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The radius of gyration of a branch of a uniform star polymer

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Abstract. We use Monte Carlo methods and perturbation calculations to study the mean-square radius of gyration of a branch of a uniform star, with excluded volume, as a function of the number (f) of branches and of the number (n) of monomers per branch. We show that the mean-square radius of gyration $\langle S(n,f)^2\rangle$ scales like $A(f)n^{2\nu}$, f fixed, $n\to\infty$, where the exponent is independent of f. We estimate the amplitude ratios $A(f)/A(1)$ for various values of f and show that these ratios are lattice independent. The amplitude ratio increases as f increases, but the effect is small. The numerical agreement between the two methods is good, especially for small values of f.

1. Introduction

A uniform star polymer has f branches with n monomers in each branch. It is now possible to synthesise such f-stars with a controlled number of monomers in each branch (Roovers *et al* 1983) and measurements of the radius of gyration have been carried out for various values of f (Bauer *et al* 1980, Huber *et al* 1984). In order to model the behaviour under theta conditions the radius of gyration has been calculated for random walk models (Zimm and Stockmayer 1949). In the good solvent regime an appropriate model must incorporate excluded-volume effects and such calculations have been carried out by renormalisation group methods (Miyake and Freed 1983, Vlahos and Kosmas 1984) and by Monte Carlo techniques (Zimm 1984, Whittington *et al* 1986). There is general agreement that the ratio (g) of the mean-square radius of gyration for an f-star divided by that for a linear polymer with the same *total* degree of polymerisation ($N=nf+1$) depends only weakly on the solvent, i.e. excluded-volume effects do not have a large effect on the value of g. However, the Monte Carlo results have established that there is considerable interference between the branches which results in an expansion of the branch as f increases at constant n. This is apparent in the mean-square end-to-end length of a branch $\langle R_n(f)^2\rangle$ which scales like $B(f)n^{2\nu}$, as $n\to\infty$. The ratio $B(f)/B(1)$ is a lattice-independent quantity which increases as f increases (Whittington *et al* 1986).

The mean-square radius of gyration of a branch of a star should show similar behaviour. We expect it to scale like $A(f)n^{2\nu}$ and the amplitude ratios $A(f)/A(1)$ should increase with f. This might be observed experimentally by carrying out neutron scattering measurements on an f-star with a single branch deuterated. In this paper we report the results of the first calculations which have been carried out for this problem. Using both first-order perturbation calculations and Monte Carlo methods,

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we establish that the effect exists (i.e. the appropriate amplitude ratio increases with increasing f) and obtain good agreement between the results of the two approaches.

2. First-order perturbation calculation about $d = 4$

The mean-square radius of gyration of a branch of a uniform star can be written in terms of the squares of the inter-monomer distances as

$$\langle S(n,f)^2 \rangle = \sum_{i=1}^{n-1} \sum_{k=i+1}^{n} \langle (\boldsymbol{R}_{i1} - \boldsymbol{R}_{k1})^2 \rangle / n^2 \tag{2.1}$$

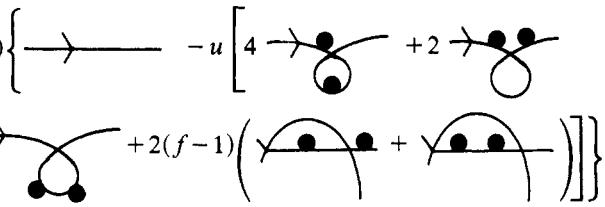
where $\boldsymbol{R}_{ij}$ is the position vector of the ith monomer in the jth branch. In calculating the average $\langle \ldots \rangle$ account must be taken of the interactions between monomers in the same branch and between monomers in different branches. In the Gaussian model with excluded volume the probability distribution of the configuration $\{\boldsymbol{R}_{ij}\}$ is given by

$$P\{\boldsymbol{R}_{ij}\} = (d/2\pi a^2)^{Nd/2} \exp\Bigg(-(d/2a^2) \sum_{i=0}^{n-1} \sum_{j=1}^{f} (\boldsymbol{R}_{i+1,j} - \boldsymbol{R}_{ij})^2 - u \sum_{k=1}^{f} \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \delta^d(\boldsymbol{R}_{ik} - \boldsymbol{R}_{jk}) - u \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\substack{k=1 \\ k \neq l}}^{f} \sum_{l=1}^{f} \delta^d(\boldsymbol{R}_{ik} - \boldsymbol{R}_{jl}) \Bigg) \tag{2.2}$$

and the average $\langle \ldots \rangle$ with respect to $P\{\boldsymbol{R}_{ij}\}$ implies integration over all position vectors.

As u increases the polymer chain goes from the ideal state corresponding to a random walk ($u = 0$) to an expanded state corresponding to a self-avoiding walk ($u > 0$). Each of these two states is characterised by a specific value (u^*) of the interaction parameter, and the properties of the chain exhibit power-law behaviour with universal characteristic exponents. Calculations to second order in u, with the requirement of power-law behaviour, yield to first order in $\varepsilon = 4 - d$ the characteristic values $u^* = 0$ for the ideal state and $u^* = \varepsilon/16$ for the expanded state (Kosmas 1981). u^* is universal in the sense that it does not depend on specific constraints such as the architecture of the polymer (Vlahos and Kosmas 1984) or the presence of an interacting wall (Kosmas 1985). It is a useful parameter since knowledge of u^* to order ε allows the calculation of critical exponents and universal amplitude ratios to the same order in ε, using first-order perturbation expansions (in the parameter u) about $d = 4$.

In order to determine the mean-square radius of gyration of a branch, the mean-square distances of all pairs of monomers in the branch have to be calculated. To zeroth order in u the ideal random walk result $\langle (\boldsymbol{R}_{i1} - \boldsymbol{R}_{j1})^2 \rangle_0 = a^2(i-j)$ is found from (2.2). The first-order terms require the evaluation of all diagrams with one loop. There are two classes of such diagrams, those coming from intra-branch interactions when both interacting units lie in the same branch, and those coming from inter-branch interactions when the interacting units are in different branches. In diagrammatic form the mean-square radius of gyration of a branch can be written as

$\langle S(n,f)^2 \rangle = (a^2/n^2)\Big\{$  $\Big\}$. (2.3)

The first diagram corresponds to the unperturbed star, the next three to intra-branch interactions and the final two to inter-branch interactions. The dots correspond to a pair of monomers in the same branch and imply a summation over the square distances between such pairs of monomers (equation (2.1)), while the loop is formed from two points in either one or two branches. The diagrams all have the form $-(\text{common part})^2/(\text{length of loop})^{1+d/2}$. (See Fixman (1955) for a treatment of the $d=3$ case.) After replacing the summations by integrations these can be evaluated at $d=4$ and their values are given in table 1. Substituting the values of these diagrams in (2.3) gives

$$\langle S(n,f)^2\rangle = (na^2/6)\{1+2u[\ln n - \tfrac{13}{12} + (f-1)(\tfrac{35}{8} - 6\ln 2)]\}. \tag{2.4}$$

For large n the $\ln n$ term dominates in the coefficient of u, and is the first term in the expansion of $n^{2\nu}$ where $\nu = \frac{1}{2} + u^* = \frac{1}{2} + \varepsilon/16 + O(\varepsilon^2)$ is the critical exponent of the linear chain. The remaining f-dependent part is significant when we calculate the

Table 1. Forms and values of the diagrams for $d=4$.

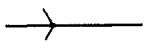
	$= \int_0^n dl \int_l^n dk\,(l-k) = n^3/6$
	$= -\int_0^n di \int_i^n dj \int_0^i dk \int_i^j dl\,(l-i)^2/(j-i)^3 = -n^3/18$
	$= -\int_0^n di \int_i^n dj \int_0^i dk \int_j^n dl\,(j-i)^{-1} = -n^3(\ln n - \frac{11}{6})/6$
	$= -\int_0^n di \int_i^n dj \int_i^j dk \int_k^j dl\,(l-k)^2/(j-i)^3 = -n^3/72$
	$= -\int_0^n di \int_0^n dj \int_0^i dk \int_i^n dl\,(i-k)^2/(i+j)^3 = n^3(7\ln 2 - 5)/6$
	$= -\int_0^n di \int_0^n dj \int_0^i dk \int_k^i dl\,(l-k)^2/(i+j)^3 = n^3(\frac{5}{2} - 4\ln 2)/24$

Table 2. Estimates of the amplitude ratio $A(f)/A(1)$.

f	Equation (2.5) with $\varepsilon = 1$	SC	BCC
2	1.027		1.025 ± 0.002
3	1.054	1.044 ± 0.003	1.044 ± 0.005
4	1.081	1.060 ± 0.004	
5	1.108	1.072 ± 0.005	
6	1.135	1.085 ± 0.01	1.08 ± 0.01
8	1.189		1.10 ± 0.02

amplitude ratio. We obtain

$$A(f)/A(1) = 1 + (\varepsilon/8)(f-1)(\tfrac{35}{8} - 6\ln 2) \tag{2.5}$$

to first order in ε. This amplitude ratio increases linearly with f and the numerical results for various values of f and $\varepsilon = 1$ ($d = 3$) are shown in table 2.

3. Monte Carlo calculations

In this section the uniform star is modelled as f self- and mutual-avoiding walks, starting at a common vertex (the origin, say) of a three-dimensional lattice. The self- and mutual-avoiding conditions mimic the excluded-volume effect. We use an inversely restricted sampling technique (Rosenbluth and Rosenbluth 1955) to generate a sample of f-stars up to $f = 6$ on the simple cubic (SC) lattice and up to $f = 8$ on the body-centred cubic (BCC) lattice. We have also considered the cases $f = 1$ and $f = 3$ on the face-centred cubic (FCC) lattice. Sample sizes used were typically between 300 000 and 900 000 and maximum branch lengths were between 30 and 50.

When $f = 1$ we have a self-avoiding walk, where we expect that

$$\langle S(n,1)^2 \rangle = A(1) n^{2\nu} [1 + D(1) n^{-\Delta} + O(n^{-1})] \tag{3.1}$$

where ν is about 0.588 and Δ is about 0.47 (Le Guillou and Zinn-Justin 1980). If we plot $\ln\langle S(n,f)^2 \rangle$ against $\ln n$ we obtain a set of parallel straight lines for the various values of f. This strongly suggests that the exponent ν is independent of f and we assume the value 0.588 throughout the analysis. (In our previous work (Whittington *et al* 1986) we found that the estimated values of amplitude ratios were essentially independent of the assumed value of ν in the range 0.58–0.6.)

With this assumption about the value of the exponent ν we have plotted $\langle S(n,f)^2 \rangle / n^{1.176}$ against n in figure 1 for the BCC lattice. The asymptotic regime is reached remarkably quickly, especially for small values of f. To estimate the amplitude ratios $A(f)/A(1)$ we have plotted $\langle S(n,f)^2 \rangle / \langle S(n,1)^2 \rangle$ against n in figures 2 and 3 for the SC and BCC lattices, respectively. This ratio should tend to $A(f)/A(1)$ for n large

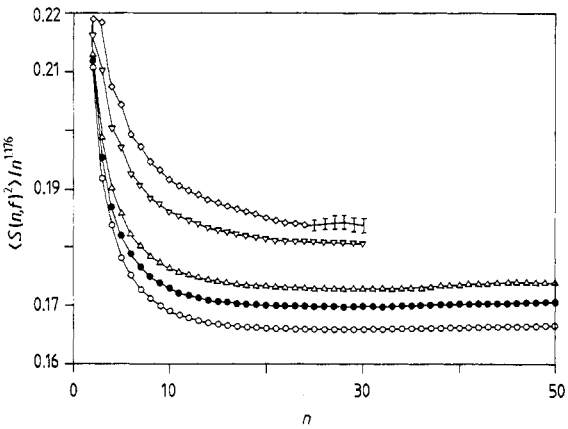


Figure 1. Reduced mean-square radius of gyration of a branch of an f-star for the BCC lattice. ○, $f = 1$; ●, $f = 2$; △, $f = 3$; ▽, $f = 6$; ◇, $f = 8$. For $f < 8$ the error bars (one standard deviation) are no larger than the size of the symbols.

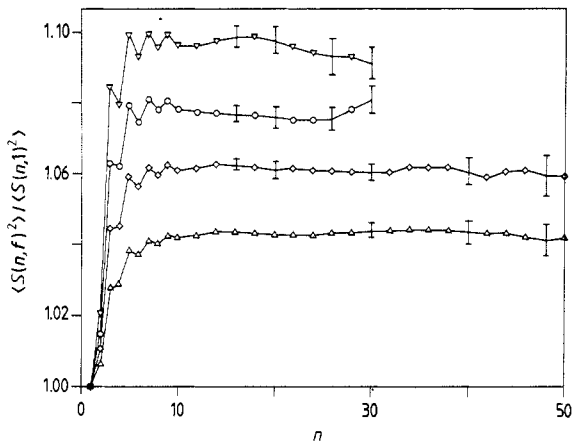


Figure 2. Ratio of the mean-square radius of gyration of a branch of an f-star to that of a self-avoiding walk for the SC lattice. △, $f=3$; ◇, $f=4$; ○, $f=5$; ▽, $f=6$.

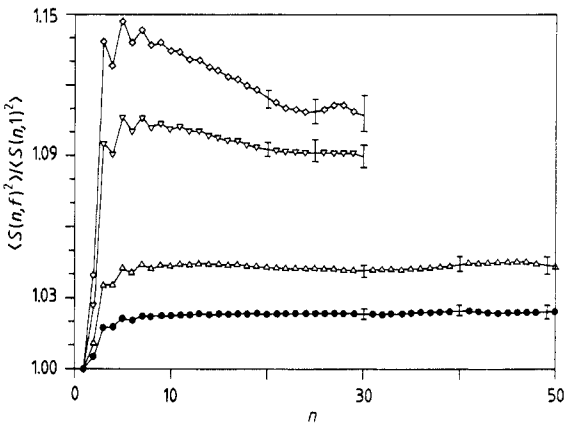


Figure 3. Ratio of the mean-square radius of gyration of a branch of an f-star to that of a self-avoiding walk for the BCC lattice. ●, $f=2$; △, $f=3$; ▽, $f=6$; ◇, $f=8$.

provided that the exponent ν is independent of f. Our estimates of the amplitude ratios are given in table 2. It appears that the amplitude ratios are lattice independent. We have examined this possibility further by estimating the amplitudes for $f=1$ and 3 for the FCC lattice. The n dependence is shown in figure 4 and we estimate that the amplitude ratio $A(3)/A(1)=1.045\pm0.01$, in close agreement with that for the other two lattices.

Since the amplitude ratios are lattice independent they are universal quantities, suitable for comparison with experimental results and with the results of the first-order perturbation calculations. The agreement between the two methods is quite good, especially at small f. As f increases the differences become more marked and we note that values from the first-order perturbation calculations are larger than the Monte Carlo results. In both cases the results indicate an increase in the amplitude ratio with increasing f which is related to the increased interference between the branches. A

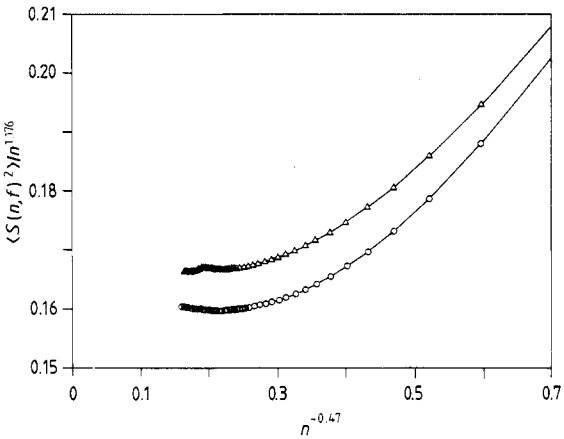


Figure 4. Reduced mean-square radius of gyration of a branch of an f-star extrapolated against $n^{-0.47}$ for the FCC lattice. ○, $f=1$; △, $f=3$. Error bars (one standard deviation) are no larger than the size of the symbols.

similar effect is seen in the estimates of the statistics exponent $\gamma(f)$ (Wilkinson *et al* 1986).

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