fraction rather than the volume fraction for the interference term. The second step is to break the line of $N = N_0 + xN_x$ sites into $N^{2/3}$ lines each of $N^{1/3}$ sites. The problem of placing the N_x molecules on these $N^{2/3}$ lines is the same as the problem of placing N_x molecules in a three-dimensional cubic lattice when the molecules all have the same orientation. It is easy to show that to first order in N the entropy is the same for the $N^{2/3}$ lines of length $N^{1/3}$ as for the one line of length N.
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Role of Excluded Volume in the Configurational Properties of Uniform Star Polymers: Iterative Convolution and Monte Carlo Simulation

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ABSTRACT: The dimensional properties of three-dimensional uniform athermal self-avoiding star polymers of small to intermediate molecular weight are determined in the iterative convolution (IC) approximation. The results are compared with continuum Monte Carlo (MC) simulations and with lattice-based and renormalization group (RG) estimates that relate to the large-N limit. In particular, the present analysis provides direct structural and dimensional assessment of the interior star regimes proposed by Daoud and Cotton, which are inaccessible to the lattice-based and RG treatments. We find no evidence to support the Daoud–Cotton proposals. On the basis of the iterative convolution approximation, the central core structure of the star terminates at a density discontinuity followed by secondary radial structural features. These features are confirmed by Monte Carlo simulation. The relative mean square radii of gyration $g(f) = \langle S_N^2(f)\rangle / \langle S_N^2(1)\rangle$ is determined as a function of branching number f, and contrary to the Daoud–Cotton proposals we find $g \sim f^{-1}$ for small-to-intermediate uniform star systems. The particle scattering function $P(Q)$ is also determined, and comparisons are made with its random walk counterparts for a variety of star configurations.

Introduction

Interest in the theoretical description of the configurational properties of star-branched polymers has developed considerably with the increasing body of experimental data, largely based on recent light-scattering[1] and rheological/hydrodynamic studies.[2] Since the classic paper of Zimm and Stockmayer[3] based on the random-walk model (RW) of a polymer star, subsequent attention has been focused largely on the incorporation of the excluded volume effects appropriate to a real molecule. Notwithstanding these attempts, considerable attention has been devoted to the configurational statistics of star polymers in Θ solvents, and these studies have been complemented by experimental studies in Θ solutions. However, as has been frequently observed, there may not exist a unique Θ point at which the Zimm–Stockmayer theory would be appropriate due to the strong radial variation in monomer concentration about the star's vertex. Indeed, Daoud and Cotton[4] identify three distinct concentration regimes outward along a radial vector from the star center: in the central close-packed core the monomer concentration is essentially constant, while at intermediate distances interbranch effects dominate, excluded-volume effects are effectively screened, and the behavior is assumed to be Gaussian. In the outermost regions the full intrachain excluded-volume effect obtains, and in conjunction with a variable blob size representation of the sequence along each star branch, Daoud and Cotton established a functional form for the radial distribution of monomer concentration on the basis of scaling arguments in terms of the number of branches f and distance from the central vertex. Implicit in their treatment is the assumption of a monotonically decreasing monomer concentration along a radius vector, together with a somewhat arbitrary choice of blob size. Despite these objections, some of their results are in good agreement with light-scattering data[1] and recent exact enumeration studies,[6] although the model remains open to the above criticisms. Two of the characteristics of scaling arguments are their restriction to a power law representation of the configurational properties upon density and molecular weight and their inability to predict prefactors and distribution functions; in this regard the analysis of Daoud and Cotton is no exception. Indeed, many of the power law exponents are independent of the number of branches, the structure of the star polymer emerging solely from the prefactors, clearly emphasising the importance of their explicit determination.

More recently a chain conformational renormalization group (RG) technique has been applied to star polymers by Miyake and Freed[5] whose specific objectives were to

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determine the principal configurational properties of uniform f-branched polymers, including prefactors and the full crossover dependence of all quantities on the strength of the excluded-volume interaction and the chain length. The calculation proceeds by the usual excluded volume perturbation expansion with subsequent expansion in $\epsilon = 4 - d$, where d is the number of dimensions and the preoccupation is with the case $\epsilon = 1$. We note from the outset that these Gell-Man-Low type renormalization group estimates are all to $\mathcal{O}(\epsilon)$ and, indeed, coincide with the Zimm-Stockmayer result in $d = 4$. Moreover, because of the assumed form of intra- and interchain interaction, the renormalization group technique is inherently incapable of describing hard-core packing fractions $> \sim 20\%$ in the vicinity of the vertex, where the details of the monomer interaction are significant, and to this extent is likely to misrepresent configurational properties of star systems in which the packing details of the central core constitute an important component of the overall structure. Miyake and Freed suggest their calculations are accordingly restricted to branch numbers $f \leq 7$: this, however, is in the limit $N \rightarrow \infty$, and core contributions are likely to be of considerably greater significance for finite star systems.

These latter observations appear to be confirmed by recent three-dimensional lattice-based exact enumeration and Monte Carlo representations of self-avoiding f-branched star polymers by Whittington et al.,[6] according to which the RG estimates show a progressive overestimate of the gyration ratio $g(f)$ for $f \geq 3$, an effect that may be attributable to the inadequate description of the close packing regime at the vertex, which suggests that the details of central core packing may be significant even when the primary objective is the determination of the asymptotic dimensional exponents as $N \rightarrow \infty$.

In this study we present an iterative convolution description of uniform finite star polymers in dilute solution, with particular emphasis on the determination of the dimensional and scattering properties of the system as a function of branch length n and number f. The iterative convolution determinations include all uniform stars having $f \leq 6$, $n \leq 10$, while the Monte Carlo simulations are effectively restricted to substantially smaller branching lengths and numbers due to severe attritional losses. Indeed, the successful generation of uniform stars of high functionality (e.g., $f = 6$, $n > 3$) was so unlikely as to yield no opportunity for statistical averaging. Accordingly, comparisons between the IC and MC analyses are restricted to those regions of (f,n) for which there is an adequate MC data base. The molecular weight of the uniform stars is taken to be $N = nf + 1$, with a central monomer located at the vertex. Other geometrical branching structures such as nonuniform stars, combs, etc., may be readily handled by the same methods, but here we restrict ourselves to uniform systems of f identical branches of n monomers. In addition to the dimensional properties of star polymers, we determine the radial segment density distribution about the vertex, since this appears to be the subject of some controversy—and indeed, we compound the controversy with the identification of a discontinuity not previously predicted but nevertheless confirmed by our continuum Monte Carlo studies. The internal concentration regimes proposed by Daoud and Cotton are investigated in detail, complementing the limiting analyses ($N \rightarrow \infty$) that describe the long-range structure of large stars.

Theoretical Background

A detailed description of the iterative convolution (IC) technique has been given elsewhere,[7] and a wide variety of applications have been previously reported in the literature.[8] Here we restrict ourselves to those aspects that are relevant to the description of uniform star systems and refer the reader to the original paper[7] for details of the theoretical procedure. Basically, the IC technique describes finite *linear* heterogeneous sequences of segments in terms of the normalized spatial probability distribution $Z(ij|N)$ developed between segments i and j within the N-mer (Figure 1). (We denote r_{ij} by ij throughout, without ambiguity.) The only input quantity required is the specification of the interaction matrix $[\Phi_{ij}]$, which describes the full set of intersegmental pair potentials developed within the sequence. In the case of linear homogeneous sequences the specification of the interaction matrix is particularly simple, and we shall restrict ourselves to such homogeneous systems. Sequential connectivity and preservation of the contour length of the sequence is ensured by setting $Z(i,i\pm1|N) = \delta(r_{i,i\pm1}-D)$, where D is the separation of sequentially adjacent monomers: it should be pointed out, however, that any well-behaved functional form for $Z(i,i\pm1|N)$ may be specified—harmonic functions, for example—although here we restrict ourselves to the fixed contour length implied in the adoption of δ bonds between adjacent segments.

The coupled set of integral equations relating the interaction matrix to the distribution functions has been given elsewhere,[7] but we nevertheless repeat the fundamental ansatz here for the purposes of subsequent discussion. The spatial probability distribution between segments i,j within the system is given as

$$Z(ij|N) = H(ij)\Pi' \int Z(ik|N)\, Z(kj|N)\, \mathrm{d}\mathbf{k} \qquad (1)$$

where Π' represents a mean of the product of convolution integrals and $H(ij) = \exp(-\Phi_{ij}/kT)$. As it stands, eq 1 is not in iterative form; however, by substitution of the equation into itself

$$Z(ij|N) = H(ij) \int H(ik)\Pi' \int Z(il|N)\, Z(lk|N)\, \mathrm{d}\mathbf{l} \; H(kj)\Pi' \int Z(km|N)\, Z(mj|N)\, \mathrm{d}\mathbf{m}\, \mathrm{d}\mathbf{k} \qquad (2)$$

the set of coupled integral equations may be solved iteratively by fast Fourier transform techniques. It should be emphasised that eq 1 expresses the *direct* interaction $H(ij)$ between particles i and j and all *indirect* routes of propagation involving from 1 up to the remaining $N - 2$ particles in the sequence.[7] While the distributions and their various principal moments appear to be in the best reported agreement with Monte Carlo estimates for linear hard-sphere sequences, eq 1 is nevertheless an approximation, and it is appropriate to identify those features that are of particular relevance in the discussion of uniform star polymers.

Previously,[7] in formation of the mean Π' in eq 1 all convolution products between a given pair of segments, i,j say, where mediated through every field point $1 \leq k \neq i,j \leq N$ *with equal weight*. Now while every field-point k should participate in the total convolution product, they should not, in general, arise with equal weighting, and this is a characteristic feature of the iterative convolution approximation. In particular, the formation of a short-range distribution $Z(i,i\pm n|N)$ ($n \ll N$) will at some stage involve the convolution of long-range products, which in fact should play a subordinate role in the formation of $Z(i,i\pm n|N)$. The net effect of this as it stands is to progressively enhance the long-range form of these internal distributions with increasing chain length. This will be of particular concern later when we make comparisons of

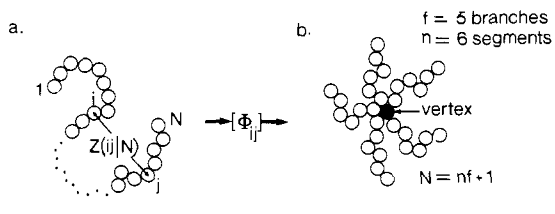

Figure 1. (a) Geometry of a linear polymer sequence. (b) Application of the interaction matrix $[\Phi_{ij}]$ to the linear sequence (a) yields the transformation to a uniform star polymer.

stars of high molecular weight (large N) with their linear counterparts. Accordingly we differentially weight the convolution product between points i,j mediated through field-point k all within the system by the factor $(|n_{ik}n_{kj}|)^{-1}$, where n_{ik} is the number of links between segments i,k in forming Π'. This has the effect of subordinating the contribution of long-range convolutions involving field points whose contour distance between i,j is great. Although segments i,j may have a substantial contour length separating them, they may, of course, still find themselves in close proximity, if they are on adjacent branches, for example. However, the weighting factor is meant to reflect the substantial differences in *range* accessible to a given i,j pair, and therefore the differential probabilities of the various mediating paths of propagation of correlation. Nevertheless, we are restricted to stars of intermediate molecular weight, contrary to the preoccupation in the literature with the limiting properties as $N \rightarrow \infty$. This is so since the IC technique is an approximation, and the long-range spatial distributions that arise in systems of high molecular weight suffer progressively from cumulative errors that develop in the formation of the convolution product of all shorter range distributions. How serious this becomes at large N is not known, and we tend to restrict our IC analyses to those systems that may be conveniently investigated by complementary MC simulations. This restriction to low to intermediate molecular weights is in fact a distinct advantage since it enables us to investigate the internal regimes of the star described by Daoud and Cotton, but which remain inaccessible to the renormalization group and lattice-based analyses.

The IC approximation effectively replaces the $(N-2)$-fold integral by a weighted mean of a product of $(N-2)$ one-dimensional integrals, and the approximation inevitably embodies a loss of fidelity in the expression of self-interaction within the sequence. Unfortunately this is hard to quantify, and the best assessment we can make at this stage is a qualitative comparison with simulation data: this we shall do throughout the present analysis.

We are primarily concerned with excluded volume effects within the system, and here we consider a linear sequence of flexibility connected hard spheres of diameter $\sigma = 1.0$: sequential connectivity is ensured by setting $Z(i,i\pm1|N) = \delta(r_{i,i\pm1}-D)$, with $D = \sigma = 1.0$. Designating the first segment 0 and recalling that any well-behaved form of interaction between any pair of segments may be specified, we form an f-branched uniform star polymer with n monomers per branch by replacing the δ bond between sequential segments $(bn,bn+1)$ within branch b $(1 \leq b < f)$ by the nonsequential hard-sphere interaction, while additionally specifying δ bonds between segments $(0,bn+1)$. Such a specification of the interaction matrix transforms the homogeneous linear sequence into the uniform star polymer shown in Figure 1. Other specifications would, of course, yield other branching geometries such as nonuniform stars, combs, etc., but we shall not investigate these here. We note at this stage that the segment diameter is effectively a crossover parameter since $0 \leq \sigma \leq 1.0$ yields the crossover behavior between the Gaussian ($\sigma = 0$) and full excluded volume ($\sigma = 1.0$) limits, although we shall not pursue this aspect here.

Monte Carlo Simulation of Uniform Stars

There have been relatively few simulations of star molecules that incorporate excluded volume effects, and these have generally been restricted to lattice-based analyses. Here we consider three-dimensional continuum systems of perfectly flexible uniform star polymers. First we outline the growing algorithm.

Stars with f branches of n segments (f,n) are grown by placing f segments randomly about the vertex segment (with a uniform distribution over the surface of the sphere for each) and then adding one segment at a time to each branch in turn, the added segment uniformly distributed about the previous segment in its branch. Only configurations that have no overlaps are accepted and added to statistics for (f,n).

Note that smaller stars are generated in the process of growing large ones. For example, if a (3,6) star is being grown, placing the third segment on the second branch forms a (2,3) star, which can be accepted as a (2,3) configuration provided there are no overlaps among the seven segments (including the vertex) of the subset corresponding to the smaller star, regardless of whether the entire (3,6) configurations are successful or not.

The program always sets out to grow a star of (max f, max n), checking appropriate subsets for overlaps and accumulating statistics for smaller f and n as it goes. Note that once any segment on a given branch has caused a violation with its own or earlier branches, adding more segments to that branch or following branches is pointless, as the violation will remain. It is, however, still possible to accumulate other acceptable substars of the entire configuration by continuing to build on earlier branches.

In this way uniform (f,n) stars are grown, and the principal configurational statistics accrued. In particular, the radial distribution of segments per branch about the vertex $\rho(r|f,n)_b$, the mean square radius of gyration $\langle S_N^2(f)\rangle$, the mean square branch length $\langle R_n^2(f)\rangle$, and the mean branch length $\langle R_n(f)\rangle$ are determined. Where possible, 40000 successful configurations per uniform star were taken, but for some of the larger stars substantially smaller samples were enforced. In all cases 95% confidence limits on the geometrical quantities were determined. There is, of course, no distinction between a two-branched star and a linear chain. This identity was used as a confirmation of the MC technique adopted here: the present growing algorithm yielded identical geometrical properties for $(2,n)$ stars as for conventional linear $2n + 1$ segment chains.

In addition the scattering function $P(Q)$ (eq 5) was determined on the basis of these excluded-volume Monte Carlo simulations. Although the ensemble average $\langle \sin Qr_{ij}/Qr_{ij}\rangle$ could have been determined, it was computationally easier to form the Fourier transforms of the set of distributions $Z(ij|f,n)$. While there have been numerous Monte Carlo simulations of $P(Q)$ data, these are generally based on unperturbed RISM sequences in which local rotational features of the chain are modeled, but long-range excluded-volume effects are neglected. Here we are modeling a perfectly flexible hard-sphere system in which excluded volume features are explicitly incorporated.

Radial Distribution of Monomer Concentration

The IC technique is ideally suited to the determination of the structure of stars of low-to-intermediate molecular weight and in particular is able to describe those interior regimes proposed by Daoud and Cotton that are inaccessible to techniques that depend on the limiting condition $N \to \infty$.

Clearly, a knowledge of the complete set of intersegmental spatial probability distributions $Z(ij|f,n)$ ($N = fn + 1$) within the star enables us to determine all the principal dimensional properties of the system, including the radial distribution of monomer concentration about the central vertex, this being one of the major structural features of star polymers yet to be unequivocally resolved. In their analysis, Daoud and Cotton first introduce their "blob" concept within which the average geometrical properties of the sequence are related to the local monomer concentration. The dimension of the blob is a variable parameter and is assumed to increase monotonically with distance from the vertex. They then identify three distinct concentration regimes, within each of which a different functional dependence on branching number f and radial distance from the vertex is proposed (Figure 2a). In the central close packed core ($r < f^{1/2}$) excluded-volume processes dominate, and the monomer concentration is taken to be effectively constant, with the branches virtually fully extended. At intermediate distances from the vertex ($f^{1/2} < r < \upsilon^{-1}f^{1/2}$) intrachain processes are modified by the presence of adjacent branches that effectively act as a solvent. In this semidilute regime geometric screening is presumed to induce Gaussian behavior within the blobs, and the radial variation of concentration dependence is taken to be of Zimm–Stockmayer form: $\phi(r) \sim f^{1/2}/r^{-1}$. Finally, at large radial distances from the central vertex ($r > \upsilon^{-1}f^{1/2}$), where υ is the excluded volume associated with a monomer, intrachain processes are assumed to dominate, with interbranch effects being relatively unimportant. In this regime Daoud and Cotton describe the branches as isolated linear sequences with excluded-volume effects present within the blobs, and the functional form of the concentration dependence is taken to be $\phi(r) \sim f^{2/3}\upsilon^{-1/3}r^{-4/3}$. Notwithstanding the good agreement between some of their predicted results and light-scattering experiments,[1] the proposal of three distinct concentration regimes is open to criticism not only on the basis of the somewhat ad hoc prescription for their location but also because the model denies the essentially continuous radial response of the sequence to its local environment. Again, the size of the blobs is somewhat arbitrarily determined, and this has an immediate bearing upon the local monomer concentration and, indeed, its functional form. However, it is difficult to justify a close-packed extended-chain regime at all branching numbers as Daoud and Cotton assert. Miyake and Freed attribute to this packing anomaly the substantial discrepancy between the Daoud–Cotton model and the RG estimates which are expected to most appropriately describe small branching numbers at low packing fractions (<20%) where details of the monomer packing are relatively unimportant.

At intermediate distances from the vertex the assumption of Gaussian behavior on the basis of screening processes of the kind proposed in semidilute solutions can only be regarded as a caricature of the true behavior, and there is no evidence that a spatially extended regime of this type can exist within a uniform star system: indeed, it is somewhat easier to argue *against* the existence of such a regime in a star polymer than in a uniform semidilute system of linear chains. Certainly Miyake and Freed did not observe this kind of screening in their RG calculations, nor was it observed in our own Monte Carlo simulations. Finally, while such scaling arguments attempt to express the power law dependence upon molecular weight, branching number, etc., they are inherently incapable of

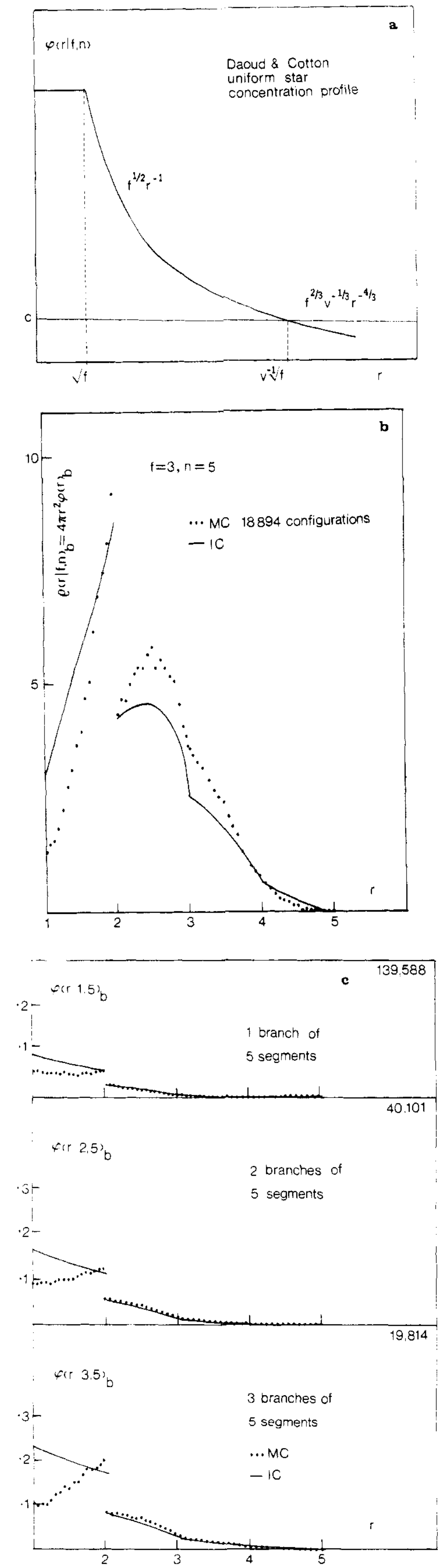

Figure 2. (a) Schematic form of $\phi(r)$ assumed by Daoud and Cotton. (b) Radial distribution of monomers $\rho(r|f,n)$ within a branch about the central vertex for $f = 3$, $n = 5$ incorporating excluded volume, determined on the basis of iterative convolution (IC) and Monte Carlo techniques. (c) Concentration of monomers (number of segments/unit volume) per branch $\phi(r|f,n)_b$ about the central vertex for $f \leq 3$, $n = 5$ in the excluded volume limit.

yielding the prefactors, without which quantitative comparison of distribution functions and the principal dimensional properties of the system cannot be made.

The radial distribution of monomer concentration within a branch b ($1 \le b \le f$) is defined by

$$\rho(r|f,n)_b = 4\pi \sum_{i=1}^{n} Z(0i|f,n) r_{0i}^{2} \quad (3)$$

where $Z(0i|f,n)$ is the normalized spatial probability distribution of the ith segment relative to the central vertex within a uniform f-branched star each containing n monomers per branch. Clearly, the radial monomer distribution is identical for each of the f branches within a given uniform star, and in Figure 2b we present $\rho(r|f,n)_b$ for a uniform star having $f = 3$ branches each of length $n = 5$ monomers and determined in the full excluded-volume limit $\sigma = 1$. Although the IC analyses extend to include uniform (6,10) stars, meaningful comparison with MC data is unfortunately restricted to (3,5) systems on account of the extremely high attrition rates encountered in trying to form MC systems of high functionality. The distributions have the required property that

$$n = 4\pi \int_0^{\infty} \rho(r|f,n)_b r^2 \, dr$$

Two striking features of the distribution are immediately apparent. First, the radial distribution of monomer concentration is a much more structured function of distance from the central vertex than assumed by Daoud and Cotton, and second, there is a pronounced discontinuity in the distribution at one segment diameter beyond the central monomer with the development of subsequent structure in the form of discontinuities of gradient at integral radial separations from the vertex. The amplitude of the principal discontinuity develops strongly with increasing branch number and appears convincingly confirmed on the basis of Monte Carlo simulation, as does the subsequent radial structure. It should be emphasized that this discontinuity is *not* an artifact of either the IC or the MC analyses. Indeed, the existence of the discontinuity has been demonstrated analytically[11] and is a straightforward consequence of the uniform distribution of the first and second branch segments about the vertex particle. The result is confirmed by correctly conducted continuum Monte Carlo simulation. The discontinuity cannot be resolved on the basis of discrete lattice representations due to the essential coarseness of the spatial resolution.

It is not generally appreciated that this discontinuity develops in random-walk stars, although *not* when the intersegmental distributions $Z(ij|N)$ are represented by Gaussian functions. The exact form for the random-walk distribution function[22]

$$Z(r) = [2^{n+1}(n-2)!\pi r]^{-1} \sum_{k=0}^{(n-r)/2} (-1)^k \binom{n}{k} (n-2k-r)^{n-2} \quad (4)$$

where $n = |j - i|$ is the number of links between i,j, assumes the Gaussian form only as $n \gg 1$ and is therefore inappropriate for the description of the core region of random-walk stars and indeed for any of the small-to-intermediate-sized RW stars considered here. In fact, all $Z(i,i{\pm}2)_{RW}$ exhibit a pronounced discontinuity at the end of their range, and although the amplitude of the RW discontinuity does not develop with f, of course, it is nevertheless a pronounced feature of the random-walk segment density profile for the range of uniform stars considered here.

Direct comparison with the density profile of Daoud and Cotton (Figure 2a) is made in terms of the function $\phi(r)_b = \rho(r)_b/4\pi r$ (Figure 2c) and represents the radial variation of monomer concentration per branch (i.e., number of segments/unit volume). Both the IC curve and MC data disagree substantially with the proposed form of Daoud and Cotton in three essential respects. First, the central core structure terminates in a density discontinuity in $\phi(r)_b$ at one segment diameter from the vertex. This is predicted on the basis of the IC calculations and is clearly confirmed on the basis of the MC analyses. The amplitude of the discontinuity appears to develop with branch number f but not with branch length n, which confirms the association of the discontinuity with the packing in the immediate vicinity of the central monomer.

The existence of the discontinuity in uniform star systems appears not to have been anticipated in the literature, although such a feature has been identified on the basis of the iterative convolution technique in the case of terminally attached sequences at a rigid boundary.[10] The discontinuity was subsequently confirmed both analytically[11] and on the basis of continuum Monte Carlo analyses:[12] this feature is unequivocally attributed to geometric packing effects, and the reader is directed to the earlier papers[11,12] for details of its development. Suffice it to say here, however, that the discontinuity arises from the distribution of segment $i + 2$ about $i + 1$, where the latter is contiguously attached to the vertex particle 0. A similar phenomenon was reported on the basis of the IC description of ring polymers.[8]

We observe that at low branching numbers the distribution is far from constant within one segment diameter of the vertex particle, and only with increasing f does the core tend toward the constant close-packing concentration assumed by Daoud and Cotton (Figure 2a). However, we believe the monomer concentration at contact with the vertex particle is consistently overestimated in the IC approximation and is attributed to a degree of monomer interpenetration that arises in the IC approximation at all packing densities:[11] this conclusion appears supported by the MC data and is an aspect of the IC approximation that was anticipated previously.

Accordingly, we strongly suspect that the negative gradient in $\phi(r|f,n)_b$ within one segment diameter of the vertex determined on the basis of the IC approximation should be substantially reduced, if not reversed, and this conclusion appears to be supported by the MC data on the basis of which the contact value $\phi(r{=}1)_b \sim 0.1$ at the central monomer for all $f > 1$, regardless of branch length n. This implies that the monomer concentration *per branch* in the immediate vicinity of the vertex segment remains constant, while the concentration within the central core $1 < r \le 2$ steadily increases with branching number but not with length.

With increasing f at constant branch length n the distribution extends radially, indicating that a given branch expands away from the close-packed central core as the number of branches increases (Figure 2c): we shall return to this aspect below. While the principal discontinuity forms at all degrees of branching, the subsequent structure appears to develop with increasing f and is regarded as an unequivocal feature of the concentration profile. The existence of the principal discontinuity and the subsequent radial structure and the dependence of the distribution upon the branching parameters (f,n) determined on the basis of the IC technique appear fully supported by the Monte Carlo data.

Beyond the central core, the density distribution $\rho(r|f,n)_b$ and its concentration counterpart $\phi(r|f,n)_b$ both show distinct structural features, confirmed by Monte Carlo simulation and at variance with the Daoud–Cotton proposals. In particular there appear discontinuities of *gradient* in both $\phi(r|f,n)_b$ and $\rho(r|f,n)_b$ at integral radial distances from the central vertex and somewhat analogous with the radial distribution in a hard-sphere fluid. Undoubtedly these arise from geometrical packing effects in the vicinity of the core region and suggest that any theory incapable of accounting for excluded-volume features in the vicinity of the vertex must inevitably forfeit any description of star properties that are dependent on the features of central core packing, in particular the renormalization group and lattice-based techniques, which cannot accommodate the detailed features of close geometrical packing. It is perhaps in this respect that the distinction between the IC and Dauod–Cotton descriptions of the interior structure of uniform stars is at its greatest, and the experimental resolution of the differences most important. Basically, the IC description predicts structure attributable to geometrical packing effects, while the Daoud–Cotton model suggests a random-walk behavior characterized by Gaussian spatial distributions. These possibilities should be readily distinguished by scattering studies, and we return to a calculation of the scattering function below.

It should be said, however, that for systems of high molecular weight whose geometrical properties are essentially determined by the configurational properties of dilute extended branches in which the core region is of subordinate importance, we would expect that the renormalization group and lattice-based analyses to agree well with each other and with experiment for systems of high molecular weight.

The iterative convolution analysis, restricted to systems of low-to-intermediate weight, is particularly suited to the investigation of the interior regimes proposed by Daoud and Cotton: the interior features of the star are, of course, inaccessible to those analyses that require passage to the limit $N \to \infty$. Assessment of Daoud and Cotton's scaling predictions for the radial monomer concentration is best made in terms of the g ratios discussed in the next section. We shall therefore postpone detailed discussion until later and simply restrict ourselves here to the observation that their scaling predictions are not supported by the IC determinations.

Particle-Scattering Function for Star Polymers

In dilute solution the particle-scattering function $P(Q)$ for a system of N identical point scatterers can be written as[17]

$$P(Q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle \exp(i\mathbf{Q}\cdot\mathbf{r}_{ij})\rangle$$

where $\mathbf{Q} = (4\pi/\lambda)\sin(\theta/2)$ is the reduced scattering vector between the incident and scattered coherent beams and $\mathbf{r}_{ij}$ is the vector connecting scattering centers i and j within the molecule. λ is the wavelength of the scattered radiation in the medium. Averaging over all orientations of $\mathbf{r}_{ij}$, the above equation reduces to

$$P(Q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle \sin(Qr_{ij})/Qr_{ij}\rangle \qquad (5)$$

where the broken brackets represent the spatial average over the scalar separation r_{ij}. This, of course, is nothing other than the Fourier transform of $Z(ij|N)$, which is routinely determined in the course of the evaluation of the convolution integrals (eq 1), and so the scattering function is a natural product of the IC technique.

Given the novel structure of the radial monomer concentration predicted in the previous section, it is of interest to see whether the discontinuity can be resolved from scattering studies and to determine the effect of branching number f and molecular weight N upon the particle-scattering function $P(Q)$.

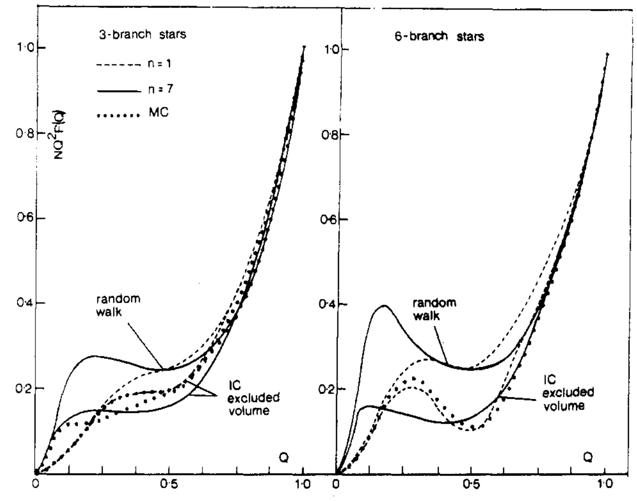

Figure 3. Kratky plots of $P(Q)Q^2N$ versus Q for uniform stars (a) $f = 3$, MC(n = 1, 7); (b) $f = 6$, MC(n = 1).

There have been earlier attempts to calculate the particle scattering function of linear systems ab initio, but a number of simplifications have to be introduced, not least of which is the neglect of excluded volume. And while developments of the generator matrix method of Flory et al.[18] have recently been made in an attempt to incorporate the self-avoiding feature,[19] the technique can only be applied consistently in the case of zero excluded volume. In general, the determination of $P(Q)$ requires the combination of eq 5 with a realistic chain model: these two features come together naturally in the IC approximation.

In Figure 3 we plot $P(Q)Q^2N$ versus Q for a variety of star configurations (f,n). These so-called Kratky plots are determined on the basis of the exact random-walk (eq 4) and IC excluded-volume treatments, and their comparison provides a useful means of identifying the role of the excluded volume processes in the scattering from a uniform star polymer. Beyond $Q \sim 0.5$ the RW and IC set of curves each becomes independent of star configuration (f,n) and molecular weight, although in both cases the plots coincide at $Q = 1.0$. Scattering at large wave vectors relates to the scale of the monomer units, and is obviously independent of macromolecular structure.

At small Q, in the so-called Guinier scattering region, eq 5 may be expanded:

$$P(Q) \simeq 1 - \frac{Q^2\langle S_N{}^2\rangle}{3} + \ldots$$

Clearly, this region of the curve relates to the macromolecular structure of the system, and in both the large and small Q limits the random-walk and excluded-volume Kratky plots are qualitatively similar. It is at intermediate Q relating to local configurational structure on the scale of several monomer units within the star where the major discrepancies between the RW and excluded-volume structures occur. It is clearly apparent that the Kratky function develops a pronounced maximum at $Q \sim 0.2$ with increasing branch length at given f for RW stars, while for excluded-volume systems the curve develops a plateau region as n increases. This strongly suggests qualitatively different behavior within the two systems over intermediate spatial scales and would appear not to sustain the Daoud–Cotton proposition of a Gaussian interior regime since for our intermediate-size stars substantial scattering should arise from Daoud and Cotton's region II. Nor, moreover, do these results support the proposition that the RW description affords an acceptable representation of excluded volume systems as has been suggested elsewhere:[6] the discrepancy appears to increase with increasing molecular weight. It may well be that there is nevertheless some coincidence in the gross geometrical features of the random-walk and excluded-volume systems, but this does not entitle the presumption of similar configurational structures within the star: indeed, the present results suggest they are qualitatively distinct. Also shown in Figure 3 are the corresponding Kratky plots for Monte Carlo excluded volume systems for $f = 3$, $n = 1, 7$, and $f = 6$, $n = 1$. These results are in good agreement with the IC determinations, confirming the qualitative distinction between the RW and excluded-volume systems. We point out the small quantitative discrepancy between the IC and MC predictions at intermediate Q, which we attribute to the known slightly imperfect IC representation of the monomer–monomer distribution at close separations.

Experimentally, proposed configurational structures of such systems may be tested by exploiting contrast factors in small-angle neutron scattering. Here, however, we may readily identify the origin of various features in the Kratky plot by restricting the double sum in eq 5 to certain subsets of the Fourier transforms and observing the effect on $NQ^2P(Q)$. Thus we are able to identify the pronounced peak in the RW Kratky plot at intermediate Q with interbranch scattering.

The fundamental distinction between interbranch scattering in random-walk and excluded-volume systems is that in the former case there is no branch–branch interference. Indeed, the only common feature of the two systems is the preservation of branch contour length, and presumably any differences must be attributed to excluded volume effects.

In their analysis of small-angle neutron scattering from a polystyrene-*b*-poly(methyl methacrylate) diblock copolymer, Edwards et al.[21] model the dimer as a spherical central core of poly(methyl methacrylate) with diametrically opposed isolated polystyrene chains attached to the surface. Such a structure may be described as a two-branch star with a large central core, and these authors find that Monte Carlo simulations of an impenentrable spherical core of 50-Å diameter with two diametrically opposed 50-segment RISM chains attached yielded a particle-scattering function in close agreement with the SANS data and in qualitative agreement with the theoretical particle-scattering functions determined here. The RISM chains embodied no excluded volume, however, and a direct comparison between our homogeneous $(2,n)$ star systems and the highly heterogeneous diblock copolymer of Edwards et al. is not appropriate. Of course, quantitative agreement would not be expected from such dissimilar systems, although the same behavior for the experimental diblock copolymer of Edwards et al. with increasing molecular weight was observed in the present studies.

Relative Mean Square Radius of Gyration

The mean square radius of gyration $\langle S_N^2(f)\rangle$ of a uniform f-branched star polymer of molecular weight N may be determined by light-scattering techniques,[1] as may its linear counterpart $\langle S_N^2(1)\rangle$. Their ratio

$$g(f) = \langle S_N^2(f)\rangle / \langle S_N^2(1)\rangle \qquad (6)$$

determined in the limit $N \to \infty$, provides a measure of the relative deployment of monomer concentration of the star polymer with respect to a linear sequence of the same molecular weight. The random-walk result, obtained by Zimm and Stockmayer,[3] leads to the following relation between g and the number of branches f in a uniform star:

$$g = (3f - 2)/f^2 \qquad (7)$$

a result recovered by Miyake and Freed in their RG description when $\epsilon = 4$ and/or when their crossover parameter is 0. An analogous quantity g', based on the intrinsic viscosity ratio of branched and linear chains, has been related to the g ratio by a number of workers.[1,9] While each worker predicts a different functional relationship, they nevertheless agree that g' increases with increasing g. However, given the uncertainty, we restrict ourselves to the geometrical ratio g. Daoud and Cotton predict that

$$g \sim f^{-4/5} \qquad (8)$$

for long branches in a good solvent, and this is confirmed to within 1% by the lattice-based MC enumerations of Whittington et al.[6] and is further supported by experimental data,[1] and although the RG estimates of Miyake and Freed appear not to support the proposition, this may be attributed to the systematic and substantial discrepancy in their g ratios with increasing f. For our purposes we are more concerned with stars of intermediate molecular weight, for which the Daoud and Cotton model predicts

$$g \sim f^{-1/2} \qquad (9)$$

while for sufficiently small systems ($f \sim n^2$) such that the core constitutes the whole star, Daoud and Cotton propose

$$g \sim f^{-2} \qquad (10)$$

These relations form important criteria in the assessment of Daoud and Cotton's scaling analysis in regions inaccessible to other theoretical treatments and scattering investigations and will be investigated in detail below. The definition of the mean square radius of gyration for a system of identical monomers is

$$\langle S_N^2\rangle = \frac{1}{N(N-1)}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\langle r_{ij}^2\rangle \qquad (11)$$

and the development of the ratio g as a function of branch number f is presented in Table I for uniform star polymers comprised of unit hard-sphere monomers: both $\langle S_N^2(f)\rangle$ and $\langle S_N^2(1)\rangle$ are determined on the basis of the iterative convolution and Monte Carlo analyses. The IC estimates extend to branch lengths $n = 10$ for all branching numbers, and these small-to-intermediate $g(f)$ ratios are presented in Table I. Even so, it is difficult to resist forming a least-squares fit to the IC data and determining a limiting estimate of $g(f)$ as $N \to \infty$. These are also presented in Table I. While the legitimacy of these extrapolated values may be questioned, it is nevertheless evident that these limiting estimates must inevitably be less than the finite molecular weight values, which are already smaller than all other estimates except for our continuum Monte Carlo values. The Monte Carlo continuum estimates reported here relate to (f,n) values of (3,10), (4,8), (5,6), and (6,3), reflecting the rapidly declining success rate in forming successful star configurations as branching increases. We note the generally closer agreement between the IC/continuum MC than the RG/lattice MC results. And while the g ratio decreases steadily with branching number in every case, it is interesting to note that both the IC and MC estimates are invariably smaller than the random-walk results of Zimm and Stockmayer, indicating that the IC and MC descriptions of the excluded volume systems are relatively more compacted with respect to their linear

Table I
Limiting Ratios ($N \rightarrow \infty$) for $g(f) = \langle S_N^2(f)\rangle / \langle S_N^2(1)\rangle$

		f (number of branches)			
		3	4	5	6
this work[a]	IC	0.739_{10} $(0.721)_\infty$	0.571_{10} $(0.545)_\infty$	0.459_{10} $(0.429)_\infty$	0.370_{10} $(0.341)_\infty$
	MC	0.678_{10} $(0.692)_\infty$	0.546_8 $(0.536)_\infty$	0.444_6 $(0.447)_\infty$	0.395_3[d]
lattice	MC_∞	0.76 ± 0.01	0.60 ± 0.01	0.51 ± 0.01	0.43 ± 0.01
	RG_∞	0.798	0.667	0.58	0.519
eq 7	RW_∞	0.778	0.625	0.520	0.444
exptl	Bauer et al.[1]		0.633, 0.65		0.458, 0.46
	Huber et al.[1]	0.761[b] 0.69[c]			

[a] The subscripts represent the $g(f)$ value determined on the basis of n_{max} monomers per branch: $()_\infty$ indicates the extrapolated limiting ratio. [b] θ solvent. [c] Good solvent. [d] No extrapolation attempted.

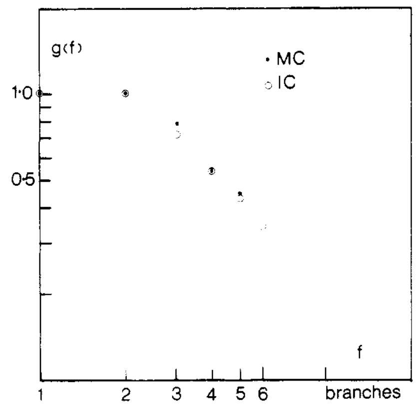

Figure 4. Plot of ln g against ln f.

counterpart than are the random-walk descriptions. Nevertheless, the closeness of the RG, lattice-based, and RW g ratios lead Whittington et al.[6] to conclude that for uniform stars the g ratios seem insensitive to excluded volume effects.

As we observed previously, the monomer concentration in the vicinity of the vertex particle is consistently overestimated in the IC approximation, which will undoubtedly lead to an underestimate in $\langle S_N^2(f)\rangle$, and this is apparent from Figure 5a. Moreover, $\langle S_N^2(1)\rangle$ is known to be overestimated in the IC approximation for $N > 12$,[7] both these features tending to depress the g ratio. Nevertheless, the agreement with the MC remains good, and we conclude that the low g ratios are not artifacts of the approximation and indeed agree well with the Monte Carlo estimates. Obviously the limiting ratios as $N \rightarrow \infty$ will be even smaller, and estimates of these are also shown in Table I: these latter values bear the most immediate comparison with other estimates shown in the table. It is appropriate to point out that at $f = 3$, for which the MC statistics are good (541 000 configurations at $n = 1$ to 40 100 configurations at $n = 10$), $g(3)$ is already substantially below other estimates, and g can only be expected to decrease with increasing f, although we do acknowledge that the restriction to MC six-branched stars of only three monomers per branch prevents an unequivocal extrapolation to MC systems of high functionality. These ratios, which differ substantially from the random-walk estimates, do not enable us to conclude that uniform star ratios are insensitive to excluded-volume processes, at least for the small systems investigated here. Certainly the particle-scattering functions $P(Q)$ reveal very different interior processes operating within the random-walk and excluded-volume systems (Figure 3).

It is not easy to identify the basis for the significantly larger renormalization group ratios obtained by Miyake and Freed. Whittington et al. suggest that it may arise from an overestimate of $\langle S_N^2(f)\rangle$ due to an overstatement of the excluded volume effect, which would imply that the discrepancy should increase with f, which it does. However, the RG ratios of Miyake and Freed are only correct to $\mathcal{O}(\epsilon)$ and this may account for the discrepancy: certainly the RG discrepancies are even more severe in two dimensions,[6] suggesting that omission of the $\mathcal{O}(\epsilon^2)$ term may be responsible.

In Figure 4 we plot ln g against ln f, from which we conclude that a relationship of the form $g \sim f$ would provide the most appropriate description, contrary to the Daoud–Cotton proposals for small-to-intermediate-sized

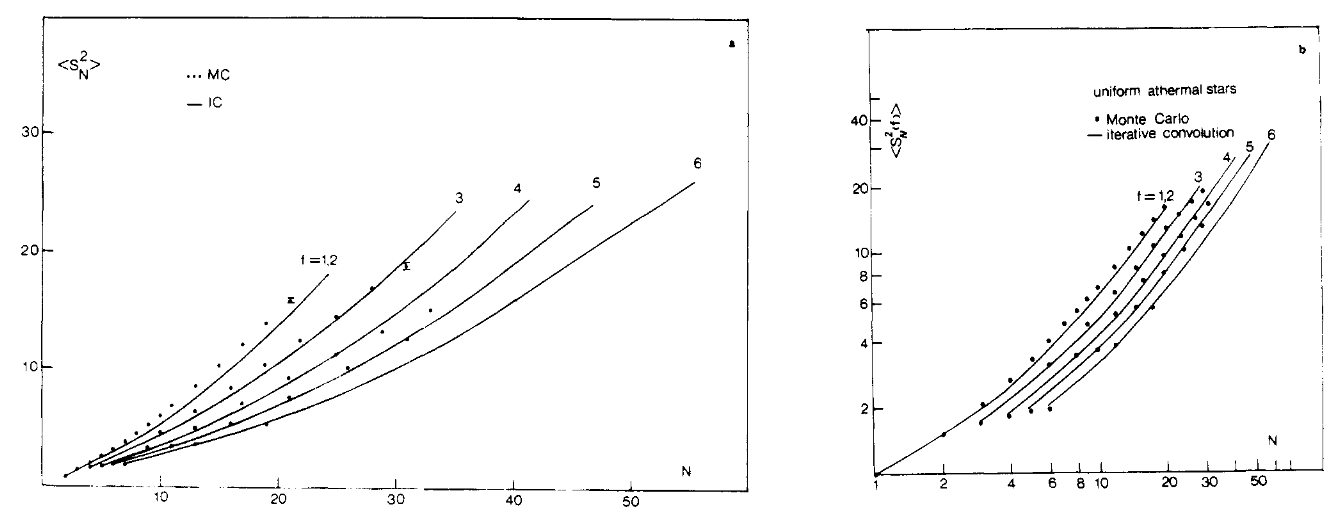

Figure 5. (a) Mean square radius of gyration $\langle S_N^2(f)\rangle$ as a function of molecular weight N and degree of branching f (error bars represent 95% confidence limits). (b) log–log plot of $\langle S_N^2(f)\rangle$ as a function of molecular weight N and degree of branching f.

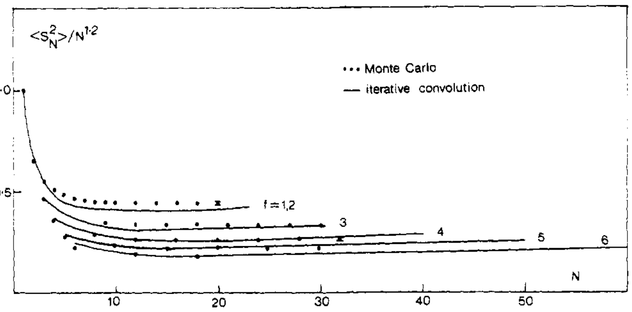

Figure 6. Plot of ratio $\langle S_N^2(f)\rangle/N^{1.2}$ (error bars represent 95% confidence limits).

stars (eq 9 and 10) and accordingly conclude that the structure of these interior regions is not as proposed by Daoud and Cotton. This conclusion is, moreover, supported by our MC simulations. In particular we find that the central core is not characterized by constant monomer density, nor do we observe the intermediate-range screening proposed by these authors.

Mean Square Radius of Gyration

The mean square radius of gyration $\langle S_N^2(f)\rangle$ has been the subject of considerable experimental[1] and theoretical[4-6] attention, and in Figure 5a we show the dependence of this function upon degree of polymerization N and branching number f, both on the basis of Monte Carlo simulation and iterative convolution approximation. The agreement is seen to be good. In Figure 5b the corresponding log–log plot of the IC and MC data is presented, from which we observe that the plots are essentially parallel, independent of f. Both these results concur with the lattice-based analysis of Whittington et al.,[6] and while our results are for substantially smaller stars, it is again difficult to resist a least-squares fit and extrapolation of our IC data, from which we conclude that the exponent in the relation

$$\langle S_N^2(f)\rangle = A(f)N^{2\nu(f)} \qquad (12)$$

$$\lim N \to \infty$$

is $\nu \sim 1.1$, independent of f and in close agreement with the RG (1.125)[5] and (1.176)[14] and lattice-based (1.20) estimates, the latter of which appears to correspond to the exponent for a linear chain. In Figure 6 we test this hypothesis by plotting $\langle S_N(f)\rangle/N^{1.2}$, from which we see that both the IC and MC data are consistent with this description at intermediate N. At a given degree of polymerization it is apparent that $\langle S_N^2(f)\rangle$ decreases with increasing f, corresponding to a reduction in the deployment of the segments as f increases, as we might expect.

On the basis of a knowledge of the limiting exponents $\nu(f)$, it is possible to estimate the prefactor $A(f)$ in eq 12. However, such estimates are not justified in the present case, given the range of application of the IC technique; we therefore confine ourselves to the observation that at a given degree of polymerization $A(f)$ decreases rapidly with increasing f (Figure 5a), and in this respect concurs with the other asymptotic estimates ($N \to \infty$).[5,6]

Dimensions of Branches of Uniform Stars

The second moments of the normalized distributions $Z(0,n|f,n)$ and $Z(i,j|f,n)$ $(0 < i \neq j < n)$ yield the mean square end-to-end $\langle R_n^2(f)\rangle$ and internal $\langle R_{i,j}^2(f)\rangle$ separations within a branch, respectively.

The mean square end-to-end length of a branch provides us with a direct means of assessing the Daoud–Cotton proposal, according to which

$$\langle R_n^2(f)\rangle f^{-1/2}N^{-1} = \text{constant} \qquad (13)$$

should hold for stars of intermediate size. However, we find no evidence to support such a relation and conclude that the geometric screening assuming by these authors does not exist, at least not in the form proposed. Again, for small stars of core size we should have[4]

$$\langle R_n^2(f)\rangle N^{-1} = \text{constant} \qquad (14)$$

and this too does not appear to be substantiated by the MC or IC determinations. We therefore regard this as additional evidence against the internal concentration regimes proposed by Daoud and Cotton, although for large stars of high molecular weight the lattice-based MC estimates[6] appear to support their proposed structure for the outermost regime.

In fact, $\langle R_n^2(f)\rangle$ appears to develop more strongly than $n^{1.2}$ over the range of uniform star configurations investigated on the basis of the iterative convolution approximation ($n \leq 10$, $f \leq 6$), and a similar conclusion has been drawn by Whittington et al. based on MC lattice enumerations. Only for branch lengths $n > 30$ does the limiting from $\langle R_n^2(f)\rangle \sim n^{1.2}$ appear to be achieved.[6] What the IC and lattice-based results clearly show is the strong radial expansion of the interior in qualitative agreement with the Daoud and Cotton proposal, but scaling differently.

Conclusions

The iterative convolution technique was applied to a system of uniform athermal perfectly flexible hard-sphere stars of small-to-intermediate molecular weight. The three-dimensional continuum systems incorporated excluded volume effects and were compared with their simulated Monte Carlo counterparts. The agreement was generally good, although the known interpenetration effects of the IC approximation at high packing fractions in the vicinity of the vertex were observed.

The IC and MC analyses provided an assessment of the Daoud–Cotton scaling predictions for the interior regions of uniform stars incorporating excluded volume effects. These regions are generally inaccessible to lattice-based or renormalization group estimates since these are valid only in the limit of high molecular weight when the exterior regions of the star dominate the metrical properties of the system.

From the outset we observe that no evidence to support the Daoud–Cotton proposals was found over the range of branch lengths and branching numbers (n, f, respectively) investigated on the basis of either the IC or MC techniques. Indeed, the radial concentration profile exhibits a discontinuity with subsequent radial structure that may be directly attributed to geometrical packing effects in the interior, while Daoud and Cotton propose a uniform density core with a subsequent monotonically decreasing radial concentration of monomers.

The ratio $g(f) = \langle S_N^2(F)\rangle/\langle S_N^2(1)\rangle$ appears to show a steady decrease with increased branching f for all systems considered in Table I. The IC and MC values appear significantly and consistently smaller than their lattice-based renormalization group and random-walk counterparts, and although our IC and MC estimates are restricted to systems of low-to-intermediate molecular weight, the ratio is only likely to decrease further with increasing N.

Now since the exponent ν in eq 12 appears independent of branching number f, it follows that $g(f)$ is determined by the ratio $A(f)/A(1)$. The magnitude of the prefactor A is determined by two competing processes: (1) "confinement" of the monomers to a localized region around the vertex attributable to both sequential connectivity and degree of branching for a system of given molecular weight; (2) excluded volume, which will tend to delocalize the system. In the case of random-walk systems only the confinement process operates, and the reduction in the radius of gyration of a star polymer relative to its linear counterpart of identical molecular weight may be directly attributed to the structural reorganization alone.

If excluded-volume effects are now introduced, the expansion of the more weakly confined linear system may well exceed that of its more tightly confined star counterpart, in which case g(excluded volume) < g(random walk) at given (f,n). This we find on the basis of our IC and MC analyses (Table I). Clearly, the behavior of these ratios depends on a subtle balance between these competing agencies: the effective interaction, explicit or implicit, adopted in the various theoretical approaches would seem to be largely responsible for the various ratios obtained.

The Daoud-Cotton predictions for the branching dependence of g appear unsubstantiated for stars of small-to-intermediate size on the basis of the present analyses, concurring with our earlier conclusions regarding the interior structure of uniform stars. (It should be said, however, that in the case of large stars, Whittington et al. support Daoud and Cotton's prediction for long branches in a good solvent (eq 8)). We therefore conclude that the packing and screening processes envisaged by Daoud and Cotton as operating in the core and intermediate regions of a uniform star are not supported by the present IC and MC analyses.

Finally, the mean square length of a branch appears to develop more strongly with n than its isolated counterpart for stars of small-to-intermediate molecular weight. This concurs with the lattice-based observations of Whittington et al. and reflects the high monomer concentration in the vicinity of the vertex. Only for $n > 30$ do these latter authors find that a branch regains the $n^{1.2}$ dependence characteristic of isolated linear self-avoiding sequences, and this appears to be the case regardless of branching number $(f \leq 6)$.

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Kinetics of Swelling of Spherical and Cylindrical Gels

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ABSTRACT: The theory of kinetics of swelling of a gel previously developed by Tanaka and Fillmore for spherical samples has been generalized to the case of cylindrical samples. The effect of a nonnegligible shear modulus has been included in the derivation. The values of the cooperative diffusion coefficient obtained from macroscopic swelling experiments in spherical and cylindrical polyacrylamide and poly(dimethylsiloxane) gels show good agreement with results of quasielastic light-scattering experiments.

Introduction

The kinetics of swelling of spherical neutral gels have been studied both theoretically and experimentally by Tanaka and Fillmore, who showed that the macroscopic swelling behavior was described by a diffusion equation with a diffusion coefficient D given by[1]

$$D = M_{os}/f = (K_{os} + 4\mu/3)/f \qquad (1)$$

where M_{os}, K_{os}, and μ are the osmotic longitudinal modulus, the osmotic compressional modulus, and the shear modulus of the gel, respectively, and f is the friction coefficient describing the viscous interaction between the polymer and the solvent. In their derivation, Tanaka and Fillmore have assumed that the shear modulus μ of the gel was negligible compared to the osmotic bulk modulus. Recently, we have extended the model of these authors to the case of spherical gels with a nonnegligible shear modulus.[2] The purpose of the present paper is to study the kinetics of swelling for cylindrical gels in the limit of infinite height or infinite diameter and to compare the theoretical predictions to swelling experiments performed in polyacrylamide gels swollen by water and in poly(di-

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