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Publisher *Taylor & Francis*

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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Whittington, S. G. and Soteros, C. E.(1992) 'Uniform Branched Polymers in Confined Geometries', *Journal of Macromolecular Science, Part A*, 29: 6, 195 – 199

**To link to this Article:** DOI: 10.1080/10101329208054582

**URL:** <http://dx.doi.org/10.1080/10101329208054582>

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## UNIFORM BRANCHED POLYMERS IN CONFINED GEOMETRIES

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### ABSTRACT

We review some rigorous results on the behaviour of branched polymers when confined in a slab and in a prism, and when interacting with a surface, and introduce some new results on the corresponding problem for vesicles.

### INTRODUCTION

The characteristic feature of linear polymer molecules in dilute solution is their high degree of conformational freedom. When a polymer molecule is confined in some way, such as being restricted to a pore or slit, some conformations will be forbidden by the geometrical constraint. This leads to a decrease in the conformational entropy of the molecule. For a linear polymer (modelled, for instance, as a self-avoiding walk on a lattice) this loss in conformational entropy has been carefully investigated using a variety of techniques [1, 2, 3, 4].

This paper will be primarily concerned with uniform branched polymers. For example uniform stars are polymers with a single branch point of degree  $f$  and  $f$  branches, all of which have the same length, meeting at this branch point, and uniform combs are polymers with  $t$  branch points of degree 3 arranged along a backbone with each of the  $2t + 1$  branches having the same length. In the same way that linear polymers can be modelled as self-avoiding walks (SAWs) on a lattice, such uniform branched polymers can be modelled as embeddings of graphs with each branch being a self-avoiding walk and with the branches being mutually avoiding. We can ask for the number of embeddings of such graphs as a function of the number of edges  $n$  in each branch, and we shall be particularly interested in the large  $n$  behaviour. We can also study the number of embeddings with a geometrical constraint and ask how the large  $n$  behaviour depends on this constraint.

For any such uniform branched polymer type we can show that the loss in conformational entropy, when the branched polymer is confined to lie in a slab, is the

same as the corresponding conformational entropy loss for a self-avoiding walk in the same slab [5]. However, if the branched polymer is confined to a prism, the conformational entropy loss is larger than the conformational entropy loss for a self-avoiding walk in the same prism [6].

The theory of the adsorption of linear polymers, modelled by self-avoiding walks interacting with a surface, is relatively well understood [7, 8]. In the infinite  $n$  limit there is a phase transition in the model [7] and the location of the phase transition has been estimated numerically [9, 10, 11]. We show that for any fixed branched polymer type the temperature dependence of the free energy is identical to that for the self-avoiding walk [5, 12] so that, in particular, the phase transition corresponding to adsorption occurs at the same temperature.

The corresponding treatment for linear and branched polymers interacting with a line in two dimensions shows that the thermodynamics is different in the two cases [5, 12]. This result suggests that the codimension (the difference between the dimension of the space and the dimension of the embedded object) plays an important role. This has implications for vesicles interacting with a surface. It turns out that the thermodynamics of a vesicle (topologically equivalent to a sphere) interacting with a surface is different from that of a membrane with free boundaries (topologically equivalent to a disc) interacting with a surface.

### UNIFORM BRANCHED POLYMERS IN SLABS AND PRISMS

In lattice models the primary quantity of interest is the number of ways in which a particular kind of graph can be embedded in a lattice. We shall be mainly concerned with the three dimensional case and consider the simple cubic lattice. Let  $c_n$  be the number of ways in which an  $n$ -step SAW can be embedded in this lattice. For instance  $c_1 = 6$ ,  $c_2 = 30$ ,  $c_3 = 150$ ,  $c_4 = 5 \times 150 - 6 \times 4 = 726$ . The number of walks rises exponentially with  $n$  so that [13]

$$0 < \lim_{n \rightarrow \infty} n^{-1} \log c_n = \kappa < \infty. \quad (1)$$

$\kappa$  is the reduced limiting conformational entropy per edge and we shall often refer to  $\kappa$  as the *conformational entropy*. The numerical estimate [14] of  $\kappa$  is 1.544.

Let the number of self-avoiding walks confined to lie in a slab on the simple cubic lattice, i.e. between two parallel planes  $z = 0$  and  $z = L$ , be  $c_n(L)$ . It can be shown [4] that  $\lim_{n \rightarrow \infty} n^{-1} \log c_n(L) = \kappa(L)$  with  $\kappa(L) < \kappa(L+1) < \kappa$  and  $\lim_{L \rightarrow \infty} \kappa(L) = \kappa$ . This implies that as the planes are brought closer together there is a successive loss in conformational entropy.

We can specify a branched polymer type by specifying a graph with fixed homeomorphism type (e.g. a star, comb, tadpole, theta or dumbbell). For this fixed homeomorphism type  $\tau$  let  $g_n(\tau)$  be the number of embeddings of  $\tau$  in the simple cubic lattice with  $n$  edges in each branch. Then it can be shown [5] that

$$\lim_{n \rightarrow \infty} N^{-1} \log g_n(\tau) = \kappa \quad (2)$$

where  $N$  is the total number of edges in the embedding (e.g. for a comb with  $t$  'teeth'  $N = (2t + 1)n$ ). Let  $g_n(\tau, L)$  be the corresponding number of embeddings in a slab of width  $L$ . Then, provided that  $L$  is large enough for one embedding of  $\tau$  to fit in the slab ( $L \geq 2$  is certainly a sufficient condition),

$$\lim_{n \rightarrow \infty} N^{-1} \log g_n(\tau, L) = \kappa(L) \quad (3)$$

for all  $\tau$ . This means that all uniform branched polymer types lose the same amount of conformational entropy when confined in a slab, in the large  $n$  limit. The proofs of equations (2) and (3) rely on concatenation of unfolded SAWs in wedges.

For a prism the situation is quite different. To be specific consider the prism which is the subset of the lattice between the pair of planes  $z = 0$  and  $z = L_1$  and the pair of planes  $y = 0$  and  $y = L_2$ . If we write  $c_n(L_1, L_2)$  for the number of self-avoiding walks in this prism and  $g_n(\tau, L_1, L_2)$  for the number of embeddings of  $\tau$  in the prism then [6]

$$\lim_{n \rightarrow \infty} n^{-1} \log c_n(L_1, L_2) = \kappa(L_1, L_2) \quad (4)$$

and

$$\limsup_{n \rightarrow \infty} N^{-1} \log g_n(\tau, L_1, L_2) < \kappa(L_1, L_2), \quad (5)$$

for every  $\tau$  except that corresponding to a self-avoiding walk, so that self-avoiding walks lose less conformational entropy than any other uniform branched polymer when confined in a prism. Physically this can be understood as being due to the interference between the branches caused by the prism constraint. In a prism the branches are effectively constrained to extend in a single direction while in a slab they can extend in two directions. The formal proof of equation (5) relies on a 'pattern' theorem argument.

## ADSORPTION OF UNIFORM BRANCHED POLYMERS

A useful model for the adsorption of linear polymers is a self-avoiding walk in the simple cubic lattice interacting with a plane. Specifically we consider the number  $c_n(m)$  of  $n$ -step SAWs which begin at the origin, are confined to the half-space  $z \geq 0$  and have  $m + 1$  vertices in the plane  $z = 0$ . The appropriate partition function is  $Z_n(\beta) = \sum_m c_n(m) e^{\beta m}$  and one can show [7] that the reduced limiting free energy per edge

$$A(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log Z_n(\beta) \quad (6)$$

exists.  $A(\beta)$  is continuous and convex but is a non-analytic function of  $\beta$  so that the model exhibits a phase transition at some  $\beta_0 > 0$ , corresponding to adsorption [7].

If we consider uniform embeddings of graphs of homeomorphism type  $\tau$  we can show [5] that the corresponding reduced limiting free energy

$$A(\tau, \beta) = \lim_{n \rightarrow \infty} N^{-1} \log \sum_m g_n(\tau, m) e^{\beta m} \quad (7)$$

where  $g_n(\tau, m)$  is the number of embeddings of  $\tau$  with  $n$  edges in each branch and  $m+1$  vertices in the plane  $z=0$ , is equal to  $A(\beta)$  for every  $\tau$ . This implies that the temperature dependence of the free energy is the same as for SAWs and in particular the adsorption transition occurs at the same temperature.

This turns out not to be true in two dimensions [5]. In this case we have a SAW on the square lattice interacting with a line and the free energy is again continuous, convex and non-analytic [7]. For any fixed homeomorphism type  $\tau$  we find that the free energy is independent of  $\beta$  and  $\tau$  for  $\beta \leq 0$  but for  $\beta > 0$  we can show [5] that the free energy is less than or equal to that of SAWs and the inequality becomes strict for  $\beta$  sufficiently large. Hence for an attractive interaction with a surface and sufficiently low temperature the thermodynamics depends on the type of branched polymer. The essential physical feature is that one branch when adsorbed in the surface can prevent other branches from reaching the surface in two dimensions. A branch, which is a one dimensional object, can leave and return to the surface and create a region of the two dimensional space which is not accessible to another branch. If the space is three dimensional this separation phenomenon does not occur. (This is essentially the Jordan curve theorem.)

### ADSORPTION OF VESICLES

In the adsorption of branched polymers the crucial factor in determining whether the free energy is the same as for SAWs is the codimension of the space. Although for the polymer problem the two dimensional case is not of practical significance, an analogous effect occurs in the adsorption of vesicles at a surface, since a vesicle is a two dimensional object in a three dimensional space and the codimension is one.

A convenient model for a vesicle is a connected set of plaquettes (elementary squares on the simple cubic lattice) homeomorphic to a sphere [15, 16]. Let  $v_n$  be the number of embeddings of a vesicle with  $n$  plaquettes (i.e. with area  $n$ ) in the simple cubic lattice (e.g.  $v_6 = 1$  and  $v_{10} = 3$ ). It can be shown that  $0 < \lim_{n \rightarrow \infty} n^{-1} \log v_n = \chi < \infty$ . If  $v_n(m)$  is the number of vesicles with  $n$  plaquettes confined to a half-space and having  $m$  plaquettes in  $z=0$  then the free energy is given by

$$\mathcal{A}(\beta) = \lim_{n \rightarrow \infty} n^{-1} \log Q_n(\beta) \quad (8)$$

where  $Q_n(\beta)$  is the partition function given by  $Q_n(\beta) = \sum_m v_n(m) e^{\beta m}$ . It can be shown by a concatenation argument that the limit in equation (8) exists for  $\beta < \infty$ . Similarly it is easy to show that the free energy is convex and continuous.

Since for  $\beta \leq 0$ ,  $v_{n-4} e^{\beta} = v_n(1) e^{\beta} \leq Q_n(\beta) \leq Q_n(0) = v_n$ , then  $\mathcal{A}(\beta) = \chi$  for all  $\beta \leq 0$ . Since for  $\beta > 0$ ,  $e^{\beta m_{max}} \leq Q_n(\beta) \leq v_n e^{\beta m_{max}}$ , where  $m_{max} = n/2 + o(n)$ , then  $\beta/2 \leq \mathcal{A}(\beta) \leq \chi + \beta/2$ . This establishes the existence of a phase transition since  $\mathcal{A}(\beta)$  is a non-analytic function of  $\beta$  for some positive  $\beta$ .

If we consider a membrane with free boundaries and homeomorphic to a disc and write  $d_n(m)$  for the number of embeddings of a disc with  $n$  plaquettes confined to a half-space and having  $m$  plaquettes in  $z=0$  then a similar argument shows that  $\liminf_{n \rightarrow \infty} n^{-1} \log \sum_m d_n(m) e^{\beta m} \geq \beta$ . This implies that the thermodynamics must be different from that of a vesicle at sufficiently large  $\beta$ .

## DISCUSSION

We have reviewed some rigorous results on the behaviour of linear and uniform branched polymers with geometrical constraints, including the phenomenon of adsorption at a surface, in the large  $n$  limit. The behaviour for intermediate values of  $n$  is much less well understood and there is considerable scope both for computer investigations and experimental studies. For instance a Monte Carlo study of the entropy loss for uniform stars or combs in slabs and prisms seems to us to be an appropriate next step. Similarly we are not aware of any experimental work on the adsorption of uniform branched polymers at a surface.

## ACKNOWLEDGEMENTS

The authors are grateful to NSERC of Canada for financial support.

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