Dimensions of the branches of a uniform brush polymer

1989 J. Phys. A: Math. Gen. 22 5109

(http://iopscience.iop.org/0305-4470/22/23/015)

J. Phys. A: Math. Gen. 22 (1989) 5109–5116. Printed in the UK

Dimensions of the branches of a uniform brush polymer

M K Kosmas†, D S Gaunt‡ and S G Whittington§

† Department of Chemistry, University of Ioannina, Ioannina, Greece
‡ Department of Physics, King's College, Strand, London WC2R 2LS, UK
§ Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received 26 June 1989

Abstract. Excluded volume effects increase the dimensions of the various branches of a uniform brush polymer to different extents. We use Monte Carlo methods and perturbation calculations to study the mean-square end-to-end branch lengths of a uniform brush with two branch points, as a function of the number (n) of monomers in a branch and the functionalities (f_1 and f_2) of the branch points. The mean-square end-to-end length $\langle R_n^2 \rangle$ of a branch scales like $Bn^{2\nu}$ and we investigate how the amplitude (B) varies for the different types of branch as f_1 and f_2 vary. The amplitude ratios are expected to be lattice independent and we find good agreement between our numerical estimates of these ratios from perturbation and Monte Carlo calculations.We have extended the perturbation calculations to make predictions for the corresponding amplitude ratios for the mean-square radii of gyration of the various branches.

1. Introduction

Branched polymers with a specified architecture and the same number of monomers in each branch have been receiving considerable attention of late (e.g. Ohno and Binder 1988 and references therein). Earlier work focused on excluded volume effects in uniform f-stars, which are polymers with f branches (meeting at a vertex of degree f) and n monomers in each branch. The statistics, dimensions and dynamics of these have been studied by the renormalisation group (Miyake and Freed 1983, Vlahos and Kosmas 1984, Ohno and Binder 1988), conformal invariance (Duplantier 1986), exact enumeration (Wilkinson *et al* 1986), Monte Carlo (Whittington *et al* 1986, Wilkinson *et al* 1988) and molecular dynamics techniques (Grest *et al* 1987). Where comparisons can be made between the results of these various approaches the agreement is generally good. In particular, there is agreement that g, the ratio of the mean-square radius of gyration of an f-star to that of a linear polymer with the same total degree of polymerisation, is insensitive to effects of excluded volume. Nevertheless, excluded volume effects are important in determining the dimensions of such polymers and, in particular, the branches of a uniform star are expanded (relative to a random walk model) by excluded volume effects within and between branches. This can be seen both in the mean-square end-to-end length of a branch (Miyake and Freed 1983, Whittington *et al* 1986), and in the mean-square radius of gyration of a branch (Whittington *et al* 1988).

In this paper we study the dimensions of the branches of uniform brushes with two branch points. A (k_1, k_2)-brush has two branch points with functionalities $k_1 + 2$

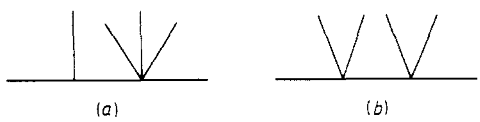


Figure 1. Examples of uniform brushes: (a) (1,3)-brush, (b) (2,2)-brush.

and $k_2 + 2$. See figure 1 for some examples. In such structures there are in general (for $k_1 \neq k_2$) three distinct types of branch which we call k_1-branches, k_2-branches and the internal branch. These are expected to be expanded by different amounts and the degree of expansion will depend on k_1 and k_2. In section 2 we investigate the magnitude of this effect on the mean-square end-to-end length of a branch using Monte Carlo techniques and, in section 3, compare these results with those obtained by a perturbation calculation. The agreement is very satisfactory. In section 4 we extend the perturbation calculations to the mean-square radius of gyration of a branch, which could in principle be measured by neutron scattering experiments on suitably deuterated samples.

2. Monte Carlo calculations

In this section we describe Monte Carlo results for uniform brushes weakly embeddable in the simple cubic lattice. We study the mean-square end-to-end length $\langle R_n(k_1, k_2, \alpha)^2 \rangle$ of a branch of a (k_1, k_2)-brush with n edges in each branch, where $\alpha = 0, 1, 2$ according to whether the branch is the internal one (between the two branch points), a branch from a vertex of degree 1 to the branch point of degree $(k_1 + 2)$, or from a vertex of degree 1 to the branch point of degree $(k_2 + 2)$.

We used an inversely restricted sampling technique (Rosenbluth and Rosenbluth 1955) to generate brushes with $k_1 = 1$, $k_2 = 1, 2, 3$ and 4, with $n \leq 20$. Sample sizes ranged between 500,000 and 2,000,000. Samples for the various values of n were uncorrelated.

By analogy with self-avoiding walks we expect that

$$\langle R_n(k_1, k_2, \alpha)^2 \rangle = B(k_1, k_2, \alpha) n^{2\nu} [1 + C(k_1, k_2, \alpha) n^{-\Delta} + O(n^{-1})] . \tag{2.1}$$

Log–log plots of $\langle R_n(k_1, k_2, \alpha)^2 \rangle$ against n give a set of parallel lines, indicating that ν is independent of k_1, k_2 and α, and consistent with a value of ν equal to that for a self-avoiding walk, i.e. 0.588. In the subsequent analysis we assume that $\Delta = 0.47$ (Le Guillou and Zinn-Justin 1980).

If $\langle R_n^2 \rangle$ is the mean-square end-to-end length of an n-step self-avoiding walk, and B is the corresponding amplitude, we are primarily interested in the amplitude ratios

$$\mathscr{B}(k_1, k_2, \alpha) \equiv B(k_1, k_2, \alpha)/B = \lim_{n\to\infty} \langle R_n(k_1, k_2, \alpha)^2 \rangle / \langle R_n^2 \rangle \tag{2.2}$$

which are expected to be lattice independent and which can therefore be compared with results from experiments and from continuum calculations.

In figures 2 and 3 we show the n dependence of $\langle R_n(1, k, \alpha)^2 \rangle / \langle R_n^2 \rangle$ for $\alpha = 0$ (the internal branch) and for $\alpha = 2$, for $k = 1, 2, 3$ and 4. The values of $\langle R_n^2 \rangle$ for the self-avoiding walk are taken from Guttmann (1987). We see that, for each k, the internal branch is more expanded than the external branch and, in both cases, the degree of extension increases as k increases.

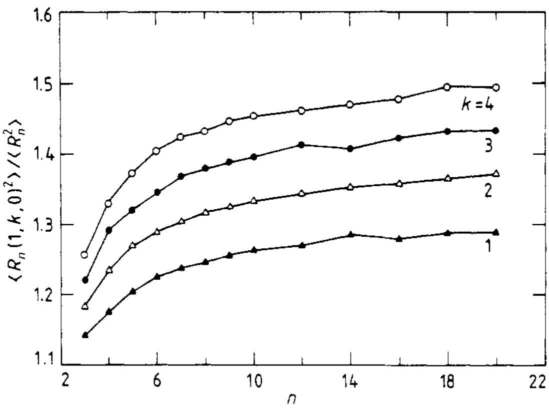


Figure 2. The n-dependence of the reduced mean-square end-to-end length of the internal branch of a $(1, k)$-brush. Error bars (one standard deviation) are no larger than twice the size of the symbols.

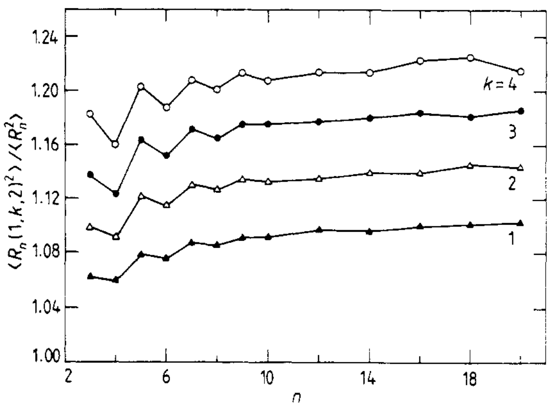


Figure 3. The n-dependence of the reduced mean-square end-to-end length of the external branch ($\alpha = 2$) of a $(1, k)$-brush. Error bars (one standard deviation) are no larger than twice the size of the symbols.

Table 1. Comparison of estimates of amplitude ratios of branches of a $(1, k)$-brush from Monte Carlo (MC) and first-order ϵ-expansion (RG) calculations.

	$\mathscr{B}(0)$		$\mathscr{B}(1)$		$\mathscr{B}(2)$	
k	MC	RG	MC	RG	MC	RG
1	1.35±0.05	1.305	1.128±0.010	1.119	1.128±0.010	1.119
2	1.45±0.05	1.402	1.13±0.01	1.124	1.16±0.02	1.175
3	1.52±0.04	1.499	1.13±0.02	1.128	1.21±0.02	1.230
4	1.58±0.06	1.596	1.13±0.03	1.132	1.26±0.03	1.285

In order to estimate $\mathscr{B}(1, k, \alpha)$ we plot $\langle R_n(1, k, \alpha)^2\rangle / \langle R_n^2\rangle$ against $n^{-0.47}$. A typical plot is shown in figure 4. The value of $\mathscr{B}(1, k, \alpha)$ is estimated from the intercept and numerical estimates for various values of k and α are given in table 1.

3. Perturbation calculation for $\langle R_n(k_1, k_2, \alpha)^2 \rangle$

In this section we present a perturbation calculation of the mean-square end-to-end length of a branch of a uniform (k_1, k_2)-brush, to first order in $\epsilon = 4 - d$, where d is the dimensionality of the space.

We use the Gaussian model with excluded volume interactions according to which the probability distribution $P\{\boldsymbol{R}_{ij}\}$ of the set of position vectors of the ith monomer in the jth branch is given by

$$P\{\boldsymbol{R}_{ij}\} = P_o\{\boldsymbol{R}_{ij}\} \exp\left(-u \sum_{k=1}^{b} \sum_{i=1}^{n} \sum_{j \neq i}^{n} \delta^d(\boldsymbol{R}_{ik} - \boldsymbol{R}_{jk}) - u \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{b} \sum_{l \neq k}^{b} \delta^d(\boldsymbol{R}_{ik} - \boldsymbol{R}_{jl}) \right)$$

$$\equiv P_o\{\boldsymbol{R}_{ij}\} \exp(-u\Phi) \tag{3.1}$$

where $P_o\{\boldsymbol{R}_{ij}\}$ is the ideal probability, which includes connectivity effects but not excluded volume terms. N is the total number of monomers, b is the total number of branches in the brush and u is an excluded volume parameter.

To first order in u the mean-square end-to-end length of the α-branch is equal to

$$\langle R^2(\alpha) \rangle = \langle R^2(\alpha) \rangle_o - u[\langle R^2(\alpha)\Phi \rangle_o - \langle R^2(\alpha) \rangle_o \langle \Phi \rangle_o] \tag{3.2}$$

where we have suppressed the dependence on k_1 and k_2 and where

$$\langle \ldots \rangle_o = \frac{\int \ldots P_o \Pi \mathrm{d}\boldsymbol{R}_{ij}}{\int P_o \Pi \mathrm{d}\boldsymbol{R}_{ij}} . \tag{3.3}$$

Clearly $\langle R^2(\alpha) \rangle_o$ is proportional to n.

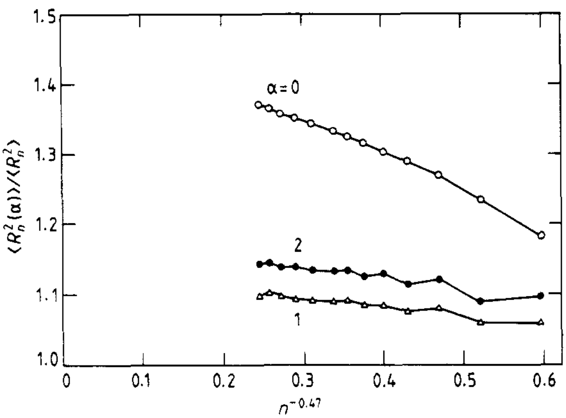
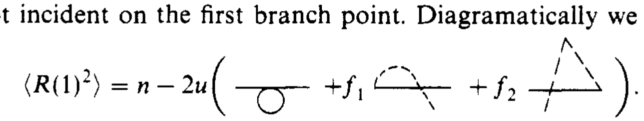


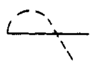
Figure 4. Extrapolation against $n^{-\Delta}$ of the reduced mean-square end-to-end length of the branches of a (1,2)-brush.

For $\alpha = 1$ the u term in (3.2) has three contributions. These are an intra-branch term, $f_1 = k_1 + 1$ interactions between the branch and a second branch incident on the same branch point, and $f_2 = k_2 + 1$ interactions between the branch and one of the f_2 branches not incident on the first branch point. Diagramatically we can write this as



(3.4)

Interchanging f_1 and f_2 gives $\langle R(2)^2 \rangle$. For the internal branch ($\alpha = 0$) there are again three contributions to the u term. These are an intra-branch term, $(f_1 + f_2)$ interactions between the internal branch and any of the other branches, and $f_1 f_2$ interactions between pairs of branches, one incident on each branch point. This can be written as

$$\langle R(0)^2 \rangle = n - 2u\Big(\quad$$  $$+ (f_1 + f_2)$$  $$+ f_1 f_2$$  $$\Big). \tag{3.5}$$

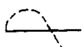
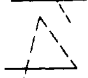
A factor of $(d/2na^2)^{d/2}$ has been absorbed in u to make u and $\langle R(\alpha)^2 \rangle$ dimensionless.

All of the diagrams have a single loop and are of the form $-C^2/L^{(d/2)+1}$ where L is the length of the loop and C is the length of the common part of the branch being considered and the loop (Fixman 1955). The forms and values of these diagrams are given in table 2. Using these we find

$$\langle R(1)^2 \rangle = n\{1 - 2u[-\ln n + 1 + f_1(\tfrac{1}{4} - \ln 2) + f_2(\tfrac{1}{12} + 3\ln 2 - 2\ln 3)]\} \tag{3.6}$$

$$\langle R(0)^2 \rangle = n\{1 - 2u[-\ln n + 1 + (f_1 + f_2)(\tfrac{1}{4} - \ln 2) - \tfrac{1}{6} f_1 f_2]\}\,. \tag{3.7}$$

Table 2. Forms of the diagrams required for $\langle R_n(\alpha)^2 \rangle$, and their values for $d = 4$.

Diagram	Form	Value
	$-\int_0^n \mathrm{d}i \int_i^n \mathrm{d}j\, 1/(j-i)^{(d/2)-1}$	$n(-\ln n + 1)$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j\, i^2/(i+j)^{(d/2)+1}$	$n(\frac{1}{4} - \ln 2)$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j\, i^2/(i+j+n)^{(d/2)+1}$	$n(\frac{1}{12} + 3\ln 2 - 2\ln 3)$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j\, n^2/(i+j+n)^{(d/2)+1}$	$-\frac{1}{6}n$

Setting $f_1 = f_2 = 0$ gives the self-avoiding walk result, then taking ratios and replacing u by its fixed point value $u^* = \epsilon/16$ (Kosmas 1981) gives

$$\mathscr{B}(0) = 1 + \tfrac{1}{8}\epsilon[0.443(f_1 + f_2) + 0.167 f_1 f_2] \tag{3.8}$$

$$\mathscr{B}(1) = 1 + \tfrac{1}{8}\epsilon[0.443 f_1 + 0.034 f_2] \tag{3.9}$$

$$\mathscr{B}(2) = 1 + \tfrac{1}{8}\epsilon[0.034 f_1 + 0.443 f_2]. \tag{3.10}$$

In table 1 we give the numerical values of these amplitude ratios for $f_1 = 2$, $f_2 = k + 1$, for $k = 1, 2, 3$ and 4, and for $\epsilon = 1$. The agreement with the Monte Carlo estimates is generally satisfactory, in that all the ϵ-expansion results are within one standard deviation of the Monte Carlo estimates.

4. Mean-square radius of gyration

The expansion of the end-to-end length of a branch of a brush, which we discussed in sections 2 and 3, is a result of interference between the branches. This interference will also lead to expansion of the radius of gyration of a branch; we study this phenomenon in this section using perturbation techniques. In principle this should be observable experimentally by neutron scattering studies of a brush with one branch suitably deuterated.

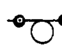
The mean-square radius of gyration of the jth branch can be expressed as

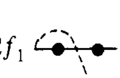
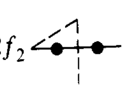
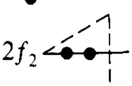
$$\langle S_j^2\rangle = n^{-2}\sum_{i=1}^{n-1}\sum_{k=i+1}^{n}\langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\rangle$$
$$\simeq n^{-2}\int_o^n \mathrm{d}i\int_i^n \mathrm{d}k\langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\rangle. \tag{4.1}$$

To first order in u

$$\langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\rangle = \langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\rangle_o - u[\langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\Phi\rangle_o - \langle(\boldsymbol{R}_{ij}-\boldsymbol{R}_{kj})^2\rangle_o\langle\Phi\rangle_o] \tag{4.2}$$

For $\alpha = 1$ the mean-square radius of gyration can be written in diagrammatic form as

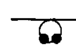
$\langle S_n(1)^2\rangle = (na^2/6) - (ua^2/n^2)\Big(2$  $+ 2$  $+ 4$ 

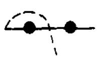
$+ 2f_1$  $+ 2f_1$  $+ 2f_2$  $+ 2f_2$  $\Big)$ (4.3)

where 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. The forms and values of the diagrams are given in table 3. These lead to

$$\langle S_n(1)^2\rangle = (na^2/6)\{1 + 2u[\ln n - \tfrac{13}{12} + f_1(\tfrac{35}{8} - 6\ln 2) + f_2(\tfrac{251}{24} - 36\ln 3 + 42\ln 2)]\} \tag{4.4}$$

$\langle S_n(2)^2\rangle$ is given by interchanging f_1 and f_2 in (4.4). For the internal branch the corresponding result is

$\langle S_n(0)^2\rangle = (na^2/6) - (ua^2/n^2)\Big(2$  $+ 2$  $+ 4$ 

$+ 2(f_1 + f_2)$  $+ 2(f_1 + f_2)$  $+ 2f_1f_2$  $\Big)$

$$= (na^2/6)\{1 + 2u[\ln n - \tfrac{13}{12} + (f_1 + f_2)(\tfrac{35}{8} - 6\ln 2) + \tfrac{1}{12}f_1f_2]\}. \tag{4.5}$$

We write

$$\mathscr{G}(\alpha) = \lim_{n\to\infty}\langle S_n(\alpha)^2\rangle/\langle S_n^2\rangle \tag{4.6}$$

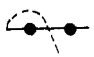
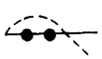
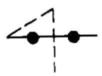
where $\langle S_n^2\rangle$ is the mean-square radius of gyration of a self-avoiding walk. Then, replacing u by its fixed-point value $(\epsilon/16)$ and dividing by the self-avoiding walk result (obtained by setting $f_1 = f_2 = 0$), we obtain

$$\mathscr{G}(0) = 1 + \tfrac{1}{8}\epsilon[0.216(f_1 + f_2) + 0.083f_1f_2] \tag{4.7}$$

$$\mathscr{G}(1) = 1 + \tfrac{1}{8}\epsilon[0.216f_1 + 0.020f_2] \tag{4.8}$$

$$\mathscr{G}(2) = 1 + \tfrac{1}{8}\epsilon[0.020f_1 + 0.216f_2]. \tag{4.9}$$

Table 3. Forms of the diagrams required for $\langle S_n(\alpha)^2\rangle$, and their values for $d = 4$.

Diagram	Form	Value
	$-\int_0^n \mathrm{d}i \int_i^n \mathrm{d}j \int_0^i \mathrm{d}k \int_j^n \mathrm{d}l\,(j-i)^{1-(d/2)}$	$n^3(-\ln n + \frac{11}{6})/6$
	$-\int_0^n \mathrm{d}i \int_i^n \mathrm{d}j \int_i^j \mathrm{d}k \int_k^j \mathrm{d}l\,(l-k)^2/(j-i)^{(d/2)+1}$	$-\frac{1}{72}n^3$
	$-\int_0^n \mathrm{d}i \int_i^n \mathrm{d}j \int_0^i \mathrm{d}k \int_i^j \mathrm{d}l\,(l-i)^2/(j-i)^{(d/2)+1}$	$-\frac{1}{18}n^3$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j \int_0^i \mathrm{d}k \int_i^n \mathrm{d}l\,(i-k)^2/(j+i)^{(d/2)+1}$	$n^3(7\ln 2 - 5)/6$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j \int_0^i \mathrm{d}k \int_k^i \mathrm{d}l\,(l-k)^2/(j+i)^{(d/2)+1}$	$n^3(\frac{5}{2} - 4\ln 2)/24$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j \int_0^i \mathrm{d}k \int_i^n \mathrm{d}l\,(i-k)^2/(j+i+n)^{(d/2)+1}$	$n^3(-13 + 44\ln 3 - 51\ln 2)/6$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j \int_0^i \mathrm{d}k \int_k^i \mathrm{d}l\,(l-k)^2/(j+i+n)^{(d/2)+1}$	$n^3(\frac{61}{6} - 32\ln 3 + 36\ln 2)/24$
	$-\int_0^n \mathrm{d}i \int_0^n \mathrm{d}j \int_0^n \mathrm{d}k \int_k^n \mathrm{d}l\,(l-k)^2/(j+i+n)^{(d/2)+1}$	$-\frac{1}{72}n^3$

5. Discussion

Excluded volume effects give rise to differential expansion of the various types of branches in a uniform brush. The perturbation calculations described in sections 3 and 4 show that this is due to two contributing effects. The first is the interaction between a distinguished branch and the remaining branches. The effect of the remaining branches is smaller when they are further away from the distinguished branch. The second effect, which acts only on the internal branch, is due to repulsion between branches attached to the internal branch at different branch points. This repulsion leads to an 'extensive force' on the internal branch.

The effect on the mean-square radius of gyration is only about half as big as the effect on the mean-square end-to-end length. See equations (3.8)–(3.10) and (4.7)–(4.9). This arises from the averaging in the radius of gyration over all lengths up to and including the maximum.

This work, as well as our previous work (Whittington *et al* 1988) on the internal dimensions of uniform stars, shows that perturbation calculations agree well with Monte Carlo estimates and provide reliable results, at least for small functionalities.

Acknowledgments

DSG and SGW are grateful to NATO (grant no RG85/0067) for partial financial support. SGW and MKK were partially supported by NSERC of Canada and by the Greek Ministry of Research and Technology, respectively.

References

Duplantier B 1986 *Phys. Rev. Lett.* **57** 941

Fixman M 1955 *J. Chem. Phys.* **23** 1656
Grest G S, Kremer K and Witten T A 1987 *Macromol.* **20** 1376
Guttmann A J 1987 *J. Phys. A: Math. Gen.* **20** 1839
Kosmas M K 1981 *J. Phys. A: Math. Gen.* **14** 931
Le Guillou J C and Zinn-Justin J 1980 *Phys. Rev.* B **21** 3976
Miyake A and Freed K F 1983 *Macromol.* **16** 1228
Ohno K and Binder K 1988 *J. Physique* **49** 1329
Rosenbluth M N and Rosenbluth A W 1955 *J. Chem. Phys.* **23** 356
Vlahos C H and Kosmas M K 1984 *Polymer* **25** 1607
Whittington S G, Lipson J E G, Wilkinson M K and Gaunt D S 1986 *Macromol.* **19** 1241
Whittington S G, Kosmas M K and Gaunt D S 1988 *J. Phys. A: Math. Gen.* **21** 4211
Wilkinson M K, Gaunt D S, Lipson J E G and Whittington S G 1986 *J. Phys. A: Math. Gen.* **19** 789
—— 1988 *Macromol.* **21** 1818