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Monte Carlo calculations on off-lattice polymer chains. The influence of variation of the excluded volume

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Abstract. Monte Carlo calculations on off-lattice chains with various ratios λ of bead diameter to bond length show that γ and γ' in $\overline{h^2} = aN^{\gamma}$ or $\overline{r^2} = a'N^{\gamma'}$, respectively, are not 6/5 throughout but depend on λ. It is generally accepted that the theoretical predictions of the two-parameter theory do not depend on the kind of interaction potential between non-bonded beads. This assumption, however, proves to be wrong. The hard-sphere potential employed in this work yields results inconsistent with those of the perturbation theory using a pseudopotential with a δ function.

1. Introduction

The influence of the excluded volume on the configuration of macromolecules has been the subject of numerous theoretical investigations during the last three decades. Yet this problem could not be solved satisfactorily, due to the enormous mathematical difficulties. These require simplifications whose effect on the final result can hardly be estimated. The starting point of the theories is almost exclusively the so called segment model, where both the bond angles and the angles of rotation can assume any value with the bond length fixed. This model is often simplified by introducing Gaussian distributed bond lengths. The potential between two non-bonded segments is usually written

$$\omega(\boldsymbol{r}_{ij}) = kT\beta\delta(\boldsymbol{r}_{ij})$$

where δ is a three-dimensional Dirac delta function, and the binary cluster integral

$$\beta = \int [1 - \exp(-\omega(\boldsymbol{r}_{ij})/kT)]\, \mathrm{d}\boldsymbol{r}_{ij}.$$

If further assumptions are dispensed with, a mathematical treatment similar to the Ursell–Mayer theory of real gases leads to a power series containing only two parameters, Na^2 (N = number of bonds, a = effective bond length) and $N^2\beta$. This series has been accepted to be exact within the framework described and to be convergent. Recent work (Domb and Joyce 1972, Edwards 1975, Gordon *et al* 1976, Aronowitz and Eichinger 1976), however, has cast considerable doubt on this, because it could be shown that the calculation of cluster integrals beyond second order generates infinite terms.

Previously the series was believed to converge very slowly even in the limit of small perturbations, its applicability thus being confined to the vicinity of the Θ temperature. For that reason it has been of some interest to get closed expressions valid

for a somewhat larger range. The diversity of the relevant results published up to now is due to the fact that authors have decoupled the many-body problem in different ways. Converting their results for $z \gg 1$, with

$$z = \left(\frac{3}{2\pi a^2}\right)^{3/2} \beta N^{1/2},$$

into the form $\overline{h^2} = aN^{\gamma}$, values of 1·15 (Yamakawa 1971b), 1·195 (de Gennes 1972), 1·2 (Flory 1949, Edwards 1965, Flory and Fisk 1966, Fujita *et al* 1967, Yamakawa 1968, Kurata 1968, Alexandrowicz 1968, Yamakawa 1971a), 1·25 (Bueche 1953, Yamakawa and Tanaka 1967), 1·33 (Kurata *et al* 1960, Ptitsyn 1961, Fixman 1962) are obtained for γ.

It is not possible to decide by experiment which of the theories should be preferred, because β and hence the parameter z are not directly observable quantities. The development of high-speed electronic computers permitted the approach to this problem to be made in a quasi-experimental way. For that purpose two methods have been evolved: the exact enumeration of possible configurations of short walks on a lattice supplemented by extrapolation of interesting quantities to infinitely long walks, and Monte Carlo calculations. Domb (1969) has given a comprehensive bibliography of both methods in a review.

The corresponding results of both methods calculated for different lattices resulted in $\gamma = 6/5$ (in the three-dimensional case). Authors working with polymer chains in the continuum (pearl necklace model), did not get the same definite statement about γ. Grishman (1973) for instance got a value of 6/5 within confidence limits whereas Stellman and Gans (1972) published data somewhat higher than 6/5. Nevertheless $\gamma = 6/5$ is generally accepted and considered as supporting strongly those approximate theories supplying this value asymptotically.

Thus it is evident there is something common to all the approximate theories: γ does not depend on the excluded volume. Starting from an arbitrary value of β and diminishing it successively, γ should remain constant and become unity in a discontinuous manner if $\beta \to 0$ (random flight chain). By intuition one expects another behaviour, namely a gradual decrease to the random flight value. Such a presumption is supported by a publication of Fleming (1967), who found a certain dependence of γ on the diameter of segments in his Monte Carlo calculations on off-lattice chains. It should be added, however, that at that time great significance could not be attributed to these results because the chains used had been too short (20–100 segments). A further reference to the dependence of γ on the size of the structural units is due to Warvari *et al* (1972). Recently this problem has been treated in an extensive investigation by Smith and Fleming (1975) and in a short communication—published almost simultaneously—by me (Bruns 1975). Here the information given earlier will be explained in a more profound way and the consequences pointed out.

2. Generation of chains

2.1. Basic chains

As in earlier publications of the present author (Bruns 1969, 1970, 1972, 1975, 1976, Bruns and Naghizadeh 1976), a pearl necklace model was used with a hard-sphere potential between non-bonded beads. A chain consisted of $N+1$ spheres of diameter

d indexed from 0 to N, which are connected by N bonds of length $l = 1$. The centre of the zeroth bead was chosen as origin of a three-dimensional coordinate system with the z axis directed to the first bead, the centre of the second bead being in the x–z plane, the bond angle $(\pi - \theta_1)$ determining its x and z coordinates. θ_1 was produced by a random number generator in such a manner that $\cos\theta_1$ was equally distributed between

$$\tfrac{1}{2}d^2 - 1 \leqslant \cos\theta_1 \leqslant 1 \qquad \text{for } d/l \equiv \lambda = 0{\cdot}1, 0{\cdot}3, 0{\cdot}5, 1{\cdot}0$$

or

$$1 - (2/d^2) \leqslant \cos\theta_1 \leqslant 1 \qquad \text{for } \lambda = 2{\cdot}0.$$

The choice of the lower limit of $\cos\theta_1$ deviating from -1 ensured no intersections with the zeroth bead in the case of $\lambda \leqslant 1{\cdot}0$. If $\lambda = 2{\cdot}0$ an intersection between the beads 0 and 2 cannot be avoided. The range given for $\cos\theta_1$ then means that the two segments intersect each other only within their common neighbour. The direction towards the third bead was determined by the supplement of the bond angle θ_2 and the angle of rotation ϕ_2, both being randomly generated. Because the direction of the bonds was intended to be equally distributed over the surface of a sphere, $\cos\theta_2$ and ϕ_2 $(0 \leqslant \phi_2 < 2\pi)$ had to be equally distributed. The range of $\cos\phi_2$ was chosen as above for the reasons already discussed. θ_2 and ϕ_2 are angles with regard to an auxiliary coordinate system with its origin in the centre of the first bead, the z axis coinciding with the direction to the second bead, the x axis directed in such a manner that angle $\phi_2 = 0$ corresponds to the *trans*position of the beads 0, 1, and 2. The coordinates of the third bead are (0, 0, 1) in terms of the auxiliary system attached to the second bead, and must be transformed into the coordinates of the laboratory system by rotation and translation.

After that the proposed position of the third bead was checked for intersection with the zeroth bead: the chain was discarded in favour of a fresh start from the origin if the distance of the centres of the two beads happened to be smaller than d. The checking system will be described later in this paper. If there was no intersection the fourth, fifth, . . . , eighth beads were added in the same manner. The coordinates of the $(j+1)$th bead, $\mathbf{r}_{j+1}$, may be calculated recursively:

$$\mathbf{r}_{j+1} = \mathbf{r}_j + \left(\prod_{i=1}^{j} \mathbf{A}_i\right)\begin{pmatrix}0\\0\\1\end{pmatrix} \qquad j = 1, 2, \ldots$$

with

$$\mathbf{A}_i = \begin{pmatrix} -\cos\theta_i\cos\phi_i & \sin\phi_i & \sin\theta_i\cos\phi_i \\ -\cos\theta_i\sin\phi_i & -\cos\phi_i & \sin\theta_i\sin\phi_i \\ \sin\theta_i & 0 & \cos\theta_i \end{pmatrix}$$

and $\phi_1 = 0$.

To produce $\sin\phi$ and $\cos\phi$ it is possible to generate ϕ and then to calculate its trigonometric functions. Considerably more efficient, however, is a method described by Fluendy (1970) which is slightly modified here. Two equally distributed random numbers $\xi[-1, 1]$ and $\eta[0, 1]$ are generated. They must satisfy the condition $r^2 \equiv \xi^2 + \eta^2 \leqslant 1$, otherwise a new pair is generated. Thus equally distributed points within the upper half of an unit circle are generated. The angle between the radius vector and the abscissa is set as $\phi/2$. In this way $\sin\phi = 2\xi\eta/r^2$ and $\cos\phi = (\xi^2 - \eta^2)/r^2$.

After a successful construction of a chain, the coordinates of the beads, their distances from the origin and the elements of the final matrix of rotation were stored on a disc and some quantities of interest (end-to-end distance, etc) calculated. 38 400 chains were generated in this manner corresponding nearly to the capacity of the disc. The method just described seems to be less effective than that of Grishman (1973) because of its numerous matrix multiplications. Grishman generates the random directions in space by three random numbers representative of a point within an unit sphere. This procedure, however, has the following disadvantage: the probability of intersection of two beads decreases with increasing difference of their indices. It has its maximum value for a proposed jth bead, with regard to the $(j-2)$th bead, and amounts to 25% in the case $\lambda = 1$, as is easily seen by geometrical considerations. By our method an intersection with the last but one neighbour is avoided and the probability of chain discarding is diminished.

2.2. Chain prolongation

Alexandrowicz (1969) and Alexandrowicz and Accad (1971) developed an effective procedure for generating long chains. This 'dimerisation' method was used here.

Two of the chains with $N = 8$ produced in the first run were randomly selected and coupled by fusing the eighth bead of the first with the zeroth bead of the second chain. The direction of the new bond $8 \rightarrow 9$ was created by random choices of the corresponding angles of bond and rotation. If tests on intersection between the beads of the two partial chains were negative, the data of the chain now consisting of 16 bonds were stored on a second disc after calculation of interesting quantities. The capacity of this second disc was exhausted after storing the data of $38\,400/2 = 19\,200$ chains. The dimerisation was continued up to chains with $N = 1024$ bonds. A sample of 300 such chains was obtained.

In order to get a pre-estimation of the standard deviation of the mean-square end-to-end distance for chains with $N = 1024$, the variance of the appropriate distribution, assumed to be nearly Gaussian, was considered and found to be $\frac{2}{3}(\overline{h^2})^2$. The standard deviation of the mean-square itself is then $\sqrt{6}/(3\sqrt{n})$ (where n is the size of the sample). If n is taken as 2100, a relative standard deviation of the order of 1·8%may be expc ted. This seems to be sufficient, therefore the procedure described above was performed seven times.

The chain generation just described was repeated several times inserting other ratios λ, thus varying the hard-sphere potential. λ was taken as 0·1, 0·3, 0·5, 1·0, and 2·0.

2.3. Test on self-intersection

This is the most time-consuming step of the computation. The beads i and j $(i \leqslant j-3)$ with the coordinates $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ intersect if $|\boldsymbol{r}_j - \boldsymbol{r}_i| < d$. Necessary (but not sufficient) conditions for satisfying the inequality are $|\Delta x| < d$, $|\Delta y| < d$, $|\Delta z| < d$. This gives a testing scheme which takes the shortest computation time for short chains. If the chains are long, this method is too time-consuming, since the number of tests increases quadratically with the number of beads. In this case a hash-code procedure has proved to be very favourable. Some modifications of it have already been described (Gans 1965, Fleming 1967, Jurs and Reissner 1971, Grishman 1973). In this investigation concentric sphere shells of thickness 1 were put around the origin. A list was

kept of which shells are occupied by the centre of a bead and which are not. In the beginning the list is empty. An 'occupied' notice is made successively in the list for each bead of the chain, and simultaneously given a reference, at which place on a second list the appropriate indices can be found. In this second list it is marked, if a further bead is positioned in the same shell and where its index (in the second list likewise) can be found. If a part of a chain free from intersections has already been registered and a new bead is added, the test on intersection runs as follows. It is ascertained in which shell the centre of the bead to be checked is positioned. The first list gives an indication of whether this shell has already been occupied by preceding beads. If so, the second list gives information about their indices. Only these beads need be checked in the way described for short chains. The same has to be done with the neighbour shells, because beads positioned there may intersect with the bead to be added.

2.4. Random number generator

The random number generator used is part of the software package of the TR 440 computer. It is one of the type $x_{i+1} = (ax_i + b) \bmod n$. a and b have been chosen respectively so as to optimise the spectral test or to minimise the serial correlation coefficient between x_i and x_{i+1}. Further tests (test for uniformity, difference test, run-up test, inter-arrival test) are met.

3. Results

Mean-square end-to-end distances, $\overline{h^2}(N, \lambda)$ and mean-square radii of gyration, $\overline{r^2}(N, \lambda)$, as well as their variances, $\sigma^2_{\overline{h^2}}$ and $\sigma^2_{\overline{r^2}}$, were calculated for each of the samples for different N(8, 16, 32, 64, 128, 256, 512, 1024) and λ (0·1, 0·3, 0·5, 1·0, 2·0) (tables 1, 2). Attempts were made, as usual, to fit the above to the equations

$$\overline{h^2}(N, \lambda) = aN^{\gamma} \tag{1a}$$

and

$$\overline{r^2}(N, \lambda) = a'N^{\gamma'} \tag{1b}$$

respectively. To calculate $a(a')$ and $\gamma(\gamma')$ the equations were linearised:

$$\ln \overline{h^2} = \ln a + \gamma \ln N. \tag{2}$$

Table 1. Mean-square end-to-end distances $\overline{h^2}(N, \lambda)$ and variances for different N and λ.

N \ λ	0·1	0·3	0·5	1·0	2·0
8	8·029±0·01211	8·610±0·01254	10·20±0·01342	15·83±0·01151	34·66±0·02041
16	17·30±0·03752	19·17±0·04006	24·27±0·04590	40·28±0·04762	99·40±0·1121
32	35·80±0·1127	41·53±0·1249	55·88±0·1543	97·00±0·1877	249·5±0·5220
64	73·51±0·3322	89·54±0·3818	127·4±0·5020	227·3±0·7004	586·7±1·993
128	148·4±0·9535	192·1±1·149	289·0±1·620	526·2±2·520	1344±6·910
256	298·4±2·708	412·1±3·447	646·8±5·213	1199±8·727	2997±22·48
512	598·8±7·651	895·7±10·29	1453±16·51	2737±28·79	6727±73·52
1024	1235±21·24	1960±33·15	3342±53·35	6364±98·17	14880±236·7

Table 2. Mean-square radii of gyration $\overline{r^2}(N, \lambda)$ and variances for different N and λ.

N \ λ	0·1	0·3	0·5	1·0	2·0
8	1·486±0·001281	1·565±0·001300	1·779±0·001318	2·471±0·0009697	4·435±0·001367
16	3·073±0·004022	3·346±0·004177	4·054±0·004469	6·160±0·003995	12·83±0·007471
32	6·182±0·01196	7·048±0·01292	9·109±0·01490	14·87±0·01630	34·26±0·03957
64	12·46±0·03500	14·91±0·03911	20·54±0·04849	35·15±0·06261	85·52±0·1659
128	24·90±0·1004	31·75±0·1168	46·23±0·1545	82·26±0·2308	204·7±0·6184
256	50·15±0·2876	68·33±0·3450	103·3±0·4949	189·4±0·8130	469·4±2·106
512	100·7±0·8128	147·1±1·023	233·2±1·576	431·8±2·733	1067±6·988
1024	202·9±2·237	323·6±3·271	531·4±5·093	994·3±8·978	2407±22·53

γ and $\ln a$ were determined so as to minimise

$$M = \sum_i (\ln \overline{h_i^2} - \ln a - \gamma \ln N_i)^2 / \sigma_i^2 \tag{3}$$

with $\sigma_i^2 = \sigma_{\overline{h_i^2}}^2 / \overline{h_i^2}$. M follows a χ^2 distribution with $g-2$ degrees of freedom (g = number of means). To test the goodness of fit, however, the unmodified equations were used:

$$\chi^2 = \sum_i (\overline{h_i^2} - aN_i^\gamma)^2 / \sigma_{\overline{h_i^2}}^2. \tag{4}$$

Similar equations are yielded for $\overline{r^2}$. Figures 1 and 2 give respectively the dependences of the mean-square end-to-end distance and the mean-square radius of gyration on the number of bonds. The values for $N = 1$ and 2 are theoretical. As can be seen, mainly in the case of the end-to-end distances, the curves become linear only

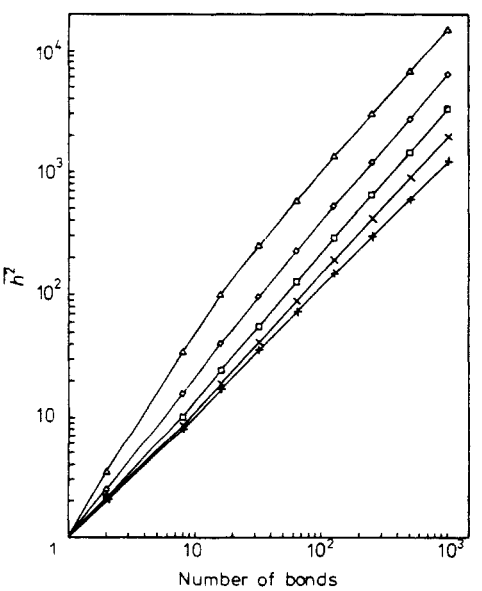

Figure 1. The dependence of the mean-square end-to-end distance on the number of bonds for $\lambda = 0{\cdot}1$ (+), 0·3 (×), 0·5 (□), 1·0 (◇), 2·0 (△).

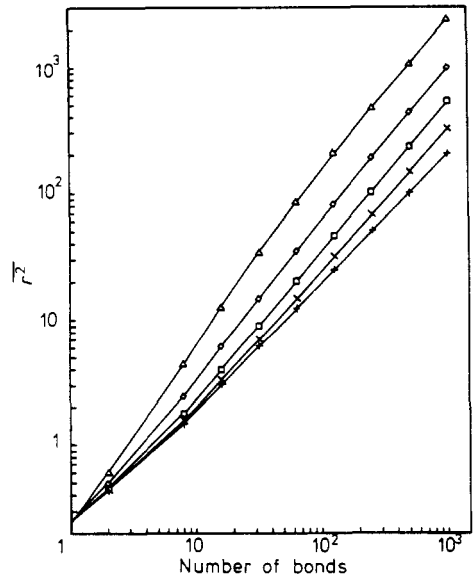

Figure 2. The dependence of the mean-square radius of gyration on the number of bonds for $\lambda = 0{\cdot}1$ (+), $0{\cdot}3$ (×), $0{\cdot}5$ (□), $1{\cdot}0$ (◇), $2{\cdot}0$ (△).

after an 'induction range'. It is for this reason that the present author (Bruns 1969, 1970) had obtained a value for γ somewhat greater than 1·2 for chains with $\lambda = 1{\cdot}0$, because he had available only chains up to bond numbers of about 100. In any case it is obvious that equation (1) is valid only asymptotically with regard to off-lattice models. Therefore in order to calculate a and γ, short chains were not considered, and the χ^2 test (equation (4)) was taken as a criterion. As can be seen the fit is sufficiently good for $N \geq 64, \ldots, 128$. The influence of λ is clearly perceptible, the slope of the curves increasing with increasing λ. Table 3 shows the parameters of the curves together with their standard deviations.

Though the χ^2 test is satisfied in all these cases, one cannot be sure that the curvature observable for each of the curves has become small enough to draw the conclusion that the values estimated for γ are valid in the limit of large N. Truly the curvature must disappear gradually, otherwise the slope would not converge, and the question is to what extent are the values of γ influenced by the curvature in the range $N > 128$. This can be answered with certainty only by generating still longer chains. A

Table 3. Values of a, a', γ, γ' from the relations $\overline{h^2} = aN^{\gamma}$ and $\overline{r^2} = a'N^{\gamma'}$, respectively, and their dependence on λ.

λ	a	γ	a'	γ'
0·0	1·000	1·000	0·1667	1·000
0·1	1·089±0·022	1·013±0·004	0·1904±0·0025	1·005±0·003
0·3	0·8650±0·0031	1·113±0·007	0·1442±0·0032	1·111±0·004
0·5	0·966±0·018	1·174±0·004	0·1586±0·0017	1·169±0·002
1·0	1·603±0·050	1·194±0·006	0·2460±0·0045	1·198±0·003
2·0	4·87±0·16	1·159±0·006	0·641±0·012	1·189±0·004

very rough estimation was performed by fitting the data points repeatedly, always omitting those which belong to the lowest N respectively. The results are shown in figures 3(*a*)–(*e*). As can be seen, the values of γ do not change much, the data being

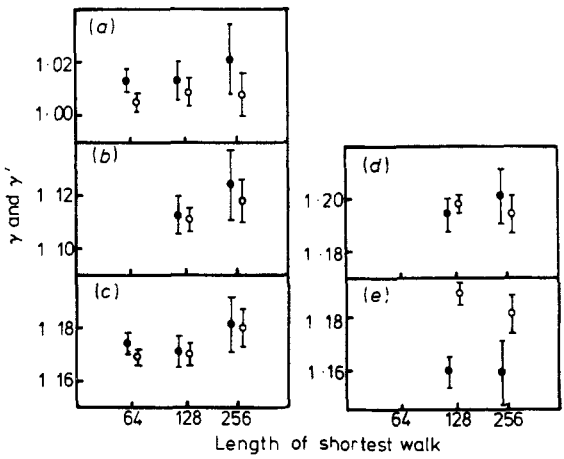

Figure 3. Values of γ(●) and γ'(○) as a function of the length of the shortest walks included in the sample for computing the fit. Error bars indicate the standard deviation. Values of λ are: (*a*) 0·1, (*b*) 0·3, (*c*) 0·5, (*d*) 1·0, (*e*) 2·0.

too scattered for further statements to be made. The values in table 3 do not agree very well with those published by Smith and Fleming (1975). The reason may be that they have used chains up to about 100 bonds, i.e. values taken from the 'induction range', to estimate the parameters. Nevertheless the trend is the same in both cases: γ and γ' increase from 1·0 to 1·2, as λ increases from 0·0 to 1·0. One expects now a further increase in γ and γ' if $\lambda > 1{\cdot}0$ to an upper limit of 2·0 (rod-like chains). The decrease observed here for $\lambda = 2{\cdot}0$ is surprising therefore. It is not as yet clear whether this ambiguous behaviour will always be found for any $\lambda > 1{\cdot}0$, or whether a broader 'induction range' exists here. The values of γ and γ' for the same λ scarcely differ except for $\lambda = 2{\cdot}0$. The question of whether the difference is significant, was elucidated by an F test on the expression

$$\ln \overline{h^2}/\overline{r^2} = \ln a/a' + (\gamma - \gamma') \ln N. \tag{5}$$

The hypothesis $\gamma - \gamma' = 0$ was checked against the alternative $\gamma - \gamma' \neq 0$ on a confidence level of 0·95. It could be shown that γ and γ' are equal for $\lambda \leqslant 1{\cdot}0$ within the confidence limit given. Only for $\lambda = 2{\cdot}0$ is the difference significant. This contradicts with the results of Smith and Fleming (1975), who found considerable differences between the two exponents, and those of Stellman and Gans (1965). From the results obtained here, the ratio $\overline{h^2}/\overline{r^2}$ is expected to converge to a value different from zero. The dependence of this ratio on λ was investigated, and $\overline{h^2}/\overline{r^2}$ fitted against $1/N$ by spline functions in figure 4. The shape of the curves does not allow a reliable extrapolation to $1/N = 0$, the more so, since the ratios most relevant for an extrapolation belonging to long chains have considerable standard deviations (~0·12 for $N = 1024$). There is some probability that

$$6{\cdot}0 < (\overline{h^2}/\overline{r^2})_\infty < 6{\cdot}4$$

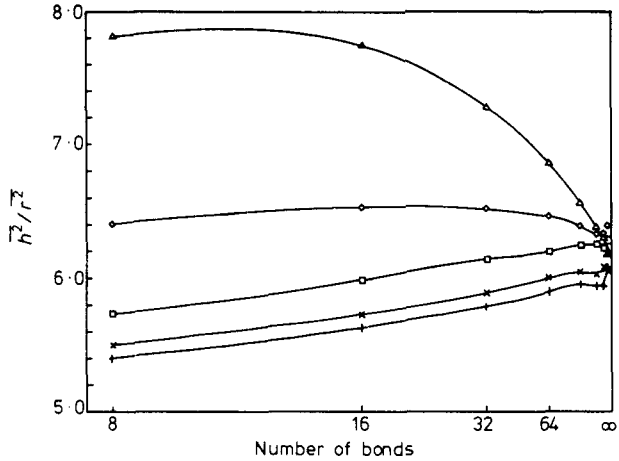

Figure 4. The dependence of the ratio mean-square end-to-end distance to mean-square radius of gyration on the number of bonds for $\lambda = 0{\cdot}1$ (+), $0{\cdot}3$ (×), $0{\cdot}5$ (□), $1{\cdot}0$ (◇), $2{\cdot}0$ (△).

for all λ, the ratio thus being greater than that for unperturbed chains. It cannot be answered with certainty, if the dependence of $\overline{h^2}/\overline{r^2}$ on λ ascertained for low bond numbers also exists in the asymptotic case.

The data produced here offer a good possibility to examine the validity of current theories dealing with the dependence of the expansion factors

$$\alpha_h^2 = \overline{h^2}/\overline{h_0^2} \qquad \text{and} \qquad \alpha_r^2 = \overline{r^2}/\overline{r_0^2}$$

($\overline{h_0^2} = Na^2$ and $\overline{r_0^2} = N(N+2)a^2/[6(N+1)]$ in terms of the segment model) on z. The following expressions were examined:

$\alpha^5 - \alpha^3 = 2{\cdot}60z$	Flory, original (FO) $\alpha_h = \alpha_r = \alpha$
$\alpha_h^5 - \alpha_h^3 = \frac{4}{3}z$ $\alpha_r^5 - \alpha_r^3 = \frac{134}{105}z$	Flory, modified (FM)
$\alpha_h^2 - 1 = \frac{4}{3}\alpha_h z$ $\alpha_r^2 - 1 = \frac{134}{105}\alpha_r z$	Bueche and James (BJ)
$\alpha_h^3 - \alpha_h = 2{\cdot}053z\ (1 + 1/(3\alpha_h^2))^{-3/2}$	Kurata, Stockmayer and Roig (KSR)
$\frac{1}{5}\alpha_h^5 + \frac{1}{3}\alpha_h^3 - \frac{8}{15} = \frac{4}{3}z$	Kurata (K)
$\alpha_h^4 - \alpha_h^2 = \frac{48}{69}z[1 + 2/(3\alpha_h^2) + 1/(4\alpha_h^4)]$	Bueche (B)
$\alpha_h^5 - 0{\cdot}4931\alpha_h^3 - 0{\cdot}2499\alpha_h^{-1{\cdot}332} \sin(1{\cdot}0731 \ln\alpha_h)$ $-0{\cdot}5069\alpha_h^{-1{\cdot}332}\cos(1{\cdot}073 \ln\alpha_h) = 2{\cdot}630z$	Fujita, Okita and Norisuye (FON)
$\alpha_h^3 - 1 = 2z$ $\alpha_r^3 - 1 = 1{\cdot}914z$	Fixman (F)
$4{\cdot}67\alpha_h^2 - 3{\cdot}67 = (1 + 9{\cdot}34z)^{2/3}$ $5{\cdot}12\alpha_r^2 - 4{\cdot}12 = (1 + 9{\cdot}79z)^{2/3}$	Ptitsyn (P)

$$\left.\begin{aligned}\alpha_h^2 - 0{\cdot}572 &= 0{\cdot}428(1+6{\cdot}23z)^{1/2}\\ \alpha_r^2 - 0{\cdot}541 &= 0{\cdot}459(1+6{\cdot}04z)^{0{\cdot}46}\end{aligned}\right\}$$ Yamakawa and Tanaka (YT)

$$\alpha_h^{6{\cdot}67} - 1 = 4{\cdot}45z$$ Yamakawa (Y)

The expansion factors could be calculated from the Monte Carlo data, whereas z could not. Indeed a (=1) and N are known but β is not. For lattice models this quantity can be equated to the volume per lattice point. For off-lattice models, with a hard-sphere potential, however, β can only be estimated:

$$v_0 < \beta \leqslant 8v_0$$

with v_0 the volume of a bead.

For this reason the relations given above were examined by a method previously used (Bruns 1970). The equations were transformed to

$$f(\alpha) = CN^{1/2}. \tag{6}$$

The constant C includes quantities originating from the equation itself as well as $[3/(2\pi)]^{3/2}$ and β due to z. The graph of $f(\alpha)$ against $N^{1/2}$ then has to be a straight line through the origin. C can be estimated by a least-squares method and the goodness of fit by a χ^2 test. Thus there are two criteria available, the test on linearity and the quantity β evaluated from C, which must have a value of physical relevance. In table 4 only those equations which passed the test on linearity are listed.

Table 4 shows that the equations of Bueche and James, Kurata, Stockmayer and Roig, Fixman, and Ptitsyn do not satisfy the condition of linearity in each case. None of the theories can describe the data for

$$\lambda = \begin{cases} 0{\cdot}1 & \alpha_h \text{ and } \alpha_r \\ 1{\cdot}0 & \alpha_r \end{cases}$$

satisfactorily.

In many cases the theories yield values of β, exceeding the upper limit $8v_0$. Flory's original equation possesses the best properties for α_h, followed by the equation of Kurata. The properties of each equation concerning α_r are insufficient. If the values of γ and γ' combined in table 3, are assumed not to change essentially for chains still longer than those used here, none of the equations is valid. Each of them becomes asymptotically $\alpha^2 \sim N^{\gamma''}$. γ'', however, does not depend on the excluded volume, but is a constant, contrary to the Monte Carlo results. Without that the validity of the closed expressions is still discussed. In spite of the doubts about the correct form of the perturbation equation—already mentioned in the introduction of this paper—the single contact coefficients of the equations

$$\begin{aligned}\alpha_h^2 &= 1 + 1{\cdot}333z(-2{\cdot}075z^2 + 6{\cdot}459z^3 - \ldots)\\ \alpha_r^2 &= 1 + 1{\cdot}276z(-2{\cdot}082z^2 + \ldots)\end{aligned} \tag{7}$$

are still accepted (Aronowitz and Eichinger 1976), the other coefficients being uncertain at present. In the case of $\lambda = 0{\cdot}1$ the values of z calculated by means of the estimation of β already used are small enough even for large N. In this range terms with higher powers of z are not expected to contribute essentially. The coefficient of z can therefore be tested for correctness. Table 5 shows the results. $\alpha_{h\mathrm{MC}}^2$ and $\alpha_{r\mathrm{MC}}^2$ are

Table 4. Tests on closed expressions published up to the present. Quantities relevant in a physical sense have been marked by exclamation marks in parentheses.

λ	$v_0=\beta_{min}$	$8v_0=\beta_{max}$	Equation	β
α_h				
0·1	$5{\cdot}24\times10^{-4}$	$4{\cdot}19\times10^{-3}$	—	—
0·3	0·0141	0·113	FO	0·0940 (!)
			FM	0·183
			B	0·184
			FON	0·144
			YT	0·157
			Y	0·172
0·5	0·0654	0·523	FO	0·423 (!)
			FM	0·824
			K	0·421 (!)
			B	0·787
			FON	0·562
			YT	0·608
			Y	0·806
1·0	0·524	4·19	FO	2·56 (!)
			FM	5·00
			K	1·82 (!)
			B	4·10 (!)
			FON	2·96 (!)
			YT	2·86 (!)
2·0	4·19	33·52	FO	32·5 (!)
			FM	63·5
			K	16·4 (!)
			B	35·8
			FON	34·0
			YT	23·0 (!)
			Y	143
α_r				
0·1	$5{\cdot}24\times10^{-4}$	$4{\cdot}19\times10^{-3}$	—	—
0·3	0·0141	0·113	FO	0·0878 (!)
			FM	0·179
			YT	0·196
0·5	0·0654	0·523	YT	0·720
1·0	0·524	4·19	—	—
2·0	4·19	33·52	YT	30·66 (!)

Table 5. Tests on the equations of perturbation theory (equation (7)).

N	z_{min}	z_{max}	α^2_{hmin}	α^2_{hmax}	α^2_{hMC}	α^2_{rmin}	α^2_{rmax}	α^2_{rMC}
64	0·00138	0·0111	1·0018	1·0145	1·149	1·0018	1·0139	1·150
128	0·00196	0·0156	1·0026	1·0203	1·159	1·0025	1·0194	1·158
256	0·00277	0·0221	1·0037	1·0285	1·167	1·0035	1·0272	1·171
512	0·00391	0·0313	1·0052	1·0399	1·170	1·0050	1·0379	1·178
1024	0·00553	0·0443	1·0073	1·0555	1·206	1·0070	1·0524	1·188

Monte Carlo data. As can be seen, equations (7) are not valid for hard-sphere potentials. The objection that the values of N may not be large enough, will be refuted in § 4.

4. Discussion

Monte Carlo calculations on off-lattice models with hard-sphere potential show that the exact equations of the two-parameter theory supplied with appropriate values of excluded volume do not give correct expansion factors. Furthermore they make evident that each closed expression derived up to the present fails in one point or another. This seems to contradict partially the statements of Alexandrowicz and Accad (1973). They had examined some closed expressions (FM, YT, K, P) and the perturbation equations by means of a lattice model. A self-intersection, instead of being excluded, had been accorded a variable Boltzmann factor. This was related to the excluded volume, which now could be varied by variation of the Boltzmann factor. The results are as follows.

(*a*) The Monte Carlo data were fitted satisfactorily by the perturbation equation $\alpha^2 = 1 + 1{\cdot}333z$ (without terms of higher order) if $z < 0{\cdot}23$ and $N \geqslant 64$. This means that chains of $N = 64$ seem to be long enough for the requirements of the perturbation theory.

(*b*) The closed expression of Alexandrowicz and Kurata (K) proved to be the best.

(*c*) $\overline{h^2}$ is a function of $\beta N^{1/2}$.

The reason for this apparent contradiction to the results presented here can be cleared up. The difference between a lattice model and an off-lattice model is irrelevant here, though the latter is nearly always used in theory as a prototype of a polymer chain. The essential difference is in the potentials employed. Usually a pseudopotential is applied by theory: segments are considered as points, which interact only if two of them take the same vertex in space. Only then is the excluded volume β effective. Such a potential is easily introduced into Monte Carlo calculations by means of a lattice model (Kron and Ptitsyn 1964, Alexandrowicz and Accad 1973) and therefore confirms consistently the equations of the two-parameter theory. There are other circumstances with regard to an off-lattice model. When generating a chain it is impossible that two segments have exactly the same coordinates. Therefore the pseudopotential just mentioned cannot be introduced here. The hard-sphere potential, however, leads to completely different results as could be shown in § 3. The predictions made by the two-parameter theory are connected implicitly with the pseudopotential. The opinion, generally accepted, that any interaction potential leads to the same results as the pseudopotential provided the short-range nature is preserved, should obviously be revised.

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References

Alexandrowicz Z 1968 *J. Chem. Phys.* **49** 1599–502
—— 1969 *J. Chem. Phys.* **51** 561–5
Alexandrowicz Z and Accad Y 1971 *J. Chem. Phys.* **54** 5338–45
—— 1973 *Macromolecules* **6** 251–5

Aronowitz S and Eichinger B E 1976 *Macromolecules* **9** 377–85
Bruns W 1969 *Makromol. Chem.* **124** 91–102
—— 1970 *Makromol. Chem.* **134** 193–207
—— 1972 *Makromol. Chem.* **158** 177–89
—— 1975 *Makromol. Chem.* **176** 813
—— 1976 *Colloid Polymer Sci.* **254** 325–8
Bruns W and Naghizadeh J 1976 *J. Chem. Phys.* **65** 747–51
Bueche F 1953 *J. Chem. Phys.* **21** 205–8
Domb C 1969 *Adv. Chem. Phys.* **15** 229–59
Domb C and Joyce G S 1972 *J. Phys. C: Solid St. Phys.* **5** 956–76
Edwards S F 1965 *Proc. Phys. Soc.* **85** 613–24
—— 1975 *J. Phys. A: Math. Gen.* **8** 1171–7
Fixman M 1955 *J. Chem. Phys.* **23** 1656–9
—— 1962 *J. Chem. Phys.* **36** 3123–9
Fleming R J 1967 *Proc. R. Soc.* **90** 1003 – 9
Flory P J 1949 *J. Chem. Phys.* **17** 303–10
Flory P J and Fisk S 1966 *J. Chem. Phys.* **44** 2243–8
Fluendy M 1970 *Markov Chains and Monte Carlo Calculation in Polymer Science* ed. G G Lowry (New York: Dekker)
Fujita H, Okita K and Norisuye T 1967 *J. Chem. Phys.* **47** 2723–7
Gans P J 1965 *J. Chem. Phys.* **42** 4159–63
de Gennes P G 1972 *Phys. Lett.* **38A** 339–40
Gordon M, Ross-Murphy S B and Suzuki H 1976 *Eur. Polymer J.* **12** 733–40
Grishman R 1973 *J. Chem. Phys.* **58** 220–5
James H M 1953 *J. Chem. Phys.* **21** 1628–36
Jurs P C and Reissner J E 1971 *J. Chem. Phys.* **55** 4948
Kron A K and Ptitsyn O B 1964 *Vysokomol. Soedin.* **6** 862–7
Kurata M 1968 *J. Polymer Sci.* A **6** 1607–12
Kurata M, Stockmeyer W H and Roig A 1960 *J. Chem. Phys.* **33** 151–5
Ptitsyn O B 1961 *Vysokomol. Soedin.* **3** 1673–83
Smith N C and Fleming R J 1975 *J. Phys. A: Math. Gen.* **8** 929–58
Stellman S D and Gans P J 1972 *Macromolecules* **5** 516–26
Stockmayer W H 1960 *Makromol. Chem.* **35** 54–74
Warvari H E, Knaell K K and Scott III R A 1972 *J. Chem. Phys.* **57** 1161–8
Yamakawa H 1968 *J. Chem. Phys.* **48** 3845–9
—— 1971a *J. Chem. Phys.* **54** 2484–7
—— 1971b *Modern Theory of Polymer Solutions* (New York: Harper and Row) equation (15.96)
Yamakawa H and Tanaka G 1967 *J. Chem. Phys.* **47** 3991–9