of γ vs. the quantity $\sigma\phi$ (which depends on the lattice and goodness of the solvent via the amount of attractive energy between segments) was found to coincide with the corresponding curve previously found for the case of linear polymers. Therefore, γ is independent of branching of the polymer. In particular, the point at which $\gamma = 1$, which defines the theta point, is independent of branching. From the calculated squared radii, the g ratio and expansion factors were calculated, and their values were found to disagree with the values calculated from analytical theories. At the theta conditions, the calculated g values are from 6 to 15% greater than those calculated according to the Zimm–Stockmayer theory. However, the g values for moderately good solvents ($\sigma\phi = 1.1$) agree well with the values obtained from the Zimm–Stockmayer theory for random flight model of a star.

Our calculations predict that the expansion factor is less for stars than for linear polymers and that it decreases with increasing number of branches, while analytical theories predict the opposite behavior. We believe that this disagreement is due to the use of the random walk model in analytical theories of polymers at their theta condition.

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Span of a Random-Flight Model of a Star-Branched Polymer Chain

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ABSTRACT: An expression is derived for the probability distribution function of the span of a random-flight model of a star-branched polymer molecule. The model consists of f random flight chains, each containing N steps, which emanate from a common point. Numerical results showing the form of the distribution function as a function of the number of branches are presented.

In this paper we continue our investigation of spans of random flight models of polymer chains.[2a] The spans of a polymer chain are defined to be the lengths of the sides of the smallest box with edges parallel to the coordinate axes which contain the entire chain. Daniels[2b] was the first to determine the distribution function and moments of what he called the "extent" and what we choose to call the span of a random walk (or polymer chain). Later, and independently, Feller[3] and Kuhn[4,5] treated the same or equivalent problems. There is now an extensive literature on this subject.[6–13] Interest in these extreme dimensions arises from several directions. First, the typical or average spanning rectangular box is far from cubic.[12–14] This asymmetry must affect solution properties of polymer chains in which there is relative motion between the solvent and the polymer chain. Second, the notion of the span of polymer chains enters in theories of gel permeation chromatography in which separation of polymer chains according to molecular weight is envisaged as arising from a partition or exclusion of the chains in small pores on the basis of size or span.[15–17]

In this paper we calculate the distribution function of the span of a star-branched random-flight chain. Casassa,[17] using an observation of van Kreveld,[18] determined the first moment without explicitly finding the distribution function. Using an argument which is implicit in Daniel's paper[2b] and which was elaborated on by Rubin, Mazur, and Weiss,[2a] we obtain the distribution function of the span, show how it appears in the calculations of Casassa and Tagami,[16] and thus verify Casassa's formula[17] for the average span of a star-branched polymer chain.

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Span of a Star-Branched Polymer Chain

In this paper we assume a random-flight model of a star-branched polymer chain (star) in which f random flight chains, each consisting of N steps, emanate from a common point. We derive an expression for $P(R_1,R_2,R_3,N)$, the joint probability distribution function (pdf) of the three spans of a star in the directions of the coordinate axes x_1, x_2, x_3. The pdf $P(R_1,R_2,R_3,N)$ is the probability that the star has a span in the x_i direction which lies between R_i and $R_i + dR_i$, $i = 1, 2, 3$. Let $R_i > 0$, $i = 1, 2, 3$, define the lengths of the edges of a rectangular box $\Omega(R_1,R_2,R_3)$ which spans the star, has a corner located at the origin of the x_1, x_2, x_3 coordinate system, and has its edges parallel to the coordinate axes. For any configuration of the star, label the coordinates of the central point by $x_1^{(0)}$, $x_2^{(0)}$, $x_3^{(0)}$ and the coordinates of the tips of the branches by $x_1^{(k)}$, $x_2^{(k)}$, $x_3^{(k)}$ for $1 \leq k \leq f$.

In the limit of large N, the pdf for any one of the branches of the star is governed by the equation

$$\frac{\partial v}{\partial N} = \frac{1}{6}\left(\frac{\partial^2 v}{\partial x_1^2} + \frac{\partial^2 v}{\partial x_2^2} + \frac{\partial^2 v}{\partial x_3^2}\right) \tag{1}$$

where $v \equiv v(x_1,x_2,x_3;N)$ and where absorbing boundary conditions are imposed on the walls of the box, $\Omega(R_1,R_2,R_3)$, i.e., $v = 0$ on the walls of the box for $N \geq 0$. The probability that a branch starts in the box at $x_1^{(0)}$, $x_2^{(0)}$, $x_3^{(0)}$ and reaches x_1, x_2, x_3 at step N without ever leaving the box is[19-21]

$$v_{x_1^{(0)},x_2^{(0)},x_3^{(0)}}(x_1,x_2,x_3;N) = \prod_{i=1}^{3}\left\{\frac{2}{R_i}\sum_{n_i=1}^{\infty}\sin\left(\frac{n_i\pi x_i}{R_i}\right) \times \sin\left(\frac{n_i\pi x_i^{(0)}}{R_i}\right)\exp\left(-\frac{n_i^2\pi^2 N}{6R_i^2}\right)\right\} \quad (2)$$

The pdf for a configuration of the star is the product

$$V_{x_1^{(0)},x_2^{(0)},x_3^{(0)}}(x_1^{(1)},\ldots,x_3^{(f)};N) = \prod_{k=1}^{f} v_{x_1^{(0)},x_2^{(0)},x_3^{(0)}}(x_1^{(k)},x_2^{(k)},x_3^{(k)};N) \quad (3)$$

In order to calculate the pdf of the spans of a star, we first add together the probabilities of all configurations of the star inside the box $\Omega(R_1,R_2,R_3)$ by forming the integral

$$\Psi(R_1,R_2,R_3;N) = \prod_{k=0}^{f}\left\{\int_0^{R_1} dx_1^{(k)}\int_0^{R_2} dx_2^{(k)}\int_0^{R_3} dx_3^{(k)}\right\} \times V_{x_1^{(0)},x_2^{(0)},x_3^{(0)}}(x_1^{(1)},\ldots,x_3^{(f)};N) \quad (4)$$

It is clear from the product forms in eq 2 and 3 that the expression for $\Psi(R_1,R_2,R_3;N)$ can also be written as a product of three independent identical factors,

$$\Psi(R_1,R_2,R_3;N) = \prod_{i=1}^{3}\psi_f(R_i;N) \quad (5)$$

where

$$\psi_f(R;N) = \left(\frac{4}{\pi}\right)^f \sum_{n_1=0}^{\infty}\cdots\sum_{n_f=0}^{\infty} \times\left\{\prod_{k=1}^{f}\left(\frac{\exp\left[-\frac{\pi^2 N}{6R^2}(2n_k+1)^2\right]}{2n_k+1}\right)\right\} R \times \int_0^1 dy \prod_{j=1}^{f}\sin[(2n_j+1)\pi y] \quad (6)$$

$$\psi_f(R;N) = RK_f(R;N) \quad (7)$$

Equation 5 is a quantity which is proportional to the total number of distinct configurations of star molecules contained in $\Omega(R_1,R_2,R_3)$. Included among these configurations, there are exactly

$$(R_1-\rho_1)(R_2-\rho_2)(R_3-\rho_3)P(\rho_1,\rho_2,\rho_3;N)\,d\rho_1\,d\rho_2\,d\rho_3 \quad (8)$$

configurations whose spanning box is $\Omega(\rho_1,\rho_2,\rho_3)$ where $0 \leq \rho_i \leq R_i$, $i = 1, 2, 3$. Thus, the following integral relation[2] exists between $\Psi(R_1,R_2,R_3;N)$ and $P(\rho_1,\rho_2,\rho_3;N)$

$$\Psi(R_1,R_2,R_3;N) = \int_0^{R_1} d\rho_1\int_0^{R_2} d\rho_2\int_0^{R_3} d\rho_3\,(R_1-\rho_1) \times (R_2-\rho_2)(R_3-\rho_3)P(\rho_1,\rho_2,\rho_3;N) \quad (9)$$

The solution of this simple integral equation is

$$P(R_1,R_2,R_3;N) = \prod_{i=1}^{3}\left\{\frac{d^2}{dR_i^2}\psi(R_i;N)\right\} \quad (10)$$

Daniels[2b] obtained the product form in eq 10 for the joint pdf of the spans of a simple unbranched chain in the limit $N \gg 1$. In the present case of a star molecule we rewrite eq 10 as

$$P(R_1,R_2,R_3;N) = \prod_{i=1}^{3} p^{(f)}(R_i;N) \quad (11)$$

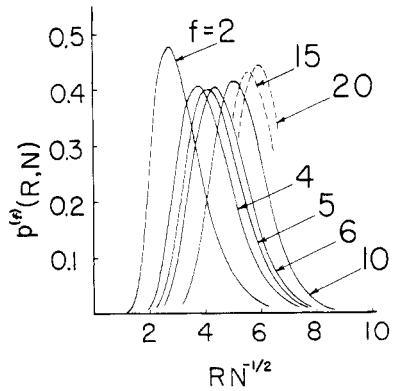

Figure 1. The pdf $p^{(f)}(R;N)$ is plotted vs. $RN^{-1/2}$ for values of f = 2, 4, 5, 6, 10. In addition values of $p^{(15)}(R;N)$ and $p^{(20)}(R;N)$ are plotted in the vicinity of the maximum of each.

Thus the pdf of the span in any of the directions x_i is

$$p^{(f)}(R;N) = \frac{d^2}{dR^2}\psi_f(R;N) \quad (12)$$

where $\psi_f(R;N)$ is given in eq 6.

In case $f = 1$, eq 12 yields the result first obtained by Daniels[2b] for the pdf of the span of a random-flight chain of N steps,

$$p^{(1)}(R;N) = \frac{d^2}{dR^2}\frac{8}{\pi^2}R\sum_{n=0}^{\infty}(2n+1)^{-2} \times \exp\left[-\frac{\pi^2 N}{6R^2}(2n+1)^2\right] \quad (13)$$

In case $f = 2$, it is readily verified that

$$p^{(2)}(R;N) = p^{(1)}(R;2N) \quad (14)$$

We have evaluated $p^{(f)}(R;N)$ in eq 12 numerically. The results are displayed in Figure 1 for f = 2, 4, 5, 6, 10 where values of $p^{(f)}(R;N)$ are plotted vs. the reduced variable $RN^{-1/2}$. In addition the pdf's for f = 15 and 20 are shown in the vicinity of the maximum of each. For each value of f, the maximum step extension (branch tip to branch tip) of the star molecule is $2N$. It can be seen that the most probable value of the span increases with increasing f as should be expected. However, there is a second more subtle trend which can be seen in Figure 1. The probability associated with the most probable value of the span passes through a minimum for $f = 5$, and thereafter increases with increasing f. In effect, for $f \geq 5$ the span distribution function becomes more sharp as the number of branches increases.

The nth moment of the span can be determined in a straightforward manner from eq 12,

$$\langle R^n\rangle = \int_0^{\infty} d\rho\,\rho^n\frac{d^2}{d\rho^2}\psi_f(\rho;N) = \lim_{\rho\to\infty}\left\{\rho^n\frac{d}{d\rho}\psi_f(\rho;N) - n\rho^{n-1}\psi_f(\rho;N)\right\} + n(n-1)\int_0^{\infty} d\rho\,\rho^{n-2}\psi_f(\rho;N) \quad (15)$$

In the case of the first moment, (15) reduces to

$$\langle R\rangle = \lim_{\rho\to\infty}\left\{\rho\frac{d}{d\rho}\psi_f(\rho;N) - \psi_f(\rho;N)\right\} \quad (16)$$

and in terms of the quantity $K_f(R;N)$ in eq 7

$$\langle R\rangle = \lim_{\rho\to\infty}\left\{\rho^2\frac{d}{d\rho}K_f(\rho;N)\right\} \quad (17)$$

The function $K_f(\rho;N)$ which is defined in eq 6 and 7 also appears in the work of Casassa and Tagami[16] (their eq 4). These authors have obtained the following value of $K_f(\rho;N)$ in the vicinity of $\rho = \infty$ (their eq 13 which is corrected in footnote 18 of Casassa[17]),

$$K_f(\rho;N) \sim 1 - 2\psi(f)(fN/6\rho^2)^{1/2} + O(N/6\rho^2) \quad (18)$$

where

$$\psi(f) = \left(\frac{f}{\pi}\right)^{1/2} \int_0^\infty [\mathrm{erf}(t^{1/2})]^{f-1} e^{-t}\, dt \quad (19)$$

Inserting (18) in (17), the following formula proposed by Casassa[17] for the average value of the span is obtained,

$$\langle R \rangle = 2(2Nf/3)^{1/2}\psi(f) \quad (20)$$

It is readily verified by combining (18) and (15) that the span distribution is properly normalized, i.e., the zeroth moment is equal to unity. Finally, we remark that it is possible in principle to obtain higher order correction terms to the expression for $K_f(\rho;N)$ of Casassa and Tagami[16] which is reproduced in eq 18. For each additional correction term, it will be possible to calculate an additional moment of the span pdf from eq 15.

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Monte Carlo Study of a Self-Interacting Polymer Chain

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ABSTRACT: A Monte Carlo study of the Domb–Joyce Model of a polymer chain was made by simulating random walks on the simple cubic lattice. It is shown that the recent formula advanced by Domb and Barrett for the expansion factor α^2 as a function of an intramolecular potential (for weak perturbations) is in excellent agreement with the computer simulations. The behavior of the partition function for such a model is also investigated.

An important problem in polymer physics is the configurational characteristics of long flexible chains in dilute solution. Early models of such systems treated the chain as a normal random walk (NRW). This model is primitive since it neglects self-exclusions in the chain. To account for such "excluded volume" effects a self-avoiding walk (SAW) model of the polymer chain must be studied. The self-avoiding walk model mathematically is a non-Markovian process and very complicated. Nevertheless, by application of both analytic and numerical techniques[2-4] some conclusions concerning the behavior of configurational properties of both NRW and SAW models have been advanced. In particular, it has been found that for models studied in three dimensions the mean-square end-to-end distance, $\langle R_N^2 \rangle$, of such chains obeys the following simple asymptotic formulas

$$\langle R_N^2 \rangle_0 = AN \qquad \text{(NRW)} \quad (1)$$

$$\langle R_N^2 \rangle \sim AN^{1.20} \qquad \text{(SAW)} \quad (2)$$

where A is a model dependent constant and the exponent is only dimensionally dependent or universal. Equation 2 has been found to be strictly true for ordinary SAW walks simulated on three-dimensional lattices. Domb[5] advanced the hypothesis that the exponent in eq 2 is a universal parameter of polymer systems and should therefore be insensitive to models studied in a given dimension. This idea is supported by the studies of Hioe[6] and Watson.[7] The general form of eq 2 is retained for models considering finite intramolecular interactions[8,9] and varying excluded volume,[10-16] but in general the exponent appears to be a function of the intermolecular potential and excluded volume effects. Moreover, the connection between the simple form of eq 2 and the many formulas advanced for the expansion factor of the end-to-end distance α^2 where,

$$\alpha_N^2 = \langle R_N^2 \rangle / \langle R_N^2 \rangle_0 \quad (3)$$

is not straightforward. Thus a fundamental problem remaining is an understanding of the behavior of the self-interacting chain.

Recently Domb and Joyce[17] have specified a lattice version of the expansion factor problem. They have shown that α^2 may be expressed as a perturbation series in the interaction parameter ω of the form;

$$\alpha^2 = 1 + \sum_i K_i \omega^i \quad (4)$$

where the K_i's are functions of $N^{i/2}$. Here $\omega = 0$ corresponds to the NRW and $\omega = -1$ to the SAW. They note that the continuum model may also be expressed as a power series in