trifluorosilane, considered as a perfect gas at 1 atmos pressure, were calculated for four different temperatures from 243°K (bp) to 600°K. The translational, rotational, vibrational, and torsional (hindered rotational) contributions are listed separately in Table V. The torsional contribution is rather uncertain, since the evidence for the torsional frequency is not very strong.

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Monte Carlo Calculation of the Average Extension of Molecular Chains

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The behavior of chains of very many molecules is investigated by solving a restricted random walk problem on a cubic lattice in three dimensions and a square lattice in two dimensions. In the Monte Carlo calculation a large number of chains are generated at random, subject to the restrictions of no crossing or doubling back, to give the average extension of the chain $\langle R^2\rangle_{\mathrm{Av}}$ as a function of N, the number of links in the chain. A system of weights is used in order that all possible allowed chains are counted equally. Results for the true random walk problem without weights are obtained also.

I. INTRODUCTION

An attempt is made to simulate the behavior of chains of very many molecules by solving a restricted random walk problem[1] on a cubic lattice (or on a square lattice on two dimensions). The average squared extension of the chain as a function of the number of links is calculated. The random walk problem is set up as described below.

To the best of the authors' knowledge the first numerical calculations of chain length were made by Dr. Ei Teramoto of Kyoto University, who performed the remarkable feat of evaluating chain lengths in the two-dimensional case up to $N=20$ by a hand calculation cataloging all possible chains. After completion of the present work it was brought to the authors' attention by Dr. R. J. Rubin that machine calculations similar to ours have been performed by Wall, Hiller, and Wheeler.[2] They calculated somewhat different lattices (a cubic lattice with the bond angle restricted to 90° and a tetrahedral lattice) and used a different statistical procedure, more straightforward but probably more time consuming.

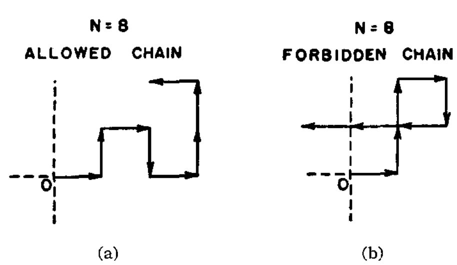

FIG. 1. Examples of an allowed chain and a forbidden chain for $N=8$ in two dimensions.

[1] W. Kuhn, Kolloid-Z. **68**, 2 (1934).
[2] Wall, Hiller, and Wheeler, J. Chem. Phys. **22**, 1036 (1954).

II. DESCRIPTION OF STATISTICAL PROCEDURE

For a given number of links N in the chain, any configuration consisting of N links laid out joined and in succession on a cubic lattice is considered. Regarded as a random walk problem, at any stage of m links ending at the position (x,y,z), all six of the positions $(x\pm1, y\pm1, z\pm1)$ are *a priori* equally likely at stage $m+1$. The excluded volume effect is simulated by the requirement that the chain not be allowed to cross itself or double back on itself at any stage (see Fig. 1 for an example of an allowed and a forbidden configuration in the two-dimensional case). Consequently, at any stage there are at most five possible subsequent positions. In statistical equilibrium all configurations of a given number of links satisfying the above requirements are equally probable, and are to be weighted equally in calculating $\langle R^2\rangle_{\mathrm{Av}}$ (the average squared extension of the chain) as a function of N. $\langle R^2\rangle_{\mathrm{Av}}$ is of importance in calculating such properties as the viscosity of the molecular chains.

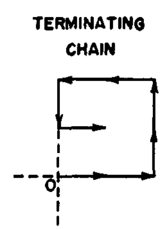

FIG. 2. A terminating chain in two dimensions. For $N>8$, if such a chain is generated, its weight is zero and a new chain is begun from the origin.

The mathematical random walk problem is solved by a Monte Carlo procedure carried out on the Los Alamos high speed electronic computer Maniac. In the calculation a large number of suitable configurations are successively generated at random according to the following scheme, and averages are taken over these configurations.

(1) For simplicity the first link is placed from (0,0,0) to (1,0,0).

(2) Any satisfactory set of m links reaching from the origin to position $(x,y,z)_m$ is associated with a weighting function W_m calculated at each step according to procedure (3) below. The weighting function is necessary since some configurations are generated more often than others, and a weighting function must be introduced so that all configurations are counted equally. After N links are obtained by procedure (3), with a final position $(x,y,z)_N$ and weight W_N, the value of $\langle R_N^2\rangle_{\text{Av}}=x_N^2+y_N^2+z_N^2$ is weighted with W_N in a statistical average of many such chains.

(3) At any stage of m links reaching to $(x,y,z)_m$, as was mentioned in the foregoing, the six positions $(x\pm1, y\pm1, z\pm1)$ must be considered. One of these six positions is $(x,y,z)_{m-1}$ and is ruled out immediately. Any of the other five possible positions at $m+1$ may be among the values of $(x,y,z)_i$ for $i=m-3, m-5, m-7, \cdots$ (geometrical considerations exclude coincidences between $m+1$ and $m, m-2, m-4, m-6, \cdots$). If comparison shows such to be the case, a modification of the weight W_m must be made to obtain W_{m+1}. There are really three possibilities:

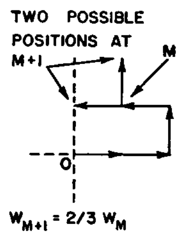

FIG. 3. An example in two dimensions of the modification of the weight in going from stage M to stage $M+1$. Only two positions at $M+1$ are possible instead of the maximum number of three.

(a) All six possible new positions are occupied (see Fig. 2 for an example in two dimensions, where only four new positions are available). The process is then terminated with a weight $W=0$, and a new chain must be generated, starting again from (0,0,0).

(b) All five positions (the position at $m-1$ being excluded) are unoccupied. Then

$$W_{m+1}=W_m(W_1=1). \quad (1)$$

One of these five positions is picked at random to give $(x,y,z)_{m+1}$. (In the actual calculation a random number which assumes one of the six values $0, 1, \cdots, 5$ is generated, corresponding one-to-one to the six positions $(x\pm1, y\pm1, z\pm1)$. If the random number happens to correspond to $(x,y,z)_{m-1}$, a new independent random number is generated and the process repeated until one of the unoccupied positions is chosen.)

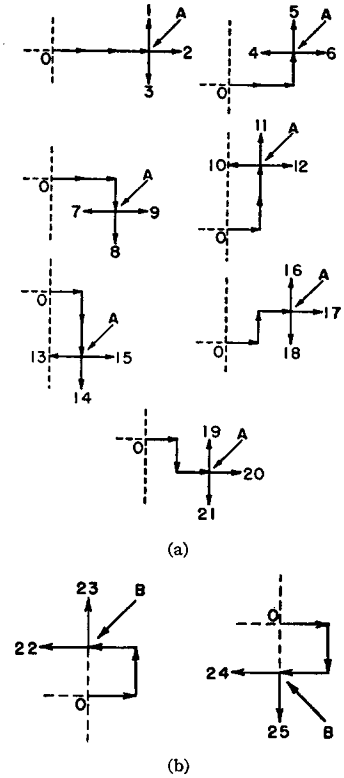

FIG. 4. All suitable configurations for $N=4$ in two dimensions [with the first link always from (0,0,0) to (1,0,0)]. In the modified random walk problem, if a configuration shown in Fig. 4(a) is generated it is given weight 1; however, if one of the configurations of Fig. 4(b) is generated it is given weight $\frac{2}{3}$.

(c) Only n new positions are unoccupied, with $0<n<5$. Then

$$W_{m+1}=(n/5)W_m(W_1=1). \quad (2)$$

(In two dimensions $0<n<3$ and $W_{m+1}=(n/3)W_m$.) A random number is used to pick one of the n positions just as in (b) above (see Fig. 3).

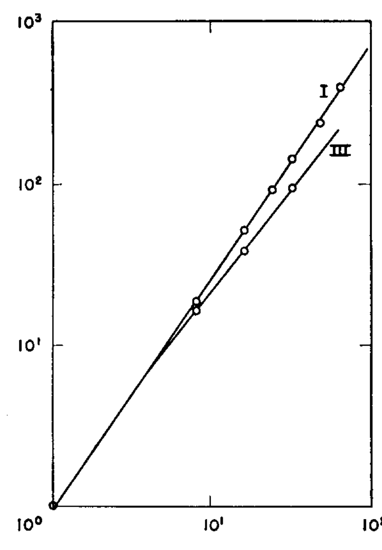

FIG. 5. Values of $\langle R^2\rangle$ *versus* N on a log-log polt for the two-dimensional case. Curve I represents $\langle R^2\rangle$ for the modified random walk problem with weights, and curve III gives values for the true random walk problem without weights.

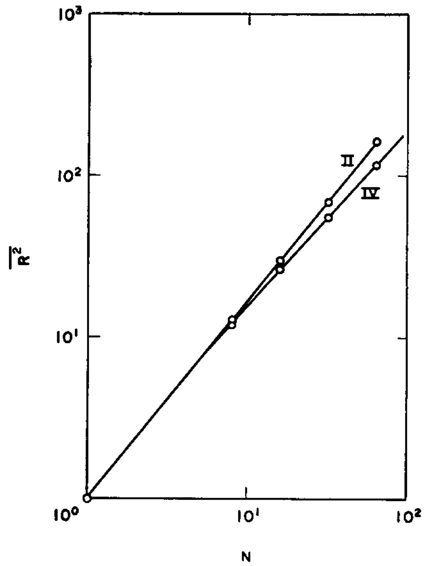

FIG. 6. Values of $\langle R^2 \rangle$ *versus* N on a log-log plot for the three-dimensional case. Curve II corresponds to averages taken with the weighting function W_N, and curve IV to direct averages without weights.

The weight W_m is calculated so that all possible allowed configurations of a given N are counted equally. Tentatively, the number of such configurations (if the chains were allowed to cross themselves but not to double back) would be $(5)^{N-1}$. This number must be multiplied by the average value of W_N, $\langle W_N \rangle_{\text{Av}}$, to obtain the true number of possible configurations of N links.

To see why Eq. (2) is correct for the weighting function, consider the simple case $N=4$ in two dimensions. All suitable configurations are shown in Figs. 4(a) and 4(b). The twenty-five possible configurations are weighted equally to give an average value of $\langle R^2 \rangle_{\text{Av}}$ of 7.04. However, any of the four configurations in Fig. 4(b) will be generated in the random walk scheme three-halves as often as any configuration of Fig. 4(a). [A point (A) is reached just as often as a point (B), but from a point (A) any of three configurations can be generated instead of only two, as from one of the points (B)]. Therefore, configurations of Fig. 4(b) have the weight $\frac{2}{3}$, as follows automatically from prescription (C), Eq. (2) above.

TABLE I. Values of $\langle R^2 \rangle_{\text{Av}}$ and $\langle W \rangle_{\text{Av}}$ as functions of N, for two-dimensional random walk problem with weights.

N	Total No. of chains	$\langle R^2 \rangle_{\text{Av}}$	$\bar{W}$
8	11 547	18.80	0.679
16	9565	51.98	0.316
24	6662	92.92	0.140
32	15 051	143.60	0.0618
48	4986	239.88	0.01065
64	5332	402.09	0.00222

TABLE II. Values of $\langle R^2 \rangle_{\text{Av}}$ and $\langle W \rangle_{\text{Av}}$ as functions of N, for three-dimensional random walk problem with weights.

N	Total No. of chains	$\langle R^2 \rangle_{\text{Av}}$	$\bar{W}$
8	11 307	12.81	0.828
16	7736	29.80	0.544
32	7369	68.35	0.214
64	4769	162.40	0.0296

III. RESULTS

The problem was calculated for two and for three dimensions, with various values of N. Results for $\langle R^2 \rangle_{\text{Av}}$ as a function of N are shown in Fig. 5, curve I, for two dimensions, and in Fig. 6, curve II, for three dimensions.

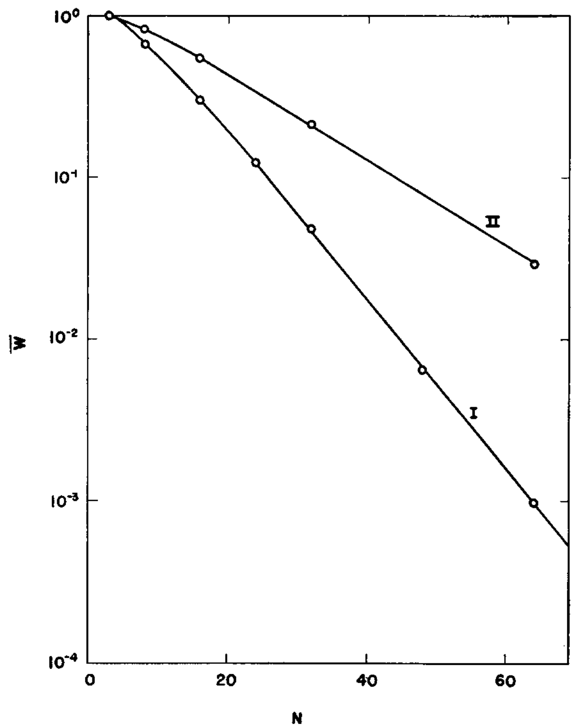

FIG. 7. Values of the average weight, $\langle W \rangle_{\text{Av}}$, *versus* N on a semilog plot. Curve I represents the two-dimensional case, corresponding to the values of $\langle R^2 \rangle$ given in Fig. 5, curve I; curve II gives three-dimensional results corresponding to curve II of Fig. 6. Both curves, of course, correspond to the modified random walk problem with weights.

Curves for $\langle W_N \rangle_{\text{Av}}$ as a function of N are shown as curves I and II of Fig. 7. As discussed above, the average weights, when multiplied by $(5)^{N-1}$ in three dimensions or $(3)^{N-1}$ in two dimensions, give the total number of configurations of length N which exist.

Approximate fits are given by

$$\langle R_{\text{I}}^2 \rangle_{\text{Av}} = 0.917(N)^{1.45} \quad \text{two} \quad (3)$$

$$\langle W_{\text{I}} \rangle_{\text{Av}} = 2.14(0.887)^N \quad \text{dimensions} \quad (4)$$

$$\langle R_{\text{II}}^2 \rangle_{\text{Av}} = (N)^{1.22} \quad \text{three} \quad (5)$$

$$\langle W_{\text{II}} \rangle_{\text{Av}} = 1.46(0.941)^N \quad \text{dimensions.} \quad (6)$$

The numerical values (good probably to a few percent) obtained for $\langle R^2\rangle_{Av}$ and $\langle W\rangle_{Av}$ are given in Table I, (for two dimensions) and Table II (for three dimensions). The total number of chains generated for each value of N is listed also.

For mathematical interest a comparison problem was also run, the true random walk problem without crossing or doubling back, but with all generated configurations being given a weight 1. For small values of N, the presence or absence of a weight calculated according to Eq. (2) is negligible. However, for increasing N, $\langle R^2\rangle_{Av}$ drops below the values given by Eqs. (3) and (5), as shown in curves III and IV of Figs. 5 and 6. Numerical values are given in Tables III and IV. Statistics here are fairly poor. Fits here are

$$\langle R_{III}^2\rangle = 1.18(N)^{1.26} \text{ (two dimensions)} \qquad (7)$$

$$\langle R_{IV}^2\rangle = 1.26(N)^{1.09} \text{ (three dimensions).} \qquad (8)$$

TABLE III. Values of $\langle R^2\rangle_{Av}$ as a function of N, for two-dimensional random walk problem without weights.

N	Total No. of chains	$\langle R^2\rangle_{Av}$
8	3226	16.47
16	1379	38.39
32	1381	95.21

The maximum values of N for which the problem can be attempted are limited not only by the number of terminating chains encountered (see Fig. 2), but in the weighted case by the increasing occurrence of very low weights and resultant large statistical fluctuations. Also, of course, the machine running time increases rapidly with N. Roughly, some twenty hours of machine-calculating time were used.

TABLE IV. Values of $\langle R^2\rangle_{Av}$ as a function of N, for three-dimensional random walk problem without weights.

N	Total No. of chains	$\langle R^2\rangle_{Av}$
8	5646	11.97
16	2576	26.18
32	1229	55.24
64	1186	116.17

IV. CONCLUSION

It is found that the restricted random walk problem on a cubic lattice for chains of length up to sixty-four links predicts an average squared extension in the three-dimensional case of

$$\langle R^2\rangle = N^{1.22}$$

and in the two-dimensional case

$$\langle R^2\rangle = 0.917(N)^{1.45}.$$

The total number of configurations of a given length is also calculated.

While these chain lengths are quite small, the above results give a remarkably good fit over the entire range. Moreover, when we consider the results of Wall, Hiller, and Wheeler,[2] it is now found that the same exponent, 1.22, applies to three different types of lattice. This is certainly suggestive of some general law. It is still an open question whether a different ratio of excluded radius to link size would affect these results. In view of the rather complete study being made by Wall, Hiller, and Wheeler the authors of the present paper do not intend to pursue this subject further.