A General Treatment of Random-Flight Statistics with and without Excluded Volume

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ABSTRACT: We present a new formulation for the distributions of the one-, two-, and three-dimensional radii of gyration of linear and branched random-flight chains, and show how it can be extended to include the excluded volume effect. The formulation is shown to be especially suited for numerical methods. As an example, the excluded volume problem is then solved numerically for random-flight chains with up to 100 statistical segments in the limit of small z, $[z = n^{1/2}b(n/4\pi\langle S^2\rangle_0)^{3/2}]$, where n is the number of statistical segments, b is the binary cluster integral, and $\langle S^2\rangle_0$ is the mean-square radius of gyration of the assembly of unperturbed chains. The results show that the equation for the chain expansion factor, $\alpha_S{}^2 = 1 + (^{134}/_{105})z - \ldots$, is adequate only for $n > 10^3$. Indeed the coefficient $(^{134}/_{105})$ is in error by as much as 30–10% for polymers of n in the range of 10–100. We suggest the following correction to the above equation: $\alpha_S{}^2 = 1 + (^{134}/_{105})[1 + (0.885/n^{0.462})]z - \ldots$.

Distribution functions characterizing the one-, two-, and three-dimensional radii of gyration of random-flight chains have been intensively studied over the last several years.[1–14] This is not unexpected because of the vital role that these distributions play in various aspects of polymer science. Until now, only the statistics of linear chains had been considered in detail. The problem of determining the distribution of the radius of gyration or its square S^2, for linear chains, has been approached from various points of view. Fixman[1] and Coriell and Jackson[5] obtained Fourier transforms (characteristic functions) of the distribution of S^2 and then used different mathematical techniques to give approximate solutions of the problem for various ranges of S^2. Forsman and Hughes[2–4,10] formulated the problem in terms of a series of convolution integrals and gave approximate solutions over similar ranges of S^2. Later, Fujita and Norisuye[11] inverted Fixman's[1] characteristic function analytically in terms of Bessel functions for low and high values of $S^2/\langle S^2\rangle_0$ (where $\langle S^2\rangle_0$ is the unperturbed mean-square radius of gyration). They observed agreement with Fixman's values for low $S^2/\langle S^2\rangle_0$ but disagreement in the range of high $S^2/\langle S^2\rangle_0$. All these results, however, were valid only for sufficiently large values of n (the number of statistical segments in a polymer chain).

The first complete solutions for the one-, two-, and three-dimensional distributions of the radii of gyration as functions of n were given by Hoffman and Forsman,[7–9] who presented numerical solutions to the convolution integrals of Forsman and Hughes.[2–4] Their solutions agreed well with the asymptotic solutions derived earlier by Fixman,[1] Forsman,[2,4] and Forsman and Hughes.[3] Hoffman and Forsman[8] also presented numerical results for the distribution of the one-dimensional radius of gyration, $S_x{}^2$ for short, linear random-flight chains (n = 2, 4, and 10). Coriell and Jackson,[6] however, reported an analytic solution for the distribution for n = 2 which was in substantial disagreement with the numerical solution.[8] Later, Gupta and Forsman[14] showed that the discrepancy was the result of errors in the normalization constant, and tabulated corrected distribution functions.

In this paper, we present a new, general formulation for the distribution of the one-, two-, and three-dimensional radii of gyration of assemblies of random-flight chains of any type of branching. The method is applicable to finite as well as infinite chains. We also show that the formulation gives a general solution to the excluded-volume problem for branched as well as linear chains. The analysis is then used to generate solutions to the excluded-volume problem for assemblies of linear chains with emphasis on chain-length effects.

Although many of the essential features of the solution to the excluded-volume problem were given in the earliest publications,[15–19] this problem is far from being satisfactorily solved, and indeed previous treatments have been limited to chains with infinite segments. The excluded-volume effect is measured in terms of two expansion factors α_L and α_S, the ratios of the root-mean-square end-to-end distance and the radius of gyration to those of the unperturbed assembly of molecules. Existing theories for prediction of the expansion factors may be classified according to the following statistical mechanical models which serve as their starting points.

The most rigorous model applied to date[17–24] assumes polymer molecules in dilute solution to act as an assembly of Kuhn chains with polymer–solvent and polymer–polymer interactions written as a potential of mean force acting between nonbonded masses of the chain backbone. We will

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(24) F. Bueche, *ibid.*, **21**, 205 (1953).

designate this simply as the Kuhn model. Zimm, Stockmayer, and Fixman,[17,18,22] Yamakawa, *et al.*,[21,23] and Bueche[24] used the cluster expansion technique equivalent to that applied in the theory of dilute gases[25] to give the expansions

$$\alpha_S^2 = 1 + \frac{134}{105}z - 2.082z^2 + \dots \quad (1)$$

$$\alpha_L^2 = 1 + \frac{4}{3}z - \left(\frac{16}{3} - \frac{28\pi}{27}\right)z^2 + 6.459z^3 + \dots \quad (2)$$

where

$$z = n^{1/2}b(n/4\pi\langle S^2\rangle_0)^{3/2} \quad (3)$$

In eq 3, b is the binary cluster integral (defined later in this paper), n is the number of Kuhn segments, and $\langle S^2\rangle_0$ is the mean-square radius of gyration of the assembly of unperturbed chains. Recently Chikahisa[26] used the cumulant expansion method to give the next term in eq 2 as $-1.3438z^4$. Since for real polymer systems $n > 100$, eq 1 and 2 hold for small interactions indeed. They are, however, rigorous expressions for the limiting behavior at vanishing b.

An important result of the segment cluster theory is that the coil expansion is a function of only one dimensionless parameter z which incorporates both energy and chain length dependences. One would thus be tempted to interpret eq 1 and 2, therefore, as also representing the behavior of α_S and α_L with decreasing chain length. This is, of course, not correct, since they were both derived in the limit of infinite chain length. In this paper we will show that for chain lengths of most interest chain expansion is a function of both z and n.

We should like to add that in recent years a number of investigators[27-34] have attacked the excluded-volume problem for the Kuhn model with a variety of mathematical techniques. Since only one method has given a solution for chain expansion,[27,30] the other methods must, at present, be considered as new formulations of the problem which show promise for future development, and will not be considered further here. Alexandrowicz,[27,30] however, has used an integral equation approach to show that α_L increases as $n^{0.118}$ as $n \to \infty$. This result is in good agreement with predictions of the segment cloud model described below.

The segment could model,[11,15,16,35-38] introduced by Flory,[15,16] is less fundamental in its description of polymer chains in infinitely dilute solution than the Kuhn model discussed above. It offers the considerable advantage, however, of being far more mathematically tractable. Flory[15,16] assumed that the free energy of a polymer molecule could be expressed as the sum of two terms, the free energy of mixing of a cloud of segments and an entropy term derived from the theory of rubber elasticity. The model suffers from a major conceptual difficulty. The contiguous nature of the chain molecule enters into the theory both through the rubber elasticity term and through application of the Flory-Huggins[16] theory in the free energy of mixing term.[39] Flory[15,16] obtained the following closed expression for α_L

$$\alpha_L^5 - \alpha_L^3 = \frac{3\sqrt{3}z}{2} \quad (4)$$

Equation 4 was derived by maximizing the distribution of α_L rather than integrating to obtain moments of the distribution, a procedure that was certain to introduce some (unknown) error, but which gave results in a convenient form.

Forsman and Hughes[35] were the first to obtain α_S^2 by determining the second moment of the distribution of S in the presence of polymer–solvent and intramolecular polymer–polymer interactions. They found the following expression for the asymptotic behavior with increasing z

$$\alpha_S^2 = (3/\pi^{4/5})z^{2/5} + 0.243 \quad (5)$$

which was applicable for values of α_S greater than about 2.

It may be mentioned here that many workers[40-43] have used Monte Carlo methods to study the excluded-volume problem. Though their results are valid only for a relatively small number of steps, they observe α^5 proportional to $n^{1/2}$, which is the same functionality given in eq 4 and 5.

The excluded-volume problem at nonvanishing z has never been solved for the Kuhn model. For lack of better information, therefore, it was suggested[44] that the Flory expression be modified to agree with the more rigorous results of the segment cluster method given in eq 1 and 2 in the limit of vanishing z. The result is

$$\alpha_S^5 - \alpha_S^3 = \frac{134z}{105} \quad (6)$$

which is in good agreement with the asymptotic form given in eq 5.

We take this approach here, but will show that $(\alpha_S^5 - \alpha_S^3)/z$ is not then a constant but a function of n.

Generalized Expression for the Distribution of Radii of Gyration for Linear and Branched Chains

We assume the usual Kuhn model of $n + 1$ masses (numbered from 0 to n) connected by n statistical segments (numbered from 1 to n) of mean-square length l^2 each. The gaussian parameter characterizing the end-to-end distance of the assembly of chains is denoted by β^2 and for the individual statistical segments by $n\beta^2$. In this model, the probability of observing any configuration in the unperturbed state is given by

$$(\sqrt{n}\beta/\sqrt{\pi})^{3n} \exp\left[-n\beta^2 \sum_{j=1}^{n}(x_j^2 + y_j^2 + z_j^2)\right] \times \prod_{j=1}^{n} dx_j dy_j dz_j \quad (7)$$

where x_j, y_j, and z_j represent the components of the vector defining the jth statistical segment. In matrix notation, eq 7

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(33) H. Yamakawa, *ibid.*, **48**, 3845 (1968).
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(36) P. J. Flory and S. Fisk, *ibid.*, **44**, 2243 (1966).
(37) M. Kurata, W. H. Stockmayer, and A. Roig, *ibid.*, **33**, 151 (1960).
(38) S. K. Gupta, R. F. Hoffman, R. E. Hughes, and W. C. Forsman, to be submitted to *J. Polym. Sci.*
(39) Equation 4 was originally derived in terms of parameters introduced in the Flory–Huggins theory. It was shown, however, that it could be equally well written in terms of z (ref 17).
(40) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 637 (1959).
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may be written as

$$W^0_{x,y,z}(\mathbf{x}, \mathbf{y}, \mathbf{z})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}\mathrm{d}\mathbf{z} = (\sqrt{n}\beta/\sqrt{\pi})^{3n} \exp[-n\beta^2(\mathbf{x}^T\mathbf{x} + \mathbf{y}^T\mathbf{y} + \mathbf{z}^T\mathbf{z})]\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}\mathrm{d}\mathbf{z} \quad (8)$$

Here

$$\mathbf{x}^T = [x_1, x_2, \ldots, x_n] \quad (9)$$

and

$$\mathrm{d}\mathbf{x} = \mathrm{d}x_1\mathrm{d}x_2 \ldots \mathrm{d}x_n \quad (10)$$

with similar equations for the y and z components. Equation 8 must first be transformed into center of mass coordinates, $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ where

$$\hat{\mathbf{x}}^T = [\hat{x}_1, \hat{x}_2, \ldots, \hat{x}_n] \quad (11)$$

We shall present the transformation equations first for linear polymer molecules and, in the next section, for branched chains. For linear chains

$$x_j = \hat{x}_j - \hat{x}_{j-1} \quad (12)$$

and, for $j = 1$, using the definition of the center of mass

$$x_1 = \hat{x}_1 - \hat{x}_0 = 2\hat{x}_1 + \hat{x}_2 + \hat{x}_3 + \ldots + \hat{x}_n \quad (13)$$

with equivalent expressions in y and z coordinates. Equations 12 and 13 may thus be written as

$$\mathbf{x} = \mathbf{P}\hat{\mathbf{x}}, \quad \mathbf{y} = \mathbf{P}\hat{\mathbf{y}}, \quad \mathbf{z} = \mathbf{P}\hat{\mathbf{z}} \quad (14)$$

with

$$\mathbf{P} = \begin{bmatrix} 2 & 1 & 1 & 1 & \ldots & 1 & 1 \\ -1 & 1 & 0 & 0 & \ldots & 0 & 0 \\ 0 & -1 & 1 & 0 & \ldots & 0 & 0 \\ . & . & . & . & \ldots & . & . \\ 0 & 0 & 0 & 0 & \ldots & -1 & 1 \end{bmatrix} \quad (15)$$

Appropriate expressions for $\mathbf{P}$ for branched chains will be discussed later, and we will show that the following treatment is completely general and can be applied to molecules with any type of branching. The jacobian of the transformation from the $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$, to the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ system is a constant, and so eq 8 becomes

$$W^0_{\hat{x},\hat{y},\hat{z}}(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}} = C(\sqrt{n}\beta/\sqrt{\pi})^{3n} \exp[-n\beta^2(\hat{\mathbf{x}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{x}} + \hat{\mathbf{y}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{y}} + \hat{\mathbf{z}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{z}})]\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}} \quad (16)$$

where C is the normalization constant.

To get the distribution of S^2, eq 16 must be integrated over all values of $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ consistent with the constraint

$$S^2 = \frac{1}{n+1}\sum_{j=0}^{n} (\hat{x}_j^2 + \hat{y}_j^2 + \hat{z}_j^2) \quad (17)$$

In the center of mass coordinates, the summation in eq 17 for the x component is given as

$$\sum_{j=0}^{n} \hat{x}_j^2 = \sum_{j=1}^{n} \hat{x}_j^2 + \left[\sum_{j=1}^{n} x_j\right]^2 = \mathbf{x}^T\mathbf{M}\mathbf{x} \quad (18)$$

where

$$\mathbf{M} = \begin{bmatrix} 2 & 1 & 1 & 1 & . & . & 1 \\ 1 & 2 & 1 & 1 & . & . & 1 \\ 1 & 1 & 2 & 1 & . & . & 1 \\ . & . & . & . & . & . & . \\ 1 & 1 & 1 & 1 & . & . & 2 \end{bmatrix} \quad (19)$$

with equivalent expressions in y and z. Note that $\mathbf{M}$ is the same for branched chains. On using the Fourier representation of the δ function[45] in eq 16 we get

$$W^0(S^2) = C\int_{-\infty}^{\infty}\int \ldots \int \exp[-n\beta^2(\hat{\mathbf{x}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{x}} + \hat{\mathbf{y}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{y}} + \hat{\mathbf{z}}^T\mathbf{P}^T\mathbf{P}\hat{\mathbf{z}})] \exp\left[2\pi i\omega\left\{\frac{\hat{\mathbf{x}}^T\mathbf{M}\hat{\mathbf{x}} + \ldots}{n+1} - S^2\right\}\right]\mathrm{d}\omega\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}} \quad (20)$$

or

$$W^0(S^2) = C\int_{-\infty}^{\infty} \ldots \int \exp[-n\beta^2(\hat{\mathbf{x}}^T\mathbf{D}\hat{\mathbf{x}} + \hat{\mathbf{y}}^T\mathbf{D}\hat{\mathbf{y}} + \hat{\mathbf{z}}^T\mathbf{D}\hat{\mathbf{z}})] \exp[-in(n+1)\beta^2S^2\phi]\mathrm{d}\phi\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}} \quad (21)$$

where we have defined

$$\mathbf{D} = \mathbf{P}^T\mathbf{P} - i\phi\mathbf{M} \quad (22)$$

and

$$\phi = \frac{2\pi\omega}{n(n+1)\beta^2} \quad (23)$$

Equation 21, on integrating over $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ gives[46]

$$W^0(S^2) = C\int_{-\infty}^{\infty} \frac{\exp[-in(n+1)\beta^2S^2\phi]\mathrm{d}\phi}{|\mathbf{D}(\phi)|^{3/2}} \quad (24)$$

Equation 24 is a completely general statement of the unperturbed distribution of radii of gyration of assemblies of random-flight chains. We note that only the real part of $\mathbf{D}$ is a function of the nature of the branching. Finally, from the theory of characteristic functions, expressions for the distributions of the one- and two-dimensional radii can be obtained from eq 24 by replacing the denominator in the integrand by $|\mathbf{D}(\phi)|^{1/2}$ and $|\mathbf{D}(\phi)|$, respectively.

$W^0(S^2)$ for Linear Chains

For a linear chain, we may write eq 25 from eq 15 and 22.

$$\mathbf{D}(\phi) = \begin{bmatrix} 5-2i\phi & 1-i\phi & 2-i\phi & 2-i\phi & \ldots & 2-i\phi & 2-i\phi \\ 1-i\phi & 3-2i\phi & 0-i\phi & 1-i\phi & \ldots & 1-i\phi & 1-i\phi \\ 2-i\phi & 0-i\phi & 3-2i\phi & 0-i\phi & \ldots & 1-i\phi & 1-i\phi \\ 2-i\phi & 1-i\phi & 0-i\phi & 3-2i\phi & \ldots & 1-i\phi & 1-i\phi \\ . & . & . & . & \ldots & . & . \\ 2-i\phi & 1-i\phi & 1-i\phi & 1-i\phi & \ldots & 3-2i\phi & 0-i\phi \\ 2-i\phi & 1-i\phi & 1-i\phi & 1-i\phi & \ldots & 0-i\phi & 2-2i\phi \end{bmatrix} \quad (25)$$

The determinant $|\mathbf{D}(\phi)|$ may be simplified by a series of elementary row and column transformations to give a five-

(45) A. Papoulis, "The Fourier Integral and its Applications," 1st ed, McGraw-Hill, New York, N. Y., 1962.
(46) R. Bellman, "Introduction to Matrix Analysis," 2nd ed, McGraw-Hill, New York, N. Y., 1970.

banded determinant given in an earlier paper[14] and may be written as a continued product using a formula due to Bellman[46] as

$$|\mathbf{D}(\phi)| = \prod_{j=1}^{n}\left[4 - 2i\phi + \left\{2\cos\left(\frac{j\pi}{n+1}\right)\right\}\left\{2\cos\left(\frac{j\pi}{n+1}\right) + 4 - i\phi\right\}\right] \quad (26)$$

The normalization constant may be obtained using a theorem in Fourier transform theory[45]

$$\langle\psi^0\rangle = 2\pi F(0) = \frac{2\pi C}{|\mathbf{D}(0)|^{3/2}} = \frac{2\pi C}{(n+1)^3} \equiv 1 \quad (27)$$

where $F(\phi)$ is the characteristic function of $W^0(S^2)$ and

$$\psi = n(n+1)\beta^2 S^2 \quad (28)$$

Finally, we obtain

$$W^0(S^2) = \frac{(n+1)^3}{2\pi}\int_{-\infty}^{\infty}\frac{\exp[-in(n+1)\beta^2S^2\phi]d\phi}{|\mathbf{D}(\phi)|^{3/2}} \quad (29)$$

The numerical solution of eq 29 has already been presented for short chains.[14] It was observed that for n greater than about 10, the above formulation incorporating the continued product representation of $|\mathbf{D}(\phi)|$ (eq 26) was far more efficient than the multiple convolution method used previously.[7-9] Further details on the analysis and computations can be found elsewhere,[47] along with proof that eq 29 is mathematically equivalent to other formulations for the distribution of the radii of gyration of assemblies of finite and infinite random-flight chains.

$W^0(S^2)$ for Branched Chains

Equation 24 can be applied to assemblies of branched chains by determining the appropriate matrix **P** relating the description of the chains in the **x** and $\hat{\mathbf{x}}$ spaces. This procedure is relatively simple. For example, consider the branched chain shown in Figure 1. Equation 13 still applies. Equation 12 applies to all the statistical segments except numbers 9 and 10, since (in one dimension) we note that

$$x_9 = \hat{x}_9 - \hat{x}_6 \quad (30)$$

and

$$x_{10} = \hat{x}_{10} - \hat{x}_4 \quad (31)$$

For this example, therefore, **P** is given by eq 32. Equation

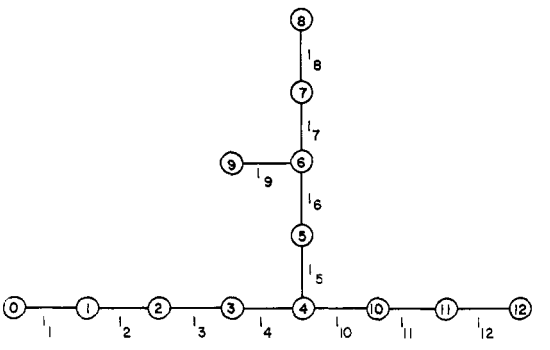

Figure 1. A branched chain.

32 differs only slightly from eq 15 for linear chains. In rows 9 and 10 of eq 32, the -1 appears in columns 6 and 4, indicating that statistical segments 9 and 10 extend between masses 6 and 9 and masses 4 and 10, respectively. We thus observe a simple one-to-one correspondence between the **P** matrix and the molecular architecture. Note, however, that the first row is determined by the center of mass criterion and thus is independent of branching.

The construction of **P** can be systematized to accommodate any form of branching. The first row is always the same. All $P_{i,i}$'s except $P_{1,1}$ are unity. All $P_{i,i-1}$'s equal -1 with the following exception. The masses are assumed to be numbered sequentially. If we count off the masses from zero to n, we will have to jump off the backbone at the *end* of each branch. Each row corresponding to the index of the mass j *following* each jump has a -1 in the column with an index equal to that of the mass to which mass j is connected. All other elements are zero.

The formulation presented here is a generalization of the matrix method for treating chain statistics published previously.[48] It was shown that for assemblies of any type of branched molecules, the one-dimensional radius of gyration S_x could be written in the following form[48] (The notation used here is not the same as in ref 48, but was selected to be compatible with this paper and other more recent publications.)

$$n(n+1)S_x^2 = \mathbf{x}^T\mathbf{F}\mathbf{x} \quad (33)$$

and

$$n(n+1)\langle S_x^2\rangle = \langle x^2\rangle \quad \text{trace } \mathbf{F} \quad (34)$$

$$\mathbf{P} = \begin{bmatrix}
2 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
-1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1
\end{bmatrix} \quad (32)$$

(47) S. K. Gupta, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pa., 1972.

(48) W. C. Forsman, *Macromolecules*, 1, 343 (1968).

or

$$n(n+1)\langle S^2\rangle = 3\langle x^2\rangle \quad \text{trace } \mathbf{F} \tag{35}$$

Since

$$(n+1)S_x{}^2 = \mathbf{x}^{\mathrm{T}}\mathbf{M}\mathbf{x} \tag{36}$$

it is straightforward to show that

$$\mathbf{F} = n(\mathbf{P}^{-1})^{\mathrm{T}}\mathbf{M}\mathbf{P}^{-1} \tag{37}$$

Whereas the **F** matrices are difficult to work with, the **P** matrices are far simpler.

We should also like to point out that if eq 37 is rearranged to give

$$\mathbf{M} = n^{-1}\mathbf{P}^{\mathrm{T}}\mathbf{F}\mathbf{P} \tag{38}$$

P can be expressed as follows

$$\mathbf{D} = \mathbf{P}^{\mathrm{T}}(\boldsymbol{\delta} - i\phi n^{-1}\mathbf{F})\mathbf{P} \tag{39}$$

where $\boldsymbol{\delta}$ is the Kronecker delta matrix. Substituting eq 39 into eq 24 gives a characteristic function that yields eq 35.

For linear chains, it is possible to show that eq 24 is equivalent to every other formulation of $W^0(S^2)$ because $|\mathbf{D}(\phi)|$ can be written as a continued product.[47] It remains to be seen, however, whether or not similarly tractable expressions can be found for $|\mathbf{D}(\phi)|$ for various classes of branched chains. It would be satisfying to one's sense of mathematical order if this were the case. Nevertheless, from a practical point of view, eq 24 and its one- and two-dimensional analogs contain all the information the random-flight model for unperturbed chains is capable of giving. Except for asymptotic behavior, distributions must be determined numerically. Subsequent publications will be devoted to a detailed treatment of various classes of branched chains.

In the next section we will show that the above formulation of chain statistics can be extended to include polymer–solvent and intramolecular polymer–polymer interactions for linear and branched chains. The development will then be applied to linear chains with emphasis on chain-length effects.

A Generalized Treatment of the Excluded-Volume Effect

We now modify the formulation for the unperturbed distribution to solve for the excluded-volume effect. We shall develop this for the general case first and then present results for linear chains.

To get the distribution function for the perturbed case, a Boltzmann factor, $\exp(-V/kT)$, must be included in the integrand in eq 21. If we represent the total potential energy V for a polymer chain as a sum of pairwise interaction potentials V_{pq} acting between the backbone masses, we get

$$e^{-V/kt} = \exp\left[-\sum_p\sum_q V_{pq}/kT\right] = \prod_{p,q}[1 + (e^{-V_{pq}/kt} - 1)] = 1 + \sum_{q=1}^{n}\sum_{p=0}^{q-1} f_{pq} + \dots \tag{40}$$

where

$$f_{pq} = \exp[-V_{pq}/kT] - 1 \tag{41}$$

and f_{pq} is a function only of the relative positions of the pth and qth masses. Including the Boltzmann factor then gives the following expression for the perturbed distribution $W(S^2)$ corrected to the first order in interaction energy

$$W(S^2) = C\int\int_{-\infty}^{\infty}\int \exp[-n\beta^2(\hat{\mathbf{x}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{x}} + \hat{\mathbf{y}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{y}} + \hat{\mathbf{z}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{z}}] \times \exp(-i\psi\phi)\left[1 + \sum_p\sum_q f_{pq}\right]\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}}\mathrm{d}\phi \tag{42}$$

where C is not the same normalization constant as in eq 21. Equation 42 can be written as the sum of two terms, the first being a constant times the unperturbed distribution.

$$W(S^2) = C\left(\frac{\pi}{n\beta^2}\right)^{3n/2}\int_{-\infty}^{\infty}\frac{\exp(-i\psi\phi)\mathrm{d}\phi}{|\mathbf{D}(\phi)|^{3/2}} + Y \tag{43}$$

where

$$Y = C\sum_{q=1}^{n}\sum_{p=0}^{q-1}\int\int_{-\infty}^{\infty}\exp[-n\beta^2(\hat{\mathbf{x}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{x}} + \hat{\mathbf{y}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{y}} + \hat{\mathbf{z}}^{\mathrm{T}}\mathbf{D}\hat{\mathbf{z}})]\exp(-i\psi\phi)f_{pq}\mathrm{d}\phi\mathrm{d}\hat{\mathbf{x}}\mathrm{d}\hat{\mathbf{y}}\mathrm{d}\hat{\mathbf{z}} \tag{44}$$

The above integral is solved first for $p \neq 0$.

If we write $\mathbf{r}_q = \mathbf{r}_p + \mathbf{r}$ (with related components $\hat{\mathbf{x}}_q = \mathbf{x}_p + \hat{x}$, etc.), then

$$Y = C\sum_{q=1}^{n}\sum_{p=0}^{q-1}\int\int_{-\infty}^{\infty}\cdots\int \exp[-n\beta^2(\hat{\mathbf{x}}_q{}^{*\mathrm{T}}\mathbf{D}_{pq}{}^*\hat{\mathbf{x}}_q{}^* + \hat{\mathbf{y}}_q{}^{*\mathrm{T}}\mathbf{D}_{pq}{}^*\hat{\mathbf{y}}_q{}^* + \hat{\mathbf{z}}_q{}^{*\mathrm{T}}\mathbf{D}_{pq}{}^*\hat{\mathbf{z}}_q{}^*)]\exp(-i\psi\phi)\exp[-n\beta^2\{\hat{x}(\dots + \hat{x}d_{qq}) + \hat{y}, \hat{z}\text{ terms}\}]f_{pq}\mathrm{d}\phi\mathrm{d}\hat{\mathbf{x}}_q{}^*\mathrm{d}\hat{\mathbf{y}}_q{}^*\mathrm{d}\hat{\mathbf{z}}_q{}^*\mathrm{d}\hat{x}\mathrm{d}\hat{y}\mathrm{d}\hat{z}\} \tag{45}$$

$\mathbf{D}_{pq}{}^*(\phi)$ is an $(n-1)$ by $(n-1)$ matrix as shown in eq 46 and $\mathbf{x}_q{}^*$ is an $(n-1)$ by 1 column vector with $\hat{x}_q$ missing. Similar definitions hold for $\hat{\mathbf{y}}_q{}^*$ and $\hat{\mathbf{z}}_q{}^*$. The elements $d_{t,s}$ are the same as those in the matrix **D** in eq 25.

$$\mathbf{D}_{p,q}{}^* = \begin{bmatrix} d_{1,1} & d_{1,2} & \dots & (d_{1,p}+d_{1,q}) & \dots & d_{1,q-1} & d_{1,q+1} & \dots & d_{1,n} \\ d_{2,1} & d_{2,2} & \dots & (d_{2,p}+d_{2,q}) & \dots & d_{2,q-1} & d_{2,q+1} & \dots & d_{2,n} \\ \cdot & \cdot & \dots & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ (d_{p,1}+d_{q,1}) & (d_{p,2}+d_{q,2}) & \dots & d_{p,p}+d_{p,q}+d_{q,p}+d_{q,q} & \dots & (d_{p,q-1}+d_{q,q-1}) & d_{p,q+1}+d_{q,q+1} & \dots & d_{p,n}+d_{q,n} \\ \cdot & \cdot & \dots & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ d_{q-1,1} & d_{q-1,2} & \dots & d_{q-1,p}+d_{q-1,q} & \dots & d_{q-1,q-1} & d_{q-1,q+1} & \dots & d_{q-1,n} \\ d_{q+1,1} & d_{q+1,2} & \dots & d_{q+1,p}+d_{q+1,q} & \dots & d_{q+1,q-1} & d_{q+1,q+1} & \dots & d_{q+1,n} \\ \cdot & \cdot & \dots & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ d_{n,1} & d_{n,2} & \dots & d_{n,p}+d_{n,q} & \dots & d_{n,q-1} & d_{n,q+1} & \dots & d_{n,n} \end{bmatrix} \tag{46}$$

$p \neq 0$

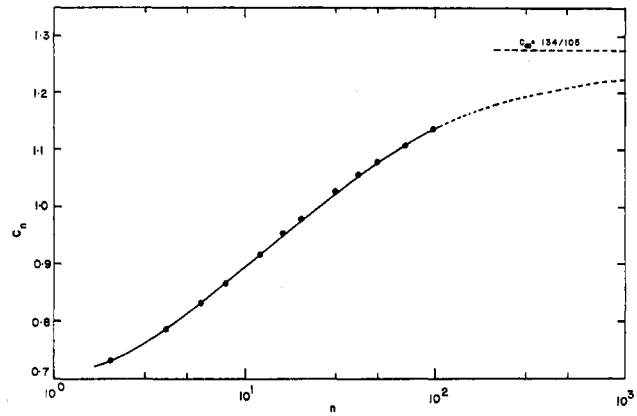

Figure 2. C_n as a function of n: (●) calculations, (- - - -) extrapolation of eq 57.

Since the potentials V_{pq} are short ranged, f_{pq} becomes zero at very small values of $\hat{x}$, $\hat{y}$, $\hat{z}$. At high values of $\mathbf{r}$, f_{pq} is zero, whereas at low values the exponential term is essentially unity. The integration over $\hat{x}$, $\hat{y}$, $\hat{z}$ may therefore be replaced by

$$\int\int\int f_{pq}\mathrm{d}\hat{x}\mathrm{d}\hat{y}\mathrm{d}\hat{z} \tag{47}$$

which may be recognized as the negative of the binary cluster integral[25] b. Integrating over $\hat{\mathbf{x}}_q^*$, $\hat{\mathbf{y}}_q^*$, and $\hat{\mathbf{z}}_q^*$, we obtain[46]

$$Y = Cb\left(\frac{\pi}{n\beta^2}\right)^{\{3(n-1)/2\}} \sum_{q=1}^{n}\sum_{p=0}^{q-1}\int_{-\infty}^{\infty} \frac{\exp(-i\psi\phi)\mathrm{d}\phi}{|\mathbf{D}_{pq}^*(\phi)|^{3/2}} \tag{48}$$

A similar procedure for the case of $p = 0$ gives eq 49.

$$\mathbf{D}_{0q}^*(\phi) = \begin{bmatrix} (d_{1,1} - {}^1/_2d_{1,q} - {}^1/_2d_{q,1} + {}^1/_4d_{q,q}) & \cdots & (d_{1,q-1} - {}^1/_2d_{1,q} - {}^1/_2d_{q,q-1} + {}^1/_4d_{q,q}) & (d_{1,q+1} - {}^1/_2d_{1,q} - {}^1/_2d_{q,q+1} + {}^1/_4d_{q,q}) & \cdots \\ (d_{2,1} - {}^1/_2d_{2,q} - {}^1/_2d_{q,1} + {}^1/_4d_{q,q}) & \cdots & (d_{2,q-1} - {}^1/_2d_{2,q} - {}^1/_2d_{q,q-1} + {}^1/_4d_{q,q}) & (d_{2,q+1} - {}^1/_2d_{2,q} - {}^1/_2d_{q,q+1} + {}^1/_4d_{q,q}) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ (d_{q-1,1} - {}^1/_2d_{q-1,q} - {}^1/_2d_{q,1} + {}^1/_4d_{q,q}) & \cdots & (d_{q-1,q-1} - {}^1/_2d_{q-1,q} - {}^1/_2d_{q,q-1} + {}^1/_4d_{q,q}) & (d_{q-1,q+1} - {}^1/_2d_{q-1,q} - {}^1/_2d_{q,q+1} + {}^1/_4d_{q,q}) & \cdots \\ (d_{q+1,1} - {}^1/_2d_{q+1,q} - {}^1/_2d_{q,1} + {}^1/_4d_{q,q}) & \cdots & (d_{q+1,q-1} - {}^1/_2d_{q+1,q} - {}^1/_2d_{q,q-1} + {}^1/_4d_{q,q}) & (d_{q+1,q+1} - {}^1/_2d_{q+1,q} - {}^1/_2d_{q,q+1} + {}^1/_4d_{q,q}) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} \tag{49}$$

We have now established $\mathbf{D}_{pq}^*$ for all the possible cases. If we absorb $(\pi/n\beta^2)^{3n/2}$ in the normalization constant C and use the definition of z as in eq 3, we can write eq 43 as

$$W(S^2) = C\int_{-\infty}^{\infty} \exp(-i\psi\phi)\left[\frac{1}{|\mathbf{D}(\phi)|^{3/2}} - \frac{z}{n^{1/2}}\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{1}{|\mathbf{D}_{pq}^*(\phi)|^{3/2}}\right]\mathrm{d}\phi \tag{50}$$

The term in parenthesis is the characteristic function $F(\phi)$ for the distribution of ψ. From the theory of distribution functions,[45] the mean value of ψ is given by

$$\langle\psi\rangle = n(n+1)\beta^2\langle S^2\rangle = -iF'(0)/F(0) \tag{51}$$

Therefore

$$\langle S^2\rangle = \frac{3i}{2n(n+1)\beta^2}\left[\frac{|\mathbf{D}'(0)|}{|\mathbf{D}(0)|^{5/2}} - \frac{z}{n^{1/2}}\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{|\mathbf{D}_{pq}^{*\prime}(0)|}{|\mathbf{D}_{pq}^*(0)|^{5/2}}\right]\left[\frac{1}{|\mathbf{D}(0)|^{3/2}} - \frac{z}{n^{1/2}}\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{1}{|\mathbf{D}_{pq}^*(0)|^{3/2}}\right]^{-1} \tag{52}$$

TABLE I

n	C_n	n	C_n
2	0.730	30	1.028
4	0.785	40	1.058
6	0.830	50	1.079
8	0.866	70	1.107
12	0.918	100	1.133
16	0.954	∞[a]	1.275[a]
20	0.979		

[a] Fixman's theory for an infinite chain.

Expanding the denominator as a binomial and performing algebraic manipulations gives

$$\alpha_S^2 = 1 + \frac{z}{n^{1/2}}|\mathbf{D}(0)|^{3/2}\left[\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{1}{|\mathbf{D}_{pq}^*(0)|^{3/2}} - \frac{|\mathbf{D}(0)|}{|\mathbf{D}'(0)|}\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{|\mathbf{D}_{pq}^{*\prime}(0)|}{|\mathbf{D}_{pq}^*(0)|^{5/2}}\right] \tag{53}$$

which is in the form of $\alpha_S^2 = 1 + C_nz$. Equation 53 is a completely general expression for α_S^2 and it can be evaluated numerically by using the appropriate expression for the transformation matrix $\mathbf{P}$.

Excluded Volume for Linear Chains

In order to obtain C_n for linear chains, we must use eq 25 for $|\mathbf{D}(\phi)|$. From eq 26, we have

$$|\mathbf{D}(0)| = (n+1)^2 \tag{54}$$

and

$$|\mathbf{D}'(0)| = -in(n+1)^2(n+2)/6 \tag{55}$$

and we get from eq 53

$$C_n = \frac{(n+1)^3}{n^{1/2}}\left[\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{1}{|\mathbf{D}_{pq}^*(0)|^{3/2}} - \frac{6i}{n(n+2)}\sum_{q=1}^{n}\sum_{p=0}^{q-1}\frac{|\mathbf{D}_{pq}^{*\prime}(0)|}{|\mathbf{D}_{pq}^*(0)|^{5/2}}\right] \tag{56}$$

Equation 56 was solved numerically, and the results are shown in Table I.[47] Figure 2 presents C_n plotted as a function of n and offers evidence that the limit, as $n \to \infty$, of $C_n = ({}^{134}/_{105})$, as is required by the asymptotic solution.

The excluded volume effect for branched chains may similarly be obtained. The results for typical branched chains will be presented in a subsequent publication.

Discussion

The computed results for linear chains are plotted in Figure 3 as log $[({}^{134}/_{105}) - C_n]$ *vs.* log n. By accepting the linear extrapolation shown for $n > 100$, we found that for $n > 10$,

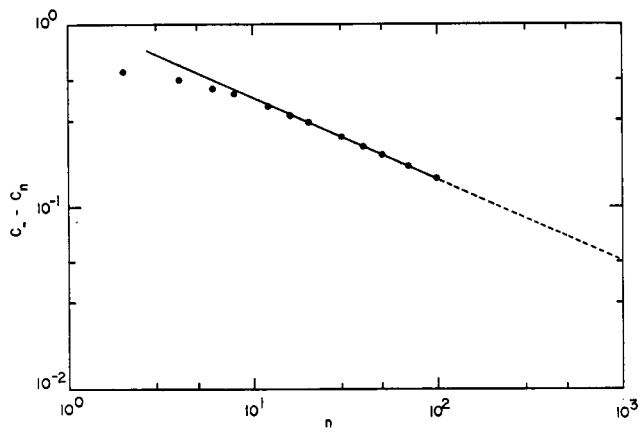

Figure 3. $^{134}/_{105} - C_n$ as a function of n: (●) calculations, line represents eq 57 (extrapolated for $n > 100$).

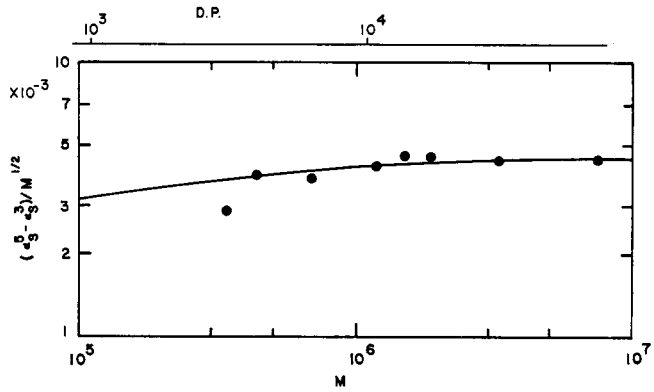

Figure 4. $(\alpha_S{}^5 - \alpha_S{}^3)/M^{1/2}$ *vs.* M for poly(α-methylstyrene) in toluene at 25°: (●) data of Nagasawa, *et al.* (ref 53), line represents eq 58.

the following empirical equation adequately described the behavior

$$C_n = \frac{134}{105}\left(1 - \frac{0.885}{n^{0.462}}\right) \tag{57}$$

When $n = 10$, 100, and 1000, C_n is lower than C_∞ by about 30, 10, and 5%, respectively. Rigorous interpretation of these results in terms of molecular weight is, however, impossible. In principle, n can be selected with considerable latitude, subject to only two restrictions. Although enough repeat units must be taken per statistical segment to assure that they can be characterized by a gaussian distribution of end-to-end distances, few enough repeat units must be taken per statistical segment to assure that all the mass of each chain can be assumed to be concentrated at the ends of the statistical segments. With this latitude in the definition of n, no theoretical predictions containing n explicitly can be given unequivocal interpretation. We assert, however, that a reasonable qualitative test for the effect of molecular weight on C_n is to interpret eq 57 with n defined by the minimum number of repeat units per statistical segment that gives a gaussian distribution. Work reported by Flory[49] and more recently by Allegra and Avitabile[50] indicates that for vinyl chains 25 repeat units only crudely approximate gaussian behavior, whereas 100 repeat units obey gaussian statistics quite well. For the sake of argument, therefore, we will test eq 57 for the importance of molecular weight effect by assuming the conservative value of 30 repeat units per statistical segment for typical vinyl polymers. If we assume a molecular weight of about 100 for a repeat unit, $n = 10$, 100, and 1000 correspond to molecular weights of about 3×10^4, 3×10^5, and 3×10^6. Clearly, the presently accepted excluded-volume treatment for small z is applicable, in most instances, only to molecular weights greater than 10^6. Indeed substantial errors are introduced for $M < 3 \times 10^5$.

The above treatment applies only in the limit as $z \to 0$. We will therefore adopt the point of view suggested by Stockmayer[44] and use the Kuhn model results to give the proper limiting behavior of the approximate segment cloud equation of Flory. The result is

$$\alpha_S{}^5 - \alpha_S{}^3 = \frac{134}{105}\left(1 - \frac{0.885}{n^{0.462}}\right)z \tag{58}$$

the above equation describes the observed increase in $(\alpha_S{}^5 - \alpha_S{}^3)/z$ with increasing M reported in early work.[51-54] As a test of the proposed molecular weight dependence, Figure 4 compares the recent light-scattering results of Nagasawa, *et al.*,[53] on dilute poly(α-methylstyrene) solutions with predictions from eq 58 by taking 80 repeat units per statistical segment. Considering the experimental error (discussed by Nagasawa, *et al.*[53]), the predicted molecular weight dependence is clearly indicated.

We conclude that the presence of n explicitly in eq 57 and 58 indicates that the Kuhn model is inadequate to describe the excluded-volume problem except in the limit as $n \to \infty$. Until a more detailed theory is available, we suggest that these two equations can be used to correlate data on coil expansion by allowing the number of repeat units per statistical segment to be a semiempirical curve-fitting parameter.

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