Markoff Chains and Excluded Volume Effect in Polymer Chains

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ture, are reproducible after further heating of the oven in vacuum. This may be due either to continued reduction with the formation of a second solid or liquid phase or to the formation of a stable oxide which does not undergo further reduction at the partial pressure of oxygen maintained in the oven under the conditions of the experiment.

(5) The "steady state" may again be oxidized if it is heated in an atmosphere of oxygen exceeding a critical pressure, which no doubt is a function of temperature.

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Markoff Chains and Excluded Volume Effect in Polymer Chains

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In most of the theoretical work on statistical properties of polymer chains one includes (for mathematical simplicity) configurations which correspond to several monomers located at the same point. Here a mathematical method based on the theory of Markoff chains is used to eliminate short-range excluded volume effects in polymer chains formed on space lattices. Those aspects of the theory of Markoff chains which are important in this problem are briefly reviewed.

If $a_s(s=j-k)$ is the correlation coefficient between the x component of the position of the jth monomer and that of the kth, then the root-mean-square distance between ends of a chain of degree of polymerization N is proportional to $N^{\frac{1}{2}}$ (as $N\rightarrow\infty$) provided that $a_s\rightarrow 0$ more rapidly than $A/s^{1+\epsilon}$ (as $s\rightarrow\infty$). Here A is a constant and ϵ is an arbitrarily small positive constant. This condition is satisfied in a chain in which any group of n_0 successive monomers do not overlap each other or any monomers in neighboring groups of n_0 provided $n_0 \ll N$.

A detailed analysis of a polymer chain on a square lattice is given.

I. INTRODUCTION

A KNOWLEDGE of the geometrical configuration of polymer chains and the distribution of monomer elements in such chains is necessary for theoretical investigations of polymer solutions and of the elastic behavior of polymers. In most of the current polymer literature configuration and distribution problems are solved with the assumption that polymers are formed by the successive addition of C—C bonds in a random manner with the restriction that bond angles have specified values (and perhaps that attractive or repulsive forces act between monomer elements twice removed). This mode of conceptual construction of a chain does not prohibit the formation of configurations in which several atoms exist in the same place. Hence the standard polymer models have particle densities larger and root-mean-square lengths shorter than those of real polymers.

In this paper we shall discuss a mathematical scheme for the investigation of statistical properties of polymer chains whose carbon atoms lie on points of a periodic space lattice. By application of the theory of Markoff chains, we can treat models in which the short-range overlapping of atoms is eliminated. Our detailed calculations will be restricted to chains whose carbon atoms lie on a square lattice. They are now being extended to chains on simple cubic and diamond type lattices. It seems that an analogous mathematical method using integral equations can be employed in the analysis of chains which are not restricted to lattices.

We shall introduce those formulas from the theory of Markoff chains[1] that will be needed for our application. For completeness a brief discussion of long-range order in Markoff chains will be included in the Appendix.

Let us consider polymer chains which can be formed on a square lattice; that is, two-dimensional polymers with bond angles of 90° and with a constant bond distance between monomers. Several of the configurations drawn in Fig. 1 (b, c) cannot exist because they contain lattice points which are occupied by two monomers.

Those overlaps which occur when a monomer four removed from a given monomer returns to the position of the given monomer will be called first-order overlaps (see b in Fig. 1). Overlaps of monomers 12 removed (see c) will be called second-order overlaps, etc. Inasmuch as first-order overlaps are so much more probable than those of higher order one can expect them to be the primary source of the deviations from random models.

It is known that the mean square distance between two distant points in a random model of a polymer chain is proportional to the number of monomers be-

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[1] For a more detailed discussion of the general theory see, for example, M. B. Hostinsky, *Methodes Générales du Calcul des Probabilités* (Gauthier-Villars, Paris, 1931); M. Frechet, *Reserches Théoriques Modernes sur le Calcul des Probabilités* (Gauthier-Villars, Paris, 1938); or E. Montroll, Ann. Math. Stat. 18, 18 (1947).

tween the two points. We shall now, in a heuristic way, find the conditions under which the same result is obtained in a chain with correlations between configurations of bonds in the chain. Physically these correlations may result from an attraction or repulsion (which leads to excluded volume effects) between monomers or indirectly through the interaction of the chain with its solvent or neighboring chains.

If x_j represents the x component of the vector connecting the jth and $j+1$st monomers, then the x component of the length of the chain is given by

$$X_n = x_1 + x_2 + \cdots + x_n.$$

The possible values of x_j for a chain on a quadratic lattice are $-a$, 0, a (where a is the bond length). The mean value $E(x_j)$ of x_j is zero. We represent the mathematical expectation or average value of X_n^2 by $E(X_n^2)$. Then

$$E(X_n^2) = \sum_{j=1}^{n} E(x_j^2) + 2\sum_{j=1}^{n-1}\sum_{k=j+1}^{n} E(x_j x_k),$$

where $E(x_j x_k)$ is the correlation coefficient between the jth and kth components. In very long chains end effects are of secondary importance; hence as $n\to\infty$ we can assume that $E(x_j x_k)$ is a function of $(k-j)$ when j and k are not too close to the ends of the chain. Then if $(k-j)=s$, we have as $n\to\infty$

$$E(X_n^2) \sim n a_0 + 2\sum_{s=0}^{n-1} (n-s) a_s; \quad a_s = E(x_j x_k).$$

In a random chain all correlation coefficients a_s $(s>0)$ are zero and the classical result $E(X_n^2)\sim n a_0$ follows. By using several examples, we can show that $E(X_n^2)$ is proportional to n in chains whose long-range correlations decrease faster than $a_s = A/s^{1+\epsilon}$, where ϵ is an arbitrarily small positive number. Let $a_s \sim A\exp(-Bs)$ as $s\to\infty$ $(B>0)$. Then

$$\sum_{s=1}^{n-1}(n-s)A\exp(-Bs) \sim nAe^{-B}/(1-e^{-B}).$$

Hence

$$E(X_n^2) \sim n\{a_0 + 2Ae^{-B}(1-e^{-B})^{-1}\}.$$

When $a_s \sim A/s^B$ $(B>0)$, we have

$$\sum_{s=1}^{n-1}(n-s)A/s^B \simeq \begin{cases} An/(B-1) \text{ if } B>1 \\ An\log n \text{ if } B=1 \\ An^{2-B}/(2-B)(1-B) \text{ if } 0<B<1. \end{cases}$$

Therefore $E(X_n^2)\sim n[a_0 + 2A(B-1)^{-1}]$ if $B>1$, $2An\times\log n$ if $B=1$ and $2An^{2-B}/(2-B)(1-B)$ if $B<1$.

A correlation coefficient A/s is somewhat analogous to long-range Coulomb forces and one of the form As^{-B} $(B<1)$ involves long-range order of the type observed in a crystal lattice. One of the fundamental questions in the theory of excluded volume effects is: Are the long-range effects large enough to make $E(X_n^2)$ of order greater than n? After making several approximations, Flory[2] has obtained an expression for $E(X_n^2)$ of the form An^{2-B} where $1>B>0.8$. It is important that more research be done on some polymer model to completely settle this point one way or the other. We shall show at the end of this paper that if one constructs a chain by joining smaller chains of n_0 monomers each, in such a way that each monomer in a given subchain is influenced only by other monomers in its own and neighboring subchains, then the root-mean-square distance between the ends of the chain is proportional to $n^{\frac{1}{2}}$(as $n\to\infty$) no matter how large n_0 is chosen to be. The punch card investigations of configurations of polymer chains now being pursued by Dr. Gilbert King[3] should be helpful in deciding a form for the long-range correlation functions.

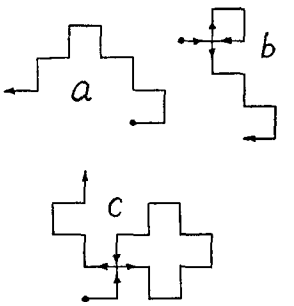


FIG. 1. Sample configurations of chains on a square lattice.

In the remaining analysis we shall limit ourselves to models which exclude first-order overlaps but which permit the much less probable overlaps of higher order. Our analysis can, in principle, be generalized to include any desired order of overlap, but this generalization leads to the determination of characteristic values and vectors of matrices of very high order.

Our main calculation will be equivalent to an investigation of a random walk on a square lattice in which the walker (a) must turn to the left or right after each step (retreating is prohibited!), (b) is not allowed to reoccupy any lattice point in four steps, (c) has a two-step memory such that his nth step is influenced by his $(n-2)$nd.

This model corresponds to the wanderings of an ill-mannered random walker who is not allowed to return to any lattice point he has passed until a time longer than that required for him to take 11 steps. After that time he is forgiven and is again allowed to revisit old points.

First we shall compare the number of possible paths under these limitations with the number of paths which are possible when (b) is relaxed. We can restrict our calculation to paths which start with a step in the positive x direction (or in polymer language with chains whose first bond lies in the x direction and whose second bond is connected to the right end of the first). By symmetry the ratio of the number of restricted paths to

[2] P. J. Flory, J. Chem. Phys. 17, 303 (1949).
[3] G. King, ONR progress reports.

that of the number of random paths in this case is exactly the same as it is when the first step is in the negative direction or in the positive or negative y directions.

Those paths which are consistent with (a) and (b) can be represented by a sequence of right (R) and left (L) turns such as LLRLRLLRLR (see a in Fig. 1) which do not contain three successive R's or L's (three successive turns in a given direction yield a first-order overlap). A polymer of degree of polymerization $(n+2)$ has $(n+1)$ bonds and can be represented by a sequence of n R's and L's. Below we enumerate the possible sequences for $n=1$, 2, and 3.

$n=1$			L		R	
$n=2$	LL		LR	RL		RR
$n=3$	LLR	LRL	LRR	RLL	RLR	RRL.

Every possible sequence ends in either class (i) LR or RL, or (ii) LRR or RLL. If $n=4$ all sequences of class (i) can be constructed by attaching an L(R) to those of $n=3$ which end in R(L). Those of class (ii) can be formed by adding RR (LL) to those sequences of $n=2$ which end in L (R). Hence if y_n is the number of possible $(n+2)$-mers, we have $y_4=y_3+y_2$. In general it is clear that similar reasoning leads to the difference equation $y_n=y_{n-1}+y_{n-2}$ subject to $y_1=2$ and $y_2=4$.

The solution of this equation is

$$y_n=[1+3\cdot 5^{-\frac{1}{2}}]x_1^{n-1}+[1-3\cdot 5^{-\frac{1}{2}}]x_2^{n-1};$$
$$x_j=\tfrac{1}{2}[1-(-1)^j 5^{\frac{1}{2}}].$$

Since the number of unrestricted $(n+2)$-mers is 2^n, the fraction of these without first-order overlap is (as $n\to\infty$) $f_n\sim 1.171(0.809)^{n-1}$.

Even when n is as small as 10, $f_n\sim 178/1024=0.18$. Hence we see that *most* of the configurations counted in a random model are forbidden when only first-order overlaps are taken into account.

II. THEORY OF MARKOFF CHAINS

1. Characterization of a Simple Markoff Chain

Let the infinite set of dependent variables z_0, z_1, z_2, $\cdots$ be related so that the probability distribution of z_j is uniquely defined by that of z_{j-1} and the law of dependence is independent of j. Chains of variables with these properties are called simple Markoff chains after the Russian mathematician who first studied them systematically.

Let the possible values of z_j $(j=0, 1, 2, \cdots)$ be a_1, a_2, $\cdots a_n$. Then the probability distribution of z_j is defined by

$$p_m(j)=pr(z_j=a_m) \quad m=1, 2, \cdots N \text{ and } j=0, 1, 2, \cdots. \quad (1)$$

(We follow the common notation of the theory of probability and read the symbol $pr(z_j=a_m)$ as the probability that z_j equals a_m.)

These numbers can be represented as components of an N-vector

$$\mathbf{P}(j)=\{p_1(j), p_2(j), \cdots, p_N(j)\}. \quad (2)$$

Inasmuch as z_j is postulated certainly to have one of the values of the set a_1, a_2, $\cdots$, a_N we have

$$\sum_{m=1}^{N} p_m(j)=1 \text{ for all } j. \quad (3)$$

A simple Markoff chain is completely characterized by $P(0)$, the probability distribution of z_0, and the N^2 *transition probabilities*

$$p(n\to m)=p_{mn}=pr(z_{j+1}=a_m \text{ if } z_j=a_n) \quad (4)$$
$$p_{mn}\geq 0 \text{ if } 1\leq n, m\leq N.$$

Since $z_j=a_n$ implies with certainty that z_{j+1} has one of the values a_1, a_2, $\cdots$, a_N, we have

$$\sum_{m=1}^{N} p_{mn}=1 \text{ for } n=1, 2, \cdots, N. \quad (4a)$$

The probability of the simultaneous occurrence of two compatible events is the product of the unconditional probability of the occurrence of one of the events by the conditional probability of the other assuming that the first has occurred. Hence

$$pr(z_{j+1}=a_m \text{ and } z_j=a_n)=p_{mn}p_n(j). \quad (5)$$

Inasmuch as the probability of the occurrence of a given event is the sum of the probabilities of the mutually exclusive ways in which the event can happen, we have

$$p_m(j+1)=\sum_{n=1}^{N} p_{mn}p_n(j) \text{ for } m=1,\cdots, N \text{ and } j=0, 1, \cdots. \quad (6)$$

The distribution of z_{j+2} follows immediately from that of z_j by iteration of (6). Then

$$p_m(j+2)=\sum_{n=1}^{N} p_{mn}p_n(j+1)$$
$$=\sum_{n_2=1}^{N}\left(\sum_{n_1=1}^{N} p_{mn_1}p_{n_1n_2}\right)p_{n_2}(j). \quad (7a)$$

In general,

$$p_m(j+k)=\sum_{n_1=1}^{N}\sum_{n_2=2}^{N}\cdots\sum_{n_k=1}^{N} p_{mn_1}p_{n_1n_2}\cdots p_{n_{k-1}n_k}p_{n_k}(j). \quad (7b)$$

Hence $p_m(k)$ can be obtained from the initial distribution $p_m(0)$ by application of (7) when $j=0$. The multiple summation process is unwieldy for direct computation. To avoid it we express these relations in matrix form.

The transition probabilities p_{mn} which characterize a simple chain are completely exhibited in the Markoff

or stochastic matrix

$$\mathbf{P}=(p_{mn}). \tag{8}$$

By a direct computation it is clear that the components of $\mathbf{P}\cdot\mathbf{P(j)}$ are $p_m(j+1)$ $(m=1, 2, \cdots, N)$. Hence $\mathbf{P}\cdot\mathbf{P(j)}=\mathbf{P(j+1)}$ and

$$\mathbf{P(j+k)}=\mathbf{P}\cdot\mathbf{P(j+k-1)}=\mathbf{P}^2\cdot\mathbf{P(j+k-2)}=\cdots=\mathbf{P}^k\cdot\mathbf{P(j)}. \tag{9}$$

Now let $\mathbf{r}_1, \cdots, \mathbf{r}_N$ be the set of right-hand characteristic vectors (r.c.v.) of $\mathbf{P}$; $\mathbf{s}_1, \cdots, \mathbf{s}_N$ the set of left characteristic vectors (l.c.v.); and $\lambda_1, \cdots, \lambda_N$ the corresponding characteristic values (c.n.). These quantities satisfy the equations

$$\mathbf{P}\mathbf{r}_k=\lambda_k\mathbf{r}_k \quad \text{and} \quad \mathbf{s}_k\mathbf{P}=\lambda_k\mathbf{s}_k. \tag{10}$$

It is well known that $\mathbf{s}_j\cdot\mathbf{r}_k=0$ if $\lambda_j\neq\lambda_k$ and that the sets $\{\mathbf{s}_j\}$ and $\{\mathbf{r}_j\}$ can be normalized so that $\mathbf{s}_j\cdot\mathbf{r}_j=1$.

The characteristic vector $\mathbf{s}_1=(1, 1, \cdots, 1)$ is a l.c.v. of every Markoff matrix, for by (8) and (4a) we have

$$\mathbf{s}_1\cdot\mathbf{P}=\left(\sum_m p_{m1}, \sum_m p_{m2}, \cdots, \sum_m p_{mN}\right)=(1, 1, \cdots, 1)=\mathbf{s}_1.$$

The c.n. of $\mathbf{s}_1=\mathbf{1}$ is $\lambda_1=1$. The modulus of every c.n. of a Markoff matrix is ≤ 1. Let the components of a r.c.v., $\mathbf{r}$, be $x_1, x_2, \cdots, x_N$. Then $\sum_n p_{mn}x_n=\lambda x_m$, and $|\lambda||x_m|=|\sum_n p_{mn}x_n|\leq\sum_n|p_{mn}||x_n|$ for every m. Hence

$$|\lambda|\sum_m|x_m|=\sum_{m,n}p_{mn}|x_n|\leq\sum_n|x_n|\sum_m p_{mn}=\sum_n|x_n|$$

so that $|\lambda|\leq 1$. It is convenient to order the c.n.'s of $\mathbf{P}$ so that $1=\lambda_1\geq|\lambda_2|\geq|\lambda_3|\geq\cdots\geq|\lambda_N|$.

The probability distribution vector $\mathbf{P(0)}=\{p_1(0), \cdots, p_N(0)\}$ can be expanded in a Fourier series in the r.c.v. $\{\mathbf{r}_j\}$:

$$\mathbf{P(0)}=\sum_{j=1}^{N}c_j\mathbf{r}_j, \quad \text{where} \quad c_j=\mathbf{s}_j\cdot\mathbf{P(0)}. \tag{11a}$$

Clearly the normalization condition (3) implies that

$$c_1=\mathbf{s}_1\cdot\mathbf{P(0)}=(1, 1, \cdots, 1)\cdot\{p_1(0), \cdots, p_N(0)\}=1. \tag{11b}$$

Hence $\mathbf{P(0)}=\mathbf{r}_1+\sum_2^N c_j\mathbf{r}_j$. Since $\mathbf{P}^k\mathbf{r}_j=\lambda_j\mathbf{r}_j$, the probability distribution vector $\mathbf{P(k)}$ has a simple Fourier series:

$$\mathbf{P(k)}=\mathbf{P}^k\mathbf{P(0)}=\mathbf{P}^k\mathbf{r}_1+\sum_2^N c_j\mathbf{P}^k\mathbf{r}_j=\mathbf{r}_1+\sum_{j=2}^{N}\mathbf{c}_j\lambda_j{}^k\mathbf{r}_j. \tag{12a}$$

If the components of $\mathbf{r}_j$ are $\{r_{j1}, r_{j2}, \cdots, r_{jN}\}$, then

$$pr(z_k=a_m)=r_{1m}+\sum_{j=2}^{N}c_j\lambda_j{}^k r_{jm}. \tag{12b}$$

When several c.n. of a Markoff matrix are equal, the matrix has the same number of linearly independent c.v. corresponding to c.n. as the degree of its degeneracy. By taking the appropriate linear combinations of these c.v.'s the validity of (12) is preserved.

2. Averages over Markoff Chains

The average value of a function $f_k=f_k(z_k)$ is given by

$$E(f_k)=\sum_{m=1}^{N}f_k(a_m)pr(z_k=a_m)=\mathbf{f}_k\cdot\mathbf{r}_1+\sum_{j=2}^{N}c_j\lambda_j{}^k(\mathbf{f}_k\cdot\mathbf{r}_j), \tag{13}$$

where $\mathbf{f}_k$ is the vector whose components are $f_k(a_m)$. The average value of a function $f_{ks}(z_k, z_s)$ where $s>k$ is given by

$$E(f_{ks})=\sum_{m,t=1}^{N}f_{ks}(a_m, a_t)pr(z_k=a_m)pr(z_s=a_t \text{ if } z_k=a_m)=\sum_{m,t=1}^{N}\left[r_{1m}+\sum_{u=2}^{N}c_u r_{um}\lambda_u{}^k\right]f_{ks}(a_m, a_s)\times\left[r_{1t}+\sum_{j=2}^{N}s_{jm}r_{jt}\lambda_j{}^{s-k}\right]. \tag{14}$$

Similar expressions exist for averages of functions of more than two variables.

A special case of (14) that will be needed later is obtained by letting (a) $f_{ks}(z_k, z_s)=x(z_k)x(z_s)$, (b) $E(x(z_k))=0$ for every k, and (c) $|\lambda_j|<1$ if $j>1$. Under these conditions (13) implies that

$$-\mathbf{x}\cdot\mathbf{r}_1=\sum_2^N c_j\lambda_j{}^k(\mathbf{x}\cdot\mathbf{r}_j).$$

Since this is true for every k, $\mathbf{x}\cdot\mathbf{r}_1=0$. Therefore (14) reduces to

$$E(x_kx_s)=\sum_{m=1}^{N}\left(r_{1m}+\sum_{u=2}^{N}c_u r_{um}\lambda_u{}^k\right)x(a_m)\sum_{j=2}^{N}s_{jm}(\mathbf{x}\cdot\mathbf{r}_j)\lambda_j{}^{s-k}=O[\exp-a(s-k)]; a>0. \tag{14a}$$

The distribution function of the sum

$$\sum_n=U(z_0, z_1)+U(z_1, z_2)+---+U(z_{n-1}, z_n) \tag{15}$$

can be expressed in terms of

$$f_n(w)=\sum_{a_0=1}^{N}\cdots\sum_{a_n=1}^{N}pr(x_j=a_0)\prod_{j=0}^{n-1}\{pr(z_j=a_j \text{ if } z_{j-1}=a_{j-1})\exp[iwU(a_j, a_{j+1})]\}. \tag{16a}$$

By repeating the type of analysis used at the beginning of this section one has:

$$f_n(w)=\sum_{k=1}^{N}\{\mathbf{s}_k(w)\cdot\mathbf{P(0)}\}\{\mathbf{1}\cdot\mathbf{r}_k(w)\}\Lambda_k{}^n(w), \tag{16b}$$

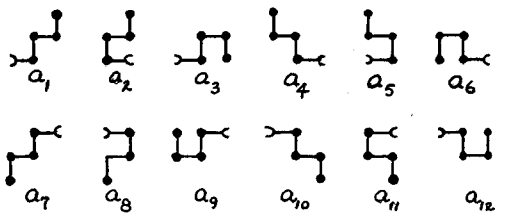


FIG. 2. The possible configurations of four successive bonds (with the first bond horizontal). The bond that is to be attached to the preceding part of the chain is the one connected to the open semicircle.

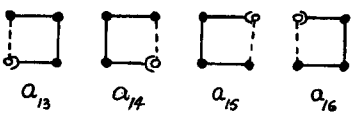


FIG. 3. The impossible configurations of four successive bonds.

where $\mathbf{s}_k(w)$ and $\mathbf{r}_k(w)$ are respectively the l.c.v. and r.c.v. of the matrix whose elements are $[pr(z_j=a \text{ if } z_{j-1}=b)]\exp[iwU(a,b)]$ and $\Lambda_k(w)$ is the corresponding characteristic value. Indeed, when s and t are points of continuity of the distribution function of $\sum_n$

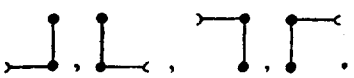
$$pr(s<\sum_n \leqslant t)=\lim_{T\to\infty}\frac{1}{2\pi i}\int_{-T}^{T}(e^{-iws}-e^{-iwt})f(w)dw/w. \quad (17)$$

It can be shown that in the limit as $n\to\infty$, $pr(\sum_n \leq t)$ becomes Gaussian provided that the transition probability matrix $\mathbf{P}$ has a single c.n. of modulus unity.

This summary of the properties of Markoff chains is based on the three papers of reference 1. Hostinsky's little monograph was the first to give a detailed analysis of the characteristic value theory of Markoff chains.

III. STATISTICAL PROPERTIES OF POLYMER CHAINS ON SQUARE LATTICES

Now let us find the root-mean-square distance between ends of chains which do not contain first-order overlaps. All those chains whose first bond lies in the x direction can be constructed by the successive addition of the following links



Of the 16 possible four-bond chains that can be formed from pairs of these only the 12 in Fig. 2 do not contain first-order overlaps. The four in Fig. 3 are forbidden. If the construction of these forbidden configurations is started the fourth bond in a_{13} must be placed so that a_5 results; a_{14} becomes a_2, a_{15} becomes a_{11}, and a_{16} becomes a_8.

For the purpose of describing a polymer chain as a Markoff chain, it is convenient to imagine long chains as a sequence of 4-mers. Indeed they can be represented by the sequence $z_0z_1z_2\cdots z_n$ where each z_j is a 4-mer of the set $a_1, a_2, \cdots, a_{12}$.

To find the $pr(z_0=a_k)$ let us construct 4-mers in such a manner that the probability of the sth particle being as far away from the $(s-3)$rd as possible is β while that of it being as near as possible (without overlap) is $\alpha=1-\beta$. The configuration a_1 can be constructed by first placing a bond to the right of the starting point. The probability of this placement is one-half. The probability of the second bond going to the left of the direction of the first is also one-half. The probability of the third going to the right is β, as is also that of the fourth going to the left. Hence $pr(z_0=a_1)=(\frac{1}{4})\beta^2$. In a similar manner we obtain

$$p_k(0)=pr(z_0=a_k)=\begin{cases}(\frac{1}{4})\beta^2 & \text{if } k=1,4,7,10\\ (\frac{1}{4})\alpha & \text{if } k=2,5,8,11\\ (\frac{1}{4})\alpha\beta & \text{if } k=3,6,9,12.\end{cases}$$

$$\mathbf{P}(0)=(\tfrac{1}{4})\{\beta^2,\alpha,\alpha\beta,\beta^2,\alpha,\alpha\beta,\beta^2,\alpha,\alpha\beta,\beta^2,\alpha,\alpha\beta\}. \quad (18)$$

The transition probabilities (p_{jk}) can be computed in a straightforward manner. Let us find $p_{13}=pr(z_{j+1}=a_1 \text{ if } z_j=a_3)$. The first new bond added to a_3 is forced to the left of path direction to prevent overlap (see b in Fig. 4). The probability of the second new bond going to the left is α. The third is forced to the left and the fourth goes to the left with a probability β. Hence $p_{13}=\alpha\beta$. Some transition probabilities are zero; for example, an a_1 followed by an a_6 yields a first-order overlap. The complete transition probability matrix is

$$\mathbf{P}=\begin{bmatrix}A_1 & A_2 & A_3 & A_4\\ A_2 & A_1 & A_4 & A_3\\ A_3 & A_4 & A_1 & A_2\\ A_4 & A_3 & A_2 & A_1\end{bmatrix}, \quad (19a)$$

where

$$\mathbf{A}_1=\begin{bmatrix}\beta^4 & \beta^4 & \alpha\beta\\ \alpha^2 & \alpha^2 & 0\\ \alpha\beta^3 & \alpha\beta^3 & \alpha^2\end{bmatrix} \quad \mathbf{A}_2=\begin{bmatrix}\alpha\beta^2 & \alpha\beta^2 & 0\\ \alpha\beta^2 & \alpha\beta^2 & 0\\ \alpha^2\beta & \alpha^2\beta & 0\end{bmatrix}$$

$$\mathbf{A}_3=\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & \alpha\beta\\ 0 & 0 & 0\end{bmatrix} \quad \mathbf{A}_4=\begin{bmatrix}\alpha\beta^2 & \alpha\beta^2 & \beta^3\\ 0 & 0 & 0\\ \alpha^2\beta & \alpha^2\beta & \alpha\beta^2\end{bmatrix}. \quad (19b)$$

It is easy to verify that the sum of the elements of each column is equal to unity. Of course the fact that $\alpha+\beta=1$ must be used.

The characteristic values of $\mathbf{P}$ are the same as those of $\mathbf{Q}=\mathbf{R}^{-1}\mathbf{P}\mathbf{R}$ where

$$\mathbf{R}=\frac{1}{2}\begin{bmatrix}(1) & (1) & (1) & (1)\\ (1) & (-1) & (1) & (-1)\\ (1) & (1) & (-1) & (-1)\\ (1) & (-1) & (-1) & (1)\end{bmatrix}=\mathbf{R}^{-1}; \quad (1)=\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}. \quad (20)$$

If $\mathbf{r}$ and $\mathbf{s}$ are the r.c.v. and l.c.v. of $\mathbf{P}$, then those of $\mathbf{Q}$ are $\mathbf{R}^{-1}\mathbf{r}$ and $\mathbf{sR}$. The matrix $\mathbf{Q}$ is of the form

$$\mathbf{Q}=\begin{pmatrix}\mathbf{Q}_1 & 0 & 0 & 0\\ 0 & \mathbf{Q}_2 & 0 & 0\\ 0 & 0 & \mathbf{Q}_3 & 0\\ 0 & 0 & 0 & \mathbf{Q}_4\end{pmatrix} \tag{21}$$

where

$$\left.\begin{aligned}\mathbf{Q}_1&=\begin{pmatrix}\beta^4+2\alpha\beta^2 & \beta^4+2\alpha\beta^2 & \alpha\beta+\beta^3\\ \alpha^2+\alpha\beta^2 & \alpha^2+\alpha\beta^2 & \alpha\beta\\ \alpha\beta^3+2\beta\alpha^2 & \alpha\beta^3+2\beta\alpha^2 & \alpha^2+\alpha\beta^2\end{pmatrix}\\ \mathbf{Q}_2&=\begin{pmatrix}\beta^4-2\alpha\beta^2 & \beta^4-2\alpha\beta^2 & \alpha\beta-\beta^3\\ \alpha^2-\alpha\beta^2 & \alpha^2-\alpha\beta^2 & \alpha\beta\\ \alpha\beta^3-2\beta\alpha^2 & \alpha\beta^3-2\beta\alpha^2 & \alpha^2-\alpha\beta^2\end{pmatrix}\end{aligned}\right\} \tag{21a}$$

$$\left.\begin{aligned}\mathbf{Q}_3&=\begin{pmatrix}\beta^4 & \beta^4 & \alpha\beta-\beta^3\\ \alpha^2+\alpha\beta^2 & \alpha^2+\alpha\beta^2 & -\alpha\beta\\ \alpha\beta^3 & \alpha\beta^3 & \alpha^2-\alpha\beta^2\end{pmatrix}\\ \mathbf{Q}_4&=\begin{pmatrix}\beta^4 & \beta^4 & \alpha\beta+\beta^3\\ \alpha^2-\alpha\beta^2 & \alpha^2-\alpha\beta^2 & -\alpha\beta\\ \alpha\beta^3 & \alpha\beta^3 & \alpha^2+\alpha\beta^2\end{pmatrix}.\end{aligned}\right\} \tag{21b}$$

Now the characteristic vectors of $\mathbf{Q}$ can be divided into four classes such that those in a given class correspond to the c.n. of a single $\mathbf{Q}_j$. Then

$$\mathbf{r}_j=\mathbf{R}\cdot\{\xi_j^{(1)},\xi_j^{(2)},\xi_j^{(3)},0,0,0,\cdots,0\}\quad j=1,2,3 \tag{22a}$$

$$\mathbf{r}_j=\mathbf{R}\cdot\{0,0,0,\xi_j^{(1)},\xi_j^{(2)},\xi_j^{(3)},0,0,\cdots,0\}\quad j=4,5,6 \tag{22b}$$

$$\mathbf{r}_j=\mathbf{R}\cdot\{0,0,0,0,0,0,\xi_j^{(1)},\xi_j^{(2)},\xi_j^{(3)},0,0,0\}\quad j=7,8,9 \tag{22c}$$

$$\mathbf{r}_j=\mathbf{R}\cdot\{0,0,\cdots,0,\xi_j^{(1)},\xi_j^{(2)},\xi_j^{(3)}\}\quad j=10,11,12, \tag{22d}$$

where the ξ_j's are the r.c.v. of the $\mathbf{Q}_k$'s. The same distribution of zeroes exists in the corresponding s_j's.

In order to find the root-mean-square distance between pairs of monomer elements in our chains we need the Fourier coefficients $\{c_j\}$ of the expansion

$$\text{prob}(z_0=a_m)=\sum_{j=1}^{N} c_j r_{jm}\quad\text{where}\quad c_j=\mathbf{s}_j\cdot\mathbf{P}(\mathbf{0}), \tag{22a}$$

and $\mathbf{P}(\mathbf{0})$ is given by (18). Since $c_j=(\mathbf{s}_j\cdot\mathbf{R})\mathbf{R}^{-1}\mathbf{P}(\mathbf{0})$, and $\mathbf{R}^{-1}\cdot\mathbf{P}(\mathbf{0})=\frac{1}{2}\{\beta^2,\alpha,\alpha\beta,0,0,\cdots,0\}$ we see that $(\mathbf{s}_j\cdot\mathbf{R})$ is orthogonal to $\mathbf{R}^{-1}\cdot\mathbf{P}(\mathbf{0})$ when $j>3$. Hence $c_4=c_5=\cdots=c_{12}=0$. From the expressions for $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ that we shall obtain later it follows that $c_1=1$, $c_2=\alpha^3$, and $c_3=0$; therefore

$$\mathbf{P}(\mathbf{k})=\mathbf{r}_1+\alpha^{4k+3}\mathbf{r}_2. \tag{23b}$$

The x component, $x(a_1)$, of the distance between the two ends of a 4-mer in configuration a_1 is $2a$; and that of the y component is also $2a$. The corresponding components for all configurations are given by the vectors $\mathbf{x}$ and $\mathbf{y}$ whose elements are $x(a_k)$ and $y(a_k)$

$$\mathbf{x}=2a(1,0,1,-1,0,-1,-1,0,-1,1,0,1) \tag{24a}$$

$$\mathbf{y}=2a(1,1,0,1,1,0,-1,-1,0,-1,-1,0). \tag{24b}$$

On some occasions $\mathbf{x}$ and $\mathbf{y}$ will be represented by column vectors with the same elements as (24). Equation (22) implies that

$$\mathbf{x}\cdot\mathbf{r}_j=\mathbf{s}_j\cdot\mathbf{x}=0\quad\text{unless}\quad j=10,11,12 \tag{25a}$$

$$\mathbf{y}\cdot\mathbf{r}_j=\mathbf{s}_j\cdot\mathbf{y}=0\quad\text{unless}\quad j=7,8,9. \tag{25b}$$

If we let $\mathbf{R}_n$ be the vector which connects the two ends of a chain of n 4-mers, we have $\mathbf{R}_n=\mathbf{i}X_n+\mathbf{j}Y_n$ where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors in the x and y direction and

$$X_n=\sum_{k=0}^{n-1}x(z_k)\quad\text{and}\quad Y_n=\sum_{k=0}^{n-1}y(z_k). \tag{26}$$

The average value of the vector $\mathbf{R}_n$, $E\{\mathbf{R}_n\}=\mathbf{i}\sum_k E\{x(z_k)\}+\mathbf{j}\sum_k E\{y(z_k)\}$ vanishes from symmetry considerations. This result can easily be verified by combining (13), (23), and (25).

The mean square distance between ends of our polymer chain is given by

$$E\{R_n^2\}=E\{X_n^2+Y_n^2\}=\sum_{j=0}^{n-1}E\{x^2(z_j)+y^2(z_j)\}$$
$$+2\sum_{k=0}^{n-2}\sum_{j=k+1}^{n-1}E\{x(z_j)x(z_k)+y(z_j)y(z_k)\}. \tag{27}$$

The $x^2(z)+y^2(z)$ vector is $\mathbf{U}=4a^2(2,1,1,2,1,1,2,1,1,2,1,1)$. Hence (13) and (23) imply

$$E\{x^2(z_j)+y^2(z_j)\}=\mathbf{U}\cdot\mathbf{r}_1+\alpha^{4j+3}\mathbf{U}\cdot\mathbf{r}_2 \tag{28}$$

when $j>k$, we find by application of (13), (23), and (25) that

$$E\{x(z_j)x(z_k)+y(z_j)y(z_k)\}$$
$$=\sum_{t,m=1}^{12}[r_{1m}+\alpha^{4k+3}r_{2m}][x(a_m)x(a_t)$$
$$+y(a_m)y(a_t)]\left[r_{1t}+\sum_{u=2}^{12}s_{um}r_{ut}\lambda_u{}^{j-k}\right]$$
$$=\sum_{m=1}^{12}[r_{1m}+\alpha^{4k+3}r_{2m}]$$
$$\times\left\{\sum_{u=2}^{12}s_{um}\lambda_u{}^{j-k}[x(a_m)\mathbf{x}\cdot\mathbf{r}_u+y(a_m)\mathbf{y}\cdot\mathbf{r}_u]\right\}. \tag{29}$$

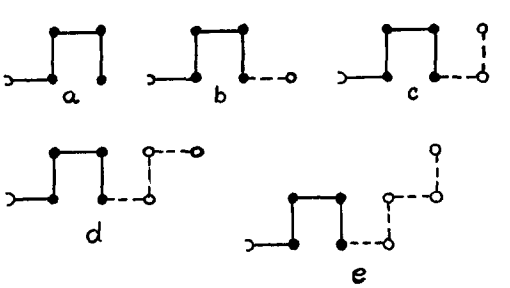


FIG. 4. Steps in the construction of an a_1 which follows an a_3.

In order to complete our calculation, we must find the c.v. and c.n. of $\mathbf{Q}$. Since $\mathbf{x}\cdot\mathbf{r}_j=\mathbf{y}\cdot\mathbf{r}_j=0$ if $j=4, 5, 6$, we do not need the c.v. which correspond to the c.n. of $\mathbf{Q}_2$. Furthermore each of the matrices $\mathbf{Q}_j$ have a c.n. $\lambda=0$. We shall represent these by $\lambda_3=\lambda_6=\lambda_9=\lambda_{12}=0$. Equations (28) and (29) indicate that the corresponding c.v. do not enter into our problem.

We can determine the c.n. and c.v. of $\mathbf{P}$ in the usual manner. Those which correspond to the c.n. of $\mathbf{Q}_1$ are

$$\lambda_1=1, \quad \mathbf{r}_1=[1/4(1+\alpha)]\{\beta,\alpha,\alpha,\beta,\alpha,\alpha,\beta,\alpha,\alpha,\beta,\alpha,\alpha\} \tag{30a}$$

$$\mathbf{s}=(1,1,1,1,1,1,1,1,1,1,1,1) \tag{30b}$$

$$\lambda_2=\alpha^4, \quad \mathbf{r}_2=-[1/4\alpha(1+\alpha)] \times\{\beta,-1,\alpha,\beta,-1,\alpha,\beta,-1,\alpha,\beta,-1,\alpha\} \tag{31a}$$

$$\mathbf{s}_2=(\alpha,\alpha,-1,\alpha,\alpha,-1,\alpha,\alpha,-1,\alpha,\alpha,-1) \tag{31b}$$

$$\lambda_3=0, \quad \mathbf{s}_3=(\alpha,0,-\beta,\alpha,0,-\beta,\alpha,0,-\beta,\alpha,0,-\beta). \tag{32}$$

The c.n. of $\mathbf{P}$ which are c.n. of $\mathbf{Q}$ are $\lambda_7=\alpha^2\exp-\varphi$ and $\lambda_8=\alpha^2\exp\varphi$ and $\lambda_9=0$, where $\varphi=\cosh^{-1}\{1+\frac{1}{2}\beta^4\alpha^{-2}\}$ and λ_7 and λ_8 satisfy

$$\lambda^2-\lambda(\beta^4+2\alpha^2)+\alpha^4=0, \quad \lambda_9=0. \tag{33}$$

These characteristic values are plotted in Fig. 5 as a function of α. The corresponding c.v. of $\mathbf{P}$ are ($k=7, 8$)

$$\mathbf{r}_k=\frac{1}{4(\alpha\beta^6-q_k^2)}\{\beta^4, w_k, \alpha\beta^3, \beta^4, w_k, \alpha\beta^3, -\beta^4, -w_k, -\alpha\beta^3, -\beta^4, -w_k, -\alpha\beta^3\} \tag{34a}$$

$$\mathbf{s}_k=(q_k, q_k, \beta^3, q_k, q_k, \beta^3, -q_k, -q_k, -\beta^3, -q_k, -q_k, -\beta^3), \tag{34b}$$

where $q_k=\alpha^2-\alpha\beta^2-\lambda_k$ and $w_k=-(q_k+\beta^4)$. The c.n. of $\mathbf{Q}$ also satisfy (33). We choose $\lambda_{10}=\lambda_7$ and $\lambda_{11}=\lambda_8$.

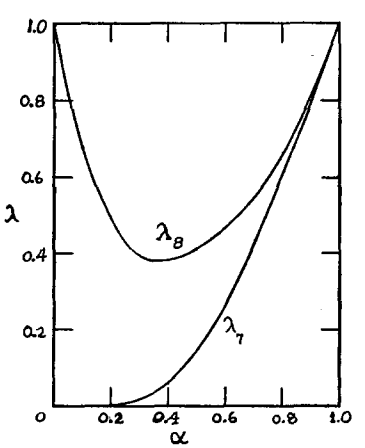


FIG. 5. The variation of the characteristic values λ_7 and λ_8 as a function of the interaction constant α. As $\alpha\to 0$ monomers show increasingly strong attraction, as $\alpha\to 1$ strong repulsion. The random case corresponds to $\alpha=\frac{1}{4}$.

Then, for $k=10, 11$, we have

$$\mathbf{r}_k=-\frac{1}{4(n_k^2+\alpha\beta^6)}\{\beta^4, m_k, \alpha\beta^3, -\beta^4, -m_k, -\alpha\beta^3, -\beta^4, -m_k, -\alpha\beta^3, \beta^4, m_k, \alpha\beta^3\} \tag{35a}$$

$$\mathbf{s}_k=(n_k, n_k, -\beta^3, -n_k, -n_k, \beta^3, -n_k, -n_k, \beta^3, n_k, n_k, -\beta^3) \tag{35b}$$

where $n_k=\alpha^2+\alpha\beta^2-\lambda_k$ and $m_k=-(\beta^4+n_k)$.

Equation (23b) can now be verified by application of Eqs. (30–32) to (23a). We also find that

$$\mathbf{x}\cdot\mathbf{r}_u=-2a\beta^3/(n_u^2+\alpha\beta^6) \quad \text{if} \quad u=10, 11$$

$$\mathbf{y}\cdot\mathbf{r}_u=2aq_u/(q_u^2-\alpha\beta^6) \quad \text{if} \quad u=7, 8.$$

$$\sum_{m=1}^{12} r_{jm}x(a_m)s_{um}=\frac{2a\beta(-\alpha)^{1-j}}{(1+\alpha)}(n_u-\alpha\beta^2) \quad \text{if } u=10, 11; j=1, 2.$$

$$\sum_{m=1}^{12} r_{jm}y(a_m)s_{um}=\frac{2aq_u}{1+\alpha} \text{ if } u=7, 8 \text{ and } j=1, 2.$$

Since $\lambda_7=\lambda_{10}$, $\lambda_8=\lambda_{11}$, $n_{10}=q_7+2\alpha\beta^2$ and $n_{11}=q_8+2\alpha\beta^2$.

The definition of q_u and the characteristic equation (33) imply that

$$2E\{x(z_j)x(z_k)+y(z_j)y(z_k)\}=\frac{8a^2}{(1+\alpha)(\beta^4+4\alpha^2)}\cdot\sum_{u=7}^{8}\lambda_u^{j-k}[2-\beta\alpha^{2+4k}]W_u \tag{36a}$$

where

$$W_u=[\alpha^3(\beta^2-2\alpha)+\lambda_u(2\alpha^2+\beta^4+\alpha\beta^2)]/(\lambda_u-\alpha^2). \tag{36b}$$

Hence Eqs. (27), (28), (30), (31), and (36) imply that

$$E\{R_n^2\}=\frac{8a^2}{(1+\alpha)}\left\{n-\frac{\beta\alpha^2}{2(1-\alpha^4)}(1-\alpha^{4n}) +\frac{1}{\beta^4+4\alpha^2}\sum_{u=7}^{8}\sum_{k=0}^{n-2}\sum_{j=k+1}^{n-1}\lambda_u^{j-k}[2-\beta\alpha^{4k+2}]W_u\right\}. \tag{37}$$

We need the sums

$$\sum_{k=0}^{n-2}\sum_{j=k+1}^{n-1}\lambda^{j-k}=\frac{n\lambda}{1-\lambda}-\frac{\lambda}{1-\lambda^2}+\frac{\lambda^{n+1}}{(1-\lambda)^2} \tag{38}$$

$$\sum_{k=0}^{n-2}\sum_{j=k+1}^{n-1}\alpha^{4k}\lambda^{j-k}=\frac{\lambda}{(1-\alpha^4)(1-\lambda)}-\frac{\lambda^{n+1}}{(1-\lambda)(\lambda-\alpha^4)} +\frac{\lambda\alpha^{4n}}{(1-\alpha^4)(\lambda-\alpha^4)}. \tag{38a}$$

When these expressions are substituted into (37) and the relations $\lambda_7\lambda_8=\alpha^4$ and $\lambda_7+\lambda_8=\beta^4+2\alpha^2$ are employed

one obtains (see Appendix II)

$$E\{R_n^2\}=\frac{8a^2}{(1+\alpha)}\left\{\frac{n(1+\alpha^2)}{2\alpha\beta}+\frac{\alpha^6-\alpha^4-6\alpha^3-\alpha^2-1}{8\beta^2\alpha^2(1+\alpha)}\right.$$
$$-\frac{\alpha^{4n+2}}{4\beta(1+\alpha)}+\frac{a_{n+1}}{8\alpha^2\beta^2}(1-\alpha+2\alpha^2+4\alpha^3-\alpha^4-\alpha^5)$$
$$\left.-\frac{b_{n+1}}{8\alpha^2\beta^2}(1-11\alpha+2\alpha^2+8\alpha^3-5\alpha^4+\alpha^5)\right\}, \quad (39)$$

where $a_n=(\lambda_7{}^n-\lambda_8{}^n)/(\lambda_7-\lambda_8)$ and $b_n=-\alpha^4(\lambda_7{}^{n-1}-\lambda_8{}^{n-1})/(\lambda_7-\lambda_8)$. If N is the degree of polymerization of our polymer, then $N=4n$. Since $\lambda_7=\alpha^2\exp-\varphi$ and $\lambda_8=\alpha^2\exp\varphi$ where $\varphi=\cosh^{-1}(1+\frac{1}{2}\beta^4\alpha^{-2})$, we can also write a_n and b_n as $a_n=\alpha^{2(n-1)}(\sinh n\varphi)/\sinh\varphi$ and $b_n=\alpha^{2n}[\sinh(n-1)\varphi]/\sinh\varphi$.

In the limit as $n\to\infty$ (39) reduces to (provided that $\alpha\neq 0, 1$)

$$\frac{1}{N}E\{R_n^2\}\sim\frac{a^2(1+\alpha^2)}{\alpha(1-\alpha^2)}. \quad (39a)$$

In a chain in which first-order overlaps are allowed the corresponding result can easily be shown to be

$$(1/N)E\{R_n^2\}\sim a^2\beta/\alpha. \quad (40)$$

Qualitatively this equation has the correct form because (a) when $\alpha=\beta=\frac{1}{2}$ there is no correlation between successive bonds. Hence

$$E\{R_n^2\}=E\{x_0^2+\cdots+x^2{}_{n-1}+y_0^2+\cdots+y^2{}_{n-1}\}=Na^2$$

(here the x's and y's represent x and y components of bonds and not 4-mers); (b) as $\alpha\to 0$ the probability of a first-order overlap approaches zero. Hence (40) must approach (39a) in the limit; as it does; (c) as $\beta\to 0$ the chain becomes a square with sides of length a so that $N^{-1}E\{R_n^2\}\to 0$.

The root-mean-square distance between ends of very long chains with and without first-order overlaps on a square lattice are compared in Fig. 6. It is to be noted that even in the random case, $\alpha=\frac{1}{2}$, the average chain length is increased by a factor 1.8 by excluding first order overlaps. This type of result was first suggested by Kuhn.[4]

An important feature of (39) is that $E\{R_n^2\}$ is proportional to N for all $0<\alpha<1$. In the limit as $\alpha\to 0$ or 1 the asymptotic expression (39) is not correct, for other λ's beside λ_1 have the value unity. Indeed, when $\alpha=1$, $E\{R_n^2\}=\frac{1}{4}N^2a^2$ and when $\alpha=0$, $E\{R_n^2\}=\frac{1}{2}N^2a^2$.

Now it is interesting to determine how large the degree of polymerization, N, must be in order for the asymptotic Eq. (39a) to give a good estimate to $E\{R_n^2\}$. The smallest value of N that allows one to use (39a) to estimate (39) with a relative error of less than 10 percent has been obtained by comparing (39a) with (39). This value of N is plotted in Fig. 7 as a function of α. Even in the almost random range of $\alpha\simeq\frac{1}{2}$, N must be $\simeq 50$. This result is also valid for intermediate monomers in a long chain. Hence, on a square lattice the asymptotic formula (39a) cannot be applied to intermediate monomers unless they are separated by more than 50 bonds.

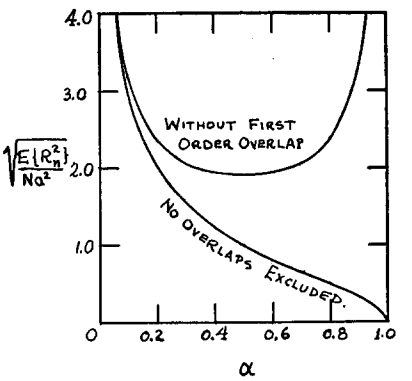


FIG. 6. Root-mean-square distance between ends of very long chains, $[E(R_n^2)]^{\frac{1}{2}}$, as a function of α. a=bond length and N =degree of polymerization.

It can be shown that the mean square distance between the ends of any chain formed on a space lattice with the restriction that overlaps up to some finite order are excluded has the form of (39):

$$E\{R_n^2\}=An+B+\sum c_j e^{-nd_j}$$

where the real part of d_j is positive. The considerations which lead to the An term are given below. Equation (39) is valid only for degrees of polymerization of the form $4n=N$; it can be generalized to all values of N by adding one, two, or three bonds to all possible configurations of a $4n$-mer and computing the proper averages. On this basis one actually obtains different values of B and c_j for each set of the form $N=4n+j$ $(j=1-3)$.

Let us consider a Markoff chain with a single characteristic value of modulus 1. This chain has the property (14a):

$$E(x_k x_s)=O[\exp-a(s-k)]. \quad a>0.$$

Now suppose one constructs a polymer chain on a space lattice by piecing together subchains of degree of polymerization n_0, where n_0 is as large as one desires. If (a) these individual subchains are restricted to have configurations with no overlap and (b) the transition probability of a given configuration of a subchain being followed by another configuration of a subchain is set equal to zero when these two configurations would lead to an overlap, then one would have a Markoff chain of the type considered in our earlier discussion. The case of interest has been $n_0=4$. The configurations of a subchain in the general case could be represented by $a_1, a_2, \cdots, a_m$ and the analysis of the problem would proceed in the manner outlined in Section II. The

[4] W. Kuhn, Kolloid Zeits. 87, 3 (1939).

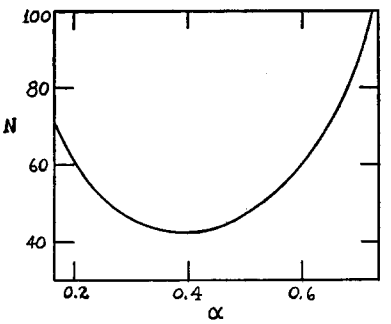


FIG. 7. Minimum degree of polymerization, N, necessary for asymptotic expression (39a), the mean square distance between chain ends, to have a relative error of less than 10 percent. This is plotted as a function of α.

matrices involved would be of considerably larger order than those obtained when $n_0=4$ and indeed when $n_0>10$ it might be hopelessly complicated to find the c.n. and c.v. of the (p_{ij}) matrix. However no matter how large n_0 might be, the correlation coefficient $E(x_k, x_s)$ decays exponentially with $(k-s)$ and the introductory discussion of this paper implies that as $n\to\infty$, $E(X_n^2)\to nA=N(A/n_0)=N\times$(constant) where $N=nn_0=$degree of polymerization of our model.

In the above model rather long-range effects can be taken into account. On the basis of the model the author doubts that one can change the relation $E(X_n^2)/N\to$ constant as $N\to\infty$. It would seem that by increasing the complication of the model one would merely increase the accuracy of the constant of interest.

We shall now describe a model experiment that could be set up to give a clearer indication of whether $E(X_n^2)/N\to$constant or, as is stated by Flory, $E(X_n^2)/N^c\to$constant where $c\neq 1$. Let strings of identical beads be constructed with the number of beads varying from about 100 to 1000. If a particular string of beads were placed in a viscous fluid and the fluid agitated, the string would go through a large number of configurations, but the individual monomers, the beads, could never penetrate one another. By painting the end beads with luminous paint, one could photograph the strings at regular intervals and observe projections of the distance between the ends. After a large number of photographs are taken, the mean square distance between a projection of the ends could be computed. This could be done for strings of various lengths and the variations of $E(X_n^2)$ with n could be determined. The experiment could also be performed with the luminescent beads at various points on the string.

In principle the exact distribution function of R_n^2 can be derived from a direct application of Eqs. (16) and (17). However, it has not yet been obtained by the author for chains on a square lattice because of the analytical complexity of the resulting expressions. However, the limiting distribution as $n\to\infty$ is Gaussian. This result follows from the central limit theorem for Markoff chains[1] or from the more general results of Bernstein[5] for the distribution of the x component of the distance X_n between ends of a chain of degree of polymerization $N=4n$, is given by

$$pr\left\{X_n<\left[\frac{N(1+\alpha^2)}{2\alpha(1-\alpha^2)}\right]^{\frac{1}{2}}ta\right\}\sim\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{t}\exp(-\tfrac{1}{2}t^2)dt.$$

By symmetry Y_n has the same distribution.

Since as will be discussed below, X_n and Y_n are independent variables, the distribution of $\mathbf{R}_n$ follows directly from that of X_n and Y_n. The correlation coefficient between X_n and Y_n is given by

$$E(X_nY_n)=\sum_{j=1}^{n-1}E(x_jy_j)+\sum_{i\neq j}E(x_jy_i).$$

By direct calculation one finds that

$$E(x_jy_j)=\sum_k x_j(a_k)y(x_k)pr(z_j=a_k)=0.$$

It can also be shown that $E(x_iy_j)=0$ when $i\neq j$. Qualitatively this is to be expected because the vector x has the same symmetry as the characteristic vectors of λ_{10}, λ_{11}, and λ_{12} while y has that of the vectors of $\lambda_1-\lambda_9$. Since the r.c.v. of $\lambda_{10}-\lambda_{12}$ are orthogonal to the l.c.v. of $\lambda_7-\lambda_9$, we have $E(x_jy_k)=0$.

One can obtain corrections to the Gaussian distribution by computing higher moments of the distribution by the methods used here for the calculation of $E\{R_n^2\}$ and substituting these moments into the Gram-Charlier series (the expansion of a distribution function as a linear combination of Hermite polynomials).

The application of the theory of Markoff chains to the excluded volume problem in polymers is being investigated independently by King[3] who is using punch card techniques. The author is grateful to Dr. Gilbert King for several interesting discussions of his work.

APPENDIX I. LONG-RANGE ORDER IN MARKOFF CHAINS

The distribution $\mathbf{P}(\mathbf{k})=\mathbf{r}_1$ is stationary; that is, if $\text{prob}(x_0=a_m)=r_{1m}$, then $\text{prob}(x_k=a_m)=r_{1m}$ for every integer k. This observation is a direct consequence of the fact that $\mathbf{r}_1=\mathbf{P}\mathbf{r}_1=\mathbf{P}^2\mathbf{r}_1=\cdots=\mathbf{P}^k\mathbf{r}_1$. A uniform distribution $p_m(j)=1/N$ is stationary when

$$\sum_{n=1}^{N}p_{mn}=1$$

for all m.

We shall now show how the distribution of x_k is related to that of x_0 for various classes of distributions of the c.n.'s of P of modulus 1.

(a) $\lambda_1=1$ *is the only c.n. of modulus 1.*—Since $|\lambda_j|<1$ for $j\neq 1$, we see that as $k\to\infty$ each term in the summand of (12b) tends exponentially to zero. Hence as $k\to\infty$

$$pr(x_k=a_m)\sim r_{1m}.$$

This result is independent of the initial distribution of x_0. $\mathbf{P}(\mathbf{k})=\mathbf{r}_1$

[5] S. Bernstein, Math. Ann. **97**, 1 (1926). See also P. A. P. Moran, Quart. J. Math. (Oxford) **19**, 140 (1948); Proc. Cam. Phil. Soc. **44**, 342 (1947).

is the only stationary distribution in this case. Every Markoff chain of this type approaches its stationary state as $k\to\infty$.

(b) $\lambda_1=\lambda_2=\cdots=\lambda_f=1 (f>1)$ *are the only c.n. of modulus 1.*—Since $|\lambda_j|<1$ for $j>f$, as $k\to\infty$ we have

$$pr(x_k=a_m)\sim r_{1m}+\sum_{j=2}^{f} c_j(0)r_{jm}.$$

The appearance of the $c_j(0)$'s, which depend on the distribution of x_0, implies that as $k\to\infty$ the distribution of x_k approaches a stationary value. However, this *stationary distribution depends on the distribution* of x_0 so that there is a correlation between the distributions of x_k and x_0 for all k no matter how large. In the phraseology of the theory of cooperative phenomenon *long-range order* exists in a Markoff chain which has several c.n. equal to unity. This class of chains also differs from those discussed in (a) in that several stationary distributions are possible. Indeed, every distribution of the form

$$p_m(k)=r_{1m}+\sum_{j=2}^{f} c_j r_{jm}$$

such that $\Sigma_m p_m(k)=1$ and $p_m(k)\geqslant 0$ is stationary.

(c) *The numbers* $\lambda_j=\exp(2\pi ij/q)$ *with* $q\leqslant N$, *and* $j=0, 1, \cdots, q-1$ *are the only c.n. of unit modulus.*—As $k\to\infty$, Eq. (12b) becomes

$$pr(x_k=a_m)\sim r_{1m}+\sum_{j=2}^{q-1} c_j(0)r_{jm}\exp(2\pi ij/q).$$

Hence the asymptotic distribution of x_k is periodic with period $q\leqslant N$. This periodic distribution depends on the distribution of x_0 so that long-range order exists in this case. The only stationary distribution is $p_m(k)=r_{1m}$.

It can be proven** that the only c.n. of modulus unity of a Markoff matrix of order n are roots of unity, $\exp 2\pi ij/q$, with $q\leqslant N$. Several cycles of c.n. can exist, but even in this general case the asymptotic distribution is either stationary or periodic depending on the initial distribution of x_0. For a detailed discussion of this case the reader is referred to Frechet.[1]

In general a dependence of the distribution of x_k on that of x_0 as $k\to\infty$ (that is, long-range order) exists if and only if more than one of the c.n. of the Markoff matrix are of modulus unity.

Several theorems on the roots of Markoff matrices are of interest for the discussion of long-range order. The first of these is a theorem of Frobenius: Let $p_{mn}>0$ for all m and n. Then the c.n. $\lambda_1=1$ is simple and is the only c.n. of modulus 1. Its r.c.v. is the only r.c.v. of (p_{mn}) whose components are all non-negative. A second is due to Frechet.[1] Let $p_{mn}>0$ for all m, and let λ be a c.n. of (p_{mn}). Then either $\lambda=1$ or $|\lambda|<1$.

Frobenious' theorem leads immediately to the result that long-range order cannot exist in a chain whose Markoff matrix has only positive elements.

** V. Romanovsky, Acta Math. **66**, 147 (1936) and N. Dmitriev and E. Dynkin, Comptes Rendus U.S.S.R. **49**, 159 (1945).

APPENDIX II. REMARKS ON DERIVATION OF EQ. (39)

Equation (39) was derived by combining (36)–(38). A number of symmetric functions of λ_7 and λ_8 had to be calculated. For example, the contribution of the term $n\lambda/(1-\lambda)$ of (38) to (37) required the evaluation of

$$A_1=\sum_{u=7}^{8}\frac{\lambda_u W_u}{1-\lambda_u}=\sum_u\left[\alpha^3(\beta^2-2\alpha)+\lambda_u(2\alpha^2+\beta^4+\alpha\beta^2)\right]\frac{\lambda_u}{(1-\lambda_u)(\lambda_u-\alpha^2)}$$
$$=\alpha^3(\beta^2-2\alpha)f_1+(2\alpha^2+\beta^4+\alpha\beta^2)(f_1-1),$$

where

$$f_1=\frac{\lambda_7}{(\lambda_7-\alpha^2)(1-\lambda_7)}+\frac{\lambda_8}{(\lambda_8-\alpha^2)(1-\lambda_8)};$$

but $\lambda_7\lambda_8=\alpha^4$ and $\lambda_7+\lambda_8=\beta^4+2\alpha^2$. Hence

$$(\lambda_7-\alpha^2)(\lambda_8-\alpha^2)=-\alpha^2\beta^4$$
$$(1-\lambda_7)(1-\lambda_8)=4\alpha\beta^2,$$

and

$$f_1=-\frac{1}{4\alpha^3\beta^6}\{[\alpha^4-\alpha^2\lambda_7][1-\lambda_8]+[\alpha^4-\alpha^2\lambda_8][1-\lambda_7]\}$$
$$=-\frac{1}{4\alpha\beta^6}\{2\alpha^2+2\alpha^4-(\lambda_7+\lambda_8)(1+\alpha^2)\}=(1+\alpha^2)/4\alpha\beta^2.$$

This expression for f_1 implies that

$$A_1=f_1(2\alpha^2+\beta^4+\alpha\beta^2+\alpha^3\beta^2-2\alpha^4)-(2\alpha^2+\beta^4+\alpha\beta^2)$$
$$=(\beta^4+4\alpha^2)(f_1-1)+(\alpha\beta^2-2\alpha^2)[-1+(1+\alpha^2)f_1]$$
$$=(\beta^4+4\alpha^2)(\beta^2+2\alpha^2)/4\alpha\beta.$$

The quantity A_1 also appears in the contribution of the first term of (38a) to (37).

The contribution of the remaining terms of (38a) and (38b) can be obtained in a similar manner. It is convenient for this purpose to write ($u=7, 8$)

$$\lambda_u{}^n=a_n\lambda_n+b_n,$$

where a_n and b_n are defined under Eq. (39). The validity of this equation follows from the expressions for $\lambda_7\lambda_8$ and $\lambda_7+\lambda_8$. In terms of a_n and b_n one can establish the following relations for each term in the double sum of (37):

$$\sum_{u=7}^{8}\frac{\lambda_u W_u}{(1-\lambda_u)^2}=\frac{(\beta^4+4\alpha^2)}{16\alpha^2\beta^4}\{\beta(1+\alpha^2)(\beta^2+2\alpha^2)$$
$$-\alpha^2(2\alpha^2+\beta^4+\alpha\beta^2+\alpha^3\beta^2-2\alpha^4)\}$$

$$\sum_{u=7}^{8}\frac{\lambda_u{}^{n+1}W_u}{(1-\lambda_u)^2}=\frac{(\beta^4+4\alpha^2)}{16\alpha^2\beta^3}\{a_{n+1}(1-2\alpha+7\alpha^2-4\alpha^3+11\alpha^4+2\alpha^5+\alpha^6)$$
$$+\beta b_{n+1}(1+3\alpha+6\alpha^2-10\alpha^3+5\alpha^4-\alpha^5)\}$$

$$\sum_{u=7}^{8}\frac{\lambda_u{}^{n+1}W_u}{(1-\lambda_u)(\lambda_u-\alpha^4)}=\frac{(\beta^4+4\alpha^2)}{4\alpha^4\beta^2}\{\alpha^3 a_{n+1}+(\alpha-\beta^2)b_{n+1}\}$$

$$\sum_{u=7}^{8}\frac{\lambda_u W_u}{(\lambda_u-\alpha^4)}=\frac{(\beta^4+4\alpha^2)}{4\beta^2}(3\beta^2+\alpha-\alpha^3).$$