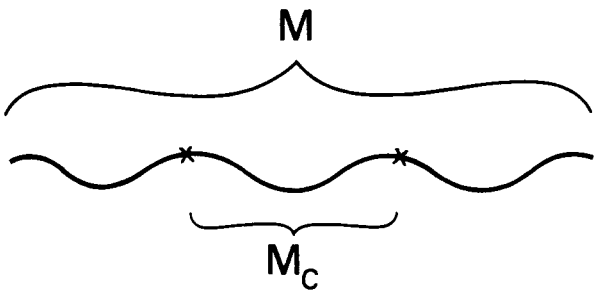

Figure 8. Sketch suggesting the structure of a polyethylene chain in a gel at $c \simeq c^*$, with the cross-links (crystallites) shown by the ×'s. A large fraction of such a chain would be in the two dangling ends, which are elastically ineffective.

in calculations of this type. In any case, M_c makes up a considerable fraction of the total M, as is shown schematically in Figure 8. Thus, there may be only two or three cross-links per chain, which is of course consistent with their preparation at $c \simeq c^*$. Also, a considerable portion of each chain is in the form of dangling ends, which are elastically ineffective. This indicates that the gels are extremely fragile not only because of their very low polymer content but also because a great deal of the polymer present is in the form of elastically ineffective material.

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References and Notes

(1) Edwards, C. O.; Mandelkern, L. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 355.
(2) Okabe, M.; Isayama, M.; Matsuda, H. *J. Appl. Polym. Sci.* **1985**, *30*, 4735.
(3) Domszy, R. C.; Alamo, R.; Edwards, C. O.; Mandelkern, L. *Macromolecules* **1986**, *19*, 310.
(4) Koltisko, B.; Keller, A.; Litt, M.; Baer, E.; Hiltner, A. *Macromolecules* **1986**, *19*, 1207.
(5) Chan, E. K. M.; Mandelkern, L. *Polym. Prepr.* **1987**, *28*, 130.
(6) Smith, P.; Lemstra, P. J.; Pijpers, J. P. L.; Kiel, A. M. *Colloid Polym. Sci.* **1981**, *259*, 1070.
(7) Sawatari, E.; Okumura, T.; Matsuo, M. *Polym. J.* **1986**, *18*, 741.
(8) Russo, P. S. *Reversible Polymeric Gels and Related Systems*; American Chemical Society: Washington, DC, 1987.
(9) Hiltner, A. In *Order in the Amorphous "State" of Polymers*; Keinath, S. E., Miller, R. L., Rieke, J. K., Eds.; Plenum Press: New York, 1987.
(10) McKenna, G. B.; Guenet, J.-M. *Polym. Commun.* **1988**, *29*, 58.
(11) Shukla, P.; Muthukumar, M. *Polym. Eng. Sci.* **1988**, *28*, 1304.
(12) Matsuda, H.; Kashiwagi, R.; Okabe, M. *Polym. J.* **1988**, *20*, 189.
(13) Hoffman, H.; Ebert, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 902.
(14) McKenna, G. B.; Guenet, J.-M. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 267.
(15) Smith, P.; Lemstra, P. J.; Booij, H. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 877.
(16) Lemstra, P. J.; Smith, P. *Br. Polym. J.* **1980**, *12*, 212.
(17) Lemstra, P. J.; van Aerle, N. A. J. M.; Bastiaansen, C. M. *Polym. J.* **1987**, *19*, 85.
(18) Takahashi, A.; Nakamura, T.; Kagawa, J. *Polym. J.* **1972**, *3*, 207.
(19) Glotin, M.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 807.
(20) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Oxford University Press: Clarendon, 1975.
(21) Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*; Wiley-Interscience: New York, 1988.
(22) Popli, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 441.
(23) Ferry, J. D. *Adv. Protein Chem.* **1948**, *4*, 1.
(24) Ferry, J. D. *J. Am. Chem. Soc.* **1948**, *70*, 2244.
(25) Walter, A. T. *J. Polym. Sci.* **1954**, *13*, 207.
(26) Lehaine, S. A.; Pain, G. S. *Eur. Polym. J.* **1983**, *19*, 1147.
(27) Guenet, J. M.; McKenna, G. B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2499.
(28) Smith, P.; Lemstra, P. J.; Pijper, P. L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2229.
(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(30) Timoshenko, S.; Goodier, J. N. *Theory of Elasticity*; McGraw Hill: New York, 1951.

Thermodynamic Properties of Star Polymers: Good Solvents

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ABSTRACT: We present the results of a high-precision Monte Carlo analysis of star polymers on the face-centered cubic lattice with up to $f = 6$ arms and up to an overall polymerization of $Nf \simeq 400$. With the help of an improved dimerization method we were able to increase the accuracy of previous investigations significantly. This is the first numerical investigation on stars, which analyzes a rather complete set of physical quantities ranging from the radius of gyration to the initial decay of the scattering function, including hydrodynamic properties.

1. Introduction

Star polymers have found a considerable interest in the literature both from experiment[1-11] and from theory.[12-33] From a theoretical point of view they are an interesting testing ground of modern scaling ideas as well as renormalization group calculations. These concepts can be tested and analyzed by computer simulations of star polymers. Typical quantities like the radius of gyration have also been measured by light[5,6,8,9] and neutron scattering.[8,10] Simulations up to now either are concerned with stars of relatively many arms[32] or only consider a rather selected set of physical quantities.[16,18,23-25,28,29,31] Lipson et al.[28,29] investigate star polymers on a lattice by the Rosenbluth–Rosenbluth Monte Carlo method.[34] This method also called biased sampling is known to be dangerous for good solvent chains[35] and consequently it is

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confined to rather small systems. The authors calculate the exponent γ of the partition function and the size of star. Freire et al.[23,24] mainly are concerned with the hydrodynamic properties under varying solvent conditions; however, they consider stars with very short arms (N = 3 for f = 18). Also Barett and Tremain[31] confine themselves to the g factor and the exponent γ. They also use the Rosenbluth–Rosenbluth algorithm even for stars with very high polymerization. The recent molecular dynamics simulation of many-arm star polymers of Grest et al.[32] gives a rather complete description of static and dynamic properties of stars with $f \geq 10$. However, there no hydrodynamic interaction was considered in the simulation and by a constraint of the numerical method the exponent γ was not obtained. They are mainly aiming at systems where the Daoud–Cotton[17] scaling is expected to work well.

Giving this short summary, we think that there is a strong need for a complete and high-precision investigation of model star polymers by means of a Monte Carlo method. Here we use a new modified version of the dimerization method of Suzuki[36] and Alexandrowicz.[37] For the exponent γ we are able to reduce the error bars of Lipson et al.[28] by an order of magnitude. We generated stars on a fcc lattice (face-centered cubic) with up to f = 6 arms and overall polymerization of $Nf \simeq 400$ (N is the number of monomers per arm). The stars are modeled as a self-avoiding walk on this lattice, starting from a common center. Since we are interested here in the good solvent properties besides the excluded-volume condition no further interaction is taken into account. Additional interactions modeling the collapse transition will be considered in a subsequent publication.[43]

The paper is organized as follows. First we give a definition of the model and describe the algorithm. We then show that this can directly be used to estimate the exponent γ without considering the effective coordination number q_{eff} of the walks. We then discuss the Daoud–Cotton scaling and check its applicability to our systems, which have relatively few arms; we calculated the density decay $\rho(r)$, the radius of gyration $\langle R_G^2(N,f)\rangle$, and the center end distance $\langle R^2(N,f)\rangle$ of the arms. We then investigate internal bond correlations as well as the asphericities of the stars as a function of arm length and number of arms f. Then we turn to the structure function, and finally we calculate the hydrodynamic radii as well as the initial decay of the structure function.[19] For all these systems we consider the linear chain as a limiting case.

2. Model and Partition Function: Modified Dimerization

In search for an effective algorithm for the MC simulation of stars,[38] we have to take into account their special topology as well as the higher monomer density in the central region. The reptation algorithm,[40] e.g., although highly efficient for dense systems, evidently cannot work. Since we are interested in an precise determination of the critical exponent $\gamma(f)$, only static algorithms can be considered. The biased sampling algorithm of Rosenbluth and Rosenbluth[34] was shown to be of no use for polymerization $Nf > 200$,[35] as the relative error of both the partition function and the directly measurable physical quantities (radius of gyration, structure function, etc.) increases exponentially with the polymerization. However, one needs large systems in order to extrapolate to the $N \rightarrow \infty$ limit, which is needed for scaling.

Up to now the longest self-avoiding walks (SAW) have been built by the dimerization algorithm.[37,36] In the first step two-halfs of a chain are built by a method that introduces no bias (the simple sampling algorithm, e.g., builds random walks and keeps the self-avoiding ones). Then they are linked together. The resulting chain is discarded, if it intersects itself. Those that are still self-avoiding can be used for further dimerization iteration steps. The method is completely unbiased if one does not use chains of failed dimerization steps again (this was not the case in the original work of Alexandrowicz[37]). The high efficiency of the method is due to the fact that loops are mostly avoided. They are possible only around the link. (One may not conclude though from this discussion that the "last loop deletion" algorithm gives the correct distribution of self-avoiding walks.[38,39])

For $N >> 1$, i.e., in the case where corrections to scaling are negligible, the partition function of the linear chain $Z(N)$ has the scaling form[41]

$$Z(N) = C q_{\text{eff}}^N N^{\gamma-1} \tag{1}$$

where C is some lattice-dependent constant of the order one. q_{eff} is the effective coordination number of the walk and is also lattice dependent. If now, for instance, one wants to calculate γ by the ratio of successful to tried chains in a simple sampling or Rosenbluth–Rosenbluth algorithm,[42] one typically uses the ratio method in order to avoid uncertainties from the high q_{eff} power. However, one still needs good estimates for q_{eff}. In the dimerization method this problem does not occur. Here the probability $p(N \rightarrow 2N)$ of a successful link of two strands of length N is simply given by

$$p(N \rightarrow 2N) \propto (N/2)^{1-\gamma} \tag{2}$$

Solving this for γ and extrapolating $1/N \rightarrow 0$, one neither needs to know q_{eff} nor C.

The dimerization method, however, is impractical for technical reasons and has not been used very frequently. One typically stores a huge number of chains as a reservoir for every dimerization step. In addition one needs a time at least proportional to N to decide whether two strands intersect themselves (this is for a lattice, for off lattice chains one needs a time of order $N \ln N$). However, there is a way to evade this problem. We restrict ourselves to a short desription and to one dimerization step. The generalization will be given in a subsequent publication.[44] We first generate the first self-avoiding part of the chain by the simple sampling algorithm. The second part is immediately continued at the end of the first part. If this second part intersects itself, one may start again at the end of the first part as the second part was not self-avoiding. If the second part intersects the first one and after that also itself, one may again start in the middle for the same reason. Only in the case where the second part intersects the first one but not itself, the dimerization process failed and one has to build the chain from the very beginning. This procedure is completely equivalent to dimerization but needs no I/O and has the additional advantage of giving all information about any intersections immediately.

For stars we first built the arms by a two-step dimerization. Every new arm was linked to the previous ones by exactly the same method, where each arm can be considered as a new part in the dimerization procedure, similar to the linear case.

The partition function of a star is given by[28,33]

$$Z(N) = C(f) q_{\text{eff}}^N N^{\gamma(f)-1} \tag{3}$$

The result of the $1/N \rightarrow 0$ extrapolation mentioned previously is given in Figure 1 and shows that the effective corrections to eq 2 are very small. The comparison to results of other authors are represented in Figure 2 and Table I. The statistical error of the chosen method is 1

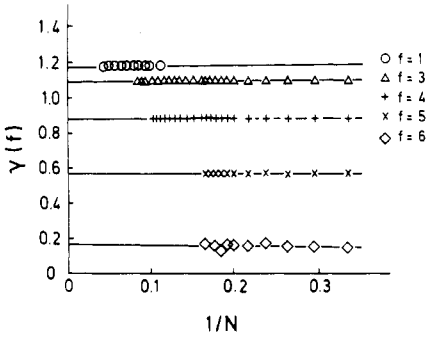

Figure 1. Determination of the critical exponent $\gamma(f)$ for $f = 1$, 3, 4, 5, and 6 by use of eq 2.

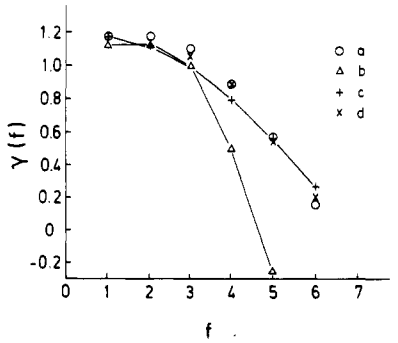

Figure 2. Critical exponent $\gamma(f)$ for $f = 1$, 3, 4, 5, and 6 for various models. (a) Dimerization, the error bars are smaller than the symbol size; (b) ϵ expansion in first order;[22] (c) expansion with an effective expansion parameter;[33] (d) Rosenbluth–Rosenbluth method.[28] The solid lines represent the analytic calculations.

Table I
Comparison of the Values for $\gamma(f)$ of Various Authors

	γ			
f	this work	Wilkinson et al.[28]	Miyake and Freed[22]	Ohno[33]
1	1.171 ± 0.001		1.125	
3	1.089 ± 0.001	1.05 ± 0.03	1	1.11
4	0.879 ± 0.001	0.88 ± 0.03	0.75	0.98
5	0.567 ± 0.002	0.55 ± 0.05	0.375	0.79
6	0.16 ± 0.01	0.20 ± 0.05	−0.125	0.55

order of magnitude smaller than that of the other data in the figure.[28] There are clear deviations to the first order in ϵ expansion calculation of Miyake and Freed,[22] although this expansion is made for the limit of a small number of arms. The use of an effective expansion parameter of Ohno[33] leads to

$$\gamma(f) = 1 + (\gamma(1) - 1)f - \tfrac{1}{3}(\gamma - 1)^{1/2}[f(f-1)]^{3/4} \quad (4)$$

and to results fairly consistent with the Monte Carlo calculations, although this equation is a summation limit for many arms.

3. The Size of Stars: Simulation and Scaling Arguments

Although the ϵ expansion represents a very interesting approach to many problems in polymer physics, it is often known to be inaccurate, for quantitative analysis. Therefore it is necessary to use scaling arguments for the system under consideration. In our case this was done by Daoud and Cotton[17] and by Birshtein and Zhulina.[26] The main task is to find the local screening length or blob size $\xi(r)$, inside which a part of an arm is not disturbed by the existence of the other arms. From geometrical considerations one gets

$$\xi(r) = rf^{-1/2} \quad (5)$$

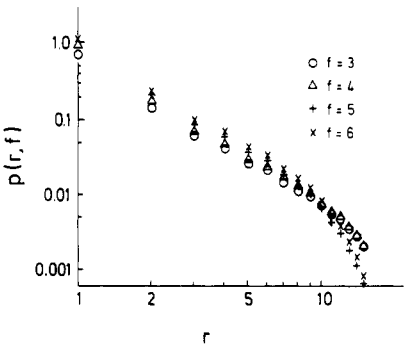

Figure 3. Density profile $\rho(r,f)$ versus r for various stars; because of the fractal nature of the objects, the slope of the curves is $\propto d_F - d$ for $r < R_G$, with $d_F = 1/\nu$ and $d = 3$ in the double-logarithmic plot. After $r > R_G$, the density decays exponentially.

in the case of many arms, since f arms cut the surface of a sphere at radius r. This leads to an f-dependent local density $\rho(r,f)$ (r is the distance from the center of the star)

$$\rho(r) = f^{(3\nu-1)/(2\nu)}r^{1/\nu-3} \quad (6)$$

The radius of gyration $\langle R_G^2\rangle$is defined by

$$\langle R_G^2\rangle = \left\langle \frac{1}{M^2}\sum_{i,j}^{M}(\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle = \left\langle \frac{1}{M}\sum_{i}^{M}(\mathbf{r}_i - \mathbf{r}_{CM})^2 \right\rangle \quad (7)$$

($M = Nf + 1$ $\mathbf{r}_{CM}$ is the center of mass vector), the last expression being more convenient for computational purposes. Integrating the local density (eq 6) up to $\langle R_G^2(N,f)\rangle$ gives the overall polymerization M, and therefore one obtains for the f dependence of the radius of gyration of a star

$$\langle R_G^2(N,f)\rangle \propto N^{2\nu}f^{1-\nu} \quad (8)$$

By a similar argument, the center to end distance of the arms $\langle R_{arm}^2(N,f)\rangle$ also follows a power law

$$\langle R_{arm}^2(N,f)\rangle \propto N^{2\nu}f^{1-\nu} \quad (9)$$

Daoud and Cotton expected these results to hold only in the outer part regime of a star. They argue that there exist two more regimes, a central core of constant density and a intermediate region resembling a concentrated solution. It should be pointed out that the *simultaneous* existence of the last two regimes could not be seen yet either in a molecular dynamics simulation[32] modeling up to $f = 50$ arms or in a Monte Carlo simulation including attractive interactions between the monomers.[43] According to Daoud and Cotton one finds for the radius r_1 of the boundary between the excluded volume and the unswollen regime $r_1 \propto f^{1/2}/v$ ($v \propto |(T-\Theta)|/\Theta$ is the excluded-volume parameter; T and Θ are the temperature and the Θ temperature, respectively). This in combination with the facts mentioned above means one has only then a chance to observe the crossover at r_1, if one investigates stars with very many arms in the neighborhood of $T = \Theta$. In addition the arms have to be extremely long, so that the Θ blobs can be distinguished from the ones of eq 5 caused by the star geometry. In other words there are four length scales that have to be at least by an order of magnitude different from each other, if one wants to investigate the crossover at r_1. First there is the persistence length of the walk, second the size of the Θ blobs, third the size of the blobs due to the star geometry, and fourth the radius of gyration of the hole star.

We now turn to the results of the Monte Carlo calculation. The density profile $\rho(r,f)$ versus r is shown in Figure 3 for $f = 3, \ldots, 6$. In Figure 4 the same data are scaled as

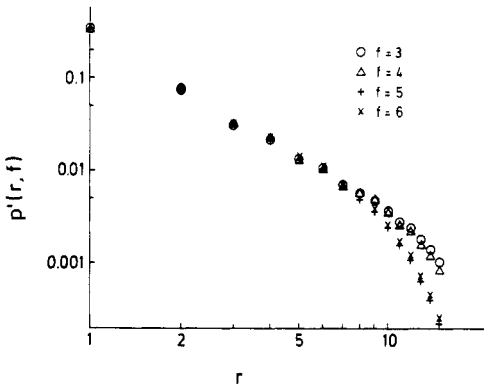

Figure 4. Same data as in Figure 3 but scaled according to eq 6: $\rho'(r,f) = \rho(r,f)f^{(1-3\nu)/(2\nu)}$.

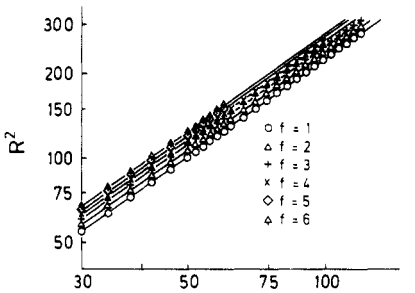

Figure 5. End to end distance $\langle R^2(N,f)\rangle$ versus N of the linear chain and the center end distances of stars. The apparent exponent $\nu_{app} = 0.592$ is slightly higher than the one obtained after taking into account corrections to scaling.

in eq 6. The agreement to the predictions of Daoud and Cotton is remarkable. Very good agreement was also found in a simulation of many-arm stars,[32] where it is rather expected. In our case, however, it is not clear how valid the model is, and one might be suspicious about the reasons of such a good agreement. We will return to this point at the end of the section.

In the Daoud–Cotton picture the correlation length critical exponent ν turns out to be the same as for the linear chain. Figure 5 shows the dependence of the center to end distance of the arms. The cases $f = 1$, 2 representing the linear chain were also examined to serve as a reference ensemble. All data seem to lie with extremely high accuracy on straight lines. Nevertheless one should still be carefull about extracting ν from the slope of the double-logarithmic plot, since corrections to scaling, although not visible, might shift its value (in fact if no care is taken about any corrections to scaling, ν turns out to be equal to 0.592). Since we are using a fcc lattice, we can compare our results for the linear chain with those obtained by exact enumeration methods of Majid et al.[45] Writing

$$\langle R^2(N,f=1)\rangle = AN^{2\nu}\left[1 + \frac{B}{N^{\Delta}} + \frac{C}{N}\right] \qquad (10)$$

and adopting their calculated values for B, Δ, and C ($B = -0.29$, $\Delta = 0.47$, $C = 0.25$), one obtains $\nu = 0.5876 \pm 0.0003$. This is in very good agreement with the result calculated by Majid et al. ($\nu = 0.5875 \pm 0.0015$) and also with the one of the renormalization group approach of LeGuillou and Zinn-Justin ($\nu = 0.588 \pm 0.0015$).[46] The numbers show that carefully carried out Monte Carlo simulation can lead to results of extremely high accuracy, which is better than series analysis.

We note furthermore that the N dependence of the persistence length $\langle R^2(N,f)\rangle/N^{2\nu}$ of the arms is given by straight lines even for $f \neq 1$ (Figure 6) if plotted against $B/N^{\Delta} + C/N$. This need not be the case of course, since B, C, and Δ in principle may be f dependent.

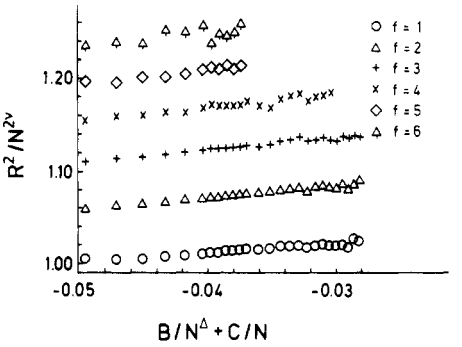

Figure 6. Same data as in Figure 5 but divided by $N^{0.5876}$ and plotted versus $B/N^{\Delta} + C/N$. The values of the amplitudes B and C and of the exponent Δ are taken from exact enumeration.[45]

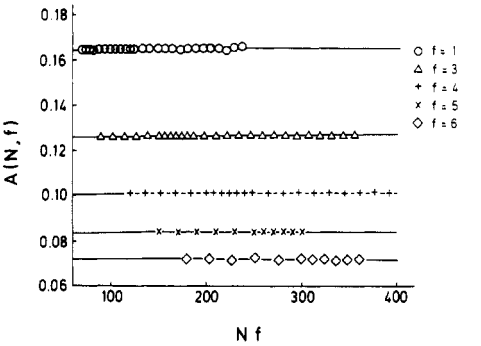

Figure 7. $A(N,f) = \langle R_G(N,f)/(Nf)^{2\nu}\rangle$ with $\nu = 0.5876$ versus Nf. The amplitude of the corrections to scaling seems to be almost zero for the fcc lattice used.

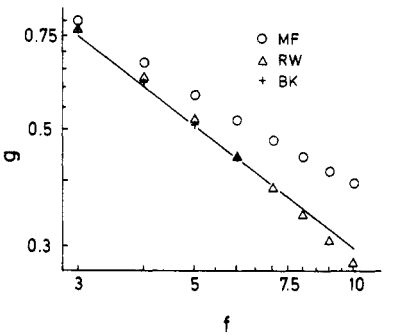

Figure 8. g factor of eq 11 of various calculations: MF, Miyake and Freed;[22] RW, the random-walk model;[12] BK, this work; the full line represents the scaling result of Daoud and Cotton.[17]

For the calculation of the f dependence of the radius of gyration, we also obtain the ratios $\langle R_G^2\rangle/(Nf)^{2\nu}$ plotted in Figure 7. This sensitive way of analyzing the data shows that there are no corrections to scaling worth mentioning to $\langle R_G^2(N,f)\rangle$ for the lattice used.

The size of stars is usually given in terms of the size of the linear chain of equal polymerization. We thus define the universal ratios

$$g(f) = \lim_{N\to\infty} \frac{\langle R_G^2(N,f)\rangle}{\langle R_G^2(Nf,f=1)\rangle} \qquad (11)$$

and

$$g_{arm}(f) = \lim_{N\to\infty} \frac{\langle R^2(N,f)\rangle}{\langle R^2(N,f=1)\rangle} \qquad (12)$$

In the random-walk model g_{arm} is of course independent of f, while $g(f) = (3f-2)/f^2$.[12] The Daoud–Cotton scaling theory yields via eq 8 $g(f) \propto f^{1-3\nu}$ and $g_{arm} \propto f^{1-\nu}$. These

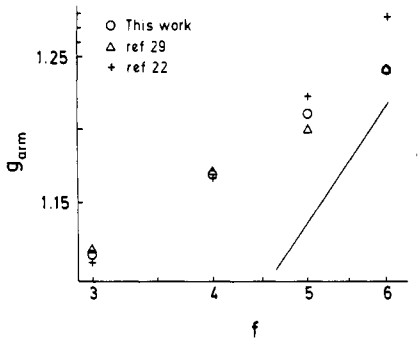

Figure 9. g_{arm} factor of eq 12 of various calculations: the full line represents the scaling result of Daoud and Cotton.[17] In this case the agreement of MC calculations to the predictions of the ϵ expansion is much better.

Table II
Comparison of Values for the Amplitude
$g = \langle R_G^2(N,f)\rangle/\langle R_G^2(Nf,f=1)\rangle$

	f			
ref	3	4	5	6
this work (MC)	0.766	0.611	0.508	0.439
12 (RW)	0.777	0.625	0.52	0.44
16 (MC)	0.70	0.63		0.3
18 (MC)	0.80	0.63		0.43
25 (MC)		0.63		0.45
29 (MC)	0.76	0.60	0.51	0.43
31 (MC)		0.65		
23 (MC)				0.44
32 (MD)				0.412
22 (ϵ-exptl)	0.798	0.667	0.580	0.519
2 (exptl)		0.633		0.451
6 (exptl)	0.69			
11 (exptl)	0.75	0.61		0.44

Table III
Comparison of Values for the Amplitude
$g_{arm} = \langle R^2(N,f)\rangle/\langle R^2(N,f=1)\rangle$

	f			
ref	3	4	5	6
this work (MC)	1.116	1.168	1.21	1.24
29 (MC)	1.12	1.17	1.20	1.24
22 (ϵ-exptl)	1.111	1.166	1.222	1.277
12 (RW)	1.000	1.000	1.000	1.000

curves are plotted together with our data and the predictions of the renormalization group treatment in Figures 8 and 9. A comparison to values of other authors and also to experiments is given in Tables II and III. At this point it should be emphasized that stars in Θ solvents do not obey they random-walk statistics, leading to $g = (3f - 2)/f^2$.[43] One of the very peculiarities of these objects is that the random-walk behavior agrees much better for the good solvent case (for few arms) than for the Θ solvent.

The data show a striking agreement in $g(f)$ between the Monte Carlo calculation and the random-walk model. Actually this was also found in the work Whittington et al.[29] and of Barett and Tremain.[31] Clear discrepancies occur only for $f > 10$. We think that this agreement is a rather accidental one. For if one tries to recalculate $g(f)$ in the way done by Zimm and Stockmayer but using $\nu = 0.59$ rather than $\nu = {}^1/_2$, the result is poorer.[47] In addition it is quiet clear from Figure 9 that the arms are elongated, even for $f = 3$, which means that their mutual interference is important even for very few arm stars. One can still push this further: Even in the case $f = 2$, $\langle R^2(N)\rangle$ increases. That means that the first half of a linear self-avoiding walk knows that there exists a second half. On the other hand, this mutual interaction effect between arms is not so dominant that it leads immediately to the

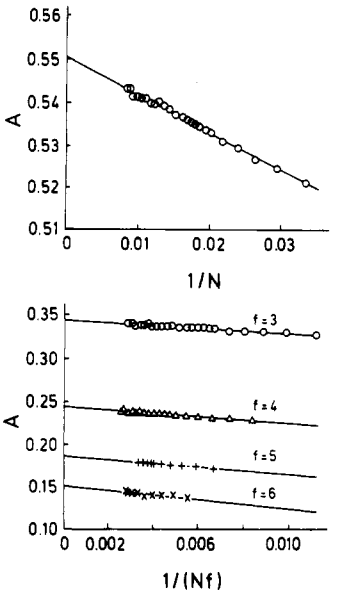

Figure 10. Asphericity A for linear chains and for stars $f = 3$, 4, 5, and 6. As expected, stars become more and more spherical with higher f.

predicted behavior of the scaling ansatz for g_{arm}. The simulation of Grest et al.[32] shows that the scaling behavior for the arms is reached only for $f > 30$.

Dealing with $g(f)$ returns us to the question of the density decay. Why do the global properties $\rho(r,f)$ and $g(f)$ of the stars scale nicely according to the Daoud–Cotton picture even for very few arms? In our opinion the answer is simple: In the scaling picture both quantities are derived assuming a spherically symmetric object. This is not the case here, especially for few-arm stars. As the mutual arm interaction of few-arm stars is not as strong as needed for the star scaling theory, stars should consequently be smaller than predicted. They are not, since the effect of asphericity enlarges them again. The line of arguments should hold for the density decay as well.

4. The Asphericities of Stars

Let x_i, y_i, z_i be the Cartesian components of the distance vector of the monomer i from the polymer center of mass. We further define

$$r_1^2 = \sum_i x_i^2 \qquad r_2^2 = \sum_i y_i^2 \qquad r_3^2 = \sum_i z_i^2 \tag{13}$$

$S = r_1^2 + r_2^2 + r_3^2$, and $M = r_1^2r_2^2 + r_2^2r_3^2 + r_3^2r_1^2$. In order to obtain a measure for the asymmetry of polymers, Gaspari and Rudnick[56] defined the asphericity of chains by

$$A = \frac{\langle S^2 - 3M\rangle}{\langle S^2\rangle} \tag{14}$$

This way of determining the asymmetry of a chain is more convenient than calculating the values of the three components of the diagonalized tensor of inertia, since the latter one involves ordering the components and makes analytic calculations difficult even for random walks (the asphericity of a random walk is calculated to $A = 0.526$[56,57]).

As self-avoiding walks are fractal objects, the value of the asphericity A should be independent of the polymerization. Nevertheless corrections to scaling might be important and the extrapolation to the limit $N \to \infty$ is always required. Figure 10 shows the result of such an extrapolation for linear and stars polymers. The value of A for $f = 1$ is a little bit higher than the one obtained by Bishop[57] ($A = 0.546 \pm 0.008$ for $N = 401$), where no extrapolation

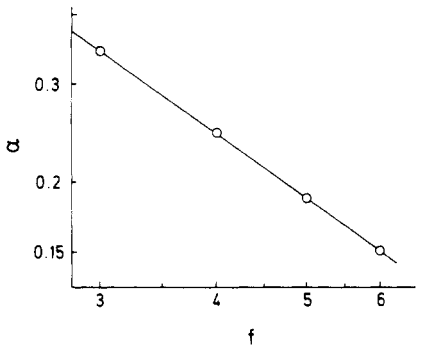

Figure 11. Ratio $\alpha(f)$ of the asphericity of a star to the linear chain. The power of the decay with increasing f is equal to 1.19.

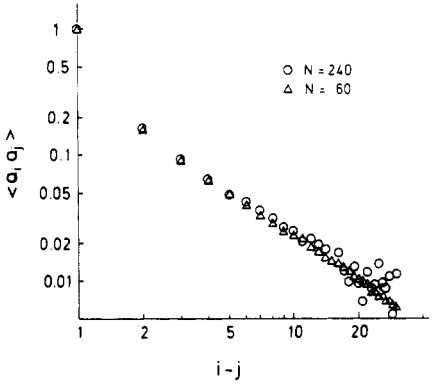

Figure 12. Bond correlations for the linear chain. $\langle \mathbf{a}_i \mathbf{a}_j \rangle$ seems to follow a power law with the power $p = -1.15$.

was carried out. As was mentioned before, and as one can easily expect, stars become more and more spherical with increasing number of arms. The ratio

$$\alpha = A(f)/A(f = 1) \tag{15}$$

is found to obey a power law already for few arm stars with $\alpha \propto f^{1.19}$, as is demonstrated in Figure 11.

5. The Bond Correlations

If $\mathbf{a}_i$ is the bond vector of bond i, this influences the direction of bond $\mathbf{a}_j$ having the distance of $|j - i|$ along the chain. We describe this dependency by the bond correlation function $\langle \mathbf{a}_i \mathbf{a}_j \rangle$. For linear three-dimensional chains, this has only received very little attention.[58] For purely random walks there is of course no correlation, whereas for nonreversal random walks on a lattice (random walks without direct back-folding) the correlations decay exponentially, $\langle \mathbf{a}_i \mathbf{a}_j \rangle \propto C^{|i-j|}$, where C is some constant less than one. If we assume a power law dependence for the self-avoiding case $\langle \mathbf{a}_i \mathbf{a}_j \rangle \propto |i - j|^p$, one can calculate the exponent p by comparison with the end to end distance

$$\langle R^2 \rangle = \sum_{i,j} \langle \mathbf{a}_i \mathbf{a}_j \rangle \propto N^{2\nu} \tag{16}$$

Changing the summation into an integration gives for p

$$p = -2(1 - \nu) \simeq -\frac{4}{5} \tag{17}$$

This is not consistent with our Monte Carlo calculations. We analyzed $\langle \mathbf{a}_i \mathbf{a}_j \rangle$ for linear chains of length between $N = 60$ and $N = 240$ monomers. We chose one of the two bonds exactly in the middle of the chain to avoid corrections to scaling. In fact Figure 12 shows that there is not much difference in the results between $N = 60$ and $N = 240$. We do find a power law but with the power $p = -1.15$. However, it still might be possible that the deviation is due to very slow decaying corrections to scaling.

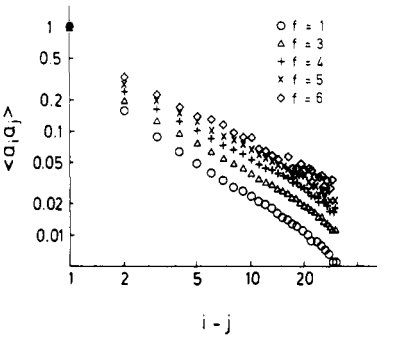

Figure 13. Bond correlations for stars. As the arms are forced to the outer part of the star, $\langle \mathbf{a}_i \mathbf{a}_j \rangle$ decays more slowly with increasing f.

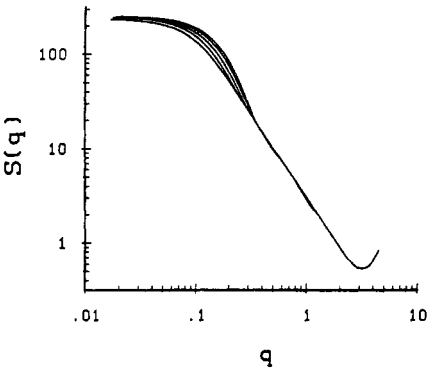

Figure 14. $S(q)$ versus q for $f = 1$, 3, 4, 5, and 6 and $Nf = 240$. $S(q)$ was calculated in the program for 60 equidistant q values on a logarithmic scale. The points are connected by spline functions.

For stars, one expects that the amplitudes of the correlations decay more slowly with increasing f, since the arms are forced to grow away from the center. This is in fact the case as can be seen in Figure 13. In addition the corresponding powers p seem to decrease with increasing f. This cannot be true, if eq 17 holds, and supports the conjecture of having large corrections to scaling.

6. Structure Functions: Statics and Initial Decay

Because of the special geometry of stars, one expects some pronounced effects considering the structure function defined by

$$S(\mathbf{q}) = \frac{1}{Nf + 1} \left| \sum_{j}^{Nf+1} \exp(i\mathbf{q}\mathbf{r}_j) \right|^2 \tag{18}$$

For a star without excluded-volume interactions, $S(\mathbf{q})$ has been computed already in 1953 by Benoit.[13] For stars with a different number of arms but constant overall polymerization, the main effect consists in an overshooting in the crossover behavior connecting the regimes $qR_G << 1$ with $S(q) = Nf + 1$ and $qR_G >> 1$ with $S(q) \propto q^{-d_F}$ ($d_F = 1/\nu$ is the fractal dimension). This overshooting results from the decreasing radius of gyration with increasing f and is of course expected to occur also in stars with excluded volume (Figure 14). This behavior can be seen much more clearly in the Kratky plot[19] $S(q)q^{1/\nu}$ versus q, see Figure 15, and has actually been prooven in neutron scattering experiments.[10]

The full scaling behavior of many-arm stars with excluded volume including two more scaling regimes is described by Grest et al.[32] In our case this is of course not detectable. This full scaling was not completely seen even with 50-arm stars. Nevertheless one can show by using $S(q)$ even for few-arm stars the effect of the excluded

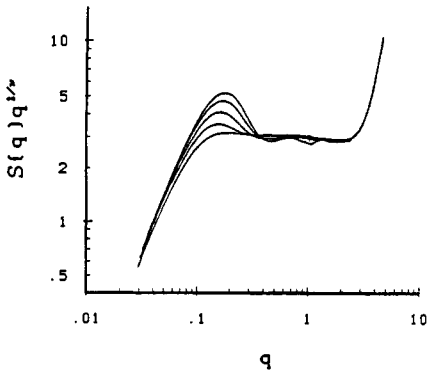

Figure 15. Same data as in Figure 14 plotted in the more sensitive Kratky plot.

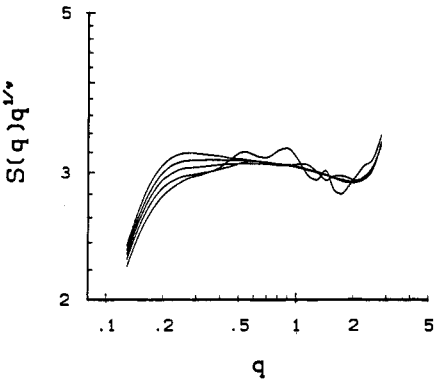

Figure 16. $S(q)q^{1/\nu}$ versus q for two arms consisting of $N = 80$ monomers of an f-arm star. $f = 2, ..., 6$. The sample size is rather small at $f = 6$ (2000 chains), leading to large fluctuations.

volume resulting in the stretching of arms. For this we calculate the structure function of single arms. Since their radius of gyration decreases with increasing f, one should be able to see this difference at $qR_{G,arm} \simeq 2\pi$ in the sensitive Kratky plot. In order to obtain more clear results we take the structure function of two arms of a f arm star; i.e., we investigate how much the linear chain with $f = 2$ is disturbed by the existence of the other arms. The results shown in Figure 16 indicate the slowly increasing size of the arms.

The initial decay rate $\Gamma^{(0)}$

$$\ln S(\mathbf{q},t) = \ln S(\mathbf{q},t=0) - \Gamma^{(0)}t \pm ... \tag{19}$$

of the dynamic structure function $S(\mathbf{q},t)$

$$S(\mathbf{q},t) = \frac{1}{Nf}\sum_{i,j}\langle \exp[i\mathbf{q}(\mathbf{r}_i(t) - \mathbf{r}_j(0))]\rangle \tag{20}$$

is also of great importance and can be calculated rigorously from the static properties, as was shown by Akcasu and Gurol:[48,19]

$$\Gamma^{(0)} = -\frac{\mathrm{d}}{\mathrm{d}t}\ln S(\mathbf{q},t)|_{t=0} = \frac{\sum_{i,j}\langle \mathbf{q}\boldsymbol{D}_{ij}\mathbf{q}\,\exp[i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)]\rangle}{\sum_{i,j}\langle \exp[i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)]\rangle} \tag{21}$$

Preaveraging the Oseen tensor gives for D_{ij} (see, e.g., ref 49):

$$D_{ij} = \frac{kT}{\zeta}\left[\delta_{ij} + (1 - \delta_{ij})\frac{\zeta}{8\pi\eta_0|\mathbf{r}_i - \mathbf{r}_j|}\left(1 + \frac{(\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j)}{(\mathbf{r}_i - \mathbf{r}_j)^2}\right)\right] \tag{22}$$

(ζ, friction coefficient; η_0, viscosity of the solvent; k, Boltzmann constant; T, temperature; the terms kT/ζ and $\zeta/(8\pi\eta_0)$ are set equal to one in the simulation).

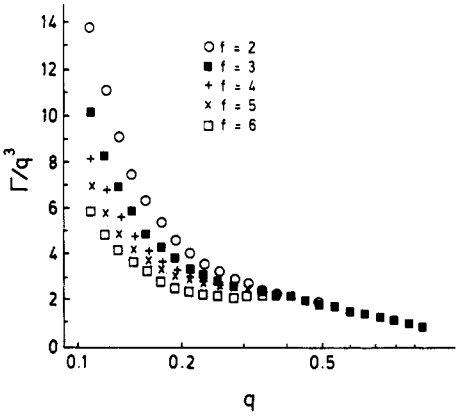

Figure 17. Initial decay rate $\Gamma^{(0)}$ for stars of various numbers of arms of equal length $N = 40$. $\Gamma^{(0)}$ is independent of f in the regime $qR_G >> 1$, as a monomer of an arm does not realize the existence of the other arms.

In the cases $qR_G << 1$ and $qR_G >> 1$, one obtains the well-known results[49]

$$\Gamma^{(0)} = D_G q^2; \qquad qR_G << 1 \tag{23}$$

with

$$D_G = \frac{kT}{6\pi\eta_0}\int_0^{Nf}\frac{di}{Nf}\int_0^{Nf}\frac{dj}{Nf}\left\langle\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right\rangle \tag{24}$$

and

$$\Gamma^{(0)} = C\frac{kT}{\eta_0}q^3; \qquad qR_G >> 1 \tag{25}$$

The constant C depends on the exponent ν ($C(\nu = {}^1/_2) = 0.0625$, $C(\nu = {}^3/_5) = 0.0788$).

The crossover regime between these two limiting behaviors is especially interesting for stars: A monomer of an arm can move on the average a distance of the order of magnitude of the screening length $\zeta(r)$, without realizing the connection of its own arm to the other ones. For larger distances (i.e., with decreasing q) it must drag along more and more of the whole star. This is expressed by the reduction of the internal diffusion rate for $qR_{G,arm} \simeq 1$ (de Gennes correlation holes[50]). This effect first described by Burchard[19] for stars is clearly demonstrated in the simulation and could also be measured in neutron scattering experiments[10] (Figure 17).

7. The Hydrodynamic Radius

In the Kirkwood theory[51] the diffusion constant D is given by

$$D = \frac{kT}{M\zeta} + \frac{kT}{6\pi\eta}\frac{1}{R_H} \tag{26}$$

($M = Nf + 1$) where $R_H(N,f)$ is the hydrodynamic radius defined by

$$\frac{1}{R_H} = \frac{1}{M}\sum_{i\neq j}^{M}\left\langle\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right\rangle \tag{27}$$

Our main purpose in this section is to show the very slow approach to the asymptotic behavior $R_H \propto N^\nu$ with $\nu = 0.5876$, i.e., the same ν as for end to end distance. Such a slow approach has been in fact already proposed by Weill and des Cloizeaux,[52] although the experimentally measured exponent ν is about 0.55[53,54] (a discussion is given in ref 49). The high accuracy of our results allows for a very precise verification of this fact, while this was not possible

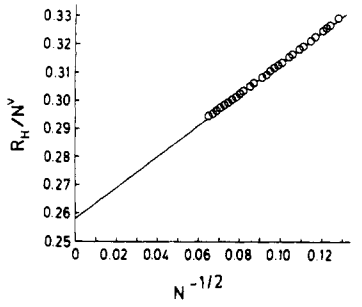

Figure 18. $R_H(N)/N^\nu$ versus $1/N^{1/2}$ for linear chains. Using the value $\nu = 0.5876$, one obtains a clear demonstration of the slow approach to the asymptotic scaling behavior of R_H.

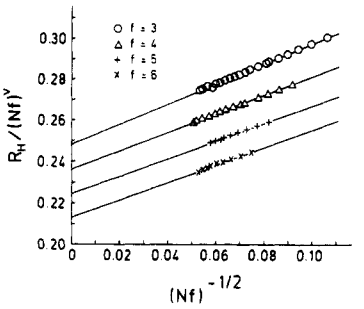

Figure 19. Same plot as in Figure 18 for stars with $f = 3, ..., 6$. The parallel lines indicate that the amplitude of the correction to scaling term is independent of f.

in the simulation of Rey et al.[23] because of data scattering. In Figures 18 and 19 we plotted the $R_H(N,f)/N^\nu$ for linear chains and stars versus $N^{-1/2}$. Both figures show that the dominant power of the corrections to scaling is porportional to $N^{-1/2}$. The reason of this slow approach to the asymtotic value may be found in the very special way of defining R_H. Since the hydrodynamic radius is the harmonic mean of the distances between the monomers, the weight of the small distances having large corrections to scaling is much higher than in arithmetic means like the radius of gyration. Figure 20 shows the behavior of the ratio $h(f)$

$$h(f) = \frac{R_H(N,f)}{R_H(Nf,f=1)} \tag{28}$$

For random walks $h(f)$ is calculated as[55]

$$h(f) = \frac{f^{1/2}}{2 - f + 2^{1/2}(f-1)} \tag{29}$$

The data suggest that no simple power law can be fitted for few-arm stars, while this has to be the case in the many-arm limit.

We also calculate the ratio $\rho(f)$

$$\rho = R_G^2(N,f)/R_H(n,f) \tag{30}$$

For random walks one finds[61]

$$\rho = \left(\frac{3f-2}{f\pi}\right)^{1/2} \frac{8[2 - f + 2^{1/2}(f-1)]}{3f} \tag{31}$$

For Θ solvents the random-walk ansatz is known to give results about 15% higher than the experimental values.[62] This fact is also found in our case for the $f = 3$ star (see Figure 21). If the measured point in Figure 21[6] is accurate enough, this would mean that the effect of corrections to scaling of R_H is not the reason of this discrepancy. In any case one should be very careful in analyzing ρ: Since here the leading powers of R_H and R_G proportional to N^ν cancel, both corrections to scaling and data scattering lead to strong uncertainties in the results.

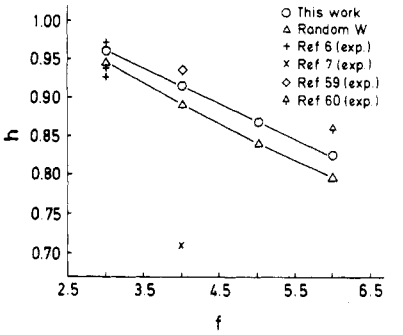

Figure 20. Ratio $h = R_H(N,f)/R_H(Nf,f=1)$ versus f. The agreement of the random-walk result to the MC calculations is not as good as for the analogous ratios $g(f)$ of the radii of gyration (see Figure 8). The error bars of the MC simulation are smaller than the symbol size. Comparison to experiments[6,7,59,60] is difficult because of data scattering.

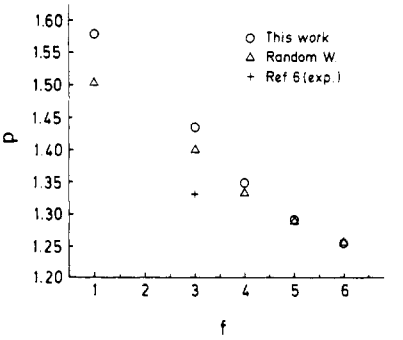

Figure 21. Ratio $\rho = R_G(N,f)/R_H(N,f)$ versus f. No good agreement of the random-walk result to the MC calculations is found. The data give rise to the assumption that for $f > 6$ the value of the good solvent stars is higher than that of the random-walk stars.

8. Conclusions

By the use of a modified version of the dimerization method, which is also capable of generating very effectively star polymers, we were able to extent previous results significantly. For the exponent γ we were able to reduce the error bars of previous investigations by an order of magnitude. The approximate equation of Ohno turned out to describe the stars much better than the Miyake and Freed equation. The overall configurational properties turned out to be in good accord to the Daoud–Cotton scaling, although this approach originally is designed for many arms f. Deviations from this concept then can be seen by analyzing properties of single arms, such as the average center end distances of the arms. Similar to earlier simulations of many-arm stars, only the outer extended regime of the scaling was found. One of the most important result is concerned with the hydrodynamic properties of star polymers as well as linear polymers. For the hydrodynamic radius we show that the leading correction to scaling is proportional to $1/N^{1/2}$ for stars as well as for linear chains. Using this both systems yield also from this quantity an excellent estimate of the exponent ν. As can be seen from the figures this correction is fairly strong. A reanalysis of experiments should yield a common extrapolation by using the asymptotic exponent ν. Such an analysis using numerical data to our knowledge was not done yet. The earlier simulations for stars were confined to arms, which did not significantly exceed the persistence length. We also considered the initial decay of the dynamic structure function. With increasing arm number f, we find a clear indication of the de Gennes correlation hole, as was

also found for more arms by neutron scattering. To conclude, we presented an extensive rather general analysis of the asymptotic properties of star polymers on the fcc lattice. Corrections to scaling were taken into account. We calculate several properties, which are not only of theoretical interest but can directly be checked by experiment, such as hydrodynamic radii, scattering functions, and others.

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References and Notes

(1) Burchard, W. *Macromolecules* **1974**, *7*, 841. Burchard, W.; Kajiwara, K.; Nerger, D.; Stockmayer, W. *Macromolecules* **1984**, *17*, 222.
(2) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(3) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.
(4) Kanjiwara, K.; Burchard, W. *Macromolecules* **1982**, *15*, 660.
(5) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(6) Huber, K. H.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(7) Xuexin, C.; Zhongde, X.; von Meerwall, E.; Seung, N.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 1343.
(8) Huber, K.; Bantle, S.; Burchard, W.; Fetters, L. J. *Macromolecules* **1986**, *19*, 1404.
(9) Khorramian, B. A.; Stivala, S. S. *Polym. Commun.* **1986**, *27*, 184.
(10) Richter, D.; Stühn, B.; Ewen, B.; Nerger, D. *Phys. Rev. Lett.* **1987**, *58*, 2462.
(11) Khasat, N.; Pennisi, R.; Hadjichristidis, N.; Nerger, D.; Fetters, L. J., preprint, 1987.
(12) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(13) Benoit, H. *J. Polym. Sci.* **1953**, *9*, 507.
(14) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(15) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(16) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.
(17) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.
(18) Kolinski, A.; Sikorski, A. *J. Polym. Sci.* **1982**, *20*, 3147; *J. Polym. Sci.* **1984**, *22*, 97; *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 177.
(19) Burchard, W. *Adv. Polym. Sci.* **1983**, *48*, 1.
(20) Vlahos, C.; Kosmas, M. K. *Polymer* **1984**, *25*, 1607.
(21) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854.
(22) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228; *Macromolecules* **1984**, *17*, 678.
(23) Freire, J. J.; Prats, R.; Pla, J.; Torre, J. G. *Macromolecules* **1984**, *17*, 1815. Freire, J. J.; Rey, A.; Torre, J. T. *Macromolecules* **1986**, *19*, 457. Rey, A.; Freire, J. J.; Torre, J. G. *Macromolecules* **1987**, *20*, 342.
(24) Freire, J. J.; Pla, J.; Rey, A.; Prats, R. *Macromolecules* **1986**, *19*, 452.
(25) Zimm, B. H. *Macromolecules* **1984**, *17*, 795.
(26) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453.
(27) Birshtein, T. M.; Zhulina, E. B.; Borisov, O. V. *Polymer* **1986**, *27*, 1078.
(28) Lipson, J. E. G.; Whittington, S. G.; Wilkinson, M. K.; Martin, J. L.; Gaunt, D. S. *J. Phys. A* **1985**, *18*, L469. Wilkinson, M. K.; Gaunt, D. S.; Lipson, J. E. G.; Whittington, S. G. *J. Phys. A* **1986**, *19*, 789.
(29) Whittington, S. G.; Lipson, J. E. G.; Wilkinson, M. K.; Gaunt, D. S. *Macromolecules* **1986**, *19*, 1241.
(30) Halperin, A.; Alexander, S. *Macromolecules* **1986**, *20*, 1146.
(31) Barett, A. J.; Tremain, D. L. *Macromolecules* **1987**, *20*, 1687.
(32) Grest, G. S.; Kremer, K.; Witten, T. A. *Macromolecules* **1987**, *20*, 1376. Grest, G. S.; Kremer, K.; Milner, S.; Witten, T. A. *Macromolecules* **1989**, *22*, 1904.
(33) Ohno, K.; Binder, K. *J. Phys. Fr.* **1988**, *49*, 1329.
(34) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356.
(35) Batoulis, J.; Kremer, K. *J. Phys. A* **1988**, *21*, 127.
(36) Suzuki, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 561.
(37) Alexandrowicz, Z. *J. Chem. Phys.* **1969**, *51*, 561.
(38) Binder, K.; Kremer, K. *Comp. Phys. Rep.* **1988**, *7*, 259.
(39) Lawler, G. F.; Duke *Math. J.* **1980**, *47*, 655; **1986**, *53*, 249.
(40) Kron, A. K. *Polym. Sci. USSR* **1965**, *7*, 1361.
(41) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(42) Baumgärtner, A. In *Monte Carlo Methods in Statistical Physics, Topics Current Physics*; Binder, K., Ed.; Springer: Berlin, Heidelberg, New York, Tokyo, 1984; Vol. 36, p 145.
(43) Batoulis, J., Kremer, K. *Europhys. Lett.* **1988**, *7* (8), 683.
(44) Batoulis, J., manuscript in preparation.
(45) Majid, I.; Djordjevic, Z.; Stanley, H. E. *Phys. Rev. Lett.* **1983**, *51*, 1282.
(46) LeGuillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95; *Phys. Rev. B21* **1980**, 3976.
(47) Batoulis, J. PhD Thesis, Mainz 1987, unpublished. For this calculation we assume that the star is built up by $f/2$ double arms. One double arm has the size of an ordinary self-avoiding walk; i.e., it does not interfere with the others. The result for arbitrary ν is $g(f) = [(2^{2\nu+1} - 1)f - 2(2^{2\nu} - 1)]/f^{2\nu+1}$, which gives the Zimm–Stockmayer result for $\nu = {}^1/_2$.
(48) Akcazu, Z.; Gurol, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1.
(49) Doi, M.; Edwards, S. F. The *Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(50) de Gennes, P.-G. *Physica* **1959**, *25*, 825.
(51) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1.
(52) Weill, G.; des Cloizeaux *J. Phys.* **1979**, *40*, 99.
(53) Adam, M.; Delsanti, M. *J. Phys.* **1976**, *37*, 1045; *Macromolecules* **1977**, *10*, 1229.
(54) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 584, 1184. Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 425.
(55) Stockmayer, W. H.; Fixman, M. *Ann. N.Y. Acad. Sci.* **1953**, *57*, 334.
(56) Rudnick, J.; Gaspari, G. *J. Phys. A* **1986**, *19*, L191.
(57) Bishop, M.; Saltiel, C. preprint, 1988.
(58) Grassberger, P. *Phys. Lett.* **1982**, *89A*, 381.
(59) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(60) Roovers, J.; Toporowski, P. M. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 1907.
(61) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 580, 1265.
(62) Schmidt, M.; Burchard *Macromolecules* **1981**, *14*, 210.