

Layer Hopping by Chains in Polymeric Smectics?

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A new, nonperturbative, feature of chain conformations in strongly ordered polymeric smectics is found. Like the solitary hairpin defects in polymeric nematics, these features arise from the confinement of the chain, in our case spatial confinement by the smectic layers as well as the directional restrictions of the nematic. This liquid-crystalline reduction in chain entropy is resisted by layer hopping. Consequent exponential variation of chain dimensions is given by a simple kink argument, in accord with a systematic analysis.

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We investigate a general phenomenon in polymeric liquid crystals—the competition between lack of molecular rigidity, a large source of entropy, and mesogenic ordering. This competition distinguishes polymers qualitatively from their monomeric analogs, for instance in the nature of their transitions.^{1,2} Another important consequence is the nonperturbative, nonlinear behavior of chain conformations in nematics (hairpins^{3,1}), and a new feature for smectics predicted below. Both as a specific example and to introduce the model that we shall extend to smectics, we shall discuss, in terms of barrier penetration, these resultant solitary defects in nematic chain conformation. Our main result, exponential variation in chain dimensions in strong smectic fields, is shown to arise from layer hopping. It is obtained by mapping onto the simplest possible band-structure problem. Small-angle neutron and x-ray scattering is required to test these ideas.

Polymeric nematics differ from their conventional, rodlike counterparts in that their length, on the scale of their persistence length, is long enough to exhibit flexibility. The drive to explore many molecular conformations characterizes most polymer properties, but is in conflict with the tendency toward orientational order required by the packing and interaction of the mesogenic moieties comprising the chain.

In backbone (BB) molecules where mesogenic units are lineally incorporated in the main chain, this concept of competition has been recognized by de Gennes³ via the introduction of hairpins and pursued, via a model of wormlike nematics,⁴ by Warner, Gunn, and Baumgärtner.¹ The tangent vector $\hat{u}(s)$ of such a chain evolves with arc length s on the unit sphere. The rotational diffusion equation describing $\hat{u}(s)$ is of the Schrödinger type with an equatorial potential resulting from the nematic mean field. The confinement of the tangent vector to the polar regions leads, in the limit of strong fields,¹ to rodlike dimensions in the ordering direction z . Transitions from one pole to another are molecular hairpins [see Fig. 1(a)], the activated equatorial barrier hopping corresponding qualitatively to de Gennes's Boltzmann factor of hairpin energy. The quantum analog is¹ of tunneling from one

pole to another, solved by WKB approximation in the strong-field limit. Exponential behavior of chain dimensions is accordingly no surprise. Phase behavior and transitions are found² to be qualitatively different from simple nematics because of the interplay between molecular ordering and the internal entropy reservoir of molecules. Examples are large latent entropies and drastic expansions of molecular dimensions. Comb, or side-chain (SC), polymers have stiff, mesogenic elements attached by molecular hinges to the main chain, itself capable of exhibiting various degrees of flexibility according to its composition. Several types of nematic order have been found,⁵ one of which, N_I , is where the side-chain ordering is dominant and where, when the hinge constrains the main chain and side chain to be close to perpendicular, the main chain is confined toward the plane perpendicular to the ordering direction. This assumes that the side-chain spacing along the main chain is less than a persistence length so that the hinge constraint effectively acts along the whole main chain; see c in (3). On the tangent unit sphere the repulsive potential is now in the polar regions and the tangent vector resides in the tropics [see Fig. 1(b)]. Unlike the prolate case, this oblate case ex-

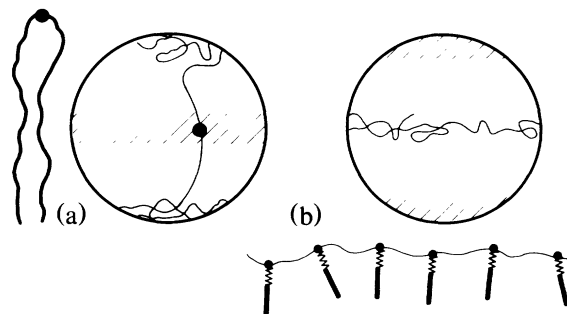


FIG. 1. (a) Nematic backbone polymer with a hairpin change in direction indicated by a dot. The corresponding trajectory on the tangent unit sphere shows the hairpin (dot) as the transition from one pole to another through the equatorial repulsive potential (shown shaded). (b) Nematic comb polymer with side chains attached to the main chain by hinges (small dot plus zig-zag). The main-chain tangent sphere shows localization around the equator by the polar potentials.

hibits no exponential change in chain dimensions—as the field grows the z dimension shrinks and the perpendicular dimension becomes that of a 2D random walk. These comb nematics lead to the smectic- A phases we consider here.

Pendant smectogenic moieties induce a polymeric smectic phase. The modulation of the density in the z direction by the side chains restricts main-chain freedom still further than in the particular oblate SC nematic described above. The restriction is not only in the directions that the chain tangent can adopt (the nematic field), but also in the z position (the smectic field). In the limit of strong smectic fields we predict interesting qualitative behavior, exponential chain dimensions arising because of chain hopping (tunneling) between layers [see Fig. 2(a)], in contrast to the tunneling in tangent space of BB nematics. Now there is conflict between the drive toward maximizing the internal entropy of a chain and the smectic field confining it toward exploring only two dimensions. The resolution again yields exponential dependence of chain dimensions in the layer-normal (z) direction,

$$\langle r_z^2 \rangle = l \exp\{-\beta E_L\} L, \quad (1)$$

where E_L is a barrier energy, L is the chain length, l is an effective step, and $\beta = (k_B T)^{-1}$.

We now outline the theory leading to this new aspect (1) of molecular combs. In the BB partition function Z_B we can identify the competing influences in the sum over conformations:

$$Z_B = \int \delta \hat{u}(s) \delta \mathbf{r}(s) \exp\{-\beta H_B\} \prod_s \delta[\hat{u}(s) - \dot{\mathbf{r}}(s)], \quad (2)$$

$$H_B = \int_0^L ds \left\{ \frac{1}{2} \epsilon \dot{\mathbf{u}}^2(s) + c P_2(u_z(s)) + b \sigma \cos[k_0 r_z(s)] \right\}. \quad (3)$$

The main chain is represented as a wormlike trajectory $\mathbf{r}(s)$ with tangent vector $\hat{u}(s)$ given by $\dot{\mathbf{r}}(s)$, the dot denoting $\partial/\partial s$. The arc length s varies between 0 and L . The first term in the energy H_B represents chain-bend elasticity,³ ϵ being the modulus. We neglect torsional modes of the main chain since, although important, they do not contribute to changes in the chain dimension. The second is the mean fields of nematic order and bend from the hinges with P_2 the second Legendre polynomial. The constant c contains,⁵ in addition to nematic coupling constants of the Maier-Saupe and Flory types, the order parameters of the nematic components, main and side chains. For simplicity we shall only consider here the smectic- A -nematic (Sm_A -N) transition and will also assume that the nematic order is already high and, further, changing little with temperature. Then c is a positive constant for the particular nematic phase to which we are restricted. The third term of (3) shows a smectic mean field inducing a density wave in the z direction

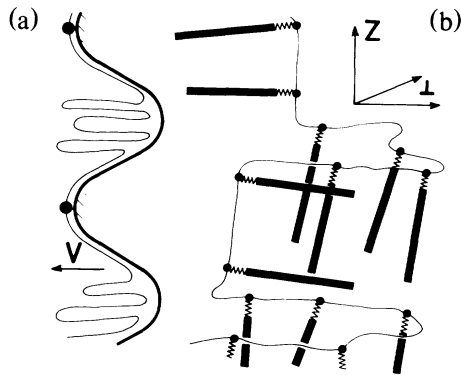


FIG. 2. (a) Additional confinement of such combs by a smectic cosinusoidal potential V . The layer normal, z , is also the polar direction in Fig. 1(b). Main-chain deviation from the z direction now involves layer hopping (dot) in the smectic potential and a random walk in the z -direction results. (b) The comb, with side chains now shown, illustrates how layer hopping by the main chain necessarily involves bringing side chains in conflict with the nematic field. This is the repulsive polar potential of Fig. 1(b).

because the chain is attached more or less rigidly to the side groups undergoing smectic ordering. The smectic order parameter is $\sigma = \langle \cos k_0 r_z(s) \rangle$ and the coupling constant b is assumed to subsume the effect of nematic-smectic cross coupling, negligible if the nematic order is saturated and thence uncorrelated with $\cos(k_0 r_z)$. The smectic wave vector is $k_0 = 2\pi/d_0$ with d_0 the layer periodicity imposed by the side-chain ordering.

The number of hops in the random-walk dimension (1) contains the exponential factor. A heuristic justification considers E_L to be the energy of a chain making a single transition from one smectic well to the next. When we take the nematic and smectic energies in (3) and minimize their sum, the optimal trajectory has

$$r_z(s) = (2d_0/\pi) \tan^{-1} \exp[(b\sigma k_0^2/3c)^{1/2} s], \quad (4)$$

with an associated energy

$$E_L = 4\sqrt{q}/\beta \equiv 8(3b\sigma c)^{1/2}/k_0. \quad (5)$$

Rapid transition through smectic potentials are dictated by b but involve the chain tangent moving toward the poles, the main chain heading in the z direction, which brings the side chains perpendicular to the nematic field and is penalized by c [see transitions in Fig. 2(b)]. The geometric mean $(b\sigma c)^{1/2}$ of (5) is characteristic of an Euler-Lagrange minimization. The hopping probability is then proportional to the Boltzmann factor $\exp(-\beta E_L)$. We show below that this is indeed the major effect but that temperature, bend fluctuations, and hop overlap have a more subtle role. The simplest evidence of this is that (1) is not proportional to d_0^2 as the above analysis would suggest.

The Green's function G equivalent to (3) obeys⁶ the

Fokker-Planck-type equation

$$\{\partial/\partial L - D\nabla_{\hat{u}}^2 - \beta c P_2(\zeta) - \zeta \partial/\partial z - \beta b \sigma \cos(k_0 z)\} G = \delta(L) \delta(\zeta - \zeta_0) \delta(z - z_0), \quad (6)$$

where $\zeta \equiv u_z$, $z \equiv r_z$. The first term of (3) corresponds to $D\nabla^2$ in (6), where $D = (2\beta\epsilon)^{-1}$ is the rotational diffusion constant and is also the inverse persistence length of the worm with no fields.¹ The second term in (3) confines \hat{u} to the tropics and the first three terms in (6) together are the spheroidal wave equation in tangent space¹ yielding the oblate chains of the underlying N_I phase.⁵ We denote the eigenvalues of the eigenequation corresponding to the spheroidal part of (6) by $\lambda_n^{(0)}$, the eigenfunctions by $Sp_n(\zeta)$. The partition function can be recovered from G by summing over initial and final coordinates. G also yields conformations and order parameters. We shall suppress the partition function for side chains since the nematic order is assumed saturated with the smectic phase being at low temperatures.

Since real-space properties such as chain dimensions and smectic order interest us, we project out the tangent dependence of the distribution in (6). This can be done systematically by use of Bloch perturbation theory⁷ for infinitely degenerate states which, when applied to Fokker-Planck equations for overdamped systems, is equivalent to the Chapman-Enskog procedure used to eliminate fast variables from kinetic equations.⁸ The method works in underdamped systems⁹ and is quite general, summarized in this context by Renz,⁹ and leads to asymptotic series. We change variables $k_0 z = 2y$ and divide (6) through by D . The projection then yields the equivalent eigenequation in real space

$$[B_n \partial^2/\partial y^2 - (\beta b \sigma/D) \cos 2y] \psi_\nu(y) = (\lambda_{\nu,n} - \lambda_n^{(0)}) \psi_\nu(y), \quad (7)$$

where B_n , giving a spatial diffusion constant of $B_n D (2/k_0)^2$, is⁸

$$B_0 = \left(\frac{k_0}{2D} \right)^2 \left(\sum_m^{\text{odd}} \frac{\zeta_{m0}^2}{\lambda_m^{(0)} - \lambda_0^{(0)}} \right) = \left(\frac{k_0}{2D} \right)^2 f_0 \quad (8)$$

for the ground state $n=0$. The matrix element ζ_{m0} is taken with respect to Sp_m and Sp_0 . This procedure depends on the magnitude of (8), the ratio of the square of two lengths: the worm persistence length D^{-1} reduced by the oblate nematic confining potential (the f_0 factor), and the layer spacing, $d_0 = 2\pi/k_0$. The result (7) corresponds to the classic scaling result of Edwards—if the step length of a walk is short compared with a relevant length scale, here d_0 , then the walk can be replaced with a Wiener process. Indeed, the diffusive part of (7) can be derived heuristically by comparison with the result⁵ for the z dimension of an oblate chain in the strong N_I limit, $\langle r_z^2 \rangle$

$= D^{-1} L / (2\Delta^2)$, where Δ^2 is the nematic coupling⁵ $3c\epsilon\beta^2$. The oblate nematic field allows only small excursions away from the equator [Fig. 1(b)] and hence the z -step length is shrunk by $(2\Delta^2)^{-1}$ from D^{-1} . By identification of diffusion constants, we have $B_0 = (k_0/2D)^2 / (4\Delta^2)$, consistent with limiting values of ζ_{m0} and $\lambda_{m0}^{(0)}$ inserted into (8).

This is the first time we have seen the use of a physical and mathematical reduction of a worm chain to a Wiener process. It proves very useful though we emphasize that one cannot use Wiener processes in real space at the outset in liquid crystal problems. This is because of four physical aspects absent in the Wiener measure, namely, nematic coupling to the tangent vector, chain stiffness as a precondition for mesophases, hinged side chains restricting the main chain tangent vector, and rod dimensions susceptible of approach.^{1,2}

If we divide (7) by B_0 and now write

$$q = b\sigma / (\epsilon k_0^2 f_0) \quad (9)$$

and the new eigenvalue $a_\nu = (\lambda_{\nu,n} - \lambda_n^{(0)}) / B_0$, then (7) is cast into the conventional Mathieu form,⁹ a prototype Schrödinger equation for band electrons in a lattice:

$$\{-\partial^2/\partial y^2 + 2q \cos(2y)\} \psi_\nu(y) = a_\nu \psi_\nu(y). \quad (10)$$

The q of (9) is the same as that defined by (5) in the limit of strong nematic fields, that is, where $f_0 = (4\Delta^2)^{-1}$. The qualitative aspects of chains in a smectic phase now emerge and we merely sketch the details. The required Green's function is expressed as products of eigenfunctions of (10), including the solutions $\psi_{\nu k}$ with $k \neq 0$ away from the band center, by exponentials of eigenvalues times chain lengths. For long chains we have ground-state dominance,¹ the lowest values of λ appear in G , and we take the $n=0, \nu=0$ ground state of the spheroidal or Mathieu equations with only the parabolic region about the band minimum, $k=0$. All that is important, in all strengths of smectic order, is the curvature, that is, the effective mass.

Strong ordering, q large, corresponds to tight binding whereupon ψ_k is constructed in the usual way with ψ_{00} arising from semiclassical estimates of the wave functions in each well, or from parabolic cylinder functions of periodic argument.¹⁰ The dispersion relation for the eigenvalues, $a_{0k} = \Delta a \sin^2(k\pi/2)$, is characterized by the exponentially small bandwidth Δa describing barrier hopping by the chain. The resultant chain dimension and order parameter derive from G with ψ and a inserted. The scaled bandwidth $B_0 \Delta a$ deter-

mines $\langle r_z^2 \rangle = f_0 D^{-1} L \pi^2 \Delta a / 2$. We obtain

$$\Delta a = 2^5 (2/\pi)^{1/2} q^{3/4} \exp(-4\sqrt{q}) \quad (11)$$

whereupon (1) results, with the activation energy e_L (5) in the strong oblate limit for f_0 . The nonperturbative result (11) is consistent with (5) and (1). The effective step l is the oblate nematic step $D^{-1}/2\Delta^2$ scaled by $q^{3/4}$, a nonintuitive result.

Asymptotically the order parameter σ is

$$\sigma = \langle \cos k_0 z \rangle = 1 - 1/2 q^{1/2} + \dots \quad (12)$$

a cubic self-consistency equation for σ . The temperature at which solutions first (discontinuously) appear is an upper bound on first-order transitions N_I to Sm_A . Unfortunately this occurs for $q \sim 0.6$ where it is unwise to use (12). The assertion of first order and the bound are hence unreliable. Low-order perturbation theory asserts a second-order transition. Further comments on the transition await a numerical analysis.

Since this work was completed an experimental investigation has appeared¹¹ demonstrating that chain dimensions perpendicular to smectic layers are very strongly reduced. It would be interesting to know if in this strong smectic limit any activated behavior is seen.

In summary, we have established a striking result for chain conformations in strong smectics as a result of conflicts between smectogenic and polymer properties. Relation (1) for chain size can be tested by small-angle x-ray or neutron scattering from labeled chains in melts and would test our hopping idea. Our method projects the chain problem into real space and a bandlike problem results. Away from the hopping regime numerical analysis or nearly-free-electron analysis would be relevant, the former to describe the

transition, the latter for the important case of comb polymers in smectic solvents.

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