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1986 J. Phys. A: Math. Gen. 19 987

(http://iopscience.iop.org/0305-4470/19/6/026)

J. Phys. A: Math. Gen. 19 (1986) 987-999. Printed in Great Britain

A Monte Carlo analysis of terminally attached self-avoiding polymer sequences in the vicinity of a rigid boundary

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Received 4 January 1985, in final form 3 July 1985

Abstract. A Monte Carlo analysis of terminally attached hard sphere sequences of $N \leqslant 24$ segments in the vicinity of a rigid plane is presented. The principal configurational properties of the system are determined, in particular the segment density distribution $\rho(z|N)$ normal to the boundary, the mean square end-to-end length $\langle R_{1N}^2 \rangle$, the mean square radius of gyration $\langle S_N^2 \rangle$ and the mean thickness of the adsorbed layer $\langle z_{1N} \rangle$. Comparisons with a previously presented iterative convolution analysis are made and the existence of a density discontinuity in $\rho(z|N)$ is confirmed. Exponent representations of the data suggest $\langle R_{1N}^2 \rangle \sim (N-1)^\gamma$ with $\gamma \sim 1.2$, consistent with lattice-based analyses. The boundary configurations are resolved into loop, train and tail components and their dependence upon chain length determined. Good agreement with the convolution analysis is found, the results being consistent with earlier analyses by Roe and Chan *et al*, and the experimental investigations of Cosgrove *et al*.

1. Introduction

Analyses of chain conformations in the vicinity of a rigid boundary have generally been restricted to lattice-based investigations in which partial account is taken of excluded volume processes in finite sequences. Earlier work based on random lattice walk models does not concern us here; these results have been reviewed by Barber and Ninham (1970).

The lattice-based analyses may be further resolved into exact enumeration studies (Lax 1974, Mark and Windwer 1974, Whittington 1975, Middlemiss and Whittington 1976, Torrie *et al* 1976, Guttmann *et al* 1978, Hammersley *et al* 1982) and Monte Carlo estimates based on self-avoiding lattice walks (Clark and Lal 1978, 1981, Dickinson and Lal 1980); comparative discussion of some of these results will be given below.

In addition, a variety of continuum analyses have been proposed with partial or complete neglect of excluded volume processes operating within the sequence (Forsman and Hughes 1963, Edwards 1965, Silberberg 1967, de Gennes 1969, Chan *et al* 1975). It is not appropriate to review these treatments here; instead we refer the reader to Dickinson and Lal (1980) for an appraisal. In all cases the preoccupation is with the asymptotic properties of the sequences as the number of steps $N \to \infty$. Despite the importance of the problem in the description of a wide range of systems ranging from biological cell boundary phenomena to colloidal stability against flocculation, relatively

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little interest has been shown in the configurational properties of finite self-avoiding continuum sequences in the vicinity of a rigid boundary. An analysis by the present author based on a convolution integral technique has been previously reported (Croxton 1981, 1983), although in the absence of any extensive Monte Carlo analysis of the problem with which to compare the results. In these convolution estimates the effect of a rigid plane was introduced by allowing the diameter of the first segment $\sigma_0 \to \infty$, whilst for the remaining sequence $\sigma_1, \ldots, \sigma_N = 1$ was adopted. It was found that the configurational properties of the chain rapidly approached an asymptotic form with increasing σ_0, and in practice $\sigma_0 = 64$ was assumed. The Monte Carlo estimates, on the other hand, were determined for a terminally attached sequence $\sigma_1, \ldots, \sigma_N = 1$ at a rigid plane; the discrepancy between the curvilinear and the cartesian volume elements in the two models is negligible for the sequence lengths investigated here. Accordingly we regard r_{0i} and z_i as equivalent representations of the normal separation of segment i from the rigid boundary.

Certainly exact enumeration studies are available, and whilst useful, the inherent 'coarse-grained' nature of the lattice in which the sequence is embedded prohibits immediate comparison with any continuum analysis. Indeed, some aspects of the lattice distribution are inevitably unresolved; a case in point concerns the hard sphere segment density distribution $\rho(z|N)$ normal to the boundary for a terminally attached sequence. On the basis of the convolution approximation, $\rho(z|N)$ should show a pronounced discontinuity at a distance of one segment diameter from the boundary with a weakly resolved secondary structure associated with geometric layering of the segments (Croxton 1985) whilst the lattice-based distribution is essentially structureless. Recent Monte Carlo calculations for strongly adsorbed perfectly flexible self-avoiding sequences have been reported by Higuchi *et al* (1983). Where appropriate we shall make reference to these results, although direct comparison cannot be made with the present analysis which relates to zero chain-plane attraction.

In this paper we present a Monte Carlo analysis of perfectly flexible self-avoiding hard sphere sequences terminally attached to a rigid plane. In particular, the segment density distributions $\rho(z|N)$ normal to the plane are determined for $N \leqslant 24$, as are the mean and mean square segment-segment and segment-boundary separations. Whilst adsorption as such does not occur in this system, the mean thickness of the boundary layer of polymer segments, the normal location of the centre of gravity and the radius of gyration of the sequence are determined. Finally, a detailed analysis of the development of specific structures (loops, trains and tails) at the boundary is presented; in all cases the N dependence of these quantities is investigated.

2. The Monte Carlo analysis

The geometry of the system is shown in figure 1. A perfectly flexible hard sphere sequence of identical segments diameter $\sigma = 1$ is terminally attached to a rigid planar boundary. We identify the *accessible boundary* which represents the locus of closest approach of any segment centre to the rigid boundary. It is with respect to this boundary that we measure normal separation z in units of σ.

The centre of the Nth hard sphere segment is distributed uniformly over the accessible spherical surface $r_{N-1,N} = \sigma$, any attrition in the accessible area being due to the presence of the rigid boundary or interference with non-adjacent segments within

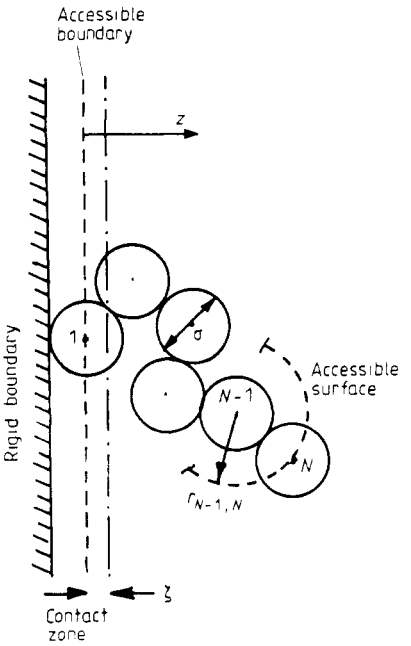

Figure 1. Geometry of terminally attached sequence. The accessible boundary represents the locus of closest approach of the hard sphere segments to the rigid plane. The contact zone ζ is also indicated. Segment N is distributed uniformly over the accessible spherical surface defined by $r_{N-1,N}$, subject to geometrical interference.

the sequence. The centre of the terminally attached segment is located at (0, 0, 0). The correct procedure for locating the Nth segment (Knuth 1969) involves the independent selection of x, y, z coordinates relative to the centre of the $(N-1)$th segment *normally* distributed over the interval $(-1, 1)$, whereupon

$$r = (x^2 + y^2 + z^2)^{1/2}$$

giving the location of the Nth segment (x', y', z') where

$$x' = x/r \qquad y' = y/r \qquad z' = z/r.$$

This procedure ensures that the Nth segment is uniformly distributed over the accessible surface of the $(N-1)$th. Provided there is no violation of the excluded volume condition in the system the sequence of N segments is considered an acceptable configuration from the point of view of compilation of statistics. If a violation does occur, then the entire sequence is rejected; nevertheless, the statistics of the 'successful' sequence of $N-1$ segments must of course be retained. Repeated attempts to 'successfully' extend the $N-1$ sequence is essentially incorrect since it asserts that the distribution of the earlier segments are unmodified by the presence of subsequent extensions of the chain, which of course they are.

It is also incorrect to select the (x, y, z) coordinates *uniformly* over the interval $(-1, 1)$. Points uniformly distributed in three-dimensional Euclidian space are *not* uniformly distributed in the two-dimensional curved space defined by $r_{N-1,N}$.

Naturally many more shorter sequences will be successfully generated than longer ones, and we find the number of successful sequences range as follows:

N	Number of successful configurations
2	334 355 290
5	78 779 290
10	8 815 913
15	1 052 673
20	129 912
24	24 773

Obviously the statistical averages determined are better defined for the shorter sequences. Nevertheless, a good quantitative description is obtained over the entire range of sequences investigated.

3. Results

3.1. Segment density distributions

In figure 2 we present the normalised MC segment density distribution $\rho(z|N)$ for a terminally attached sequence of 15 hard sphere segments in the vicinity of a rigid

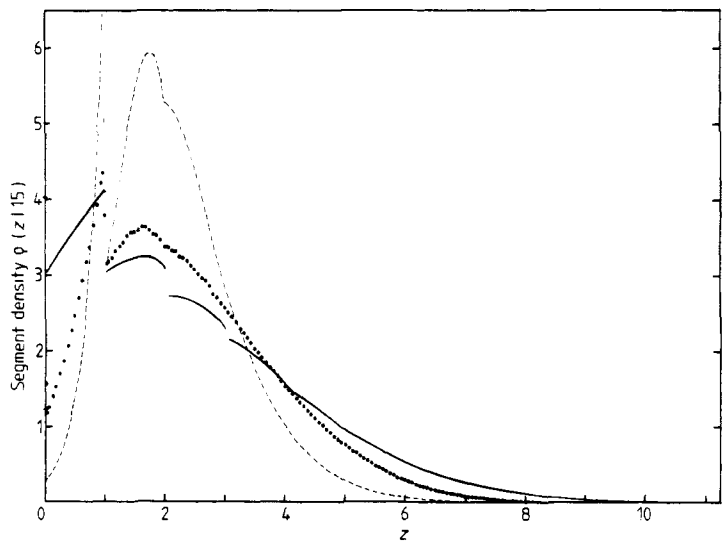

Figure 2. Comparison of the Monte Carlo segment distribution $\rho(z|15)$ with the C and IC estimates. The IC distribution is seen to be in better overall agreement with the Monte Carlo data, but substantially over-estimates the chain-plane contact probability. The C approximation conversely under-estimates the contact probability and over-estimates the distribution in the vicinity of the discontinuity. ——, IC, - - -, C; · · ·, Monte Carlo after 1052 673 configurations.

plane. The normal distance z is measured in units of the segment diameter from the plane $z=0$, coinciding with the accessible boundary (figure 1).

The existence of a discontinuity in $\rho(z|N)$ at $z=1$, first predicted on the basis of the convolution approximation (Croxton 1981, 1983, 1985) is confirmed by the Monte Carlo results for the entire range of N investigated. The amplitude of the discontinuity $\Delta\rho$ decreases slightly with increasing N but is of the order of ~ 1.25 throughout.

In all cases the discontinuity is preceded by a steep rise in $\rho(z|N)$ $(0<z<1)$, and for $N>8$ is followed by a maximum $(z>1)$ corresponding to a weakly resolved second layer and for longer simulated sequences $(N \geqslant 11)$, evidence of a third layer. All these features have been previously predicted (Croxton 1981, 1983) and differ substantially from distributions based on *a priori* considerations and from lattice-based analyses, both of which suggest an essentially structureless distribution (Dickinson and Lal 1980). It is appropriate to note that the *continuum* (off-lattice) Monte Carlo computations of Higuchi *et al* (1983) also show no evidence of a discontinuity in the segment density profile. However, as we observed in a previous publication (Croxton 1983), in the case of strong chain-plane attraction $\rho(z|N)$ is collapsed towards the boundary and the discontinuity, whilst still present, is nevertheless absorbed into the principal maximum. Higuchi's analysis for strongly adsorbed sequences does not resolve a discontinuity in $\rho(z|N)$ for such systems and confirms the qualitative form of the distributions reported earlier (Croxton 1983). It should be emphasised, however, that the geometrical processes responsible for the discontinuity continue to operate.

For the purposes of comparison the results of a more recent iterative convolution (IC) approximation (Croxton 1984) are shown (figure 2); the IC technique is seen to predict the structure semi-quantitatively, although the somewhat over-collapsed nature of the approximation is apparent. More particularly, the IC approximation appears to suggest a more highly structured distribution than is evident from the MC simulations, although more extended runs may resolve this structure. The principal discontinuity at $z=1$ is clearly confirmed, however.

The highly structured nature of the hard sphere IC distributions may be directly attributed to the form of the component distributions $Z(z_i|N)$

$$\rho(z|N)=\sum_{i=2}^{N} Z(z_i|N)$$

where $Z(z_i|N)$ represents the normalised spatial probability distribution of the ith segment within the N-mer normal to the accessible boundary. We find for $2<i\leqslant 5$, the $Z(z_i|N)$ indicate that the ith segment is strongly expelled from the vicinity of the boundary—a direct consequence of the 'entropic repulsion' (Silberberg 1967, Croxton 1983) associated with the reduction in accessible chain conformations by the presence of the boundary. As a result the component distributions $Z(z_i|N)$ for small i are distorted into a saw-tooth form, with the maximum displaced towards the end of the range $(Z_i^{\max}\sim(i-1)\sigma)$. The saw-tooth form of $Z(z_i|N)$ relaxes with increasing i, though it is nonetheless responsible for the short-range serrations in $\rho(z|N)$. Now, whilst these serrations are not clearly resolved in the MC data, the IC calculations nonetheless identify the agent responsible for the fine structure in the simulated density distributions.

It is appropriate here to make a detailed comparison of the convolution (C) (Croxton 1983) and iterative convolution (IC) (Croxton 1984) estimates of the segment density distributions normal to the boundary in the context of the Monte Carlo data reported here. In particular we observe that the overall agreement with the MC distribution is

better for the IC approximation (figure 2); specifically, the density discontinuity, the secondary maximum and the tail structure are better represented. However, the contact density at the boundary, corresponding to adsorbed sequences, is substantially over-estimated in the IC approximation with respect to the MC distribution. This represents the primary distinction between the C and IC estimates, the former approximation substantially under-estimating the adsorbed component (Croxton 1983, figure 2). Both approximations are known to yield over-collapsed distributions; IC appears to identify these near-boundary configurations primarily as trains, whilst C identifies them as loops.

3.2. *Mean square end-to-end distance*

The mean square separation of the terminally attached and terminal segments $\langle R_{1N}^2 \rangle$ was determined, and the results are shown in figure 3. For comparison the Monte

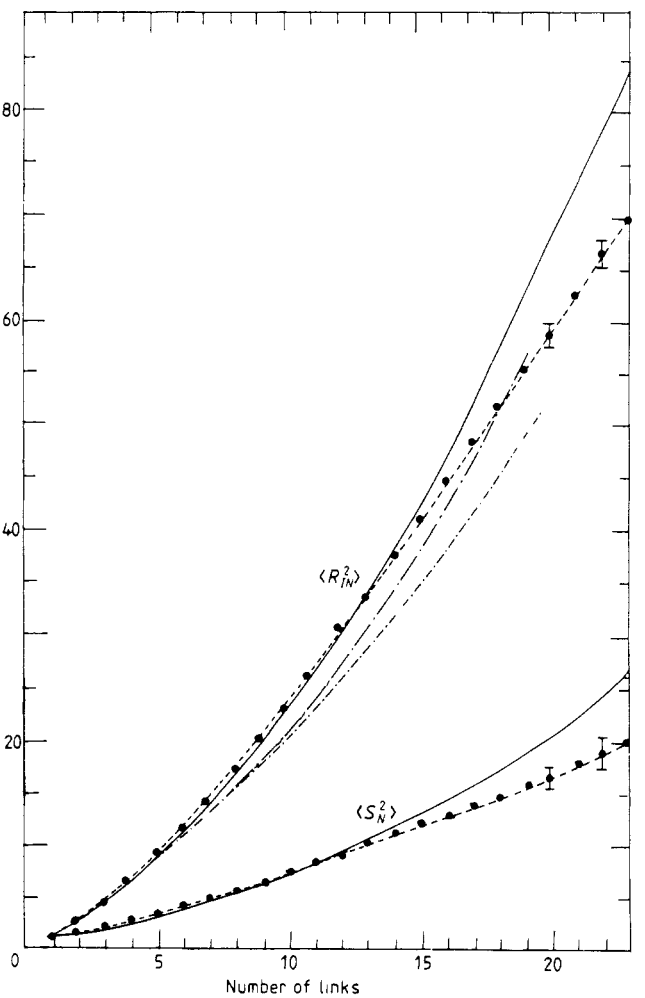

Figure 3. The mean square end-to-end separation $\langle R_{1N}^2 \rangle$ and radius of gyration $\langle S_N^2 \rangle$ on the basis of the MC and IC analyses. The isolated chain counterparts are shown for comparison. ——, IC (terminally attached); —·—, IC (isolated); - - -, MC (terminally attached); -·-, MC (isolated).

Carlo results for an isolated, but otherwise identical, sequence are shown. The confined sequence is consistently expanded with respect to its isolated counterpart, as might be expected from the reduction in accessible volume due to the boundary. However, there is no reason to presuppose that the mean segment densities of the terminally attached and isolated sequences should be identical; it is not a foregone conclusion therefore that $\langle R_{1N}^2 \rangle$ should necessarily be greater than its isolated counterpart, although Mark and Windwer (1974) have suggested that such would be the case for walks restricted to the half-space.

$\langle R_{1N}^2 \rangle$ calculated on the basis of the iterative convolution (IC) approximation for a terminally attached sequence is also shown, together with the corresponding results for an isolated sequence. The relative expansion of the terminally attached sequence is clearly illustrated, and is seen to be in good agreement with the Monte Carlo estimate. The error bars in figure 3 indicate the 95% confidence interval.

We have also estimated the mean square length exponent γ in the relation

$$\langle R_n^2 \rangle \sim n^{\gamma}$$

where $n = N - 1$. We form the estimate on the basis (Whittington 1975)

$$\gamma_n = \tfrac{1}{2} n(\langle R_{n+2}^2 \rangle / \langle R_n^2 \rangle - 1) \tag{1a}$$

and these are shown in figure 4. A least squares quadratic fit to the data suggests a limiting value $\gamma_\infty \sim 1.20$ which concurs with the exact enumeration results of Whittington (1975) ($\gamma_\infty \sim 1.2$) and Guttmann *et al* (1978) ($1.19 < \gamma_\infty < 1.22$) determined on a variety of lattices. It should be emphasised that in off-lattice Monte Carlo studies, unlike their lattice-based exact enumeration counterparts, the γ_n are subject to statistical error. To place error estimates upon the γ_n would require numerous re-runs of the entire simulation, which would, of course, be computationally prohibitive. Any conventional specification of error associated either with the γ_n or the estimate of γ_∞ is therefore impossible on the basis of the present data set.

Lax (1974) had previously asserted that in the absence of a soft chain-plane interaction, γ retains its isolated chain value ($\gamma_{iso} = 1.20$); our result appears fully consistent with Lax's assertion and contradicts the claim of Mark and Windwer (1974) that the exponent should increase when the walk is restricted to the half-space $z > 0$.

3.3. *Radius of gyration*

The mean square radius of gyration of the chain was determined on the basis of the expression

$$\langle S_N^2 \rangle = \sum_i \sum_j R^2(ij|N)/N(N-1)$$

and the results are shown in figure 3. Assuming a chain length dependence of the form

$$\langle S_N^2 \rangle \sim n^{\gamma^*}$$

we estimate the exponent on the basis of

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

It is apparent from figure 4 that the radius of gyration and mean square length exponents γ_n^* and γ_n appear to be converging with increasing chain length. Whilst earlier analyses on isolated chains suggest that the mean square length and gyration exponents may

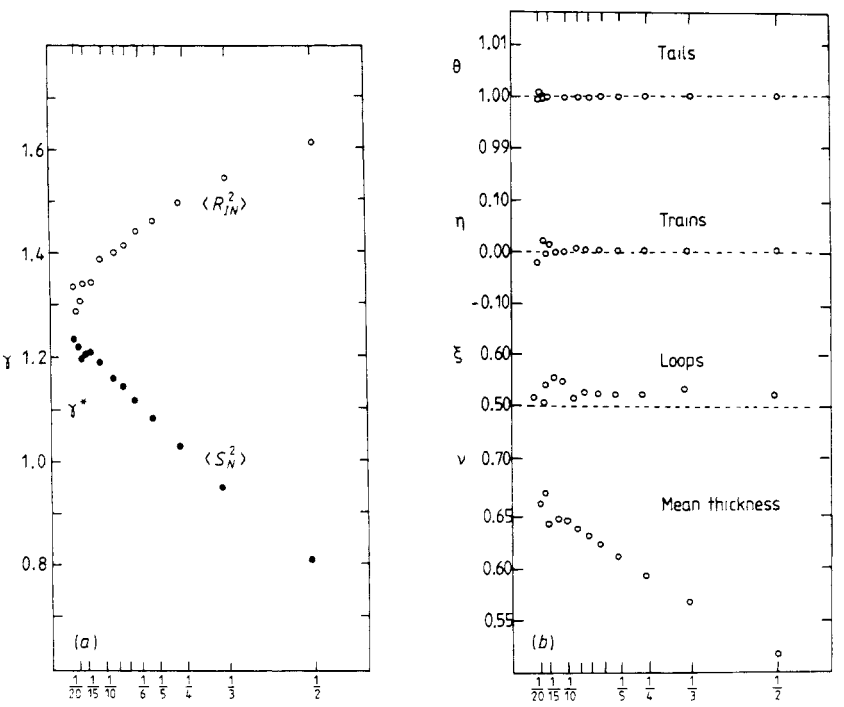

Figure 4. (*a*) Exponent estimates γ_n and γ_n^* for the mean square chain length and radius of gyration as a function of inverse chain length. (*b*) Loop, train, tail and mean thickness exponents as a function of inverse chain length.

be identical, we cannot yet draw the same conclusion for terminally attached sequences. An estimate formed on the basis of a least squares fit to the MC data suggests $\gamma_\infty^* > 1.2$; we emphasise however the reservations which must be placed upon such an estimate, as discussed above. Nevertheless, this value is consistent with the proposition $\gamma_\infty = \gamma_\infty^*$.

3.4. Development of loops, trains and tails

The configuration of the terminally attached sequence at the boundary may be resolved into three distinct classes: loops, trains and tails (figure 5). The precise classification

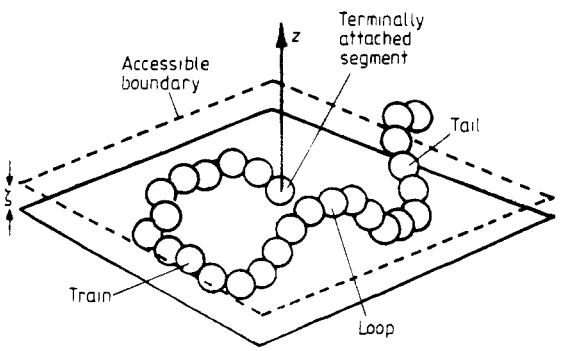

Figure 5. Resolution of chain conformation into loop, train and tail components.

depends upon the width of the contact zone ζ (Higuchi *et al* 1983). Segments whose z coordinates are within ζ of the accessible boundary surface are classified as being adsorbed, and as such constitute a *train*. Segments whose centres $z > \zeta$ form either *loops* or *tails*, depending whether one or more of the subsequent centres of the desorbed sequence do or do not return to within ζ of the accessible plane. Clearly the partitioning of the sequence into loops, trains and tails depends sensitively upon the ratio ζ/σ, particularly since the segment density distribution $\rho(z|N)$ varies rapidly in the vicinity of the boundary (figure 2). Accordingly, we present results for two choices of ζ.

The presence of a rigid boundary substantially reduces the number of accessible chain conformations with respect to its isolated counterpart. Indeed, the associated rise in boundary excess free energy in the vicinity of the plane may be regarded as an entropic repulsion between segments and boundary (Middlemiss *et al* 1977, Croxton 1983). This provides a particularly useful concept in the analysis of loop, train and tail formation.

In table 1 we present the number/size distribution of loops, trains and tails for a terminally attached hard sphere sequence of 16 segments (691 654 successful configurations; $\zeta = 0.0078\sigma$). These results are typical of all sequence lengths investigated in the range $2 \leq N \leq 24$.

Table 1. Numbers and sizes of loops, trains and tails for $N = 16$ (691 654 successful configurations; $\zeta = 0.0078\sigma$).

Size	Loops	Trains	Tails
1	0	3100	130
2	819	0	108
3	434	0	85
4	250	0	99
5	177	0	83
6	123	0	100
7	129	0	83
8	79	0	128
9	104	0	123
10	87	0	180
11	93	0	253
12	84	0	433
13	108	0	811
14	131	0	3 071
15	310	0	685 655

3.4.1. Trains. First we note that entropic repulsion accounts for the strong predisposition against trains; desorbed configurations in the form of loops and tails, particularly the latter, account almost entirely for the observed chain conformations (table 1, figure 6(b, c)), in good agreement with the experimental work of Cosgrove *et al* (1983) and observed in a number of lattice-based analyses embodying weak or zero chain-plane attraction (e.g. Lal and Stepto 1977, Dickinson and Lal 1980). Trains, if they do occur, are never more than one link in length (figure 6(a)) regardless of chain length. The bound fraction of the sequence decreases rapidly with increasing N (figure 6(b, c)); attrition in chain conformation with adsorption of a single segment develops rapidly with chain length and the associated free energy penalty ensures a decreasing fraction of the sequence in the form of trains with increasing N.

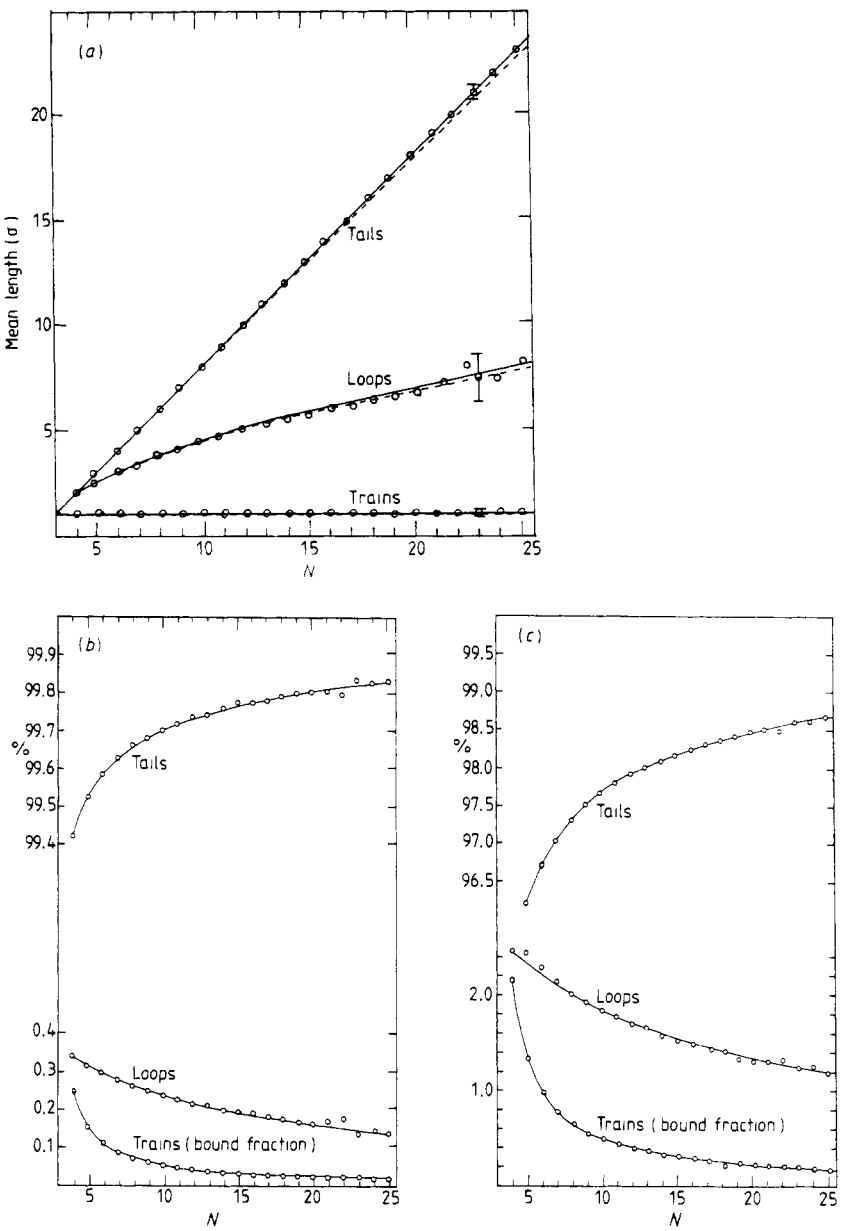

Figure 6. (*a*) Mean component lengths as a function of chain length. The error bars indicate the 95% confidence intervals. Loops form primarily in denominations of maximal or minimal size, accounting for the very large confidence interval for loop formation (table 1). - - -, $\xi = 0.0625\sigma$; ——, $\zeta = 0.007\,28\sigma$. (*b*) Component fractions as a function of chain length, expressing percentage of chain in loop train and tail form. $\zeta = 0.007\,28\sigma$. (*c*) Component fractions as a function of chain length, expressing percentage of chain in loop, train and tail form. $\zeta = 0.0625\sigma$.

An exponent representation of the form $\langle l_{\text{train}} \rangle \sim (N-1)^{\eta}$ suggests an asymptotic ($N \to \infty$) value $\eta \sim 0$ (figure 4). As emphasised previously, the MC data are not susceptible to any conventional assessment of error as far as exponent estimates are concerned, based on relations of the form $1(a, b)$. However, the data presented in figure 4 are consistent with Roe's (critical) value $\eta_c = 0$, determined on the basis of the divergent generalised partition function method (Roe 1965a, b) in which excluded volume is neglected. Roe identifies the critical condition as one for which a weak chain-plane attraction counters the entropic repulsion at the plane, yielding a zero excess free energy.

3.4.2. Tails. Desorbed sequences in the form of loops and tails represent the preferred conformations at the boundary, particularly the latter (table 1) which account for more than 99% of the observed structure (figure 6(b)). The configurational attrition associated with returns to the plane, relative to the totally desorbed sequence, increases rapidly with chain length and accounts for the increasing predisposition for the formation of tails with increasing N. Clearly, theories which ignore the presence of tails would appear incapable of providing an adequate description of the configurational behaviour of finite length sequences (Simha *et al* 1953). It is evident that a strong segment-boundary attractive interaction would be required to substantially modify the ratio of adsorbed to desorbed configurations.

Fitting an exponent representation of the form $\langle l_{\text{tail}} \rangle \sim (N-1)^{\theta}$ suggests a value $\theta \sim 1$ (figure 4) for asymptotically long sequences, again consistent with Roe's critical estimate $\theta_c = 1.0$. This is not a general result of course, and will depend upon adsorption energy (Lal and Stepto 1977).

3.4.3. Loops. From table 1 we see that very short and very long loops are more probable than those of intermediate length, within a given sequence. This distribution of loop lengths is characteristic of all sequence lengths investigated. The return of an intermediate segment to the plane effects a relatively greater attrition of chain conformations than does a return at either end of the sequence. Given the overall predisposition towards the formation of tails, short loops are favoured with respect to those of larger denomination. One consequence of this bimodal distribution of loop lengths is that the variance in $\langle l_{\text{loop}} \rangle$ is enormous (figure 6(a)) making any definitive assessment of dependence upon chain length difficult. However, the progressive predisposition towards shorter rather than longer loops with increasing chain length is nevertheless clearly apparent. An exponent representation of the form $\langle l_{\text{loop}} \rangle \sim (N-1)^{\xi}$ suggests an exponent $\xi \sim 0.52$ for asymptotically long sequences (figure 4), again in good agreement with Roe's critical value $\xi_c = 0.5$.

3.4.4. Thickness of the boundary layer. The mean thickness of the boundary layer $\langle z_{1N} \rangle$ as a function of chain length was also determined, and is found to increase slowly with N (figure 7) which we interpret as evidence of lateral spreading of the sequence with increasing chain length. The mean square normal separation $\langle z_{1N}^2 \rangle$ supports this conclusion. For an isolated, spherically symmetric sequence $\langle z_{1N}^2 \rangle \equiv \langle R_{1N}^2 \rangle$. However, we find that $\langle z_{1N}^2 \rangle$ is substantially less than $\langle R_{1N}^2 \rangle$ for a terminally attached chain—a result consistent with lateral spreading of desorbed sequences rather than normal growth away from the boundary.

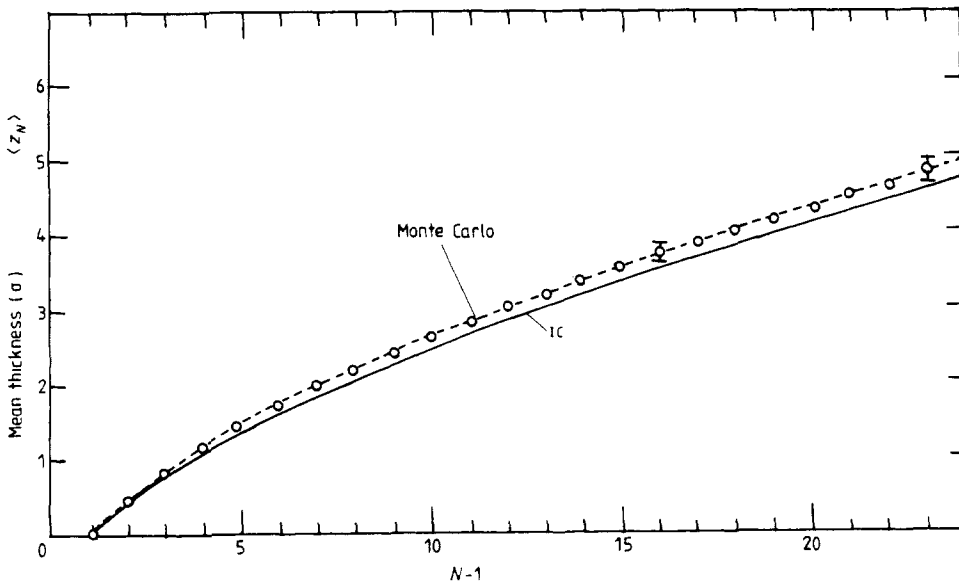

Figure 7. The mean thickness $\langle z_{1N} \rangle$ of boundary layer as a function of chain length.

An analysis of the mean normal span $\langle z_n \rangle$ on the basis of

$$\langle z_n \rangle \sim n^{\nu}$$

and

$$\nu_n = \tfrac{1}{2} n(\langle z_{n+2} \rangle / \langle z_n \rangle - 1)$$

suggests $\nu_\infty \sim 0.67$ (figure 4). Unfortunately no exact enumeration data are available for comparison. However, Chan *et al* (1975) report $\nu_\infty = 0.5$ for a terminally attached sequence, weakly attracted to a rigid plane. This result, determined on the basis of a divergent partition function analysis, neglects excluded volume, in which case a somewhat stronger n dependence might be anticipated, particularly in the absence of chain-plane attraction.

3.4.5. Effect of contact zone thickness ζ. Two choices of contact zone thickness were chosen, $\zeta = 0.00728\sigma$ and 0.0625σ, within which a segment centre was considered to be adsorbed to the plane. Whilst the qualitative dependence of the loop, train and tail fractions upon N was relatively insensitive to the choice of ζ, the quantitative effects arising from the reclassification were considerable. This may be directly attributed to the short-range form of $\rho(z|N)$ which increases rapidly over the range $0 < z < 1$. The bound fraction (trains) increases by an order of magnitude (figures 6(*b*, *c*)), although $\langle l_{\text{train}} \rangle$ remains essentially unmodified. With this relaxation in the adsorption criterion, configurations previously classified as tails are now reclassified as loops, increasing the loop fraction by ~60%. This reclassification is, of course, at the expense of tails which show a far less dramatic dependence upon the choice of ζ.

On the basis of MC analyses of terminally attached continuum sequences, Higuchi *et al* (1983) have determined the ζ dependence of the various boundary structures discussed above. They find that resolution into loop, train and tail components is sensitively dependent upon the choice of ζ. However, the stringent criteria for adsorption adopted here ($\zeta = 0.0625, 0.00728$) provide an unequivocal resolution of the various

boundary structures. As Higuchi *et al* observe, however, under conditions of strong chain-plane attraction the development of relatively thick boundary layers introduces ambiguity into the choice of ζ and the associated resolution of loops, trains and tails.

Acknowledgments

I should like to thank Ruby Turner for performing the numerical analysis and ARGS for financial support.

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