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Lattice Walk Models of Uniform Star Polymers with Many Arms

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ABSTRACT: A high coordination random lattice walk serves as the basis of a model of a uniform star polymer with from 1 to 24 branches. Monte Carlo results are presented for two classes of walk which exhibit significantly different excluded volume characteristics. The effects of excluded volume and functionality on stars and star fragments are observed and interpreted in light of theoretical predictions and experiment. Results provide a fairly complete picture of excluded volume effects in uniform stars, in partial agreement with the scaling results of Daoud and Cotton. The success of the Zimm–Stockmayer equation in describing real stars is discussed.

1. Introduction

When several linear polymers are brought together at a point, called the *branch point*, a star polymer is formed. If each of the branches or arms of the star has the same chemical length, then the star is said to be *uniform*. Stars are fascinating objects. Within the same molecule one finds compact, highly structured fragments and extended, linear ones. A star is dense near the branch point and dilute far from the branch point. Polymer dimensions are known to be dependent on concentration; the dimensions of stars and fragments of stars depend on the concentration profile within the star. At the same time, uniform stars have an idealized structure. They are far simpler than almost all natural and synthetic branched polymers and provide a natural framework for the study of the physics of large molecules.

Following some notable studies of stars over many years,[1-3] several recent works have considered the effects of excluded volume[4-8] and have furnished a number of intriguing predictions. Many of these can only be adequately tested on stars with many arms. Some fascinating experimental work on such stars has been done by Fetters and his associates,[9,10] who have produced uniform polystyrene stars with as many as 18 branches. Theorists too have sought to confirm scaling and renormalization group predictions by numerical means, and results are now available for stars with up to 12 arms.[11-17]

In the present work, a non-nearest-neighbor lattice walk[18] is used to model uniform star polymers with up to 24 branches, using Monte Carlo techniques. Both self-avoiding (SA) and neighbor-avoiding (NA) walks, which differ considerably in their excluded volume properties, are simulated. It is hoped that by observing stars with a larger number of branches, using models with widely disparate excluded volume characteristics, it will be possible to learn enough about the effects of excluded volume in stars to permit intelligent assessment of the arguments which have been put forward. It is further hoped that some conclusions might be drawn concerning the significance of the various concentration regimes within the star.

2. Theory

Configurational properties of particular interest include the mean square radius of gyration $\langle S_N^2(f)\rangle$ of the star, the mean square end-to-end length of a single branch or arm $\langle R_n^2(f)\rangle$, and the mean square distance $\langle R_{ij}^2(f)\rangle$ between two sites i and j within the star. Also of interest is the number of configurations of uniform stars s_N. Here n is the number of monomer units or segments per branch, N is the number of monomer units in the star, and f is the *functionality* or number of branches. Clearly $N = nf$. If N is large, then these quantities are expected to satisfy relations of the form

$$\langle S_N^2\rangle \sim A(f)N^{2\nu} \tag{1}$$

$$\langle R_n^2\rangle \sim B(f)n^{2\nu} \tag{2}$$

and

$$s_N \sim \lambda(f)^N N^{\gamma(f)-1} \tag{3}$$

It is expected that $\langle R_{ij}^2\rangle$ obeys a law similar to eq 2. The analogy with scaling laws for isolated, linear chains is clear. Power laws such as eq 1 and 2 display both an exponent and a prefactor or amplitude. The exponent is characteristic of a fundamental physical process and therefore universal. This means that the same exponent ν should apply to all equations relating to chain dimensions. Numerous studies put the value of ν close to the Flory value: $^3/_5$. Recent renormalization group analysis yields a value of 0.588.[19]

The amplitude on the other hand is characteristic of functionality and such model-dependent details as monomer structure, permitted bond angles, and short-range interaction. It is possible to eliminate these model-dependent details by forming the ratios

$$g(f) = \frac{A(f)}{A(1)}$$

and

$$g'(f) = \frac{B(f)}{B(1)}$$

One expects then that both g and g' will be universal functions of f. We will assume that for large f, the prefactors $A(f)$ and $B(f)$ can be described by power laws:

$$A(f) \sim f^{\delta} \qquad B(f) \sim f^{\delta}$$

It is especially important to note that these equations

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imply that star polymers are subject to excluded volume in essentially the same way as linear polymers, except that the amplitude of the swelling is modified by the presence of the many arms. It is a relatively simple matter to establish bounds for the exponent δ, by employing scaling arguments. If we assume that the local monomer density is equal to that of an isolated chain, then each of the f branches will occupy a cone whose volume equals that occupied by an isolated chain of n segments. Ignoring prefactors, we have

$$n^{9/5} \cong R_n^3 f^{-1}$$

whence

$$B(f) \sim f^{2/3} \tag{4}$$

This argument surely underestimates the local monomer concentration, so we take the value of $^2/_3$ as an upper bound. A lower bound may be obtained by overestimating the local monomer concentration. If the star is a very concentrated object, then each branch may be considered as an ideal chain of n/m "blobs" of size ξ, following the methods outlined by de Gennes.[20] A blob is assumed to encompass m consecutive monomers which essentially obey isolated chain statistics. That is, a blob is a region sufficiently small that

$$\xi \sim m^{3/5}$$

The dimensions of the branch are given by

$$R_n \cong \frac{n^{1/2}}{m^{1/2}}\xi$$

Now we impose the condition that the star volume is the volume of nf/m blobs. Then

$$R_n^3 \cong f\frac{n}{m}\xi^3$$

Eliminating m and ξ from the last two equations yields

$$B(f) \sim f^{-2/5} \tag{5}$$

We assert then that $-^2/_5 < \delta < ^2/_3$. Unfortunately these bounds are somewhat weak. One can well imagine that near the center of the star, the concentration may be such that eq 5 applies, while near the outer extremities eq 4 should be more appropriate. Note that this implies that there is a region within the star whose dimensions diminish with increasing functionality and another whose dimensions increase with functionality. Daoud and Cotton[4] have come to similar conclusions. They identify three separate excluded volume regimes: (i) a close packed core where the branches are extended; (ii) an intermediate, "concentrated" regime where the excluded volume is screened to some extent; and (ii) a "dilute" outer region where the branches behave essentially as self-avoiding chains.

By considering that the monomer concentration diminishes with distance from the branch point, they obtain $\delta = ^2/_5$. This should be compared with the result obtained by Miyake and Freed,[5] based on the ϵ expansion:

$$g' = \frac{B(f)}{B(1)} = 1 + \frac{(f-1)(4\ln 2 - 1)}{32} + \mathcal{O}(\epsilon^2) \tag{6}$$

This implies that $\delta = 1$, which is surely too large. It should be noted, however, that Miyake and Freed do not expect this result to be valid for any but small f.

The ratio g' scales as does $B(f)$, but g scales as $A(f)f^{-6/5}$. This is because the denominator of g, unlike that of g', involves a chain with $N = nf$ segments. Since $A(f)$ can be expected to scale like $B(f)$, this implies the Daoud–Cotton result:

$$g(f) \sim f^{-4/5} \tag{7}$$

Consider now the ratios g and g' for a star composed of Gaussian segments. Since in this case $B(f)$ is independent of f, we expect g' to be a constant. However, the denominator of g contains a factor f, so we expect g to scale as f^{-1}. This is reflected in the Zimm–Stockmayer equation,[1] proposed some 40 years ago for ideal (i.e., no excluded volume) uniform stars.

$$g(f) = \frac{3f-2}{f^2} \tag{8}$$

Now, at least for the values of f which have been studied, f^{-1} is not too different from $f^{-4/5}$, so it is not surprising that experimental and numerical values of g indicate a relative insensitivity to excluded volume. However, this insensitivity is in part due to mathematical artifact and must not be interpreted as meaning that star polymers are not subject to excluded volume effects.

Consider now eq 3. Wilkinson et al.[16] have shown that $\lambda(f) = \mu^f$. Here μ is the growth constant for a linear self-avoiding walk. It is convenient to think of μ as being the growth constant "per branch". The quantity $\gamma(f)$ is expected to be a decreasing function of f, reflecting the increased difficulty of formation of stars as the number of arms increases. The following formula is proposed, also by Miyake and Freed:[5]

$$\gamma(f) = 1 + \frac{1}{8}\left[1 - \frac{(f-1)(f-2)}{2}\right] + \mathcal{O}(\epsilon^2) \tag{9}$$

The remainder of this article describes a Monte Carlo experiment designed to shed further light on the quantities ν, g, g', μ, and γ and to determine the relative significance of the various concentration regimes proposed by Daoud and Cotton.

3. Model and Computational Details

A random walk on a *simple cubic* lattice may be characterized by the triplet (100), representing the set of permitted steps

$$\{(1,0,0),(-1,0,0),(0,1,0),(0,-1,0),(0,0,1),(0,0,-1)\}$$

It can be seen that a (100) walk has a coordination of 6, indicated by the three possible permutations of the digits 1,0,0, multiplied by the two possible signs (±) of the non-zero digit. In a like manner, a *non-nearest-neighbor walk* may be characterized by a triplet (pqr), where p,q,r are positive integers. Such a walk has a coordination of 6, 8, 12, 24, or 48 depending on the values of p,q,r. For example, a (112) walk has a coordination of $3 \times 2^3 = 24$, while a (013) walk has a coordination of $3! \times 2^2 = 24$. Further details on (pqr) walks are given in ref 18.

In this study, stars are generated by using self-avoiding (112) and (113) walks and neighbor-avoiding (112) walks. All these walks have a coordination of 24. The neighbor-avoiding (NA) walks have considerably more excluded volume than do the self-avoiding (SA) walks. For more details on NA walks, the reader is referred to the articles by Torrie and Whittington.[21] For purposes of illustration, examples of two-dimensional self-avoiding walks, non-nearest-neighbor walks, and neighbor-avoiding walks are shown in Figure 1.

The Monte Carlo method used is that of Rosenbluth and Rosenbluth,[22] also called inversely restricted sampling. Samples of from 80 000 to 500 000 stars with f branches of n segments per branch were generated. The function-

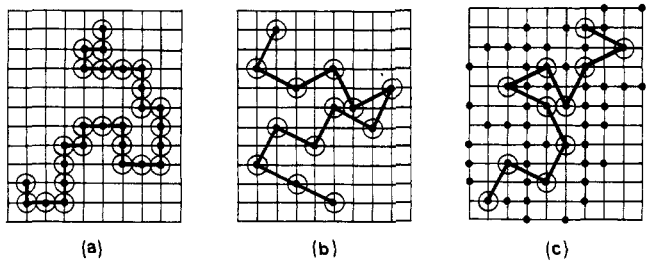

Figure 1. (a) (01) SA, (b) (12) SA, (c) (12) NA walks. The symbol ● indicates an additional site forbidden to the walk, being a (12) neighbor of a site already visited.

ality f was varied, in increments of 4, from 1 to 24 for the (112) and (113) SA walks and from 1 to 16 for the (112) NA walks. The value of n was chosen as 100 except for the 24 branch SA walks and the 16 branch NA walks. In these cases only, $n = 80$.

The smaller sample sizes apply to the larger stars, those with the greater number of arms. Since more suitable sample sizes are precluded by the natural limits on computer time, we have had to be content with those obtained. While we have a reasonable confidence in the results reported, the reader should be aware that the precision of the reported results diminishes with increasing f. The reliability of the numerical results is discussed in greater detail in section 5.

4. Numerical Analysis of Results

It is difficult to establish the value of the exponent ν (defined in eq 1) for (112) and (113) walks. While one fully expects that ν will have the usual self-avoiding walk value, this has yet to be shown rigorously. Numerical confirmation is difficult as well. On the one hand, the high coordination number precludes the generation of exact series to a length sufficient to permit precise extrapolation. On the other hand, the longer series produced by Monte Carlo methods have too much scatter for the extrapolation methods usually applied to exact series to be of much use. Moreover, simple logarithmic plots display significant curvature for the lengths of chain under discussion, thus making estimates of ν by this approach unreliable. However, it has been noted by Igloi[23] that a considerable smoothing occurs if the series is summed. That is, if $a_m \sim m^{\nu}$, then $\sum_{m=1}^{M} a_m \sim M^{1+\nu}$. This method was applied to form simple ratio plots (see e.g., ref 24) of ν_N vs. $1/N$ and ν_n' vs. $1/n$ where

$$\nu_N = \frac{N}{2}\left[\frac{\sigma_{N+1}}{\sigma_N} - 1\right] \tag{10}$$

$$\nu'_n = \frac{n}{2}\left[\frac{\sigma'_{n+1}}{\sigma'_n} - 1\right] \tag{11}$$

and where

$$\sigma_N = \sum_{j=1}^{N} \frac{\langle S_j^2 \rangle}{j}$$

$$\sigma'_n = \sum_{j=1}^{n} \frac{\langle R_j^2 \rangle}{j}$$

Typical results may be seen in Figure 2.

Once the dominant exponent has been ascertained, it is possible to estimate the prefactors $A(f)$ and $B(f)$. This, too, is a very delicate affair and much depends on what has become known as "corrections to scaling", by which we mean corrections to the asymptotic expressions (1)–(3).

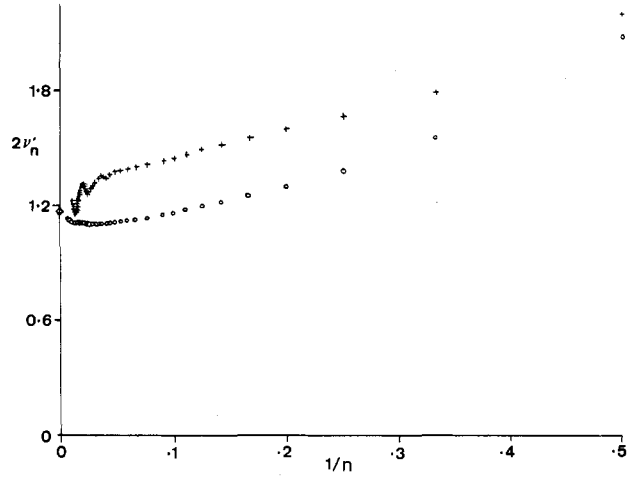

Figure 2. $2\nu'_n$ vs. $1/n$ for $f = 2$: (O) 113, (+) 112 NA.

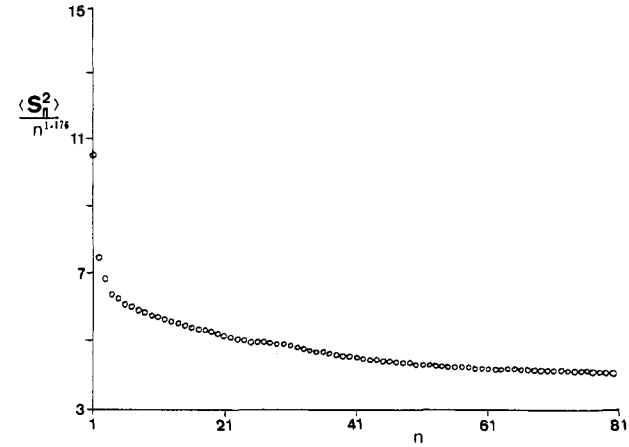

Figure 3. Plot of $\langle S_n^2(f)\rangle/n^{1.176}$ vs. n for $f = 24$.

The corrections are expected to be lattice dependent, that is, nonuniversal. While they do not seem to greatly affect results for the nearest-neighbor walks,[25,26] such corrections are known to be significant for non-nearest-neighbor walks. Unfortunately there is considerable confusion over the most appropriate form of corrections, so in this work $A(f)$ has been estimated by fitting $\langle S_N^2(f)\rangle$ to a number of plausible models:

(i) $$\ln \langle S_N^2(f)\rangle = \ln A + 2\nu \ln N$$

(ii) $$\frac{\langle S_N^2\rangle}{N^{1.176}} = A + \frac{B}{N^{\epsilon}}$$

(iii) $$\frac{\langle S_N^2\rangle}{N^{1.176}} = A + \frac{B}{N^{\epsilon}} + \frac{C}{N}$$

(iv) $$\frac{\langle S_N^2\rangle}{N^{1.176}} = A + \frac{B}{N} + \frac{C}{N^2} + \ldots$$

(v) $$\frac{\langle S_N^2\rangle}{N^{1.176}} = A + \frac{B}{N^{0.5}} + \frac{C}{N} + \ldots$$

Models (i), (iv), and (v) were fit by using linear least squares, while models (ii) and (iii) were fit by using the method of differential corrections.[27]

The values of $g(f) = A(f)/A(1)$ presented in Figure 4 are averages of the various estimates. Similar procedures were followed for $B(f)$ and $g'(f)$.

The quantities μ and $\gamma(f)$ are estimated by fitting to the equation

$$\ln s_N = N \ln \mu + (\gamma - 1) \ln N$$

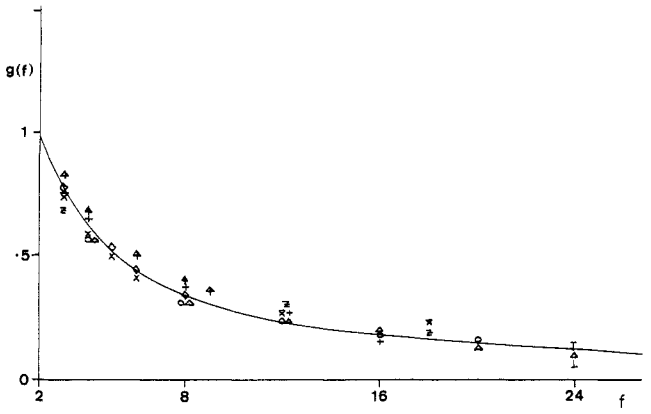

Figure 4. $g(f)$ vs. f: (○) 112, (△) 113, (+) 112 NA, (×) MC ref 17. (⏃) MC, ref 13; (◇) RG, ref 6. (⊠) experiment: Θ-solvent, ref 10. (Z) Experiment good solvent, ref 10. Solid line: Zimm–Stockmayer equation, ref 1. For $f \geq 4$, the curve lies very close to $1.86f^{-4/5}$. Estimated error bars have been added to one point for reference. See section 5.6.

Table I
Results for $\gamma(f)$[a]

	$\gamma(f)$		
f	112	113	MF[b]
1	1.16	1.15	1.13
2		1.17	1.13
4	0.71	0.91	0.75
8	−0.99	−0.30	0.50
12	−4.07	−2.56	−5.75
16	−8.80	−5.71	−12.0
20	−15.4	−12.3	−20.25
24		−20.0	−30.5

[a] $\mu = 22.49$ (112); $\mu = 22.36$ (113). [b] Reference 5.

No attempt has been made to account for subdominant correction terms to s_N. Results are displayed in Table I.

5. Results

5.1. Exponent ν. Linear log–log fits of $\langle S_N^2 \rangle$ vs. N or $\langle R_n^2 \rangle$ vs. n consistently yield values of ν less than 0.588 for the self-avoiding walks and greater than 0.588 for the neighbor-avoiding walks. This is not particularly surprising, given the residual curvature in the plots. We conclude that the "asymptotic linear region" has not yet been attained. A study of Figure 2 will indicate the remarkable smoothing which occurs when the ratios of sums (defined in eq 10 and 11) are plotted. Also remarkable is the curvature and oscillation present in these simple plots which indicates that very long series indeed will be required to establish the limiting values. One of the graphs shown in Figure 2 is for a self-avoiding walk, and the other is for a neighbor-avoiding walk. This latter graph displays considerable scatter for n greater than about 20. While similar plots for higher functionalities show somewhat greater scatter, it is not unfair to say that the limiting value could possibly be 0.588 in all cases. It is however not possible to determine ν with any precision on the basis of these plots. We have therefore *assumed* the accepted value $\nu = 0.588$ for fitting models (ii)–(v).

5.2. Branch Growth Constant μ. For the (112) and (113) walks, we have chosen to accept the respective values of 22.49 ± 0.05 and 22.36 ± 0.05 determined in a previous study.[18] For the (112) NA walk, we have determined $\mu = 17.2 \pm 0.2$. This is a value significantly lower than that for the (112) SA walk and gives a good indication of the increase in the excluded volume condition. If μ represents an "effective" coordination number, we can intuitively see that there are fewer sites available to the NA walk than to the SA walk, and this is entirely due to additional space occupied by previous steps of the walk.

Table II
Values for $g' = B(f)/B(1)$

f	112	113	112 NA	MF
2		1.07	1.28	1.06
4	1.19	1.08	1.43	1.17
8	1.47	1.20	1.54	1.39
12	1.71	1.27	1.80	1.61
16	1.48	1.43	1.74	1.83

Table III
$\langle R_{j,j+10}^2 \rangle$ for 113 and 112 NA Walks[a]

	$j = 0$		$j = 10$		$j = 80$	
f	113	112 NA	113	112 NA	113	112 NA
1	11.4	19.2	11.8	22.0		19.6
4	12.8	21.8	12.4	20.8	11.7	20.8
8	13.9	23.1	12.9	17.9		19.0
12	14.4	23.9	12.2	19.0	11.9	17.3
20	14.7		11.9	17.6	11.5	

[a] Isolated chains: $\langle R_{10}^2 \rangle = 18.2$ (112 NA); $\langle R_{10}^2 \rangle = 11.3$ (113).

5.3. Exponent $\gamma(f)$. While the values of $\gamma(f)$ differ somewhat from the predictions of Miyake and Freed, eq 9, the same strong "downward" tendency is clear from a study of Table I. It should be noted that good estimates of γ require precise estimates of μ, and these are currently not available. The values of γ for (112) NA walks show considerable scatter, and a direct analysis has not been attempted.

5.4. Ratios $g(f)$ and $g'(f)$. A crude estimate of the amplitude $A(f)$ may be obtained by plotting values of $\langle S_N^2(f) \rangle$ vs. n as shown in Figure 3 and extrapolating. It can be seen that, despite the small sample sizes, the data are smooth and well-behaved. The values of $g(f)$ plotted in Figure 4 have been found by fitting the numerical data to the functional forms assumed in section 4 and then taking the algebraic mean of the ratios $A(f)/A(1)$ thus obtained. The error bars sketched for the $f = 24$ point indicate the maximum and minimum fitted values. As can be seen, the estimates obtained for both the SA and NA walks all lie close to the Zimm–Stockmayer curve, which provides an adequate expression for g over the accessible range of f. For $f \geq 4$, it is virtually impossible to distinguish the Zimm–Stockmayer curve from the fitted function:

$$g = 1.86f^{-4/5}$$

As explained in section 2, it is not at all surprising that this should be so.

It was hoped that the Monte Carlo data would indicate a clear choice between the Miyake and Freed prediction that g' should scale as f and the Daoud and Cotton one that g' should scale as $f^{2/5}$. However, the variation due to the uncertainty in fitting for larger f is such as to preclude any attempt to accurately assess the value of the exponent. Moreover, the Miyake–Freed formula gives values for low f which are consistent with the data obtained (see Table II). A numerical resolution of this question was therefore not possible.

5.5. Intrachain Moments. It is not possible to make any quantitative predictions based on the results for intrachain moments. However, it is possible to draw some *qualitative* conclusions. It is immediately clear from a study of Table III, in which is presented the measured value of $\langle R_{j,j+10}^2 \rangle$ for various j, that there is a significant expansion near the branch point, and this expansion diminishes with distance from the branch point. As might

Table IV
Angle Subtended by Monomers j and $j + 1$

	$j = 10$		$j = 80$		
f	113	112 NA	113	112 NA	ref
4	45	53	74	76	90
12	51	58	74	78	60
16		59		77	53
20	54		76		48

be expected, the swelling is more marked for the NA walks than for the SA walks.

Table IV shows the average angle (in degrees) subtended at the branch point by monomers j and $j + 10$ within a branch. It can be seen that subchains initially have a transverse compression which relaxes as one progresses toward the outer region of the star. There appears to be some interpenetration of branches, particularly near the outer extremities of the star, which increases as f increases. This can be surmised from the reference angle displayed in the last column of Table IV. This is the maximum angle subtended at the branch point by one of f noninterpenetrating branches. While the angle between monomers appears to be relatively constant, this reference angle diminishes steadily with f.

5.6. Quality of the Data. A 24-branch star with 80 steps per branch represents a very large self-avoiding walk. Admittedly, 80 000 such objects are a very small sample. These considerations require that the properties estimated be "numerically stable", that, is not particularly sensitive to fluctuations in the data. One such quantity is the amplitude $A_n(f) = \langle S_n^2(f) \rangle / n^{1.176}$, whose limiting value is the principal object of study in this work. Figure 3 shows that, even for 24 arms, the estimated value of A_n is smooth and well-behaved for all n. In this case, for instance, the variance for the point at $n = 80$ is estimated to be 0.1.

The *maximum* possible error in the plotted points is the sum of the uncertainty in the numerical data and the uncertainty due to the fitting procedure used. This sum is greater than the error indicated in Figure 4. However, we have chosen to accept the maximum and minimum fitted values as being a reasonable indication of the *probable* error of $g(f)$.

6. Discussion

The measurements reported here, combined with the information gleaned from previous theoretical and experimental studied, provide a reasonably consistent picture of the configurational anatomy of a uniform star polymer. There is a *small* core in which the chain segments radiating from the branch point are very extended relative to the dimensions of isolated chains of comparable length. Although the core itself does not extend for more than a few segments, the radial extension of subchains persists to the extremities of the star branches. The fragment dimensions diminish steadily until at the end of the branch they are very like those of a chain of comparable length. However, it is important to note that *any* n-segment fragment of the star has a greater end-to-end extension than the corresponding isolated chain. One expects such chain expansion even at the outer regions of the star since there the dimensions of the subchain will be affected by the presence of an attached end chain of some considerable size.

At the same time, the fragments undergo a *transverse* compression near the branch point which diminishes as one progresses away from the core. It is this transverse compression which appears to best correspond to the Daoud–Cotton scaling predictions, in contrast to the radial dimensions which do not behave at all as Daoud and Cotton might predict. Their argument is based on a "blob" which expands *uniformly* with radial distance. The Monte Carlo results, however, are consistent with chain fragments occupying a cigar-shaped volume near the branch point and becoming more nearly spherical at the outer reaches of the star. We conclude that the concentration gradient forcing the chains outward is more potent than any screening of excluded volume due to the concentration itself. As there is no transverse concentration gradient, there may well be "transverse screening" of excluded volume.

It is useful to consider the relative importance of the different excluded volume regimes. Although it is not possible to discuss this matter with any precision, it is possible to make some remarks of a qualitative nature. First of all the core, in which the chain fragments are very extended, is of relatively little importance. Indeed, for stars with sufficiently long arms, its effect on chain dimensions is negligible. The other two regimes, which Daoud and Cotton refer to as the "unswollen" and the "swollen" regimes, respectively, are not at all insignificant. The question arises however as to whether such regimes are identifiable as distinct regions within the star. We think not. While there is a region where effective screening of excluded volume surely does occur in a transverse sense, this is the same region where the radial expansion is close to its maximum. We would prefer to think of the entire region outside the central core as being one regime in which expansion and compression occur in a complementary fashion.

Another very interesting question concerns the apparent insensitivity of the ratio $g(f)$ to excluded volume and the success of the Zimm–Stockmayer equation for real stars. This has already been discussed at some length in section 2 where it was pointed out that, by coincidence, the scaling behavior of g for Gaussian stars does not differ greatly from that for real stars; any differences over the accessible range can be accounted for by adjustments to the amplitude. We conclude on the basis of our data that the Daoud–Cotton scaling prediction is well satisfied. Certainly it is sufficiently accurate that any discrepancy between it and the true scaling law will not be detected by numerical or experimental means for some time to come.

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Configuration of Terminally Attached Chains at the Solid/Solvent Interface: Self-Consistent Field Theory and a Monte Carlo Model

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ABSTRACT: Segment density distributions, root mean square (rms) thicknesses, and bound fractions have been calculated for terminally attached chains at the solid/solvent interface. The effects of coverage, solvent quality, and adsorption energy are considered. Both the self-consistent field theory of Scheutjens and Fleer and a Monte Carlo method have been used. The results show a marked difference between systems with adsorption energies above and below the cricital value. Solvency has a significant effect on the variation of the rms thickness with chain length. At high coverages, polymer configurations with small bound fractions and highly extended tails are found. Differences between the two models are discussed.

Introduction

The configuration of terminally attached polymers at the solid/solvent interface has attracted a great deal of interest both experimentally and theoretically.[1] This interest is in-line with the increased use of these polymers as dispersion stabilizers, adhesives, etc. Experimentally, only small-angle neutron scattering[2] (SANS) has been used successfully to measure the segment density distribution of a terminally attached polymer at the solid/solvent interface.[3,4] The data for terminally attached polystyrene on silica in carbon tetrachloride[4] showed a clear maximum in the density distribution away from the interface. This could be interpreted in terms of a low χ_s[1,4] (the difference in the energy of adsorption of a segment and a solvent molecule in units of kT) and a high grafted amount. For physically adsorbed polystyrene on silica, however, a monotonically decreasing density distribution was found.

Theoretically, a large number of different approaches have been used to describe these systems. These can be divided into isolated chain[5-7] and interacting chain models.[8-10] Some of these models have used a lattice to constrain the number of chain conformations generated. An advantage of a lattice model is that the energy originating from nearest-neighbor interactions can easily be calculated.

For a single terminally attached chain, Hesselink[5] has given an analytical form for the density distribution, but no account is taken of the solvent or surface interactions. In the exact enumeration self-avoiding walk procedure,[6] the surface interaction is included and the critical adsorption energy χ_{sc} was determined. Croxton[7] has developed a self-avoiding hard-sphere model for terminally attached chains not constrained by a lattice. A monotonically decreasing segment density profile is found at high χ_s, whereas a profile with a pronounced maximum is found at low χ_s. The profiles however show a marked discontinuity near the interface.

For chemically grafted chains, there are often high chain densities at the interface, and single-chain models are unsatisfactory. Hesselink,[5] de Gennes,[10] and Dolan and Edwards[8] have discussed the influence of lateral interactions between chains. However, they have only considered the case for $\chi_s = 0$. Levine et al.[9] have combined the self-consistent field approximation with the matrix representation method of DiMarzio and Rubin.[11] In their paper, they calculate segment density profiles for terminally attached chains between two plates for different values of χ_s. They do not give any data for a single surface or a breakdown of the distribution in terms of segments in trains and loops. Clark and Lal[12] have used the Monte Carlo method with the periodic boundary constraint to mimic the effect of coverage. In their simulation, they generate new chain conformations from a parent distribution by a four-bond rotation; only the good solvent case is considered.

In this paper we compare a Monte Carlo approach with that of the Scheutjens–Fleer lattice model, extended to the case of terminally attached chains.

Monte Carlo Simulation

The Monte Carlo simulation for terminally attached chains was carried out by generating a large sample of self-avoiding walks on a simple cubic lattice. The surface was taken as a plane which the walks cannot cross. The first segment was attached at the origin (i,j,k = 1,0,0). At each point on the walk, the surrounding lattice sites were tested for previous visits before the next step was generated. The probability of making a step to any adjacent free site depends on the number of free sites available.[13] For example, in an "open" walk, where five of the surrounding positions are free, the probability of a step is $^1/_5$. In a "compact" walk, where, say, only two adjacent sites

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