Configurational properties of self-interacting linear polymer chains in a three-dimensional continuum. II. Internal distributions, radius of gyration

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Configurational properties of self-interacting linear polymer chains in a three-dimensional continuum: II. Internal distributions, radius of gyration

Clive A Croxton

Department of Mathematics, University of Newcastle, Newcastle, NSW, 2308 Australia

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Abstract. The internal distributions within a freely pivoted self-avoiding polymer are determined on the basis of a simple diagrammatic convolution technique in conjunction with a superposition approximation. It is found that the mean square lengths of internal subsets are expanded with respect to their isolated values to an extent depending upon the proximity of the subset to either end of the chain. For chains of length much greater than the length of subset, asymmetric screening by the tail 'crowds-in' the internal subset, and shows signs of incipient collapse—a result familiar in dense fluid systems.

1. Introduction

Despite its close relation to the experimentally more accessible characteristics of dilute polymer solutions, such as diffusion, viscosity and light scattering, the mean square radius of gyration $\langle S^2 \rangle$ of an isolated polymer has received relatively little attention in comparison with the more readily calculable, but experimentally generally inaccessible, mean square end-to-end distance $\langle R^2 \rangle$. Such attention as the radius of gyration has received has been restricted almost exclusively to Monte Carlo or exact enumeration studies of self-avoiding walks on regular lattices. Certainly the calculation of $\langle S^2 \rangle$ for a perfectly flexible chain of segments incorporating excluded volume effects is a substantially more ambitious task than is the calculation of the mean square end-to-end separation. A determination of $\langle S^2 \rangle$ requires a knowledge of all the internal distributions $Z(i, i+k)$ which, in general, will differ from the distribution of an *isolated* chain of k segments. Moreover, the internal distribution may be expected to depend both on the number of segments N in the entire chain, $Z(i, i+k|N)$, and on the location of the subset within the chain, i.e. $Z(i, i+k|N) \neq Z(m, m+k|N)$, $i \neq k \neq m$, $1 < i, m, k < N$, although presumably certain of the internal distributions are symmetrical.

Monte Carlo and exact enumeration studies on regular lattices seem to suggest that for a self-avoiding walk on a regular lattice $\langle S_n^2 \rangle = bn^{\gamma'}$, where b is a lattice-dependent constant, $n = N - 1$ is the number of links in the chain, and γ' is an exponent. Moreover, γ' appears to be identical to γ, the exponent appearing in the expression $\langle R_n^2 \rangle = an^{\gamma}$ for lattice walks, at least to within 'experimental' error. The equality of the two exponents has not, however, been demonstrated convincingly for self-avoiding walks in a continuum (see references to Monte Carlo and exact enumeration studies in Croxton (1979), hereafter referred to as I).

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The only exact analytic result available is for the case of zero excluded volume, in which case $\langle S_n^2 \rangle = n(n+2)/6(n+1)$. Since there is no self-interference within the chain, all internal distributions developed between elements separated by k links are identical to the isolated end-to-end distribution of a k-link chain, and this simplification enables the analysis to proceed. In this paper we investigate various models for the internal distribution and determine their associated radii of gyration.

2. The internal distributions $Z(i, i+k|N)$

It is straightforward to show that the radius of gyration may be expressed as

$$\langle S_n^2 \rangle = \sum_{i,j=1}^{N} \sum^{N} \frac{\langle R_{ij}^2 \rangle}{2N},$$

that is, as a double sum over all the internal mean square separations. Despite the various machine determinations of the dependence of $\langle S_n^2 \rangle$ on chain length, no explicit discussion has appeared in the literature regarding the internal distributions themselves. Presumably, in the presence of excluded volume effects we may anticipate that the internal distributions will differ from their isolated values. Thus $\langle R^2(i, i+k)|N \rangle \neq \langle R^2(k) \rangle$. If we assume that the internal mean square lengths satisfy an exponent relation of the same form as for the isolated distributions, then

$$\langle S_n^2 \rangle = \left(A \sum_{i=1}^{n} (N-i) i^{\bar{\gamma}_{\text{int}}} \right) \Big/ N^2, \tag{1}$$

where $\bar{\gamma}_{\text{int}}$ is some mean internal exponent.

In making this assumption we have excluded the possibility that an internal distribution for, say, a subset of m segments depends upon the *location* of the subset within the chain. Moreover, we are also assuming that the internal distributions are independent of the length N of the chain. To produce an exponent $\gamma_S \sim 1{\cdot}2$, a widely reported value on the basis of machine simulation, we find that $\bar{\gamma}_{\text{int}}$ needs to be $\sim 1{\cdot}38$: the internal distributions are, generally speaking, *expanded* with respect to their isolated form.

3. The internal distributions $Z(1i|N)$, $Z(ij|N)$

The fully bonded diagram of, for example, order 5 is

(2)

and, by neglecting certain of the internal bonding configurations as described in I, we have been able to establish a lower bound on the mean square end-to-end separation, and the associated probability distribution. We now consider the internal distributions $Z(1i|N)$ for such a system, and for simplicity we take the case $Z(13|5)$. As in the theory of classical fluids there is a hierarchical relationship between two- and three-segment

distribution functions: for example, we may write

$$Z(1i|N) = \int Z(1iN)\,\mathrm{d}\boldsymbol{N}, \tag{3}$$

where $Z(1i|N)$ represents the $1i$ segment distribution in an N-mer, and $Z(1iN)$ represents the three-segment $(1iN)$ distribution. Generally, $Z(1i|N) \neq Z(1i)$; that is, the internal distributions differ from the isolated functions. However, for the perfectly flexible ($\gamma = 1$) and perfectly stiff ($\gamma = 2$) chains we do have $Z(1i|N) \equiv Z(1i)$. It remains to express $Z(1iN)$ in terms of known functions, and a form of Kirkwood superposition approximation (KSA) would appear to be the obvious choice. Consideration of diagram (2) in conjunction with a KSA might suggest

$$Z(1i|N) = Z(1i) \int Z(iN)H(1N)\,\mathrm{d}\boldsymbol{N} \tag{4}$$

(where H represents the exclusion bond defined in I); however, it is immediately apparent that much of the important cross-correlation between $Z(1i)$ and $Z(iN)$ is neglected. In other words, approximation (4) assumes that the component correlations develop as if in isolation. Indeed, the only accurate internal distribution function would be

$$\begin{aligned} Z(1j|j+1) &= Z(1j) \int Z(j, j+1)H(1j+1)\,\mathrm{d}(\boldsymbol{j+1}) \\ &= Z(1j) \int \delta(j, j+1)H(1, j+1)\,\mathrm{d}(\boldsymbol{j+1}). \end{aligned} \tag{5}$$

A substantial improvement would be

$$Z(1j|N) = Z(1j|N-1) \int Z(jN|N-1)H(1N)\,\mathrm{d}\boldsymbol{N}, \tag{6}$$

where $Z(jN|N-1) = Z(j-(j-1), N-(j-1)|N-1)$ by symmetry. Starting from $N = 3$ and increasing the chain length segment by segment, all functions on the RHS of (6) are known and $Z(1j|N)$ may be determined. For the specific case mentioned earlier ($N = 5$) we would have

$$Z(13|5) = Z(13|4) \int Z(35|4)H(15)\,\mathrm{d}\boldsymbol{5}, \tag{7}$$

where, of course,

$$Z(35|4) \equiv Z(13|4).$$

We note that, provides the distributions are correctly normalised, they correctly yield

$$Z(1i|N)_{\epsilon=0} = Z(1i)_{\epsilon=0} \tag{8}$$

for the zero excluded volume case.

This series of linked equations, which may be readily evaluated by Fourier transform techniques, describes the *cumulative* interference of the last segments ($j+1 \to N$) with the subset ($1 \to i$) under consideration.

A straightforward extension of the treatment outlined above for an entirely internal subset leads us to propose

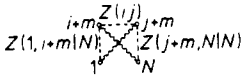
$$Z(ij|N) = Z(i-1, j-1|N-1) \int Z(1i|N-1)H(1N)\,\mathrm{d}\mathbf{1}, \tag{9}$$

where again, working inwards from either end of the chain, we incorporate the cumulative effects of the interference of the two tails $(1 \to i-1)$ and $(j+1 \to N)$ with the subset $(i \to j)$. Equation (9) correctly reduces to

$$Z(ij|N)_{\epsilon=0} = Z(ij)_{\epsilon=0} \tag{10}$$

in the zero excluded volume limit, provided the distributions are correctly normalised. Equation (9) is, of course, also amenable to fast Fourier transform techniques. Moreover, it is immediately apparent from (9) that the *location* of an internal subset of $|i-j|$ particles within the chain will affect the distribution, since clearly the convolutions

and



will differ, even though both internal distributions involve $|i-j|$ segments, the latter subset being translated by m units along the chain.

Nevertheless, we anticipate from the outset that the superposition product of three two-particle correlations determined on the above basis will yield internal distributions *collapsed* with respect to the exact internal functions, since cross-correlation of particles within the subsets is partially neglected.

A comparison of isolated and internal eight-particle subsets is shown in figure 1. We see that the amplitude of the distribution at $r = 1$ is largest for the isolated chain, indicating a net expansion of the chain. The expansion appears to increase with the length of the tail, two short tails effecting a greater expansion than a single longer tail comprising the same number of segments. $Z(r_{18} = 1)$ is the end-to-end contact probability of forming an eight-particle loop in the case of an isolated chain or an entanglement in the case of an internal distribution.

4. The internal mean square lengths $\langle \boldsymbol{R}^2_{i,i+k}|\boldsymbol{N}\rangle$

We observed in § 2 that the *overall* behaviour of the internal distributions appeared to be a general expansion and an effective stiffening characterised by an effective internal exponent $\bar{\gamma}_{\mathrm{int}} \geqslant \gamma_{R,S}$. It is clear that, while this represents the overall behaviour, the actual behaviour, at least on the basis of equation (9), is much more complicated, depending not only on the number of segments within the subset, but also on the location of the subset within the chain, and the length of the chain N.

In figure 2 we show the internal expansions $\langle R^2_{1i|N}\rangle - \langle R^2_{1i}\rangle$ for $\sigma = 1$. In the case $\sigma = 0$ the superposition approximations (6) and (9) correctly yield internal mean square lengths which are identical to the isolated value. In the case of a perfectly flexible chain of hard sphere segments ($\sigma = 1$) the expanded mean square lengths $\langle R^2_{1i|N}\rangle$ are seen gradually to attain an asymptotic expansion. Closer examination shows that there is a gradual collapse of $\langle R^2_{1i|N}\rangle$, at least for $i \ll N$, $N \gg 1$, although there is evidence that this behaviour occurs for all internal distributions. The initial expansion is clearly attributable to the interference of the tail with the subset under consideration, prohibiting certain of the collapsed configurations attainable if the subset were in isolation.

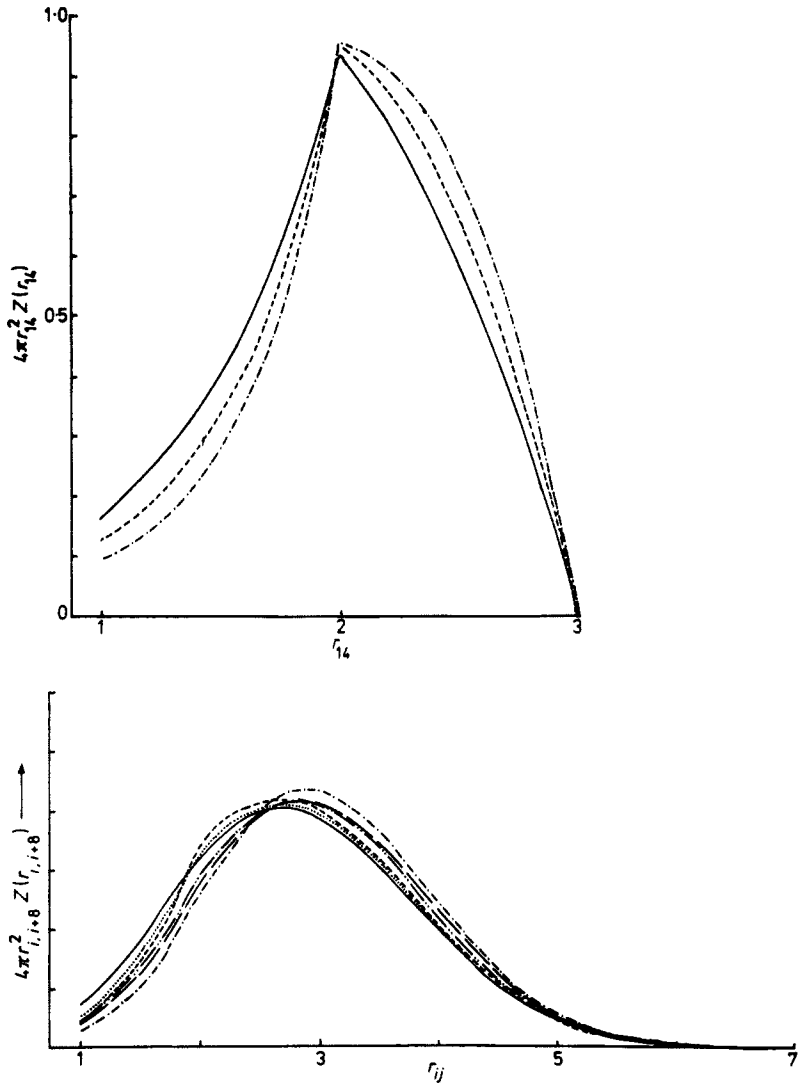


Figure 1. (*a*) Internal four-particle distributions for $N = 4, 5, 6, 10$: —— $Z(1, 4|4)$; – – – $Z(1, 4|17)$, $Z(1, 4|12)$; – · – $Z(9, 12|20)$. (*b*) Internal eight-particle distributions for $N = 8, 9, 10, 14, 20$: ——— $Z(1, 8|8)$; ····· $Z(1, 8|9)$; – – – – $Z(2, 9|10)$; — · · — · · $Z(1, 8|14)$; — — $Z(1, 8|20)$; — · — · $Z(7, 14|20)$.

Increasing the tail length has a diminishing effect, and the expansion of the subset reaches a limiting value, and eventually initiates a *collapse* of the subset—a result familiar from conventional hard sphere fluid systems arising from the 'crowding-in' or asymmetrical screening of the set of segments under consideration.

The behaviour and development of the internal distributions is considerably more complex, as anticipated, the expansion of a given subset depending both on N and on the location of the subset within the chain. Moreover, a purely internal subset is subjected to the combined effects of *two* tails, whose qualitative behaviour follows that outlined above for single-tailed subsets. As we might expect, the subset attains its

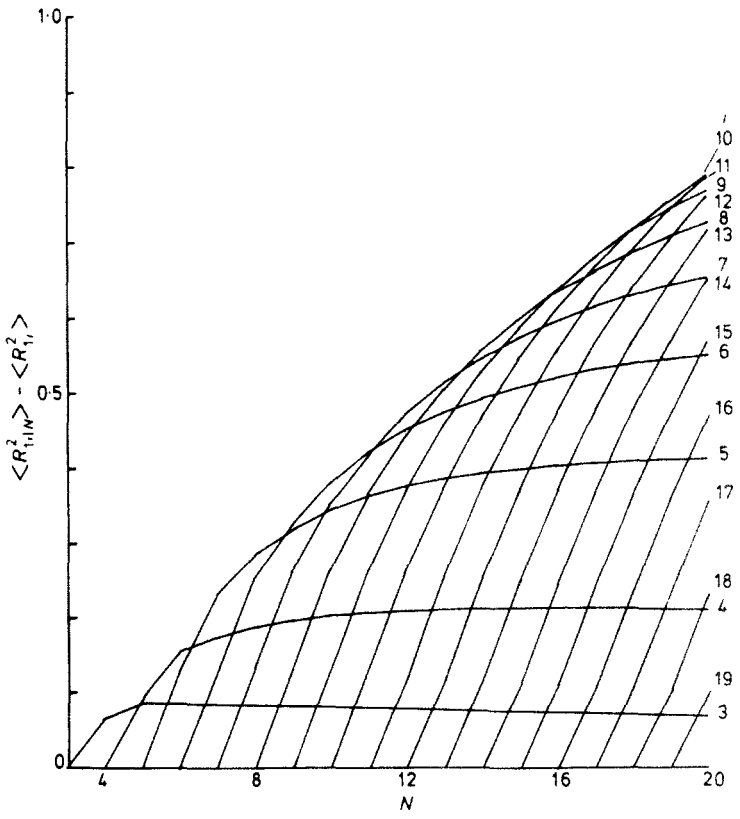


Figure 2. The relative internal expansions $\langle R^2_{1i|N}\rangle - \langle R^2_{1i}\rangle$.

greatest expansion when the two tails are of equal length. In figures 3 and 4 we show the expansions $\langle R^2_{ij|N}\rangle - \langle R^2_{ij}\rangle$ for $|i-j|=4$ and $|i-j|=8$ respectively. We see at once that the eight-particle segments show a greater relative expansion throughout. Points with only one line leading out to the right are cases where both tails are the same length. Where two lines lead to the right from a point, the line with the steeper slope arises from adding one particle to the smaller of the two tails; the other line arises from adding one particle to the longer tail. In the case of the eight-segment subchain, the second particle added to a tail appears to make more difference to the length than does the first (i.e. $\langle R^2_{18|10}\rangle > \langle R^2_{29|10}\rangle$), which means that there is a lot of crossing over and back in the lines where all the tails are small.

5. Radius of gyration

It is straightforward to show that the radius of gyration is related to the internal mean square lengths (Tanford 1961)

$$\langle S^2_n\rangle = \sum_{1=i}^{N}\sum_{j=1}^{N}\frac{\langle R^2_{ij}\rangle}{2N^2}. \tag{11}$$

In the case of a perfectly flexible chain with zero excluded volume ($\sigma = 0$), the internal

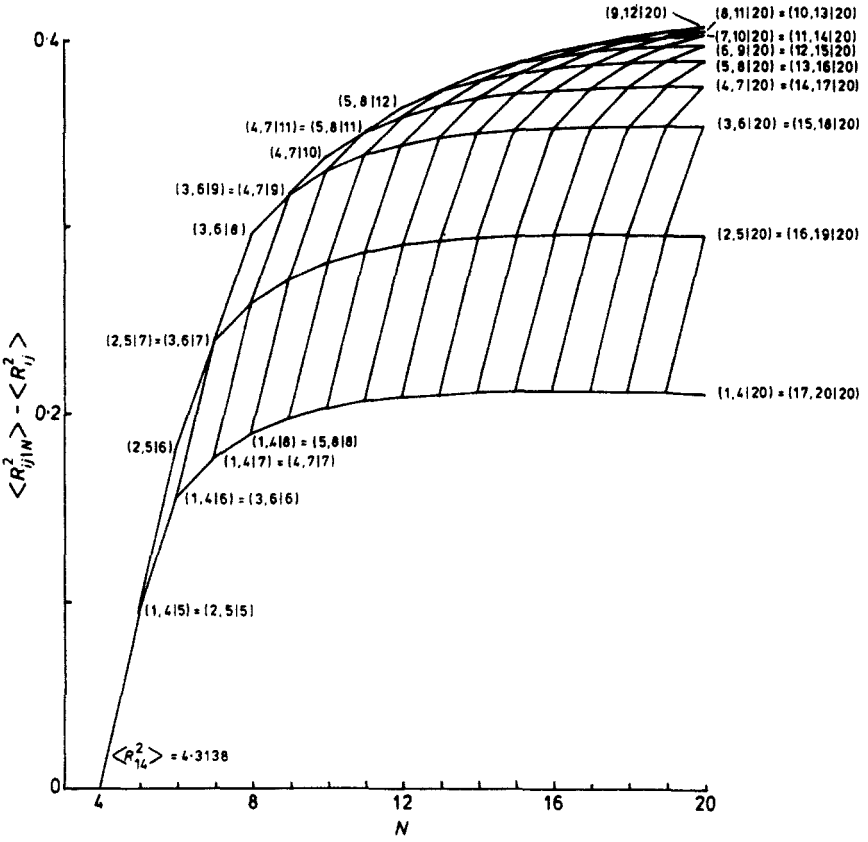


Figure 3. The relative internal expansions $\langle R^2_{ij|N}\rangle - \langle R^2_{ij}\rangle$ for four-particle subsets.

mean square lengths are identical to their isolated values ($\gamma_R = 1$), and we have

$$\langle S_n^2 \rangle = n(n+2)/6(n+1), \tag{12}$$

whereupon, for long chains, $\gamma_S = 1$. For perfectly rigid chains ($\gamma_R = 2$), again no excluded volume effects arise, and equation (11) leads to the result

$$\langle S_n^2 \rangle = n(n+2)/12. \tag{13}$$

On the basis of the internal mean square lengths reported in the previous section we are able to calculate the radius of gyration for polymer chains for which $\sigma = 1$. A calculation of γ on the basis of the linearisation of the exponent relation $\langle S_n^2 \rangle = bn^{\gamma}$ yields, for the nth estimate of γ,

$$\gamma_n = (\langle S_{n+1}^2 \rangle / \langle S_n^2 \rangle - 1)n.$$

When plotted against $1/n$ this yields the smoothly varying curve shown in figure 5. As reported in I, we expect over-collapsed configurations to contribute to the calculation of the radius of gyration, which will, in consequence, be consistently too small. Moreover,

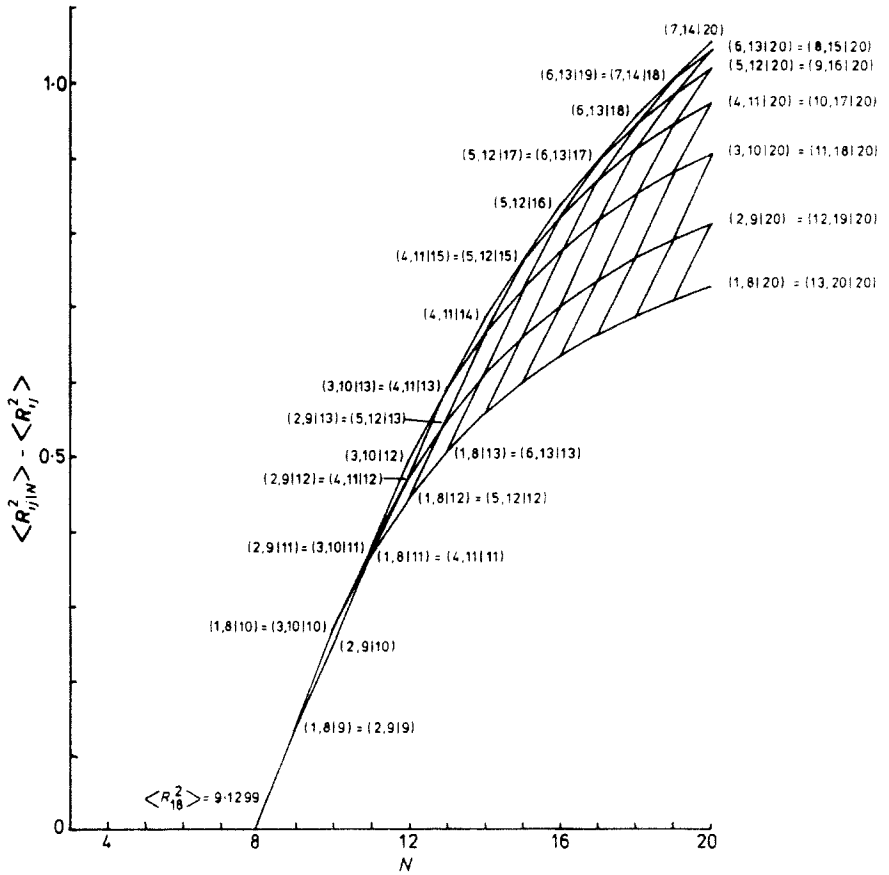


Figure 4. The relative internal expansions $\langle R^2_{ij|N} \rangle - \langle R^2_{ij} \rangle$ for eight-particle subsets.

as the fraction of bonds omitted increases with increasing N, we expect the results to tend to the zero excluded volume result as $N \to \infty (1/n \to 0)$. These results are shown only for completeness; we shall not attempt to draw any conclusions regarding the exponent γ.

6. Conclusions

On the basis of a convolution approximation together with a superposition approximation, the internal distributions within a polymer chain incorporating excluded volume effects are calculated. It is found that the mean square lengths of internal subsets of particles are expanded with respect to their isolated values to an extent depending on the proximity of the subset to either end of the chain.

As the length of the chain increases, a subset at a given location from one end of the polymer becomes progressively indifferent to the long tail, and tends asymptotically to a limiting expansion. Ultimately, however, for chains of length much greater than the length of subset, the tail 'crowds-in' the internal subset, and the expansion begins to decrease slowly—a result familiar in classical dense fluid systems.

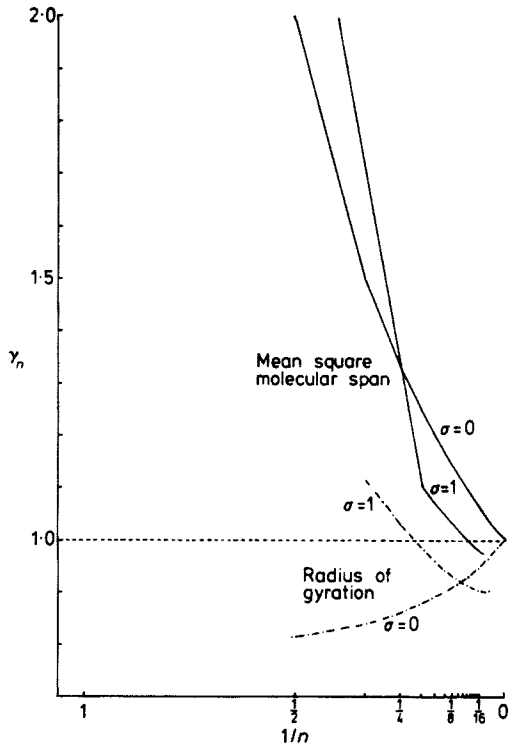


Figure 5. Comparison of various γ_n estimates for the radius of gyration and mean square end-to-end distance.

References

Croxton C A 1979 *J. Phys. A: Math. Gen.* **12**
Tanford C 1961 *Physical Chemistry of Macromolecules* (New York: Wiley)