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 β = 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

$$0_{\beta\neq0}(J) \sim J^{-2.2} \quad (22)$$

(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.

(24) F. T. Wall, L. A. Hiller, and D. J. Wheeler, *J. Chem. Phys.*, **22**, 1036 (1954).

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-

(1) F. T. Wall, L. A. Hiller, and D. J. Wheeler, *J. Chem. Phys.*, **22**, 1036 (1954); F. T. Wall and J. Erpenbeck, *ibid.*, **30**, 637 (1959).
(2) Z. Alexandrowicz and Y. Accad. *J. Chem. Phys.*, **54**, 5338 (1971).

cently the probability of actual intersections was studied[3] in lattice chains with which the self-intersection is not strictly excluded, it is accorded instead a Boltzmann factor $1 > \omega > 0$. All such Monte-Carlo results bear upon the basic assumptions of excluded volume theories and for that reason, it seems worthwhile to examine the following question.

The probability of a contact between a pair of segments k and l—as it appears in the real chain theories—is weighted by the Boltzmann factor of interactions occurring among any other segments. But, is the probability of the k, l contact weighted as well by the Boltzmann factor due to the interaction among the k and l segments themselves, or, is it not?

To examine the question let us follow Fixman's[4] exposition of the basic theory. The configurational partition function is written as eq 1, where $V(L_{ij})$ stands for the

$$Z = \text{const}\int\cdots\int \exp\left[-\sum_{i>j}\sum V(L_{ij})/kT\right] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \quad (1)$$

pairwise interaction among the segments, while f^0 is the random-flight function for the set of n segment vectors, $\mathbf{r}^n$. With this notation the probability of a k, l contact is as shown in eq 2, where the delta function $\delta(\mathbf{L}_{kl})$ limits

$$P(0_{kl}) = \int\cdots\int \delta(\mathbf{L}_{kl}) \exp\left[-\sum_{i>j}\sum V(L_{ij})/kT\right] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \Big/ \int\cdots\int \exp\left[-\sum_{i>j}\sum V(L_{ij})/kT\right] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \quad (2)$$

the segments to a contact. The question whether the probability is, or is not, weighted by the Boltzmann factor of the contact itself, depends therefore on whether the sums of exponential coefficients in the above equation do, or do not, contain $V(L_{kl})$. The answer lies in the further development of Fixman's theory. Introduction of the binary cluster approximation leads to

$$\exp[-V(L_{ij})/kT] = 1 - \beta\delta(\mathbf{L}_{ij}) \quad (3)$$

where β is the "excluded volume." Hence the Boltzmann factor in eq 1 becomes

$$\exp\left[-\sum_{i>j}\sum V(L_{ij})/kT\right] = \prod_{i>j}\prod[1 - \beta\delta(\mathbf{L}_{ij})] \quad (4)$$

Upon the introduction of a further approximation (the nature of which is not made very precise), Fixman also notes that

$$\exp\left[-\sum_{i>j}\sum V(L_{ij})/kT\right] \simeq \exp\left[-\beta\sum_{i>j}\sum \delta(\mathbf{L}_{ij})\right] \quad (5)$$

This second less accurate, form of the Boltzmann factor is irrelevant to Fixman's perturbation theory. It has been invoked for the formulation of the starting equation in several approximate theories, notably in Fixman's theory,[5] in the author's first theory[6] (AI) and in his second theory,[7] which is identical with a theory independently derived by Kurata[8] (A-K). As we shall presently see, however, this employment of the less accurate Boltzmann factor (eq 5) is quite unnecessary, and even unfortunate, since it tends to confuse the question at issue.

For the sake of illustration, take the derivation of the A-K theory. This starts from a differentiation, with respect to β, of the (log of) partition function (the latter is actually restricted to given end-to-end distance but this is irrelevant for our purpose). Taking eq 4 for the Boltzmann factor leads to eq 6. The double product in the numerator

$$\partial \log Z/\partial\beta = -\sum_{i>j}\sum \int\cdots\int \delta(\mathbf{L}_{kl}) \prod_{i>j}\prod[1 - \beta\delta(\mathbf{L}_{ij})] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \Big/ \int\cdots\int \prod_{i>j}\prod[1 - \beta\delta(\mathbf{L}_{ij})] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \quad (6)$$

contains no kl term; the denominator contains $1 - \delta(L_{kl})$, but, its mean value over the entire space (*not* restricted to a kl contact) is effectively equal to one. Hence (eq 2), the above result is equal to

$$\partial \log Z/\partial\beta = -\sum_{k>l}\sum P(0_{kl}) \quad (7)$$

not weighted by $V(L_{kl})$. The rest of the derivation can now be carried on exactly as in the original A-K theory. On the other hand, if the differentiation is carried out with the less accurate Boltzmann factor of eq 5, the result becomes

$$\partial \log Z/\partial\beta = -\sum_{k>l}\sum \int\cdots\int \delta(\mathbf{L}_{kl}) \exp\left[-\beta\sum_{i>j}\sum \delta(\mathbf{L}_{ij})\right] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n \Big/ \int\cdots\int \exp\left[-\beta\sum_{i>j}\sum \delta(\mathbf{L}_{ij})\right] f^0(\mathbf{r}^n)\mathrm{d}\mathbf{r}^n = -\sum_{k>l}\sum P(0_{kl}) \quad (8)$$

weighted by $V(L_{kl})$. Fixman's derivation of his differential equation[5] proceeds in a very similar manner, *viz.*, *via* a differentiation with respect to β, which leads to contacts probabilities. The same argument establishes therefore that, although the employment of the less accurate Boltzmann factor implies a probability as in eq 8, with the more exact form the probability is as in eq 7. Lastly, examination of theory AI shows that, although the Boltzmann factor of eq 5 is used to begin with, a stepwise expansion of the exponent is subsequently applied which, in effect, brings it back to the form of eq 4! The expansion progressively "annihilates" the $\delta(L_{kl})$ terms, for one segment after another, turning these into respective contacts probabilities. The latter therefore are similar to those of eq 7.

In conclusion, when the polymer theories are based upon the more accurate formulation of Fixman's partition function, with the Boltzmann factor given by eq 4 and not by eq 5, it turns out that the relevant contacts probabilities, for segments k and l, are *not* weighted by a factor due to the interaction of k and l themselves. Insofar as Monte-Carlo results are for contacts probabilities which are so weighted,[3] comparison requires that the latter should be converted into the former through dividing out $\exp[-V(L_{kl})/kT]$. Results at a given β will be merely rescaled by a constant factor, but, the dependence of β will become different.

(3) Z. Alexandrowicz and Y. Accad, *Macromolecules*, **6**, 251 (1973).
(4) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).
(5) Appendix to ref 4 above; also M. Fixman, *J. Chem. Phys.*, **36**, 3123 (1962).
(6) Z. Alexandrowicz, *J. Chem. Phys.*, **46**, 3789 (1967).
(7) Z. Alexandrowicz, *J. Chem. Phys.*, **49**, 1599 (1968).
(8) M. Kurata, *J. Polym. Sci., Part A-2*, **6**, 1607 (1968).