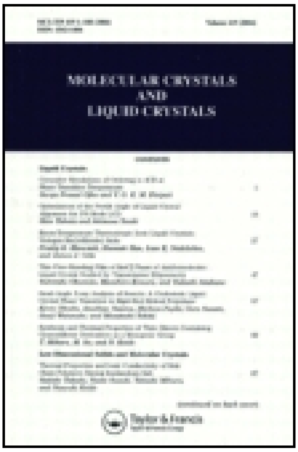

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Molecular Ordering in Nematics: The Modular Formulation of the Potential of Mean Torque

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Molecular Ordering in Nematics: The Modular Formulation of the Potential of Mean Torque

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The general framework for the description of orientational ordering of (flexible) molecules in the nematic phase in terms of ordering properties of submolecular units in a modular fashion is presented. Various choices of the elementary submolecular units (segments) leading to different representations of the potential of mean torque are discussed. Transformations among such representations are studied in order to clarify the physical significance of intersegmental correlation terms. It is shown that for *n*-alkane solutes and chains pendant to nematogenic cores in neat materials, the uncorrelated bond representation (each C—C bond segment individually interacts with the nematic mean field) used in most of the previous studies of this type gives a poor description of chain ordering. The introduction of orientational correlations among bond segments (particularly nearest neighbor correlations) improves the quality of fits of the order parameter profiles and explains the difficiency of previous models. The NMR data are described accurately by a representation wherein the potential is additive with respect to slightly biaxial CH_2 (CH_3) "atom-blocks." When the biaxiality of the blocks is neglected one obtains a potential which is additive with respect to the chord segments (i.e. segments joining the mid points of adjacent C—C bonds) which also gives fairly accurate results. The results indicate that the ordering of the chain is driven essentially by the alignment of individual chord segments, an ordering mechanism that is consistent with excluded volume considerations.

I. INTRODUCTION

The potential of mean torque is a quantity of central importance to the description of orientational order of molecules in the nematic phase. The orientational probability distribution[1–4] $f(\theta)$ of a rigid, uniaxial, "solute" molecule interacting with the nematic "solvent" is related to the potential of mean torque $V(\theta)$ according to the well known relation

$$f(\theta) = Z^{-1}\exp[-V(\theta)/kT], \tag{1}$$

where θ is the angle between the solute molecular axis and the nematic director,

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and Z is the normalization factor. In principle $V(\theta)$ can be expressed rigorously by a series expansion in Legendre polynomials $P_l(\cos\theta)$ (of even l due to the apolarity of the nematic phase). The dominant contribution to the ordering in a nematic phase comes from the $l = 2$ term of the expansion.[4] (The $l = 4$ term is known to have detectable effects near the low temperature end of the nematic range, whereas the $l > 4$ contributions are negligible.) Accordingly, the simplest, yet rather successful, model for the potential of mean torque of a uniaxial molecule in the nematic phase corresponds to the angular dependence of the second degree Legendre polynomial, $V(\theta) \sim P_2(\cos\theta)$. The proportionality factor is determined by the strength of the coupling between the solute molecule and the nematic solvent environment, and by the degree of ordering of the latter. In the mean field approximation one obtains a specific form for the proportionality factor, namely

$$V(\theta) = -wSP_2(\cos\theta) \tag{2}$$

where w is the intermolecular (solvent-solute) coupling constant and S is the nematic solvent order parameter. The angular dependence of $V(\theta)$ does not by itself reflect the precise nature of the intermolecular interactions (aside from their anisotropy). Thus both dispersion and steric (excluded volume) interactions lead to the same $P_2(\cos\theta)$ dependence[1,2] for the dominant contributions to $V(\theta)$. The treatment of biaxial solutes at this level of accuracy entails only an additional coupling constant.[3,4] The representation of the potential of mean torque for a rigid molecule of any shape is therefore a matter of locating the molecular principal axes and of determining the two coupling constants.

Flexible molecules such as alkanes (and alkyl chains attached to rigid mesogenic cores) that can assume a large number of conformations cannot be treated along the above lines since this would require the specification of a set of principal axes and coupling constants for each of the conformations. Attempts to generate systematically these sets of conformer characteristic from simple geometrical features, such as the conformer polarizability tensor,[5] the conformer inertia tensor,[6] the circumference of its projection on a plane normal to the director,[7] its end-to-end vector,[8] etc., lead to rather crude descriptions of the molecular alignment. An alternative approach is to regard the flexible molecule as a collection of rigid submolecular segments that assume different relative positions according to the molecule's conformation, and to formulate the potential of mean torque of the entire molecule in a modularly additive fashion, i.e., by adding up tensor contributions pertaining to the orientability of such segments. The segments could in principle be associated with atoms, groups of atoms, atom-atom bond vectors (chemical bonds), etc. as long as the local structure defining a segment is fixed for all conformations.

For molecules involving a limited number of nonequivalent segment types, this modular approach leads to compact representations of the potential of mean torque in terms of a few segment coupling constants. Furthermore, it offers the possibility of describing a wide variety of molecular structures (flexible or rigid) in terms of a small number of "modules." In implementing the modular additivity hypothesis, however, it is necessary to consider carefully the significance of the additive tensor contributions in connection with the chosen subdivision of the molecule into rigid segments. A rigorous formulation of the potential of mean torque should manifestly preserve the equivalence between representations based on different subdivisions. In other words, the potential of mean torque should not depend on the way one chooses to subdivide the molecule. Now since one is rarely able to retain all the terms of a rigorous expansion of the potential, it is important that the subdivision be such as to allow a physically sensible and a computationally reasonable truncation of the expansion. It will be emphasized herein that a truncated expression for the potential of mean torque will assume a simple form for certain ways of molecular subdivision and a more complicated one for others.

The purpose of this paper is to expand on this point and to explore the physical significance of various representations of the potential of mean torque and their implications on the nature of the intermolecular forces that produce molecular alignment in the nematic phase. We focus attention on flexible alkane solutes in nematics and the alkyl chain component of mesogens. The essential finding of this work is that the alignment of the alkyl chain is a result of excluded volume interactions. These interactions are shown to be described very successfully by a segment-wise additive potential of mean torque wherein the aligning units are identified with (slightly biaxial) atom-block segments associated with the carbon atoms of the chain. In the limit of vanishing biaxiality these atom-block segments reduce to the chord segments (vectors connecting successive bonds in the chain) previously introduced by the present authors[9,10] to describe deuterium NMR data.

II. MODULAR REPRESENTATION AND TRANSFORMATIONS OF THE POTENTIAL OF MEAN TORQUE

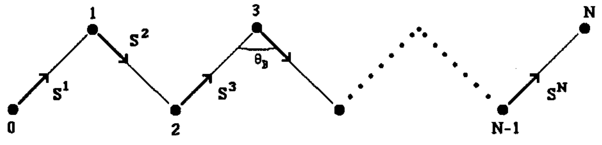
a. Bond Representation

Consider a linear chain molecule consisting of $N + 1$ identical united atoms labeled by $i = 0, 1, 2, \ldots N$ (for example an n-alkane if we ignore the slight inequivalence between the methylene and methyl carbons at the ends). The state of such a solute molecule in a nematic solvent is completely specified given, say, the set of N bond vectors $\mathbf{s}^i$ that join successive atoms in the chain (see Figure 1a). It is straightforward to show[9] that the most general form of the potential of mean torque, accurate to tensor rank 2, is given by

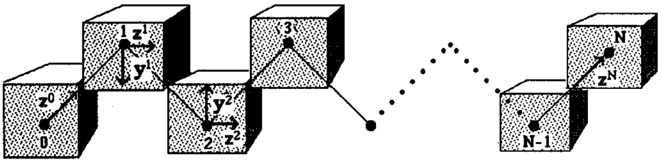
$$V(\omega,n) = -\sum_{m=0}^{N-1}\sum_{i=1}^{N-m} \tilde{w}_m P(\mathbf{s}^i,\mathbf{s}^{i+m}) \tag{3}$$

where ω represents the orientation of the solute molecular frame relative to the nematic director, n is the conformation label and $P(\mathbf{s}^i,\mathbf{s}^{i+m}) = (3\cos\theta^i \cos\theta^{i+m} - \mathbf{s}^i \cdot \mathbf{s}^{i+m})/2$, with θ^i denoting the angle between the ith bond vector $\mathbf{s}^i$ and the nematic director.

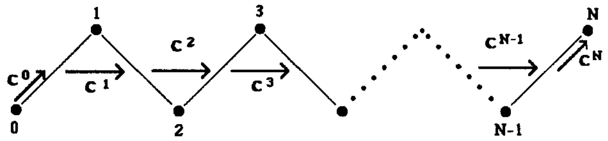
The expression of Equation 3 is rigorous (within the context of second rank tensor angular dependence) and is dictated by mathematical and symmetry con-



(a) Bond Representation



(b) Atom-block Representation



(c) Chord Representation

FIGURE 1 Representations of an alkyl chain with $N+1$ carbon atoms. (a) Bond vector representation; (b) atom-block representation; (c) chord vector representation.

siderations. Comparison of the predictions of $V(\omega,n)$ of Equation 3 for the segmental order parameters with experimental NMR measurements on n-alkanes[9] indicates that the dominant contributions come from the terms associated with $\tilde{w}_0$ and $\tilde{w}_1$. The $\tilde{w}_2$ terms are found to have a small but measurable contribution, and $\tilde{w}_3$, $\tilde{w}_4$, . . . do not have detectable effects on the computed order parameters. Hence, according to these findings, a sufficiently accurate description of the alkane solute can be given by

$$V(\omega,n) = -\tilde{w}_0 \sum_{i=1}^{N} P(\mathbf{s}^i,\mathbf{s}^i) - \tilde{w}_1 \sum_{i=1}^{N-1} P(\mathbf{s}^i,\mathbf{s}^{i+1}). \tag{4}$$

Before we discuss the physical significance of these terms, it is necessary to recall that the use of the bond vectors $\mathbf{s}^i$ as basic segmental elements in the formulation of $V(\omega,n)$, although simple and convenient, is by no means the only possibility, and does not necessarily imply that the alignment of the chain is physically driven by the alignment of the individual bond segments in the nematic field. We shall present two alternative possibilities of subdividing the chain molecule into rigid segments. They provide mathematically equivalent representations to the bond segment representation of $V(\omega,n)$ given in Equation 4, but are suggestive of a concrete, physical interpretation of the alignment mechanism.

b. Atom-Block Representation

This representation is obtained by subdividing the chain into $N-1$ blocks pertaining to the inner atoms. Each block is assigned a set of local Cartesian axes $\mathbf{x}^i$, $\mathbf{y}^i$, $\mathbf{z}^i$, as shown in Figure 1b. For convenience the $\mathbf{z}^i$ axis is chosen to join the mid points of adjacent bonds at atom i and the $\mathbf{y}^i$ axis to be in the plane of these bonds ($\mathbf{y}^i$ therefore subtends the bond valence angle θ_B). For the blocks corresponding to the outermost atoms ($i = 0$ and $i = N$) the $\mathbf{z}^i$ axis is chosen along the direction of the respective terminal C—C bonds (i.e., coincident with the bond vectors $\mathbf{s}^1$ and $\mathbf{s}^N$). The directions of $\mathbf{x}^0$, $\mathbf{y}^0$, $\mathbf{x}^N$, $\mathbf{y}^N$ are irrelevant due to the assumed cylindrical symmetry of these bonds.

By using the relations

$$\begin{aligned} \mathbf{s}^i &= \sin\left(\frac{\theta_B}{2}\right)\mathbf{z}^i - \cos\left(\frac{\theta_B}{2}\right)\mathbf{y}^i \\ \mathbf{s}^{i+1} &= \sin\left(\frac{\theta_B}{2}\right)\mathbf{z}^i + \cos\left(\frac{\theta_B}{2}\right)\mathbf{y}^i \end{aligned} \tag{5}$$

it is straight forward to transcribe $V(\omega,n)$ of Equation 4 into the atom-block module representation.

$$\begin{aligned} V(\omega,n) = &-\frac{1}{2}\tilde{w}_0[P(\mathbf{z}^0,\mathbf{z}^0) + P(\mathbf{z}^N,\mathbf{z}^N)] \\ &- \sum_{i=1}^{N-1}\{(A+B)P(\mathbf{z}^i,\mathbf{z}^i) + B[P(\mathbf{x}^i,\mathbf{x}^i) - P(\mathbf{y}^i,\mathbf{y}^i)]\} \end{aligned} \tag{4'}$$

with

$$A = \sin^2\left(\frac{\theta_B}{2}\right)(\tilde{w}_0 + \tilde{w}_1), \text{ and } B = \cos^2\left(\frac{\theta_B}{2}\right)(\tilde{w}_1 - \tilde{w}_0)/2.$$

In comparing the (mathematically equivalent) forms of Equation 4 and 4′ it is essential to note that the summations in the two representations are over different objects (bonds in 4 and atoms in 4′), and, more importantly: whereas in Equation 4 there are terms pertaining to pairs of bonds (i.e., the $\tilde{w}_1$, or "nearest neighbor correlation" terms), in Equation 4′ the potential of mean torque results from the addition of terms involving only *single* atom-block segments. In this case the modular formulation reduces to a simple segment-wise additive scheme. The orientational ordering of the inner atom-bloc, segments is biaxial (due to the fact that successive bonds $\mathbf{s}^i$ and $\mathbf{s}^{i+1}$ are not colinear) with biaxiality

$$\eta = \frac{B}{A+B} = \frac{\tilde{w}_1 - \tilde{w}_0}{2\tan^2\left(\frac{\theta_B}{2}\right)(\tilde{w}_1 + \tilde{w}_0) + \tilde{w}_1 - \tilde{w}_0} \tag{6}$$

Fits of n-alkane NMR order parameter profiles show that $\tilde{w}_1$ is only slightly smaller than $\tilde{w}_0$ indicating that the atom block biaxiality is small ($\eta \approx -0.03$). According to the above description, the orientational ordering of the chain is driven by the tendency of the atom blocks to align their longitudinal axis $\mathbf{z}^i$ parallel to the director. This interpretation, in conjunction with the slight biaxiality of the atom blocks, is consistent with the space filling picture of the chain molecule whereby alignment is produced by sterically accommodating the chain's global contour along the nematic field in order to minimize excluded volume conflicts with the solvent molecules.

c. Chord-segment Representation

In the limit of vanishing biaxiality of the atom-blocks ($\tilde{w}_1 = \tilde{w}_0$) one obtains a representation in terms of the $\mathbf{z}^i$ vectors only. These vectors are then identified with the directions $\mathbf{c}^i$ of the chords of the chain (i.e., the lines joining the midpoints of adjacent bonds; see Figure 1c). The expression for the potential of mean torque is in this case

$$V(\omega,n) = -\frac{1}{2}\tilde{w}_0[P(\mathbf{c}^0,\mathbf{c}^0) + P(\mathbf{c}^N,\mathbf{c}^N)] - 2\tilde{w}_0\sin^2\left(\frac{\theta_B}{2}\right)\sum_{i=1}^{N-1} P(\mathbf{c}^i,\mathbf{c}^i) \qquad (4'')$$

The form of $V(\omega,n)$ in the chord representation indicates that (apart from end effects) the chain behaves as a linear collection of cylindrical segments whose axes (coincident with the chain chords) align independently along the nematic field. This is a very simple picture of chain alignment that requires a single coupling parameter, namely the chord coupling strength, $2\tilde{w}_0\sin^2(\theta_B/2)$. A picture of comparable formal simplicity, but of quite different physical implications, is provided by the "independent bond model" obtained by setting $\tilde{w}_1 = 0$ in Equation 4. This latter model originally introduced by Marcelja[11a] has been used extensively[12,13] to describe alkyl chain alignment in the nematic phase mainly because of its formal and computational simplicity. According to the form of $V(\omega,n)$ in the independent bond model, the alignment of the alkyl chain results from the alignment of individual C—C bonds in an uncorrelated fashion. The only physical justification of this derives from the assumption that the orientational ordering of the chain is dominated by dispersion forces that may be readily evaluated with additive (uniaxial) bond polarizabilities. Moreover, the independent bond model, when viewed in the context of the atom-block representation of Equation 4′, corresponds to a huge block biaxiality $\eta \approx -0.3$ (obtained by setting $\tilde{w}_1 = 0$ in Equation 6). However, comparison with experiment shows clearly[9] that w_1 is much closer to w_0 than to 0, thus favoring the chord model and its physical interpretation for chain alignment, i.e., excluded volume interactions dominate. These findings provide a clear physical rationalization of Marcelja's[11b] *ad hoc* choice of the chord segment to construct a potential of mean torque for lipid membranes that proscribes that the mean direction of chain propagation be along the bilayer normal.

It should become clear from the above examples that, for a given representation of the potential of mean torque, the existence of significant contributions from terms involving pairs of segments (such as the $\tilde{w}_1$ terms in Equation 4) is a manifestation of the fact that the physically aligning segments are considerably different from the "mathematical" segments used to obtain that representation. The criterion of which molecular subdivision comes closer to describing the "physically aligning units" is thus set by the degree to which one may neglect contributions of the "correlation" terms among pairs of such units in the expansion of $V(\omega,n)$. Herein comparisons between calculations based on the different representations of $V(\omega,n)$ and experiment show unambiguously that the widely used independent bond model is qualitatively inferior to representations that include bond orientational correlations.

In order to illustrate the significance of nearest neighbor correlation terms in connection with the bond representation and to make explicit contact with commonly encountered[11-13] expressions of $V(\omega,n)$ using reduced spherical harmonics, we discuss in Appendix A the following simple, but exaggerated, example: a freely jointed chain consisting of two identical uniaxial segments (see Figure 2a). We compare the values of $V(\omega,n)$, in the representation of Equation 4, for the following two idealized configurations: $\{i\}$ an extended conformation with the two segments parallel to the director and $\{ii\}$ a folded conformation with one segment parallel and one antiparallel to the director (see Figure 2b). We have from Equation A7 in the Appendix A, $V\{i\} = -2\tilde{w}_0 - \tilde{w}_1$ and $V\{ii\} = -2\tilde{w}_0 + \tilde{w}_1$. Thus, with only the $\tilde{w}_0$ term, the two arrangements, although obviously of quite different shape and alignment tendency, are characterized by identical values of the potential of mean torque. The energetic distinction between the two arrangements is reflected entirely by the $\tilde{w}_1$ term.

Of course, since it is possible to transcribe easily $V(\omega,n)$ from one representation

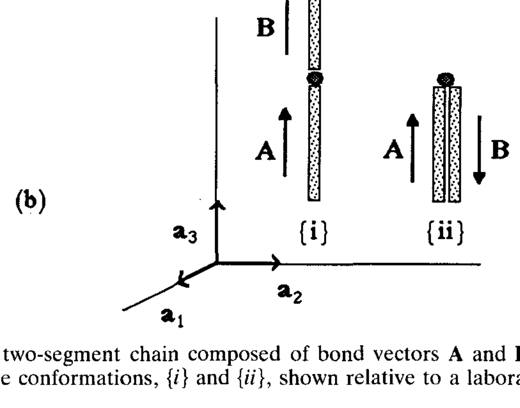


FIGURE 2 An ideal two-segment chain composed of bond vectors **A** and **B**; (a) arbitrary conformation; (b) two extreme conformations, $\{i\}$ and $\{ii\}$, shown relative to a laboratory frame.

to another, one may work with any representation one finds convenient, as long as segment pair correlation terms are not discarded *ad hoc*. Finally, it is emphasized that the modular approach is rather general, allowing one to transcribe models of $V(\omega,n)$ that are based on global molecular properties into modular form. This is demonstrated in Appendix B where we consider a global property that has been proposed before[8] to be relevant to the ordering of flexible molecules, namely, the end-to-end vector, **R**, shown in Figure 3.

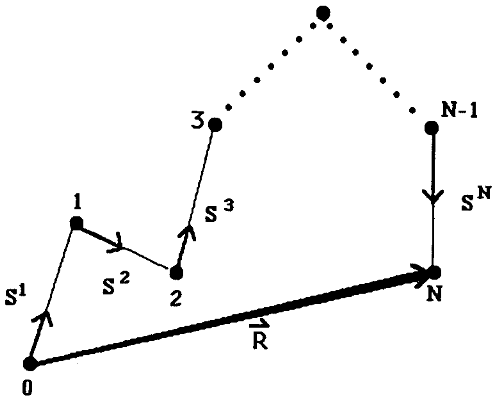


FIGURE 3 The end-to-end vector, **R**, a global property of an arbitrary alkyl chain configuration.

III. CHAIN ORDER PARAMETER CALCULATIONS

The potential of mean torque $V(\omega,n)$ as formulated in the previous section determines the orientational probability distribution for each conformer of a solute molecule. To calculate the thermal average of any quantity $F(\omega,n)$ that depends on the orientation and/or conformation of the solute molecule, one needs to generate all the conformations and their statistical weights. In the present calculations this is carried out within the context of the standard rotational isomeric state (RIS) model[14] of the chain. For alkyl chains there are two basic RIS parameters, the trans-gauche energy difference E_{tg} and the gauche dihedral rotation angle about the C—C bonds ϕ_g. The nominal values for these parameters are $E_{tg} \approx 0.5$ kcal/mol and $\phi_g \approx 113°$. These values, along with standard geometrical data on bond lengths and bond angles,[14,15] are used in order to determine the energy $E(n)$ and geometry of the conformers. The conformer generation process is carried out by affecting all possible rotations by $\pm\phi_g$ about the C—C bonds. Conformations leading to self intersection of the molecule and $g \pm g$ conformations of the chain are rejected.

The conformer energy $E(n)$ together with the potential of mean torque $V(\omega,n)$ are then used to determine the probability distribution $f(\omega,n)$ for the conformations and orientations of the solute molecule as follows,

$$f(\omega,n) = \frac{1}{\zeta} G(n)\exp[-(E(n) + V(\omega,n))/kT] \tag{7}$$

where ζ is the usual normalization factor (we use the normalization $\Sigma_n \int d\omega f(\omega,n) = 1$) and $G(n)$ is the conformer rotational kinetic energy factor.[10] The thermal average $\langle F \rangle$ of any quantity $F(\omega,n)$ is obtained by averaging over all orientations and conformations of the solute molecule according to

$$\langle F \rangle = \sum_n \int d\omega \, F(\omega,n) \, f(\omega,n) \tag{8}$$

To test the modular approach to the formulation of the potential of mean torque we have calculated the order parameters of the C—^{2}H bonds of the alkyl chain and compared the results with the values obtained by ^{2}H NMR measurements. The comparison between calculation and experiment, in addition to testing the theory, provides the values of $\tilde{w}_0$, $\tilde{w}_1$ . . ., which in turn can give insights into the microscopic mechanism of alignment, and in particular, into whether the ordering is primarily driven by C—C bond alignment ($\tilde{w}_1 << \tilde{w}_0$, dispersion forces) or by chord alignment ($\tilde{w}_1 \approx \tilde{w}_0$, excluded volume). Calculations were performed on both free chains (alkane solutes in a nematic solvent) and pendant chains on a mesogenic core (neat nematic liquid crystals).

VI. RESULTS AND DISCUSSION

a. *n*-Alkanes

Table I shows the results of three different fits of experimental C-^{2}H order parameter profiles of octane, $\langle P_2(\cos\theta_j)\rangle_{\text{expt}}$, dissolved in the nematic solvent phase-V at 300 K. The fit quality as monitored by the percent mean square deviation of the calculated splittings from the measured ones[10] (Table I, column 1), namely by the quality factor

$$R_{\%} = 100 \left\{ \sum_j \left[\langle P_2(\cos\theta_j)\rangle_{\text{expt}} - \langle P_2(\cos\theta_j)\rangle_{\text{calc}} \right]^2 \right\} / \sum_j |\langle P_2(\cos\theta_j)\rangle_{\text{expt}}|^2, \tag{9}$$

with j running over all the deuterated carbon sites.

TABLE I

Deuterium NMR quadrupolar splittings of *n*-octane-d$_{18}$ in the nematic solvent phase V at 300 K

Quadrupolar Splittings (kHz)			
		Calculated	
Measured	$\tilde{w}_0 = 0.23$[a] $\tilde{w}_1 = 0.18$	$\tilde{w}_0 = \tilde{w}_1$ $= 0.21$	$\tilde{w}_0 = 0.44$ $\tilde{w}_1 = 0$
−10.53	−10.78	−10.31	−14.07
−32.76	−31.24	−31.15	−31.20
−38.09	−38.34	−38.51	−35.63
−40.52	−41.29	−41.68	−37.81
Quality Factor	$R_{\%} = 1.2\%$	$R_{\%} = 1.4\%$	$R_{\%} = 5.7\%$

[a] In kcal/mol.

The second column of Table I shows the results of the calculation using the biaxial atom block segmental representation of $V(\omega,n)$ in Equation 4′. The optimal values of $\tilde{w}_0 = 0.23$ kcal/mol and $\tilde{w}_1 = 0.18$ kcal/mol yield for the inner block biaxiality, according to Equation 6 (with $\theta_B = 112°$), $\eta = -0.029$.

The value of $R_{\%}$ ($=1.2\%$) is close to the experimental uncertainty of the data ($\sim 1\%$). This indicates that the biaxial atom block potential of mean torque provides a good description of the ordering of the chain. It should be noted that this fit (and the others on Table I) is obtained without making any adjustments of the nominally accepted values of the RIS parameters E_{tg} and ϕ_g.

In order to investigate the extent of the influence of atom-block biaxiality on the calculated profiles (equivalently, the sensitivity of order parameter profiles to block biaxiality) we have carried out fits with the (uniaxial) chord model potential of Equation 4″ (i.e., with $\tilde{w}_0 = \tilde{w}_1$). The results are shown in column 3 of Table I. The accuracy is only slightly reduced relative to the biaxial atom-block calculation. This suggests that the block biaxiality observed in the fit of column 2 is not a critical factor to the alignment of the chain in the nematic environment.

Finally, to test the validity of the alignment mechanism of the independent (uncorrelated) bond model, we have made fits using the bond model potential (i.e., $V(\omega,n)$ of Equation 4 but with $\tilde{w}_1 = 0$). It is obvious from the results in column 4 of Table I ($R_{\%} = 5.7\%$) that this model gives a rather poor description of the order parameter profiles.

b. Nematogen-Pendant Alkyl Chains

To assess the generality of the conclusion reached for *n*-alkane solutes we have studied the orientational order profiles of the deuterated chain attached to the mesogen octylcyanobiphenyl (8-CB). The segment-wise additive potential of mean torque $V(\omega,n)$, in this case, has to be extended in order to include contributions from the alignment of the cyanobiphenyl (CB) core. This is done at a minimal level of detail by adding to the potential of the chain a term $\tilde{w}_{\mathrm{core}}\, P_2(\cos\theta_{\mathrm{core}})$, where $\tilde{w}_{\mathrm{core}}$ measures the anisotropic coupling of the CB core to the nematic field and θ_{core} is the angle between the CB para axis and the nematic director. As the ^{2}H-NMR data is not sufficient to reveal clearly the details of the aligning mechanism we have neglected contributions from the CB core biaxiality and also from atom-block biaxiality (i.e., we have used $\tilde{w}_0 = \tilde{w}_1$ for the chain, leading to the chord model of Equation 4″). The basic submolecular units that produce, in an additive manner, the alignment in this simplified interaction picture of the nematogen are shown in Figure 4a. The results of the calculations are shown in Figure 4b. For comparison with the predictions of the independent bond model,[12,13,16] we have made calculations with $\tilde{w}_1 = 0$ for the chain potential. The latter results exaggerate the even-odd oscilations in the computed order parameter profile and are inferior to those obtained with the chord model, although the inadequacy of the bond model is not as marked as in the case of *n*-alkanes. This is due to the fact that in 8-CB the orientational ordering of the molecule is dominated by the alignment of the CB core (which is treated identically in both the independent bond model and the chord model).

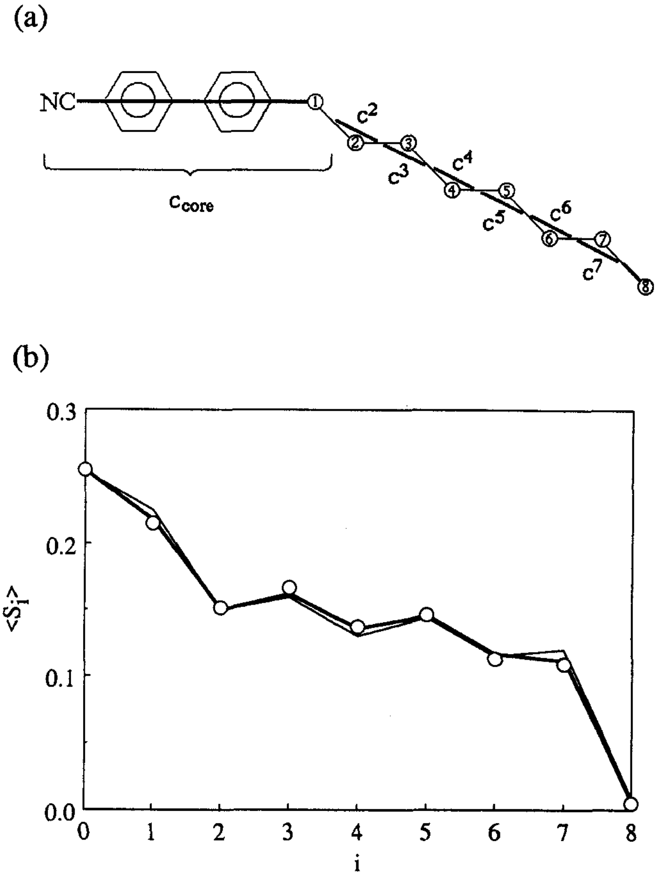


FIGURE 4 (a) Molecular geometry and interacting modules of the 8-CB molecule in the chord model; (b) Orientational order parameter profile of 8-CB in the nematic phase at $T = T_{NI} - 4°C$. The open circles represent measured values from Reference 16. The bold line gives the calculated profile according to the chord model with optimized parameters $\tilde{w}_{core} = 1.38$ kcal/mol and $\tilde{w}_0 = \tilde{w}_1 = 0.16$ kcal/mol (the quality factor $R_{\%} = 0.6\%$). The fine line gives the calculated profile according to the independent bond model ($\tilde{w}_1 = 0$) with $\tilde{w}_{core} = 1.49$ kcal/mol and $\tilde{w}_0 = 0.36$ kcal/mol (in this case $R_{\%} = 1.7\%$). For the octyl tail chain ($i = 1, 2, \ldots, 8$), $\langle S_i \rangle = -\langle P_2(\cos\theta^i \; C\text{-}^2H) \rangle$ gives the magnitude of the order parameter of the ith C-^2H bond of the chain (with carbon atom numbering as in 4(a)). The order parameter of the cyanobiphenyl para-axis, reduced by 50% for plotting convenience, is represented by $\langle S_0 \rangle = (1/2) \langle P_2(\cos\theta_{core}) \rangle$.

V. CONCLUDING REMARKS

We introduce for the first time the *biaxial* atom block representation, of which the chord and C—C bond modules are special (extreme) cases. Moreover, by studying the transformations among these representations we show that the strength of intersegment (intermodule) correlations is dictated by the choice of modules and, conversely, the "correct" choice minimizes such correlations. The results presented in the previous section show that the modular approach to the formulation of the potential of mean torque can be successfully applied to the description of the orientational ordering of flexible alkyl chains (both free solute chains and pendant mesogen chains) in the nematic phase. The simplest case of the modular formulation, i.e., the (uncorrelated) segment-wise additive formulation, is fairly accurate in describing the C-^{2}H order parameter profiles, provided that the additivity is over the *chord* segments (or atom blocks). These results also show that ordering arises essentially by the alignment of the chain chords, in accordance with expectations based on the excluded volume picture of the molecular ordering. Transcription of the chord representation of the potential of mean torque into the bond representation shows that $\tilde{w}_1 = \tilde{w}_0$ and, therefore, that the nearest neighbor bond correlation terms in the expansion of $V(\omega,n)$ are as important as the single (direct) bond orientation terms and not a mere correction that could be left out in a coarse approximation. The fact that orientational correlations of adjacent bonds are important when the alignment is driven by the chords is intuitively clear: each chord is attached to two adjacent bonds and thus its reorientation corresponds to simultaneous reorientation of both of these bonds.

The consistency, transferability and generality of the modular approach, even in its simplest implementation (the chord model), and its biaxial generalization (the atom-block representation), has been applied to the alkanes,[9,10] mesogens such as n-CB and n-OCB,[17] and is being studied in substituted alkanes, dimer mesogens and even rigid solutes.[18] In the latter only transferabilty of the modular properties is relevant. The modular formulation of the potential of mean torque successfully describes the temperature dependence and chain length dependence in alkane solutes and in neat monomer and dimer mesogens; it also exhibits accurate predictive capabilities when applied to rigid fused-ring hydrocarbons. Additionally, this description of flexible molecules enables us to critically examine the rotational isomeric state approximation itself by contrasting the comprehensive proton dipolar coupling data set of n-hexane dissolved in a nematic solvent.[19] In short, the modular approach appears to offer a significant improvement in efforts to understand molecular ordering in nematics with a potential of mean torque.

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APPENDIX A

In order to illustrate the physics (and mathematics) of the "additional" term in Equation 4 relative to the independent bond model (Equation 4 with $\tilde{w}_1 = 0$), we carry out a detailed calculation with a simple example, a chain comprised of two identical segments **A** and **B** (see Figure 2a). Our goal is to identify how this additional term enters into the coupling constant used in traditional expressions[11–13] of the potential of mean torque and to emphasize how this term influences the orientational energy of different conformations of this simple chain.

For the two-segment chain, Equation 4 written out explicitly becomes

$$V(\omega,n) = -\tilde{w}_0[P(\mathbf{A},\mathbf{A}) + P(\mathbf{B},\mathbf{B})] - \tilde{w}_1 P(\mathbf{A},\mathbf{B}) \tag{A1}$$

where **A**, **B** are the unit vectors describing the directions of the two segments in a macroscopic frame (with **z** along the nematic director **N**). According to the definitions of $P(\mathbf{s}^i,\mathbf{s}^{i+1})$ we have:

$$\begin{aligned} P(\mathbf{A},\mathbf{A}) &= \frac{3}{2}(\mathbf{A}\cdot\mathbf{N})^2 - \frac{1}{2}, \\ P(\mathbf{B},\mathbf{B}) &= \frac{3}{2}(\mathbf{B}\cdot\mathbf{N})^2 - \frac{1}{2}, \end{aligned} \tag{A2}$$

and

$$P(\mathbf{A},\mathbf{B}) = \frac{3}{2}(\mathbf{A}\cdot\mathbf{N})(\mathbf{B}\cdot\mathbf{N}) - \frac{1}{2}(\mathbf{A}\cdot\mathbf{B}).$$

With $\mathbf{a}_\mu$ ($\mu = 1,2,3$) denoting the unit vectors along the three axes of a molecular-fixed frame we may switch to molecular frame components A_μ, B_μ according to

$$\begin{aligned} \mathbf{A} &= \sum_\mu (\mathbf{A}\cdot\mathbf{a}_\mu)\mathbf{a}_\mu = \sum_\mu A_\mu \mathbf{a}_\mu \\ \mathbf{B} &= \sum_\mu B_\mu \mathbf{a}_\mu \end{aligned} \tag{A3}$$

Obviously the molecular frame components depend only on the conformation of the two-segment chain, i.e., $A_\mu = A_\mu(n)$, $B_\mu = B_\mu(n)$. Using Equations A2 and A3 we may rewrite Equation A1 as follows:

$$\begin{aligned} V(\omega,n) = -\sum_{\mu,\nu} \Bigg\{ & \frac{\tilde{w}_0}{3}(3A_\mu A_\nu - \delta_{\mu\nu} + 3B_\mu B_\nu - \delta_{\mu\nu}) + \frac{\tilde{w}_1}{3}\Bigg[\frac{3}{2}(A_\mu B_\nu \\ & + A_\nu B_\mu) - (\mathbf{A}\cdot\mathbf{B})\delta_{\mu\nu}\Bigg]\Bigg\} \left\{\frac{3}{2}(\mathbf{a}_\mu\cdot\mathbf{N})(\mathbf{a}_\nu\cdot\mathbf{N}) - \frac{1}{2}\delta_{\mu\nu}\right\} \end{aligned} \tag{A4}$$

This expression of the potential of mean torque in Cartesian notation may be readily translated in terms of molecular-fixed frame rotation matrices $C_{\mu,\nu}(\omega)$ and conformation dependent coupling tensors $\varepsilon^n_{\mu,\nu}$:

$$V(\omega,n) = -\sum_{\mu,\nu} \varepsilon^n_{\mu,\nu} C_{\mu,\nu}(\omega) \tag{A4$'$}$$

In order to carry out this transcription we have used the following definitions (from Equation A4 above):

$$\varepsilon^{n}_{\mu,\nu} \equiv \left\{ \frac{\tilde{w}_0}{3}\,(3A_\mu A_\nu - \delta_{\mu\nu} + 3B_\mu B_\nu - \delta_{\mu\nu}) + \frac{\tilde{w}_1}{3}\left[\frac{3}{2}\,(A_\mu B_\nu + A_\nu B_\mu) - (\mathbf{A}\cdot\mathbf{B})\delta_{\mu\nu}\right]\right\} \tag{A5}$$

and

$$C_{\mu,\nu}(\omega) \equiv \left\{\frac{3}{2}\,(\mathbf{a}_\mu\cdot\mathbf{N})(\mathbf{a}_\nu\cdot\mathbf{N}) - \frac{1}{2}\,\delta_{\mu\nu}\right\}. \tag{A6}$$

Let's examine in detail the implications of this development by considering two extreme conformations of the freely-jointed two-segment chain shown in Figure 2b. In both conformations $\{i\}$ and $\{iI\}$, $\varepsilon^{n}_{\mu,\nu}$ is diagonal in the indicated molecular-fixed frame. The diagonal components of $\varepsilon^{n}_{\mu,\nu}$ in each conformation are given by

$$\begin{aligned} \varepsilon^{\{i\}}_{3,3} &= -\frac{2}{3}\,(2\tilde{w}_0 + \tilde{w}_1), \quad \varepsilon^{\{i\}}_{1,1} = \varepsilon^{\{i\}}_{2,2} = -\frac{1}{2}\,\varepsilon^{\{i\}}_{3,3} \\ \varepsilon^{\{ii\}}_{3,3} &= -\frac{2}{3}\,(2\tilde{w}_0 - \tilde{w}_1), \quad \varepsilon^{\{ii\}}_{1,1} = \varepsilon^{\{ii\}}_{2,2} = -\frac{1}{2}\,\varepsilon^{\{ii\}}_{3,3} \end{aligned} \tag{A7}$$

Obviously if one sets $\tilde{w}_1 = 0$, then the two conformations will have identical $\varepsilon^{n}_{\mu,\nu}$ tensors, i.e., they will behave identically as far as their orientational order in the nematic solvent is concerned. Therefore, by ignoring the $\tilde{w}_1$ terms one is treating the two segments as if—with regard to their alignment energy—they were completely independent (i.e., as if they did not belong to the same chain) and one is in effect ignoring *excluded volume effects* on the orientational order.

It is trivial to switch from Cartesian to spherical tensor notation,

$$\sum_{\mu,\nu} \varepsilon^{n}_{\mu,\nu} C_{\mu,\nu}(\omega) \rightarrow \sum_{m} \varepsilon^{n}_{(2),m} C_{(2),m}(\omega),$$

where

$$\varepsilon^{n}_{(2),0} \sim \varepsilon^{n}_{3,3},$$

$$\varepsilon^{n}_{(2),\pm 1} \sim \varepsilon^{n}_{3,1} \pm i\varepsilon^{n}_{3,2},$$

$$\varepsilon^{n}_{(2),\pm 2} \sim \varepsilon^{n}_{1,1} - \varepsilon^{n}_{2,2} \pm 2i\varepsilon^{n}_{2,1}.$$

but the latter tends to be less convenient for the description of segmental correlations.

It is important to note in Equations A4 and A4′ that $\varepsilon^{n}_{\mu,\nu}$ is the most general second rank tensor that can be constructed from quadratic contributions of the components of the equivalent vectors **A**, **B** (the equivalence meaning that these vectors describe segments with identical interactions with the nematic mean field and accordingly the tensor should be symmetric to the exchange **A** → **B**). In the past, however, the $\varepsilon^{n}_{(2),m}$ coefficients in the spherical tensor expansion of $V(\omega,n)$ have been identified directly with the single bond interactions[11–13] (in what we refer to as the independent bond model). In view of the preceding discussion, however, such an identification clearly ignores arbitrarily the $\tilde{w}_1$ part of $\varepsilon^{n}_{\mu,\nu}$ (or $\varepsilon^{n}_{(2),m}$). The physical difficiencies that result from ignoring the $\tilde{w}_1$ term are important; a cursory examination of the orientational potential energy of these two extreme conformers of the idealized two-segment chain emphasizes the implications of ignoring the $\tilde{w}_1$ terms (see text).

APPENDIX B

One very simple model of molecular ordering in nematics wherein a global property might be relevant is the end-to-end vector model (Figure 3), in which the molecular alignment is assumed to result from the tendency of the vector spanning the length of the molecule to align parallel to the director according to the following potential of mean torque:

$$V_R(\omega,n) = -\tilde{w}_R P_2(\cos\theta_R) \tag{B1}$$

where θ_R is the angle between the nematic director and the end-to-end vector **R**.

We express **R** in terms of bond vectors (of length s), i.e., $\mathbf{R} = s\,\Sigma_i\,\mathbf{s}^i$, which, when substituted in Equation B1, gives the following expression for the V_R in the bond segment representation:

$$V_R(\omega,n) = -\tilde{w}_R\left(\frac{s^2}{R^2}\right)\left\{\sum_{i=1}^{N} P(\mathbf{s}^i,\mathbf{s}^i) + 2\sum_{m=1}^{N-1}\sum_{i=1}^{N-m} P(\mathbf{s}^i,\mathbf{s}^{i+m})\right\} \tag{B2}$$

In the language of the modular approach (Equation 3), this corresponds to equal magnitudes for all the coupling constants pertaining to segmental pair correlations, irrespective of their separation along the chain. Furthermore, the correlation couplings are twice as large as the direct (single segment) coupling, i.e.

$$\tilde{w}_1 = \tilde{w}_2 = \tilde{w}_3 \ldots = 2\tilde{w}_0 = \tilde{w}_R\left(\frac{s^2}{R^2}\right) \tag{B3}$$

This is in marked contradiction with the behavior of the couplings as obtained from fittings of NMR data on *n*-alkanes, according to which the correlation couplings diminish rapidly with pair distance and, except for $\tilde{w}_1$, their values are well below that of $\tilde{w}_0$. This discrepancy is not surprising in view of the obvious inadequacy of the end-to-end vector to describe the shape and alignment tendencies except for linear conformers. For the majority of the conformers assumed by a sufficiently long alkane molecule, the bulk of the molecular volume lies outside of the end-to-end axis (see Figure 3) and furthermore different conformers may satisfy the same end-to-end vector. Note also that according to Equation B3, the end-to-end vector representation implies that the couplings $\tilde{w}_m$ could be conformation dependent ($\sim w_R/R^2$).

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