastically jointed rods so that a bend energy remains in the problem. This is the opposite choice from that of Croxton [7-9] who models limited flexibility by freely jointed rods with a maximum cone angle allowed. This is an athermal choice, that is there is no energy or temperature associated with rod bending. His theory has one energy scale, that of the nematic potential.

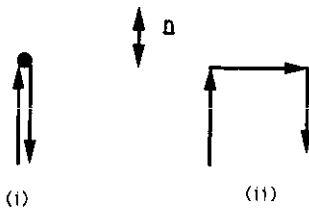


Figure 2. Possible reversals of direction for a discrete chain: (a) a bend of π at a single joint (\bullet); (b) a bend of $\pi/2$ at two successive joints.

Figure 2 sketches the simplest possibilities for a hairpin: (a) involves twice as much elastic energy as (b) (assuming that U_{el} is harmonic in the angular difference $(\theta_i - \theta_{i-1})$) but (b) involves the nematic potential p for the intermediate rod. This

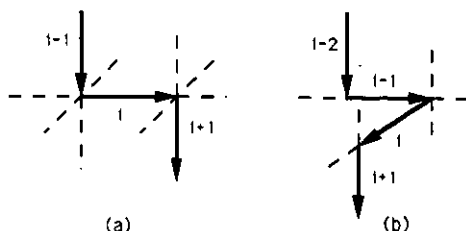


Figure 3. (a) A section of jointed chain. The bond i had six possibilities: up, down and four transverse states. (b) Two consecutive rods ($i-1$ and i) in their transverse states (required to illustrate the structure of the transition matrix).

is the first indicator that q and p enter separately in their own Boltzmann factors rather than in the form of their geometric mean \sqrt{qp} in a single Boltzmann factor.

To encapsulate the possibilities of figure 2 we need a model allowing up, down and g transverse states, see figure 3 for a simple cubic realization with $g = 4$. In models of nematics with discrete orientations of rods one must take care with the values of g and P_2 given to a discrete representation. If $P_2(\uparrow) = P_2(\downarrow) = 1$ (so as to get for perfect order $Q \equiv 1$) then for transverse directions $P_2(\leftrightarrow)$ must be $-2/g$ (to get $\langle P_2 \rangle_{\text{isotropic}} = 0$). Representing $pQ/k_B T = \alpha$ then the partition function for a single rod is

$$Z = 2e^\alpha + ge^{-2\alpha/g} \equiv 2e^\alpha \left(1 + \frac{g}{2} \exp \left[- \left(\frac{2}{g} + 1 \right) \alpha \right] \right) \equiv 2e^\alpha (1 + te^{-r}) \quad (6)$$

where $t = g/2$ and $r = (2/g + 1)\alpha$. Expanding $\ln(Z)$ in a series in Q , that is α , to get the free energy one obtains for the term cubic in Q

$$-\frac{1}{6} \frac{t}{1+t} + \frac{1}{2} \left(\frac{t}{1+t} \right)^2 - \frac{1}{3} \left(\frac{t}{1+t} \right)^3. \quad (7)$$

The cubic term is what distinguishes nematics from simpler dipolar systems such as magnets. For $t = 1$ the coefficient of α^3 , i.e. Q^3 , in the free energy vanishes, that is for $g = 2$. This degree of transverse freedom ($g = 2$) corresponds to a total of two dimensions, one up and down, the other transverse. The eigenfunctions of \hat{L}^2 (\hat{L} being the angular momentum operator, generating rotations in space) are $\sin(n\phi)$ in two dimensions. For these functions positive and negative values are geometrically equivalent, eliminating cubic terms in the free energy and giving a second-order phase transition. We shall adopt $g = 4$, but any value of $g > 2$ will give the correct first-order behaviour. Thus $P_2(\leftrightarrow)$ is $-\frac{1}{2}$. When introducing elastic interactions later we shall check at each stage that the nematic symmetry of the problem is retained.

We wish now to solve the relevant polymer problem by jointing such rods together and then adding an elastic interaction between consecutive rods. Since this is a one-dimensional problem along the chain with nearest-neighbour interactions and a nematic mean field it can be solved exactly using the transfer matrix technique. We shall do this but project the problem (approximately) down to that of a 3×3 matrix in order to have analytic solutions. It is important that at each stage of approximation we retain the nematic symmetry of the problem. The partition function of the jointed-rod

chain is

$$Z = \sum_{n_i} \prod_i \exp \left\{ \frac{\alpha}{2} [P_2(n_{i-1}) + P_2(n_i)] - \frac{\beta}{2} (n_i - n_{i-1})^2 \right\} \tag{8}$$

$$\equiv \sum \prod \exp[-H(n_i, n_{i-1})]$$

where the possible values of $n_i = \pm 1$ for \uparrow or \downarrow and $n_i = 0$ for the g transverse states specify the state of the i th rod. We write $q/k_B T = \beta$ for the reduced elastic interaction. \sum_{n_i} indicates a sum over all rod possibilities and we employ periodic boundary conditions $n_{N+1} = n_1$. The nematic interaction has been split into two parts so that a factor $\alpha P_2(n_i)$ appears as $(\alpha/2)P_2$ in two consecutive terms in \prod_i .

Z can be re-expressed as

$$Z = \dots M_{\xi\eta}^{(i-1)} M_{\eta\zeta}^{(i)} M_{\zeta\delta}^{(i+1)} \dots \tag{9}$$

where repeated subscripts indicate summation (tracing) and the matrix M is

$$M_{\eta\zeta}^{(i)} = \langle n_{\eta}^{(i-1)} | e^{-\hat{H}} | n_{\zeta}^{(i)} \rangle. \tag{10}$$

The six states of the i th rod are denoted by $|n_{\xi}^{(i)}\rangle$ whence M is a 6×6 matrix. The action of the operator \hat{H} on $|n\rangle$ generates the Boltzmann factor of (8). We now reduce this problem to that of a 3×3 matrix:

(a) *The freely jointed nematic polymer.* The (6×6) matrix M is

$$M^{(i)} = \begin{pmatrix} a^4 & [a]^\dagger & a^4 \\ [a] & \{a^{-2}\} & [a] \\ a^4 & [a]^\dagger & a^4 \end{pmatrix} \tag{11}$$

where $a = e^{\alpha/4}$, $[a]^\dagger = (a, a, a, a)$, $\{a^{-2}\}$ is the 4×4 matrix of elements a^{-2} , and \dagger denotes transposition. $[a]$ represents consecutive rods $(i-1)$, i with $(i-1)$ up or down and i transverse, or vice versa. The Boltzmann factors, split in the manner of (8) are thus $e^{\alpha/2 - \alpha/4} = e^{\alpha/4} \equiv a$. $\{a^{-2}\}$ represents $(i-1)$ and i both in transverse states and the Boltzmann factors are $e^{-\alpha/4 - \alpha/4} = e^{-\alpha/2} \equiv a^{-2}$. a^4 represents $\uparrow\uparrow$, $\downarrow\downarrow$, $\uparrow\downarrow$ or $\downarrow\uparrow$ for $(i-1)$ and i weighted by $e^{\alpha/2 + \alpha/2} = e^\alpha \equiv a^4$.

If one replaces M by the 3×3 matrix

$$M = \begin{pmatrix} a^4 & 2a & a^4 \\ 2a & 4/a^2 & 2a \\ a^4 & 2a & a^4 \end{pmatrix} \tag{12}$$

one can see that the tracing over a sequence analogous to (9) generates the same set of states as (9) itself. Two examples illustrate this: take $\dots M_{\xi\eta}^{(i-1)} M_{\eta\zeta}^{(i)} \dots$ with ξ , η and ζ equal to one of 1, 0 or -1 where, when they take the value 0, a $g = 4$ degenerate transverse state is implied. (i) The sequence of the type of figure 3(a) is contained in $M_{\pm 1, 0}^{(i-1)} M_{0, \pm 1}^{(i)}$ and results in the correct degeneracy of four associated with the choice of the states of the intermediate rod i . (ii) The example of figure 3(b) with two consecutive transverse rods $(i-1)$, i is described by $M_{10}^{(i-1)} M_{00}^{(i)} M_{01}^{(i+1)}$ and yields the correct value of 16 associated with the transverse degeneracy, this appearing as $2 \times 4 \times 2$, the individual factors being associated with the respective M s.

The trace of the product of the N matrices \mathbf{M} is

$$Z = \sum_{i=1,2,3} \lambda_i^N \quad (13)$$

where the λ_i are the three eigenvalues of the matrix \mathbf{M} . For the freely jointed case we are considering, the eigenvalues of (12) are

$$\lambda = 0, 0, 2a^4 + 4/a^2. \quad (14)$$

As $N \gg 1$ (13) is dominated by the largest of these whence

$$Z = (2e^\alpha + 4e^{-\alpha/2})^N \quad (15)$$

which by identification with (6) is clearly indeed the partition function for N freely jointed nematic rods and hence has the correct α^3 behaviour, that is it has a first-order phase transition. The latter, and the absence of an α term, is sensitively dependent on the correct choice of degeneracy factors in \mathbf{M} (12).

(b) *Elastically jointed rod polymers.* If we now take $\beta \neq 0$ then to each $\pi/2$ bend we associate the Boltzmann factor $b = e^{-\beta/2}$ in the partition function Z (8), since one of n_i or n_{i-1} must be ± 1 and the other 0. If we have bends of $\pi/2$ between transverse states (an example is in figure 3(b)) then $n_i = n_{i-1} = 0$ but we still associate b with the matrix element $\langle 0|e^{-\hat{H}}|0\rangle$. Likewise bends of π (reversals of direction) are weighted by $b^4 = e^{-2\beta}$. These are associated with the sequences $n_i = \pm 1, n_{i-1} = \mp 1$ between up/down states, and similar π bends connecting successive rods both lying in the transverse plane. The $(\pm 1, 0)$ and $(0, \pm 1)$ elements ($\pi/2$ bends to and from the transverse plane) clearly pick up a factor of b and the $(\pm 1, \mp 1)$ elements (π bends down to up and vice versa) b^4 (this is exact). The problem is that in the 3×3 representation of a 6×6 problem there is no unique prescription for putting these factors into the transverse states—a 4×4 block of the $6 \times 6 \mathbf{M}$ in (11) is now subsumed into a single number, the $(0, 0)$ element of the $3 \times 3 \mathbf{M}$ in (12). Referring to figure 3(b), if we model the polymer orientations by putting it on a cubic lattice, then there are four non-bent intermediate configurations, eight bent by $\pi/2$ and four by π . Accordingly the weight of these states in $\dots M_{10} M_{00} M_{0-1} \dots$ now becomes

$$e^{-\beta/2}(4 + 8e^{-\beta/2} + 4e^{-2\beta})e^{-\beta/2}. \quad (16)$$

The term at each end denoting the bend to or from the transverse plane and the middle factor the intermediate transverse states. Taking out a factor of two for each $e^{-\beta/2}$ factor in M_{10} and M_{01} one is left with $M_{00} = (1 + 2b + b^4)/a^2$ whence \mathbf{M} is now

$$\mathbf{M} = \begin{pmatrix} a^4 & 2ba & b^4 a^4 \\ 2ba & c/a^2 & 2ba \\ b^4 a^4 & 2ba & a^4 \end{pmatrix} \quad (17)$$

with $c = (1 + 2b + b^4) = 4$ when $b = 1$ (the freely jointed case $\beta = 0$). This choice replicates the full enumeration of the chain on a cubic lattice. Other choices of lattice would require a different combination of factors in c .

The partition function is again simply given by the largest eigenvalue of the matrix M (17), the root of a cubic equation. We denote this by λ_{\max} and the next largest roots by λ_1 and λ_2 :

$$\begin{aligned} \lambda_{\max} &= \frac{1}{2} \left\{ a^4(1 + b^4) + c/a^2 + \sqrt{[a^4(1 + b^4) - c/a^2]^2 + 32b^2a^2} \right\} \\ \lambda_1 &= a^4(1 - b^4) \\ \lambda_2 &= \frac{1}{2} \left\{ a^4(1 + b^4) + c/a^2 - \sqrt{[a^4(1 + b^4) - c/a^2]^2 + 32b^2a^2} \right\}. \end{aligned} \tag{18}$$

One may check that this gives a free energy of the correct form, that is with no α term and with a negative α^3 term. Taking $F = k_B T [\ln(Z) + \frac{1}{2} N \alpha^2 T']$ (with the last term being the mean field term to compensate for double counting) and T' the reduced temperature $T' = k_B T/p$, one obtains for small α :

$$\begin{aligned} F(\alpha)/N k_B T &= -\ln(1 + 4e^{-\beta/2} + e^{-2\beta}) + \frac{1}{2} [T' - \frac{1}{6}(1 + e^{\beta/2} + e^{-3\beta/2})] \alpha^2 \\ &\quad - \frac{1}{144} e^{-3\beta} (1 + 2e^{3\beta/2} + 2e^{2\beta} - 2e^{3\beta} + 2e^{7\beta/2} + e^{4\beta}) \alpha^3 \\ &\quad + \frac{1}{1728} e^{-9\beta/2} (1 + e^{3\beta/2} + e^{2\beta})^3 \alpha^4 + \dots \end{aligned} \tag{19}$$

The first term is due to the bend elasticity contribution when the polymer is in the isotropic state. The second term largely gives the first-order nematic-isotropic phase transition temperature T'_{NI} , which depends on the bend elasticity. If it is written in the form $\frac{1}{2} [T' - T'^*] \alpha^2$ then T'_{NI} is very close to the pseudo second-order phase transition T'^* , exceeding T' by an amount depending on the coefficients of α^3 and α^4 . Experimentally this difference is less than 1 K. As β approaches zero, T'_{NI} is reduced to that in the freely jointed rod system.

4. Chain dimensions

The central concern of this paper is the expansion of the chain at low temperatures. This is not revealed by the free energy (calculated earlier) but by a calculation of the mean square dimension $\langle R_z^2 \rangle$. In units of the rod length one has

$$\langle R_z^2 \rangle = \left\langle \left(\sum_i n_i \right)^2 \right\rangle \equiv \sum_{i,j} \langle n_i n_j \rangle. \tag{20}$$

Such averages are easy to evaluate using the Schwinger technique which we illustrate with the one-rod problem. Add a term $-\gamma n$ to the Hamiltonian: $H \rightarrow -\alpha P_2(n) - \gamma n$ whence Z becomes

$$Z = \sum_{n=-1,0,1} \exp[\alpha P_2(n) + \gamma n]. \tag{21}$$

Since we have

$$\langle n^2 \rangle = \left. \frac{\sum n^2 e^{\alpha P_2(n) + \gamma n}}{\sum e^{\alpha P_2(n) + \gamma n}} \right|_{\gamma=0} \tag{22}$$

then

$$\langle n^2 \rangle = \left. \frac{\partial^2 \ln Z(\alpha, \gamma)}{\partial \gamma^2} \right|_{\gamma=0} + \langle n \rangle^2. \tag{23}$$

We have $Z(\alpha, \gamma) = (e^{\alpha+\gamma} + e^{\alpha-\gamma} + 4e^{-\alpha/2})$, whence it can be seen that

$$\langle n \rangle = \partial \ln Z / \partial \gamma |_{\gamma=0} = 0 \tag{24}$$

as it should be for a nematic where the quadrupolar symmetry means that \uparrow and \downarrow are indistinguishable. $\langle n \rangle = 0$ is a result used for polymers. (23) then yields

$$\langle n^2 \rangle = \frac{1}{1 + 2e^{-3\alpha/2}} \tag{25}$$

and a direct calculation of the order parameter $Q = \langle P_2(n) \rangle_n$ gives

$$Q = (1 - e^{-3\alpha/2}) / (1 + 2e^{-3\alpha/2}) \tag{26}$$

whereupon, eliminating $e^{-3\alpha/2}$, one has

$$\langle n^2 \rangle = \frac{1}{3}(2Q + 1). \tag{27}$$

This is also essentially the result for an N -rod freely jointed polymer,

$$\langle R_z^2 \rangle = \sum_{i,j} \langle n_i n_j \rangle = \frac{N}{3}(2Q + 1) \tag{28}$$

that is there always remains a random walk in the Z -direction, the elongation of the polymer coming purely from the orientation of its elements rather than from correlations between them.

For the elastically jointed chain, elongation is primarily due to the infrequency of reversal of chain direction rather than the above bias of the rod directions. In the worm picture the energy cost of reversal was the geometric mean of the bend and nematic penalties. Here, one can see from figure 2 it can be either purely bend (i) or bend and nematic (ii) depending on their relative cost. The Schwinger term for the polymer is put in the symmetrized form $-\gamma(n_i + n_{i-1})/2$ whence in $M_{\xi\eta}^{(i)}$ one has an additional multiplicative term of $d^2 (\equiv e^\gamma)$ for $\xi = \eta = \uparrow$, d^{-2} for $\xi = \eta = \downarrow$, d for $\xi = \uparrow, \eta = 0$ and $\xi = 0, \eta = \uparrow$, d^{-1} for $\xi = \downarrow, \eta = 0$ and $\xi = 0, \eta = \downarrow$, and d^0 for 0, 0. Thus the transfer matrix \mathbf{M} becomes, instead of (17),

$$\begin{pmatrix} a^4 d^2 & 2abd & a^4 b^4 \\ 2abd & c/a^2 & 2ab/d \\ a^4 b^4 & 2ab/d & a^4/d^2 \end{pmatrix} \tag{29}$$

and now λ_{\max} and λ_1 are functions of γ as well as of p and q . We find, since $\langle n \rangle = 0$, that $\langle R_z^2 \rangle$ reduces to

$$\langle R_z^2 \rangle = \left. \frac{\sum_i [N(N-1)\lambda_i^{N-2}\lambda_i'^2 + N\lambda_i^{N-1}\lambda_i'']}{\sum_i \lambda_i^N} \right|_{\gamma=0} \tag{30}$$

where the summation is over the three eigenvalues λ_{\max} , λ_1 , λ_2 and prime denotes $d/d\gamma$.

The determinantal equation for the eigenvalues λ_i of the new M (29) is of the form

$$f(\lambda) + \gamma^2 g(\lambda) = 0 \tag{31}$$

as $\gamma \rightarrow 0$, where $f(\gamma) = 0$ is determinantal equation to be solved when $d = 1$, discussed above in (17) and (18). Equation (31) takes the form it does because of the symmetry of the appearance of the d and d^{-1} terms in (29). Terms in the determinant are functions of $d^2 + d^{-2}$ and $d + d^{-1}$. Equivalently, turning the polymer over lets $n \rightarrow -n$ or equally $\gamma \rightarrow -\gamma$ in the Schwinger terms. However $\langle R^2 \rangle_z$ is unchanged by this and hence the λ_i that determine $\langle R^2 \rangle_z$ must be functions of γ^2 . From (31) it is clear that the $\gamma = 0$ values of the eigenvalues, λ_i^0 say, are shifted by

$$\lambda_i \rightarrow \lambda_i^0 - \gamma^2 g(\lambda_i^0) / f'(\lambda_i^0) + O(\gamma^4) \tag{32}$$

where $f'(\lambda_i^0)$ is $df/d\lambda|_{\lambda=\lambda_i^0}$. We thus have $\lambda_i'|_{\gamma=0} = 0$ and

$$\lambda_i''|_{\gamma=0} = -2g(\lambda_i^0) / f'(\lambda_i^0). \tag{33}$$

The vanishing first derivatives simplify (30) considerably to

$$\frac{\langle R_z^2 \rangle}{N} = \frac{\sum_i \lambda_i^{N-1} \lambda_i''}{\sum_i \lambda_i^N} \Big|_{\gamma=0} \tag{33}$$

where the left-hand side is normalized so that the random walk result is $\langle R_z^2 \rangle / N = 1$. It is now clear why we also retain the second largest eigenvalue λ_1 : although in Z (and hence F) (13) shows that for large N the term λ_{\max}^N dominates over λ_1^N in (30), the balance in (34) for R_z between terms of order N (random walk) and order N^2 (rod-like) can be effected by λ_1 .

The drastic expansion of the chain is associated with $b \rightarrow 0$, that is large values of the elastic constant q . We hence explore this limit of (34). From equation (18) we see that λ_{\max}^0 and λ_1^0 tend to a common value $\bar{\lambda} = a^4$ as $b \rightarrow 0$. Denote the deviations of λ_{\max}^0 and λ_1^0 from $\bar{\lambda}$ by $\delta\lambda_i$. These deviations, from (18) can be seen to be $\delta\lambda_{\max} \sim O(b^2/a^2) + O(a^4b^4)$ and $\delta\lambda_1 = -a^4b^4$ and are hence small as $b \rightarrow 0$. Correspondingly the difference in the eigenvalues, $\lambda_{\max}^0 - \lambda_1^0 \equiv \delta\lambda_{\max} - \delta\lambda_1$ is also $O(b^2)$, denote it by Δ . Since $f(\lambda)$ has the λ_i^0 as its roots it must be $f = (\lambda_{\max}^0 - \lambda)(\lambda_1^0 - \lambda)(\lambda_2^0 - \lambda)$ whence we find that the derivatives are

$$\begin{aligned} f'(\lambda_{\max}^0) &= -(\lambda_1^0 - \lambda_{\max}^0)(\lambda_2^0 - \lambda_{\max}^0) \equiv -\Delta \cdot (\lambda_{\max}^0 - \lambda_2^0) \\ f'(\lambda_1^0) &= +\Delta \cdot (\lambda_1^0 - \lambda_2^0) \end{aligned} \tag{35}$$

From these expressions, in (33) we immediately see that the second derivatives at $\gamma = 0$ are

$$\lambda_{\max}''|_{\gamma=0} = -\lambda_1''|_{\gamma=0} = \frac{2g(\bar{\lambda})}{\Delta(\bar{\lambda} - \lambda_2^0)} \tag{36}$$

where we have set $\lambda_{\max}^0 = \lambda_1^0 = \bar{\lambda}$ in places where they appear insensitively.

Returning to $\langle R_z^2 \rangle / N$ (34), inserting λ_i'' and neglecting λ_2^N compared with the much larger λ_{\max}^N and λ_1^N we have

$$\frac{\langle R_z^2 \rangle}{N} = \frac{2g(\bar{\lambda})}{\Delta(\bar{\lambda} - \lambda_2^0)} \frac{(\lambda_{\max}^0)^{N-1} - (\lambda_1^0)^{N-1}}{(\lambda_{\max}^0)^N + (\lambda_1^0)^N}. \quad (37)$$

We set $\lambda_{\max}^0 = \lambda_1^0 = \bar{\lambda}$ (the value of the λ_i^0 at $b = 0$ for $i = \max$ and $i = 1$) for simplicity in the denominator of (37). Expanding about $\bar{\lambda}$ we obtain $(\lambda_i^0)^{N-1} \sim \bar{\lambda}^{(N-1)} [1 + (\delta\lambda_i/\bar{\lambda})(N-1) + \dots]$, and hence in the numerator we obtain for the difference $(\lambda_{\max}^0)^{N-1} - (\lambda_1^0)^{N-1} \sim \bar{\lambda}^{N-2}(N-1)\Delta$. One thus obtains

$$\frac{\langle R_z^2 \rangle}{N} = \frac{g(\bar{\lambda})(N-1)}{\bar{\lambda}^2(\bar{\lambda} - \lambda_2^0)}. \quad (38)$$

This is the rod result we have sought. The coefficient of N^2 in $\langle R_z^2 \rangle$ can be assembled: from (18) $\bar{\lambda} = a^4$ and $\bar{\lambda} - \lambda_2^0 = a^4 - 1/a^2$ (ignoring terms in b here since a is large). The additional term $g(\lambda)$ in (31) thus is

$$g(\lambda) = \lambda[4(ab)^2 - a^4c + a^4\lambda] \rightarrow \bar{\lambda}^3 \quad (39)$$

whence the coefficient of N^2 (see (38)) is precisely one. There are corrections to this pure rod value of $O(b)$. Extracting the rod limit from the apparently random walk result (34) depended on the two largest eigenvalues merging. In fact the closeness of the eigenvalues λ_{\max} and λ_1 determines the crossover between random walk and rod behaviour. This is the same phenomenon as in the worm-like chain where this is demonstrated by a semi-classical analysis of an analogue problem, the quantum rotator in a quadrupolar potential [3]. The requirement for a crossover is that the expansion of $(\lambda_i^0)^{N-1}$ after (37) about $\bar{\lambda}$ can be truncated as indicated. The condition that subsequent terms are small is, to within terms of $O(\ln(N))$, simply that $N(\Delta/\bar{\lambda}) \ll 1$, that is

$$\Delta/\bar{\lambda} \sim 2b^4 + \frac{8b^2}{a^6 - 1} + \frac{16b^3}{(a^6 - 1)^2} + \dots \ll 1/N \quad (40)$$

on expanding out and keeping large terms as $a \rightarrow \infty$, $b \rightarrow 0$. The final condition is then, to leading order,

$$2b^4 + 8b^2/a^6 = 2e^{-2\beta} + 8e^{-\beta-3\alpha/2} \ll 1/N. \quad (41)$$

The terms of the left-hand side can be identified with figures 2(a) and 2(b) respectively. When the larger of these (the more probable hairpin process) occurs on average more than once along the chain (i.e. the probability per rod of a bend occurring is $\geq 1/N$) then the chain as a whole begins take up a random walk rather than giant rod character. The important conclusion is that in the discrete picture one does not find the worm result \sqrt{qp} , but rather q and p occurring separately in Boltzmann factors. Thus worm and discrete models appear fundamentally different. Despite this, the basic hairpin process of stretching chains from random walks to rods as they become stiffer, or the nematic field becomes stronger, is as in the worm case. Note, however, that simply having a flexible chain ($q = 0$) in a strong nematic field ($p \rightarrow \infty$) is not sufficient ($2b$ is recovered) to get a rod, q must be large enough to

prevent figure 2(a) dominating. One needs $p > q$ in order to prevent the nematic field allowing 2(b) to provide a way around 2(a).

Direct comparison of our model with that of Croxton [7–9] is difficult since bend does not enter in his model as an energetic penalty, but rather as an entropic restriction (on accessible angles). However Croxton also notes that if there is no restriction on bend, even arbitrarily high nematic potentials cannot force the polymer to the rod limit. His converse result [7] that there are restrictions on bend sufficient to make nematic polymers always rodlike independently of how long they become is not borne out by these or earlier [4] investigations. We explore above how the rod limit is a delicate balance of Boltzmann factors of bend and nematic potential with the length N of the chain. It is clear that N must ultimately enter expressions for the rod-coil transition since these are one-dimensional systems that have no phase transition in the $N \rightarrow \infty$ limit. Croxton notes that his simulation study has difficulty attaining equilibrium at the lower temperatures.

Experiment in the rapid expansion of dimensions of main chain nematics has thus far been limited to one neutron scattering study [1]. Expansions, rapidly increasing as T is reduced, have been seen up to about $\times 16$ in $\langle R_z^2 \rangle$. We have speculated that there should be a drastic hairpin effect seen in dielectric [10] and NLO [11] experiments. It remains to be seen if these experiments can distinguish between the various models of nematic polymers.

In conclusion we have shown that having a worm or a discrete model depends on whether the characteristic hairpin size $\lambda = \sqrt{\epsilon v/Q}$ or $l_0 \sqrt{q/pQ}$ is larger than the length of the component rods in the polymer. If it is, a worm model seems appropriate. If not, a discrete model is better. We have analysed an extreme limit of a discrete model here, namely where the bend constant is large. Where the bend constant is smaller one can model the spacer as a section of worm chain of reasonable length. This has been treated elsewhere as the 'non-homogeneous chain' where the dependence on molecular parameters has been more fully explored [12].

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