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Assessment of Bond Rotation Interdependence in Polymer Chains: An Information Theory Approach

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ABSTRACT: Measures of randomness from information theory are adapted so that they test the correlation of rotational states in a chain molecule. One term measures the equiprobability of the rotational states. This term is simply the well-known expression for the entropy of mixing of an ideal solution, recast in the jargon of information theory. The more interesting second term measures the interdependence of the bond rotations. This term arises from the contribution of preferential nearest-neighbor interactions to the entropy of mixing of a nonideal one-dimensional system. The behavior of these two terms is examined in detail for infinitely long simple chains in which bonds are subject to symmetric threefold rotation potentials. In the special case of linear polyethylene, the distribution becomes more equiprobable upon an increase in temperature, but there is virtually no change in interdependence due to the nearly exact compensation of two competing effects. Illustrative calculations for poly(vinyl acetate) demonstrate that microstructure can have a large influence on both the equiprobability and the interdependence of the distribution of rotational states.

Introduction

Many configuration-dependent physical properties of unperturbed chains are successfully rationalized by application of the rotational isomeric state approximation.¹⁻³ The most common situation, in which rotations about consecutive bonds are interdependent, can be treated to any desired degree of approximation by formulation of the configuration partition function as a product of statistical weight matrices. Bonds are independent in the special case where each statistical weight matrix has identical rows.

While it is easy to distinguish between chains with independent and interdependent bonds, it is often a more difficult task to assess which of two real chains has the greater degree of interdependence of bond rotations. For example, in which member of the following pairs of chains are the bond rotations more interdependent: Polyethylene with 10 and 20 bonds? Long polyethylene chains at 300 and 400 K? *meso*- and *rac*-poly(vinyl acetate)? Poly(vinyl bromide) and poly(vinyl chloride)? Poly(oxyethylene) and poly(vinylidene chloride)? Unambiguous answers to these questions are possible if there is access to a single quantitative measure of the interdependence of bond rotations that can be applied to all of these chains. An appropriate measure can be formulated by utilization of concepts from information theory. The formulation is accomplished here. Illustrative applications are made to simple chains with threefold rotation potentials and to poly(vinyl acetate).

Measures of Equiprobability and Interdependence

Rotational States as Characters of an Alphabet. The discussion is in terms of a chain that has ν rotational

states for each internal bond. Several common chains have $\nu = 3$, with the rotational states designated as t (trans), g^+ (gauche⁺), and g^- (gauche⁻). Each real chain of n bonds may be mapped as a sequence of $n - 2$ characters selected from ν possibilities. This map bears an analogy to an information message encoded by a string of characters (such as the present text), where the maximum number of distinguishable characters is ν . However, this analogy is limited, because the information in the conformation of a polymer chain is not targetted to a receiver, in contrast with a DNA sequence, which contains a measurable quantity of information in the sequence of nucleotides that is transmitted to the cellular protein synthetic machinery through the messenger RNA.

Measures of Randomness from Information Theory. The a priori probability for a specified pair of rotational states at bond $i - 1$ and i , denoted by $p_{\xi\eta;i}$, is easily extracted from Z by matrix methods that evaluate the partial derivative shown in eq 1.^{2,3} In eq 1 $w_{\xi\eta;i}$ is the

$$p_{\xi\eta;i} = \partial \ln Z / \partial \ln w_{\xi\eta;i} \quad (1)$$

statistical weight for bond i in state η when bond $i - 1$ is in state ξ . The first-order probability, $p_{\eta;i}$, that bond i is in state η is given by eq 2, and the second-order conditional probability, $q_{\xi\eta;i}$, is given by eq 3. Averages over all choices

$$p_{\eta;i} = \sum_{\xi=1}^{\nu} p_{\xi\eta;i} \quad (2)$$

$$q_{\xi\eta;i} = p_{\xi\eta;i} / p_{\xi;i-1} \quad (3)$$

for the subscript i are denoted more simply by p_{η} and $q_{\xi\eta}$.

An alternative notation for $q_{\xi\eta}$ is $p(\eta/\xi)$, which denotes the conditional probability that η follows ξ .

A basic tenet of information theory is that information is a measurable quantity. A hypothetical "chain configuration source" (which is not a physical device) is assumed to output sequences of a particular length. The configuration partition function determines the proportion and composition of these sequences. Parametric measures of information, which are functions of probabilities defined above, characterize the "chain configuration source".⁴ Interest here is in two information theoretic parameters that can be used to contrast the distribution of rotational states in different types of rotational isomeric state chains. The first of these parameters, D_1 , measures the tendency of the chain to use certain rotational states in preference to others. The second measure, D_2 , measures the tendency of the chain to use certain pairs of rotational states over others. Thus, a chain in which all states are weighted equally has $D_1 = 0$. A chain with independent bond rotational potentials would have $D_2 = 0$, but D_1 might be zero or nonzero. Chains with interdependent rotational potentials have $D_2 > 0$.

Definitions of D_1 and D_2 . A convenient starting point is Shannon's quantitative measure of information⁵

$$H_1 = -k \sum_{i=1}^{\nu} p(i) \log_2 p(i) \quad (4)$$

where H_1 is the Shannon entropy corresponding to the probability distribution $p(i)$, k is a constant normally chosen as unity, and ν is the number of distinct characters in the sequences. A more familiar choice of k might be Boltzmann's constant, as in the expression for the entropy of mixing an ideal solution. The unit measure of Shannon entropy is bit when the base of the logarithm is chosen as 2. This unit will be used here. The maximum value of H_1 occurs when all characters are equiprobable. Its value is

$$H_1^{\max} = \log_2 \nu \quad (5)$$

The deviation from randomness due to unequal values of $p(i)$, i.e., the divergence from equiprobability, is denoted by D_1 and is given by⁴

$$\begin{aligned} D_1 &= H_1^{\max} - H_1 \\ &= \log_2 \nu + \sum_{i=1}^{\nu} p(i) \log_2 p(i) \end{aligned} \quad (6)$$

For the special case of a simple chain with a symmetric threefold rotation potential, eq 6 becomes

$$D_1 = \log_2 (3) + p_t \log_2 p_t + (1 - p_t) \log_2 [(1 - p_t)/2] \quad (7)$$

which clearly depends on p_t alone. However, if the threefold rotational potential lacks symmetry

$$D_1 = \log_2 (3) + p_t \log_2 p_t + p_{g^+} \log_2 p_{g^+} + (1 - p_t - p_{g^+}) \log_2 (1 - p_t - p_{g^+}) \quad (8)$$

which depends on both p_t and p_{g^+} . In general, D_1 might be a function of as many as $\nu - 1$ of the a priori probabilities. Symmetry, however, may cause D_1 to depend on fewer of the a priori probabilities.

H_1 depends exclusively upon the distribution of single characters. One may define higher order Shannon entropies, H_2 , H_3 , etc., based on the distribution of doublets, triplets, etc. The significance of H_2 is analogous to the component of the entropy of mixing of a nonideal one-dimensional "solution" that arises from preferential nearest-neighbor interactions. The deviation from randomness due to the interdependence of characters, i.e., the

divergence from independence, is a function of second-order Shannon entropy and is given by

$$D_2 = H_2^{\max} - H_2 = H_1 - H_M \quad (9)$$

where H_M (which denotes H Markov) is given by

$$H_M = -\sum_{i=1}^{\nu} \sum_{j=1}^{\nu} p(i)p(j/i) \log_2 p(j/i) \quad (10)$$

For a chain with a symmetric threefold rotation potential, the result is

$$\begin{aligned} D_2 &= p_t \{q_{tt} \log_2 q_{tt} + (1 - q_{tt}) \log_2 [(1 - q_{tt})/2] - \log_2 p_t\} \\ &+ (1 - p_t) \{q_{g^+t} \log_2 q_{g^+t} + q_{g^+g^+} \log_2 q_{g^+g^+} + (1 - q_{g^+t} - q_{g^+g^+}) \log_2 (1 - q_{g^+t} - q_{g^+g^+}) - \log_2 [(1 - p_t)/2]\} \end{aligned} \quad (11)$$

which depends on a single a priori probability and three conditional probabilities. In general, D_2 can depend on as many as $\nu - 1$ a priori probabilities and $\nu(\nu - 1)$ conditional probabilities. Symmetry may reduce these numbers.

Higher order divergences (D_3 , D_4 , etc.) may similarly be defined, but they are not necessary if the objective is assessment of the degree of interdependence of the bond rotations. If m is the largest order of interactions considered in the formulation of the configuration partition function, then the total divergence from the state of maximum entropy, i.e., the information density, is $D_1 + D_2 + \dots + D_m$.

Calculations

Illustrative results are presented for simple chains with symmetric threefold rotation potentials and for *meso*- and *rac*-poly(vinyl acetate). The well-known statistical weight matrix for polyethylene⁶ was also used for other chains with a symmetric threefold rotation potential.

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (12)$$

Specific application to polyethylene requires that energies of 500 and 2000 cal/mol be used in the evaluation of σ and ω , respectively. Both σ and ω are treated as variable in the generalized discussion of simple chains with bonds subject to threefold rotation potentials. Sundararajan's model was used for poly(vinyl acetate).⁷ He described several sets of parameters for use in the configuration partition function. Preexponential factors from Sundararajan's Table IV and interaction energies from his Figure 10 are used here.

Using customary methods,³ we calculated a priori and conditional probabilities for chains of 4 to 100 bonds and also for chains that contain an infinite number of bonds. The same bonds (3 through $n - 1$) were included in the evaluation of both types of averages in the chains with a finite number of bonds. Use of unequal ranges for evaluation of the two types of probabilities can produce a violation of Shannon's fundamental inequality, proved by Khinchin's theorem,⁸ that $H_1 \geq H_M$.

Results and Discussion

Contour Map for D_1 . Figure 1 depicts a contour map for D_1 as a function of σ and ω for simple chains that have symmetric threefold rotation potentials. All states are equally probable when $\sigma = \omega = 1$, and therefore $D_1 = 0$ when $\ln \sigma = \ln \omega = 0$. D_1 is also zero at other combinations of σ and ω that yield $p_t = 1/3$.

D_1 increases as one moves up or to the right from the contour line where $D_1 = 0$. In this region of the contour diagram, the chains have an excess of gauche states. A

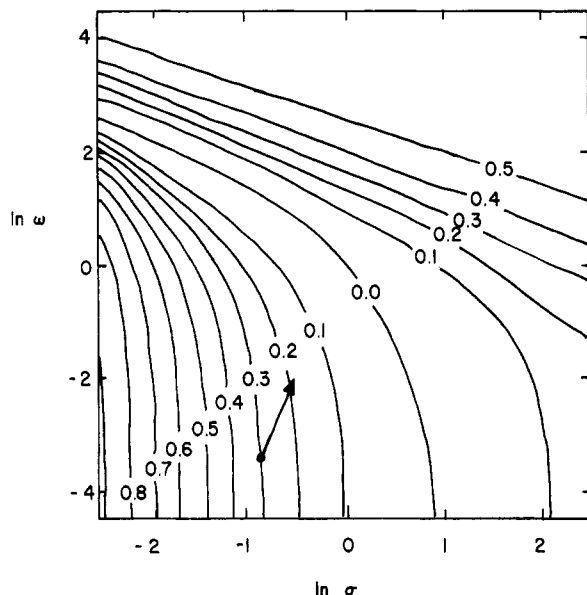


Figure 1. Contour map of D_1 for infinitely long simple chains with a symmetric threefold rotation potential. The arrow is discussed in the text.

plateau, where $0.5 < D_1 < 0.585$, is clearly evident at the top of Figure 1. If this figure were extended to the right, it would show that the plateau at large ω merges with a plateau of the same height at large σ . The molecular origin of the plateau is easily seen. Trans placements are completely suppressed at sufficiently large σ and/or ω . When trans placements are suppressed, eq 7 becomes

$$D_1 = \log_2(3) + \log_2(1/2) = 0.585 \quad (13)$$

which is the maximum value of D_1 on the plateau.

D_1 also increases as one moves left or down from the contour line where $D_1 = 0$. The chain then has an excess of trans states. The value of p_t increases as σ and ω decrease, and p_t approaches 1 as σ approaches zero. The D_1 specified by eq 7 approaches $\log_2(3) = 1.585$, and D_1 approaches this limit faster at smaller ω . The lower left quadrant is especially pertinent because an important real chain, polyethylene, has $\sigma < 1$ and $\omega < 1$.

Contour maps for D_1 and p_t (the latter not shown here) have minima at different locations. Minima for D_1 are seen at finite σ and ω in Figure 1, but the minima for p_t occur when σ and ω are infinite. Nevertheless, any contour line on the p_t contour map has an exact counterpart on the D_1 contour map because D_1 is completely specified by p_t when the bonds have a symmetric threefold rotation potential, as shown by eq 7. The contour line at $p_t = 1/3$ is superimposable on the contour line for $D_1 = 0$.

Contour Map for D_2 . Figure 2 depicts the contour map for D_2 for the chains that were considered in Figure 1. The condition $\omega = 1$ is sufficient for $D_2 = 0$ because bond rotations are then independent. (In terms of the analogy with the entropy of mixing, $D_2 = 0$ corresponds to an ideal solution where the entropy of mixing is simply $-R \sum x_i \ln x_i$.) The dependence of D_2 on σ is much stronger for $\omega < 1$ than for $\omega > 1$. This behavior can be rationalized as follows. Attention is directed first to the region where ω is large. As ω increases at constant σ , trans placements are suppressed and the dominant chain configuration becomes the one comprised exclusively of gauche placements that alternate in sign. In this limit, eq 11 reduces to $-\log_2(1/2) = 1$. While this limit is not attained for ω of the size used in Figure 2, the approach to the limit is clearly evident. The observed D_2 along the top of Figure 2 fall below the limit because a few g^+t , tg^+ , and g^+g^+ pairs persist at

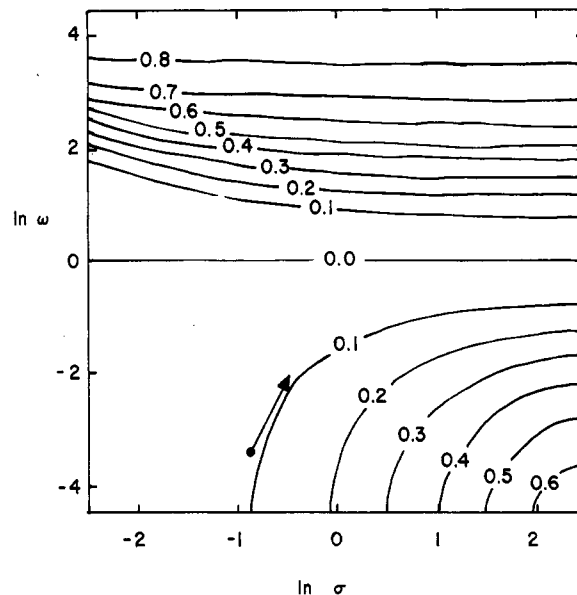


Figure 2. Contour map of D_2 for infinitely long simple chains with a symmetric threefold rotation potential. The arrow is discussed in the text.

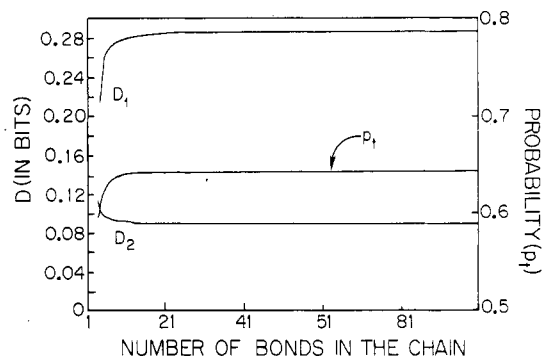


Figure 3. Chain length dependence of p_t , D_1 , and D_2 when the statistical weights are those expected for linear polyethylene at 298 K.

the largest σ considered. The g^+t and tg^+ pairs are most important at small σ , and the g^+g^+ pairs are responsible for lowering D_2 at the larger σ . The combined effect of the g^+t , tg^+ , and g^+g^+ pairs is nearly independent of σ , causing the size of D_2 to also be nearly independent of σ at large ω .

The reason that D_2 depends strongly on σ when ω is small can be seen by consideration of the dominant chain configurations in the lower left and lower right portions of the contour diagram. Trans placements are dominant when σ and ω are both small. The role of a small ω is discrimination against g^+g^+ pairs. However, these pairs are already of rare occurrence at very small σ , and the additional discrimination produced by a small ω is of little consequence. Therefore D_2 is small throughout most of the lower left quadrant. The D_2 specified by eq 11 approaches zero as σ vanishes. In the lower right quadrant, trans placements are suppressed, as are gauche pairs of opposite sign. In the limit as σ goes to infinity and ω goes to zero, the expression in eq 11 approaches 1 because each chain consists entirely of gauche placements that are of the same sign. The value of D_2 is sensitive to σ at small ω because chains at the extreme lower left of Figure 1 are forced into a single configuration (all bonds in trans states), but chains at the extreme lower right may occupy either of two configurations (each chain is comprised exclusively of gauche states of the same sign, but the gauche state may

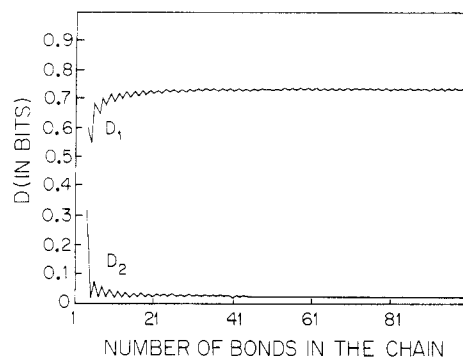


Figure 4. Chain length dependence of D_1 and D_2 for *rac*-poly(vinyl acetate) at 300 K.

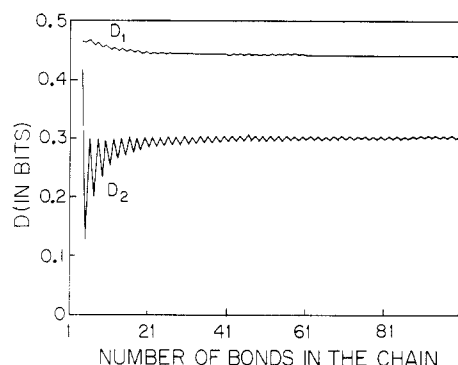


Figure 5. Chain length dependence of D_1 and D_2 for *meso*-poly(vinyl acetate) at 300 K.

be selected from g^+ and g^-).

Case of Linear Polyethylene. Figure 3 depicts D_1 and D_2 as a function of n for polyethylene chains at 298 K. The divergence from equiprobability increases by 0.073 bits from 0.214 bits for pentane to 0.287 bits for a chain of 100 bonds. In contrast, D_2 is reduced from 0.114 to 0.089 bits for the same change in n . The population of rotational states tends toward a less equiprobable (D_1 increases) but more independent (D_2 decreases) distribution as n becomes large. Equation 7 shows that the effect of chain ends on p_t is responsible for the variation in D_1 . There is a more complicated origin for the change in D_2 , which depends on three conditional probabilities as well as on p_v , as shown in eq 11. Ninety percent of the change in D_2 in Figure 3

has been accomplished at $n = 9$, but n must be 11 before there is 90% of the total change in D_1 .

An increase in temperature produces an increase in σ and ω for polyethylene. The effect on D_1 and D_2 is shown by the arrows in Figures 1 and 2. The circles at the origins of the arrows denote points where σ and ω have the values appropriate for a temperature of 298 K. The values of D_1 and D_2 are the limits obtained at large n in Figure 3. The heads of the arrows are placed at the σ and ω seen at 498 K. As the temperature increases from 298 to 498 K, there is a decrease in D_1 , but almost no change in D_2 . The population of rotational states becomes more equiprobable (D_1 decreases), but there is little change in the interdependence (D_2 is unaffected). Figure 2 clearly shows that the absence of a temperature dependence for D_2 should be attributed to compensating effects from the changes in σ and ω .

Influence of Microstructure in a Vinyl Polymer. The equiprobability and independence of rotational states can depend strongly on the microstructure, as is shown in Figures 4 and 5. These figures depict the chain length dependence of D_1 and D_2 for *meso*- and *rac*-poly(vinyl acetate). The racemic chain has the less equiprobable distribution because of the preference for *trans* states in this chain. Both *trans* and *gauche* states are of common occurrence in the *meso* chains, but they have a strong tendency for segregation into *tg* helices. It is this strong interdependence that causes the larger D_2 in the *meso* chains.

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