# Lattice models of branched polymers with specified topologies

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As a step towards understanding the thermodynamics of multi-branched polymer systems, we look at a lattice model of a uniform branched polymer with fixed topology interacting with a surface and ask for the free energy of the polymer as the number of monomers which compose the polymer goes to infinity. The conformations of a uniform branched polymer with fixed topology are modelled by embeddings of a graph in the simple cubic lattice. Rigorous results about this model are reviewed. The results suggest that large branched polymers in three dimensions interacting with a plane have the same free energy as large linear polymers interacting with a plane; the same is not true, however, for the corresponding two-dimensional problem where the polymer interacts with a line.

## 1. Introduction

Star polymer synthesis and the star-like structure of co-polymers such as micelles has prompted recent interest in extending models of linear polymers to the study of star polymers [1–6]. Also, since it is possible to tether polymer chains to surfaces and to each other, experimentalists are now studying very complicated branched polymer systems such as brushes [7] and so interest in modelling multi-branched polymer systems has grown [8–11].

The self-avoiding walk model is known to be a good model of the excluded volume effect on large linear polymers in dilute solution and hence recent models of star polymers in dilute solution have been based on self-avoiding stars. These models have focused on uniform stars where each branch has the same number of monomers, $n$, and the total number of monomers is $N = nf + 1$, where $f$ is the number of arms in the star. Whittington and Soteros [5] have obtained rigorous results in the infinite $n$ limit for a single self-avoiding star interacting with a surface on the simple cubic and square lattices. Halperin and Joanny [6] have studied a model, based on the Daoud–Cotton model for free stars, of a single star polymer interacting with a surface in two and three dimensions. The results of Whittington and Soteros are that the limiting free energy per edge of a single star interacting with a plane in three dimensions is the same as the corresponding free energy for a self-avoiding walk. In other words, when the branches of the star are long enough they act essentially like independent self-avoiding walks. In contrast, in two dimensions the limiting free energy per edge of a star strongly adsorbed to a line is less than the corresponding free energy of a self-avoiding walk. This is because, in the strong adsorption regime, a significant fraction of the vertices of a star will not be able to interact with the surface while all the vertices of a walk are free to interact with the surface. Since it is difficult to obtain rigorous results about the average size and shape of a self-avoiding star polymer, the results of Whittington and Soteros do not address the predictions of Halperin and Joanny regarding the sombrero shape of the star in intermediate interaction regimes. The results of Whittington and Soteros however do confirm the terms of order $N$ in the free energy calculations of Halperin and Joanny.

A next step towards understanding the effects of branching and topology on the properties of a polymer is to investigate whether results similar to those obtained for star polymers hold for more complex branched polymer systems. Towards this end, it has been shown [11] that the results of Whittington and Soteros can be extended to any uniformly branched polymer with fixed topology. In this paper this extension will be reviewed and some of the proofs will be outlined.

## 2. The model

We represent the topology of the polymer by a graph $\tau$ and, in order to take into account the excluded volume effect, we look at embeddings of the graph in the simple cubic lattice, $Z^3$. The results discussed here can be readily extended to corresponding models on other regular lattices; however, we focus on $Z^3$ for convenience.

A graph, $\tau$, representing the topology of a polymer is assumed to have no vertices of degree two; the *degree* of a vertex of a graph is defined to be the number of edges incident on the vertex and a loop is assumed to contribute twice to the degree of a vertex. An edge of $\tau$ is referred to as a *branch*. In the special case of a ring polymer $\tau$ is taken to be the circle graph, $\tau = \bigcirc$, and it is assumed that the circle graph has one vertex (a vertex of degree two) and one branch. Vertices of $\tau$ having degree greater than two are referred to as *branch points*; vertices of degree one are named *endpoints*.

The conformations of a polymer with topology $\tau$ are represented by embeddings of $\tau$ in the simple cubic lattice. An *embedding of $\tau$ in the simple cubic lattice* is defined to be any subgraph of the simple cubic lattice which, if one ignores vertices of degree two, is isomorphic to $\tau$. (That is, an embedding of $\tau$ is any subgraph of the simple cubic lattice which is homeomorphic to $\tau$.) Since we are concerned with embeddings of $\tau$ on the simple cubic lattice we will only be interested in $\tau \in G_6$, where $G_6$ is the set of graphs whose branch points all have degree less than or equal to six (the coordination number of the lattice). Soteros et al. [12] proved that for any $\tau \in G_6$ there exists an embedding of $\tau$ in the simple cubic lattice.

In this paper we are concerned with uniform branched polymers and hence we define a *uniform embedding of $\tau$ in the simple cubic lattice* to be an embedding of $\tau$ in the simple cubic lattice such that each branch of the embedding is composed of the same number of edges. Let $f$ be the number of branches of $\tau$ and $c$ its cyclomatic index (number of independent cycles), then by Euler's relation a uniform embedding of $\tau$ with $n$ edges per branch is composed of $N = nf - c + 1$ vertices. Note, that a necessary condition for a graph $\tau \in G_6$ to have a uniform embedding in $Z^3$ with an odd number of edges per branch is that $\tau$ have no cycles of odd length. König's theorem (see ref. [13]) implies therefore that a necessary condition for $\tau$ to have a uniform embedding in $Z^3$ with an odd number of edges per branch is that $\tau$ be bipartite (2-colourable). By constructing embeddings Soteros [11] showed that this is also a sufficient condition. Thus for any $\tau \in G_6$ and $n$ even there exists a uniform embedding of $\tau$ in $Z^3$ with $n$ edges per branch while for $n$ odd, there exists a uniform embedding of $\tau$ in $Z^3$ with $n$ edges per branch if and only if $\tau$ is bipartite.

We write $g_n(\tau)$ for the number of uniform embeddings per lattice site of $\tau$ in $Z^3$ having $n$ edges per branch. For instance, if $\tau$ is the circle graph, $\tau = \bigcirc$, then the uniform embeddings with $n$ edges per branch are self-avoiding polygons with $n$ edges and hence $g_4(\bigcirc) = 3, g_6(\bigcirc) = 22$ and $g_8(\bigcirc) = 207$. Similarly if $\tau$ is the line graph, $\tau = |$, then the uniform embeddings with $n$ edges per branch are undirected self-avoiding walks with $n$ edges and hence $g_1(|) = 3$ and $g_2(|) = 15$. Some other examples of graphs include star graphs with four branches, $\tau = \times$; theta graphs, $\tau = \ominus$; figure eight graphs, $\tau = 8$; dumbbell graphs, $\tau = \bigcirc\!\!-\!\!\bigcirc$. The number $g_n(\tau)$ is hence an estimate for the number of conformations of a polymer having topology $\tau$ and composed of $N = nf - c + 1$ monomers uniformly distributed throughout the branches of the polymer.

From the results of Hammersley and Morton [14] for directed self-avoiding walks one can show that

$$0 < \lim_{n \to \infty} n^{-1} \log g_n(|) = \kappa < \infty \,, \tag{2.1}$$

where $\kappa$ is called the *connective constant* for $Z^3$, and Hammersley [15] has shown that

$$\lim_{n \to \infty} n^{-1} \log g_n(\bigcirc) = \kappa \,, \tag{2.2}$$

where $n$ is assumed to go to infinity through the even integers. A consequence of the results to be reviewed here is that

$$\lim_{n \to \infty} N^{-1} \log g_n(\tau) = \kappa \,, \tag{2.3}$$

where, if $\tau$ is not bipartite, the limit is approached through even values of $n$ and $N = nf - c + 1$. This can be equivalently expressed as

$$g_n(\tau) = e^{\kappa N + o(N)}, \tag{2.4}$$

which indicates that the exponential growth rate of the number of conformations of a polymer with fixed topology as the size of the polymer grows is a constant independent of the topology of the polymer. Of course the unknown $o(N)$ in terms in this asymptotic expansion may depend on $\tau$ (see, for example ref. [8]).

For any graph $\tau \in G_6$ we can define $n_j$ to be the number of branch points of $\tau$ having degree, $j$, $3 \leqslant j \leqslant 6$, and $n_1$ to be the number of end points of $\tau$. (In the special case of the circle graph, $\tau = \bigcirc$, we assume that $n_2 = 1, f = 1, c = 1$ and $n_j = 0, j \neq 2$.) Euler's relation gives $n_1 = f - c - \sum_{j=2}^{6} n_j + 1$. The graph index set $\{f, c, n_j : j \geqslant 2\}$ does not, however, completely define $\tau$. In particular, the theta graph, $\tau = \ominus$ and the dumbbell graph, $\tau = \bigcirc\!-\!\bigcirc$ have the same graph index set, $f = 3, c = 2, n_3 = 2, n_j = 0, j \neq 3$. These two graphs are however not isomorphic and in particular the dumbbell graph has a *cut-edge*, an edge which when cut results in a disconnected graph, while the theta graph does not.

## 3. Uniform branched polymers interacting with a surface

We discuss next a model of a uniform branched polymer with topology $\tau$ interacting with a surface. We consider uniform embeddings of $\tau$ confined to a half-space, $z \geqslant 0$, in the simple cubic lattice and assign to each embedding an interaction energy proportional to the number of vertices of the embedding in the plane $z = 0$. We assume that the polymer contacts the surface at least once; however, the part of the polymer which contacts the surface is not specified (this specification could be made however without altering the conclusions presented here). The appropriate partition function is therefore

$$Z_n(\tau, \beta) = \sum_m g_n(\tau, m) e^{\beta m}, \tag{3.1}$$

where $g_n(\tau, m)$ is the number of uniform embeddings of $\tau$ per lattice site in the half-space with $n$ edges per branch and $m + 1$ vertices ($m \geqslant 0$) in the plane $z = 0$. In order to obtain rigorous results for this model we study the *reduced limiting free energy per monomer*,

$$A(\tau, \beta) = \lim_{n \to \infty} N^{-1} \log Z_n(\tau, \beta), \tag{3.2}$$

where the limit, if it exists, is assumed to go through even values of $n$ unless $\tau$ is bipartite. The results of Hammersley, Torrie and Whittington [16] imply that in the case $\tau = |$ the limit in eq. (3.2) exists and the function $A(|, \beta)$ is convex, continuous and is bounded as follows:

$$\max(\kappa, \kappa_2 + \beta) \leqslant A(|, \beta) \leqslant \max(\kappa, \kappa + \beta), \tag{3.3}$$

where $\kappa_2$ is the connective constant for self-avoiding walks in the square lattice,

$Z^2$. From these bounds one can conclude that there is a phase transition in the model (corresponding to adsorption) for some critical value of $\beta, \beta_c$, where $0 \leqslant \beta_c \leqslant \kappa - \kappa_2$. In fact, further arguments by Hammersley, Torrie and Whittington [16] prove that $0 < \beta_c < \kappa - \kappa_2$.

We outline next a proof that the limit in eq. (3.2) exists for all $\tau \in G_6$ and that

$$A(\tau, \beta) = A(|, \beta) . \tag{3.4}$$

Hence an adsorption transition exists for any uniform branched polymer with specified topology and the transition occurs at the same value of $\beta$, $\beta_c$, for all topologies. A more detailed proof of this result is given by Soteros [11].

We prove that the limit in eq. (3.2) exists by proving eq. (3.4). The typical approach to proving such an equation is to use a "squeezing" argument, that is one shows that $A(\tau, \beta) \geqslant A(|, \beta)$ and $A(\tau, \beta) \leqslant A(|, \beta)$. This is accomplished by obtaining lower and upper bounds respectively for the number of embeddings of $\tau, g_n(\tau, m)$, in terms of the number of undirected self-avoiding walks or self-avoiding polygons or some other type of object known to have limiting free energy $A(|, \beta)$.

The upper bound is easy to obtain by noting that each embedding of $\tau$ with $n$ edges per branch can be separated into $f$ $n$-step undirected self-avoiding walks each with at most $m + 1$ vertices in $z = 0$. Some of the $f$ undirected self-avoiding walks will have contacts with the surface and others may not. Thus we get that

$$g_n(\tau, m) \leqslant f! 2^f \sum_{k=1}^{f} g_n(|)^{f-k} \binom{f}{k} \sum_{m_i} \prod_{j=1}^{k} g_n(|, m_j) , \tag{3.5}$$

where the $f!2^f$ ensures that we are not undercounting and the $m_i$ range between 0 and $m$ such that $\sum_{i=1}^{k} m_i = m - k + 1$. Multiplying by $e^{\beta m}$ and summing over $m$ on both sides of eq. (3.5), taking logarithms, dividing by $N$ and letting $n$ go to infinity leads to

$$\lim_{n \to \infty} \sup N^{-1} \log Z_n(\tau, \beta) \leqslant A(|, \beta) . \tag{3.6}$$

Obtaining a lower bound is more difficult since we need to find a set of objects which have limiting free energy $A(|, \beta)$ and from which we can construct embeddings of $\tau$ with $n$ edges per branch and $m + 1$ vertices in $z = 0$. In this case the appropriate set of objects turns out to be a set of self-avoiding polygons in wedges and it is thus appropriate to review the known results for walks and polygons in wedges.

Define an $(\alpha, \beta, T)$-wedge for $\alpha < \beta$ to be $\{(x, y, z) \in Z^3 | 0 \leqslant x,\ \alpha x \leqslant y \leqslant \beta x + T\}$, that is a wedge bounded by three planes perpendicular to the $xy$-plane, one is the $yz$-plane, the second, $y = \alpha x$, has slope $\alpha$ and the third, $y = \beta x$, has slope $\beta$. Hammersley and Whittington [17] proved that for any $\alpha > 0$, directed self-avoiding walks and self-avoiding polygons, rooted at the origin, in a $(0, \alpha, 0)$-wedge each have connective constant $\kappa$. Their arguments can be extended to show that such walks and polygons also have limiting free energy $A(|, \beta)$.

Using the results for $(0,\alpha,0)$-wedges, Soteros [11] has proved that given $\alpha$ such that $\alpha$ or $1/\alpha$ is an integer and $\beta>\alpha$ there exists a $t$ such that self-avoiding polygons rooted at the origin in an $(\alpha,\beta,T)$-wedge each have limiting free energy $A(|,\beta)$ provided $T\geqslant t$. If $\alpha=j$, an integer, and $\beta=j+1$, then $t=j+1$ and this ensures that a polygon rooted at the origin in a $(j,j+1,j+1)$-wedge can contain edges in the positive $x$ direction.

Now let us return to obtaining a lower bound for $g_n(\tau,m)$. Suppose first that $n$ is even. There is more than one way to obtain the required embedding of $\tau$ using walks and polygons in wedges, however, perhaps the easiest construction to describe is the following. First, obtain an embedding of $\tau$ in the half-space such that

(1) exactly one edge of each branch of $\tau$ lies in the right most (maximum $x$-coordinate) plane, say $x=k$, of the embedding and so that these right most edges lie in the line $z=0, x=k, y\geqslant 0$ (such a construction exists by the arguments given in ref. [11]),

(2) each branch has an even number of edges (just divide each existing edge on the lattice into two edges) and

(3) the edges in the line $z=0, x=k$ are at least $f$ edges apart, where $f$ is the number of branches of $\tau$ (again see the construction in ref. [11]).

We thus have $f$ edges in the line $z=0, x=k, y\geqslant 0$, one from each branch, and we can label the branch whose edge in this line is closest to the $x$-axis the first branch, the branch with the next closest edge the second branch, etc. Suppose the $j$th branch has $2M_j$ edges for $j=1,\dots,f$ and suppose the resulting embedding of $\tau$ has $m^*$ vertices in the plane $z=0$. We now concatenate to the first branch a polygon in a $(0,1,1)$-wedge with $n+2-2M_1$ edges and $m_1+1$ vertices in $z=0$, and concatenate to the second branch a polygon in a $(1,2,2)$-wedge with $n+2-2M_2$ edges and $m_2+1$ vertices in $z=0,\dots$, and concatenate to the $j$th branch a polygon in a $(j-1,j,j)$-wedge with $n+2-2M_j$ edges and $m_j+1$ vertices in $z=0,\dots$, and finally concatenate to the $f$th branch a polygon in a $(f-1,f,f)$-wedge with $n+2-2M_f$ edges and $m_f+1$ vertices in $z=0$. Finally, delete the edges in the line $z=0, x=k$. This gives a uniform embedding of $\tau$ with $n$ edges per branch and $m+1=\sum_{j=1}^{f} m_j+m^*-f$ vertices in $z=0$, and we get a different embedding of $\tau$ for every distinct ordered set of $f$ polygons. Thus we have

$$\prod_{j=1}^{f} g_{n+2-2M_j}^{(j-1,j,j)}(\bigcirc,m_j)\leqslant g_n\left(\tau,\sum_{j=1}^{f} m_j+m^*-f-1\right)=g_n(\tau,m)\,, \tag{3.7}$$

where $g_{n+2-2M_j}^{(j-1,j,j)}(\bigcirc,m_j)$ is the number of $(n+2-2M_j)$-step self-avoiding polygons in a $(j-1,j,j)$-wedge with $m_j+1$ vertices in $z=0$. Multiply both sides of this equation by $\exp(\beta\sum_{i=1}^{f} m_i)$, sum over $\{m_i, i=1,\dots,f|1\leqslant m_i\leqslant n-M_i+2\}$, take logarithms of both sides, divide by $N=nf-c+1$ and let $n$ go to infinity through even values of $n$. This implies

$$A(|,\beta) \leqslant \lim_{n\to\infty} \inf N^{-1} \log Z_n(\tau,\beta), \tag{3.8}$$

where the limit is taken through even values of $n$.

If $\tau$ is bipartite one also needs the corresponding inequality where the limit is taken through odd values of $n$. If one obtains an embedding of $\tau$ satisfying the criteria (1) and (3) above and with (2) replaced by the criteria that each branch have an odd number of edges then the proof described above would be sufficient to prove eq. (3.8) for the case $n$ odd. If $\tau$ is bipartite we can label the vertices of $\tau$ with two labels (left and right say) so that no two vertices having the same label are joined by an edge in $\tau$. In ref. [11] a construction is described which yields an embedding of $\tau$ in which there exists a plane $x = k$ that intersects each branch of the embedding at exactly one vertex and these vertices of intersection lie in the $z = 0$ plane. (Note that such a construction is not possible for a graph which is not bipartite such as the circle or figure eight graph.) This embedding can be constructed so that the number of edges in each branch is odd. Concatenating an appropriate polygon to each branch will then allow one to construct an embedding of $\tau$ satisfying criteria (1) and (3) above and also satisfying the constraint that the number of edges in each branch is odd.

The conclusion is therefore that

$$\lim_{n\to\infty} N^{-1} \log Z_N(\tau,\beta) = A(|,\beta). \tag{3.9}$$

If one wants to add a constraint that the polymer is attached to the surface at a specific branch point then the above proof still works except that now for the lower bound one must start with an embedding of $\tau$ which satisfies the required constraint.

A corollary of this is that eq. (2.3) is true. This comes from the fact that $Z_N(\tau,0) \leqslant g_n(\tau)$ and an upper bound for $g_n(\tau)$ is obtained by embedding independent self-avoiding walks.

## 4. Uniform branched polymers in two dimensions interacting with a line

If we restrict ourselves even further and consider graphs embedded on the square lattice, $Z^2$, then the picture changes considerably. The analog of eq. (2.3) is still true, that is

$$\lim_{n\to\infty} g_n(\tau) = \kappa_2, \tag{4.1}$$

where now $g_n(\tau)$ represents the number of uniform embeddings of $\tau$ per lattice site on the square lattice. However, the free energy of a graph interacting with the line $y = 0$ is no longer equal to that for a self-avoiding walk. Note that in two dimensions $\tau$ is restricted to the set of planar graphs with maximum degree 4.

We start by outlining the proof of eq. (4.1). The argument used to prove eq.

(2.3), concatenating polygons in $(j-1,j,j)$-wedges, no longer works here. For example, if one considers the case that $\tau = \ominus$, the theta graph, it is clearly impossible to construct an embedding of the theta graph such that each branch has exactly one edge in a rightmost line since the middle branch cannot have any edges in a rightmost line. Instead we obtain a lower bound for $g_n(\tau)$ by constructing an embedding of $\tau$ using walks in (0,1, 0)-wedges. The upper bound is obtained as usual by separating $\tau$ into $f$ self-avoiding walks.

In this case we start with a uniform embedding of $\tau$ such that there exists a line, $x=k$, which cuts every branch of $\tau$ exactly twice (see ref. [11] for a proof that such an embedding exists). Call this embedding of $\tau$ $T$. There are hence $2f$ vertices in the line $x=k$ and we label these $v_0, \dots, v_{2f-1}$ according to the value of their $y$-coordinates such that $v_0$ has the smallest $y$-coordinate. Let $n_0$ be the number of edges per branch in $T$ with $n_0$ even.

Define $\mathcal{C}_n^M$ to be the set of rooted $n$-step directed self-avoiding walks in a (0, 1, 0)-wedge such that the walk starts at (0, 0), ends at $(M, 0)$ and the coordinates of the $i$th step satisfy $y<M-x$ for $i<n$. Define $c_n^M$ to be the number of such walks. Thus such a walk is contained in an isosceles triangle with height $M/2$ and base $M$ and the triangle contains $(\lfloor (M/2 \rfloor + 1)(\lceil M/2 \rceil + 1)$ sites of the square lattice. Let $c_n^* = \sum_{M=1}^n c_n^M$. The arguments of Whittington [18] imply that

$$\lim_{n\to\infty} n^{-1} \log c_n^* = \kappa_2 \, . \tag{4.2}$$

Thus, given an integer $\hat{n} \geqslant 4f^2$, there exists a triangle with base $M$ such that $M > 2f-1$ and such that

$$c_{\hat{n}}^M \geqslant \frac{c_{\hat{n}}^*}{\hat{n}} \, . \tag{4.3}$$

Fix such an $M$.

The idea now is to construct a uniform embedding of $\tau$ with $n$ edges per branch, $n$ even, by concatenating a sequence of walks from the set $\mathcal{C}_{\hat{n}}^M$ to the vertices in the line $x=k$ of $T$. In order to do this we must ensure that there is enough vertical space between the vertices in the line $x=k$ so that the triangles of height $M/2$ fit. First, assume $n \geqslant 4Mf(2f+1)+n_0$ and choose $p$ and $q$ such that $n = 2\hat{n}p + n_0 + 4Mf(2f+1) + 2q$. Divide $T$ along the line $x=k$ into two parts, a left part, $T_{\mathrm{L}}$, and a right part, $T_{\mathrm{R}}$, and so that the vertices $v_0, \dots, v_{2f-1}$ are duplicated with one set connected to the left part, $v_0^{\mathrm{L}}, \dots, v_{2f-1}^{\mathrm{L}}$, and the other connected to the right part, $v_0^{\mathrm{R}}, \dots, v_{2f-1}^{\mathrm{R}}$. Let $\hat{x}$ and $\hat{y}$ represent the unit vectors in the positive $x$ and $y$ directions respectively. Translate $T_{\mathrm{R}}$ so that $v_i^{\mathrm{R}} = v_i^{\mathrm{L}} + [(p+4f)M + q]\hat{x}$ for $i = 0, \dots, 2f-1$. It is possible to connect $v_i^{\mathrm{L}}$ to $v_i^{\mathrm{L}} + ((4f-1)M, iM)$ by a sequence of $2Mf(2f+1) - (i+1)M$ steps and to connect $v_i^{\mathrm{R}}$ to $v_i^{\mathrm{R}} + (M, iM)$ by a sequence of $(i+1)M$ steps (see ref. [11]) and relabel the new endpoints $v_i^{\mathrm{L}}$ and $v_i^{\mathrm{R}}$ respectively for $i = 0, \dots, 2f-1$. Now, $v_i^{\mathrm{L}}$ and $v_{i+1}^{\mathrm{L}}$ are separated by at least $M$ steps in the positive $y$-direction and similarly $v_i^{\mathrm{R}}$ and $v_{i+1}^{\mathrm{R}}$ are separated by at least $M$ steps in the positive $y$-direction. Hence a walk from the set $\mathcal{C}_{\hat{n}}^M$ can be concatenated to $v_i^{\mathrm{L}}$ and in fact $p$ such walks can be concatenated. (The resulting walk is in a slit of height $M$.) If an additional $q$ steps in the positive $x$-direction are added then $v_i^{\mathrm{L}}$ will be connected to $v_i^{\mathrm{R}}$ and doing this for each $i$ results in an embedding of $\tau$ with $n$ edges per branch. A different embedding of $\tau$ will result for each different ordered set of $2fp$ walks from $\mathcal{C}_{\hat{n}}^M$ and hence

$$[c_{\hat{n}}^M]^{2fp} \leqslant g_n(\tau)\,. \tag{4.4}$$

Taking logarithms, dividing by $N \equiv fn - c + 1$, fixing $\hat{n}$ and letting $n \to \infty$ in this equation yields,

$$\hat{n}^{-1} \log c_{\hat{n}}^M \leqslant \liminf_{n\to\infty} N^{-1} \log g_n(\tau)\,. \tag{4.5}$$

Letting $\hat{n} \to \infty$ and using eq. (4.2) leads to

$$\kappa_2 \leqslant \liminf_{n\to\infty} N^{-1} \log g_n(\tau)\,. \tag{4.6}$$

An upper bound can be obtained in terms of self-avoiding walks as in the derivation of eq. (3.5) and hence eq. (4.1) is true for the case that the limit is taken through even values of $n$. This is sufficient to prove that eq. (4.1) is true for $\tau$ not bipartite.

To prove eq. (4.1) for the case that $\tau$ is bipartite we need to get a construction which will give a uniform embedding of $\tau$ with an odd number of edges per branch. The argument is essentially the same as above except now we start with a uniform embedding of $\tau$ for which there exists a line $x = k$ which cuts every edge of $\tau$ exactly once and we assume this embedding has $n_0$ edges per branch (this embedding exists by the arguments given in ref. [11]). Now there are only $f$ vertices in the line $x = k$. Given $n$ odd, we choose $p$ and $q$ such that $n = \hat{n}p + n_0 + mf(f+1) + q$ and the proof goes through as for eq. (4.6) with $2f$ replaced by $f$ wherever it occurs.

A proof similar to the one just outlined could also have been used to prove eq. (3.8). We cannot, however, prove the analog of (3.8) for the two-dimensional case using this approach since in the embedding of $\tau$ that would result only the bottom branch of the embedding could have contacts with the line $y = 0$. Hence only the bottom branch would have free energy equal to that for a walk.

In fact in two dimensions the analogs of eqs. (3.4) and (3.8) are not true. In particular Whittington and Soteros [5] showed that they were not true for $\tau$ a 3-star and it is straightforward to generalize their argument to show that the same holds for any $\tau \neq |$. The reason for this relies on the fact that for all cases, outside the walk case, it is not possible for every vertex of the graph to lie in the line $y = 0$ and indeed a significant fraction of the vertices of the graph will be unable to contact the line $y = 0$. This "shading" effect is most important in the attractive, large $\beta$ regime. For the repulsive, $\beta < 0$, regime it is possible to show that, analogous to eq. (3.4),

$$A(\tau, \beta) = (A|, \beta) = \kappa_2, \quad \text{for } \beta \leqslant 0\,. \tag{4.7}$$

For general $\beta$ the result in two dimensions is as follows:

$$\max(\kappa_2, m^*(\tau)\beta) \leqslant \liminf_{n\to\infty} N^{-1} \log Z_n(\tau,\beta)$$
$$\leqslant \limsup_{n\to\infty} N^{-1} \log Z_n(\tau,\beta) \leqslant \max(\kappa_2, \kappa_2 + m^*(\tau)\beta)\,, \qquad (4.8)$$

where

$$m^*(\tau) = \lim_{n\to\infty} \frac{m_n^*(\tau)}{nf - c + 1} \qquad (4.9)$$

with $m_n^*(\tau) = \max\{m | g_n(\tau, m) \neq 0\}$ and $g_n(\tau, m)$ is now the number of uniform embeddings of $\tau$ on the square lattice in the half-space $y \geqslant 0$ with $n$ edges per branch and $m+1$ vertices in the line $y=0$. As usual the limit in eq. (4.9) is taken through only even values of $n$ if $\tau$ is not bipartite. The bounds involving $m^*(\tau)$ arise from the fact that for $\beta \geqslant 0$

$$e^{m_n^*(\tau)\beta} \leqslant Z_n(\tau,\beta) = \sum_{m=0}^{m_n^*(\tau)} g_n(\tau,m) e^{m\beta} \leqslant g_n(\tau) e^{m_n^*(\tau)\beta}\,. \qquad (4.10)$$

Taking logarithms, dividing by $N = nf - c + 1$, and letting $n$ go to infinity in eq. (4.10) gives the terms involving $m^*(\tau)$ in eq. (4.8). The lower bound involving $\kappa_2$ comes from considering embeddings of $\tau$ as in the construction leading to eq. (4.4) with exactly two vertices in $y=0$. The upper bound involving $\kappa_2$ comes from the fact that for $\beta \leqslant 0$, $Z_n(\tau,\beta) \leqslant Z_n(\tau,0) \leqslant g_n(\tau)$.

In the special cases $\tau = |$ and $\tau = \bigcirc$ the limit $\lim_{n\to\infty} N^{-1} \log Z_n(\tau,\beta) = A(\tau,\beta)$ has been proved to exist. One can show that $m^*(|) = 1$ and $m^*(\bigcirc) = 1/2$ and hence for $\beta > 0$, the slope of the upper bound for $A(\bigcirc,\beta)$ is less than the slope of the lower bound for $A(|,\beta)$. This indicates that there exists $\beta' > 0$ such that

$$A(\bigcirc,\beta) < A(|,\beta) \qquad (4.11)$$

for all $\beta \geqslant \beta'$. Whittington and Soteros [5] showed that $m^*(f\text{-star}) = 2/f < 1 = m^*(|)$ for $f = 3, 4$ and hence there exists $\beta' > 0$ such that

$$\limsup_{n\to\infty} N^{-1} \log Z_n(f\text{-star},\beta) < A(|,\beta) \qquad (4.12)$$

for all $\beta \geqslant \beta'$.

Consider the configuration of a uniform dumbbell with $n$ edges per branch in which all the vertices of the central branch lie in $y=0$ an half the vertices of each of the cycles lie in $y=0$. There is one such configuration for each $n$, $n$ even, having a total of $3n-1$ vertices and the maximum number of vertices, $2(n-1)+1$ vertices, in the line $y=0$ and hence $m_n^*(\bigcirc\!-\!\bigcirc) = 2(n-1)$. Hence $m^*(\bigcirc\!-\!\bigcirc) = 2/3$. Similarly one can show $m^*(\ominus) = 1/3$ and hence there exists $\beta' > 0$ such that

$$\limsup_{n\to\infty} N^{-1} \log Z_n(\ominus,\beta) < A(\bigcirc,\beta) < \liminf_{n\to\infty} N^{-1} \log Z_n(\bigcirc\!-\!\bigcirc,\beta)$$
$$\leqslant \limsup_{n\to\infty} N^{-1} \log Z_n(\bigcirc\!-\!\bigcirc,\beta) < A(|,\beta)$$

for all $\beta \geqslant \beta'$. Thus the free energy in the attractive (large $\beta$) regime is very dependent on the structure of the graph and not just on the graph index set of the graph.

Soteros [11] has shown that

$$\frac{1}{sf} \leqslant m^*(\tau) \leqslant r, \tag{4.14}$$

where $s = 1$ if $\tau$ is bipartite and $s = 2$ otherwise and $r = (f - c + n_3 + n_4 + 1)/2f$ if $\tau$ has a cut-edge and $r = \min\{(f - c + n_3 + n_4 + 1)/2f, \frac{1}{2}\}$ if $\tau$ does not have a cut-edge. Note that for any $\tau \neq |$, $r < 1$. Hence eq. (4.14) and eq. (4.8) imply that for any $\tau \neq |$ there exists $\beta' > 0$ such that

$$\limsup_{n \to \infty} N^{-1} \log Z_n(\tau, \beta) < A(|, \beta) \tag{4.15}$$

for all $\beta \geqslant \beta'$.

The upper bound in eq. (4.14) was obtained by breaking a uniform embedding of $\tau$ into a set of independent walks, 3-stars and 4-stars and using this to obtain an upper bound on the number of vertices of the graph which can lie in $y = 0$. This argument gives $r = (f - c + n_3 + n_4 + 1)/2f$. In the special case that $\tau$ does not have a cut-edge one can prove that $\lim \sup_{n \to \infty} N^{-1} \log Z_n(\tau, \beta) \leqslant A(\bigcirc, \beta)$ (see theorem 3 of ref. [11]) and that argument leads to $r = 1/2$. One obtains the lower bound $\beta/sf$ in eq. (4.14) by considering the embedding constructed in the proof of eq. (4.6) and forcing all the vertices in the bottom branch to lie in the line $y = 0$.

## 5. Discussion

The results reviewed in this paper indicate the following for *large* uniformly branched polymers with fixed topology. In three dimensions, such polymers interacting with a plane have the same free energy per monomer as large linear polymers interacting with a plane and hence the adsorption temperature is independent of the polymer's topology. In two dimensions, in the repulsive ($\beta < 0$) regime such polymers again act like large linear polymers; this is because entropic effects dominate and their entropy per monomer is the same as that of linear polymers. In two dimensions and in the attractive, large $\beta$, regime the free energy per monomer becomes strictly less than that of linear polymers. This implies that the adsorption transition occurs for a value of $\beta = \beta^*$ which is greater than or equal to $\beta_c$, the critical value for linear polymers; however, the possibility that $\beta^* = \beta_c$ has not been ruled out.

These conclusions are all based on rigorous results for the free energy per monomer in the infinite $n$ limit. So far we have been unable to say anything rigorously about the $o(n)$ terms in the free energy per monomer. Such information would help define what we mean by *large*. A computer study of various polymers with fixed topology could shed some light on this issue.

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