Monte Carlo of Long Lattice Chains. Variation of the Excluded Volume

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ABSTRACT: Self-avoiding chains on a cubic lattice are studied with the Monte-Carlo method. Thus self-intersections of the chain are accorded a Boltzmann weight factor. Variation of the factor corresponds to varying the effective excluded volume β, from one to zero. A previously described progressive "dimerization" technique is used: short chains of n links are dimerized to $2n$, the latter to $4n$, etc., until the desired chain length N is reached. Each dimerization adds a relatively small number of self-intersections; it is possible therefore to employ "importance sampling"—progressively picking the important configurations, *i.e.*, those with relatively few self-intersections. The variation of β, or of $z = CN^{1/2}\beta$ (C is a constant), is effected for chains from $N = 16$ to 4096. Measurement of the expansion coefficient α^2, at low z, enables to verify the linear perturbation theory and, at the same time, to determine C. With C fixed, the theoretical $\alpha^2(z)$ lines could be evaluated and compared with the Monte-Carlo data, for the entire sweep of z. The fit of various theories is discussed in detail. Another quantity measured is the probability of intersection, among points separated by J intervening links. The dependence of the probability of J and β is discussed.

The study of chains with excluded volume takes considerable support from the computer simulation of self-avoiding lattice walks (Monte-Carlo "experiments"). The effect of self-avoidance upon the mean-square end-to-end distance, as expressed by the coefficient α^2, is studied in particular. According to the so-called "two parameter" theories,[1] α^2 should depend on the product of the square root of the number of chain links, $N^{1/2}$, times the excluded volume, β. Thus

$$\alpha^2 = \alpha^2(z);\ z = CN^{1/2}\beta/L^3 \tag{1}$$

Here z constitutes the product "excluded volume parameter," C is a constant depending on the lattice, while β/L^3 is the effectively excluded volume scaled by the link (or lattice edge) length, L. On the face of it, therefore, an equivalent variation α^2 is obtained by varying $N^{1/2}$ or β. The parametric variation of the chain length N is obvious, that of β requires some elaboration. An (discontinuous) increase of β can be effected by excluding not only the intersection, but, also, the backfolding of nonconnected chain links to within first, second, etc., neighbor positions on the lattice. Preferably, however, a smooth variation of β is effected by varying the *intensity* of the self-avoiding effect. A self-intersection, instead of being excluded, is accorded a Boltzmann weight factor ω. By a development[2] similar to the Ursell–Mayer cluster theory, the effectively excluded volume β is related to ω as

$$\beta = (1 - \omega)L^3 \tag{2}$$

The weight factor associated with a configuration with g_i self-intersections is then

$$f_i = \omega^{g_i} = (1 - \beta/L^3)^{g_i} \tag{3}$$

Properties like α^2 are computed by averaging over a sample of configurations, each weighted by its proper f_i. Clearly ω can be varied between the limits zero to one, corresponding to the completely nonintersecting and to the random walk, respectively.

Most Monte-Carlo studies vary N at the fixed top value $\beta/L^3 = 1$, which enables to most economically extend the upper range of the $\alpha^2(z)$ variation. This is important, since great theoretical efforts are made to unravel the asymptotic increase of α^2 at large z. But a major advantage of smoothly varying β happens to be overlooked in this connection. The curve fitting of the theoretical $\alpha^2(z)$ lines to the Monte-Carlo results is aided, of course, by availability of data for the entire range of z, from zero to the largest that can be attained in practice. The theoretical lines for α^2 at small z, and especially the valuable exact result[3,4] for $z \to 0$, are, however, derived for "non-too-short chains" (the use of continuous chain statistics requiring $N^{1/2} \gg 1$); the limit of small z, therefore, really implies N finite and very small β. For that reason the fitting of the theoretical $\alpha^2(z)$ to the computer results for very short nonintersecting lattice walks, requires a great deal of caution.

An attractive alternative, therefore, would be to decrease z at constant (long enough) chain length, through smoothly varying β toward zero (increasing ω to one). Such a parametric variation has been described by Kron and Ptitsyn,[5] who have indeed demonstrated the essential equivalence of varying $N^{1/2}$ and β. Their study, however, has been limited to quite short chain lengths, due to the application of a direct Monte-Carlo method. The direct Monte-Carlo relies on random sampling of the chain configurations, followed by due weighting of the configurations in the calculation of sample averages. For example, α^2 is computed as

$$\alpha^2 = \langle h^2 \rangle / N = \sum (h_i^2/N) f_i / \sum f_i \tag{4}$$

where h_i^2 is the square end-to-end distance of individual configurations and f_i is their weighting factor due to the self-intersections (eq 3). The drawback of such a method lies in what might be termed "the nobodies effect in a democratic sampling." The overwhelming majority of the randomly sampled configurations are just nobodies, their contribution to the summation of above is practically nil, because of an exceedingly small weighting factor f_i (corresponding to a large number g_i of self-intersections). The major contribution to the summation is due to exceeding-

(1) See, for example, H. Yamakawa, "Modern Theory of Polymer Solutions," Harper & Row, New York, N. Y., Chapter 3, 1971.
(2) See, for example, M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955), with a constant $\omega = \exp(-E/kT)$ integrated over the volume L^3.
(3) E. Teramoto, *Busseiron Kenkyu*, **39**, 1 (1951).
(4) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).
(5) A. K. Kron and O. B. Ptitsyn, *Vysokomol. Soedin.* **6**, (5), 862 (1964). (1964).

ly few configurations of large f_i; this prevents a reliable evaluation of averages, unless enormous samples are constructed. The swamping with nobodies becomes increasingly acute as the total chain length increases, increasing thereby the number of self-intersections in a chain, and hence the variation of g_i from one configuration to another. In practice it becomes impossible to construct a representative sample of configurations for chains of more than a couple of hundred links. (This difficulty parallels, of course, the problem of sample attrition[6] encountered in the study of the completely nonintersecting chains, $\beta = 1$.) To avoid this difficulty, Monte-Carlo studies in other branches of physics have resorted to the so-called biased (nondemocratic) sampling, which *a priori* picks the configurations with a bias probability proportional to f_i. The averaging sums then, configurations which are *equally important*, for example

$$\alpha^2 = \Sigma'(h_i^2/N)/\Sigma'1 = S^{-1}\Sigma'(h_i^2/N) \qquad (5)$$

S being the number of configurations, and their biased sampling is indicated by the prime over the summation sign. (For details of this so-called Metropolis Monte-Carlo method, as related to the study of the lattice gas and of the Ising lattice, see elsewhere.[7])

All this is good and fine, and how does one set about picking the desired sample of configuration with the bias probability f_i, without going through the wasteful effort of first constructing an indiscriminate sample of all configurations, important and nobodies alike. Here the "dimerization" Monte-Carlo technique, devised before[8,9] in connection with the study of the nonintersecting chains can be resorted to. The long-chain configurations are constructed by means of repeated dimerization of an initial stock of subunits: couples of subunit chains $N = 16$ give upon linkage dimer chains $N = 32$, the latter linked give $N = 64$, etc.; in general a sample of chains of $N = 16 \times 2^x$ is constructed by means of x successive dimerizations of the initial subunits. In this manner each stage of the dimerization adds intersections only among the two different halves of the dimer, which constitute a relatively small number, Δg_i. In case of nonintersecting chains $\beta = 1$, this has led to a dramatic reduction of the sample attrition. In parallel, in the present case of variable β, the smallness of Δg_i assures that, at each stage of the dimerization, the difference between the important and less important configurations will not be very pronounced. The difference would become pronounced after the several dimerizations with which the long chain is assembled, this however is avoided. After each dimerization the resultant x level dimer chains are retained in the sample, or discarded, with a probability $\omega^{\Delta g_i}$, that matches exactly the incremental increase of their Boltzmann weight factor. The outcome after x dimerizations is a biased sample of *equally important configurations* in the sense of eq 5. Thus the method enables to sweep the variation of β in quite long chains (here up to $N = 4096$).

Experimental Section

The calculations have been carried out on an IBM 370/165 computer, using 300K of core. Details of the program relating to employment of the "Hash Table" procedure, for speedy checking of the intersections, follow those used before.[9] A notable departure from our previous procedure has been to carry out the entire series of the successive dimerizations in core alone, starting with a batch of $N = 16$ chains and carrying on, until $N = 4096$ has been reached. The process was repeated over and over again until the required sample of batches has accumulated. (In our previous study the batches were accumulated together at each stage of the dimerization, output onto a disk, and then brought back into the core, mixed together in different batches, for the next stage dimerization; this procedure is statistically sounder, but much more cumbersome operationally.)

The handling of the batches, for a particular value of β (or ω, eq 2), was as follows. To begin with, the subunit chains $N = 16$ are constructed with the direct Monte-Carlo method. For each chain the number of self-intersections, $\Delta g_{i,1}$ is recorded. A "draw of lots" with the probability (see eq 3)

$$P_{i,1} = \omega^{\Delta g_{i,1}} \qquad (6)$$

is then carried out, determining whether a chain should be included in the sample. (To save on time the order is actually inversed: first a random number R between 0 and 1 is obtained, then the construction of the chain is carried on, and the currently increasing value of Δg_i is recorded, failure occurring when the corresponding value of P_i becomes larger than R.) The successful subunit chains accumulate, until the quota for a batch is fulfilled. At the next stage, the trial dimerization $16 \times 2 \rightarrow 32$ are started. For each dimer the additional self-intersections, $\Delta g_{i,2}$ (those between the two newly joined halves), are recorded. This determines the probability

$$P_{i,2} = \omega^{\Delta g_{i,2}} \qquad (7)$$

of the dimer to be successfully included in the batch. The dimerizations are carried out until a specified *fixed number of trials* has been carried out. (This is important, since the alternative specification of the number of successes depends on the outcome of the dimerizations in particular batches and might bias the sample.) Thereafter, the successive dimerizations $32 \times 2 \rightarrow 64$ and so on, are pursued in exactly the same manner. In practice, we chose to specify the number of trials so that, on the average, the number of chains in a batch will decrease by 1.2 with each dimerization; starting with 150 subunits of $N = 16$ and ending up with about 35 chains of $N = 4096$.

Total sample size consisted of about sixty such batches. The entire operation required 10–40 min of computer time, depending on β (at high β the ratio of successes to trials is lower). An estimate for the standard deviation of the expansion coefficient, $\sigma(\alpha^2)$, was computed from the sample and amounted to 65–80% of α^2 itself, depending slightly on N and on β. The 2σ confidence limits for the sample average values of α^2 are therefore

$$\alpha^2 \pm 2\sigma(\alpha^2)/\sqrt{S} \qquad (8)$$

where S, the sample size, ranged from 10,000 to 2000, going from the shortest to longest chains.

Results and Discussion

Samples of the progressively dimerized walks on a six-choice cubic lattice were constructed for $\beta = 1$, 0.86, $1/\sqrt{2}$, 1/2, 1/4, 1/8, 1/20, 1/32, 1/40, 1/64, 1/128, and zero (random walk), N varying from 16 to 4096. The expansion coefficients of the mean-square end-to-end distance, α^2, have been measured for the corresponding three orders of magnitude variation of $N^{1/2}\beta$. (Expansion coefficients of the internal distances were measured as well; these follow the pattern of behavior for $\beta = 1$, reported before,[9] and are not reproduced.) The results for low $N^{1/2}\beta$ will be considered first. Perturbation theory gives the exact result[1]

$$\alpha^2 = 1 + (4/3)z + \cdots = 1 + (4/3)CN^{1/2}\beta/L^3 + \cdots \qquad (9)$$

for $z \rightarrow 0$, or, more exactly for $\beta/L^3 \rightarrow 0$ and $N^{1/2} \gg 1$ (see introduction).

In Figure 1 the results for $\alpha^2 - 1$ versus $N^{1/2}\beta$ are plot-

(6) F. T. Wall, S. Windwer, and P. J. Gans in "Methods in Computational Physics," Vol. 1, Academic Press, New York, N. Y., 1963, p 217.
(7) L. D. Fosdick in "Methods in Computational Physics," Vol. 1, Academic Press, New York, N. Y., 1963, p 245.
(8) Z. Alexandrowicz, *J. Chem. Phys.*, **51**, 561 (1969).
(9) Z. Alexandrowicz and Y. Accad, *J. Chem. Phys.*, **54**, 5338 (1971).

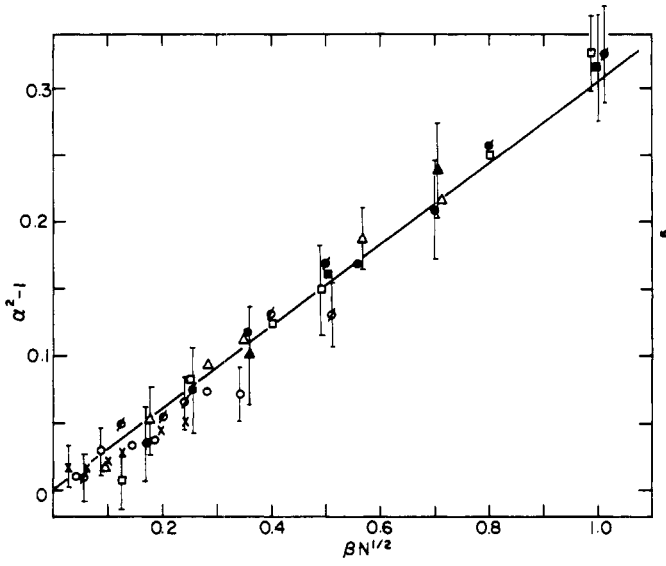

Figure 1. The initial variation of $\alpha^2 - 1$ with $\beta N^{1/2}$. Points ■, ▲, ◆, ●, □, △, ◇, ○, and x correspond to chain lengths N = 4096, 2048, 1024, 512, 256, 128, 64, 32, and 16, respectively, at various β. Vertical bars indicate confidence limits of twice the standard deviation (eq 8). The straight line corresponds to first-order perturbation expansion (eq 9), giving C = 0.23 for a six-choice cubic lattice.

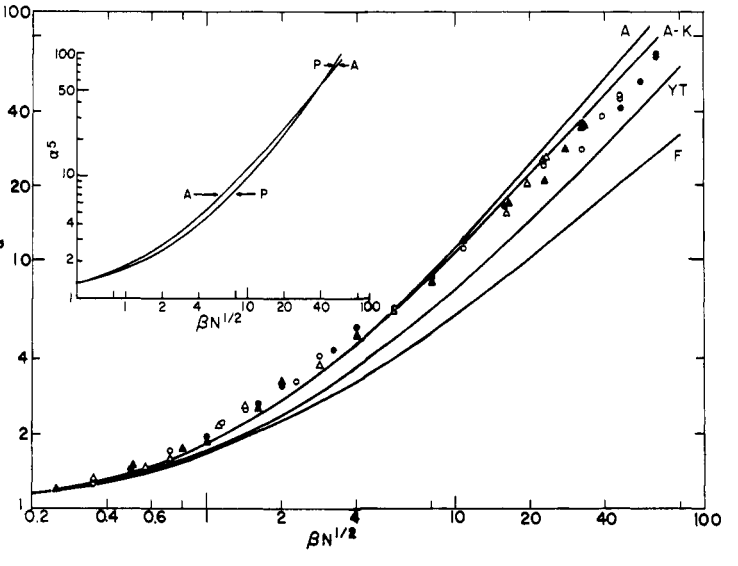

Figure 2. The variation of α^5 with $\beta N^{1/2}$. Points, ●, ○, ▲, and △ correspond to chain lengths N = 4096, 2048, 1024, and 512, respectively, at various β. The lines F, YT, A, A-K, and P (in upper corner) are computed from the theories of Flory (eq 10), of Yamakawa and Tanaka (eq 11) of Alexandrowicz (eq 12), of Alexandrowicz and (independently) of Kurata (eq 13) and of Ptitsyn (eq 14), taking C = 0.23.

ted, edge length L being unity. The $2\sigma(\alpha^2)/\sqrt{S}$ confidence limits are marked for some representative points and on the whole accord with the experimental scatter. Subject to this experimental accuracy, the following conclusions seem to follow. (a) The equivalent dependence on $N^{1/2}$, or β, holds from N = 4096 down to the remarkably low limit N = 64 and possibly even down to N = 16. (This however does not imply that the equivalent dependence might hold all the way down. For example, for N = 2 and β = 1, the theoretically exact result α^2 = 1.2 lies well below the line of Figure 1.) (b) The results obey the linear dependence of the perturbation theory. (c) The straight line slope gives C = 0.23 ± (about) 0.03, for a six-choice cubic lattice. Our main purpose of course is to apply this result to the curve fitting of theories with experimental data for the entire range of $N^{1/2}\beta$. Before proceeding, however, let's comment on the numerical significance of this result. With C = 0.23, the observed linear dependence of α^2 up to about $N^{1/2}\beta$ = 1, corresponds to z = 0.23. This is not inconsistent with the values that have been computed[1] for the first-, second-, and third-order coefficients of the perturbation series of eq 9. Also of significance is the almost perfect agreement of C = 0.23 with the probability to self-intersect for the random walk on a six-choice cubic lattice (when smoothed appropriately for even and odd number of steps), but this will be discussed later on.

The major part of our data is reproduced in Figure 2, which describes the increase of α^5 with $N^{1/2}\beta$. To avoid the insufficient length difficulty, the results are for the longest chains 512, 1024, 2048, and 4096. The results uphold the equivalent dependence on $N^{1/2}$ and β, to within the experimental error. Incidentally, the experimental scatter exceeds somewhat the confidence limits of eq 8. The following theoretical lines, computed for C = 0.23, have been added for comparison.

Line F, for Flory's (modified) theory[10]

$$\alpha^5 - \alpha^3 = (4/3)z \qquad (10)$$

(10) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); the original constant is modified to fit first-order perturbation.

Line YT, for Yamakawa and Tanaka's equation[11]

$$\alpha^2 = 0.572 + 0.428(1 + 6.23z)^{1/2} \qquad (11)$$

Line A, for Alexandrowicz's integral equation.[12] This is computed numerically at low z, and at higher z, it is approximated by (see[13])

$$\alpha^2 = 1.52z^{1/2} + 0.34 \qquad 1.1 \leq z^{1/2} \leq 12 \qquad (12)$$

Line A-K, for another integral equation that has been derived independently, by Alexandrowicz[14] and by Kurata.[15] The integrated equation is[16]

$$\alpha^5/5 + \alpha^3/3 - 8/15 = (4/3)z \qquad (13)$$

Line P, for Ptitsyn's equation[17]

$$\alpha^2 = [3.68 + (1 + 9.36z)^{2/3}]/4.68 \qquad (14)$$

(To prevent overcrowding the figure, line P is drawn on top in separate, with line A giving a relative frame reference.)

It appears that line A-K fits the Monte-Carlo data throughout the range, though its rise at high z seems to be slightly too fast. The overfast rise is more pronounced with line A and, even more so, with line P. In contrast, the rise of line YT is too slow (though its terminal slope becomes satisfactory), while the rise of line F is definitely

(11) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).
(12) Z. Alexandrowicz, *J. Chem. Phys.*, **46**, 3789 (1967).
(13) The function $\alpha(z)$ given here (Figure 2), differs slightly from that in the original publication (ref 12). The difference is due to an (unpublished) recalculation of the expansion coefficient for the *mean-square*, rather than for the *most probable*, value of the end-to-end distance. Below $\sqrt{z}$ = 1.1 the line closely resembles Fixman's; more accurately, however, it can be interpolated from the following values: for z = 0.04, 0.09, 0.16, 0.25, 0.36, 0.64, and 1.0; α^2 = 1.049, 1.11, 1.19, 1.285, 1.395, 1.64, and 1.90, respectively.
(14) Z. Alexandrowicz, *J. Chem. Phys.*, **49**, 1599 (1968).
(15) M. Kurata, *J. Polym. Sci., Part A-2*, **6**, 1607 (1968).
(16) The constant multiplying z is forced to fit first-order perturbation. The integrated form of the equation in ref 14 has been pointed out to its author by P. J. Roberts, in a private communication.
(17) O. B. Ptitsyn, *Vysokomol. Soedin.*, **3**, 1673 (1961).

too slow throughout the range. A more pronounced discrepancy would be exhibited, on one hand, by the Flory and Fisk[18] line, which rises even more slowly than Flory's line F and, on the other, by the Fixman's equation[19]

$$\alpha^3 = 1 + 2z \tag{15}$$

which rises even more quickly than line P. Still, the above conclusions concern the range of α^2 of interest to the polymer physicist, but, throw little light on the theoretical problem of the asymptotic dependence for $z \rightarrow \infty$. Thus, the best fit is exhibited by the A-K equation (13) which leads to the "Flory-like" fifth-power asymptotic dependence of α on z

$$\alpha^5 \sim z \qquad z \rightarrow \infty \tag{16}$$

But the less satisfactory fit of lines A, YT, and P does not seem to warrant their disqualification. These lines, however, lead to a 4.24-power, fourth-power, and third-power ("Fixman-like") asymptotic dependence, which about covers the range of all disputed values! It should be further pointed out in this connection that the Monte-Carlo data in Figure 2 obey indeed the fifth-power dependence in the range of $N^{1/2}\beta$ from about 6 to 60. Yet it disagrees completely with Flory's line F. The reason of course is, that, within this range the slope of F is still well below the asymptotic—corresponding to a power of α higher than the fifth by about 50%. The seemingly compelling evidence against line F is due to the wide sweep of the Monte-Carlo results, reaching very low β. In other words, fixing $C \simeq 2 \times 0.23$ would improve markedly the fit of F with the high $N^{1/2}\beta$ data (see the previous report[9] in this connection), but the disparity with the low $N^{1/2}\beta$ of Figure 2 and, especially, of Figure 1, would be complete. In this respect our conclusions disagree with those reached on somewhat similar grounds by Berry,[20] who measures the dimensions of polymer chains in solutions down to near Θ-point temperatures, and finds good agreement with the extremely slow rising Flory–Fisk line. Berry's findings however have been disputed before.[21] Of course one can also question the reliability of the Monte-Carlo methods, especially of those employing statistical subterfuges. (The reliability of the dimerization method is discussed in the previous report.[9])

To conclude, we would like to comment on the hitherto unnoticed almost perfect agreement between the A-K line (eq 13, for $C = 0.23$) with the asymptotic approximation

$$\alpha^2 = 1.067N^{1/5} - 0.092N^{-1} \tag{17}$$

which Domb[22] has derived from his exact enumeration of short walks on the cubic lattice (the deviations amount to 2% or less throughout the range). The present Monte-Carlo results are therefore fitted equally well by the A-K line and by Domb's eq 17. The fact that an extrapolation formula derived from results for $N = 1$ to 9, still holds for N thousand times as large, certainly does credit to the accuracy of Domb's numerical method.

Another quantity which could be studied within the context of the present work, not limited, to recall, to completely self-avoiding chains, is the probability of "contacts," or, of self-intersections among pairs of the chain

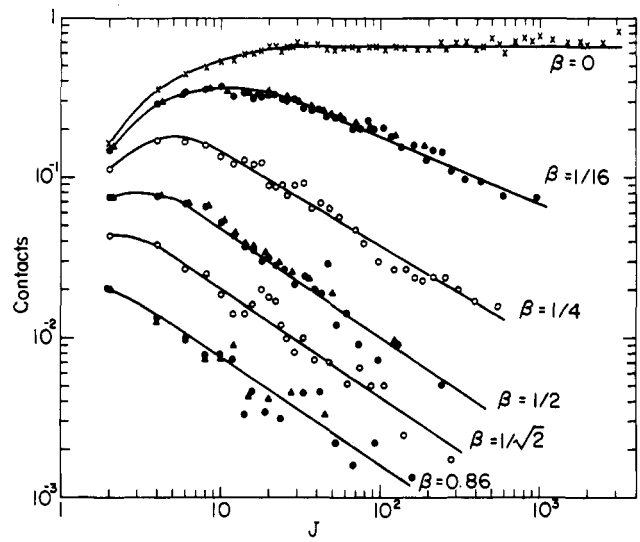

Figure 3. The probability of "contacts," or, the probability to self-intersect $0_{\beta,N}(J)$ multiplied by $(J-1)^{3/2}$, for pairs of points J links apart, as a function of J in chains $N = 4096$ and at $\beta = 0.86, 1/\sqrt{2}, 1/2, 1/4, 1/16$, and 0 (random). The triangles describe some results for $N = 512$, showing that contact probability is independent of N, for $J \ll N$. The results at $\beta = 0$ rise from 1/6 (eq 19) and attain twice the random-flight value (eq 21).

links. Let $M(J,\beta,N)$ denote the "experimental" sample average number of intersections, between links i and $i + J$, i going from 1 to $N - J$. Of course, on the cubic lattice, non-zero values of M obtain only for even J. Furthermore, M becomes exceedingly small for large J; in that case the number of self-intersections was measured for an interval of J, and the result, divided by the number of the even J within the interval, served to compute an average M for a midpoint (not necessarily integer) value of J. Finally, a smoothed probability $0_{\beta,J}(J)$, for a chain link to self-intersect, within the unit volume, with an even number of J steps, was obtained from M divided by $N - J$

$$0_{\beta,N}(J) = M/(N - J) \tag{18}$$

(the total number of links which might intersect after J steps is $N - J$, the smoothing neglects the possible effect at the chain ends). In Figure 3 the values of $0(J)$ are multiplied by $(J-1)^{3/2}$ and plotted, as "contacts" *vs.* J, for several representative β. The results are for $N = 4096$ (some are for 512), but, as it turns out, for J smaller than N by about one order of magnitude or more, $0(J)$ is independent of N. For J of the order of N it was not possible to measure $0(J)$ to within any reasonable accuracy. Incidentally, this independence of $0(J)$ of N is in accordance with the limiting behavior of intrachain distances for $J \ll N$, which has been reported elsewhere, and disagrees with the basic assumption of several theories.[9] A brief digression has to be made before further discussing the results.

For the purely random lattice walk, $\beta = 0$, the probability for a self-intersection, with two six-choice steps, should be

$$0_{\beta=0}(2) = 1/6 \tag{19}$$

Turning to the other extreme, the (gaussian) probability for a long sequence of j random-flight links to self-intersect, is

$$f^0(j) = (3/2\pi)^{3/2} j^{-3/2} \tag{20}$$

In the case of our lattice walk the probability to self-inter-

(18) P. J. Flory and S. Fisk, *J. Chem. Phys.*, **44**, 2243 (1966).
(19) M. Fixman, *J. Chem. Phys.*, **36**, 3123 (1962).
(20) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
(21) H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, *J. Phys. Chem.*, **70**, 1718 (1966); Z. Alexandrowicz, *J. Chem. Phys.*, **47**, 4377 (1967); H. Yamakawa, *ibid.*, **48**, 2103 (1968).
(22) C. Domb, *J. Chem. Phys.*, **38**, 2957 (1963).

sect is zero for all odd values of J. Hence, to assure that the smoothed probability for odd and even J combined tends to the above limit (the symmetrical six-choice walk has no "skeletal expansion"), the probability for the even (and large) J must be twice as large.

$$0_{\beta=0}(J) = 2(3/2\pi)^{3/2}J^{-3/2} \simeq 0.66J^{-3/2} \quad (21)$$

With respect to non-zero values of β we note, that, the event of self-intersection is associated with the weight factor $1 - \beta$ (see eq 2 and 3). In addition, the occurrence of a self-intersection implies a more coiled configuration of the chain, which tends to promote the occurrence of self-intersections among *other* chain links. Hence the probability of a self-intersection at $\beta \neq 0$ is expected to be $1 - \beta$ *or more* times smaller than the corresponding probability at $\beta = 0$. It is worthwhile to point out in this connection that, in computing α^2, theories on the excluded volume often deal with the *a priori* probability of a self-intersection *not* weighted by the Boltzmann factor, $1 - \beta$, associated with the intersection itself.[23]

Resuming the discussion of the experimental results in Figure 3. The probability to self-intersect in two steps 0(2), at $\beta = 0$, is indeed equal to 1/6, as in eq 19. Furthermore, at $\beta \neq 0$, this probability decreases by a factor only very slightly larger than $1 - \beta$. Thus for $\beta = 1/128$, 1/16, 1/4, 1/2, $1/\sqrt{2}$, and 0.86, the values of $(1 - \beta) \times 0(2)$ are 0.167, 0.159, 0.151, 0.148, and 0.148, respectively. Turning now to the contacts probability for $J \gg 1$, we note that, at $\beta = 0$, the results for $(J - 1)^{3/2}\, 0(J)$ are indeed scattered almost equally to both sides of the value $2(3/2\pi)^{3/2}$ of eq 21. At $\beta \neq 0$, the contacts probability decreases by more than $1 - \beta$, the more so the larger J or β. The shape of the lines seems to suggest that, for large enough J or β, the contacts probability attains an asymptotic dependence of the form

$$0_{\beta\neq 0}(J) \sim J^{-2.2} \quad (22)$$

(23) The fact that the theoretical probability of self-intersecting refers to a real chain but, is unweighted by the Boltzmann factor of the self-intersection itself, is quite clear with respect to ref 4 and, by the same token, 17 and 19. It appears that the same also applies with respect to the probability in ref 14 and 15, but, this property is obscured by fault in the derivation; see Z. Alexandrowicz, *Macromolecules*, 6, 255 (1973).

for large J or β. For comparison, the Gaussian probability at $\beta = 0$ obeys a $J^{-1.5}$ dependence. Wall and coworkers,[24] studying nonintersecting walks, $\beta = 1$, find the probability for a first intersection with the chain end (such intersection terminates the walk), obeying a J^{-2} dependence.

The last remark concerns the numerical relationship between the contacts probability, on one hand, and the constant C, giving the ratio of z to $N^{1/2}$ (eq 1), on the other. The detailed derivation of the first-order perturbation term (see,[12] for example), shows that C is simply related to the function continuously describing the probability of contacts at $\beta = 0$. Thus, for random-flight chains with the gaussian contacts probability $f^0(j)$, we have

$$f^0(j) = (3/2\pi)^{3/2}j^{-3/2} = C_{\text{gaussian}}j^{-3/2} \quad (23)$$

To recall, for the six-choice cubic lattice considered here, the probability of contacts $0(J)$ is zero, for odd J, and twice as large as $f^0(j)$, for even and large J (eq 21). (Only large values of J need to be considered in connection with C, see ref 12.) Passing to the variable $x = J/2$ we get the *smoothed* contacts probability for our lattice chain

$$0_{\beta=0}(x) = 2(3/2\pi)^{3/2}(2x)^{-3/2} = C_{\text{lattice}} \quad (24)$$

which leads to

$$C_{\text{lattice}} = 0.233 \quad (25)$$

in complete agreement with the value $C = 0.23 \pm 0.03$ which we have found from the initial slope of α^2 *vs.* $N^{1/2}\beta$ (Figure 1). The agreement strengthens of course the discussion of the theoretical lines in Figure 2 (which are computed with this particular value of C).

In conclusion, a pragmatic attitude of "if at present it is so hard to go up with the $\alpha(z)$ variation, why not go down?," enables to obtain some new information on chains with excluded volume.

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On Contacts Probability in Chains with Excluded Volume

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ABSTRACT: The theoretical derivation of probability for intersegmental contacts in chains with excluded volume is reexamined. It is concluded that, the theoretically relevant probability for a contact among a pair of segments, is *not* weighted by the Boltzmann factor due to the selfsame contact. This is important when the theoretical probability is to be compared to Monte-Carlo results on self-intersections in lattice chains.

The expansion of polymer chains due to excluded volume is closely related to the occurrence of self-intersections, or, of intersegmental contacts (the chain expands to decrease the probability of contacts). Monte-Carlo construction of lattice chains permits us to simulate the occurrence of contacts in real chains. In the case of nonintersecting chains the quantity studied was, either,[1] the probability of the "growing" chain end to intersect for the first time (which makes the construction fail), or,[2] the probability of any pair of segments to be at a small distance, without bringing about an actual intersection. Re-

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