Rod to coil transitions in nematic polymers

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Abstract. We calculate the order parameter and anisotropy (elongation) of the configurations of a nematic polymer in the nematic phase. At low temperatures we find exponentially rapid growth of chain dimensions as a function of inverse temperature. In the nematic direction the chain eventually adopts a rod-like state. The thermal activation of hairpins (abrupt reversals in chain directions) causes this behaviour. However, at even lower temperatures the deviation from rod-like alignment is governed by gentle meandering away from the mean field direction.

We construct a Maier-Saupe mean field theory of the nematic-isotropic transition, calculating for long chains the transition temperature as a function of chain properties and predicting a universal jump in the order parameter at the transition, $\Delta S_{nt} = \frac{1}{3}$.

1. Introduction

Nematic liquid crystals composed of polymer molecules have unexpected macroscopic and molecular behaviour arising from the additional element that distinguishes them from conventional rigid rod nematics, namely the internal molecular degrees of freedom. This internal entropy is responsible for the unusual properties of polymers, for instance rubber elasticity. There, a gross change in state of the fluid (extension) causes a distortion in the constituent chains and the consequent loss of freedom causes the free energy to rise.

We wish to present an analysis of chain statistics in polymeric nematics where now the fluid distortion is the existence of orientational order. The coupling of such order to the internal degrees of freedom of the chain causes a change in chain statistics, the ultimate form being the collective induction of rod-like character on intrinsically flexible chains.

Mesogenic polymers are of three types: backbone, comb and plate. We consider only the first, namely where the linear molecule has intrinsic stiffness, actual or inducible, sufficient to form a nematic liquid. An excellent review of molecular systems, experiment and theory is Ciferri *et al* (1982). One finds in such materials the features of both nematic and polymer problems; on the one hand, orientational elasticity of the nematic fluid, and on the other hand, the reaction of molecular conformation with the physical state. Additionally one finds conventional polymer properties such as (visco)-elasticity and long range spatial and temporal molecular correlations.

Backbone polymers in turn are of two types. The first, most commonly biological in origin, have rigid helical sections in equilibrium with random coil sections, the interface between the two types of chain having an associated energy. Pincus and de

Gennes (1978) recognised that this situation is analogous to the one-dimensional Ising model. They also made the important recognition that at sufficiently high chain concentrations the rigid sections will tend to orientationally order to fulfil the demands of non-overlap in their packing and the requirements of dispersion interactions. The well known incompatibility of nematic and random coil phases in turn *induces* more helical sections, leading to an additional effective rigidity of chains. Flory and Matheson (1984) attack this problem from a lattice viewpoint.

The second type of backbone is of fixed character, either uniformly stiff or consisting of stiff and less stiff sections in a fixed sequence. We, in common with most other authors, will assume that we are interested in properties relevant to sufficiently long length scales that we can characterise chains by a uniform stiffness, ε, or a persistence length, l, i.e. a worm-like chain. What has been found is that these nematic polymers can also exhibit an induced rigidity in that they increase their characteristic dimension (in the ordering direction at least) as a result of intermolecular orientational ordering. One must reiterate that within this second picture the chain structure is not changing in order to achieve this additional dimension. Flory (1978) discusses the types of molecules that could possibly conform to this picture of gradual change in the backbone direction. He then models the stiff molecule as a sequence of freely jointed rods, each with length equal to the chain persistence length, l. It is then argued that the drive to ordering is as for conventional, rigid rod, nematics, i.e. the individual rod segments pack more efficiently on average parallel to the ordering direction, the extent to which they do so being determined by their axial ratio, $x = l/d$, where d is a measure of the chain diameter. x sets a natural scale for chain segments.

We shall follow the spirit of this picture in our calculations and adopt a worm-like chain model for the polymer backbone. One important modification is required in order to discuss chain dimensions. Flory theory concerns itself with $P_2(\cos \theta)$ where θ is the angle that a segment makes with the ordering direction. For a quadrupolar fluid it is a good parameter with which to describe order. P_2 is the second Legendre polynomial. To describe the dimensions of a chain however $P_1(\cos \theta)$ is necessary, i.e. the end-to-end indistinguishability for nematic elements is violated when one comes to connect successive segments together to evaluate, say, the end-to-end dimension for the chain as a whole.

Jähnig (1979) was the first to use the worm-like chain, in the context of membrane structure, to evaluate chain properties in a nematic environment. He used a perturbative analysis for the worm equation in the presence of a potential as did ten Bosch *et al* (1983a), the latter authors also performing a perturbative analysis of the equivalent functional integral (our equation (4.1)) to derive a Landau theory (ten Bosch *et al* 1983b). We shall demonstrate that important qualitative aspects of induced rigidity, namely an essentially singular approach to the rod limit, are not accessible from a perturbative approach. de Gennes (1982) gives a useful qualitative argument for this tendency to the rod limit in terms of what he calls 'hairpins' where the chain departs from on average following the ordering direction in one sense, to following it in the opposite sense. The transition involves bending (penalised if done rapidly) and swimming across the nematic field (penalised if done too slowly). The resolution of the two competing effects is to give a value for the hairpin energy and then the transitions are considered thermally activated. Our purpose here is to describe both the perturbative and asymptotic limits within one model and to present a precise picture of the transition between rod and random walk. Ronca and Yoon (1982) also use the worm approach though their model only conserves length in a global and not a local sense,

an issue that possibly relates to the question addressed below of molecular trajectories versus local ordering direction.

All the above models make the assumption, conventional in nematics, that the local stiff unit is oriented on average about an ordering direction, the director, $\hat{n}$, and that the molecular axis is *not* to be identified with $\hat{n}$. In the worm picture we correspondingly have slack in the chains so that they can have the chemical length enabling them to fluctuate about $\hat{n}$. Consequently they are not rods in the $\hat{n}$ direction, not simply because they change their directions at hairpins, nor because backbone length is taken up by hairpins, but because they execute a random walk in the transverse direction, albeit of small extent as they stretch out in the rod limit, and therefore have finite angles, θ, with respect to $\hat{n}$. We calculate the order parameter $S = \langle P_2(\cos \theta) \rangle$ associated with these fluctuations. Contact is now made with nematic elasticity, especially splay. Within this model splay will be more difficult, because there are fewer chain ends than in a conventional nematic, but not divergently so as the chain length increases. Indeed we expect a complicated sequence of behaviours culminating in the splay being taken up by chain slack and hairpins and the modulus attaining a value independent of chain length.

It is also possible to take the opposite view (de Gennes 1982, Meyer 1982). These authors assume that there is little local freedom afforded to the worm-like molecule. The close registry in the tangent vectors of adjoining molecules in turn implies a rigid identification of director with molecular axis. Consequently nematic elasticity is then expected to be qualitatively different for polymers than for short rod molecules, the most notable example being the projected divergence of the splay constant with the length of molecules. Meyer (1982) mentions a compendium of other consequences.

Which of these two assumptions on molecular freedom is correct will be settled by experimental investigation of elasticity, flow, dielectric response and molecular conformation. We see molecular theory as being important since the deductions from either assumption are quite distinct. We make it clear that we assume a considerable degree of local chain freedom in analogy with conventional nematics and polymers.

We limit our predictions to aspects of chain configurations and some aspects of the nematic–isotropic transition. We find a description which encompasses the moderate increase of chain dimension in the ordering direction when the nematic field is weak, to a dramatic increase akin to the exponential behaviour of de Gennes (1982) when the nematic is strong. We address the problem of chain shrinkage transverse to ordering and the idea of chain slack.

In § 2 we explore the chain model (the worm) in some detail since much can be done later by analogy. We do not use the Wiener model of a chain since that model has implicit in it an infinite length of chain, manifested by one finding no limit to the extensibility, and no concomitant transverse shrinkage, when the chain is extended in one direction. For that reason it is a bad description close to the rod state where the local conservation of length is vital. Similar difficulties are encountered in the treatment of polyelectrolytes with weak screening. In § 3 we discuss the mean nematic potential experienced by a chain and in § 4 the conformations of a chain in this quadrupolar potential created by its neighbours. We demonstrate how this amounts to the diffusion on the surface of a sphere of the tangent vector and, in § 5, how chain dimensions depend on the tangent wandering around the pole (slack) or making a transition from one polar region to another (hairpins). In diffusion this transition is thermally enabled. Its frequency drops dramatically as the potential increases, thereby increasing the chain dimension. We explore this region in § 6 by looking at the analogous problem of the

quantum rotator where the transition is by tunnelling. In fact, § 6 represents a rather complete solution of the classic problem of quantum rotation of a molecule in a very strong crystal field. A Maier–Saupe theory (§ 5) is constructed to describe the nematic-isotropic transition. In § 7 we provide a summary.

2. The worm-like chain model

We shall adopt the worm-like chain as a model for the intrinsic properties of a polymer molecule, i.e. before the nematic influence is considered. Because the properties of a chain in a nematic environment can be derived in close analogy we develop the simple case in some detail.

This model, adopted also by Jähnig (1979) and Ronca and Yoon (1982), was first introduced by Saitoh *et al* (1967) and reviewed by Freed (1972). For such a chain we can represent a given point by $r(s)$ where the parameter s measures the chemical distance along the chain from one end. Since the chain is inextensible we have $|\partial r(s)/\partial s|^2 = 1$. Let us denote $\partial/\partial s$ by $'$ and further, $r'(s)$ by $u(s)$. Then $|u(s)|^2 = 1$. The bending energy is given in terms of the total curvature along the chain and an elastic modulus, ε. The energy is $\frac{1}{2}\varepsilon \int_0^L ds |u'(s)|^2$ where L is the total chain length. Let $\beta = 1/k_B T$ with T the temperature. Then an isolated chain, with no further influences on it, has a partition function given by the sum over all configurations $u(s)$, namely

$$Z_c = \int \delta u(s) \exp\left(-\tfrac{1}{2}\beta\varepsilon \int_0^L ds |u'(s)|^2\right). \qquad (2.1)$$

Given that $u(s)$ is a unit vector, as s varies along the chain, the point u wanders over the surface of a sphere. In fact since the chain folds at random, constrained only by the bending energy penalty, then (2.1) represents a kind of diffusion (Saitoh *et al* 1967, Freed 1972) over the surface of a sphere with a diffusion constant $D = (2\beta\varepsilon)^{-1}$. The sum (2.1) 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 for the diffusional process the tangent vector undergoes and can be expressed therefore in the more conventional language of the diffusion equation:

$$\left(\frac{\partial}{\partial L} - D\nabla_{\hat{u}}^2\right) G(u, u_0; L, 0) = \delta(u - u_0)\, \delta(L - 0) \qquad (2.2)$$

where $\nabla_{\hat{u}}^2$ is written explicitly with the unit vector $\hat{u}$ to indicate that it is the angular part of the Laplace operator. G is the propagator taking the tangent vector u along the chain from initial direction u_0 to the final u at the end point $s = L$. We make two remarks that are useful later. Where azimuthal variation is irrelevant, the Green function G can be written in terms of the eigenfunctions, P_l the Legendre functions, of ∇^2 thus:

$$G = \frac{1}{(2\pi)^2} \sum_l \left(\frac{2l+1}{2}\right) P_l(\cos\theta) P_l(\cos\theta_0) \exp(-\lambda_l |L|) \qquad (2.3)$$

where θ is the polar angle of u on the sphere and λ_l, the eigenvalue, is $\lambda_l = l(l+1)D$. We shall generalise this for nematics. The character of the trajectory $r(s)$ implied by G is that of a rod for L small, and an Einstein or Brownian walk for L large, L being

compared with the length of the fundamental elementary stiff unit of the chain, to be defined after (2.7). We find the rod or random walk character depending on L by noting that $r_z(L) - r_z(0) = \int_0^L ds\, u_z(s)$ where we take a given component, z, of the walk. Then $\langle [r_z(L) - r_z(0)]^2 \rangle$, related to the mean square end-to-end distance, is

$$\langle (r_z(L) - r_z(0))^2 \rangle$$

$$= \int \int_0^L ds\, ds' \langle u_z(s) u_z(s') \rangle = \int \int ds\, ds' \langle P_1(\cos\theta) P_1(\cos\theta') \rangle. \tag{2.4}$$

The average $\langle \ \rangle$ is evaluated using (2.3):

$$\int d\theta\, d\theta' \sin\theta \sin\theta' G(\theta, \theta'; s, s') P_1(\cos\theta) P_1(\cos\theta')$$

$$\times \left(\int d\theta\, d\theta' \sin\theta \sin\theta' G(\theta, \theta', s, s') \right)^{-1}$$

$$= \exp[-(\lambda_1 - \lambda_0)|s - s'|]/3 \tag{2.5}$$

where we normalise the average in preparation for the more interesting nematic case when $\lambda_0 \neq 0$ and (2.5) is not complete, as we will show in § 5. Inserting (2.5) in (2.4) we get

$$\langle (r_z(L) - r_z(0))^2 \rangle = \frac{2L}{\lambda_{1,0}} \left(1 + \frac{1}{L\lambda_{1,0}} [\exp(-\lambda_{1,0}L) - 1] \right) \Big/ 3 \tag{2.6}$$

where $\lambda_{1,0} \equiv \lambda_1 - \lambda_0 = 2D$ whence

$$\langle r_z^2 \rangle \sim L/D \qquad \text{(Einstein)} \tag{2.7a}$$

$$\sim L^2/3 \qquad \text{(rod)} \tag{2.7b}$$

for $LD \gg 1$ and $\leqslant 1$, respectively. The 'orientational diffusion constant', which has the dimensions of inverse length, defines an effective step length D^{-1} for the random walk when the molecule is long. This fundamental element of the chain can be taken to totally characterise the molecular structure and will be taken as a convenient measure of length. Before generalising this analysis to the nematic phase we discuss the additional influences acting on a chain.

3. The nematic environment and potential

In the nematic phase a molecule experiences a potential due to its environment of similarly ordered chains. We now present arguments, conventional for normal short rod nematics, for the existence of a mean field potential $V(u(s))$ appropriate for uniaxial nematics.

It is well known that nematics are invariant under reflections through the plane normal to the mean ordering direction (the director). A consequence is that the order in nematics is described by the even-order Legendre polynomials $P_2, P_4, \ldots$. The potential V felt by a molecule must perforce be of the same symmetry. A theory based solely on the soft dispersion forces between molecules with anisotropic polarisabilities (Maier and Saupe 1959) has $V(\theta) = k_B T^* S P_2(\cos\theta)$ where $k_B T^*$ is a measure of the magnitude of the forces involved (Wulf 1976). This is a mean field

approach where one replaces the interaction between pairs of molecules by P_2 of the angle, θ, a molecule makes with the ordering direction, $\hat{z}$, times the average, S, of $P_2(\cos\theta)$. Within this neglect of steric forces we shall examine the nematic to isotropic transition for polymers.

As well as these soft-core effects one has hard-core interactions, arguably more important in the drive toward ordering of molecules with rod-like character. This drive derives from the requirement that at high densities such anisodiametric molecules must have a tendency to be parallel in order to meet the constraint that they not overlap. Gelbart and Gelbart (1977) point out that an isotropic attraction, to maintain density, would produce, via this shape effect, an effective potential between molecules like

$$V(\theta) \sim aP_2(\cos\theta) + bP_4(\cos\theta) + \ldots \tag{3.1}$$

with constants $a, b, \ldots$, ascertainable from theory, such as scaled particle theory. Much earlier Flory (1956) had proposed $V(\theta) = ax\sin\theta$ where a is a constant depending on the distribution of rod orientations and x is the length-to-breadth (axial) ratio of the rod. The potential reflects the dependence of the translational freedom (entropy) of a rod on its and its neighbours' degree of orientational order. One derives the result by considering the projection of other rods onto the plane perpendicular to the rod-ordering direction. This has been criticised in at least two respects. The more natural projection for a molecule would involve $x - 1$ and not x, a consideration vital if x is not very large compared with unity (Warner 1982a). Secondly Flory's method divides the rod into different components and treats them inconsistently. Attempts to get around this have been made (Warner 1982b) with the result that the effective potential is no longer $\sin\theta$ but certainly continues to be dominated by P_2. We avoid these issues by simply taking a mean field potential of the form

$$V(\theta) = -aSP_2(\cos\theta) \tag{3.2}$$

where a is a constant of the form

$$a = k_B T^* + a_1 k_B T(D^{-1} - 1). \tag{3.3}$$

The first term measures the soft interactions and is now an energy per unit length. The second expresses the entropic potential and betrays, by the presence of the $k_B T$ term, the fact that $V(\theta)$ is really a free energy per unit length of chain. When we take $\exp(-V(\theta)/k_B T)$ then the second term contributes $\exp[a_1(D^{-1} - 1)SP_2(\cos\theta)]$ which is recognisable as expressing the entropic freedom of the chain.

An alternative justification for adopting the simple form (3.2) for the effective potential can be found in the discussion of the Maier–Saupe model by Luckhurst and Zannoni (1977) where the above ideas on the induction of such a potential form via the influence of molecular shape are expounded.

4. The equation for a chain and the nature of the solutions

We may now write the complete partition function for a chain including both the bending energy of the worm (2.1) and the effect of the nematic mean field (3.2) on the chain energy. As in (2.1) one considers a Boltzmann factor and obtains

$$Z_c = \int \delta\boldsymbol{u}(s) \, \exp\left(-\tfrac{1}{2}\beta\varepsilon \int_0^L |\boldsymbol{u}'(s)|^2 \, ds + \beta aS \int_0^L ds(\tfrac{3}{2}u_z^2(s) - \tfrac{1}{2})\right). \tag{4.1}$$

We have used $u_z = \cos \theta$ and $P_2(x) = 3x^2/2 - \frac{1}{2}$. In analogy with (2.2) there is a corresponding differential equation from which we shall work. It is

$$\left(\frac{\partial}{\partial L} - D\nabla^2 - \beta aS(\tfrac{3}{2}\cos^2 \theta - \tfrac{1}{2})\right) W(\theta) = 0. \tag{4.2}$$

We divide through by D and henceforth measure L in units of D^{-1}, the step length for the isotropic chain, and get

$$\left(\frac{\partial}{\partial L} - \nabla^2 - \Delta^2(1 - \cos^2 \theta) + \tfrac{2}{3}\Delta^2\right) W = 0 \tag{4.3}$$

where

$$\Delta^2 = -\tfrac{3}{2}Sa\beta/D = -3Sa\beta^2\varepsilon. \tag{4.4}$$

The rearrangement to the form (4.3) leads to the standard form (4.5) of the spheroidal wave equation of Meixner and Schäfke (1954) since if we put $W_n \sim \exp(-\lambda_n L)$ and note that angular part of ∇^2 is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta}$$

we get as an eigen equation

$$\left(\Lambda_n + \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} + \Delta^2(1 - \cos^2\theta)\right) W(\theta) = 0 \tag{4.5}$$

with $\Lambda_n = \lambda_n - \tfrac{2}{3}\Delta^2$. Let us denote the eigensolutions of (2.15) by $Sp_n(\theta)$, the spheroidal wavefunctions which reduce to the $P_n(\cos \theta)$ in the limit of $\Delta \to 0$ and are also normalised to $2/(2n+1)$. This equation has been extensively studied by many authors starting with Pauling (1930) who was interested in the quantum tunnelling of rotators in a quadrupolar field of a crystal. We shall exploit the formal analogy of (4.5) with this quantum problem in order to give an asymptotic analysis when the nematic potential is limitingly strong (see § 6).

The model of the worm-like chain being equivalent to the diffusion of the head of the unit tangent vector on the surface of the unit sphere is now modified. The nematic potential, $-\Delta^2 \sin \theta$ (with $\Delta^2 < 0$), acts to make the equatorial regions energetically unfavourable, reflecting the need of the molecule to avoid swimming across the nematic tide. For small Δ^2 transitions across, and residence in, the equatorial region are not uncommon. For large Δ^2, reflecting a strong potential, the tangent vector $u(s)$ is confined to the poles corresponding to the chain directed largely up or down the z axis. In diffusion thermally activated transitions over a barrier are possible, in this case over the equator.

Having established that the chain obeys a spheroidal wave equation we can write down its propagator, G, in analogy to (2.3), and use this to evaluate the partition function, i.e. the contribution of the chain's internal degrees of freedom to the total free energy of the system. G also enables us to calculate the conformations of a chain.

$$Z_c = \int dz \, dz' \, G(z, z'; L, 0)$$

$$= \int dz \, dz' \sum_n Sp_n(z) Sp_n(z') \exp(-\lambda_n L)\left(\frac{2n+1}{2}\right) \tag{4.6}$$

whereupon an expression analogous to (2.3) for the propagator G for the chain is also defined. For a free chain $Sp_n \to P_n$ and Z_c becomes $Z_c = 2$ in this picture since only the $n = 0$ term survives the sum over initial and final directions. What is important is the reduction in Z_c as a result of the action of a nematic field and we shall henceforth express Z_c in terms of the result $Z_c = 2$ for the unconstrained chain.

In a nematic field Z_c becomes

$$Z_c = \sum_n \left(\frac{2n+1}{2}\right) \left| \int dz\, Sp_n(z) \right|^2 \exp(-\lambda_n L)/2 \tag{4.7}$$

and we are forced to examine the character of the solutions to (4.5) in order to progress from the formal and useless expressions (4.6)–(4.7).

4.1. Solutions of the spheroidal wave equation

In this subsection we will present the eigenvalues and eigenvectors of the spheroidal wave equation in the limits of large and small Δ^2. These results completely specify the state of a chain, and will be used in later sections: the reader who is not interested in the details of the calculation should proceed to the next section.

For azimuthally symmetric solutions we set $m = 0$ in expressions for eigenfunctions and eigenvalues, following the notation of, say, Meixner and Schäfke (1954).

(a) *Eigenvalues.* For small nematic potentials, $\Delta^2 \to 0^-$, we can use perturbation theory about the spherical diffuser, $\{P_n\}$. We obtain for the eigenvalues Λ:

$$\Lambda_0(\Delta^2) = -\tfrac{2}{3}\Delta^2 - \tfrac{2}{135}\Delta^4 + \ldots > 0 \tag{4.8}$$

$$\Lambda_1(\Delta^2) = 2 - 2\Delta^2/5 - \frac{6}{7 \times 125}\Delta^4 + \ldots \tag{4.9}$$

giving the expected result $n(n+1)$ for $\Delta = 0$.

For $\Delta^2 \to -\infty$ we have (see Meixner and Schäfke 1954):

$$\Lambda_n = 2q|\Delta| - \tfrac{1}{2}(q^2+1) + O\left(\frac{1}{|\Delta|}\right) + \text{(non-analytic)} \tag{4.10}$$

where

$$q = n + 1 \qquad n \text{ even}$$

$$= n \qquad\quad n \text{ odd}$$

whereupon eigenvalues coalesce in pairs, the first two being

$$\Lambda_0 = \Lambda_1 = 2|\Delta| - 1 + \text{(non-analytic)}. \tag{4.11}$$

The small, non-analytic (in $1/|\Delta|$), terms survive in this difference and are a vital part of our description of chain conformations. They are derived in § 6, see (6.17). We show in figure 1 a schematic plot of $\Lambda(\Delta^2)$.

(b) *Eigenfunctions.* The eigenfunctions Sp_n are naturally expanded, for small Δ^2, in terms of the P_n appropriate to free rotational motion, this being useful for the evaluation of matrix elements of P_1, P_2 necessary for the calculation of the order parameter and chain statistics:

$$Sp_n(z) = \sum_{2r \geqslant -n}' a_{n,2r} P_{n+2r}(z) \tag{4.12}$$
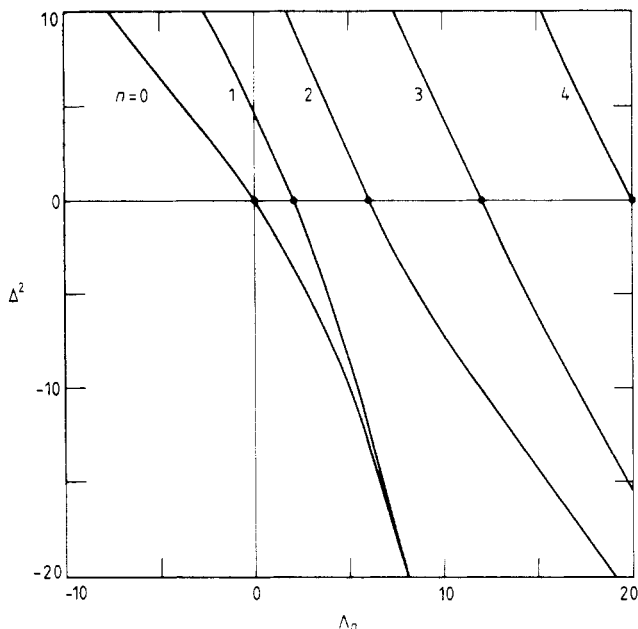
Figure 1. A schematic plot of eigenvalues Λ_n against strength Δ^2 of the quadrupolar potential. For free motion, $\Delta^2 = 0$, Λ_n takes the value $n(n+1)$. For strong nematic fields, $\Delta^2 \to -\infty$, the Λ_n coalesce in pairs with extreme consequences for chain dimensions.

where Σ' indicates that $2r$ starts at $-n$ or $2r = -n+1$ depending on n even or odd, respectively, i.e. a Sp_n depends only on P_{n+2r} which have the *same* symmetry. Since the spheroidal wave equation (4.5) tends to equation (2.2) for free diffusion as $\Delta^2 \to 0$, then $Sp_n \to P_n$. In our calculations, we will only need the expansions of Sp_0 and Sp_1. One may derive the expansions perturbatively; from Bouwkamp (1947) we find for Sp_0:

$$a_{0,0} = 1 - \Delta^4/(2 \times 3^4 \times 5) + 2\Delta^6/(3^6 \times 5 \times 7) + O(\Delta^8)$$

$$a_{0,2} = -\Delta^2/9 + 2\Delta^4/(3^4 \times 7) + 61\Delta^6/(2 \times 3^6 \times 5^2 \times 7) + O(\Delta^8) \qquad (4.13)$$

$$a_{0,4} = \Delta^4/(3 \times 5^2 \times 7) + O(\Delta^6)$$

and for Sp_1:

$$a_{1,0} = 1 - O(\Delta^4)$$

$$a_{1,2} = O(\Delta^2).$$

For $\Delta^2 \to -\infty$ we give an asymptotic analysis in § 6 of the matrix elements of P_1 and P_2 directly.

The first application of these expansions is to the partition function. For sufficiently long chains Z_c will be dominated in (4.7) by the ground state, $n = 0$, where for $\Delta^2 \to 0^-$, $\lambda_0 = \Lambda_0 + \frac{2}{3}\Delta^2 = -2\Delta^4/135$, whereupon

$$Z_c = |a_{0,0}|^2 \exp(2\Delta^4 L/135)$$

$$\equiv \left[1 - \frac{1}{9}\left(\frac{2\Delta^2}{15}\right)^2\right]^2 [1 + 2(L/135)\Delta^4] = 1 + \left(\frac{2L}{135} - \frac{8}{9 \times 225}\right)\Delta^4 + \dots . \qquad (4.14)$$

At first sight this increase in the partition function seems surprising, as one expects the number of allowed states to fall on the application of a nematic potential. However the decrease in the internal energy outweighs the decrease in entropy, causing a net decrease in the free energy.

In the opposite strong potential limit $\Delta^2 \to -\infty$, again only the lowest state enters. Although $\Lambda_1 \to \Lambda_0$ so that there is no ground-state dominance in the exponential term of (4.7), there is no P_0 term in Sp_1 and hence no contribution to the integral from $n = 1$ terms. Then the partition function becomes

$$Z_c = |a_{0,0}(\Delta^2)|^2 \exp\left(-\frac{2L\Delta^2}{3} - 2|\Delta|L\right) \equiv 4 \exp(+\tfrac{1}{2}T^*SL/T)/|\Delta|. \qquad (4.15)$$

In the second expression we have taken out the factor of D implicit in L and used the expression for Δ^2 to show that the main contribution to the partition function is from a mean potential energy per unit length of $\tfrac{1}{2}T^*S$. The pre-exponential term $|a_{0,0}|^2$ can be derived from § 6. We have also put it in terms of the chain parameters. It is of no importance in the free energy, the terms in the exponent extensive with L dominating. The smaller, positive energy term in the exponent is a consequence of hairpins in the chain and will be discussed in the next section.

In general Z_c will be given by neither limit but by (4.7). Although we shall not discuss thermodynamics further here one can see how the problem must be completed. The Sp_n and Λ_n appearing in Z_c depend on Δ and hence on the nematic order S and T. We shall show that S depends similarly on expressions involving G and hence on Sp_n and Λ_n. The free energy, a part of which is $\ln Z_c$, must therefore be minimised and the resulting S be made self-consistent. Another part of the free energy is from the translational freedom. It depends on the state of orientational order, a coupling that motivates the Flory rod potential, see § 3. Above the nematic–isotropic transition $S = 0$, and below it is finite, the transition being first-order. In what follows we shall look at chain statistics, assuming a value of S within Δ, and self-consistently solve for the order parameter within Maier–Saupe theory.

5. Chain statistics, the order parameter and Maier–Saupe theory

5.1. Chain statistics

For the isotropic worm-like chain we have unbiased random walk statistics. What do we expect with a nematic mean field acting in the z direction (say)? For a weak field there will be a tendency for segments of the chain to align along the $\pm z$ directions, thus biasing the random walk to have less arc length in the xy plane. This causes an extension of the chain in the nematic directions and a contraction in the transverse plane. In a stronger field (at lower temperatures) the morphology of the chain contains the new feature of hairpins. These arise because of the strong alignment of the chain in the $\pm z$ directions. Between the $+z$ sections and $-z$ sections, the chain must have a region transverse to the field, the hairpin. The number of hairpins is controlled by the Boltzmann factor associated with their energy, with contributions from a bending energy, trying to make the hairpin large, and nematic energy, trying to make it shrink: the balance between these determines the size. The fewer the number of hairpins, the closer to a rod the chain becomes. The remainder of this subsection will be concerned

with the calculation of chain statistics, vindicating the above conclusions and discussing some ramifications of them.

Henceforth we will only consider long chains. The limit $L \leq 1$ (remembering that L is reduced by D^{-1}) is not interesting since from (2.7) we already have rods without any inducement from the nematic field and the system obeys the laws of conventional nematics. We therefore restrict ourselves to $L \gg 1$, a truly semi-flexible polymer in the sense that the molecule is long compared with the basic stiff unit. The end-to-end correlation of a chain is expressed in (2.4) in terms of the chain tangent correlation, i.e. $\langle P_1 P_1 \rangle$. Considering conformations of the chain as a whole it is clear that the correlation function is given by

$$\langle P_1(x) P_1(x') \rangle = \int dx_0 \, dx \, dx' \, dx_f \, G(x, x_0; s)$$

$$\times P_1(x) G(x', x; s' - s) P_1(x') G(x_f, x'; L - s') / Z_c(L). \tag{5.1}$$

We now perform $\langle \ldots \rangle$ using (4.6) rather than the free expression (2.3) for G. Using the long chain limit this simplies to

$$\frac{3}{2} \left(\int dx \, Sp_0(x) P_1(x) Sp_1(x) \right)^2 \exp(-\Lambda_1 |s - s'|) / Z_c(|s - s'|). \tag{5.2}$$

The result for $\langle r_z^2 \rangle$ then resembles (2.6), namely

$$\langle r_z^2 \rangle = \frac{2L}{\lambda_{1,0}} \left(1 + \frac{1}{L\lambda_{1,0}} [\exp(-\lambda_{1,0}L) - 1] \right) \frac{3}{4} \left(\int dx \, Sp_0(x) P_1(x) Sp_1(x) \right)^2. \tag{5.3}$$

Recalling for the free worm-like chain there was a qualitative change from Einstein to rod behaviour according to whether $L\lambda_{1,0}$ was large or small, in that case, according to whether L was large or small compared with the step length. In nematics there is another path, via the nematic mean field, to making the product $L\lambda_{1,0}$ small, thereby inducing rod character. We have seen from figure 1 and from the expression (4.11) from $\Lambda_n(\Delta^2)$ that $\lambda_{1,0} \to 0$ as Δ^2 becomes large and negative, the eigenvalues of the wave equation coalescing in pairs. Therefore there is a range of values of Δ^2 where the chain becomes very rod-like with a dramatic expansion in $\langle r_z^2 \rangle$.

(a) *The weak nematic limit,* $\Delta^2 \to 0^-$. In the limit of $L \gg 1/\lambda_{1,0} \sim \frac{1}{2}$ equation (5.3) simplifies, as the expression in curly brackets becomes unity, and $\langle r_z^2 \rangle$ has the form of a random walk with effective step length L_{eff}, defined implicitly by (5.3) and

$$\langle r_z^2 \rangle = L L_{eff} / 3. \tag{5.4}$$

The integrals in the expression for L_{eff} can be readily worked out by expanding Sp_0 and Sp_1 in terms of Legendre functions (the perturbative results of (4.13)) to yield the final result (approximating $\lambda_{1,0}$ by (4.8) and (4.9)):

$$L_{eff} = 1 + 2|\Delta^2| / 9. \tag{5.5}$$

(b) *The strong nematic limit,* $\Delta^2 \to -\infty$. Inspection of (5.3) for $\langle r_z^2 \rangle$ showed that dimensions increased as the field Δ^2 became stronger. Physically it is clear why this is so; the diffusion of $u(s)$ on the surface of a sphere as s evolves is localised to the polar regions with a large potential $\Delta^2 P_2(\cos \theta)$ restricting the residence in and passage over the region of large equatorial potential. With the tangent pointing on average nearly always to one of the poles it is inevitable that the z dimension should become

like the extent of a rod. In the *xy* plane the chain retains its random walk character, $\langle r_x^2 \rangle \sim L$ but with reduced persistence length.

It is perhaps easier to visualise this problem of thermal diffusion over a barrier as that of a quantum rotator in the potential $V(\theta)$. The transition of $u(s)$ from one polar region to another would then proceed by tunnelling as *time s* evolves. Equation (4.5) then represents a time-independent version of the problem in which the eigen energies and wavefunctions are required. In § 6 we solve the problem of large nematic potentials Δ^2 by looking at the analogous quantum problem in the semiclassical limit. Here we shall simply take over these results, the most vital being the small, non-analytic, difference between the first two eigenvalues:

$$\Lambda_{1,0} = 32|\Delta|^2 \exp(-2|\Delta|)[1 - 1/|\Delta| + \ldots] = L^{*-1}. \tag{5.6}$$

Meixner and Schäfke (1954, p 221) quote this result without proof. We thus define the length $L^*(|\Delta|)$, also reduced by D^{-1} the unperturbed chain persistence length.

Two new possibilities now arise.

(1) Rods. Although $L \gg 1$, the length L^* given by (5.4) is exponentially large and we can have, for large enough $|\Delta|^2$, $\lambda_{10}L \ll 1$. The effect of this exponentially large induced effective step length in the *z* direction is to reduce (5.3) for $\langle r_z^2 \rangle$ to the rod expression

$$\langle r_z^2 \rangle = \tfrac{3}{4}L^2 \left(\int dx \, Sp_0(x) P_1(x) Sp_1(x) \right)^2 \tag{5.7}$$

for $L \ll \exp(2|\Lambda|)/32|\Delta|^2 \equiv L^*$. Taking over (6.18) for the matrix element we obtain

$$\langle r_\perp^2 \rangle = L^2 (1 - 1/|\Delta|). \tag{5.8}$$

This rod-like result differs from the coil-like result obtained in the isotropic melt by a factor of L/D^{-1}, roughly the degree of polymerisation.

(2) Random walks. If, on the other hand, Δ^2 is large but the chain is also long so that $L \geq L^*$ then (5.3) is instead reduced in a manner similar to that of (2.6) and yields a random walk, albeit greatly expanded in the *z* direction, with $\langle r_z^2 \rangle$ given by

$$\langle r_z^2 \rangle = 2(1 - 1/|\Delta|)L^*L \equiv LL_{\text{eff}}/3 \tag{5.9}$$

i.e. an effective step length is defined:

$$L_{\text{eff}} = [6 \exp(2|\Delta|)/32|\Delta|^2](1 - O(1/|\Delta|)) \propto \exp[2(3Sa\varepsilon)^{1/2}/k_B T] \tag{5.10}$$

reflecting the steps in the random walk in the *z* direction being the relatively straight sections between hairpins. We recall that without the nematic field, i.e. for an isotropic melt of such chains, $L_{\text{eff}} = 1$ (in units of D^{-1}). Accordingly L_{eff} is also the ratio of chain dimensions in the nematic melt to that in an isotropic environment. Chains are vastly expanded.

On undergoing the transition from isotropic to nematic S changes discontinuously from 0 to some $S(T)$ and from the above we see that there is a concomitant chain expansion. Chains with $L \sim L^*$ immediately become rods. Longer chains initially expand at the transition but are not yet rod-like. Further decreases in T cause L^* to increase in a very sensitive manner (like $e^{1/T}$). Although not strictly a phase transition, except for $L = \infty$ which has a transition to rod behaviour at $T = 0$ characteristic of one-dimensional systems, there is, for long enough chains, a second lower temperature region where chains experience another expansion to a final rod state. Along with this

drastic reduction in chain 'hairpins' would go a change in macroscopic properties such as elasticity and dynamical response.

5.2. Hairpin density and chain slack

Regarding (5.9) as a one-dimensional random walk with steps connected by n_h hairpins then one has

$$L_{eff}/3 \sim L/n_h \tag{5.11}$$

whence

$$n_h \sim 3L/L_{eff} \sim \left(\frac{L}{D^{-1}}\right)\frac{3Sa\varepsilon}{(k_B T)^2}\exp[-2(3Sa\varepsilon)^{1/2}/k_B T] \tag{5.12}$$

where the latter relation shows the scaling by the ratio of the total chain length to the chain stiffness. This expression makes contact with the de Gennes (1982) method of calculating the compromise between nematic and bending energy to get the energy associated with a local object and then simply using this energy in a Boltzmann factor. For example one motivates the exponential part of the partition function (4.15) in the strong field limit. The hairpin picture is an extreme limit, the validity of which depends upon the availability of chain slack to accommodate such defects in the nematic. This relates to the question of the rigid identification of chain axis with the director.

Excursions of the tangent vector from a pole without the creation of hairpins represent this slack and contribute to the transverse dimension $\langle r_\perp^2 \rangle \equiv \langle r_x^2 + r_y^2 \rangle$:

$$\langle r_\perp^2 \rangle = \int ds\,ds'\langle \sin\theta(s)\sin\theta(s')\cos(\phi(s)-\phi(s'))\rangle. \tag{5.13}$$

To average this we recognise that this involves $\langle P_1^{\pm 1}(x)\exp(\pm i\phi)P_1^{\mp 1}(x')\exp(\mp i\phi')\rangle$ necessitating the introduction of the eigenfunctions $Sp_n^m(x,\phi)$ decribing azimuthal variation in the spheroidal wave equation. The calculation proceeds in the same way as for $\langle r_z^2 \rangle$, but exponential terms $\exp[-(\Lambda_1^1 - \Lambda_0)|s - s'|]$ are obtained which, because $\Lambda_1^1 - \Lambda_0$ is never small as $\Lambda_1 - \Lambda_0$ could be, yields $2L/(\Lambda_1^1 - \Lambda_0)$ for the $\int ds\,ds'$. The result in the strong coupling limit is

$$\langle r_\perp^2 \rangle = L/(2|\Delta|^3) \tag{5.14}$$

i.e. the lateral chain extent becomes that of a random walk with a very small step length $3/(2|\Delta|^3)$.

We can now deduce that the lateral chain dimension is due to accumulated small deviations or meanderings about the z direction and not due to the transverse component of the tangent vector present during hairpin changes in direction. In turn this implies that, within this model, there is a sense to talking about local order about a director (the extent of the meanderings) as in a conventional nematic, and that there is not an identification of chain backbone with a director. Our remarks about elastic constants follow accordingly. This assertion is justified by looking at the rates of change of $\langle r_z^2 \rangle$ and $\langle r_\perp^2 \rangle$ with $|\Delta|$, the former changing most rapidly at coupling $|\Delta|^2$ such that $L^* \sim L$ (where the transition from random walk to rod occurs). The ratio of these two rates is

$$4|\Delta|^4\exp(2|\Delta|)/3. \tag{5.15}$$

Since chains are inextensible the difference in the rates can only be due to the freezing out of hairpins. The predominance of slack in determining $\langle r_\perp^2 \rangle$ is also established. We note that these conclusions are only possible in a model that conserves chain inextensibility everywhere. In the final rod-like result (5.8) for $\langle r_z^2 \rangle$ the small reduction away from L^2 is due to meanderings rather than residual hairpins since the latter would give an exponential rather than power law reduction from L^2.

5.3. The order parameter

Along with the degree of rod-like character in molecules an anisotropic fluid can be charactered by its orientation order parameter S:

$$S = \left\langle \frac{1}{L} \int_0^L \mathrm{d}s \, P_2(\cos(\theta(s))) \right\rangle. \tag{5.16}$$

This can be evaluated with the aid of normalised propagators and the change of variable $z = \cos\theta$:

$$\langle P_2(z(s)) \rangle = \int \mathrm{d}z' \, \mathrm{d}z'' \, G(z', z; L, s) G(z, z''; s, 0) P_2(z) \, \mathrm{d}z \tag{5.17}$$

which represents an average over the orientations z' and z'' at the ends of the chain and the factors G which express the probability of the propagation from one end to the point in question and then further to the other end. Referring back to (4.6) defining G in terms of spheroidal wavefunctions and to (4.12) where the spheroidal wavefunctions are defined in terms of the Legendre functions, we can integrate over the end point orientations z' and z'' whereupon only even-order terms survive and yield for long chains:

$$S = \int \mathrm{d}z \, Sp_0(z) Sp_0(z) P_2(z)/2. \tag{5.18}$$

We treat two limiting cases of this expression for S.

(a) The weak nematic limit. Expanding $Sp_0(z)$, inserting in (5.18) and integrating, one obtains for S

$$S = 2(a_{0,0}a_{0,2} + a_{0,2}^2/7 + 2a_{0,2}a_{0,4}/7 + \ldots)/5. \tag{5.19}$$

The required expressions for the a are given in (4.13). Collecting terms to $O(|\Delta|^6)$ we obtain

$$S = 2(|\Delta|^2/9 + |\Delta|^4/189 - 26|\Delta|^6/127\,575)/5. \tag{5.20}$$

(b) The strong nematic limit. To leading order the matrix element in (5.8) is clearly 1, the value of P_2 in the polar region where the tangent vector is localised. To get the next order is difficult and is performed in § 6. The result is

$$S = 1 - 3/(2|\Delta|) + \ldots. \tag{5.21}$$

5.4. The nematic-isotropic transition

This paper is concerned with molecular conformations and asymptotic behaviour in the nematic phase. We make a few comments below on the transition; an analysis is to follow (see Wang and Warner 1985). In the general expression (5.18) for S the

right-hand side is a function of Δ^2 (4.4) and thus S itself. Accordingly we can solve (5.18) self-consistently for S. It is found that solutions with $S \neq 0$ appear discontinuously below a certain temperature, the finite change in the order parameter from zero indicating a first-order transition. Both limiting expressions (5.20) and (5.21) display this first-order character and it is not clear that either of them is valid at T_{ni}. If the transition were second order Δ^2 would increase from zero, guaranteeing a region of validity of (5.20). In addition to self-consistency in S the transition requires the nematic free energy to be lower than that of the isotropic phase, a matter pursued by Wang and Warner (1985). Accordingly the T_{ni} given below represent upper bounds on a Maier–Saupe theory for the transition temperature.

At low temperatures (large $|\Delta|$) (5.21) is clearly valid and yields

$$S = 1 - 3k_B T / 2(3a\varepsilon)^{1/2}. \tag{5.22}$$

The highest temperature at which a non-zero solution of (5.21) is found is $k_B T_{ni} = 4(\varepsilon a)^{1/2}/9$ with $S_{ni} = \frac{1}{3}$ and $|\Delta|^2 = \frac{81}{16}$. This is close to the numerical estimate. On the other hand, the highest temperature, non-zero solution of (5.20) is $k_B T_{ni} = 0.4178(a\varepsilon)^{1/2}$ with $S_{ni} = 0.755$ and $|\Delta|^2 = 12.98$. It can be shown that a rigorous lower bound on the radius of convergence, $|\Delta_c|^2$, of the perturbation series of the wavefunctions is

$$|\Delta_c|^2 \geq \left(\frac{2 \int P_2 P_2 P_4}{\sqrt{6} \times \sqrt{20}} \right)^{-1} = 47.92$$

since we can place individual bounds on the number of terms at a given order, the matrix elements and the energy denominators. At the highest self-consistency temperature, where $|\Delta|^2 \sim 13$, we are well inside this bound. However, this does not guarantee that we have taken a sufficient number of terms in (5.20), three simply being the minimum required to describe a first-order transition. Further analysis (Wang and Warner 1985) shows that the next term is significant. Taking further terms will not change this order.

6. Analysis for a large nematic mean field

In this section we point out the relationship between the equation that the propagator for the tangent vector to the chain obeys and a quantum problem of a particle moving on a sphere in the presence of a strong potential, which restricts motion at low energy to the vicinity of the poles. The strength of the potential is related to the strength of the nematic mean field, and we will construct a WKB solution for the strong potential limit.

The relation of equation (4.3) to the Schrödinger equation is merely $\partial/\partial L \to i\partial/\partial t$, as usual. We find

$$\left(-\frac{1}{\sin\theta} \frac{d}{d\theta} \sin\theta \frac{d}{d\theta} + V(\theta) - \Lambda \right) \psi(\theta) = 0 \tag{6.1}$$

where

$$V(\theta) = -\Delta^2 \sin^2\theta \qquad \text{with } \Delta^2 < 0. \tag{6.2}$$

The first term in (6.1) is the kinetic energy operator for a particle on a sphere, where Λ is the energy. A realisation of this problem (of a quantum rotator in a quadrupolar

potential) is that of low temperature reorientation of a molecule in a crystal. Pauling (1930) solved it in a two-dimensional simplification which avoids a lot of the subtleties and difficulties we discuss in this section. Stern (1931) examined the three-dimensional problem, but both authors do not present a qualitative discussion for large potentials.

We are only considering azimuthally symmetric solutions here, so ϕ is ignored. In the limit of Δ tending to infinity, the potential contains very deep wells at the poles, $\theta = 0$ or π. It is physically clear that in that case the lowest two states will have almost degenerate energies, the small splitting alluded to in (4.11) being due to tunnelling through the equatorial barrier. The lowest state will be an even state with maxima at the poles, and the first excited state will be the corresponding odd state, with a nodal line around the equator. These states, labelled Sp_0, Sp_1 in § 4, result from symmetric and antisymmetric combinations of states constructed on each polar potential minimum in isolation. The aim in the rest of this section is to determine the splitting and the wavefunctions along with the matrix elements of the spherical harmonics between them, which are used to calculate the chain statistics and order parameter.

To construct the wavefunctions for the lowest two states, and hence determine their splitting, it is natural to divide the sphere into three regions: the regions near the two poles where the potential may be considered as harmonic (as a function of the angular deviation from the poles) plus anharmonic perturbations, and the equatorial region where we will use the WKB method (as discussed for double well problems in Landau and Lifshitz (1977, p 183)). The subtle point, mathematically, is checking that the regions of validity (in terms of θ) of these two approaches overlap, so that the expressions for the wavefunctions can be matched (Bender and Orszag 1978, p 504). We will solve the Schrödinger equation in the regions in the above order, and then match them.

Firstly the polar regions. Since in the limit of large potentials, $\Delta \to \infty$, we expect that the low lying states will be closely confined to the poles and the sphere will be 'flat' to a good approximation. The formal content of this remark is that we can rewrite the Laplacian of spherical polars as the Laplacian in *ordinary* polars (the first two terms in (6.3), with the radial coordinate being the old θ coordinate), plus a correction (the third term) which we will show to be a perturbation:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} = \frac{d^2}{d\theta^2} + \frac{1}{\theta} \frac{d}{d\theta} + \left(\cot \theta - \frac{1}{\theta} \right) \frac{d}{d\theta}. \tag{6.3}$$

If this correction is now expanded in powers of θ it is equivalent, of course, to the expansion of the 3D Laplacian (in powers of θ), minus the leading term. Since the first inverse factor of $\sin \theta$ in the 3D Laplacian determines the weight function for the Sturm–Liouville problem or more prosaically indicates that the problem is on a sphere, we must, when taking matrix elements and scalar products of wavefunctions, also use an element of integration (or weight function) which is the expansion of $\sin \theta$. This implies that the basis set that we will use for the perturbation theory is, in fact, not orthogonal beyond first order as the states are orthogonalised using $\theta \, d\theta$, not $\sin \theta \, d\theta$.

The last term in (6.3) is the correction. Let us initially discard it and also expand $V(\theta)$ to leading order in θ. This leaves us with the Schrödinger equation for a two-dimensional harmonic oscillator:

$$\left(-\frac{d^2}{d\theta^2} - \frac{1}{\theta} \frac{d}{d\theta} - \Delta^2 \theta^2 - \Lambda \right) \psi(\theta) = 0. \tag{6.4}$$

Of course this approximation does violence to the necessary periodicity in θ, but is allowable under the restriction of being near $\theta = 0$. The lowest energy solution to (6.4) is

$$\psi_0(\theta') = R_0 \exp(-\tfrac{1}{2}\theta'^2) \qquad R_0(\theta') = \sqrt{2} \qquad \theta' = \theta(|\Delta|)^{1/2} \qquad (6.5)$$

with energy $\Lambda = 2|\Delta|$. The first two azimuthally symmetric excited states are

$$R_2(\theta') = \sqrt{2}(\theta'^2 - 1) \qquad R_4(\theta') = \frac{1}{\sqrt{2}}(\theta'^4 - 4\theta'^2 + 2). \qquad (6.6)$$

$R_2(\theta')$ and $R_4(\theta')$ are orthogonal with $\theta \, \mathrm{d}\theta$.

We will now analyse the corrections to (6.5) perturbatively as a function of $|\Delta|^{-1}$. To facilitate this we expand the last term in (6.3) and $V(\theta)$ as functions of θ; rescale the variable θ to $\theta' = \theta\sqrt{|\Delta|}$ and divide the Schrödinger equation by $|\Delta|$. This yields, to lowest order in Δ^{-1}

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}\theta'^2} - \frac{1}{\theta'}\frac{\mathrm{d}}{\mathrm{d}\theta'} + \theta'^2 - \frac{1}{3|\Delta|}\left(-\theta'\frac{\mathrm{d}}{\mathrm{d}\theta'} + \theta'^4 \right) - \frac{\Lambda}{|\Delta|} \right]\psi(\theta') = 0. \qquad (6.7)$$

To first order in $|\Delta|^{-1}$ in perturbation theory, we find

$$\delta\Lambda_0 = 1/|\Delta|$$

$$\delta\psi_0 = \frac{1}{|\Delta|}(\tfrac{1}{12}R_0 + R_2(\theta') + \tfrac{1}{6}R_4(\theta')) \exp(-\tfrac{1}{2}\theta'^2) \qquad (6.8)$$

where the R_0 term in $\delta\psi_0$ is due to the correction to the weight function. The point of the perturbative analysis is to determine the range of validity of the approximation to the ground state (6.5). This is determined by asking when the coefficient of the Gaussian in (6.8) becomes of the order of unity. This occurs when $\theta' \simeq |\Delta|^{1/4}$, or in terms of the unscaled variable θ, $\theta \simeq |\Delta|^{-1/4}$. We should note that this is well past the classical turning point which is $(2/|\Delta|)^{1/2}$, which bodes well for matching to a WKB solution.

In the equatorial region, we use WKB. To turn (6.1) into a more amenable form we use the transformation:

$$\psi(\theta) = \chi(\theta)/(\sin \theta)^{1/2}. \qquad (6.9)$$

Substitution of this into (6.1) yields

$$\left[-\frac{1}{|\Delta|^2}\frac{\mathrm{d}^2}{\mathrm{d}\theta^2} + \sin^2\theta - \frac{1}{|\Delta|^2}\left(\frac{1}{\sin^2\theta} + 1 \right) - \frac{\Lambda}{|\Delta|^2} \right]\chi = 0. \qquad (6.10)$$

We now use the WKB form:

$$\chi(\theta) = \exp(\mathrm{i}|\Delta|S(\theta))$$

$$S(\theta) = S^{(0)}(\theta) + |\Delta|^{-1}S^{(1)}(\theta) + \dots. \qquad (6.11)$$

Then to order $|\Delta|^{-1}$, constructing the even and odd combinations of the WKB solutions emanating from each pole, we have

$$\psi_\pm(\theta) = \left(\frac{\tan \theta/2}{\sin \theta} \right)[\exp(|\Delta| \cos \theta) \pm \exp(-|\Delta| \cos \theta)]/\sqrt{2} \qquad (6.12)$$

where $\psi_+ \to (1/\sqrt{2})Sp_0$ and $\psi_- \to (\frac{3}{2})^{1/2}Sp_1$, the factors coming from the normalisation convention for the spheroidal wavefunctions.

Here we have used the fact that $\Lambda = 2|\Delta|$, to the order we are working to, from the result of the harmonic calculation (the tunnel splitting gives exponential corrections to this), and have neglected the term with coefficient $|\Delta|^{-2}$ in (6.10). The latter assumption determines the region of validity of the WKB treatment, i.e. $\theta > |\Delta|^{-1/2}$ or, in terms of the scaled variable of the polar calculation, $\theta' > 1$.

Matching is now possible, as the regions of validity of the two approximations overlap for $|\Delta|^{-1/2} < \theta < |\Delta|^{-1/4}$ or equivalently $1 < \theta' < |\Delta|^{1/4}$. It is important to guarantee the validity of the matching procedure that the range of overlap in the scaled variables becomes infinite in the asymptotic limit, $|\Delta| \to \infty$ (Bender and Orszag 1978, p 508). In fact the matching process is analogous to that at classical turning points where the 'exact' solution to the linear potential near the turning point, an Airy function, is matched to the WKB solution which diverges at the turning point: in our case we match the 'exact' solution of the quadratic potential (a Gaussian) to the WKB solution.

The actual matching is trivial: for $|\Delta|^{-1/2} < \theta < |\Delta|^{-1/4}$:

$$\psi^{\text{harmonic}}(\theta) = C\psi^{\text{WKB}}(\theta) \tag{6.13}$$

where

$$C = 4(|\Delta|)^{1/2} \exp(-|\Delta|). \tag{6.14}$$

We can check from the result of the above calculation that the main contribution to the normalisation of the ground-state wavefunction comes from the poles, and thus that the Landau and Lifshitz (1977) method for calculating the tunnel splitting is applicable. Their result is in the form of a barrier penetration factor:

$$\Lambda_{1,0} = 4\psi(\pi/2)\psi'(\pi/2) \tag{6.15}$$

where $\Lambda_{1,0}$ is the splitting.

This result assumes that the normalisation is dominated by the classically allowed region. We find in our problem

$$\Lambda_{1,0} = 32|\Delta|^2 \exp(-2|\Delta|). \tag{6.16}$$

We can now also work out the matrix elements required to specify the chain, namely $\int Sp_0 P_2 Sp_0$ and $\int Sp_0 P_1 Sp_1$. Since the main contribution arises from the polar regions we expand the Legendre functions and weight function and obtain

$$\frac{1}{2}\int Sp_0(\theta)P_2(\cos\theta)Sp_0(\theta)\sin\theta \, d\theta = 1 - 3/(2|\Delta|)$$

$$\frac{2}{\sqrt{3}}\int Sp_0(\theta)P_1(\cos\theta)Sp_1(\theta)\sin\theta \, d\theta = 1 - 1/(2|\Delta|). \tag{6.17}$$

These have corrections of order $|\Delta|^{-3/2}$. The numerical solution of (6.17) (Wang and Warner 1985) shows *post hoc* that it is very accurate, even for values of $|\Delta^2|$ smaller than where the first two eigenvalues rapidly approach each other at $|\Delta^2| \sim 10$ (see figure 1). The wide range of validity of asymptotic expansions beyond naive expectation is ubiquitous (e.g. Bender and Orszag 1978).

7. Summary

We have set up the problem of chain statistics in polymeric nematics as a problem of diffusion on a sphere and thereby solved it in the two limits of weak and strong ordering. Between these limits a simple numerical procedure yields a complete description of the chain and free energy.

At the isotropic-nematic transition the weak ordering limit is arguably valid and we observe an expansion of the chain dimensions parallel to the director, and a contraction transverse to the director. Chains of moderate length compared with their stiff units become directly rod-like, longer chains remaining a biased random walk. As the temperature is lowered these chains undergo a rapid transition to a rod-like configuration, a consequence of which would be a rapid change of the anisotropy and character of small angle neuton scattering if used to prove chain conformation.

We demonstrate that this rapid expansion is due to the freezing out of hairpins by considering the relative changes in longitudinal and transverse dimensions. We also conclude that slack in the chain, equivalent to meandering of the chain spine about the director, is more gradually eliminated. Our chain description includes inextensibility, necessary to examine such problems, rather than a model merely globally inextensible. Solving the model non-perturbatively is necessary to get drastic changes in chain dimensions.

These deductions about chain behaviour and related observations are vital to establish which picture of local chain freedom is valid. We emphasise that throughout we have made the unsubstantiated assumption that there is *not* a rigid identification of chain trajectory with director.

Along with this assumption we have also used mean fields, usual in nematic theory, and assumed that there are no long range interactions present. That a small excursion of a chain tangent is not transmitted as a nematic elastic distortion is a consequence of the chain backbone not being identified with the director; that is our underlying assumption. More serious is the potentiality that hairpins, like, say, point defects in a finite solid, interact via long range elastic distortions. As the nematic order becomes more perfect and hairpins less likely there are increasingly perturbations of regular packing and this neglected interaction may become important.

Within the assumption that chains are long compared with their stiff units we have solved self-consistency equations for the order S. This Maier-Saupe approach yields, via an asymptotic approximation, a first-order phase transition with $S_{ni} = \frac{1}{3}$ and $k_B T_{ni} = 4(\varepsilon a)^{1/2}/9$ (in agreement with a detailed numerical solution (Wang and Warner 1985)) where a is the parameter that sets the energy scale of the Maier-Saupe theory and ε is the chain stiffness. Inspection of S_{ni} shows that the phase transition is first order, in disagreement with ten Bosch *et al* (1983a, b) who obtain a second-order transition. It remains to complete a Flory description of the nematic, i.e. by calculating the steric effects on the parameter a and on the free energy.

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