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Conformational properties of terminally attached and free-floating polymer chains confined between attractive plane boundaries

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Abstract. The internal spatial distributions of self-avoiding hard sphere sequences are determined for terminally attached and free-floating systems confined between two rigid boundaries of variable attraction and separation. In all cases the terminally attached distributions are characterised by a pronounced density discontinuity and internal structure, whilst the free-floating sequences form either mono- or biglobular coils, depending upon the details of attraction, temperature and boundary separation. The role of entropic and van der Waals contributions to the structure and excess free energy are clearly resolved, and their implications for colloidal stability against flocculation discussed. The mean square molecular span and centre of gravity are also determined as a function of chain length, interaction strength and boundary separation.

1. Introduction

In a previous series of papers (Croxton 1979a, b, c, hereafter referred to as I, II and III), a diagrammatic convolution approximation to the excluded volume problem in polymer chains was developed which, for relatively short sequences ($N \leqslant 20$), exhibited what was believed to be the correct qualitative behaviour for such systems. Subsequent investigations by other workers (e.g. Redner 1980) have confirmed in detail the conclusions drawn in that series of investigations. The qualitative effect of approximation in the model was readily assessable in terms of a progressive underassessment of the exclusion processes operating within the chain with increasing length. Here, to the same degree of approximation, we extend the analysis to the problem of a perfectly flexible chain of hard sphere segments confined between two rigid boundaries, one or both of which may be attractive, whilst the chain itself is either free-floating or terminally attached to one of the boundaries. At each stage we make a direct comparison with the random walk result which allows us to form a qualitative assessment of the nature and function of excluded volume processes operating within the chain, albeit partial in the present approximation. We investigate the segment density of the N-mer $\rho(z|N)_\delta$ along the normal z to the boundary as a function of the fixed separation δ (defined below) of the two boundaries, and the results are discussed in the context of stability against flocculation of colloidal systems.

We point out that analytic and exact enumeration analyses of self-avoiding sequences in the vicinity of a rigid boundary based on a discrete regular lattice necessarily embody a mapping relating the continuous and discrete distributions.

However, in the course of the mapping, essential qualitative features of the continuous distribution are forfeited: the continuous and discrete distributions are fundamentally distinct and bear no simple relationship to each other, and some reappraisal of the role of lattice-based representations of self-avoiding sequences may be necessary. Nevertheless, comparisons of the present convolution results are made with the lattice-based analyses, for whilst the spatial distributions are quite distinct, conformationally averaged quantities are somewhat less sensitive to the details of the distribution functions, and to that extent bear comparison with the continuum results reported here.

It should be appreciated that it is not our intention to describe the behaviour of asymptotically long sequences, although the initial features associated with self avoidance should already be apparent for chains of intermediate length such as those considered here. This does not preclude comparison with the various exponent relations, however, although estimates of their limiting behaviour as $N \to \infty$ are clearly inappropriate. More important is a demonstration of the versatility and simplicity of the model, and its ability to make qualitative predictions of the properties of short to intermediate self-avoiding sequences with readily assessable physical approximations. Comparisons will be made with a continuum Monte Carlo analysis of a 12-segment sequence.

The approach of a chain towards a rigid boundary, in particular its conformational modification and development of structural features, is a problem of considerable interest in a wide variety of chemical and biophysical applications, but has received relatively little attention in the literature. Accordingly, here we concentrate on the determination of the confined distributions $Z(N)_\delta$. We also investigate the mean square molecular span $\langle R_N^2 \rangle_\delta$ as a function of both δ and the number of segments N. Another important configurational quantity determined is the location of the centre of gravity of the chain, for both terminally attached and free-floating sequences. These quantities will be compared with other reported determinations. As the chain approaches the boundary, the geometrical constraint ensures that the number of accessible conformations decreases and an estimate is made of the conformational decrease in entropy of the system as the boundary is approached. This 'entropic pressure' may be interpreted in terms of an effective repulsion exerted by the boundary on the chain and a comparison with its random walk counterpart will be made.

2. The model

In two previous papers (I, II) the internal spatial distributions $Z(1i|1N)$, $Z(ij|1N)$ of the pairs of segments $1i$, ij in a chain of $1 \ldots N$ interacting segments were determined on the basis of a diagrammatic convolution approximation, as were the end-to-end distributions $Z(1N)$. In this treatment certain of the internal interactions are neglected, enabling the properties of longer sequences to be determined on the basis of convolutions of properties of shorter chains and enabling us to exploit fast Fourier transform techniques for their numerical evaluation. Whilst no adequate account of the excluded-volume problem has been given, the present approximation unambiguously represents an almost fully self-interacting chain whose qualitative status is intermediate between that of the random walk model and the fully self-interacting systems, although much more closely that of the latter. The approximation is of a physical rather than a mathematical nature, and as such enables us to form bounded estimates of the various configurational features of the chain.

In papers I and II the internal distributions $Z(jN|1N)$, $Z(ij|1N)$ in a hard sphere sequence of N segments are given as

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

$$Z(ij|1N) = Z(ij|1, N-1) \int Z(jN|2N)H(iN)\,\mathrm{d}\boldsymbol{N} \tag{2}$$

where H is the function

$$H(ij) = \exp[-\Phi(r_{ij})].$$

$\Phi(r_{ij})$ is the reduced intersegmental pair interaction (in units of kT) and r_{ij} the intersegmental separation.

We consider both athermal (hard-sphere) and non-athermal (van der Waals attraction) interaction with the plane. Thus, in the athermal case, we have in an obvious notation

$$\begin{aligned} \Phi(r_{ij}) &= +\infty \qquad r_{ij} \leqslant \tfrac{1}{2}(\sigma_i + \sigma_j) \\ &= 0 \qquad\quad r_{ij} > \tfrac{1}{2}(\sigma_i + \sigma_j) \end{aligned} \tag{3}$$

where σ_i, σ_j are the i, j segment diameters. The H function then adopts the form of a step function, confining the chain to the region δ between the two boundaries:

$$\begin{aligned} H(1j) &= 0 \qquad r_{1j} \leqslant \tfrac{1}{2}(\sigma_1 + \sigma_j) \geqslant \delta + \tfrac{1}{2}(\sigma_1 + \sigma_j) \\ &= 1 \qquad r_{1j} > \tfrac{1}{2}(\sigma_1 + \sigma_j). \end{aligned} \tag{4}$$

In the non-athermal case we take the chain to be an athermal self-avoiding sphere sequence of $(2, \ldots, N)$ segments, each one of which interacts with the plane through an attractive van der Waals function; thus

segment–segment

$$\begin{aligned} \Phi(ij) &= +\infty \qquad r \leqslant \tfrac{1}{2}(\sigma_i + \sigma_j) \\ &= 0 \qquad\quad r > \tfrac{1}{2}(\sigma_i + \sigma_j) \qquad (i \neq j > 1) \end{aligned}$$

segment–plane

$$\Phi(1i) = -\varepsilon^*(\sigma_{1i}/r_{1i})^6 \qquad (i \geqslant 2)$$

where ε^* is a reduced van der Waals interaction parameter. Five values of ε^* were investigated ($\varepsilon^* = 0, 0.5, 1, 2, 5$) representing progressively more attractive chain–plane interaction, whilst the geometrical features of hard sphere exclusion are preserved within the chain itself.

Sequential order and intersegmental separations are established by the specification of delta-function bonds between adjacent segments within the chain; equations (1) and (2) implicitly contain these sequential ordering bonds (see paper I). The effect of a plane boundary is simply achieved by allowing the diameter of the first hard sphere segment $\sigma_1 \to \infty$; in practice we have studied the development of the distributions over the range $\sigma_1 = 1 \to 64$, and have found (Croxton 1981) that the asymptotic forms of the distributions are rapidly achieved with increasing diameter σ_1. The remainder of the chain $(2, \ldots, N)$ is confined within the region δ. $Z(1i|1N)_\delta$ then represents the spatial distribution of the ith segment in an N-mer normal to the boundary for a

given fixed range of chain confinement δ (figure 1). Moreover, the sum of the normalised component distributions

$$\rho(z|N)_\delta = \sum_{i=2}^{N} Z(1i|1N)_\delta \tag{5}$$

represents the segment density normal to the surface of segment 1 for a chain sequence $(2, \ldots, N)$ given the fixed boundary separation δ.

For the calculation of the chemical potential of the chain we shall require the unnormalised configurational sum

$$A_N = 4\pi \int_0^\infty \sum_{j=3}^{N} Z(2j|1N) r_{2j}^2 \, \mathrm{d}r_{2j}. \tag{6}$$

A clear distinction must be drawn between the various distributions and parameters used in the specification of the conformation of the chain: these are illustrated in figure 1. Principally it should be recognised that the true chain consists of the sequence $(2, \ldots, N)$ (i.e. $N-1$ segments), whilst the first segment adopts the role of a 'planar' boundary.

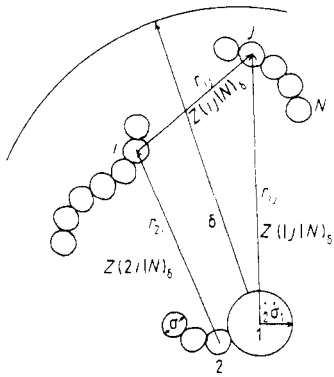


Figure 1. Geometry of the polymer-boundary systems and associated internal distributions $Z(ij|1N)_\delta$. The plane boundary configuration is achieved as $\sigma_1 \to \infty$.

The hierarchial series of linked equations (II, 6 and (II, 9) may be readily evaluated by fast Fourier transform techniques, and describe the *cumulative* interference of successive segments with the preceding sequence. We emphasise that the number of bonds or interactions omitted in this approximation at least in the specification of $\rho(z|N)_\delta$ and A_N is quite small for short to intermediate length chains. In the case of the end-to-end distributions, however, it should be noted that with increasing chain length N the fraction of neglected internal interactions increases: in other words the system tends towards the random walk result. However, for the sequence lengths under consideration here the role of excluded-volume effects is found to be substantial and accordingly we restrict our computations to chains up to 15 segments in length $(N = 16)$.

The random flight system is described exactly as a convolved sequence of uncorrelated bonds of fixed length, these representing the fixed step lengths of the random walk. The present model yields an exact description of random flight sequences when we set the interaction $H(ij) = 1$, corresponding to the complete absence of exclusion.

Comparison of analytic and the present numerical estimates for random flight quantities such as mean square end-to-end distances and radii of gyration agree to eight decimal places for isolated (free chain) sequences. This provides an assessment of the minimal numerical error engendered in the repeated convolutions for chains $N \leqslant 20$. We therefore make extensive comparison of the self-avoiding and random walk estimates at the rigid boundary, and believe the comparison to be significant from the point of view of the role of geometric processes operating within the system.

3. Results

3.1. Terminally attached sequences

The segment density distribution $\rho(z|N)_{\delta=1.5}$ for a terminally attached chain (segment 2 in contact with 1) has been determined (Croxton 1981) for a range of $\sigma_1 = 1, 16, 32, 64$; $\varepsilon^* = 0$ on the basis of which we conclude that the qualitative form of the $\sigma_1 = 64$, $\varepsilon^* = 0$ distribution is essentially that of the plane boundary problem corresponding to $\sigma_1 = \infty$. Accordingly, we set $\sigma_1 = 64$ throughout all subsequent computations. We point out that these observations relate to essentially *geometrical* effects, and remain unmodified by the subsequent application of an attractive chain-plane interaction. Nevertheless, it must be said that notwithstanding the use of a relatively large diameter σ_1, the volume elements in the region δ accessible to the chain retain *conical* rather than cylindrical symmetry. The consequences of these differing symmetries are readily apparent from a consideration of the terminally attached distribution $Z(13)_{\delta=1.5}$. This function may be determined analytically and shown to be a rectangular function at a plane boundary:

$$Z(13) = 1 \qquad z \leqslant 1.0$$
$$= 0 \qquad z > 1.0.$$

Since $Z(23)$ is simply a delta function centred on the terminally attached segment 2, the form of $Z(13)$ is reflected directly in the segment density distribution $\rho(z|13)$ (equation (5)). (The absence of a second boundary is understood in dropping the δ subscript.) We find that the effect of conical rather than cylindrical symmetry is apparent, but slight. We shall draw the reader's attention to the effects of symmetry as and when they arise.

In figure 2 we compare the Monte Carlo and convolution distributions for a terminally attached sequence of 12 hard sphere segments. The qualitative agreement is seen to be good—the discontinuity and development of secondary structure being particularly pronounced in both cases. The convolution distribution is seen to be somewhat collapsed with respect to the Monte Carlo, and this is attributed to the partial neglect of intrachain interference in the model. Nevertheless, the qualitative features are preserved and differ markedly from all previously reported determinations. It is clear that the structural features are not artefacts of the convolution approximation, the numerical process, or the effects of conical rather than cylindrical symmetry. The fact that other lattice-based analyses do not reproduce these features is simply evidence of the incommensurability of continuous distributions with those mapped into a discrete space. It is found that at all orders $N \geqslant 4$ the density distribution is structured, showing in particular a discontinuity associated with the accessible volume of the segment

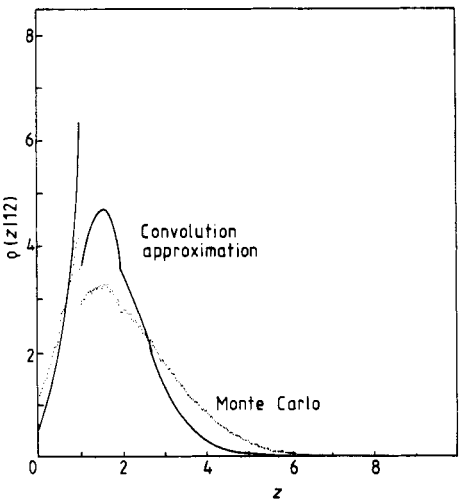


Figure 2. Comparison of the MC distribution $\rho(z|12)$ and the distribution obtained on the basis of the convolution approximation; the qualitative agreement appears good. In this and subsequent figures, z represents radial distance measured from the centre of sphere 1.

immediately adjacent to that which is terminally attached. As the length of the chain increases a second layer appears to develop and for the longest chains, an inflection, possibly indicating the development of a third, weakly resolved layer. This is confirmed in detail by Monte Carlo simulation. It is perhaps appropriate to mention at this point that the whole Monte Carlo sequence was generated anew if any violation of the exclusion condition occurred. Only in this way will the lower-order internal distributions modify their form in the presence of subsequent segments with which the initial segments have to compete for occupancy in the vicinity of the boundary.

The striking discontinuity in the segment density distribution associated with $Z(13|1N)$ warrants further comment. First of all we point out that $Z(13|1N)$ is sensitively dependent upon the number of subsequent segments in the chain. Thus, the terminally attached two-segment sequence $Z(13|13)$ may be shown analytically (discussed above) to be a rectangular function, closely reproduced in the present approximation. With increasing length, however, $Z(13|1N)$ shows a rapid increase in the amplitude of the discontinuity at $z = 1$, clearly apparent from a breakdown of the component normalised distributions of the segment density. We shall return to this point later. We see that $Z(13|1N)$ is responsible for the principal peak and discontinuity in structure for all terminally attached sequences, whilst the higher-order distributions are responsible for the secondary structure—each of the component distributions themselves being essentially structureless. Not surprisingly, the higher-order segments are responsible for the long-range form of the density distribution. Another interesting feature is the increasing contact probability of a given segment with the boundary as $N \rightarrow 16$.

The exact random walk distributions are found to be relatively less structured, although the discontinuity associated with segment 3 persists of course, being an inevitable consequence of the fixed intersegmental separation r_{23}. In particular, the principal peak associated with the first layer of segments adjacent to the plane is less well resolved in the random walk case; however, the fixed intersegmental separation

$r_{i,i+1}$ establishes the broad features of the distribution in both cases. A numerical comparison of the two structures may be given in terms of the boundary excess free energy which, in the present case, represents a measure of the entropy of the chain. The quantity

$$\mu_{N-1} = (N-1)^{-1}(\ln A_N(\infty) - \ln A_N(\delta)) \tag{7}$$

is calculated both for terminally attached and free-floating sequences as a function of boundary separation δ, and these are shown for chains of 7 and 15 segments in figure 3. The consistently higher entropy of the random walk sequences is directly attributable to the excluded-volume processes operating within the hard sphere chain.

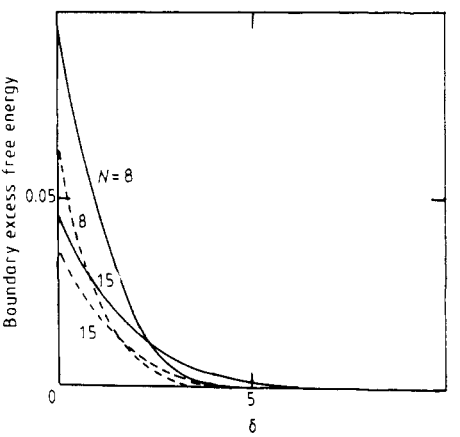


Figure 3. Development of the boundary excess free energy for terminally attached chains as a function of decreasing interplane separation δ (full curve). The corresponding random walk results are also shown (broken curve). $\varepsilon^* = 0$.

The rapid increase in μ as the chain is closely confined may be regarded as an entropic repulsion arising from the progressive configurational suppression of accessible chain conformations. This essentially geometrical effect would have to be overcome by attractive surface–segment interactions before substantial surface adsorption can take place. On the basis of this steric repulsion at the boundary we anticipate that the incorporation of excluded-volume effects will provide an additional expansion of the density distribution at the boundary with respect to the random walk result.

We are now in a position to account for the detailed structure of the density distribution curves, for whilst the discontinuity associated with the third segment is attributed to geometrical effects at the boundary and sequential constraint, the very strong increase in amplitude of the *normalised* distribution $Z(13|1N)$ at $z = 1$ with increasing chain length N has an essentially entropic origin, although this N dependence may be alternatively and equivalently understood in terms of a systematic increase in competition between the third and subsequent segments for the free volume in the immediate vicinity of the plane. We have mentioned that the chain experiences an effective entropic repulsion in the vicinity of the rigid boundary, and it follows that segments $N \geq 4$ will be expelled from the immediate vicinity of the plane, subject of course to the maintenance of sequential connection of the chain, and in so doing progressively distort the $Z(13|1N)$ distribution from its rectangular form for $N = 3$

to the highly asymmetric forms for $N \geq 4$. However, we should point out that the Monte Carlo discontinuity, whilst pronounced, does not appear to grow as strongly, and a decision as to whether this is an artefact of the convolution awaits simulation of more extended sequences. It does appear that the details of the discontinuity and its development with N becomes harder to resolve for longer chain lengths and for increasing chain–plane attraction (see below). Indeed, the discontinuity has not previously been reported on the basis of exact enumeration and Monte Carlo studies on regular lattices and so results based on these analyses should be treated with some caution.

These results bear immediate comparison with the terminally attached density profiles reported by Roe (1965) for a 1000 segment chain with no excluded volume, but a weak attractive interaction with a rigid boundary. These calculations, based upon an application of a generating function method, show that the segment density distribution maximises some distance away from the boundary, after which it decays monotonically to zero. Qualitatively similar conclusions were reached by Dickinson and Lal (1980) and Clark and Lal (1981) for the segment density profile of a 100-segment Monte Carlo chain on a tetrahedral lattice. Despite the incorporation of self avoidance in the latter calculation, there appears to be no evidence of structure in the vicinity of the plane even for non-attractive systems under the closest interplane confinements. However, as we shall see, the presence of an attractive interaction to some extent masks the discontinuity, although some reappraisal of these lattice results as a model of a self-avoiding sequence may well be necessary.

Four values of the reduced attractive interaction ($\varepsilon^* = \varepsilon/kT = 0.5, 1, 2, 5$) were investigated, representing progressively more attractive chain–plane interaction, whilst the geometrical features of hard sphere exclusion are preserved within the chain itself. Substantial conformational modification of the sequences prior to geometrical contact with the plane is anticipated on account of the long-range chain–plane interaction. In this respect the conformational properties may be expected to differ from those of a hard sphere chain interacting with a rigid plane.

We present the results for $\varepsilon^* = 5$ as being representative of the system, although we make a number of comparisons with the entire range of interaction parameters investigated. In figure 4 we show the development of the segment density distribution

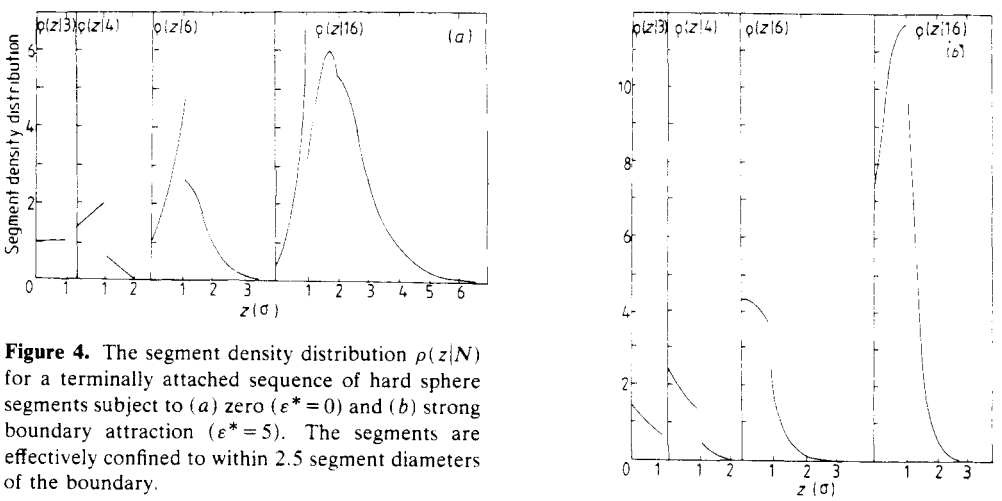


Figure 4. The segment density distribution $\rho(z|N)$ for a terminally attached sequence of hard sphere segments subject to (*a*) zero ($\varepsilon^* = 0$) and (*b*) strong boundary attraction ($\varepsilon^* = 5$). The segments are effectively confined to within 2.5 segment diameters of the boundary.

$\rho(z|N)$ for a terminally attached chain of $N = 2, \ldots, 15$ segments for $\varepsilon^* = 5$. We observe that the chain is strongly adsorbed in a largely unstructured layer of little more than one segment diameter thickness, and differs essentially from the athermal case. Certainly the probability of finding segments of the chain beyond 2.5 segment diameters is virtually zero. We note the progressive relaxation of the distribution as ε^* decreases with an associated resolution of the component $Z(13|1N)$ discontinuity as noted earlier in the athermal case.

We also calculate the segmental boundary excess free energy for terminally attached chains with decreasing δ (equation (7)). The entropic repulsion associated with the geometrical constraint imposed upon the hard sphere chain is shown in figure 3 for a sequence of 7 and 15 segments, and is seen to inhibit adsorption of terminally attached sequences for all boundary separations. The effect of attraction to one of the planes is to partially offset the steric repulsion, permitting a closer approach, but is never sufficient for the range of attractions investigated to initiate flocculation.

3.2. Free-floating sequences

We now consider hard sphere self-avoiding sequences which are no longer terminally attached, but are able to float freely between the two rigid boundaries of separation δ. In figure 6(a) we show density distributions for sequences of various lengths for $\delta = 5, 15$. As *a priori* considerations would suggest in the absence of any attraction, the segment density maximises midway between the planes. Any deviation from symmetry may be attributed to the conical symmetry of the volume element, discussed earlier. In figure 6(b) the density distribution for $N = 16$ as a function of δ is shown. The most striking feature of these distributions is the complete absence of any internal structure, which serves to confirm our earlier association of the discontinuity in terminally attached chains with the geometrical interaction of the third segment with the rigid boundary, and the constraint of sequential order.

The boundary excess free energy for a free floating chain attracted to one surface as a function of interboundary separation δ shows the same qualitative behaviour as that for terminally attached chains (figure 5). In fact, the excess free energy defined in equation (7) for given N, ε^* is somewhat greater in the case of free-floating chains since the fractional reduction in configuration freedom is greater than for one which is terminally attached. Thus, both terminally attached and free-floating sequences serve to inhibit flocculation for the range of attractions (or indeed, reduced temperatures) considered here. It should be mentioned, however, that for the shortest chains (3, 4, 5 segments) a shallow minimum in the free energy curve is observed. This is attributed to the ability of these very localised sequences to lie wholly within the long-range attractive region of the interaction, and largely evade the entropic repulsion associated with the boundaries, at least for large separations δ. Of course, with increasing N, ε^* and decreasing δ, entropic effects associated with the boundaries dominate, and the colloidal suspension is again stabilised. As we shall see below, for terminally attached sequences which experience the full effect of entropic repulsion associated with the boundary, the excess free energy curve increases monotonically with confinement (decreasing δ), even for the shortest chains, just as we might expect on the basis of our earlier argument.

Quite the reverse occurs if the chain experiences attraction to *both* boundaries, that is if we set

$$\Phi(1j) = \varepsilon^*[\sigma_1/r_{1j} + \sigma/(2 + \delta - r_{1j})]^6$$

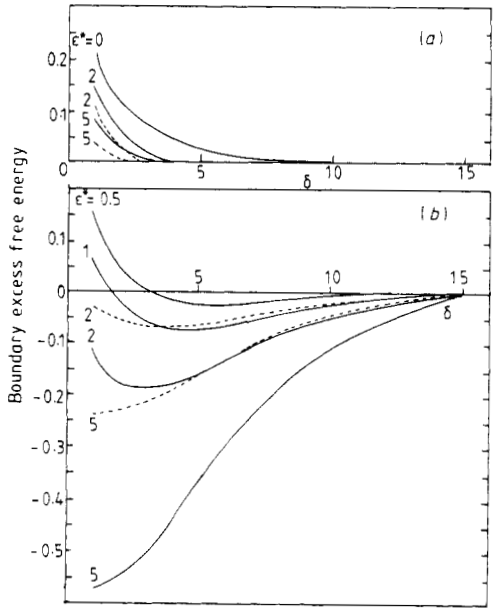
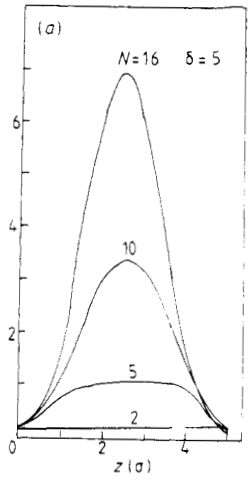
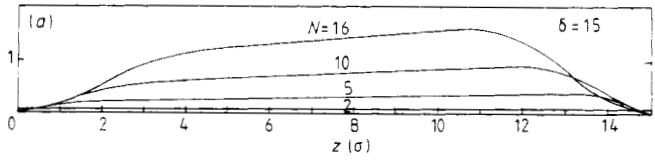


Figure 5. Development of the boundary excess free energy for terminally attached and free-floating chains for (*a*) single attractive and (*b*) double attractive boundary as a function of decreasing interplane separation δ. The full curves denote $N = 8$ and the broken curves $N = 16$.





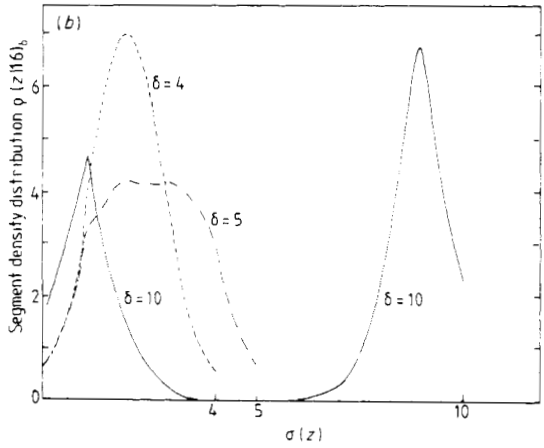


Figure 6. (*a*) Density distributions $\rho(z|N)_\delta$ for various free-floating chain ($\varepsilon^* = 0$) lengths N and non-attractive boundary separations $\delta = 5, 15$. (*b*) Free-floating density distribution for a 15-segment chain as a function of non-attractive boundary separation δ.

corresponding to an equal attraction to each boundary. In this case the repulsive entropic effects associated with geometrical chain–plane interaction are sufficiently offset by the attraction to cause the globular density distribution to broaden, and for sufficiently large ε^* and δ to become adsorbed on to one or other of the boundaries, or even to split into two separate components. Much more striking is the form of the boundary excess free energy (figure 5). At large distances the attractive force always dominates the short-range repulsive entropic component, but we see that for $\varepsilon^* = 5$ strong flocculation or adsorption of the polymer will occur, whilst for weaker attractions a looser association will develop in which it is centred on the minimum of the curve. This is in qualitative agreement with a numerical analysis by Dolan and Edwards (1974), subsequently solved analytically by Gerber and Moore (1977) under near-theta conditions corresponding here to $0 < \varepsilon^* < 1$. A recent Monte Carlo analysis for free-floating self-avoiding tetrahedral walks by Clark and Lal (1981) suggests that for close confinements the system is *totally* destabilised, even for non-attractive interactions, steric repulsion vanishing as the chains escape from between the boundaries and bulk osmotic pressure forces them together. In common with the majority of other investigations, we assume that the chains are trapped between the colloidal particles, and our results are not therefore immediately comparable with Clark and Lal's analysis. It should, perhaps, be pointed out that the form of the boundary excess free energy curves for all $\varepsilon < 0$ depends upon the *amplitude* rather than gradient of the attractive interaction. For sufficiently short-range attractions it is conceivable that the entropic repulsion arising from steric effects can lead to a weak positive maximum in the free energy at small offset distances from the boundary. However, the qualitative features reported here characterise interactions with exponents in the range 3–6, and the values of ε^* indicated.

3.3. *Mean square molecular span*

The variation of mean square molecular span $\langle R_{2N}^2 \rangle_\delta$ with with N, δ and ε^* was determined for both free-floating and terminally attached sequences, and for single and double boundary attraction.

For $\delta = 1$, the segments are effectively confined to a two-dimensional self-avoiding walk between the boundaries, whereupon $\langle R_{2N}^2 \rangle$ is independent of interaction strength ε^*. On the other hand, with increasing attraction to one boundary ($\delta = 15$, $\varepsilon^* = 5$) the system exhibits the kind of qualitative behaviour we might expect *a priori*, that is lateral spreading across the attractive boundary akin to the highly constrained ($\delta = 1$) behaviour mentioned above. This behaviour is substantially retarded in the case of the attraction to *both* boundaries. In all cases the transition of $\langle R_{2N}^2 \rangle_\delta$ from its two-dimensional behaviour varies continuously as $N > \delta \geqslant 1$. Unfortunately we cannot determine the asymptotic value of the exponent relating $\langle R_{2N}^2 \rangle_\delta$ as $N \to \infty$ since the present model degenerates to the random walk result as self-interference effects within the chain are progressively omitted.

In the case of sequences which are attracted to the plane to which they are terminally attached, their behaviour is essentially identical to those of free-floating chains, except that they are consistently expanded with respect to the latter.

More interesting, perhaps, is the location of the centre of gravity of the chain midway between the two attractive boundaries for the entire range of interaction parameters studied. As we have mentioned, the globule ranges in form from spheroidal (prolate and oblate) to dumbbell shaped; the moments of inertia and associated light

scattering properties of these various distributions would vary enormously and should be experimentally accessible, particularly as a function of temperature.

4. Conclusions

We find that for terminally attached partially self-avoiding chains of length up to 15 segments interacting with a rigid boundary, the system develops pronounced structural features. The most striking feature is the discontinuity in the density profile which may be directly attributed to the distribution of the third segment relative to the second; the segment density $\rho(z|13)$ may be shown analytically to be a rectangular function with a discontinuity at $z = 1$. The amplitude of the discontinuity develops strongly with the addition of subsequent segments, and may be associated with entropic forces acting on the body of the sequence ($N \geq 4$). The discontinuity itself, however, remains wholly attributable to the distribution of the third segment.

Analogous calculations for random walk sequences exhibit the same discontinuity, but are otherwise substantially less structured, a result confirmed by calculating the entropy deficiency developed by the self-avoiding and random chains as the boundary is approached. These results bear immediate comparison with previous lattice-based determinations based on exact enumeration, analytic and Monte Carlo calculations. In all cases the distributions show a pronounced maximum followed by a monotonic decay, although these calculations are for substantially longer sequences, and appear to show no internal structure. As we mentioned in § 1, there are grounds for seriously questioning the results of lattice-based analyses embodying as they do an implicit mapping of the continuum distribution onto a discrete lattice. It does not appear easy to devise a mapping which does not imply strongly biased transitions on a regular lattice and preserves the non-directed features of the perfectly flexible self-avoiding continuum sequence.

In the case of purely geometrical interaction with the plane ($\varepsilon^* = 0$) both terminally attached and free-floating chains exert an entropic repulsion on the planes directly attributable to the reduction in accessible conformations of the chain. In the context of colloidal suspensions these systems are stabilised against flocculation.

If the sequence is attracted to only one plane, the stabilising effect is reduced and appears quite sensitively dependent upon temperature and chain length. However, when attracted to both planes, the polymer acts to stabilise the system at high temperatures (small ε^*) and to destabilise at low temperatures (large ε^*), at least for chains of intermediate length. We conclude that flocculation will occur as the temperature is reduced. These results are in almost exact numerical agreement with recent exact enumeration studies by Middlemiss *et al* (1977).

Chan *et al* (1976) have considered a continuum model of a polymer confined between two attractive planes, but ignore excluded-volume effects. They find that the force exerted on the polymer changes from being purely repulsive to purely attractive as a function of ε^*. Here, we find a *range* of ε^* for which there is a minimum in the free energy curve, in agreement with the results of Middlemiss *et al.* This result reinforces the speculation of the latter authors that the minimum is associated with excluded-volume processes operating within the chain.

Finally we observe that the present simple model provides a sound qualitative description of polymeric systems of short to intermediate length. The versatility, simplicity and clear physical approximations involved in the model have been illustrated

in a recent series of papers. Extensions of the model to more complex situations of biophysical interest are to be published shortly.

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