Investigation of Moments of Intrachain Distances in Linear Polymers

A. J. Barrett*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.
Received July 29, 1983

ABSTRACT: We have performed Monte Carlo experiments on the intrachain moments $\langle R_{ij}^2 \rangle$ and $\langle R_{ij}^{-1} \rangle$ for linear polymer chains with excluded volume. Here R_{ij} represents the distance from the ith to the jth monomer of the chain. The results of these experiments are then combined with perturbation results to provide simple closed-form expressions for the expansion factors of the moments as functions of the excluded volume variable z. An approximate expression is also derived for the hydrodynamic radius. Finally we compare the approximate formulas with some other approximations which have been made concerning intrachain dimensions.

1. Introduction

Dramatic improvements in experimental technique have, in recent years, led to a significantly greater understanding of excluded volume in polymers.[1] It is now possible, for example, to probe the dimensions of internal portions of the chain by means of small-angle neutron scattering experiments (SANS) on deuterated block copolymers,[2] and it is to be expected that there will soon be a considerable amount of experimental data on the configurations of subchains. Recent theoretical studies of intrachain moments have also been done by a number of authors,[3-10] although the problem was first addressed by Peterlin[11] as long ago as 1955. Early work on the perturbation series of the expansion factors

$$\alpha_{ij}^2 = \langle R_{ij}^2 \rangle / \langle R_{ij}^2 \rangle_0 = \langle R_{ij}^2 \rangle / |j - i|$$

$$\alpha_{ij}^{-1} = \langle R_{ij}^{-1} \rangle / \langle R_{ij}^{-1} \rangle_0 = (\pi/6)^{1/2} \langle R_{ij}^{-1} \rangle |j - i|^{1/2}$$

(where the 0 subscript signifies that the moment is taken at the Θ point) was done by Stockmayer and Albrecht[14] and by Teramoto, Kurata, and Yamakawa.[12,13] A pioneering Monte Carlo study was performed by Wall and Erpenbeck in 1959.[15]

Internal moments appear in the formal expressions for a number of polymer characteristics,[16] notably the intrinsic viscosity, as well as friction and diffusion coefficients. They also occur in the definitions of the radius of gyration and the hydrodynamic radius. Despite their importance, these moments are not well understood, and a simple description of their behavior is not yet available.

Our aim in this paper is to produce approximate expressions for both α_{ij}^2 and α_{ij}^{-1}, using the techniques described in Domb and Barrett.[17] Such formulas provide useful quantitative descriptions of the expansion factors. Furthermore, these approximate expressions will enable us to assess the approximations which other investigators have been obliged to use in order to make useful progress.

The approximate closed expressions obtained by Domb and Barrett are interpolation formulas combining rigourous perturbation expansions for small z with numerical results on self-avoiding walks, these being representative of chains with large excluded volume (large z). Near the Θ point, where $z = 0$, an expansion factor α_{ij}^m may, for long chains, be expanded in powers of z. These perturbation series were first derived by Teramoto[12] and further developed by Zimm, Stockmayer, and Fixman[18,19] for Gaussian chains. A general formulation, which is valid for lattice chains as well, may be found in the work of Barrett and Domb.[20,21] In particular, we write

$$\alpha_{ij}^m = 1 + C_1^{(m)} z + C_2^{(m)} z^2 + \ldots \quad (m = -1, 2)$$

$C_1^{(2)}$ has been computed by Teramoto et al.,[13] while $C_1^{(-1)}$ has been computed by Barrett.[10] (Approximate expressions for $C_1^{(-1)}$ have also been obtained by Yamakawa and Kurata[22] and by Fujita, Taki, Norisuye, and Sotobayashi.[23]) Far from the Θ point, the chain is simulated by a self-avoiding walk on a lattice. In this work, we report the results of a number of Monte Carlo simulations which show clearly the dependence of α_{ij}^m on i and j and also on the length of the complete chain.

The Domb–Joyce model[25] provides a theoretical framework within which we may then interpolate smoothly between the small-z and the large-z behavior. The result is a formula of the form

$$\alpha^m = (1 + az + bz^2)^c$$

where the exponent c and the coefficient b are chosen so that α^m has the correct asymptotic behavior. The coefficient a is then chosen so that α^m has the correct expansion to first order in z. Similar formulas have previously been applied with some success to the dimensions of flexible chains.[20,21,24,26]

2. Perturbation Series

We consider an N-step random walk, on or off lattice, and assign to each self-intersection of the walk a statistical weight $1 - w$. When averages over all configurations are taken, $w = 0$ yields random walk statistics, while $w = 1$ corresponds to the statistics of self-avoiding walks.

Let the position of the ith monomer be R_i and the separation between the ith and jth monomers be $|R_i - R_j|$. Then the moments $\langle R_{ij}^m \rangle$ depend not only on $|j - i|$ but also on i (i.e., the position of the subchain within the chain) and on the total contour length N. In order to render this complex situation more tractable, we define

$$n = j - i \qquad i = \zeta n \qquad j = (1 + \zeta) n \qquad \rho = \zeta/\lambda$$

$$N = (1 + \zeta + \lambda) n$$

We shall find it convenient to express the moments either as $\langle R_{ij}^m \rangle$ or as $\langle R_n^m(\zeta,\lambda) \rangle$, as appropriate. The excluded volume variable is defined in the two-parameter limit by

$$z = h_0 n^{1/2} w$$

where $h_0 = (3/2\pi)^{3/2} g/a^3$ is a scale factor depending on the particular random walk used to model the chain. For lattice walks g is the volume per lattice site and for Gaussian walks $g = 1$. a is the step length. The problem is therefore that of an n-step chain with attached end chains of length ζn and λn, respectively (see Figure 1). Without loss of generality, we take $\zeta \leq \lambda$ and $\rho \leq 1$. In

* Present and permanent address: Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7L 2W3, Canada.

0024-9297/84/2217-1561$01.50/0

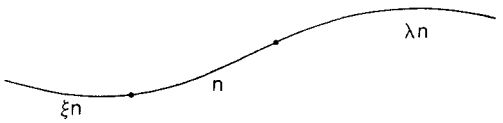

Figure 1. n-step central chain with end chains of length ζn and λn; $\lambda \geq \zeta$.

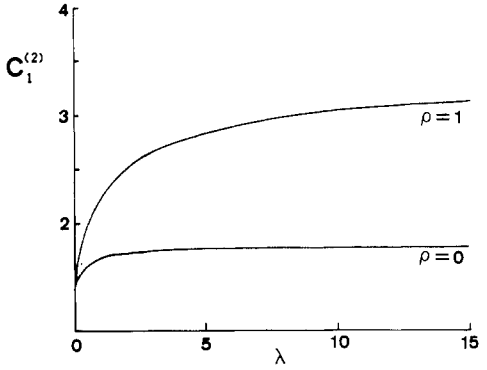

Figure 2. $C_1^{(2)}$ as a function of λ in the limits $\rho = 0$ and $\rho = 1$.

other words, we associate ζ with the shorter end chain. There are three limiting cases:

$$\zeta = \lambda = 0 \qquad \text{(no end chains)}$$

$$\zeta = 0, \qquad \lambda > 0 \qquad \text{(one end chain)}$$

$$\zeta > 0, \qquad \lambda > 0; \qquad 0 \leq \rho \leq 1 \qquad \text{(two end chains)}$$

We now write the expressions for the coefficients $C_1^{(2)}$ and $C_1^{(-1)}$ in terms of the parameters ζ and λ and consider the limiting behavior of both. From ref 13

$$C_1^{(2)} = \tfrac{4}{3}\{\tfrac{8}{3} - 4(1+\zeta)^{1/2} - 4(1+\lambda)^{1/2} + (1+\zeta+\lambda)^{-1/2} + \tfrac{8}{3}[(1+\zeta)^{3/2} + (1+\lambda)^{3/2} - \zeta^{3/2} - \lambda^{3/2}]\}$$

From ref 10

$$C_1^{(-1)} = -4\{(1+\zeta+\lambda)^{1/2} - \tfrac{1}{2}[(\zeta+\lambda)^{1/2} + \zeta^{1/2} + \lambda^{1/2}] + (\pi/4)\ln 4\zeta + \mathrm{Ti}_2(1/4\zeta) - \mathrm{Ti}_2(\zeta) + (\pi/4)\ln 4\lambda + \mathrm{Ti}_2(1/4\lambda) - \mathrm{Ti}_2(\lambda) + \tfrac{1}{2}(1+\zeta+\lambda)\tan^{-1}(\zeta+\lambda)^{1/2} - \tfrac{1}{2}(1+\zeta)\tan^{-1}\zeta^{1/2} - \tfrac{1}{2}(1+\lambda)\tan^{-1}\lambda^{1/2} - (\pi/4)\}$$

where

$$\mathrm{Ti}_2(x) = \int_0^x (\tan^{-1} y)/y \, dy$$

is the inverse tangent integral.[27]

In the limit $\zeta = \lambda = 0$, $C_1^{(2)} = {}^4/_3$, as is well-known, while $C_1^{(-1)} = \pi - 4$. In the single-end-chain limit, $C_1^{(2)}$ has the value ${}^{16}/_9$ and $C_1^{(-1)}$ the value $\pi(1 - \ln 4)$. These values are simply doubled in the two-end chain limit. (It should be noted that the two-end-chain limiting value is independent of ρ.) Figures 2 and 3 show the limiting curves for these coefficients, and we shall see that they form useful analogues for the large-z behavior of the moments.

3. Monte Carlo Algorithm

For a series of values of ζ and λ, samples of self-avoiding walks were generated by the method of Rosenbluth and Rosenbluth.[28] In this technique, the kth step of a generated walk is given a weight w_k proportional to the number of sites accessible for the next step. Thus, for an N-step walk, the weight of the walk is

$$W = \prod_{k=1}^{N} w_k$$

Let W_p be the weight of the pth walk in a given sample.

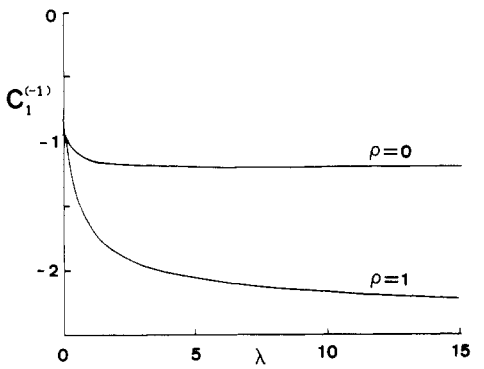

Figure 3. $C_1^{(-1)}$ as a function of λ in the limits $\rho = 0$ and $\rho = 1$.

Then for any configurational property Φ of the walk, the estimator is

$$\langle \Phi \rangle = \sum_p W_p \Phi_p / \sum_p W_p$$

where the summation is over all walks in the sample which survive to N steps.

For any N-step walk, the initial and final steps i and j of the n-step subchain may be easily determined once ζ and λ are specified. For ζ and λ fixed, and a series of values of n, one records the lengths $|R_i - R_j|$ and the weight of the walk. It is important to note that the estimates are subchain averages where the weights are those of the complete chain of N steps. One unfortunate aspect of this is that the data are those of short chains while the difficulties of chain generation are those associated with long chains.

A separate sample is required for each pair (ζ, λ). The sample size used was 100 000 walks of length $N = 300$. The set of subchain lengths chosen varied with each pair of values of (ζ, λ).

4. Asymptotic Form of $\langle R_{ij}^m \rangle$

It is reasonable to suppose that as n tends to large values

$$\langle R_n^m(\zeta,\lambda) \rangle \sim A_m(\zeta,\lambda) n^{\gamma m}$$

An interesting question concerns the value of γ_m. des Cloizeaux[4] suggests that there are three universality classes, corresponding to the three limiting cases of the previous section: no end chains, a single end chain, and two end chains. The first class has been well studied in the case of the second moment, and the exponent is widely supposed to be close to the Flory value 1.2 (recent renormalization group calculations put the value at 1.176).[29] If one accepts the Domb probability distribution[30]

$$P_N(l) = c_N l^\delta \exp -[l/\langle R_N^2 \rangle^{1/2}]^\delta$$

and that

$$\langle R_N^2 \rangle \sim A N^{2\nu}$$

then it is easy to show the scaling relation

$$\gamma_m = m\nu$$

We shall suppose this relation to hold for all three classes, which however still leaves open the value of ν for the second and third classes. Redner[7] has found some evidence for $\nu = 0.615$ in the case of a single end chain, and it is likely that ν will be larger for the case of two end chains. Nonetheless, and particularly for the chain lengths studied in this work, it is impossible to distinguish by Monte Carlo methods among possible differences of this size, so that in what follows we have assumed the Flory value for all three classes. We have further assumed that the first

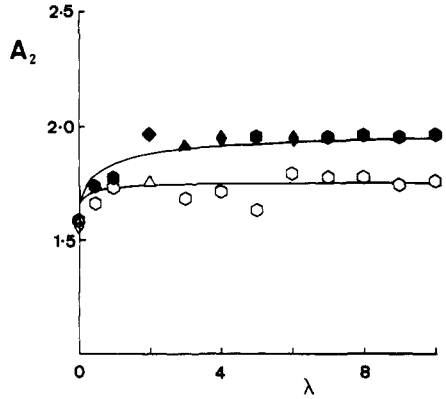

Figure 4. A_2 vs. λ in the two limiting cases $\rho = 0$ and $\rho = 1$: (○, ●) sc lattice; (◇, ◆) bcc lattice; (△, ▲) fcc lattice.

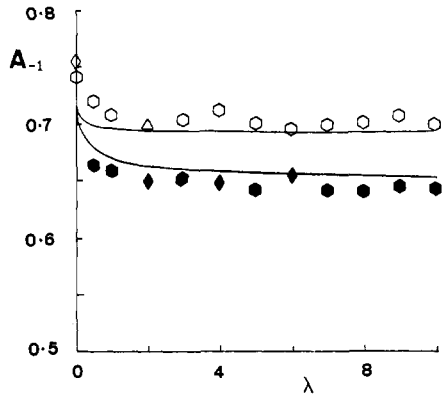

Figure 5. A_{-1} vs. λ in the two limiting cases $\rho = 0$ and $\rho = 1$. Symbols as for Figure 4.

correction term is proportional to $n^{\gamma_m - 1/2}$ and that further correction terms are of Darboux type. That is we assume that

$$\langle R_n{}^m(\zeta,\lambda)\rangle = n^{m\nu}[A_m + B_m/n^{1/2} + C_m/n + ...]$$

In the event, the constants C_m, D_m, ... do not appear to be significant, and so this expression was truncated to a linear one. The computed points were then fitted by standard least-squares methods to estimate the value of the amplitude A_m as a function of ζ, λ.

We restrict ourselves in fact to a study of the dominant amplitude A_m as a function of λ in the two limiting cases $\rho = 0$ and $\rho = 1$. Recall that $z = h_0 n^{1/2}$ for self-avoiding walks. Then if

$$\langle R_n{}^m\rangle \sim A_m n^{m\nu} = A_m (h_0 n^{1/2})^{2m\nu}/h_0{}^{2m\nu}$$

we should have

$$\langle R_n{}^m\rangle \sim E_m z^{2m\nu}$$

If two-parameter theory is valid, then E_m should not depend upon the particular class of walk used to model the polymer. We have tested this proposition by generating the samples on the three cubic lattices. As can be seen in Figures 4 and 5, all points appear to lie close to the "master curves" described in the next section.

As can also be seen from Figures 4 and 5, the behavior of E_m is not unlike the behavior of the first perturbation coefficient $C_1{}^{(m)}$, as shown in Figures 2 and 3. For both $m = 2$ and -1, the curves tend rapidly to an asymptotic value as λ increases.

5. Approximate Formulas

The approximate formulas are obtained by interpolation between the perturbation results of section 2 and the asymptotic expressions obtained in the previous section.

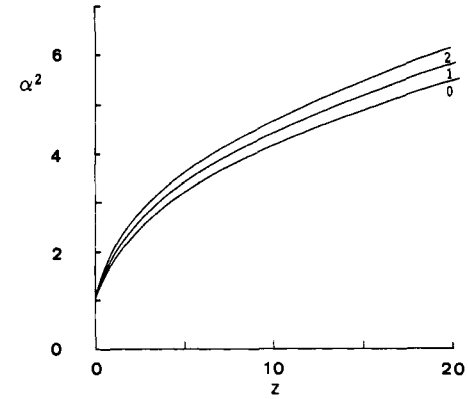

Figure 6. Approximate function for α^2, in the limit of large λ: (0) no end chains; (1) one end chain; (2) two end chains.

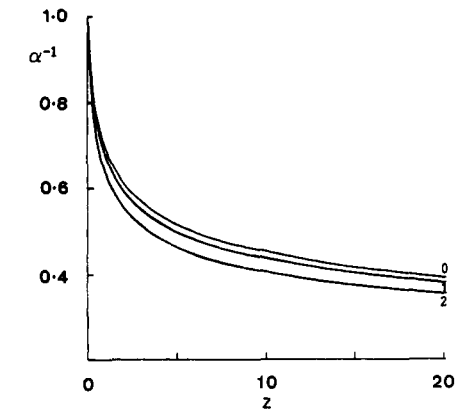

Figure 7. Approximate function for α^{-1}, in the limit of large λ. Symbols as in Figure 6.

Table I
Comparison of Approximate Formulas for $\alpha_{ij}{}^2$ with Monte Carlo Results of Wall and Erpenbeck[15]

N	n	λ	ρ	z	eq 1	ref 15
200	50	3	0	3.59	3.03	3.04
320	160	1	0	6.43	3.74	3.86
400	300	$^1/_3$	0	8.80	4.16	4.19
520	130	2	$^1/_2$	5.79	3.86	3.92
600	300	$^1/_2$	1	8.80	4.37	4.29

Similar formulas proposed for chain dimensions have been based upon a number of perturbation coefficients and an enormous body of numerical evidence.[17] In this case we have but one series coefficient and clearly much less numerical information; however, we propose the following two formulas which well fit the data we have obtained.

$$\alpha^2(\zeta,\lambda) = \left\{1 + 5C_1{}^{(2)}z\left[1 + \frac{1.89 + 2\lambda(1+\rho)}{1 + \lambda(1+\rho)}z\right]\right\}^{0.2} \quad (1a)$$

$$\alpha^{-1}(\zeta,\lambda) = \left\{1 - 10C_1{}^{(-1)}z\left[1 + \frac{2.1 + 4\lambda(1+\rho)}{1 + \lambda(1+\rho)}z\right]\right\}^{-0.1} \quad (1b)$$

These are graphed in Figures 6 and 7, and the effect of the presence of end chains may be readily observed. A comparison of the predictions of the first equation with results of Wall and Erpenbeck[15] is given in Table I.

We now consider some of the approximations other investigators have made concerning intrachain moments. Much of the work published on polymer dynamics contains one or more of these approximations,[16] and it is therefore of interest to compare them with our expressions.

Table II
Examination of the Approximation $\alpha_{ij}^{-1} = (\alpha_{ij}^2)^{-1}$; $z \gg 1$

λ	ρ	a	$1/a^{1/2}$	b
0	0	1.659	0.776	0.749
∞	0	1.78	0.750	0.678
∞	1	2.04	0.700	0.674

Table III
Comparison of the Akcasu Formula with the Approximate Formula

λ	ρ	K	z	eq 1	Akcasu
0	0	2.8	1	1.82	1.99
			5	3.22	3.32
			10	4.21	4.22
			100	10.48	9.94
1	0	3.0	1	1.92	2.03
			5	3.40	3.40
			10	4.44	4.33
			100	11.06	10.20
10	1	3.5	1	2.15	2.13
			5	3.84	3.58
			10	5.02	4.58
			100	12.49	10.83

The most common assumption made concerning α_{ij}^{-1} is that

$$\alpha_{ij}^{-1} = (\alpha_{ij}^2)^{-1/2}$$

We have in fact assumed that this is so for the exponent; however, one may usefully make a comparison of prefactors. If for large z we write

$$\alpha_{ij}^2 \sim az^{0.4} \qquad \alpha_{ij}^{-1} \sim bz^{-0.2}$$

then we want to examine the proposition that

$$b = a^{-1/2}$$

For small z, where the perturbation series is valid, this approximation is wrong, and the error should be $\mathcal{O}(z)$. It can be seen from Table II that the error incurred in the approximation is less than 10% and that it is considerably less than this over much of the chain.

The first of the two approximations concerning α_{ij}^2 that we shall examine is that of Akcasu, Benmouna, and Alkhafaji,[31] who suggest a Flory-type formula:

$$\alpha_{ij}^5 - \alpha_{ij}^3 = Kz$$

where K is a constant. We might expect this to be a reasonable choice. The curve labeled "0" in Figure 6 is simply the expansion factor for the full chain, and it will be recalled that the Flory function approximates this fairly well.[17] Since the other two curves are similar in shape, we expect that they also may be approximated by Flory-type functions. Some results obtained from the Akcasu formula are shown in Table III, and they can be seen to be in broad agreement with the values given by eq 1. The difficulty with a Flory-type formula is that it only contains a single adjustable parameter K. The choice of K determines the region where the function will give reasonably good results. We have used the following values of K, but they should not be taken too seriously:

$$\zeta = \lambda = 0 \qquad (K = 2.8)$$

$$\zeta = 0, \qquad \lambda > 0 \qquad (K = 3.0)$$

$$\zeta > 0, \qquad \lambda > 0 \qquad (K = 3.5)$$

Ullman[32] has proposed an approximation which is a modification of the Peterlin model. Peterlin[11] suggests that

$$\alpha_{ij}^2 \propto |j - i|^{\epsilon}$$

and our model is in fact equivalent to this if $\epsilon = 0.2$. Ullman suggests that ϵ should be a monotonically increasing function of $n = |j - i|$. If $n = 0$, then $\epsilon = 0.0$, whereas if $n = N$, then $\epsilon = 0.2$. This proposal, like that of Akcasu, is an attempt to improve upon the "thermal blob" theory as described by Weill and des Cloizeaux.[33] If

$$\alpha_{ij}^2 = A_n^{\gamma} = A|j - i|^{\gamma}$$

then it is clear from the results of section 4 that A is an increasing function of z for γ fixed. It is also possible to postulate that A is fixed and then one will discover that γ is an increasing function of z. The obvious advantage of this point of view is that it permits the use of Gaussian statistics for small values of z. That is to say, if the excluded-volume condition is weak or if the subchains are short, then one may take $\epsilon = 0$ without great error.

It is clear that, within a given chain, longer subchains exhibit greater excluded volume than shorter ones, and this feature is contained in a natural way in our description. Consider a chain of length N, whose excluded volume is characterized by the variable

$$Z = h_0 N^{1/2} w$$

Now subchains, which may have any contour length $0 < n \leq N$, have an excluded volume which is characterized by the variable

$$z = h_0 n^{1/2} w$$

That is to say, if Z is fixed, then w is fixed; however, z will vary directly as the root of the subchain length.

6. Radius of Gyration and Hydrodynamic Radius

The radius of gyration of a linear polymer is defined by the expression[16]

$$\langle S^2 \rangle = (1/N^2) \sum_{i<j} \langle R_{ij}^2 \rangle$$

which may be written

$$\langle S^2 \rangle = (1/N^2) \sum_{i<j}^{N} \alpha_{ij}^2 \langle R_{ij}^2 \rangle_0 = (1/N^2) \sum_{i<j}^{N} \alpha_{ij}^2 |j - i|$$

The expansion factor may then be expressed as

$$\alpha_s^2 = (6/N^3) \sum_{i<j} \alpha_{ij}^2 |j - i|$$

Then, making a change of variable $(i,j) \rightarrow (x,y)$ and replacing the sums by integrals as follows

$$x = \frac{2i}{N} - 1 \qquad y = \frac{2j}{N} - 1 \qquad \sum_i \ldots \rightarrow \frac{N}{2} \int_{-1}^{1} dx \ldots$$

we obtain

$$\alpha_s \approx \int \int_{-1}^{1} dx\, dy\, \alpha^2(x,y) |y - x|$$

The integrals were performed by using Gaussian quadrature, and Table IV compares the results obtained in this way with those given by the Domb–Barrett expression:[21]

$$\alpha_s^2 = (1 + 12.8z + 52.5z^2 + 70.3z^4)^{1/10}$$

The agreement can be seen to be most satisfactory. A similar procedure can be followed to find an approximate expression for the hydrodynamic radius, which is defined by

$$R_H^{-1} = (1/N^2) \sum_{i<j} \langle R_{ij}^{-1} \rangle = (6/\pi)^{1/2} \sum_{i<j} \alpha_{ij}^{-1} |j - i|^{-1/2}$$

so that

$$\alpha_H^{-1} \approx \frac{3(2^{1/2})}{32} \int \int_{-1}^{1} dx\, dy\, \alpha^{-1}(x,y) |y - x|^{-1/2}$$

Table IV
Comparison of α_s^2 As Determined by Summation of (1) with DB Formula

z	α_s^2(eq 1)	α_s^2(DB)
0	1	1
1	1.73	1.64
2	2.15	2.06
3	2.48	2.39
4	2.76	2.68
5	2.99	2.92
10	3.89	3.85
15	4.56	4.52
20	5.10	5.07
40	6.70	6.69
100	9.65	9.65

Table V
α_H^{-1} As Computed by Summation of (1) and with Approximate Formula

z	α_H^{-1}(eq 1)	α_H^{-1}(app)
0	1	1
1	0.80	0.79
2	0.72	0.72
3	0.68	0.67
4	0.64	0.64
5	0.62	0.62
10	0.55	0.55
20	0.51	0.51
40	0.42	0.42
100	0.35	0.35

The values thus computed are displayed in Table V. If we perform the integral by using only the large-z expression for α_{ij}^{-1}, then we may infer the asymptotic formula

$$\alpha_H^{-1} \sim 0.88z^{-0.2}$$

and combine it with the Stockmayer–Albrecht perturbation coefficient[12] to devise an approximate closed-form expression for α_H^{-1}:

$$\alpha_H^{-1} = (1 + 6.09z + 3.59z^2)^{-0.1}$$

The values which this expression gives are compared in Table V with those obtained by summation of (1), and again the agreement is acceptable.

7. Discussion

The value of the approximate formulas (1) rests, naturally enough, upon the accuracy of the Monte Carlo experiments and also on a number of assumptions. The best evidence we can offer for the correctness of the result is Table IV, wherein we compare values of α_s^2 determined from a summation of (1) with those given by the Domb–Barrett equation derived some years ago[17,20] and recently tested by experiment.[24,26] We also take comfort from the fact that the early Monte Carlo results of Wall and Erpenbeck[15] are in good agreement with (1). We have no such confirmation for α_{ij}^{-1}; however, there is no reason to suppose that this result is less reliable than that for α_{ij}^2.

It should be noted that the results presented here presuppose the validity of two-parameter theory. It is now well-known from renormalization group studies that two-parameter theory cannot be rigorously true, except in the limit of small excluded volume. Nonetheless two-parameter results have long provided useful approximations even for large excluded volume. Our results are presented in that spirit.

The principal assumption we have made is that the expansion factor follows a fifth-power law. This appears to be a satisfactory supposition for full-length chains, but the question remains open for subchains. We have also assumed that the behavior of the functions α_{ij}^2 and α_{ij}^{-1} may be adequately interpolated by (1) for $\lambda > 0$ and $0 < \rho < 1$. We have made no attempt to determine the detailed behavior of these functions except for limiting values of ρ.

In this paper we have applied our approximate formulas to derive a new expression for the hydrodynamic radius and to the assessment of other approximations which have been made concerning subchain moments. It will be interesting to see if they may also be useful in the determination of other polymer properties, for example the intrinsic viscosity and friction coefficients, when excluded volume is taken into account.

Acknowledgment. I am grateful for a number of useful discussions, particularly for those with Professor W. H. Stockmayer of Dartmouth College. I wish also to express my thanks to the Department of Chemistry, Dartmouth College, for its generosity and hospitality during 1981–1982. This work was supported, in part, by Grants CHE-8000910 and also DMR79-13227 of the Polymer Program, Division of Materials Research, National Science Foundation of the United States, and in part by CRAD Grant 3610-656, Department of National Defence, Canada.

References and Notes

(1) de Gennes P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Lodge, T. P., private communication.
(3) Baumgartner, A. *Z. Phys. B* **1981**, *B42*, 265.
(4) des Cloizeaux, J. *Phys. Rev. A* **1974**, *10*, 1665, 1980; *J Phys. (Paris)* **1974**, *41*, 223.
(5) Mattice, W. L. *Macromolecules* **1981**, *14*, 1481.
(6) Oono, Y.; Ohta, T. *Phys. Lett. A* **1981**, *85*, 480.
(7) Redner, S. *J. Phys. A* **1980**, *13*, 3525.
(8) Allegra, G.; Ganazzoli, F. *J. Chem. Phys.* **1982**, *76*, 6354.
(9) Curro, J. G.; Schaefer, D. W. *Macromolecules* **1980**, *13*, 1199.
(10) Barrett, A. J. *J. Phys. A* **1983**, *16*, 2321.
(11) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2464.
(12) Teramoto, E. *Busseiron Kenkyu* **1951**, *39*, 1.
(13) Teramoto, E.; Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *28*, 785.
(14) Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215.
(15) Wall, F. T.; Erpenbeck, J. J. *J. Chem. Phys.* **1959**, *30*, 634, 637.
(16) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(17) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179.
(18) Zimm, B. H.; Stockmayer, W. H.; Fixman, M. *J. Chem. Phys.* **1953**, *21*, 1716.
(19) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.
(20) Barrett, A. J.; Domb, C. *Proc. R. Soc. London, Ser. A* **1979**, *367*, 143.
(21) Barrett, A. J.; Domb, C. *Proc. R. Soc. London, Ser. A* **1981**, *376*, 361.
(22) Yamakawa, H. and Kurata, M. *J. Phys. Soc. Japan* **1958**, *13*, 94.
(23) Fujita, H.; Taki, N.; Norisuye, T.; Sotobayashi, H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2255.
(24) Tanaka, G. *Macromolecules* **1980**, *13*, 1513.
(25) Domb, C.; Joyce, G. S. *J. Phys. C* **1972**, *5*, 956.
(26) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(27) Lewin, L. "Dilogarithms and Associated Functions"; MacDonald: London, 1958.
(28) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356.
(29) LeGuillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(30) Domb, C.; Willis, J.; Gilmers, G. *Proc. Phys. Soc. London* **1965**, *85*, 625.
(31) Akcasu, Z.; Benmouna, M.; Alkhafaji, S. *Macromolecules* **1981**, *14*, 147.
(32) Ullman, R. *Macromolecules* **1981**, *14*, 746.
(33) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.