On the stretching of alkyl chains by nematics[a)]

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When a semiflexible chain molecule is subjected to an anistropic solvent, e.g., leads to a partial elongation and alignment of the molecule. The ordering of the CC bonds as a funciton of position along the chain was treated in an earlier communication by solving a lattice version of the rotational isomer state model in the presence of an external field. In the present paper, we extend this approach to the explicit calculation of solvent-induced size and anisotropy effects. Specifically, we determine the increase in $\langle Z_N^2\rangle^{1/2}$ as a function of chain conformation (i.e., *gauche* vs *trans*) energy ϵ and of monomer–solvent coupling strength f. Here $\langle Z_N^2\rangle^{1/2}$ is the root-mean-square value of the Z component of the end-to-end vector for an N-bond molecule (the space-fixed Z axis being taken to lie along the nematic direction). The elongation of the molecule is described in terms of the deformation of a sphere with radius $R_0 = (3\langle Z_N^2\rangle_{f=0})^{1/2}$ into an ellipsoid of revolution with eccentricity determined by $\langle Z_N^2\rangle_{f>0}$.

I. INTRODUCTION

Estimation of the size of a semiflexible chain molecule constitutes a classic problem in polymer physics. A quantitative measure of the size is most commonly taken to be $\langle r_N^2\rangle^{1/2}$, the rms end-to-end distance of the N-monomer chain. Long-range excluded volume effects give rise in general[1] to a $N^{3/5}$-dependence for $\langle r_N^2\rangle^{1/2}$. In a "theta solvent,"[2] however, the N dependence is somewhat weaker, characteristic of an "ideal" chain

$$\langle r_N^2\rangle^{1/2} = ClN^{1/2} , \quad N \gg 1 . \qquad (\text{I. }1)$$

Here l is the monomer length and C is a constant (on the order of unity) which reflects the *short*-range interferences between monomers.

For a "random flight" chain, e.g., where each monomer orientation is perfectly uncorrelated with its neighbors, $C = 1$. For a "freely rotating" chain, where the valence angle is fixed at θ, $C = (1-\cos\theta/1+\cos\theta)^{1/2}$. When in addition, the value of each dihedral angle φ is governed by a single hindered rotation potential

$$C = \left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2}\left(\frac{1+\langle\cos\varphi\rangle}{1-\langle\cos\varphi\rangle}\right)^{1/2} .$$

Finally, when the bond rotations become dependent on one another, as say in the rotational isomer state (RIS) model[3] described below, C must in general be computed numerically.

In an isotropic solvent, of course, $\langle r_N^2\rangle = 3\langle Z_N^2\rangle = 3\langle X_N^2\rangle = 3\langle Y_N^2\rangle$. In an orientationally ordered solvent, on the other hand, the semiflexible chain will be distorted from spherical symmetry. With a uniaxial liquid crystal (e.g., nematic) host, e.g., we have

$$\beta \equiv \frac{\langle Z_N^2\rangle^{1/2}}{\langle Z_N^2\rangle^{1/2}_{\text{no field}}} > 1 , \qquad (\text{I. }2)$$

i.e., the molecule will be stretched along the preferred (here Z) direction.[4] This is reminiscent of the bond ordering induced in substituent alkyl chains in *neat* liquid crystals.[5] Similar, but more complicated, distortions occur in nematic polymers[6] and in model membranes[7] where hydrocarbon tails are squeezed by neighbors whose heads are anchored to the same interface.

In a recent communication[8] we presented a molecular theory of the ordering of a semiflexible chain molecule by a liquid crystalline host. We used a simplified version of the RIS model in the presence of an external field to solve exactly for the individual bond order parameters as a function of position along the chain. The monomers at the ends of the molecule were found to be less ordered than those "inside," in agreement with experiment[4] and with intuitive expectations—each inside bond can be aligned not only by the nematic solvent but also by its neighbors. The "external field" (solvent)-induced angular correlations between pairs of monomers are found to persist over distances only a few times the "spacing" l.

In the present paper, we extend our treatment of the RIS model in a field to the case of *radial* correlations. Specifically, we compute the induced anisotropy $\beta \equiv \langle Z_N^2\rangle_f^{1/2}/\langle Z_N^2\rangle_{f=0}^{1/2}$ for reasonable values of "field" (monomer-nematic coupling) strength f, and internal conformational (*gauche* relative to *trans*) energy ϵ. By labeling each possible monomer "state" (orientation) in terms of a *space-fixed* diamond lattice direction—rather than by a dihedral angle defined with respect to the plane of the previous two—we can avoid the transformation matrices which are commonly used[3,9,10] to propagate an RIS chain conformation. The only matrix which appears is an array of Boltzmann factors which is the direct generalization of the familiar "transfer matrix" from spin Ising problems.[11] nth-nearest-neighbor effects are treated by partitioning the chain into overlapping groups of n monomers, thereby allowing the total conformational energy to be written exactly as a sum of interactions between first-nearest-neighbor n mers. The usual "pentane effect,"[3] e.g., is fully accounted for in Sec. II by dividing the chain into *trimer* sequences. From the singlet- and pair-trimer distribution functions, in the presence of a nematic field, we can solve directly for the size and anisotropy of the molecule; this

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is demonstrated in Sec. III and a brief discussion of the results is given in Sec. IV.

II. SINGLET- AND PAIR-DISTRIBUTION FUNCTIONS

To describe the semiflexible alkyl chains, we consider the three-state RIS model in which the main-chain C–C–C angle θ is tetrahedral and each C–C monomer (bond) makes a dihedral angle φ of 0° ("*trans*") or ±120° (±*gauche*) with respect to the plane of the previous two. Accordingly, each allowed conformation corresponds to a random walk on the diamond lattice. This is no longer true of course, if θ and φ are chosen to be anything other than tetrahedral and ±120°. But it is useful to forsake here the chemical fine structure (e.g., $\theta \neq \sphericalangle_{\text{tetra}}$, $\varphi \neq \pm 120°$) and focus instead on the qualitative physics of the situation. All of the monomers in an arbitrary conformation are constrained to lie along one of the four space-fixed diamond lattice directions, labeled 1, 2, 3, and 4 in Fig. 1—we choose 1 and 2 to lie as shown in the laboratory yz plane, and 3 and 4 to lie in the xy plane. Each possible chain conformation is defined by specifying an ordered sequence of monomer states (lattice directions) $m_1, m_2, \ldots, m_N$, where $m_i = 1, 2, 3$, or 4 and N = total number of C–C bonds.

The three-state rotational isomer model commonly includes short-range monomer–monomer interactions which involve first-, second-, and third-nearest neighbors. More explicitly, each time we add a C–C bond which is *gauche* (dihedral angle of ±120°) with respect to the plane of the previous two, we add ϵ ($\simeq \frac{1}{2}$ kcal/mol for polyethylene) to the chain conformational energy. (The energy associated with a *trans* bond is taken to be zero.) These *second*-nearest-neighbor interactions are trivial to handle because they lead to a total N-monomer energy which is a sum of independent contributions (ϵ from ±120° and 0 from 0°) from each of the bonds $i = 3 \rightarrow N$. With only these effects included, we would have

$$C = \left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2}\left(\frac{1+\langle\cos\varphi\rangle}{1-\langle\cos\varphi\rangle}\right)^{1/2}$$

in Eq. (I. 1). But this situation is significantly complicated by the pentane effect,[3] i.e., by *third*-nearest-neighbor interactions which effectively exclude the possibility of successive *gauche* bonds of opposite sign. (These local configurations involve steric hindrances which are large compared to kT at room temperature.) This effect can be treated exactly by expressing the total chain energy as a sum of nearest-neighbor interactions between overlapping *trimers*.

Since there are only four lattice directions (1, 2, 3, 4), and since no one of these monomer states can directly repeat itself, we need "only" allow for 4×3×3 = 36 trimer states. More explicitly, $t_i = m_i, m_{i+1}, m_{i+2}$ denotes the state of the ith trimer ($i = 1, 2, \ldots, N-2$; recall that N is the total number of monomers) and m_i (= 1, 2, 3, or 4) describes the state of the ith monomer. An arbitrary conformation of the chain is specified accordingly by an ordered sequence of overlapping trimer states: $t_1, t_2, \ldots, t_{N-2}$. The total conformation energy can then be written in the form

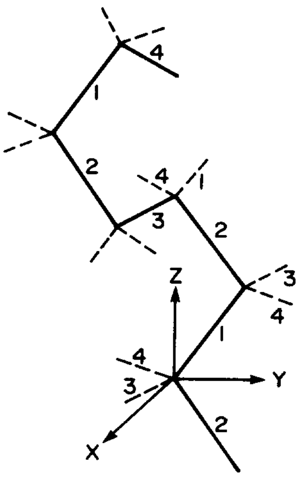

FIG. 1. The dark lines suggest part of a typical polyethylene conformation, the dashed lines showing the CH's (or CD's). The nematic field lies along the space-fixed Z axis. 1, 2, 3, and 4 refer to the four diamond lattice directions along which the CC bonds can lie; 3 and 4 lie in the space-fixed xy plane, while 1 and 2 are in the zy plane.

$$E_0(\mathrm{t}) = \epsilon_0(t_1) + \sum_{i=1}^{N-3}\left[\epsilon_0(t_{i+1}) + I(t_i, t_{i+1})\right], \tag{II. 1}$$

where $\epsilon_0(t) = 0$ if t corresponds to the *trans* state of the trimer, and $\epsilon_0(t) = \epsilon$ if the trimer is in the + or − *gauche* state; $I(t_i, t_{i+1}) = p$ if the successive trimers are both *gauche* and of opposite sign, and $I = 0$ otherwise. Since $p \gg \epsilon$ and $\epsilon \approx kT$, it is convenient to take $p \rightarrow \infty$. That is, Eq. (II. 1) is simply a sum of *trans* (0) and *gauche* (ϵ) energies, with pentane effect configurations excluded. Each time we add a monomer—say the i + 3rd—we add an energy $\epsilon_0(t_{i+1}) = 0$ or ϵ *after first checking* that we do not have $t_i, t_{i+1} = \pm$*gauche*, ∓*gauche*.

Consider now a nematic environment which exerts an aligning field on the above polymer chain. This field is of the "$P_2(\cos\theta_{m_i})$," rather than the usual "$P_1(\cos\theta_{m_i})$," type—it is the monomer's axially symmetric *polarizability tensor*, rather than its permanent *dipole moment vector*, which is "grabbed" by the orientationally ordered solvent. Accordingly, we add to Eq. (II. 1) a term

$$V(\mathrm{t}, f) = v_1(t_1, f) + \sum_{i=1}^{N-3} v(t_{i+1}, f), \tag{II. 2}$$

where

$$v(t_{i+1}, f) = -f\left[P_2(\cos\theta_{m_{i+3}}) + \tfrac{1}{2}\right] \tag{II. 2A}$$

and

$$v_1(t_1, f) = -f\left[P_2(\cos\theta_{m_1}) + P_2(\cos\theta_{m_2}) + P_2(\cos\theta_{m_3}) + \tfrac{3}{2}\right]. \tag{II. 2B}$$

Here $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$ is the second Legendre polynomial and θ_{m_i} is the angle between the ith monomer (lying along the lattice direction m_i) and the nematic field (taken to lie along the laboratory Z axis—see Fig. 1). $f = A\eta$, where A is the monomer–solvent coupling strength and η is the nematic's "P_2" order parameter. Finally, the term $\frac{1}{2}$ in square brackets in Eq. (II. 2A) is introduced so that $v = -f$ for trimer states whose third monomer has a Z component while $v = 0$ otherwise. Note that $P_2(\cos\theta_m) = \frac{1}{2}(-\frac{1}{2})$ for m = 1, 2 (3, 4). Similarly, the term $\frac{3}{2}$ in Eq. (II. 2B) assures that $v_1 = -f$, $-2f$, or $-3f$ according to whether the first trimer contains one, two, or three monomers in state "1" or "2."

From the above we have, for the chain energy in the presence of a field,

$$E(\mathbf{t},f) = \epsilon_1(t_1,f) + \sum_{i=1}^{N-3} \epsilon_I(t_i, t_{i+1}) \ , \qquad \text{(II.3)}$$

where

$$\epsilon_1(t_1,f) = \epsilon_0(t_1) + v_1(t_1, f) \qquad \text{(II.3A)}$$

and

$$\epsilon_I(t_i, t_{i+1}) = \epsilon_0(t_{i+1}) + v(t_{i+1}) + I(t_i, t_{i+1}) \ . \qquad \text{(II.3B)}$$

The probability of an arbitrary conformation $\mathbf{t}$ is then given by (here $\beta = 1/kT$ as usual)

$$P(\mathbf{t},f) = \frac{1}{Q} \exp[-\beta E(\mathbf{t},f)] \ , \qquad \text{(II.4A)}$$

where $Q = \sum_{\mathbf{t}} \exp[-\beta E(\mathbf{t})]$ is the corresponding partition function. Defining now the *trimer transfer matrix* elements

$$W(t_i, t_{i+1}, f) = \exp[-\beta \epsilon_I(t_i, t_{i+1}, f)] \qquad \text{(II.5A)}$$

and the "end"-trimer weights

$$g(t_1,f) = \exp[-\beta \epsilon_1(t_1,f)] \ , \qquad \text{(II.5B)}$$

it follows trivially that the joint probability (II.4A) can be written in the form

$$P(\mathbf{t}) = \frac{1}{Q} \exp[-\beta E(\mathbf{t})] = \frac{1}{Q} g(t_1) \prod_{i=1}^{N-3} W(t_i, t_{i+1}) \ . \qquad \text{(II.4B)}$$

The matrix $\mathbf{W}$ and vector $\mathbf{g}$ are written out in Appendix A.

In writing Eq. (II.3) for the total energy, we have suppressed the explicit dependence of the internal (*trans–gauche*) energies on the nature of the ordering field. This is in keeping with our qualitative level of description: our aim is to provide a simple, quasi-analytical theory of the stretching of semiflexible chains in anisotropic environments. Accordingly, the absolute magnitudes of the relevant energies are less important than their relative values (e.g., $\beta\epsilon$ vs βf, as compared to unity, etc.). Similarly, by asserting a directly additive form for ϵ_1 and ϵ_I—Eqs. (II.3A) and (II.3B)—we have oversimplified the interactions between solute and solvent. More explicitly, the nematic order of the host can be significantly distorted by the dissolved chains. This coupling leads to self-consistency effects which are of special importance for determining the structure of nematic polymers[6] and bilayer membranes.[7] These intriguing details are neglected in the present discussion, as we focus on the more gross features of alkyl chain stretching by nematic fields.

Summing the Boltzmann factor in Eq. (II.4B) over all states of all trimers gives the partition function ($t_1 \to u$, $t_{N-2} \to v$),

$$Q = \sum_{u,v=1}^{36} g(u)\, W^{N-3}(u, v) \ , \qquad \text{(II.4C)}$$

where $W^{N-3}(u, v)$ denotes the u, vth element of the N-3rd power of the matrix W. Similarly, the single-trimer distribution is obtained by summing the joint probability in Eq. (II.4B) over all states of all trimers but the ith; for $2 \le i \le N-3$, say, we have

$$P_i^{(t)}(r) = \frac{1}{Q} \sum_{u,v=1}^{36} g(u) W^{i-1}(u, r) W^{N-2-i}(r, v) \qquad \text{(II.6A)}$$

= probability of finding the ith trimer in the state $r(= 1 \to 36)$, $2 \le i \le N-3$.

The corresponding single-*monomer* distribution is given by

$$P_i^{(m)}(a) = \sum_r{}' P_i^{(t)}(r)$$

= probability of finding the ith monomer in the state $a(1 \to 4)$, (II.6B)

where the prime restricts the summation to those trimer states in which the first monomer is in state a. Finally the *pair* trimer–trimer distribution is (for $2 \le i \le N-3$ and $1 \le k \le N-3-i$)

$$P_{i,i+k}^{(t)}(r, s) = \frac{1}{Q} \sum_{u,v=1}^{36} g(u)\, W^{i-1}(u, r) W^{k}(r, s) W^{N-2-i-k}(s, v) \qquad \text{(II.7A)}$$

from which it follows that the corresponding *monomer–monomer* correlations are given by

$$P_{i,i+k}^{(m)}(a, b) = \sum_r{}' \sum_s{}'' P_{i,i+k}^{(t)}(r, s) \ , \qquad \text{(II.7B)}$$

where the double prime restricts the summation to those trimer states in which the first monomer is in state b.

Similar expressions obtain for the singlet and pair distributions involving trimers *at the end* of the chain. More explicitly we have

$$P_{i=1}^{(t)}(r) = P_{i=N-2}^{(t)}(r) = \frac{1}{Q}\, g(r) \sum_{r=1}^{36} W^{N-3}(r, v) \qquad \text{(II.8)}$$

and $(1 \le k \le N-3)$,

$$P_{1,1+k}^{(t)}(r, s) = \frac{1}{Q} g(r)\, W^{k}(r, s) \sum_{v=1}^{36} W^{N-3-k}(s, v)$$

$$= P_{N-2-k,N-2}^{(t)}(r, s) \ . \qquad \text{(II.9)}$$

The corresponding monomer distribution functions are given by summations identical to those in Eqs. (II.6B) and (II.7B), with $i \to 1$; see Appendix B for details.

III. CALCULATION OF SIZE AND ANISOTROPY

Consider the quantity

$$Z_N = \sum_{i=1}^{N} Z_i(a) \qquad \text{(III.1B)}$$

the Z component of the end-to-end vector.

$$Z_i(a) = l \cos\theta_i(a) \qquad \text{(III.2B)}$$

is the projection (onto the space-fixed Z axis—see Fig. 1) of the ith bond vector, $\mathbf{l}_i(a)$; $a = 1, 2, 3, \ldots, 4$ describes the state of the bond—$\mathbf{l}_i$ must lie along one of the four diamond lattice directions, as shown in Fig. 1. Then the *mean* of the square of the Z component of the end-to-end vector is given by

$$\langle Z_N^2 \rangle = l^2 \sum_i \sum_j \sum_a \sum_b \cos\theta(a) \cos\theta(b) P_{ij}^{(m)}(a, b) \ , \qquad \text{(III.2)}$$

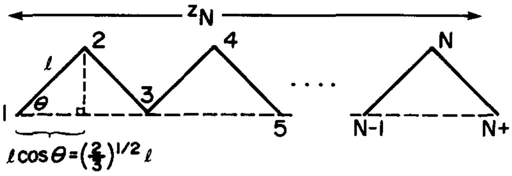

FIG. 2. All-*trans* (fully stretched, $F\to\infty$) n-alkane, depicted here for an even number (N) of C–C bonds. Z_N, the Z component of the end-to-end vector, is simply given by $N(\frac{2}{3})^{1/2}l$.

where $P_{ij}^{(m)}(a,b)$, defined by Eq. (II. 7B), is the probability of finding the ith bond (monomer) in state a and the jth in b.

Note that the bonds in states "3" and "4" make no contribution to Z_N—the directions 3 and 4 both lie in the space-fixed xy plane and hence give $\cos\theta_i(3)=0=\cos\theta_i(4)$. The direction cosines associated with states 1 and 2, on the other hand, are + or $-(\frac{2}{3})^{1/2}$—according to whether the corresponding bond vectors point up (+) or down (−), respectively. From the topology of the diamond lattice, it follows further that

$$P_{ij}^{(m)}(1^\pm,1^\pm)=P_{ij}^{(m)}(2^\pm,2^\pm)=0=P_{ij}^{(m)}(1^\pm,2^\mp) \qquad \text{(III. 3A)}$$

for $j-i=$ odd, and that

$$P_{ij}^{(m)}(1^\pm,1^\mp)=P_{ij}^{(m)}(2^\pm,2^\mp)=0=P_{ij}^{(m)}(1^\pm,2^\pm) \qquad \text{(III. 3B)}$$

for $j-i=$ even. Here 1^+ refers to a bond lying along the direction "1" and pointing "up," and so on. Finally, since $P_i^{(m)}(1^+)=P_i^{(m)}(1^-)$ and $P_i^{(m)}(2^+)=P_i^{(m)}(2^-)$, we are free to compute our statistics using only 1^+ and 2^+, i.e., we can confine ourselves to one of the two diamond sublattices. It is then straightforward to show that Eq. (III. 2) can be rewritten exactly as

$$\langle Z_N^2\rangle=\tfrac{4}{3}l^2\sum_{i=1}^{N}P_i^{(m)}(1)+\tfrac{8}{3}l^2\sum_{i=1}^{N}\sum_{k=1}^{N-i}\chi(k)\left[P_{i,i+k}^{(m)}(1,1)-P_{i,i+k}^{(m)}(1,2)\right], \qquad \text{(III. 4)}$$

where

$$\chi(k)=\begin{cases}+1, & k=\text{even}\\ -1, & k=\text{odd}.\end{cases}$$

Here we have used the additional identities

$$P_{i,i}^{(m)}(a,b)=P_i^{(m)}(a)\delta_{ab}, \quad P_{i,j}^{(m)}(1,2)=P_{i,j}^{(m)}(2,1),$$

and

$$P_{ij}^{(m)}(1,1)=P_{ij}^{(m)}(2,2).$$

In the following section we evaluate $\langle Z_N^2\rangle$ for some physically interesting choices of N (number of monomers), $G\equiv\exp(-\epsilon/kT)$ (*gauche* energy), and $F\equiv\exp(f/kT)$ (monomer–solvent coupling strength). First, though, it is illustrative to consider a couple of limiting situations for which these evaluations become analytically possible: (i) $G\equiv1$ *and* $F\equiv1$. Here we have the discrete (lattice) version of the *freely rotating chain, in zero field*. It follows that

$$P_i^{(m)}(1)=\tfrac{1}{4}$$

and

$$P_{i,j}^{(m)}(1,1)=P_{i,j}^{(m)}(1,2)=\tfrac{1}{16}$$

for $j-i>1$. (For $j=i+1$, all of the above pair functions vanish identically.) But then from Eq. (III. 4) we have that

$$\langle Z_N^2\rangle=l^2\frac{N}{3}=\frac{1}{3}\langle r_N^2\rangle$$

consistent with the $\langle r_N^2\rangle^{1/2}=ClN^{1/2}$, $C=1$ result quoted in the Introduction for a field-free, freely rotating chain. (ii) $F\to\infty$. Here, *in infinitely strong field*, every monomer must have its maximum z projection. Accordingly,

$$P_i^{(m)}(1)=\tfrac{1}{2}=P_i^{(m)}(2)$$

and

$$P_{i,j}^{(m)}(1,1)=\begin{cases}\frac{1}{2}, & \text{for } j-i=\text{even}\\ 0, & j-i=\text{odd},\end{cases}$$

$$P_{i,j}^{(m)}(1,2)=\begin{cases}0, & \text{for } j-i=\text{even}\\ \frac{1}{2}, & j-i=\text{odd}.\end{cases}$$

It follows from Eq. (III. 4) that

$$\begin{aligned}\langle Z_N^2\rangle\big|_{F\to\infty}&=\frac{4}{3}l^2\frac{N}{2}+\frac{8}{3}l^2\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{2}\\ &=\frac{4}{3}l^2\frac{N}{2}+\frac{8}{3}l^2\frac{N(N-1)}{2}\,\frac{1}{2}\\ &=\frac{2}{3}l^2N^2\,. \end{aligned} \qquad \text{(III. 5)}$$

This result for $\langle Z_N^2\rangle$ is consistent with the trigonometric fact displayed in Fig. 2

$$\langle Z_N^2\rangle\big|_{F\to\infty}=[Z_N(\text{all } trans)]^2=[(\tfrac{2}{3})^{1/2}lN]^2\,.$$

IV. NUMERICAL RESULTS AND DISCUSSION

From Eqs. (III. 4), (II. 6B), and (II. 7B) for $P_i^{(m)}(a)$ and $P_{i,i+k}^{(m)}(a,b)$, it is clear that an evaluation of $\langle Z_N^2\rangle$ follows from tabulation of the singlet- and pair-*trimer* distributions $P_i^{(t)}(r)$, $1\le i\le N-2$, and $P_{i,i+k}^{(t)}(r,s)$, $1\le i\le N-2$ and $1\le k\le N-3-i$. These latter functions are given in turn by Eqs. (II. 6A), (II. 7A), (II. 8), and (II. 9), in terms of the components of the matrix **W** and the vector **g**.

In our earlier communication we presented bond orientational order parameters for the case $N=7$, in order to compare our theoretical results against the extensive data on octane provided by Samulski's experiments[4] (n-C_8D_{18} dissolved in the nematic solvent "Merck Phase 5"). Accordingly, we have evaluated $\langle Z_N^2\rangle$ here for $N=7$. Our results are shown in Table I for $G=0.435$ (the standard choice of *gauche* energy) and for various values of F. These results can be interpreted as follows:

Consider first the case of zero field ($f\equiv0$; $F\equiv1$). The end-to-end vector $\mathbf{r}_N$ is then isotropically distributed, with $3\langle Z_N^2\rangle=3\langle X_N^2\rangle=3\langle Y_N^2\rangle=\langle r_N^2\rangle\equiv R_0^2=C^2l^2N$. That is, the semiflexible alkyl chain can be visualized as a sphere with radius

TABLE I. N is the number of "monomers" (C–C bonds), $G \equiv \exp(-\epsilon/kT)$ is the dimensionless *gauche* energy, and $F \equiv \exp(f/kT)$ is the dimensionless nematic field strength. $\langle Z_N^2\rangle$ is the mean of the square of the Z component of the end-to-end vector and $l \simeq 1.533$ Å is the C–C bond length.

	$N=7$	
	$G=0.435$	
	$\langle Z_N^2\rangle_F/l^2$	$\langle Z_N^2\rangle_F/\langle Z_N^2\rangle_{F=1}$
$F=1.0$	7.3	1.0
1.5	10.9	1.5
2.0	14.9	2.1
2.5	16.6	2.3
20	30.6	4.2
∞	$\frac{2}{3}N^2 = 32.7$	4.5

$$R_0 = \sqrt{3}\,\langle Z_N^2\rangle_{F=1}^{1/2} = \sqrt{3}(7.31)^{1/2}(l = 1.53\ \text{Å}) \simeq 7.2\ \text{Å} .$$

We now turn on the nematic field ($F = 1 \to F > 1$) and assume that the R_0 sphere is deformed, without change of volume, into an ellipsoid of revolution with semiaxes a and $b(>a)$. Denote the acentricity $1-(a^2/b^2)$ by γ. For such a body, it is easy to evaluate the average of the square of the Z component of a point on its surface. More explicitly, taking the center of the ellipsoid to lie at the origin of our previously chosen space-fixed coordinate system, we have that

$$\langle Z^2\rangle \equiv \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi [Z(\theta\varphi)]^2 \frac{1}{4\pi} = a^2 \int_0^1 dx \frac{x^2}{1-\gamma x^2} . \tag{IV.1}$$

Here $Z(\theta\varphi) = a^2\cos\theta/1-\gamma\cos^2\theta$ is the Z component of an arbitrary point on the ellipsoid surface $[(x^2+y^2)/a^2] + (Z^2/b^2) = 1$, located at the spherical polar angles θ, φ.

Writing the integral in Eq. (IV.1) as $h(\gamma)$, and associating $\langle Z^2\rangle$ with $\langle Z_N^2\rangle_F$, we have

$$\langle Z_N^2\rangle_F = a^2 h(\gamma) . \tag{IV.2}$$

But from the constancy of the molecular volume we can write

$$V_{(a,\gamma)\,\text{ellipsoid}} = V_{(R_0)\,\text{sphere}} , \tag{IV.3}$$

i.e.,

$$\tfrac{4}{3}\pi a^2 b = \tfrac{4}{3}\pi R_0^3 ,$$

or, by using

$$b \equiv a/(1-\gamma)^{1/2} ,$$

$$\langle Z_N^2\rangle_{F=0} = a^2 \frac{1}{3(1-\gamma)^{1/3}} . \tag{IV.4}$$

Finally, dividing Eq. (IV.2) by Eq. (IV.4), we have

$$\frac{\langle Z_N^2\rangle}{\langle Z_N^2\rangle_0} = 3(1-\gamma)^{1/3} h(\gamma) . \tag{IV.5}$$

Note that the above equation is satisfied in zero field for $\gamma = 0$, since $\langle Z_N^2\rangle \to \langle Z_N^2\rangle_0$ and $h(\gamma) \to \int_0^1 X^2\,dx = \frac{1}{3}$. That is, the chain is described by a sphere of radius $R_0 = a = b$. For $F > 1$, Eq. (IV.5) must be solved numerically to give the molecular acentricity associated with a given semiflexibility G and nematic coupling strength F. For $F = 1.5$, e.g., we have $\langle Z_N^2\rangle/\langle Z_N^2\rangle_0 \simeq 1.5$ and $\gamma \simeq 0.83$ ($a/b \simeq 0.41$). For $F = 2.0$, $\langle Z_N^2\rangle/\langle Z_N^2\rangle_0 \simeq 2.1$ and $\gamma \simeq 0.94$; this corresponds to the "stretching" of an $R_0 \simeq 7.2$ Å spherical octane into an $a \simeq 3.8$, $b \simeq 15.3$ Å ellipsoid.

The values of F considered above are of interest for several reasons. First, in our previous communication we showed how the singlet- and pair-monomer distribution functions could be used to calculate the individual bond alignments. We found in particular that our theoretical plots of η_i^{CD} vs i compared well with experiment for F values in the range 2–3. Here, $\eta_i^{\text{CD}} = \langle P_2(\cos\theta_i^{\text{CD}})\rangle$, where θ_i^{CD} describes the angle between the nematic direction and the CD bond on the ith carbon in n-C_8D_{18}; $P_2(\cos\theta)$ is the second Legendre polynomial, and $\langle\cdots\rangle$ denotes a conformational average. Furthermore, $F \simeq 2$–3 is consistent with an independent estimate of the nematic coupling strength made by Marčelja in his study of the orientational ordering of alkyl chains present as substituents in *neat* liquid crystals. Finally, with $F \simeq 2$–3 we find that the lesser ellipsoidal dimension is given by $a \lesssim 3.8$ Å, i.e., the semiflexible molecule is "squeezed" much as it would be by a cylindrical tube whose radius is $3.8\ \text{Å} + \frac{1}{2}\sigma_{\text{CC}} \simeq 4.6$ Å. Here $\sigma_{\text{CC}} \simeq 1.6$ Å is a distance of closest approach for two carbons. $r \simeq 4.6$ Å is indeed the radial dimension estimated by Samulski in his semiflexible-chain-in-a-repulsive-tube modeling of observed bond alignment. In any case, the *quantitative* details of our present calculations are of less interest than the emergent *qualitative* picture of molecular deformation in an anisotropic field.

APPENDIX A: TRANSFER MATRIX W AND "END" WEIGHTS g

Since t_i and t_{i+1} each run over the full set of 36 trimer states (see below), the matrix W defined by Eq. (II.5A) is 36×36. But only 84 out of its 1,296 elements are nonzero. More explicitly, consider the following enumeration of trimer states $t_i = m_i m_{i+1} m_{i+2}$ with $i = (1, 2, \ldots, N-2)$, $t = (1, 2, \ldots, 36)$ and $m = (1, 2, 3, 4)$:

1 = 121
2 = 123
3 = 124
4 = 131
5 = 132
6 = 134
7 = 141
8 = 142
9 = 143
10 = 212
11 = 213
12 = 214
13 = 231
14 = 232
15 = 234
16 = 241
17 = 242
18 = 243
19 = 312
20 = 313
21 = 314
22 = 321
23 = 323
24 = 324
25 = 341
26 = 342
27 = 343
28 = 412
29 = 413
30 = 414
31 = 421
32 = 423
33 = 424
34 = 431
35 = 432
36 = 434

What are the nonzero matrix elements of the form $W(1, t)$? Since 1 = 121, t must clearly have its first two monomers in the states 2 and 1. Thus, t must be 10 = 212, 11 = 213, or 12 = 214. A similar argument holds for each of $W(2, t)$, $W(3, t), \ldots, W(36, t)$. That is, because of overlapping of the successive trimers, the state abc can only be followed by $bcd \neq c$; otherwise $\epsilon_I(t_i, t_{i+1})$ is infinite and the associated $W_{i,i+1}$—see Eq.

(II.5A)—is identically zero. With 36 abc's and only three $bcd \neq c$'s for each of these, there can be at most $36 \times 3 = 108$ nonzero $W(t_i, t_{i+1})$'s. In addition, 24 of these 108 vanish because of the pentane effect, i.e., each *gauche* t_i—24 of the 36 trimer states—can only be followed by two (rather than three) t_{i+1}. Consider, e.g., the *gauche* trimer state 2 = 123. It can be followed by 14 = 232 and 15 = 234 *but not by* 13 = 231, since t_i, t_{i+1} = 2, 13 would involve the local conformation 1231 and hence an energy $p \gg \epsilon$.

Recalling the definitions $F \equiv \exp(f/kT)$ and $G \equiv \exp(-\epsilon/kT)$, it is then clear that each nonzero matrix element $W(t_i, t_{i+1})$ has the form $F^n G^k$: $k = 0$ or 1, according to whether $t_{i+1} = m_{i+1}, m_{i+2}, m_{i+3}$ is *trans* or *gauche*; and $n = 1$ or $m_{i+3} = 1$ or 2, and $n = 0$ otherwise. Hence,

$$\begin{array}{lll} W(1,10)=F & W(1,11)=G & W(1,12)=G \\ & W(2,14)=F & W(2,15)=G \\ & W(3,17)=F & W(3,18)=G \\ W(4,19)=FG & W(4,20)=1 & W(4,21)=G \end{array}$$

$$W(5,23)=1 \qquad W(5,24)=G$$

and so on.

Similarly, $g(t_1)$ has the form $F^M G^L$ where M is the number of 1 or 2 monomers in the first trimer, and $L = 1$ for *gauche* states ($L = 0$ otherwise). Thus,

$$\begin{array}{lll} g(1)=F^3 & g(2)=F^2G & g(3)=F^2G \\ g(4)=F^2 & g(5)=F^2G & g(6)=FG \end{array}$$

and so on.

APPENDIX B: SINGLET AND PAIR DISTRIBUTIONS

Equations (II.6A), (II.7A), (II.8), and (II.9) define the singlet- and pair-*trimer* distributions

$$P_i^{(t)}(r)\ , \quad \text{for all } 1 \leq i \leq N-2$$

and

$$P_{i,i+k}^{(t)}(r,s)\ , \quad \text{for all } 1 \leq i \leq N-3\ , \quad 1 \leq k \leq N-2-i\ .$$

The singlet- and pair-*monomer* distributions then follow from Eqs. (II.6B) and (II.7B). More explicitly, we have

$$P_i^{(m)}(1) = \sum_{r=1}^{9} P_i^{(t)}(r)\ , \quad 1 \leq i \leq N-2\ , \quad P_{N-1}^{(m)}(1) = P_2^{(m)}(1)\ , \quad P_N^{(m)}(1) = P_1^{(m)}(1)\ ,$$

$$P_{i,i+k}^{(m)}(1,\underset{[3]}{1}) = \sum_{r=1}^{9} \sum_{\substack{s=1\to 9\\ [10\to 18]}} P_{i,i+k}^{(t)}(r,s)\ , \quad \begin{array}{l} 1 \leq i \leq N-3 \\ 1 \leq k \leq N-2-i\ , \end{array} \qquad P_{i,N-1}^{(m)}(1,\underset{[2]}{1}) = \sum_{r=1}^{9} \sum_{\substack{s=10-12,19-21,28-30\\ [1-3,22-24,31-33]}} P_{i,N-2}^{(t)}(r,s)\ , \quad 1 \leq i \leq N-3$$

and

$$P_{i,N}^{(m)}(1,\underset{[2]}{1}) = \sum_{r=1}^{9} \sum_{\substack{s=1,4,7,13,16,22,25,31,34\\ [5,8,10,14,17,19,26,28,36]}} P_{i,N-2}^{(t)}(r,s)\ , \quad 1 \leq i \leq N-3\ .$$

This takes care of all $P_{i,i+k}^{(m)}$ for $i = 1 \to N-3$ and $i + k = i + 1 \to N$. There remain only

$$P_{N-2,N}^{(m)}(1,\underset{[2]}{1}) = \sum_r P_{N-2}^{(t)}(r)\ , \quad r = 1,\ 4,\ \underset{[5,8]}{7}\ , \qquad P_{N-2,N-1}^{(m)}(1,1) = 0 = P_{N-1,N}^{(m)}(1,1)\ ,$$

and

$$\underset{[N-1,N]}{P_{N-2,N-1}^{(m)}}(1,2) = \sum_r P_{N-2}^{(t)}(r)\ , \quad r = \underset{[10,19,28]}{1,\ 2,\ 3}\ .$$

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[1] See, for example, H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), Chap. 3.

[2] See, for example, H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), pp. 71–73.

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