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A random-walk model for hydrocarbon-type chains with short-range correlations

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Abstract. The conformational statistics of a normal alkane-type chain is studied by describing a random walk on a diamond lattice. The progress of the chain is governed by two probability parameters. The mathematical methods of a Markoff chain are used to calculate the expected square of the end-to-end distance for an oriented chain. The problem of excluded volume is not considered.

Since the introduction by Kuhn (1934, 1942) of the random-walk model to approximate mathematically the distributions of the configurations that flexible linear molecules might assume, the theoretical calculation of the mean dimensions of polymeric molecules has been the subject of numerous publications in recent years (Montroll 1950, Ullman and Hermans 1953, Zimm *et al.* 1953, Tobolsky and Gupta 1962, Wall *et al.* 1962). The dimensions of the polymeric chains are most conveniently characterized in terms of the mean square end-to-end separation $\langle R_n^2 \rangle$, where n is the number of steps. The knowledge of this distance is important in developing the equation of state for rubber elasticity, for deriving equations expressing intrinsic viscosity in terms of the chain length, for interpreting light scattering data from dilute solutions and for promoting the growth of other important theoretical concepts.

Recently, using the mathematical methods of Markoff chains, Tobolsky (1959) has calculated the average square length of a normal alkane-type chain. His model is the following. The n links of the chain are represented by n vectors in a diamond lattice, $R_0, R_1, R_2 \dots R_{n-1}$, the components of which (X, Y, Z) can assume only the values 1 and -1 . A property of the diamond lattice is that each successive vector is obtained from the preceding one by changing the sign of one component and leaving the two others unchanged (see appendix). The three possible orientations of a link have probabilities a or b according to whether it is placed in the trans or in one of the two gauche positions, with respect to the two preceding links. The probabilities a and b are determined by the relations

$$a + 2b = 1 \quad (1)$$

and

$$\frac{a}{b} = \exp\left(\frac{\epsilon}{KT}\right) \quad (2)$$

where $\epsilon = E_g - E_{tr}$ is the energy difference between a gauche and a trans sequence of three links. In the calculation of the average $\langle R^2 \rangle$ the chain is treated as a Markoff chain (Feller 1957) constructed from pairs of links $(R_0 R_1), (R_1 R_2), (R_2 R_3) \dots$, such that the first link of each pair is identified with the last link of the preceding pair. The transition probability matrix of this Markoff chain relates the orientation of a vector to those of two preceding ones. Hijmans and Holleman (1962) have further modified this model and included in the calculation of $\langle R^2 \rangle$ the excluded-volume effect. All conformations containing cyclohexane-type loops and most of those involving pentane-type steric hindrances are excluded.

In the present communication we consider a further modification of Tobolsky's model to consider the statistics of an oriented hydrocarbon-type chain. Again the chain describes a random walk on a diamond lattice. We consider a sequence of three consecutive links and if the last one is parallel to the first, i.e. when the sign of the same coordinate has changed, we assume that it occurs with a probability r . This is the probability of the

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orientation being destroyed. Let the other two probabilities, i.e. of preserving the orientation (in the direction indicated by the arrow in figure 1) and reversing the orientation, be designated as p and q . In other words, if two consecutive changes of sign involve the coordinates X and Y , then the next change occurs at the coordinate Y again with probability r , at the coordinate X with probability p and with probability q at the remaining

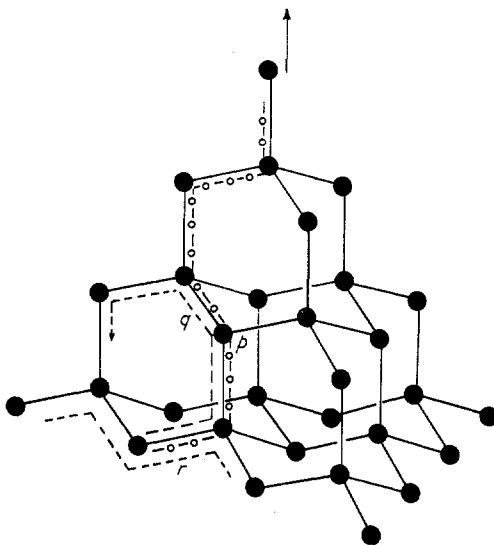


Figure 1. A hydrocarbon-type chain on a diamond lattice.

coordinate. These probability parameters are shown in the figure. The transition probability matrix P becomes

$$P = \begin{matrix} & \begin{matrix} 31 & 13 & 1-1 & -11 & -1-3 & -3-1 \end{matrix} \\ \begin{matrix} 31 \\ 13 \\ 1-1 \\ -11 \\ -1-3 \\ -3-1 \end{matrix} & \begin{vmatrix} 0 & r & 1-r & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & p+r & q & 0 \\ 0 & q & p+r & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1-r & r & 0 \end{vmatrix} \end{matrix} \quad (3)$$

Obviously $p+q+r = 1$.

The expected square of the end-to-end distance is given by

$$\langle R^2 \rangle = E\{(X_0 + \dots + X_{n-1})^2 + (Y_0 + \dots + Y_{n-1})^2 + (Z_0 + \dots + Z_{n-1})^2\} \quad (4)$$

where E stands for the expected value. The magnitude of the components is taken to be unity for simplicity of calculation:

$$\begin{aligned}
 \langle R^2 \rangle &= 3n + 2 \sum_{i=0}^{n-2} \sum_{j=i+1}^{n-1} E(X_{(i)}X_{(j)} + Y_{(i)}Y_{(j)} + Z_{(i)}Z_{(j)}) \\
 &= 3n + 2 \sum_{i=0}^{n-2} \sum_{k=1}^{n-1-i} E(X_{(0)}X_{(k)} + Y_{(0)}Y_{(k)} + Z_{(0)}Z_{(k)}).
 \end{aligned}$$

This can be written simply as

$$\langle R^2 \rangle = -3n + 2 \sum_{k=0}^{n-1} (n-k)L_k \quad (5)$$

where

$$L_k = E(X_{(0)}X_{(k)} + Y_{(0)}Y_{(k)} + Z_{(0)}Z_{(k)}). \quad (6)$$

The chain could start in any one of the six states. The weights assigned to the various states are

$$\begin{aligned} w_1 &= 3 \\ w_2 &= w_3 = 1 \\ w_4 &= w_5 = -1 \\ w_6 &= -3. \end{aligned} \quad (7)$$

With these, in general,

$$E(X_{(s)}X_{(t)} + Y_{(s)}Y_{(t)} + Z_{(s)}Z_{(t)}) = \sum_{j,k=1}^6 p_{ij}^{(s)} w_j p_{jk}^{(t-s)} w_k \quad (8)$$

where $p_{jk}^{(s)}$ is the s th step transition probability from the state j to k . To evaluate these elements, one has to evaluate first the row and column eigenvectors of the matrix. If these are $X^{(r)}$, $Y^{(r)}$, corresponding to the eigenroots λ_r , then

$$P^n = \sum_{r=1}^6 C_r^{-1} \lambda_r^n X^{(r)} Y^{(r)}. \quad (9)$$

C_r^{-1} is the inverse of the inner product of the row and column vectors. The matrix P has three eigenvectors of the symmetric pattern (x, y, z, z, y, x) , which will not contribute to L_k , and three eigenvectors of the antisymmetric form $(x, y, z, -z, -y, -x)$, which would contribute. The eigenvalues corresponding to the antisymmetric eigenvectors are -1 , λ_1 and λ_2 , where λ_1 and λ_2 are roots of

$$\begin{aligned} \lambda_1 + \lambda_2 &= q \\ \lambda_1 \lambda_2 &= q - r. \end{aligned} \quad (10)$$

The $p_{ij}^{(k)}$ elements which contribute to L_k are given below:

$$\begin{aligned} p_{11}^k &= -p_{16}^k = -p_{61}^k = p_{66}^k = (-1)^k C_1 + \lambda_1^k C_2 + \lambda_2^k C_3 \\ p_{12}^k &= -p_{15}^k = -p_{62}^k = p_{65}^k = (-1)^{k+1} C_1 + \lambda_1^{k+1} C_2 + \lambda_2^{k+1} C_3 \\ p_{13}^k &= -p_{14}^k = -p_{63}^k = p_{64}^k = (-1)^{k+1} \frac{1-r}{q} C_1 + \lambda_1^k (1-\lambda_1) C_2 + \lambda_2^k (1-\lambda_2) C_3 \\ p_{21}^k &= -p_{26}^k = -p_{51}^k = p_{51}^k = p_{56}^k = (-1)^{k+1} C_1 + \lambda_1^{k-1} C_2 + \lambda_2^{k-1} C_3 \\ p_{22}^k &= p_{11}^k = -p_{25}^k = -p_{52}^k = p_{55}^k \\ p_{23}^k &= -p_{24}^k = -p_{53}^k = p_{54}^k = (-1)^k \frac{1-r}{q} C_1 + \lambda_1^{k-1} (1-\lambda_1) C_2 + \lambda_2^{k-1} (1-\lambda_2) C_3 \\ p_{31}^k &= -p_{36}^k = -p_{41}^k = p_{46}^k = (-1)^{k+1} C_1 + \frac{q(1-\lambda_1)}{r-1} \lambda_1^{k-1} C_2 + \frac{q(1-\lambda_2)}{r-1} \lambda_2^{k-1} C_3 \\ p_{32}^k &= -p_{13}^k = -p_{35}^k = -p_{42}^k = p_{45}^k \\ p_{33}^k &= -p_{34}^k = -p_{43}^k = p_{44}^k = (-1)^k \frac{1-r}{q} C_1 + \frac{q}{r-1} (1-\lambda_1)^2 \lambda_1^{k-1} C_2 \\ &\quad + \frac{q}{r-1} (1-\lambda_2)^2 \lambda_2^{k-1} C_3 \end{aligned}$$

where

$$C_1 = \frac{q}{2(2q+1-r)}$$

$$C_2 = \frac{\lambda_1(1-\lambda_2^2)}{2(\lambda_1-\lambda_2)(2q+1-r)}$$

$$C_3 = -\frac{\lambda_2(1-\lambda_1^2)}{2(\lambda_1-\lambda_2)(2q+1-r)}$$

Now

$$\sum_{k=1}^6 p_{jk}^{(n)} w_k = 3(p_{j1}^n - p_{j6}^n) + (p_{j2}^n - p_{j4}^n) + (p_{j3}^n - p_{j5}^n) = L_{jn}. \quad (11)$$

The different values of j correspond to the chain starting in different initial states, and thus we obtain different values of L_k . Since we are interested in calculating an 'ensemble average' value of the expected square of the end-to-end distance, for each value of L_k , the calculated $\langle R^2 \rangle$ is weighted by the stationary-state probabilities of the corresponding initial starting state. The stationary-state probabilities are obtained by solving the set of equations $XP = X$ and normalizing the components of the vector P to unity, i.e. $\sum P_{ij} = 1$. For the six states the steady-state probabilities are given below:

$$\frac{q}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}, \frac{1-r}{2(2q+1-r)}, \frac{1-r}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}$$

Substituting these values, we can write

$$L_k = \frac{q}{2q+1-r} L_{1k} + L_{2k} + \frac{1-r}{q} L_{3k}. \quad (12)$$

On substituting various values, we obtain

$$L_k = \frac{q}{2q+1-r} \left\{ \frac{2C_1(-1)^k}{q^2} (2q-1+r)^2 + 32C_2\lambda_1^k + 32C_3\lambda_2^k \right\}. \quad (13)$$

We make use of the identity

$$\sum_{k=0}^{n-1} (n-k)\lambda^k = \frac{n}{1-\lambda} + \frac{\lambda^{n+1}}{(1-\lambda)^2} - \frac{\lambda}{(1-\lambda)^2}$$

and let

$$\sum_{k=0}^{n-1} (n-k)(-1)^k = A = \frac{1}{2}n + \frac{(-1)^{n+1} + 1}{4}$$

For large values of n the value of the expected square of the end-to-end distance for an oriented hydrocarbon-type molecule is reduced to a simple expression

$$\langle R^2 \rangle = \left[-3n + 2A \frac{2q(-1+r)^2}{2q+1-r} + \frac{128q}{4(2q+1-r)^2} \frac{n}{1-r} \{1 + (q-r)(1-q)\} \right] \frac{1}{3} l_0^2. \quad (14)$$

It should be possible to test the validity of this equation from measurements on light scattering, viscosity, etc., for hydrocarbons of various chain lengths. This would also permit an estimate of the various transition probability parameters, and from measurements on chains of different molecular weights the self-consistency of these parameters could be checked.

The result for the special case of Tobolsky is obtained by putting $q = \frac{1}{2}(1-r)$. In this case the above expression is reduced to

$$\langle R^2 \rangle = \frac{2n}{1-r} \frac{1}{3} (1+3r) l_0^2. \quad (15)$$

Further, if $r = \frac{1}{3}$, which implies that there is no energy difference between the trans and the two gauche configurations,

$$\langle R^2 \rangle = 2nl_0^2 \quad (16)$$

and, if $r = 0$, which implies that the trans configurations are nearly excluded,

$$\langle R^2 \rangle = \frac{2}{3}nl_0^2. \quad (17)$$

These results are well known in the theory of random walk. The problem of excluded volume is not considered here.

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Appendix

In a diamond lattice any lattice point is joined to its nearest neighbours with tetrahedral bonds (centre of a regular tetrahedron joined to four vertices). This may be illustrated as in figure 2(a). On each carbon atom four such vectors end. (In various polymer chains we come across such bonds.)

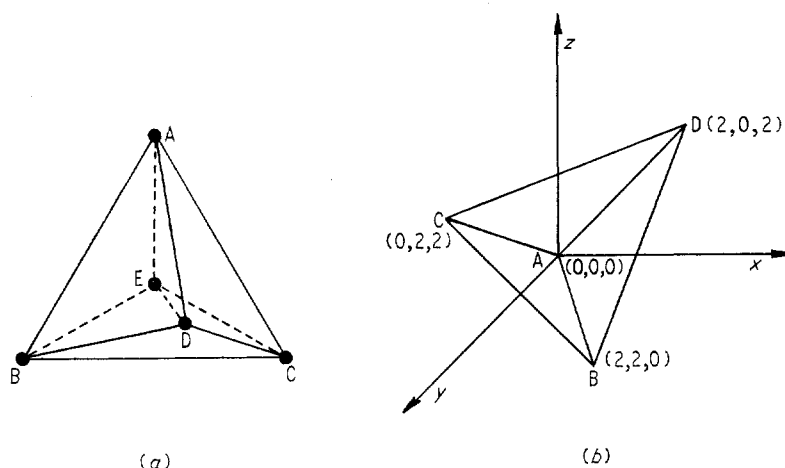


Figure 2.

Our aim here is to find a set of axes in which we can describe these bonds in a very convenient way. We shall first choose the set of axes and then show how these tetrahedral bonds can be described.

We take an orthogonal set of axes and choose four points A, B, C and D given by $(0, 0, 0)$, $(2, 2, 0)$, $(0, 2, 2)$ and $(2, 0, 2)$. Now, if we join all these points with each other, we obtain a tetrahedron. Therefore we can take them to be the atoms A, B, C and D shown in figure 2(a).

The coordinates of the centre (where the perpendiculars from any vertex to the opposite face meet) will be given by

$$\left(\frac{0+2+0+2}{4}, \frac{0+2+2+0}{4}, \frac{0+0+2+2}{4} \right) \text{ or } (1, 1, 1).$$

Hence the vector AE is given by $(1, 1, 1)$. Similarly other vectors are EB $(1, 1, \bar{1})$, EC $(\bar{1}, 1, 1)$ and ED $(1, \bar{1}, 1)$. In the case of an actual lattice we shall find other vectors also, but if we describe them with respect to the axes shown in figure 2(b) they will be

given by $(\bar{1}, \bar{1}, 1)$, $(\bar{1}, 1, \bar{1})$, $(1, \bar{1}, \bar{1})$ and $(\bar{1}, \bar{1}, \bar{1})$. Thus we obtain a set of eight vectors, which describe all the possible bonds, since in solving a problem by a 'random-walk' method these vectors also describe the direction of translation in going from one lattice point (atom) to the neighbouring one. This set can be symbolically written as $(1, 1, 1)$.

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