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The development of loops, trains and tails in a self-avoiding terminally attached molecule

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Abstract. The configuration of self-avoiding polymer molecules terminally attached to a rigid boundary is resolved into loop, train and tail components on the basis of a convolution integral analysis. The expectation lengths $\langle l_{loop} \rangle$, $\langle l_{train} \rangle$ and $\langle l_{tail} \rangle$ and the component fractions are determined as functions of chain length and chain-plane interaction. In the case of zero chain-plane attraction there is good quantitative agreement with Monte Carlo estimates, although the predicted dependence of $\langle l_{loop} \rangle$ upon chain length appears too strong.

Results are also presented for hard sphere sequences as a function of chain-plane attraction when it is found that there is a progressive redistribution amongst loop and tail states, the train exponent remaining essentially unmodified over the range of interactions investigated. Exponent representations are proposed and compared with earlier analyses. The various component structures are discussed in terms of the interplay of entropic and energetic processes at the boundary.

1. Introduction

In a previous publication (Croxton 1986a) we presented the results of a Monte Carlo analysis of the configurational properties of terminally attached self-avoiding hard sphere sequences in the vicinity of a rigid plane. The analysis was conducted to complement the various lattice-based exact enumeration and Monte Carlo treatments, and in particular to identify any fundamental differences between the continuum and discrete representations. The Monte Carlo data were compared with the results of a previously reported iterative convolution (IC) approximation (Croxton 1984), itself a development of an earlier convolution (C) approximation (Croxton 1979a, b, c, 1981, 1983). It is not appropriate to review those results here, except to say that a fundamental feature of the MonteCarlo data was the development of a pronounced discontinuity and secondary structure in the segment density distribution normal to the rigid boundary, a feature unresolved in previous discrete and continuum analyses, but nevertheless predicted on the basis of the C and IC approximation (see discussion in Croxton (1985, 1986a, b)).

Thus encouraged, we present here an analysis of the detailed structure of the terminally attached sequence in terms of its resolution into loop, train and tail components, based on the convolution approximation. Whilst we generally find that the *iterative* convolution technique yields results in closer agreement with the simulated data, this technique is substantially slower than its non-iterative counterpart, and given the very large number of spatial distributions required in the present analysis, the use

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of the simpler technique was enforced. In the case of zero chain-plane attraction, the quantitative and qualitative dependence of the component structures upon chain length are compared with the previously reported Monte Carlo analysis (Croxton 1986a); we also make comparative assessments with earlier analyses reported in the literature, in particular the recent off-lattice MC simulations of Higuchi *et al* (1983), the lattice-based statistics of Lal and Stepto (1977) and the non-numerical analyses of Roe (1965a, b) and Chan *et al* (1975).

A comparison of the C and IC approximations in the context of the Monte Carlo determinations has already been reported (Croxton 1983, 1986a). For present purposes a comparison of the C segment density distribution $\rho_C(z|N)$ normal to the boundary and the Monte Carlo data is appropriate. We have seen, for example (Croxton 1983, figure 2, Croxton 1986a, figure 2(*b*)), that both the C and IC distributions are somewhat collapsed towards the boundary with respect to the Monte Carlo distributions, although $\rho_{IC}(z|N)$ is in better overall agreement. In particular $\rho_C(z|N)$ substantially overestimates the desorbed component of the distribution (tails) resulting in a depletion of states in the vicinity of the boundary (loops, trains). Consequently, we anticipate from the outset an underestimate of the adsorbed components—loops and trains—- and an overassignment to the tail states. Whilst we believe the IC approximation would provide some appropriate reassignment of the component structures, such calculations would be prohibitively time-consuming. The present determinations are therefore conducted on the basis of the C approximation.

We adopt the same approach outlined in an earlier publication (Croxton 1983) wherein the effect of a rigid plane is introduced by allowing the diameter of the first segment $\sigma_0 \to \infty$, whilst the remaining sequence of segments $(1, \ldots, N)$ constitutes the chain proper. It was found that the configurational properties of the chain rapidly approached an asymptotic form with increasing σ_0, and in practice $\sigma_0 = 64$; $\sigma_1, \ldots, \sigma_N = 1$ was adopted.

Here the contiguous properties of the chain are expressed in terms of a binary representation wherein 1(0) represents contact (non-contact). Thus [1000011100] represents a 10 segment chain arising with probability $P^{[1000011100]}$, in which

$$\begin{array}{c} \text{train} \\ [1\underbrace{0000}\overbrace{111}\underbrace{00}]. \\ \text{loop} \quad \text{tail} \end{array}$$

Segment 1 is terminally attached to the boundary, segments 2-5 constitute a loop, segments 6-8 a train and segments 9 and 10 a tail. Loops may be readily identified as internal sequences of zeros, trains as sequences of ones and tails as terminal sequences of zeros. More particularly, the complete set of possible configurations adopted by the terminally attached chain may be enumerated in the form of a binary tree in which contact/non-contact is represented by an upward/downward branch, respectively.

Associated with a given binary branch of i bits, $[i]$, the probability $P^{[i]}$ is determined as follows. The normalised spatial distribution $Z(Oi|N)$ of segment i with respect to the boundary O may be resolved into contact/non-contact zones as shown in figure 1. Here we adopt the contact criterion

$$\begin{aligned} r_{Oi} &\leqslant \tfrac{1}{2}(\sigma_0 + \sigma_i) + \zeta \qquad \text{contact} \\ r_{Oi} &> \tfrac{1}{2}(\sigma_0 + \sigma_i) + \zeta \qquad \text{non-contact} \end{aligned} \tag{1}$$

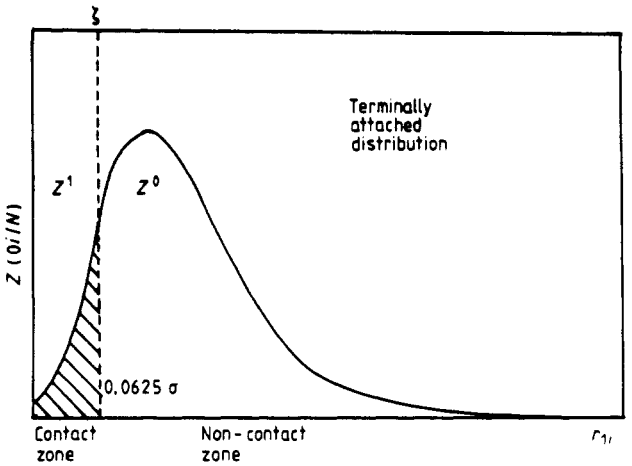

Figure 1. Resolution of the normalised spatial distribution $Z(Oi|N)$ into contact $Z^1(Oi|N)$ and non-contact $Z^0(Oi|N)$ components. The contact zone is arbitrarily set to be within $\sigma_1/16$ of the boundary plane.

with $\zeta = 0.0625\sigma_i$ which is necessarily fairly stringent if an adequate resolution of loop, train and tail processes is to be made, and this corresponds closely with the criterion for adsorption used in lattice calculations. However, Higuchi *et al* (1983) point out the effect of an arbitrary choice of ζ upon the resolution of the sequence into loop, train and tail states, and investigate a range $3.641\sigma_i \leqslant \zeta \leqslant 0.037\sigma_i$ in their Monte Carlo simulations. As these authors point out, a meaningful choice of ζ is possible only for thinly absorbed sequences which is fortunately the case for our relatively short chains: our choice of $\zeta = 0.0625\sigma_i$ closely corresponds to the most stringent criterion investigated by Higuchi *et al.* Undoubtedly substantially broader choices for the contact zone would result in a fundamental reassignment of states, and this is precisely the conclusion of these authors. The spatial distribution of the ith particle is, of course, sensitively dependent upon the configuration of the preceding sequence; this is indicated explicitly by writing $P^{[i-1,1]}$ and $P^{[i-1,0]}$ respectively, given a specific preceding sequence $[i-1]$ represented as a specific pathway through the tree to the current node.

These conditional probabilities $P^{[i]}$ are determined from the spatial distributions as follows (Croxton 1979a, b, c, 1983):

$$Z^{[i-1,i]}(Oi|ON) = Z^{[i-1,i]}(Oi|0, N-1)\int Z(i, N|1, N)H(0, N)\,\mathrm{d}\boldsymbol{N} \tag{2}$$

which, once normalised, enables the contact/non-contact probabilities to be determined (equation (4)). $H(ij) = \exp(-\Phi(ij)/kT)$, where $\Phi(ij)$ is the interaction potential between segments i, j. The convolution recursively regresses through the factor $Z^{[i-1,i]}(Oi|0, N-1)$ to the end-to-end distribution

$$Z^{[i-1,i]}(Oi|0, 1) \equiv Z^{[i-1,i]}(Oi)$$

where

$$Z^{[i-1,i]}(Oi) = H(Oi)\int Z^{[i-2,i-1]}(0, i-1)\delta(i-1, i)\mathrm{d}(\boldsymbol{i-1}). \tag{3}$$

The δ bonds in (3) ensure the sequential connectivity of the chain (Croxton 1979a, b, c, 1983). Thus $Z^{[i-1,i]}$ recursively regresses through a specific contact/non-contact

sequence $Z^{[i-2,i-1]}, \ldots, Z^{[1]}$ which are established through equations analogous to (2) and embody the convolution of the appropriate sequence of contact/non-contact functions. We draw the reader's attention to the fact that the probabilities estimated here are unconditional with respect to the subsequent configurations adopted by particles $(i+1, \ldots, N)$.

The conditional probability of contact, then, of the ith segment in an N-mer, given the preceding configuration $[i-1]$ is

$$P^{[i-1,1]}(Oi|N) = \int_{\frac{1}{2}(\sigma_0+\sigma_i)}^{0.625\sigma_i+\frac{1}{2}(\sigma_0+\sigma_i)} Z^{[i]}(Oi|0, N)\, \mathrm{d}r_{Oi} \tag{4}$$

and of non-contact

$$P^{[i-1,0]}(Oi|N) = 1 - P^{[i-1,1]}(Oi|N).$$

Since all configurations of the chain are represented on the binary tree, it follows that the probabilities at each order sum to unity, i.e. for a terminally attached 3-mer

$$P^{[111]} + P^{[110]} + P^{[101]} + P^{[100]} = 1$$

and in general

$$\sum_{\substack{\text{all} \\ \text{complexions } i}} P^{[i]} = 1 \tag{5}$$

which represents a criterion for the correct normalisation of the distributions. Finally, the conditional probabilities (4) and (5) relate to the contact probabilities of the ith segment: the probability of a particular configuration adopted by an N-mer is taken to be the product of the individual segment probabilities within the sequence

$$P^{[N]}(ON|N) = \prod_{i=2}^{N} P^{[i-1,i]}(Oi|N). \tag{6}$$

Insofar as the $P^{[i-1,i]}$ are conditional upon the structure of the preceding sequence, the product (6) only partially accounts for the interdependence of configurations and its use may be only justified *a posteriori*. However, (6) is likely to be a less serious approximation when configurations are primarily in the same classification (e.g. primarily tails). On the basis of Monte Carlo analyses (Croxton 1986a) we find that tails do account for the overwheming majority of configurations, at least for the case of zero chain-plane attraction.

2. Results

The development of loops, trains and tails within the chain are determined on the basis of systematic searches throughout the binary tree. As mentioned earlier, loops are identified as internal sequences of zeros, trains as sequences of ones and tails as terminal sequences of zeros. For any particular configuration we require their lengths to satisfy

$$l_{\text{loop}} + l_{\text{train}} + l_{\text{tail}} = l_{\text{chain}}. \tag{7}$$

This is achieved provided we measure the lengths in terms of *links* rather than segments. Thus, for the 10 segment (9 link) configuration [1000011100] we have $l_{\text{loop}} = 5$, $l_{\text{train}} = 2$, $l_{\text{tail}} = 2$, summing to 9 as it should.

A *particular configuration* $[N]$ of the N-mer will arise with probability $P^{[N]}(ON\,|\,N)$ (equations (4) and (5)) and, in general, be characterised by a number $n^{[N]}_{\text{loops}}$ of loops and $n^{[N]}_{\text{trains}}$ of trains. Moreover, the configuration $[N]$ will have a total length of loops $L^{[N]}_{\text{loops}}$ and a total train length $L^{[N]}_{\text{trains}}$. Appropriately weighting and averaging over all configurations $[N]$ yields the expectation or average quantities

$$\begin{aligned}\langle n_{\text{loops}}\rangle &= \langle n^{[N]}_{\text{loops}} P^{[N]}(ON\,|\,N)\rangle_{[N]} \\ \langle L_{\text{loops}}\rangle &= \langle L^{[N]}_{\text{loops}} P^{[N]}(ON\,|\,N)\rangle_{[N]}\end{aligned} \tag{8a}$$

and

$$\begin{aligned}\langle n_{\text{trains}}\rangle &= \langle n^{[N]}_{\text{trains}} P^{[N]}(ON\,|\,N)\rangle_{[N]} \\ \langle L_{\text{trains}}\rangle &= \langle L^{[N]}_{\text{trains}} P^{[N]}(ON\,|\,N)\rangle_{[N]}\end{aligned} \tag{8b}$$

where $\langle \ldots \rangle_{[N]}$ denotes a weighted average over the set of configurations $[N]$. The average loop length within the chain then follows as $\langle L_{\text{loops}}\rangle/\langle n_{\text{loops}}\rangle$ and similarly for trains $\langle L_{\text{trains}}\rangle/\langle n_{\text{trains}}\rangle$, designated $\langle l_{\text{loops}}\rangle$ and $\langle l_{\text{trains}}\rangle$ respectively.

A tail, on the other hand, either does or does not terminate a configuration $[N]$ and accordingly is or is not included in the expectation probability of tail formation:

$$\begin{aligned}\langle n_{\text{tail}}\rangle &= \langle P^{[N]}(ON\,|\,N)\rangle_{[N]} \\ \langle l_{\text{tail}}\rangle &= \langle L^{[N]}_{\text{tail}} P^{[N]}(ON\,|\,N)\rangle_{[N]}.\end{aligned} \tag{8c}$$

Finally, the percentages of segments within a given sequence length involved in loop, train and tail formation are determined. These quantities will be of particular use in a comparative assessment of earlier results of Roe (1965a, b) and Simha *et al* (1953).

We consider the results for three kinds of encounter separately below, each for the contact criterion $\zeta = 0.0625\sigma_i$. In particular, we investigate the development of tails, loops and trains at the boundary as a function of segment-plane attraction (Croxton 1983):

$$\Phi(Oi) = -\varepsilon^*\left(\frac{\sigma_{0i}}{r_{0i}}\right)^6 \qquad (i \geqslant 2) \tag{9}$$

where $\sigma_{0i} = \frac{1}{2}(\sigma_0 + \sigma_i)$ and $\varepsilon^* = 0, 1, 2, 5$, representing progressively a more attractive chain-plane attraction. The geometrical features of hard-sphere interaction are preserved within the chain itself. Unfortunately, there is considerable parametric diversity between the present calculations and the Monte Carlo estimates of Higuchi *et al* (1983) and Lal and Stepto (1977), and direct comparisons cannot be made. The latter authors, for example, consider tetrahedrally coordinated self-avoiding sequences on a regular lattice adsorbing from an athermal solvent and are investigated as a function of chain length and adsorption energy at the basal face of the half-lattice. The sequences are freely rotating with no *trans-gauche* conformational energy difference. Their reduced contact energies of $\varepsilon^* = 0.5, 0.9$ lie within our parametric range of interaction energies. However it should be emphasised that their sequences are not terminally attached, and direct geometrical comparisons between fixed valence bond angle and perfectly flexible sequences is not possible, even for the same number of links.

The chain-plane interaction of Lal and Stepto develops only upon contact with the basal plane which may be regarded as 'sticky' ; our analysis and the MC estimates of Higuchi *et al* (1983) both utilise more realistic continuous interactions. However these latter authors assume an inverse cubic distance dependence for the segment-plane interaction. As Higuchi *et al* observe, for the range of reduced contact energies

investigated, the chain statistics are generally insensitive to the range of solvent parameters investigated and are irrelevant for present purposes.

As we have shown elsewhere (Croxton 1983), geometric attrition of the accessible configurations of the chain in the immediate vicinity of the boundary is responsible for an entropic rise in the excess free energy of the chain μ, taking the form of an effective repulsion away from the boundary. In the case of an attractive boundary, this positive excess free energy may be partially offset and ultimately reversed for sufficiently attractive interaction parameters. However, for the range investigated ($0 \leqslant \varepsilon^* \leqslant 5$), the *gradient* of the free energy ($\mathrm{d}\mu/\mathrm{d}z$) at the boundary is always negative: in other words, in the immediate vicinity of the boundary repulsive entropic effects are responsible for a small rise in the excess free energy as the chain approaches the boundary, even though the excess free energy itself may be negative. Since μ must be zero at large distances from the boundary, it follows that the free energy passes through a local minimum in the vicinity of the boundary, and this has been observed in a variety of previously reported systems (Croxton 1983), where it is responsible for the location of the principal peak in the segment density distribution, $\rho(z|N)$.

In the case of terminally attached hard-sphere sequences and zero chain-plane attraction, we anticipate the preferential formation of tails rather than loops since the latter implicitly presuppose the existence of adsorbed sequences. However, with increasing chain-plane attraction, entropic repulsion is progressively offset, predisposing the system towards a closer association with the plane, largely at the expense of tails. Indeed, the minimum in the free energy for all $\varepsilon^* > 1$ favours the formation of *loops* rather than adsorbed trains, although adsorption will undoubtedly increase with increasing attraction. Tails, however, continue to represent the major component of the interfacial structure for the range of chain-plane attraction investigated here.

We now analyse the three classes of encounter with the plane—tails, loops and trains—in terms of these preliminary considerations.

2.1. Tails

The configurational structure of a terminally attached self-avoiding chain is primarily determined by the tail component, at least for $\varepsilon^* = 0$ (Croxton 1986a), and this appears to be confirmed experimentally for polyethylene oxide chains terminally anchored on polystyrene latex (Cosgrove *et al* 1983, Cosgrove and Vincent 1986). For weak chain-plane attraction entropic processes ensure the total desorbtion of the terminally attached sequence, and this concurs with the $\varepsilon^* = 0.5$ MC data of Lal and Stepto. With increasing attraction, however, a redistribution of tails → loops occurs, as is clearly apparent from figure 2, in agreement with the observations of Lal and Stepto. Unfortunately, Higuchi *et al* report loop, train and tail distributions only for $\varepsilon^* = 2.83$, their strongest interaction parameter. Both continuum analyses agree that $\langle l_{\text{tails}} \rangle$ increases linearly with chain length (adopting Higuchi's most stringent contact criterion $\zeta = 0.037\sigma_i$) even for the most attractive chain-plane interactions investigated. Whilst a similar lattice result is obtained by Lal and Stepto for $\varepsilon^* = 0.5$, their $\varepsilon^* = 0.9$ result is virtually independent of chain length. This difference in behaviour we attribute to the 'all-or-nothing' interaction at the 'sticky' basal plane adopted by these authors against the continuous interactions assumed in the presence and MC analyses. Undoubtedly the Metropolis sampling is very different in the two cases, and in the case of strongly attractive lattice plane interactions samples will be strongly biased in favour of adsorbed rather than desorbed structures.

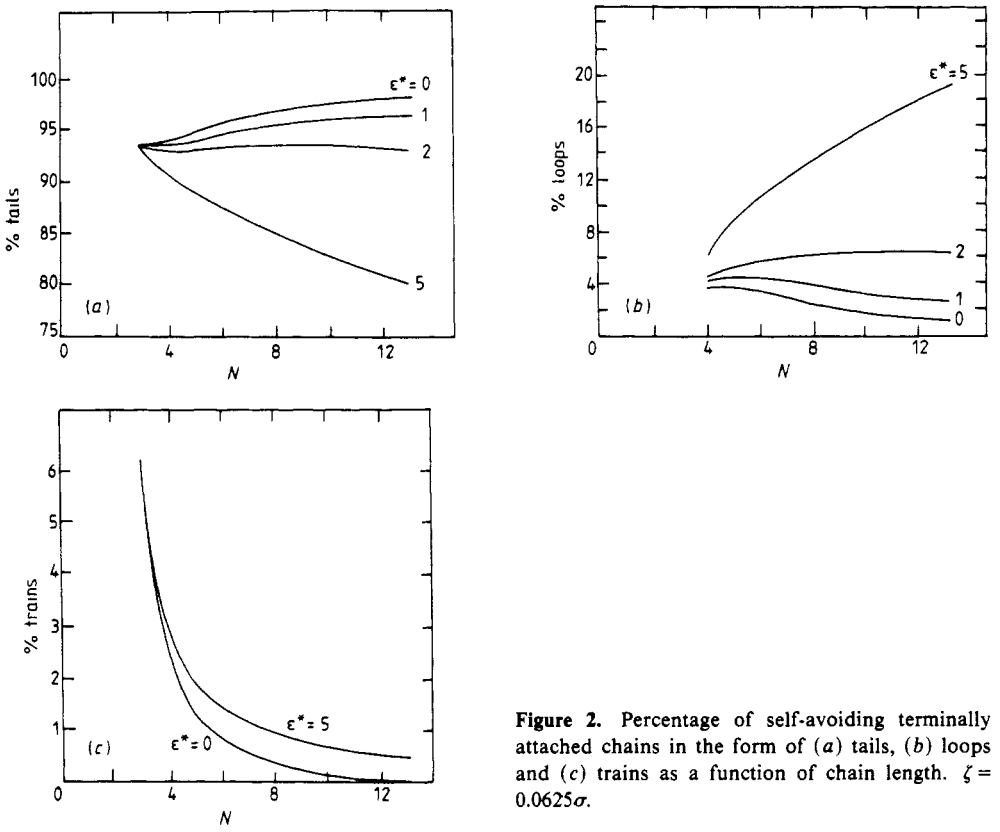

Figure 2. Percentage of self-avoiding terminally attached chains in the form of (*a*) tails, (*b*) loops and (*c*) trains as a function of chain length. $\zeta = 0.0625\sigma$.

The results of the continuum analyses corroborate Roe's (1965a, b) analysis based on a divergent generalised partition function method, initially adapted for a chain molecule by Lifson (1964). It should be noted, however, that Roe's analysis neglects the excluded volume effect, except for the nearest-neighbour interaction at the junction between adsorbed and desorbed sequences. Clearly, theories which subordinate the presence of tails would appear incapable of providing an adequate description of the configurational behaviour of finite length sequences (Simha *et al* 1953).

For weak chain-plane attraction ($0 < \varepsilon^* < 1$) we see that the fraction of the terminally attached chain in the form of tails increases with chain length N: virtually the entire sequence is in the form of totally desorbed chain with almost negligible probability of loop and/or train formation (figure 2(*a*)), and in this case the lattice and continuum analyses agree. The attrition in chain conformation involved in returns to the plane develops rapidly with N, and the associated free energy penalty ensures a growing fraction of the sequence in the form of tails with increasing chain length. Indeed, the thickness of the polymer layer is attributable almost entirely to the tail component. Roe (1965a) estimates that upwards of 70% of the sequence exists in the form of tails for all but the most strongly attractive chain-plane interactions. Whilst our estimate is somewhat higher, we point out that Roe neglects excluded volume effects which would be expected to further delocalise the sequence. However, we have anticipated from the outset that the convolution approximation consistently overestimates the tail contribution at the expense of the adsorbed components. Nevertheless, both lattice and continuum analyses report an essentially linear dependence of

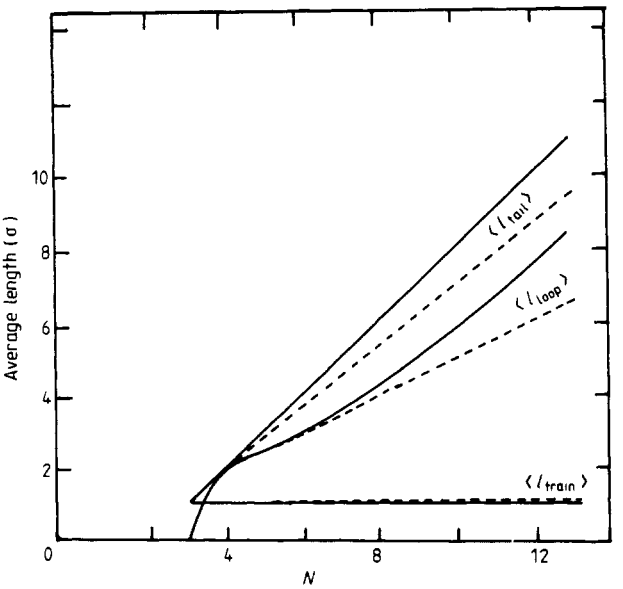

Figure 3. Average length of loops, trains and tails as a function of chain length for terminally attached sequences. Full curve: $\varepsilon^* = 0$; broken curve: $\varepsilon^* = 5$. $\zeta = 0.0625\sigma$.

$\langle l_{train} \rangle$ upon chain length, and moreover appear relatively insensitive to the range of ε^* investigated (figure 3).

2.2. Loops

For purely hard-sphere self-avoiding encounters with a rigid non-attracting plane ($\varepsilon^* = 0$), the effective entropic repulsion developed between the chain and plane predisposes the system towards the formation of tails and against loops and trains, particularly the latter. The specification of a loop presumes the existence of one or more energetically unfavourable returns to the plane, and consequently the percentage of chains in loop form steadily decreases with increasing chain length (figure 2(*b*)). The configurational attrition in forming a loop within a sequence of given length is least for loop lengths of minimum and maximum size, and accordingly we anticipate that the free energy penalty predisposes the system against the formation of loops of intermediate size—a result confirmed in the Monte Carlo analysis reported below.

With increasing chain-plane attraction however, returns to the plane either in the form of singly adsorbed segments or (much less likely) as trains are somewhat more highly favoured at the expense of tails and, in conjunction with the local minimum in the excess free energy in the vicinity of the boundary, the system is slightly more disposed towards the formation of loops (figure 2(*b*)). Whilst the average size of a loop grows steadily with chain length (figure 3), it nevertheless appears relatively insensitive to the interaction parameter ε^*, suggesting that over the range of interaction investigated, loop size is primarily determined on the basis of geometrical attritional considerations. Even so, the loop fraction increases by almost one order of magnitude as $\varepsilon^* = 0$–5 for the longest chain lengths investigated. Monte Carlo simulations ($\varepsilon^* = 0$; Croxton 1986a) revealed a bimodal distribution of loop lengths within a given sequence length: loops of maximal and minimal size would tend to develop, rather than those of intermediate length. This predisposition of the system has been discussed in terms

of configurational attrition of the sequence (Croxton 1986a) and results in a progressive increase in loop size with N. The weakly attracted tetrahedral sequence of Lal and Stepto ($\varepsilon^* = 0.5$) coincides closely with our $\varepsilon^* = 0$ Monte Carlo estimate. For stronger attractions, the results of Lal and Stepto and of Higuchi *et al* reveal a very weak dependence of $\langle l_{\text{loop}} \rangle$ upon chain length; the convolution results show a considerably stronger, linear dependence upon N, although the dependence is evidently decreasing with increasing ε^*. As we observed from the outset, the convolution approximation is known to reassign train states in favour of loop, and to a lesser extent, tail states. This may well account for the unduly strong N dependence since $\langle l_{\text{loop}} \rangle = \langle L_{\text{loop}} \rangle / \langle n_{\text{loop}} \rangle$, and $\langle n_{\text{loop}} \rangle$ is consistently underestimated. Thus, whilst the current analysis suggests $\langle l_{\text{loop}} \rangle$ depends linearly upon N for the range of ε^* investigated, Roe finds an $N^{1/2}$ dependence which concurs with our Monte Carlo ($\varepsilon^* = 0$) and the lattice-based ($\varepsilon^* = 0.5$) results.

2.3. *Trains*

The system appears strongly predisposed against the formation of trains over the range of ε^* investigated, and this is attributed to the negative spatial gradient of the excess free energy ($\mathrm{d}\mu/\mathrm{d}z$) in the immediate vicinity of the boundary. Whilst for $\varepsilon^* > 1$ the sequence may form a loose association with the plane as discussed above, nevertheless the chain is essentially desorbed and the percentage of chain length decreases rapidly with N. In fact, an asymptotic percentage of trains $\leqslant 0.5\%$ appears to be achieved by $N \sim 10$ over the range of ε^* investigated (figure 2(c)). Most interestingly, the average length of train appears virtually independent of chain length and increases slightly only for the strongest chain–plane attraction (figure 3), concurring with the results of Lal and Stepto. Whilst we have emphasised the present approximation underestimates $\langle n_{\text{trains}} \rangle$ in favour of $\langle n_{\text{tails}} \rangle$ (defined in equation (8)), trains when they do occur invariably consist of one segment only, and so $\langle l_{\text{train}} \rangle = \langle L_{\text{train}} \rangle / \langle n_{\text{train}} \rangle$ remains correctly estimated for the range of attractions investigated here. The present convolution estimates and the lattice-based and continuum Monte Carlo analyses are in total agreement regarding the very weak dependence of $\langle l_{\text{train}} \rangle$ upon N and ε^*. It is important to realise, however, that the criterion for resolution of close encounters with loops and trains will strongly influence the apparent behaviour of the system, and this is discussed in some detail by Higuchi *et al* (1983). In the present case the width of the zone ζ within which segments are considered as adsorbed is 0.0625 of a segment diameter (equation (1)). Clearly, a less stringent criterion would regard many of the loop segments as being adsorbed, whereupon a certain redistribution of percentages between figures 2(b) and 2(c) would occur, although we find the qualitative modification to be relatively small for the narrow range investigated in the Monte Carlo analysis ($\zeta = 0.0078\sigma, 0.0625\sigma$). Nevertheless, the growth in average loop length $\langle L_{\text{loop}} \rangle / \langle n_{\text{loop}} \rangle$ (equation (8)) with N would be partially transferred to the average length of trains. A consideration of the $Z(Oi \mid N)$ distribution function, however, shows that any qualitative modification of these conclusions would require the contact zone $Z^1(Oi)$ to be sufficiently broad as to include a significant component of the non-contact $Z^0(Oi)$ structure which is more highly sensitive to both ε^* and N (Higuchi *et al* 1983). Notwithstanding these observations, we note from figure 2(c) that the average *number* of trains $\langle n_{\text{trains}} \rangle$ increases by almost one order of magnitude as $\varepsilon^* = 0 \rightarrow 5$.

As we have seen, most of the segments of the terminally attached polymer extend into the solution phase in the form of tails rather than loops, in agreement with the

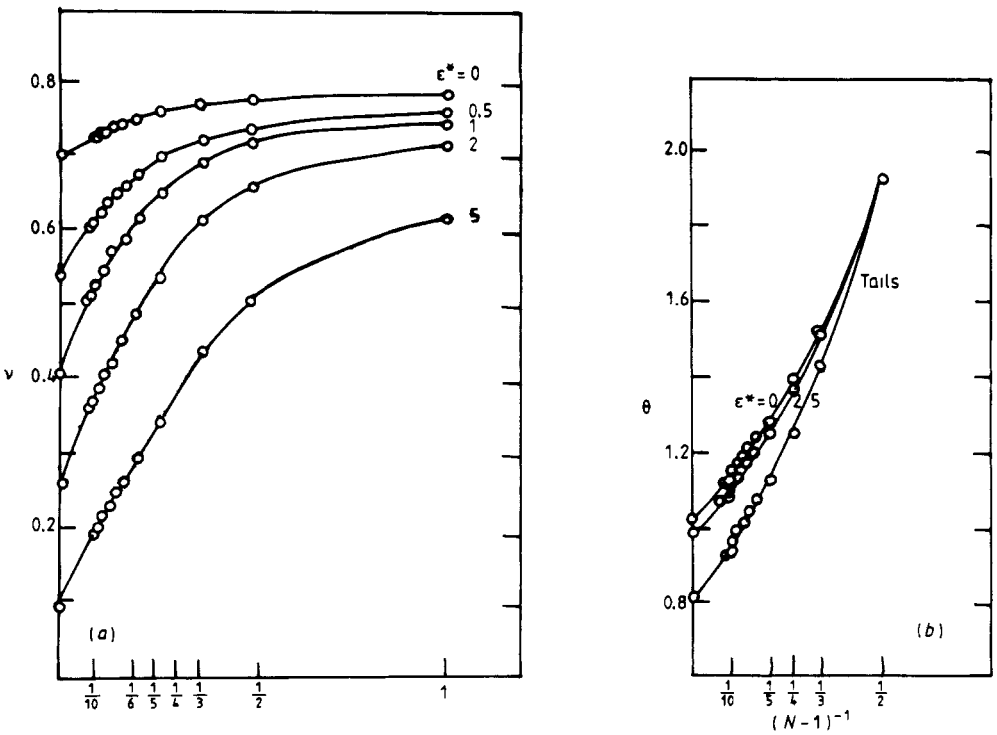

Figure 4. Quadratic fit to calculated points (○) showing asymptotic development of the exponent as a function of chain length N and interaction parameter ε^* for (a) thickness of adsorbed layer and (b) tails. $\zeta = 0.0625\sigma$.

conclusions of Roe (1965), Cosgrove *et al* (1983) and Cosgrove and Vincent (1986), but in direct contradiction to those of Simha *et al* (1953). The thickness $\langle z \rangle$ of the adsorbed layer may be related to the number of links $(N-1)$ in the N-mer by an exponent relation $\langle z \rangle \propto (N-1)^{\nu(\varepsilon^*)}$ where $\nu(\varepsilon^*)$ is dependent upon the interaction parameter. In figure 4(a) we show a least-squares quadratic fit to the convolution data, and form limiting estimates $(N \to \infty)$ of the exponent $\nu(\varepsilon)^*$. We see that the exponent steadily decreases with increasing attraction ($\nu(0) \sim 0.7$; $\nu(5) \sim 0.1$) as the sequence progressively compacts against the boundary. These results are consistent with the conclusions of Silberberg (1962) who found $\nu = 0$ for strong attraction (large ε^*) and with Simha *et al* (1953) who found $\nu = 0.5$ for weak attraction. Indeed, our MC data (Croxton 1986a) suggest $\nu \sim 0.5$ for the case of zero chain-plane attraction. The analysis of Chan *et al* (1975) based on a generating function method for the partition function also obtains exponents of 0 and 0.5 for strong and weak attraction, respectively. Certainly our estimates of the exponents are slightly higher than those of earlier analyses, but this may arise from our inclusion of excluded volume behaviour within the sequence, which the others neglect.

The zero growth in thickness of the boundary layer with increasing attraction reflects the lateral spreading of the sequence across the boundary, and this is confirmed both by our estimates of the mean square end-to-end distance $\langle R_{1N}^2 \rangle$ and the estimates of Chan *et al* which reflect a linear dependence upon N appropriate to a two-dimensional lateral spreading of the chain.

Again, the results of Higuchi *et al* reveal the N independence of the mean thickness in the case of strong attraction, and they also observe an insensitivity to solvent condition.

A similar exponent analysis $\langle l_{\text{tail}} \rangle \propto (N-1)^{\vartheta(\varepsilon^*)}$ for the N dependence of the length of tails is shown in figure 4(b), whilst the analogous exponent for trains $\eta(\varepsilon^*)$ we find to be $\sim 1, 0$ for strong and weak attraction respectively, suggesting the existence of a critical value of ε^* corresponding to adsorption/desorption. This kind of behaviour is apparent from the lattice data of Lal and Stepto and is precisely the behaviour described by Chan *et al.* Since Higuchi *et al* report $\langle l_{\text{train}} \rangle$ for only their strongest chain-plane attraction it is not possible to determine any dependence upon ε^*. However, with the predisposition towards lateral growth rather than normal extension from the boundary of strongly attracted sequences, the kind of behaviour observed in $\eta(\varepsilon^*)$ is as expected, with energetic and entropic processes dominating the large and small ε^* behaviour, respectively.

The exponents $\nu(\varepsilon^*)$, $\vartheta(\varepsilon^*)$ show a systematic decrease in magnitude with increasing chain length, and for small ε^* are fully consistent with Roe's (critical) values of $\nu_c = 0.5$, $\vartheta_c = 1.0$ and $\eta_c = 0$. Roe identifies the critical condition as one for which a weak chain-plane attraction counters entropic repulsion at the plane, yielding a zero excess free energy. We have shown elsewhere (Croxton 1983) that the excess free energy is zero in the immediate vicinity of the boundary for $\varepsilon^* \sim 0.5$ on the basis of the present interaction (equation (9)), corresponding to weak chain-plane attraction.

We see that the competing agents of energy (adsorption) and entropy (desorption) cancel *at the boundary* for $\varepsilon^* \sim 0.5$. We cannot, however, identify a unique 'theta point' at which exclusion and attrition processes cancel throughout the system as, for example, has been assumed by Silberberg (1962) in making a uniform assignment of $-k \ln 2$ to the entropy of adsorption per segment.

Roe does, however, find a critical value of the interaction parameter for which a half-power law is obeyed: $\nu = 0.5$. We find that for $1 > \varepsilon^* > 0.5$ the thickness of the adsorbate does obey a half-power law as Chan *et al* (1975) also found. It should be remembered that the analyses of Roe (1965a, b), Chan *et al* (1975), Silberberg (1962) and Simha *et al* (1953) neglect self-interference within the chain, resulting in substantially more consolidated structures at the boundary. It follows that critical behaviour is contingent upon cancellation of energy and entropy effects *at the boundary* whilst for the relatively more expanded structures reported here that a net cancellation over the thickness of the adsorbate represents the closest approach to critical behaviour. Incidentally, the consolidation of boundary structures in the absence of excluded volume concurs with McCracken's (1967) results based upon computations of terminally attached chains with attractive segment-surface interactions. Finally, in figure 5 we show the development of the mean sizes of loops, trains and tails for a self-avoiding chain, terminally attached to a rigid plane, as a function of length and chain-plane attraction. The results appear qualitatively similar to previously obtained excluded volume (Lal *et al* 1975) and random walk (Roe 1965a) sequences in the adsorbed states. The mean length of loops and tails exhibits an essentially linear decrease with increasing chain-plane attraction, whilst the size of trains shows a very gradual increase. For very strong attractions the loop and tail curves must asymptotically approach the train curve which ultimately must increase. However, entropic processes at the boundary will ensure that there will always remain loop and tail components, even for the strongest attractions.

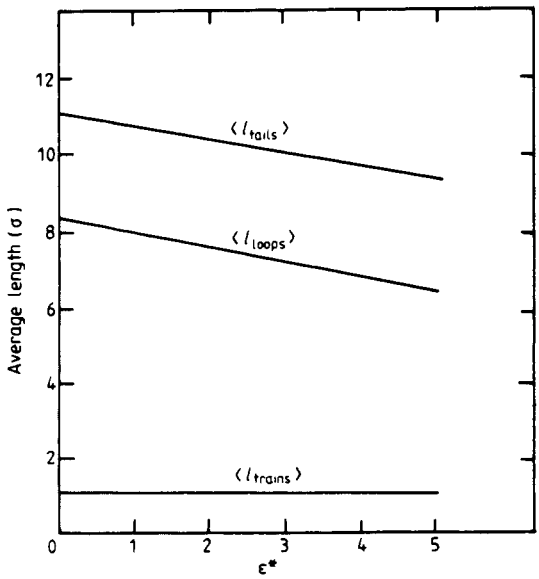

Figure 5. Average lengths of loops, trains and tails for a self-avoiding terminally attached sequence of thirteen segments as a function of chain-plane attraction.

2.4. Monte Carlo resolution of boundary structures

Unfortunately no strictly comparable Monte Carlo simulations are available with which to compare the results of the convolution approximation. Features associated with the continuum nature of the sequence and the use of continuous interaction functions obviously cannot be tested on the basis of the lattice statistics of Lal and Stepto. The continuum Monte Carlo analysis of Higuchi *et al*, whilst appropriate to the present investigation, is nevertheless somewhat preoccupied with the effect of the adsorption criterion ζ upon the resolution into loop, train and tail components rather than their dependence upon N and ε^*. A detailed MC analysis of terminally attached sequences as a function of (N, ε^*) is not yet available, although discussion in terms of the $\varepsilon^* = 0$ results is possible (Croxton 1986a).

This latter investigation revealed that the short range segment density distribution $\rho(z|N)$ normal to a rigid boundary shows a rapid rise, falling discontinuously at $z = 1$. This suggests that the resolution of adsorbed sequences will be sensitively dependent upon the contact criterion. Accordingly we investigate two values for the contact zone: $\zeta = 0.0078\sigma$ and 0.0625σ. Clearly, the former represents a more stringent criterion of adsorption than the latter. (For a detailed appraisal of the ζ dependence, see Higuchi *et al* (1983).)

On the basis of these criteria, all successful configurations generated in the course of the simulation were resolved into loops, trains and tails. The mean length dependence upon N for each classification is shown in figure 6 from which we conclude that the mean lengths are relatively insensitive to the current range of contact criteria. Comparison with the calculated quantities (figure 3) is in good agreement with tails and trains ($\varepsilon^* = 0$), though the MC loops appear to show a rather weaker N dependence.

Assuming exponent relations of the form

$$\langle l_{\text{loops}} \rangle \sim (N-1)^{\xi}$$

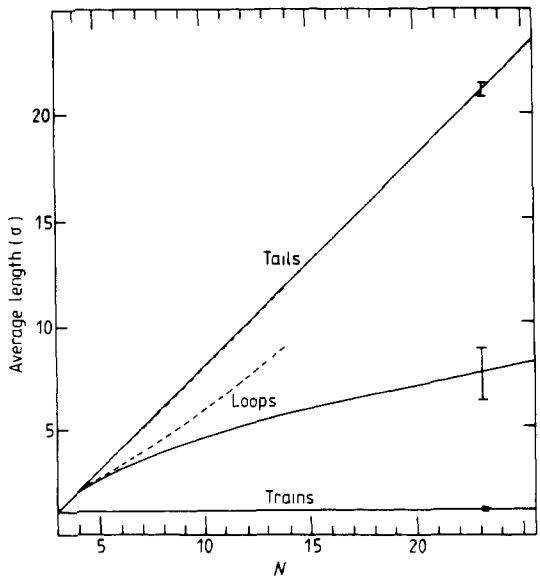

Figure 6. Monte Carlo estimates of the mean length dependence of loops, trains and tails upon N (cf figure 3; $\varepsilon^* = 0$, based on the convolution approximation). Full curve: Monte Carlo; broken curve: convolution. $\zeta = 0.0625\sigma$.

$$\langle l_{\text{trains}} \rangle \sim (N-1)^{\eta}$$

$$\langle l_{\text{tails}} \rangle \sim (N-1)^{\vartheta}$$

we find from a least-squares quadratic fit to the MC data $\xi = 0.57$, $\eta = 0.00$ and $\vartheta = 1.00$. These values are in reasonable agreement with the values estimated on the basis of the convolution approximation, except for the loop component, and are consistent with Roe's (critical) estimates for a random flight sequence weakly attracted to a boundary ($\xi_c = 0.5$, $\eta_c = 0.0$, $\vartheta_c = 1.0$).

The fractional distributions of loops, trains and tails within the sequence as a function of chain length are shown in figure 7, and are seen to be in reasonable quantitative agreement with the calculated estimates (figures 2(a, b, c); $\varepsilon^* = 0$). Clearly there is a strong predisposition against the formation of trains which we attribute to entropic effects associated with configurational attrition in the vicinity of the boundary. Trains, if they occur at all, are rarely more than one link in length regardless of chain length, and the bound fraction decreases rapidly with N (cf figure 2(c)). Attrition in the number of chain configurations with adsorption of a single segment increases dramatically with the length of the sequence, and the associated free energy penalty ensures a decreasing fraction in the form of trains with increasing N. We note from figure 2(c) that even for relatively strong segment-boundary attractions ($\varepsilon^* = 5$) the development of trains, whilst increased with respect to $\varepsilon^* = 0$, nevertheless constitutes a subordinate component of the possible boundary structures.

Desorbed sequences in the form of loops and tails clearly represent the preferred configurations at the boundary, particularly the latter which account for over 95% of the observed structure ($\varepsilon^* = 0$, figures 2(a) and 7); these desorbed configurations derive from the segment-boundary entropic repulsion. We find that loops of maximal and minimal length are more probable than those of intermediate length within a given

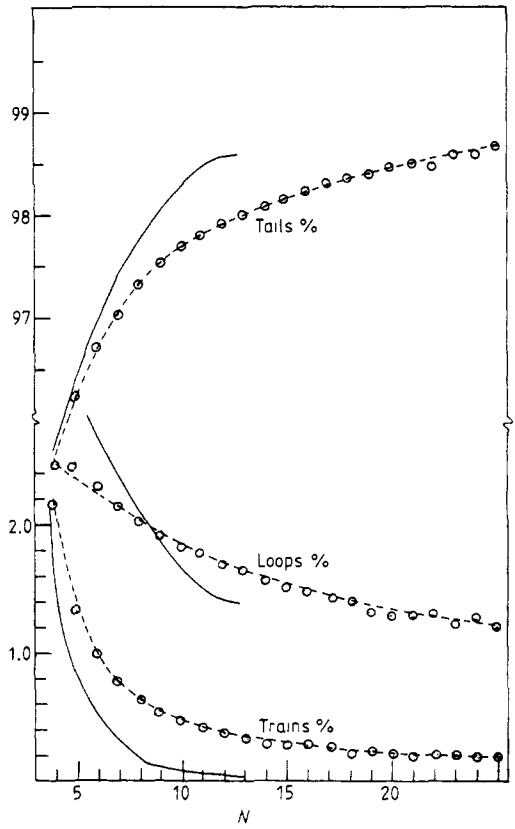

Figure 7. Monte Carlo estimates (○) of the fractional components of loops, trains and tails as a function of chain length (cf figure 2; $\varepsilon^* = 0$, based on the convolution approximation). $\zeta = 0.0625\sigma$.

sequence, and this is characteristic of all chain lengths simulated. The return of an intermediate segment to the plane effects a relatively greater attrition of chain configurations than does a return at either end of the sequence. Given the overall predisposition toward the formation of tails, short loops are favoured with respect to those of larger size. It may well be that this unusual bimodal distribution of loop lengths is partially responsible for the poor estimate of the N dependence of $\langle l_{\text{loop}} \rangle$ on the basis of the convolution approximation (figure 3).

We see from figure 7 that the fraction of the sequence in loop form decreases with increasing chain length for precisely the same reason as for trains, although somewhat less strongly.

As we anticipated in the introduction, the nature of the convolution segment density distribution $\rho_C(z \mid N)$ implies a depletion of states in the vicinity of the boundary (loops and trains) in favour of desorbed sequences. Just this reassignment of states is apparent from the component breakdown (figure 7) when compared with the Monte Carlo distribution. Clearly, the fraction of the chain in tail form is overestimated at the expense of the loop and train components, though good quantitative agreement is nevertheless obtained on the basis of the C approximation. Whilst we might expect some improvement using the iterative (IC) procedure, such calculations would be prohibitively time-consuming.

Acknowledgments

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