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Abstract. The expansion factor α_R^2 of model polymer chains 500 links long subject to excluded volume restraints has been studied using Monte Carlo techniques. The chains were synthesised in the spatial continuum, and the Wall and Erpenbeck enrichment technique was used to overcome chain attrition. The main conclusions to be drawn from the work are as follows: (i) It is possible that one of the four closed-form expressions for α_R^2 adequately represents the expansion of the chains up to $v = 0{\cdot}6$, where v is the excluded volume ratio. A necessary condition is $N \geq 100$ for $v = 0{\cdot}2$, increasing to $N \geq 500$ for $v = 0{\cdot}6$, where N is the number of links in the chain. (ii) The excluded volume should be taken as eight times the volume of the sphere representing the polymer repeat unit for chains with freely varying bond angles, and twice the sphere volume for chains with tetrahedral bond angles. (iii) The data at small v are in agreement with the perturbation theory expansion for α_R^2 up to at least $z \sim 0{\cdot}03$.

1. Introduction

The expansion factor $\alpha_R^2(N)$ for N-link polymer chains subject to excluded volume configurational constraints is defined by

$$\alpha_R^2(N) = \langle R_N^2 \rangle / \langle R_N^2 \rangle_0$$

where $\langle R_N^2 \rangle$ is the mean square end-to-end length of the chains and $\langle R_N^2 \rangle_0$ is the corresponding quantity for random walk chains, i.e. chains with zero excluded volume. This expansion has been studied by many workers since the early 1950s (Yamakawa 1971). The effective volume β excluded to one segment of the chain by the presence of another is given by

$$\beta = \int [1 - \exp(-\phi(r)/kT)] \, \mathrm{d}r \tag{1}$$

where $\phi(r)$ is the segment potential. It has usually been assumed that the intrachain forces can be represented by a three-dimensional Dirac delta function; the negative of β is called the binary cluster integral for a pair of segments. The perturbation theory development of Fixman (1955) yields

$$\alpha_R^2(z) = 1 + A_1 z + A_2 z^2 + A_3 z^3 + \ldots \tag{2}$$

where $z = (3/2\pi a^2)^{3/2} \beta N^{1/2}$ and a is the bond length, usually taken as unity. The average molecular dimensions may be expressed in terms of three parameters, namely

N, a and β, but since these parameters appear only as the two products Na^2 and $N^2\beta$ the perturbation theory is frequently called the two-parameter theory.

According to Yamakawa (1971) the series in equation (2) converges very slowly. However, several authors (Domb and Joyce 1972, Aronowitz and Eichinger 1975, 1976, Oono 1975a, b) have questioned its convergence; Edwards (1975) and Gordon *et al* (1976) claim that the expansion is only asymptotic, i.e. the series is not truly convergent for any finite nonzero z. Many authors have provided alternative closed-form expressions for $\alpha_R^2(z)$, which are supposed to be valid over a wide range of z, although subject to the condition $N \gg 1$. Some of these expressions have been compared recently by Domb and Barrett (1976). In every case it is assumed that α_R^2 is a function of z only; although the expressions predict very different $\alpha_R^2(z)$ at higher z, they have in common the result

$$\lim_{N\to\infty} \alpha_R^2(z) \propto z^{2/5}$$

or

$$\lim_{N\to\infty} \langle R_N^2 \rangle \propto N^{6/5} \tag{3}$$

It is not possible to differentiate between these expressions by comparison with experiment, because β and hence z is not directly observable. However, Monte Carlo techniques have been employed on digital computers to synthesise model chains whose configurational properties have then been analysed; a comprehensive review of this work has been written by Domb (1969). Most of the Monte Carlo data relate to 'lattice' chains, i.e. chains whose repeat units are represented by occupied vertices of some regular crystal lattice, and in which excluded volume restraints are imposed by requiring that no vertex of the lattice be visited more than once. The lattice chain data provide considerable support for the limiting behaviour given by equation (3), and also yield the result

$$\langle S_N^2 \rangle / \langle R_N^2 \rangle = \begin{cases} 0{\cdot}157 \pm 0{\cdot}002 & \text{(three dimensions)} \\ 0{\cdot}140 \pm 0{\cdot}002 & \text{(two dimensions)} \end{cases}$$

where $\langle S_N^2 \rangle$ is the mean square radius of gyration of N-link chains. Domb (1963) therefore conjectured that the dimensionality of the lattice, rather than its structural detail, largely determines the configurational properties of the chains. Based on recent developments in the theory of critical point thermodynamics, Domb and Barrett (1976) have put forward the more specific proposal that, defining $z^* = h_0 z$ where h_0 is a numerical scaling factor, $\alpha_R^2(z^*)$ is a universal function of z^* for all chains at large N. Their result is

$$\alpha_R^{10}(z^*) = 1 + \tfrac{20}{3} z^* + 4\pi z^{*2}$$

and they claim that this formula is a reasonable approximation for all z^* of practical interest. For lattice chains, h_0 is the volume per lattice site divided by β; its value for the continuum is not yet known accurately.

The synthesis of off-lattice chains on a computer is very time consuming, because more frequent violation of the excluded volume conditions leads to much greater sample attrition than for lattice chains. The available data are those of Fleming (1967), Stellman and Gans (1972a, b), Grishman (1973), Smith and Fleming (1975) and Bruns (1977, with references to earlier work). The repeat unit of the chain is usually taken as a

hard sphere, and it is convenient to define an excluded volume ratio

$$v = \text{hard-sphere diameter/bond length.}$$

Chains containing up to 1024 links have been synthesised, from $v = 0$ (random walk) up to $v = 2$, employing the enrichment (Wall and Erpenbeck 1959) and/or dimerisation (Alexandrowicz 1969) techniques to reduce the sample losses. The salient feature of the data is the dependence of the exponent γ in the equation

$$\langle R_N^2 \rangle = AN^{\gamma} \tag{4}$$

on v; it increases from unity at $v = 0$ to around $\frac{6}{5}$ at $v = 1$. Bruns (1977) compared his data with several of the two-parameter closed-form expressions, and concluded that none of them was satisfactory. He conjectured that the discrepancy arises from the use of a pseudopotential in the two-parameter theory, the chain segments being represented as points; the excluded volume is then effective only if two points coincide. This situation is accurately reproduced when synthesising on-lattice chains, and hence the agreement of the lattice Monte Carlo data with the theory. However, no two repeat units of a continuum model chain can ever occupy exactly the same volume, and thus *a priori* one should expect differences in this case.

The purpose of this paper is to present further Monte Carlo data on the configurational properties of 500-link chains constructed in the spatial continuum, with either varying bond angles (VBA) or tetrahedral bond angles (TBA), over the range $v = 0{\cdot}1$–$1{\cdot}0$. These data are significantly different from those of Bruns (1977) and Grishman (1973). However, it will be shown below that the validity of the results obtained by these authors is doubtful.

2. Synthesis of continuum chains

The method of chain synthesis was very similar to that of Smith and Fleming (1975), except that the enrichment technique was used to counteract sample attrition, rather than inversely restricted sampling. Following the suggestion of Grishman (1973), the enrichment parameters s and p were chosen to ensure that, as far as possible, the chain population showed a steady decrease at successive enrichment points. To this end, effective non-integral p were sometimes introduced by choosing between p and $p + 1$ at each enrichment point. The various s, p combinations are given in table 1.

In choosing a proposed direction for the nth bond, joining the centres of the nth and $(n + 1)$th spheres, the random number generator returned trial values of $\cos\theta_n$ and the angle ϕ_n, θ_n being the bond angle ($0 \leq \theta_n \leq \pi$ for VBA chains) and ϕ_n the angle of

Table 1. s, p parameters used in the Wall and Erpenbeck (1959) enrichment technique.

VBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
s	220	100	15	14	8	7	7
p	2	7	3·6	7	4·7	7·7	16·6
TBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
s	—	350	45	40	30	22	18
p	—	2	2	2	3	2·9	3

rotation about the bond ($0 \leq \theta_n \leq 2\pi$). In this way the probability distribution of the centre of the $(n+1)$th sphere was maintained constant over the surface of a sphere of radius unity (the bond length) centred on the nth sphere. For TBA chains $\theta = 109° 27'$, but $0 \leq \phi_n \leq 2\pi$ as before.

The method of checking for violations of the excluded volume conditions was that described by Smith and Fleming (1975).

3. Results

Mean values $\langle R_N^2 \rangle$ and $\langle S_N^2 \rangle$ were calculated, the number of R_N^2 and S_N^2 values ranging between 2500 and 20 000 with N. Checks at $v = 0{\cdot}1$ and $1{\cdot}0$ for $N = 50, 100, 150, \ldots,$ 500 showed that the variance σ_N^2 of the data varied little with v and N. The standard error in the $\langle R_N^2 \rangle$ values, defined as $\sigma_N/(\text{number of samples})^{0{\cdot}5}$, did not exceed $1{\cdot}5\%$ $\langle R_N^2 \rangle$. The same was true of $\langle S_N^2 \rangle$.

Table 2 shows the values of the constants A and γ obtained by least squares fits of the $\langle R_N^2 \rangle$ data to equation (4), using 25 points equally spaced in the range $N = 20$–500. The corresponding A' and γ' values in the equation

$$\langle S_N^2 \rangle = A' N^{\gamma'}, \tag{5}$$

are given in table 3. Equations (4) and (5) were first linearised by taking logarithms, so that the least squares fits effectively used the fractional rather than the absolute errors in the data. In this way one avoids giving disproportionate weight to the larger $\langle R_N^2 \rangle$ and $\langle S_N^2 \rangle$ values.

Figures 1 and 2 indicate respectively the accuracy of the fit between equations (4) and (5) and the Monte Carlo data, for VBA chains. The average discrepancy is about $1{\cdot}5\%$. Similar fits were obtained for TBA chains.

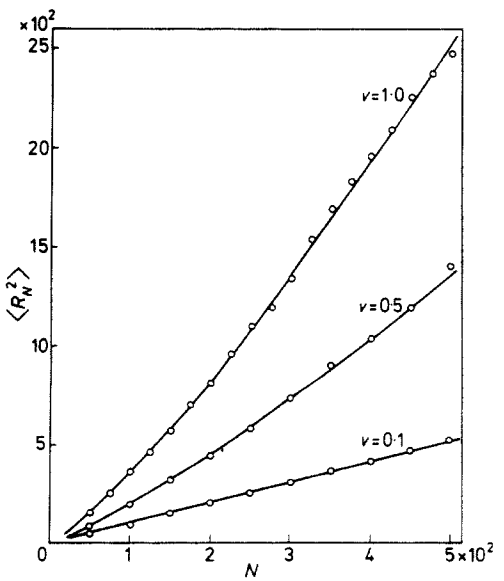

Figure 1. Variation of $\langle R_N^2 \rangle$ with N, for VBA chains. (*a*) $v = 1{\cdot}0$; (*b*) $v = 0{\cdot}5$; (*c*) $v = 0{\cdot}1$. ⊙ Monte Carlo data, ——— $\langle R_N^2 \rangle = AN^{\gamma}$, with coefficients given in table 2.

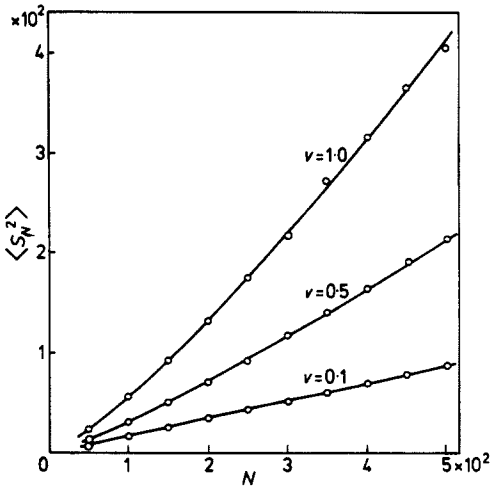

Figure 2. Variation of $\langle S_N^2 \rangle$ with N, for VBA chains. (*a*) $v = 1{\cdot}0$; (*b*) $v = 0{\cdot}5$; (*c*) $v = 0{\cdot}1$. ⊙ Monte Carlo data, ——— $\langle S_N^2 \rangle = A' N^{\gamma'}$, with coefficients given in table 3.

In order to check (at least partially) the accuracy of the computer programs, the excluded volume restraints were removed and $\langle R_N^2 \rangle_0$ values obtained up to $N = 500$ for both types of chains. The expected results are (Yamakawa 1971):

For VBA chains,

$$\langle R_N^2 \rangle_0 = N \qquad \text{(all } N\text{)}.$$

For chains with fixed bond angle θ,

$$\langle R_N^2 \rangle_0 = N\left(\frac{1-\cos\theta}{1+\cos\theta}\right) + \frac{2\cos\theta[1-(1-\cos\theta)^N]}{(1+\cos\theta)^2} \tag{6}$$

or $\langle R_N^2 \rangle_0 = 2N - 1{\cdot}5$ for TBA chains with $N \geqslant 10$. The results obtained from least-squares fits, using 25 data points as described previously, were:

for VBA chains, $\langle R_N^2 \rangle_0 = (1{\cdot}006 \pm 0{\cdot}005)N$,

for TBA chains, $\langle R_N^2 \rangle_0 = (1{\cdot}981 \pm 0{\cdot}002)N + (1{\cdot}313 \pm 0{\cdot}692)$.

This level of agreement is considered satisfactory.

There is always some risk (Domb 1963) that the use of the enrichment technique will bias the data, and therefore a further check was made by repeating some of the calculations up to $N = 100$ with much reduced enrichment levels. Once again the agreement was satisfactory; there were no indications of persistent unidirectional discrepancies between the two sets of data.

4. Discussion

4.1. Comparison with earlier data

The present $\langle R_N^2 \rangle$ values for VBA chains are consistently less than those of Bruns (1977), but consistently greater than those of Grishman (1973).

In order to eliminate excluded volume contacts between spheres $N+1$ and $N-1$, the most frequently occurring mode of violation of the excluded volume conditions, Bruns chose the bond angles θ in such a way that $\cos\theta$ was evenly distributed between $(v^2/2)-1$ and $(v^2/2)+1$. This restriction will, of course, increase $\langle R_N^2\rangle_0$. The expression corresponding to equation (6) for this restriction is not readily obtained, but it would be expected to be of the form

$$\langle R_N^2\rangle_0 = k_1 N + f(N) \tag{7}$$

with $f(N)$ being essentially constant and small in comparison with $k_1 N$ for $N \gg 1$. In order to confirm equation (7), $\langle R_N^2\rangle_0$ values were obtained with the Bruns restriction on $\cos\theta$ for $v = 0{\cdot}5$. A least-squares fit yielded

$$\langle R_N^2\rangle_0 = (1{\cdot}166 \pm 0{\cdot}002)N - (2{\cdot}492 \pm 0{\cdot}562). \tag{8}$$

It might be thought that, since Bruns generates short (eight-link) chains to use in his dimerisation process, the increase in $\langle R_8^2\rangle_0$ due to the restrictions on $\cos\theta$ would be negligible. However, for $v = 0{\cdot}5$ we obtained $\langle R_8^2\rangle_0 = 8{\cdot}86$ and $7{\cdot}92$ with and without these restrictions respectively, averaging over 20 000 chains; the analytical result in the latter case is $\langle R_8^2\rangle_0 = 8$. Clearly the effect of the $\cos\theta$ restrictions is not negligible, even for short chains.

Using equation (8) and Bruns' $\langle R_N^2\rangle$ values, one finds that the resulting α_R^2 values are consistently about 10% less than those of the present work at $v = 0{\cdot}5$. Presumably this is because the restrictions which he imposed on the bond angles decreased the effective excluded volume.

As stated above, it is thought that the use of the enrichment technique has not significantly biased the present data. Even if it has done so, the first enrichment point is at $N = 220$ for $v = 0{\cdot}1$ (VBA chains), and thus the only possible error for $N \leqslant 220$ is that due to the limited number of samples. It is reasonable to assume that the increase in $\langle R_N^2\rangle_0$ due to Bruns' bond angle restrictions would be very small at $v = 0{\cdot}1$, as also would any change in the effective excluded volume. Hence his $\langle R_N^2\rangle$ values at $v = 0{\cdot}1$ should agree with those of the present work, up to $N = 220$ at least. He generated eight-link chains without enrichment, and then used the dimerisation technique to reach $N = 1024$. Certainly the two sets of values agree well at $N = 8$, but thereafter those of Bruns are 5–10% greater. It may be that use of the dimerisation technique has biased his data.

Grishman (1973) simply rejected any bonds which led to an intersection between spheres $N-1$ and $N+1$. It is known (Fleming 1967) that such a procedure yields lower values of the exponent γ in equation (4), consistent with the lower $\langle R_N^2\rangle$ values which Grishman reports.

The data of Smith and Fleming (1975) are in good agreement with those of table 2 for $v = 0{\cdot}2$ and $v = 0{\cdot}5$, but at other values of v their $\langle R_N^2\rangle$ values are consistently 5–10% lower, for $N = 20$–100. Smith and Fleming used the inversely restricted sampling technique to offset sample loss, but pointed out that the resulting data can readily be dominated by a few chains with high statistical weights, especially at the larger v values. This effect usually produces large oscillations in the variations of $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ with N; Smith and Fleming observed such oscillations at $v = 1{\cdot}0$ for $N > 110$. However, one might expect that the data could be biased to a limited extent, due to the same cause, before such oscillations appeared. It seems likely that the results of Smith and Fleming were biased in this way.

Table 2. Values of A and γ in $\langle R_N^2 \rangle = AN^{\gamma}$.

VBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
A	0·930 ± 0·009	0·840 ± 0·010	0·786 ± 0·011	0·797 ± 0·020	0·918 ± 0·018	1·067 ± 0·039	1·336 ± 0·033
γ	1·019 ± 0·002	1·063 ± 0·002	1·159 ± 0·003	1·198 ± 0·005	1·206 ± 0·004	1·222 ± 0·007	1·215 ± 0·004
TBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
A	1·878 ± 0·020	1·801 ± 0·016	1·487 ± 0·025	1·340 ± 0·023	1·313 ± 0·008	1·412 ± 0·039	1·394 ± 0·021
γ	1·014 ± 0·002	1·027 ± 0·002	1·110 ± 0·003	1·153 ± 0·003	1·180 ± 0·002	1·189 ± 0·005	1·212 ± 0·003

Table 3. Values of A' and γ' in $\langle S_N^2 \rangle = A'N^{\gamma'}$.

VBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
A'	0·167 ± 0·002	0·152 ± 0·002	0·133 ± 0·002	0·136 ± 0·003	0·145 ± 0·003	0·168 ± 0·003	0·191 ± 0·003
γ'	1·006 ± 0·002	1·048 ± 0·002	1·150 ± 0·003	1·185 ± 0·004	1·206 ± 0·004	1·224 ± 0·004	1·235 ± 0·003
TBA chains							
v	0·1	0·2	0·4	0·5	0·6	0·8	1·0
A'	0·307 ± 0·003	0·288 ± 0·001	0·238 ± 0·002	0·216 ± 0·002	0·204 ± 0·001	0·205 ± 0·004	0·204 ± 0·003
γ'	1·016 ± 0·002	1·034 ± 0·001	1·111 ± 0·002	1·152 ± 0·001	1·184 ± 0·001	1·207 ± 0·003	1·225 ± 0·003

The data of Stellman and Gans (1972a) for TBA chains at $v = 1{\cdot}0$, obtained using the importance sampling technique of Metropolis *et al* (1953), are in excellent agreement with the results in table 2. With the exception of the $v = 0{\cdot}2$ case, so also are those of Smith and Fleming (1975); this isolated discrepancy is probably due to the weakness of the inversely restricted sampling technique discussed above.

4.2. Comparison with perturbation theory at low z

Given the doubt which has been expressed on the convergence of the perturbation theory expansion of equation (2), it is of interest to compare it with the present data for VBA chains. The immediate problem is to determine the correct value of β (see equation (1)) appropriate to a hard-sphere model. According to Bruns (1977), $v_0 < \beta \leqslant 8v_0$ where v_0 is the hard-sphere volume. Flory (1953) suggests $\beta = 8v_0$; the relationship between β and the second virial coefficient in the theory of imperfect gases (Fowler and Guggenheim 1939) also suggests $\beta = 8v_0$ (not $4v_0$ as stated by Smith and Fleming 1975), and this figure has therefore been adopted in the discussion below. This point is raised again in § 4.3.

The perturbation theory expansions (Yamakawa 1971)

$$\alpha_R^2 = \langle R_N^2 \rangle / \langle R_N^2 \rangle_0 = 1 + \tfrac{4}{3}z - 2{\cdot}075z^2 + 6{\cdot}459z^3 - \ldots \tag{9}$$

$$\alpha_S^2 = \langle S_N^2 \rangle / \langle S_N^2 \rangle_0 = 1 + 1{\cdot}276z - 2{\cdot}082z^2 + \ldots \tag{10}$$

are valid only in the limit $\beta \to 0, N \to \infty, \beta N^{1/2}$ finite. Therefore we have chosen $v = 0{\cdot}1$ and $N \geqslant 100$ for the comparison presented in table 4. Remembering that the standard error in the Monte Carlo data is about 1·5%, the data are in agreement with the perturbation theory expansion up to at least $z \sim 0{\cdot}03$.

Table 4. Comparison of perturbation theory (equations (9) and (10)) with Monte Carlo α_R^2 and α_S^2 values for VBA chains with $v = 0{\cdot}1$. $\beta = 8v_0$ assumed in equations (9) and (10).

N	z	α_R^2 (Perturbation theory)	α_R^2 (Monte Carlo)	α_S^2 (Perturbation theory)	α_S^2 (Monte Carlo)
100	0·0138	1·0180	1·0150	1·0172	1·0200
200	0·0195	1·0252	1·0285	1·0241	1·0292
300	0·0239	1·0307	1·0364	1·0294	1·0335
400	0·0276	1·0352	1·0421	1·0336	1·0361
500	0·0309	1·0392	1·0466	1·0374	1·0380

Taking $\beta = 2v_0$ for TBA chains, to be justified in § 4.3, the chain expansion at $v = 0{\cdot}1$ is too small to allow a meaningful comparison. For $v = 0{\cdot}2$ and $N = 100$ we have $z = 0{\cdot}0276$; the Monte Carlo values of α_R^2 and α_S^2 are 1·0274 and 1·0181 respectively, agreeing with the perturbation theory figures 1·0352 and 1·0336 within the standard error.

4.3. Validity of the closed-form expressions for α_R^2

The following closed-form expressions for α_R^2 were compared with the Monte Carlo data:

(i) $\alpha_R^5 - \alpha_R^3 = 2{\cdot}60z$ (Flory 1969)
(ii) $\alpha_R^5 - \alpha_R^3 = \frac{4}{3}z$ (Flory and Fisk 1966)
(iii) $\alpha_R^2 - 1 = \frac{4}{3}\alpha_R z$ (Bueche 1953, James 1953)
(iv) $(\alpha_R^3 - \alpha_R)(1 + 1/3\alpha_R^2)^{3/2} = 2{\cdot}053z$ (Kurata *et al* 1960)
(v) $\alpha_R^5/5 + \alpha_R^3/3 - \frac{8}{15} = \frac{4}{3}z$ (Alexandrowicz 1968, Kurata 1968)
(vi) $(\alpha_R^4 - \alpha_R^2)/(1 - 2/3\alpha_R^2 + 1/4\alpha_R^4) = \frac{48}{69}z$ (Bueche 1953)
(vii) $\alpha_R^3 - 1 = 2z$ (Fixman 1962)
(viii) $(4{\cdot}67\alpha_R^2 - 3{\cdot}67)^{3/2} - 1 = 9{\cdot}34z$ (Ptitsyn 1961)
(ix) $\alpha_R^{6{\cdot}67} - 1 = 4{\cdot}45z$ (Yamakawa 1968)
(x) $[(\alpha_R^2 - 0{\cdot}572)/0{\cdot}428]^2 - 1 = 6{\cdot}23z$ (Yamakawa and Tanaka 1967)
$[(\alpha_S^2 - 0{\cdot}541)/0{\cdot}459]^{2{\cdot}174} - 1 = 6{\cdot}04z$ (Yamakawa and Tanaka 1967)
(xi) $\alpha_R^{10} = 1 + \frac{20}{3}z^* + 4\pi z^{*2}$ (Domb and Barrett 1976, $z^* = h_0 z$)
(xii) $\alpha_R^5 - 0{\cdot}4931\alpha_R^3 - 0{\cdot}2499\alpha_R^{-1{\cdot}332}\sin(1{\cdot}073 \ln \alpha_R) - 0{\cdot}5069\alpha_R^{-1{\cdot}332}\cos(1{\cdot}073 \ln \alpha_R) = 2{\cdot}630z$ (Fujita *et al* 1967)
(xiii) $\alpha_R^5 - 1 = \frac{10}{3}z(1 + 2{\cdot}957z)/(1 + 3{\cdot}513z)$ (Stockmayer 1977).

Each of these expressions is valid only for $N \gg 1$. The values of z required to equate α_R^2 as given by these expressions with the Monte Carlo data were therefore calculated at $N = 500$, over the complete range of v. The implied β, expressed in units of the hard-sphere volume, varied very widely with v for all expressions except (x)–(xiii). The variations for these four are given in table 5; the β values derived from the α_S^2 values are also quoted for expression (x). The entries under $v = 0{\cdot}1$ can be disregarded, because in this case the sphere volume is so small that very small errors in the Monte Carlo data lead to large variations in the apparent β. In the range $v = 0{\cdot}2$–$0{\cdot}6$, $\beta \sim 8v_0$ for VBA chains except for the Domb and Barrett expression, while $\beta \sim 2v_0$ for all four expressions for TBA chains. $\beta = 8v_0$ is expected for VBA chains, as discussed above, but $\beta = 2v_0$ for TBA chains has not previously appeared in the literature. In figure 3 we have

Table 5. Values of β derived from four closed-form expressions for α_R^2, expressed in units of the hard-sphere volume v_0.

v	Yamakawa and Tanaka (1967)		Stockmayer (1977)	Domb and Barrett (1976)	Fujita *et al* (1967)
	from α_R^2	from α_S^2			
VBA chains					
0·1	9·55	8·08	9·58	9·30	9·36
0·2	7·55	7·46	7·54	6·82	7·10
0·4	7·75	7·89	7·71	6·31	7·11
0·5	8·10	8·35	8·23	6·63	7·70
0·6	7·64	8·29	7·98	6·38	7·57
0·8	5·88	6·87	6·46	5·14	6·25
1·0	4·57	5·75	5·27	4·18	5·16
TBA chains					
0·1	5·18	3·91	5·18	5·11	5·13
0·2	1·74	1·90	1·74	1·68	1·70
0·4	2·24	2·12	2·22	1·92	2·06
0·5	2·13	2·08	2·11	1·76	1·94
0·6	1·99	1·98	1·97	1·62	1·82
0·8	1·22	1·34	1·22	0·99	1·13
1·0	0·90	0·94	0·91	0·73	0·85

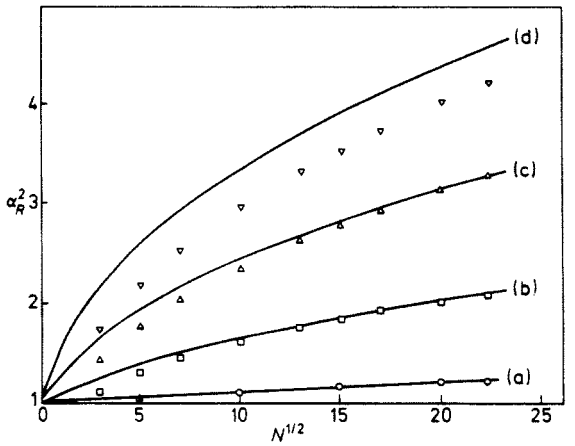

Figure 3. Variation of α_R^2 with $N^{1/2}$ for VBA chains. Monte Carlo data: ⊙ $v = 0{\cdot}2$; ⊡ $v = 0{\cdot}4$; △ $v = 0{\cdot}6$; ▽ $v = 0{\cdot}8$. Stockmayer expression (xiii) assuming $\beta = 8v_0$: (a) $v = 0{\cdot}2$; (b) $v = 0{\cdot}4$; (c) $v = 0{\cdot}6$; (d) $v = 0{\cdot}8$.

plotted some of the Monte Carlo α_R^2 for VBA chains against $N^{1/2}$, and the corresponding α_R^2 from expression (xiii) assuming $\beta = 8v_0$. At $v = 0{\cdot}2$, $0{\cdot}4$ and $0{\cdot}6$ respectively the differences between the two become less than the standard error in the Monte Carlo data for $N > 100$, 300 and 500 approximately. The discrepancies at low N almost certainly arise from the requirement $N \gg 1$ for validity of the closed form expressions. At $v = 0{\cdot}8$ the discrepancy decreases very slowly with increasing N, while at $v = 1{\cdot}0$ (not shown in figure 3) it increases. Similar situations are found for the other three expressions. It would be necessary to extend the Monte Carlo calculations to much higher N to determine whether the apparent slow convergence at $v = 0{\cdot}8$ is real, or merely due to error in the least-squares fits to equation (4). Such data would also enable one to differentiate with certainty between expressions (x)–(xiii). The Domb and Barrett expression is perhaps somewhat less attractive than the other three, because of the scaling factor h_0 which has to be evaluated for each type of chain. Its value for VBA chains appears to be approximately $0{\cdot}82$, and $0{\cdot}87$ for TBA chains.

Figure 4 shows the Monte Carlo α_R^2 as a function for $N^{1/2}$ for TBA chains, compared with the predictions of expression (xii) assuming $\beta = 2v_0$. At $v = 0{\cdot}6$ and $N = 500$ the two sets of values have not reached agreement within the error of the Monte Carlo data, contrasting with the VBA chain situation. This result is perhaps surprising, in view of the lower α_R^2 values for TBA chains. At $v = 0{\cdot}8$ and $v = 1{\cdot}0$ the discrepancy between the two sets of α_R^2 values increases steadily with increasing N, suggesting that any closed-form expression for α_R^2 based on the two-parameter theory is likely to fail for $v \geq 0{\cdot}8$.

4.4. Variation of γ and γ' with v

Tables 2 and 3 show that γ and γ' increase fairly smoothly from unity at $v = 0$ to around $\frac{6}{5}$ at $v = 1$. One immediately asks whether much longer chains would show $\gamma = \gamma'$, independent of v. In other words, do all continuum chains show the same asymptotic configurational behaviour, but with the chain length required to attain such behaviour increasing with decreasing v? The present data do not support this proposition, in that

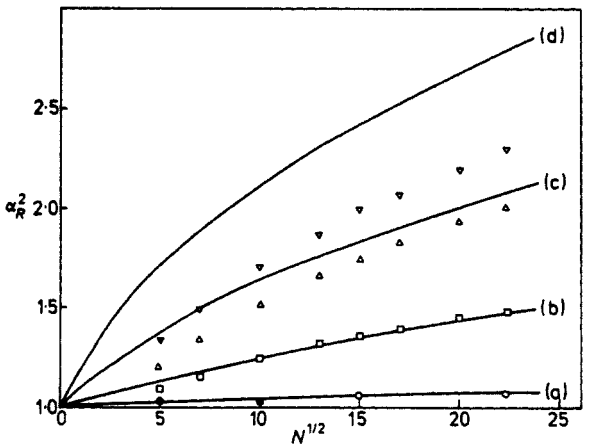

Figure 4. Variation of α_R^2 with $N^{1/2}$ for TBA chains. Monte Carlo data: ⊙ $v = 0{\cdot}2$; ⊡ $v = 0{\cdot}4$; △ $v = 0{\cdot}6$; ▽ $v = 0{\cdot}8$. Fujita *et al* (1967), expression (xii) assuming $\beta = 2v_0$: (a) $v = 0{\cdot}2$; (b) $v = 0{\cdot}4$; (c) $v = 0{\cdot}6$; (d) $v = 0{\cdot}8$.

figures 1 and 2 do not show, at $v = 0{\cdot}1$, any systematic deviation of $\langle R_N^2 \rangle$ and $\langle S_N^2 \rangle$ from equations (4) and (5) with increasing N; this is true also for $v = 0{\cdot}2$ and $v = 0{\cdot}4$. Such deviation would be expected if γ and γ' increased with N. However, if such increases were very slow, they would be detected only by generating much longer chains. We hope to undertake such a study shortly.

5. Conclusions

The following conclusions may be drawn from this work:

(i) It is possible that one of the four closed-form expressions for α_R^2, due respectively to Yamakawa and Tanaka (1967), Stockmayer (1977), Fujita *et al* (1967) and Domb and Barrett (1976), adequately represents the expansion of spatial continuum chains up to $v = 0{\cdot}6$. A necessary condition is $N \geqslant 100$ at $v = 0{\cdot}2$, increasing to $N \geqslant 500$ at $v = 0{\cdot}6$.

(ii) It is likely that any closed-form expression for α_R^2 based on the two-parameter theory fails for $v \geqslant 0{\cdot}8$.

(iii) The excluded volume β should be taken as eight times the volume of the sphere representing a repeat unit of a VBA chain, and twice the sphere volume for TBA chains.

(iv) The Monte Carlo data at small v agree with the perturbation theory expansion for α_R^2 up to at least $z \sim 0{\cdot}03$.

(v) For $20 < N < 500$, the mean square end-to-end lengths $\langle R_N^2 \rangle$ and mean square radii of gyration $\langle S_N^2 \rangle$ increase as N^{γ} and $N^{\gamma'}$ respectively, where both γ and γ' increase from unity at $v = 0$ to values slightly greater than $\frac{6}{5}$ at $v = 1{\cdot}0$.

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