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Specified polymer topologies interacting with a surface

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Abstract. We study the adsorption properties of a polymer network with a specified topology. We prove that a specified topology interacting with a surface has the same reduced free energy as a self-avoiding walk interacting with a surface.

1. Introduction

Self-avoiding walks (SAWs), k-stars and k-loops are examples of topologies, the configurational properties of which have been studied in restricted geometry. The adsorption transition of SAWs, which occurs when the vertices or edges in the walk have a sufficiently large attractive interaction with a surface, has been studied extensively using both rigorous and numerical approaches (Hammersley *et al* 1982, Guim and Burkhardt 1989, Zhao *et al* 1990, etc.). We have recently proved that k-loops, which consist of k SAWs with all initial (terminal) vertices connected together, have the same adsorption properties (reduced free energy) as a SAW (Zhao and Lookman 1990). The influence of topology on the critical properties of polymers in bulk has been studied by Gaunt *et al* (1984) and Duplantier (1986). For a general polymer network to a surface, Duplantier and Saleur (1986) have conjectured the dependence of the critical exponent γ on polymer topology. In this paper, we examine the problem of a general polymer network, with a specific topology, interacting with an adsorption surface. We prove that such a polymer network has the same reduced free energy as that for a SAW interacting with an adsorption surface.

We consider a uniform polymer network $\mathcal{G}_n(c, n_3, \ldots, n_{2d})$ which is defined on a d-dimensional hypercubic lattice and interacts with a $(d-1)$-dimensional hypersurface (either penetrable or impenetrable). The topology of such a network is specified in terms of c cycles, n_3 vertices of degree $3, \ldots, n_{2d}$ vertices of degree $2d$. These vertices will also be referred to as branch points. Using Euler's law of edges, we have

$$2c = 2 - n_1 + \sum_{i=3}^{2d} (i-2)n_i \tag{1.1}$$

and

$$2K = n_1 + \sum_{i=3}^{2d} i n_i \tag{1.2}$$

where n_1 is the number of vertices with degree 1 and K is the number of chains connecting the branch points and vertices of degree 1. Each of the K chains consists of n monomers and is an n-step SAW. The vertices of degree 2 have been suppressed since they do not affect the topology and hence the structure of the branched polymer.

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The values $\{c, n_3, n_4, \ldots, n_{2d}\}$ do not specify a unique topology since they do not uniquely determine the connectivity. More than one topology can have the same set of values for $\{c, n_3, n_4, \ldots, n_{2d}\}$ (figure 1). The case $c=0$ refers to a tree-like structure in general. However, for certain values of $\{c, n_3, n_4, \ldots, n_{2d}\}$ unique topologies are obtained. For example, $n_k=1$, $n_i=0$ for $k \neq i$ refers to a k-star, $n_3=2$, $n_i=0$, $i \geqslant 4$ refers an H-comb (figure 2). For $c=0$, each chain in such a network has a different initial and terminal vertex and each chain can have an even or odd number of monomers. The case $c \neq 0$ includes those with loops in which the initial and terminal vertices of a chain are the same (figure 1(b)). Chains forming loops or polygons are restricted to having an even number of monomers for a non-zero embedding in the hypercubic lattice. Hence, for a uniform topology with $c \neq 0$, we restrict all chains to having an even number of monomers.

For the lattice, a vertex is a point in the d-dimensional Euclidean space with integer coordinates $\boldsymbol{x}=(x_1, \ldots, x_d)$. An n-step SAW ω is a sequence of vertices $\omega = \{\boldsymbol{x}(0), \boldsymbol{x}(1), \ldots, \boldsymbol{x}(n)\}$ with $|\boldsymbol{x}(i)-\boldsymbol{x}(i+1)|=1$. We define the unit vectors by $\boldsymbol{e}_1 = (1, 0, \ldots, 0), \ldots, \boldsymbol{e}_d=(0, 0, \ldots, 1)$. The interaction surface is the hyperplane $x_1=0$. In the surface, each vertex is the intersection of $d-1$ perpendicular planes which divide the hypercubic lattice into 2^{d-1} regions, to be referred to as subsections.

Let $\mathscr{G}_n(c, n_3, \ldots, n_{2d})$ be the set of connected polymer networks with topology defined by $\{c, n_3, n_4, \ldots, n_{2d}\}$. The topology contains Kn edges since each of the K chains is an n-step SAW. We denote by $g_{Kn,m}$ the number of sich networks with a total

(a)

(b)

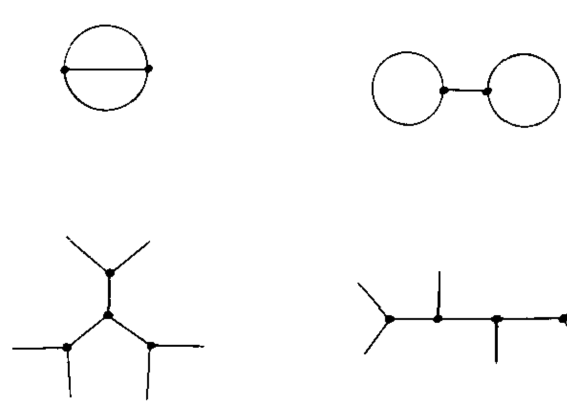

Figure 1. Examples of topologies with the same $\{c, n_3, n_4, \ldots, n_{2d}\}$: ($a$) a Θ graph and a dumb-bell with $\{2, 2, 0, 0, \ldots, 0\}$; ($b$) a tree and a comb with $\{0, 4, 0, 0, \ldots, 0\}$.

(a) (b)

Figure 2. Unique topologies for certain values of $\{c, n_3, n_4, \ldots, n_{2d}\}$; ($a$) a 4-star with $\{0, 0, 1, 0, \ldots, 0\}$; ($b$) an H-comb with $\{0, 2, 0, \ldots, 0\}$.

of m edges in the penetrable surface $x_1=0$ and define the generating function by

$$G_n(c, n_3, \ldots, n_{2d}, \omega) = \sum_{m=0}^{Kn} g_{Kn,m}\, \mathrm{e}^{m\omega}. \tag{1.3}$$

We show that

$$\lim_{n\to\infty} (Kn)^{-1} \log G_n(c, n_3, \ldots, n_{2d}, \omega) = A(\omega) \tag{1.4}$$

where $A(\omega)$ is the reduced free energy of SAWs in terms of the number of edges in the penetrable surface. For $c=0$, n can be either even or odd, for $c\neq 0$, n is even.

2. Proof of the results

We derive a lower bound for the function $G_n(c, n_3, \ldots, n_{2d}, \omega)$. By following the procedure of Gaunt *et al* (1984), such a lower bound can be obtained by using simple polymer topologies (components) to construct a polymer network with the set $(c, n_3, \ldots, n_{2d})$. In the following, we consider the case $c\neq 0$.

We have previously defined (Zhao and Lookman 1990): (i) the set of n-step SAWs, $\mathscr{B}_n$, which are totally confined in the wedge w: $1\leqslant x_2, \ldots, 1\leqslant x_{d-1}\leqslant x_d$ with $\boldsymbol{x}(0) = \boldsymbol{e}_2+\boldsymbol{e}_3+\ldots+\boldsymbol{e}_{d-1}+4\boldsymbol{e}_d$ and $\boldsymbol{x}(n)$ in the hyperplane $x_d = x_{d-1}$ (figure 3); (ii) two fixed $(d+4)$-step walks L_1 and L_2 starting at $\boldsymbol{0}$ and ending at $\boldsymbol{x}(0)$, where L_1 has no edges in the surface $x_1=0$ and L_2 is totally embedded in the surface (figure 4); (iii) two injective maps $f_{i,j}$ $(i,j\geqslant 2)$ and g_i $(i\geqslant 1)$ such that $f_{i,j}$ interchanges the coordinates x_i, x_j of a vertex $\boldsymbol{x}$ and g_i replaces x_i of $\boldsymbol{x}$ with $-x_i$. We have shown that

$$\lim_{n\to\infty} (n)^{-1} \log B_n(\omega) = A(\omega) \tag{2.1}$$

where $B_n(\omega)$ is the generating function for $\mathscr{B}_n$. Classification of walks in $\mathscr{B}_n$ by the coordinates of the end vertices yields, at most, $I=(n+1)^{d-1}(2n+1)$ subclasses. In the

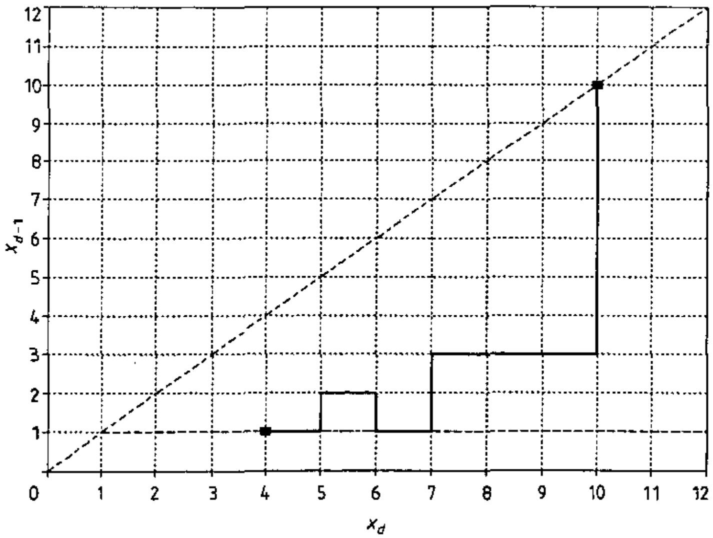

Figure 3. Example of a defined SAW in $\mathscr{B}_n$ (heavy full line). Broken lines represent the hyperplane $x_{d-1}=x_d$ and $x_{d-1}=1$.

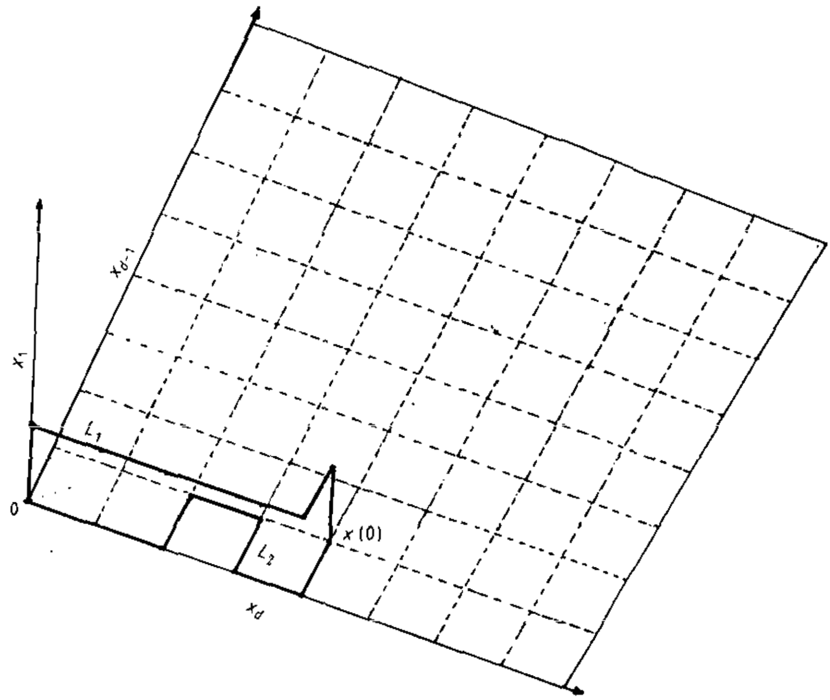

Figure 4. Heavy full lines represent the two defined $(d+4)$-step walks L_1, L_2.

ith subclass $\mathscr{B}^i_n$, the end vertex of all walks is denoted by $x(n)=(x_1(n),\ldots,x_d(n))$. By using the walks in $\mathscr{B}^i_n$, the maps $f_{i,j}$, g_i and L_1, L_2, we have previously given the construction of two components. These are:

(a) By taking two walks from $\mathscr{B}^i_n$ and concatenating with the same L_i, we can construct $(2(n+d+4)+J)$-step walks ω^1 or ω^2, where $J=3$ or $J=4$. Since we only deal with a polymer network with an even number of edges in each chain, we will let $J=4$. ω^1 and ω^2 are totally confined in the subsection s_1: $x_2\geqslant 0,\ldots,x_{d-1}\geqslant 0$, $x_d\geqslant 0$ and intersect only at their initial and terminal vertices $x(S)$ and $x(E)$, which satisfy $x(S)=\mathbf{0}$ and $x(E)=(0,\ldots,0,2x_d(n)+4)$ (figure 5). The incident edges at the two vertices for ω^1 are $[\mathbf{0},e_1]$ (or $[\mathbf{0},e_d]$) and $[x(E),x(E)+e_1]$ (or $[x(E),x(E)-e_d]$) respectively, while the incident edges at the two vertices for ω^2 are $[\mathbf{0},e_{d-1}]$ and $[x(E),x(E)+e_{d-1}]$ respectively. We will denote these walks by $\omega(e_1)$, $\omega(e_{d-1})$ and $\omega(e_d)$. For any two vertices $x(k_1)$, $x(k_2)$ in the same walk $\omega(e_i)$, we have

$$|x_j(k_1)-x_j(k_2)|\leqslant x_d(n)+1 \qquad \text{for } j\neq d \tag{2.2}$$

$$|x_d(k_1)-x_d(k_2)|\leqslant 2x_d(n)+4. \tag{2.3}$$

(b) The 'watermelon' topology consists of chains attached by their extremities such that the coordinate of any vertex on a chain lies between the two branch points (or extremes). It has previously been discussed by Zhao and Lookman (1990) and by Duplantier (1986). By using $2k$ $(2\leqslant k\leqslant d-1)$ walks from $\mathscr{B}^i_n$ and concatenating them with L_is, we can construct a uniform k-watermelon, $\ell_k(e_i,e_{i_2},\ldots,-e_{i_k})$ in which each chain has a length of $2(n+d+4)+4$ steps. The two extremes $x(S)$ and $x(E)$ are on the x_i-axis with $x(S)=\mathbf{0}$ and $x(E)=(0,0,\ldots,2x_d(n)+4,\ldots,0)$. The incident edges

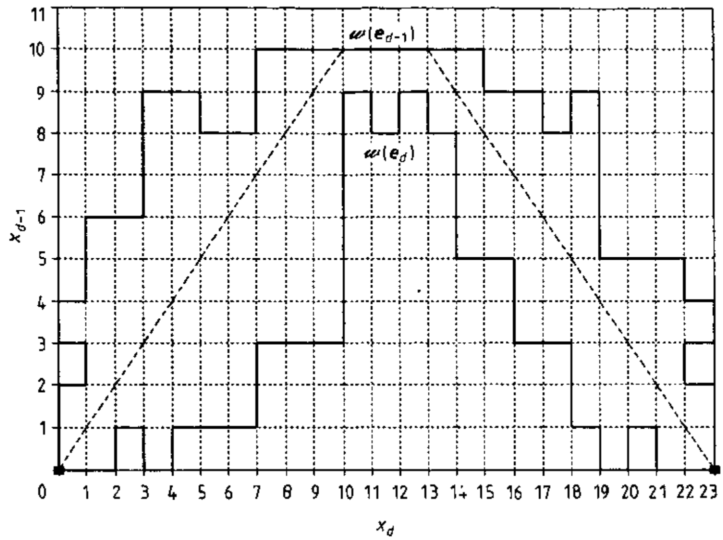

Figure 5. Example of the constructed walks $\omega(e_{d-1})$ and $\omega(e_d)$.

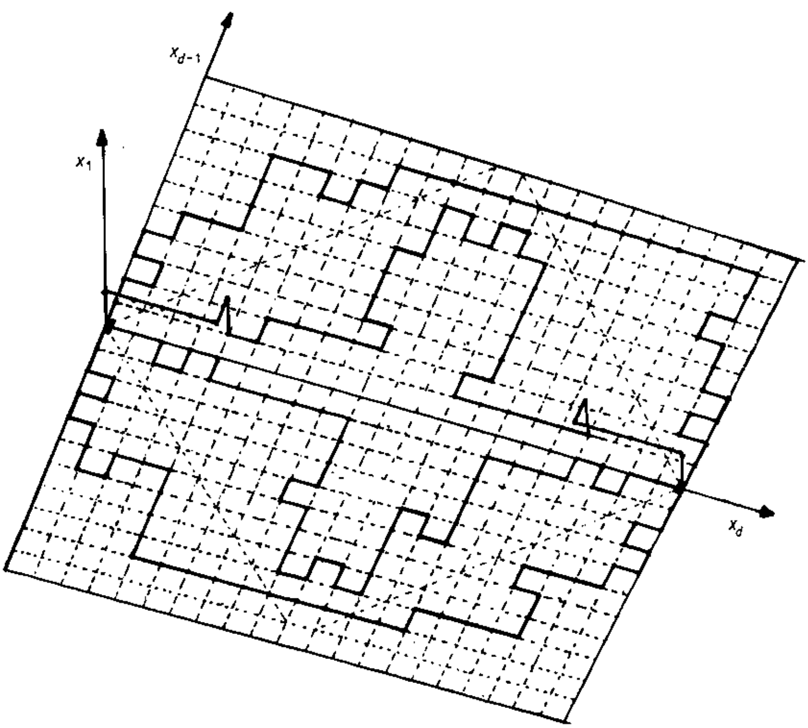

Figure 6. Example of a 4-watermelon $\ell_4(e_d, e_1, e_{d-1}, -e_{d-1})$ with its two extremes on the x_d axis. Under the map $f_{d-1,d}$, it becomes $\ell_4(e_{d-1}, e_1, e_d, -e_d)$ with its two extremes on the x_{d-1}-axis.

at $\boldsymbol{x}(S)$ and $\boldsymbol{x}(E)$ are $[\mathbf{0}, \boldsymbol{e}_i], [\mathbf{0}, \boldsymbol{e}_{i_2}], \ldots, [\mathbf{0}, -\boldsymbol{e}_{i_k}]$ and $[\boldsymbol{x}(E), \boldsymbol{x}(E)-\boldsymbol{e}_i], [\boldsymbol{x}(E), \boldsymbol{x}(E)+\boldsymbol{e}_{i_2}], \ldots, [\boldsymbol{x}(E), \boldsymbol{x}(E)-\boldsymbol{e}_{i_k}]$ respectively (figure 6). For any two vertices $\boldsymbol{x}(k_1)$, $\boldsymbol{x}(k_2)$ of ℓ, we have

$$|x_j(k_1)-x_j(k_2)| \leqslant 2(x_d(n)+1) \qquad \text{for } j \neq i \tag{2.4}$$

$$|x_i(k_1)-x_i(k_2)| \leqslant 2x_d(n)+4. \tag{2.5}$$

The special case $k=2$ is a polygon. For convenience, we refer to it as a watermelon with two uniform $(2(n+d+4)+4)$-step branches.

In addition to these two components, another component, a $(2(n+d+4)+4)$-step polygon, is also needed, which can be obtained as follows. We take two walks from $\mathscr{B}_n^i$ and concatenate both of them with L_2 (or one by L_1 and another by L_2). We denote these two walks by ω_1, ω_2 and define

$$\omega_1' = g_{i_1} \circ \ldots \circ g_{i_k} \circ f_{i,d-1} \circ f_{j,d}(\omega_1) \tag{2.6}$$

$$\omega_2' = g_{i_1} \circ \ldots \circ g_{i_k} \circ f_{d-1,d} \circ f_{j,d-1} \circ f_{i,d}(\omega_2). \tag{2.7}$$

The two new walks ω_1' and ω_2' intersect at the points $\mathbf{0}$ and $(x_1, \ldots, -x_{i_1}, \ldots, -x_{i_k}, \ldots, x_i, x_j)$ and are confined in the subsection

$$s: \qquad x_1 \geqslant 0, \ldots, x_{i_1} \leqslant 0, \ldots, x_{i_k} \leqslant 0, \ldots, x_d \geqslant 0. \tag{2.8}$$

We delete the last edge from ω_2' and join the two walks by a five-step walk: $\{\boldsymbol{x}_2'(n-1), \boldsymbol{x}_2'(n-1)+\boldsymbol{e}_{d-1}, \boldsymbol{x}_2'(n-1)+\boldsymbol{e}_{d-1}+\boldsymbol{e}_d, \boldsymbol{x}_2'(n-1)+\boldsymbol{e}_{d-1}+2\boldsymbol{e}_d, \boldsymbol{x}_2'(n-1)+2\boldsymbol{e}_d, \boldsymbol{x}_1'(n)\}$, which gives a $2(n+d+4)$-step polygon $\not{p}(\pm\boldsymbol{e}_i, \pm\boldsymbol{e}_j)$ with incident edges at $\mathbf{0}$ of $[\mathbf{0}, \boldsymbol{e}_i]$ (or $[\mathbf{0}, -\boldsymbol{e}_i]$) and $[\mathbf{0}, \boldsymbol{e}_i]$ (or $[\mathbf{0}, -\boldsymbol{e}_j]$) and $\boldsymbol{e}_i \cdot \boldsymbol{e}_j = 0$ (figure 7). For any two vertices $\boldsymbol{x}(k_1)$ and $\boldsymbol{x}(k_2)$ of $\not{p}$, one can verify that

$$|x_i(k_1)-x_i(k_2)| \leqslant x_d(n)+1 \qquad i=1, \ldots, d. \tag{2.9}$$

We denote the sets of all such walks, watermelons and polygons by $\mathscr{W}^i$, $\mathscr{L}^i$ and $\mathscr{P}^i$ respectively, where all the members are constructed from $\mathscr{B}_n^i$.

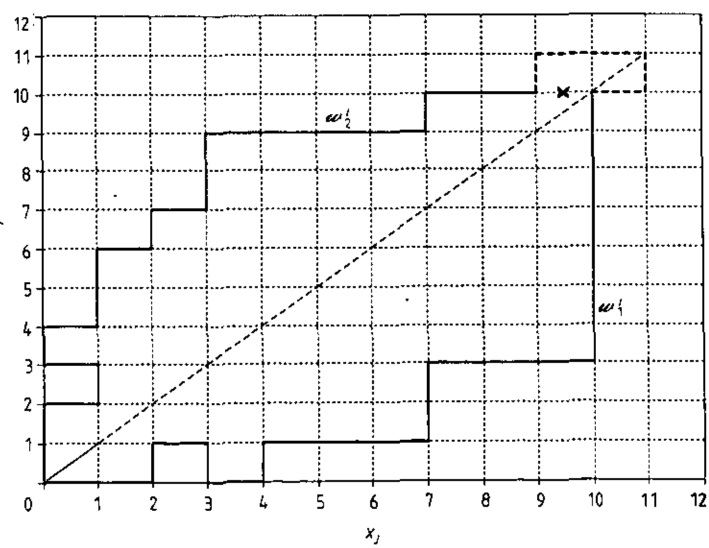

Figure 7. Example showing the joining of the two walks ω_1', ω_2' in (2.9) and (2.10) (heavy full line) by a five-step walk (heavy broken line) to form a polygon $\not{p}$. The cross indicates the edge deleted from ω_1'.

By using members from $\mathscr{P}^i$, $\mathscr{L}^i$ and $\mathscr{W}^i$, we construct appropriate precursors which are uniform polymer networks with one or no cycles and with the set of vertices $\{n'_1, n'_3, \ldots, n'_{2d}\}$, where n'_i is minimized such that

$$n'_1 = n_1 \tag{2.10}$$

and

$$n'_i \leq n_i \qquad \text{for } i \geq 3. \tag{2.11}$$

There are three such precursors (Gaunt *et al* 1984):

(i) For $n_1 = 0$, the precursor is a polygon. We take it as any member of $\mathscr{P}^i$.

(ii) For $n_1 = 1$, the precursor satisfies

$$n'_3 = n_1 \tag{2.12}$$

and

$$n'_k = 0 \qquad \text{for } k > 3 \tag{2.13}$$

which indicates that the precursor has one cycle. We take a walk ω from $\mathscr{W}^i$ and a polygon $\not{p}$ from $\mathscr{P}^i$ and join them together at the end vertex of ω.

(iii) For $n_1 \geq 2$, the precursor is a uniform tree with the set of vertices $\{n'_1, n'_3, \ldots, n'_{2d}\}$ satisfying

$$\sum_{i=3}^{2d} (i-2)(n_i - n'_i) = 2c. \tag{2.14}$$

To construct such a precursor, we take two walks $\omega_1(\boldsymbol{e}_1)$ and $\omega_2(\boldsymbol{e}_{d-1})$ from $\mathscr{W}^i$ and connect them by translating $\omega_2(\boldsymbol{e}_{d-1})$ such that its first vertex $\boldsymbol{x}(S)$ coincides with the last vertex $\boldsymbol{x}(E)$ of $\omega_1(\boldsymbol{e}_1)$. Then from $\mathscr{L}^i$, we take a $(k-2)$-watermelon $\ell_{k-2}(\boldsymbol{e}_{d-1}, -\boldsymbol{e}_1, \boldsymbol{e}_2, -\boldsymbol{e}_2, \ldots)$ (if $k = 3$, we replace the watermelon by a walk $\omega(\boldsymbol{e}_d)$ from $\mathscr{W}^i$, and use the map $f_{d-1,d}$ to let its two end vertices be on the x_{d-1}-axis). We body shift it in the $-\boldsymbol{e}_{d-1}$-direction to let the extreme $\boldsymbol{x}(E)$ coincide with the joint of the two walks. We remove the extreme $\boldsymbol{x}(S)$ and the incident edges, and then add to each branch of ℓ_{k-2} an edge in the $-\boldsymbol{e}_{d-1}$ direction, which gives a uniform tree with $n_1 = k$ and $n_k = 1$ $(k \leq 2d)$. Next, we take $\omega_3(\boldsymbol{e}_1)$ from $\mathscr{W}^i$ and $\ell'_{k'-2}(\boldsymbol{e}_{d-1}, -\boldsymbol{e}_1, \boldsymbol{e}_2, -\boldsymbol{e}_2, \ldots)$ and connect them with $\omega_2(\boldsymbol{e}_{d-1})$ at its last vertex $\boldsymbol{x}(E)$ in the same way. The definitions of the walks and watermelons together with (2.2)–(2.5) ensure that the walks and watermelons are independent of each other. By repeating the procedure, we obtain a uniform tree with the set $\{n'_1, \ldots, n'_{2d}\}$. We note that the uniform tree constructed in this way is a uniform brush with the 'backbone' consisting of $\omega_1(\boldsymbol{e}_1)$, $\omega_2(\boldsymbol{e}_{d-1})$, $\omega_3(\boldsymbol{e}_1), \ldots$ (figure 8). (A brush is a particular tree topology with a self-avoiding

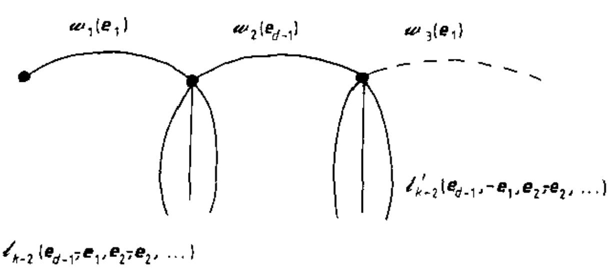

Figure 8. The construction of a uniform tree (uniform brush) as a precursor from walks and watermelons from the sets $\mathscr{W}^i$ and $\mathscr{L}^i$ respectively.

'backbone' formed by branch points of degree $\geqslant 3$ that are connected by n-step SAWs. The topology with all branch points of degree 3 is known as a comb.)

We now convert the precursors into a uniform network with the set $(c, n_3, \ldots, n_{2d})$ by using the following two constructions. We concentrate on the third case, where the precursor is a uniform tree, denoted by $\mathscr{g}'$. In $\mathscr{g}'$, the vertex $\boldsymbol{x}(S)$ of $\omega_1(\boldsymbol{e}_1)$ is the end vertex of a chain and satisfies the condition that for any vertex $\boldsymbol{x}$ of $\mathscr{g}'$, $x_d \geqslant x_d(S)$. We denote such a vertex by $\boldsymbol{x}_b$. We start with $\boldsymbol{x}_b$ of $\mathscr{g}'$, which has the incident edge $[\boldsymbol{x}_b, \boldsymbol{x}_b+\boldsymbol{e}_1]$, and all the translations that may be needed will be in the $-\boldsymbol{e}_d$ direction.

Construction 1. Adding the vertices of odd degrees to $\mathscr{g}'$. Equation (2.14) implies

$$\sum_{i=1}^{d-1} (n_{2i+1} - n'_{2i+1}) \equiv 0 \qquad (\bmod 2). \tag{2.15}$$

There remains an even number of such vertices. Starting with the highest degree, we list all of these vertices and write them in pairs. In one such pair, let the first vertex have degree i and the second vertex have degree j, so $i \geqslant j$ and $i-j=2k$. We take a $(j-1)$-watermelon $\ell_{j-1}(\boldsymbol{e}_d, \boldsymbol{e}_{k_2}, \ldots, -\boldsymbol{e}_{k_{j-1}})$ from $\mathscr{L}^i$, which has its two extremes on the x_d-axis. We translate it to let its extreme $\boldsymbol{x}(E)$ coincide with $\boldsymbol{x}_b$ of $\mathscr{g}'$, which converts $\boldsymbol{x}_b$ into a vertex of degree j. At the extreme $\boldsymbol{x}(S)$ of the watermelon, we first join it with the last vertex $\boldsymbol{x}(E)$ of a walk $\omega(\boldsymbol{e}_d)$ from $\mathscr{W}^i$ by translating $\omega(\boldsymbol{e}_d)$. We then take k polygons from $\mathscr{P}^i$ such that at $\mathbf{0}$, the incident edges of the polygons are not the edges $[\mathbf{0}, -\boldsymbol{e}_d], [\mathbf{0}, \boldsymbol{e}_d], \ldots, [\mathbf{0}, -\boldsymbol{e}_{k_{j-1}}]$, and by a translation, the polygons are confined in k of the remaining $2^{(d-2)}-1$ subsections which satisfy $x_d \leqslant x_d(S)$ at $\boldsymbol{x}(S)$ of the watermelon. By joining the polygons in this way, we convert the extreme $\boldsymbol{x}(S)$ into a vertex of degree i. Thus, we add the precursor with a vertex of degree i and a vertex of degree j, which produces $1+(i+j-6)/2$ cycles. We repeat the procedure for all pairs and obtain a uniform polymer network $\mathscr{g}''$ with n_{2i+1} of vertices with degree $2i+1$. The vertex $\boldsymbol{x}(S)$ of the last walk added becomes $\boldsymbol{x}_b$ of $\mathscr{g}''$ with incident edge $[\boldsymbol{x}_b, \boldsymbol{x}_b+\boldsymbol{e}_d]$.

Construction 2. Adding a vertex of degree $2k$ (forming $k-1$ cycles) to $\mathscr{g}''$. We first join $\boldsymbol{x}_b$ of $\mathscr{g}''$ by a walk $\omega_1(\boldsymbol{e}_{d-1})$ from $\mathscr{W}^i$ to convert it into a vertex of degree 2 with incident edges $[\boldsymbol{x}_b, \boldsymbol{x}_b+\boldsymbol{e}_{d-1}]$ and $[\boldsymbol{x}_b, \boldsymbol{x}_b+\boldsymbol{e}_d]$. We then take $k-1$ polygons from $\mathscr{P}^i$, which, at $\mathbf{0}$, have incident edges other than $[\mathbf{0}, \boldsymbol{e}_{d-1}]$ and $[\mathbf{0}, \boldsymbol{e}_d]$, and can be translated to be confined in the other 2^{d-2} subsections at $\boldsymbol{x}_b$. By joining the $k-1$ polygons at the joint vertex $\boldsymbol{x}_b$, we have thus added a vertex of degree $2k$ and $k-1$ cycles to $\mathscr{g}''$. The new $\boldsymbol{x}_b$ is the vertex $\boldsymbol{x}(S)$ of $\omega_1(\boldsymbol{e}_{d-1})$ with incident edge $[\boldsymbol{x}_b, \boldsymbol{x}_b+\boldsymbol{e}_{d-1}]$. Next, we take a walk $\omega_2(\boldsymbol{e}_d)$ from $\mathscr{W}^i$ and $k'-1$ polygons and add them to $\boldsymbol{x}_b$ to convert it into a vertex of degree $2k'$, which yields $k'-1$ cycles. The procedure is repeated until all vertices of even degree have been added.

From this procedure, we obtain a uniform polymer network $\mathscr{g}_{2(n+d+6)}(c, n_3, \ldots, n_{2d})$ with each chain constructed from two members of $\mathscr{B}_n^i$ and of length $2(n+d+6)\times$ $(=2(n+d+4)+4)$ edges. Similarly, based on the above constructions, we can convert the first two precursors into a polymer network.

Generally, we take a group of $2K$ walks $\omega_1, \omega_2, \ldots, \omega_{2K}$ from $\mathscr{B}_n^i$ where ω_i has m_i edges in the surface $x_1=0$. We first concatenate K_1 of the walks with L_1 and the rest of K_2 walks with L_2, where $K_1+K_2=2K$, and then use these walks to construct the required walks, watermelons and polygons. By following the above procedure to join these components together, we obtain a polymer network $\mathscr{g}_{2(n+d+6)}(c, n_3, \ldots, n_{2d})$

which has either $m+K_2(d+4)$ or $m+K_2(d+1)+4K$ edges in the surface, depending on the position of the end vertex $x(n)$ of the walks, where $m=m_1+\ldots+m_{2K}$. The construction of $\mathscr{g}_{2(n+d+6)}(c, n_3, \ldots, n_{2d})$ from the walks $\omega_1, \ldots, \omega_{2K}$ is considered as a standard procedure which has to be followed whenever a group of $2K$ walks from $\mathscr{B}^i_n$ are used to construct a polymer network. Hence, a distinct group of $2K$ walks will give a distinct polymer network $\mathscr{g}_{2(n+d+6)}(c, n_3, \ldots, n_{2d})$. We denote by $b^i_{n,m}$ the number of walks in the ith subclass with m edges in the surface. We obtain

$$\prod_{j=1}^{2K} b^i_{n,m_j} \leqslant g_{2K(n+d+6),m+K_2(d+4)} + g_{2K(n+d+6),m+K_2(d+4)+4K} \tag{2.16}$$

with $m=m_1+m_2+\ldots+m_{2K}$. We write

$$B_n(\omega, i) = \sum_{m=0}^{n} b^i_{n,m}\, \mathrm{e}^{m\omega} \tag{2.17}$$

as the generating function for walks in the ith subclass. From (2.16) we have

$$\begin{aligned}
(B_n(\omega, i))^{2K} &= \left(\sum_{m=0}^{n} b^i_{n,m}\, \mathrm{e}^{m\omega}\right)^{2K} \\
&= \sum_{m=0}^{2Kn} \sum_{m_1+\ldots+m_{2K}=m} \prod_{j=1}^{2K} b^i_{n,m_j}\, \mathrm{e}^{m\omega} \\
&\leqslant \sum_{m=0}^{2Kn} \sum_{m_1+\ldots+m_{2K}=m} (g_{2K(n+d+6),m+K_2(d+4)} + g_{2K(n+d+6),m+K_2(d+4)+4K})\, \mathrm{e}^{m\omega} \\
&\leqslant (2Kn)^{2K} f(\omega) G_{2(n+d+6)}(c, n_3, \ldots, n_{2d}, \omega)
\end{aligned} \tag{2.18}$$

where $f(\omega)=(1+\mathrm{e}^{4K|\omega|})\cdot \mathrm{e}^{K_2(d+4)|\omega|}$. Let $p=2K$ and $q=2K\cdot(2K-1)^{-1}$, then $p^{-1}+q^{-1}=(2K)^{-1}+(2K-1)\cdot(2K)^{-1}=1$. By Hölder's inequality, we have

$$\begin{aligned}
(B_n(\omega))^{2K} &= \left(\sum_{i=1}^{I} B_n(\omega, i)\right)^{2K} \\
&\leqslant \left(\sum_{i=1}^{I} 1^{2K/(2K-1)}\right)^{2K-1} \sum_{i=1}^{I} (B_n(\omega, i))^{2K} \\
&\leqslant I^{2K+1}(2Kn)^{2K} f(\omega) G_{2(n+d+6)}(c, n_3, \ldots, n_{2d}, \omega).
\end{aligned} \tag{2.19}$$

We now derive an upper bound for $G_n(c, n_3, \ldots, n_{2d}, \omega)$. From (1.2), we can replace the set $(c, n_3, \ldots, n_{2d})$ by the set $(n_1, n_3, \ldots, n_{2d})$, the number of all terminal and branch points of $\mathscr{g}_n$. We first classify the $\mathscr{g}_n$s according to how all the terminal and branch points are connected by chains. Let $n'=n_1+n_3+\ldots+n_{2d}$, from Gaunt *et al* (1984), there can be, at most, $2^{\binom{n'}{2}}$ ways of connecting all the points. Hence, there can be, at most, $2^{\binom{n'}{2}}$ such classes. In each class, we divide the $\mathscr{g}_n$s again by the number of chains which have at least one vertex in the surface. These two classifications give, at most, $2^{\binom{n'}{2}}\cdot 2K$ subclasses. We denote by $G_n(c, n_3, \ldots, n_{2d}, \omega, i)$ the generating function for $\mathscr{g}_n$ in the ith subclass. By following the line of argument given in Zhao and Lookman (1990), we obtain ω and as $n\to\infty$,

$$G_n(c, n_3, \ldots, n_{2d}, \omega, i) \leqslant \exp[2KnA(\omega)+\mathrm{O}(n)]. \tag{2.20}$$

Hence, we have

$$G_n(c, n_3, \ldots, n_{2d}, \omega) = \sum_i G_n(c, n_3, \ldots, n_{2d}, \omega, i)$$

$$\leqslant 2^{\binom{n}{2}}(2K)\exp[2KnA(\omega) + \mathrm{O}(n)] \tag{2.21}$$

which, together with (2.1) and (2.19), establishes (1.4).

In the above construction, we note that all of the joint vertices are in the surface with coordinates $(0, 0, \ldots, x_d)$, since the surface is penetrable and the monomers of a polymer network can be on either side of the surface. When the interaction surface $x_1 = 0$ is impenetrable, a polymer network is totally confined to one side of the surface, say $x_1 \geqslant 0$. In this case, we consider the set $\mathscr{B}_n^+$, which is the subset of $\mathscr{B}_n$ satisfying

$$x_1(i) \geqslant 0 \qquad \text{for } i = 0, 1, \ldots, n. \tag{2.22}$$

The map g_i is also restricted to $i \geqslant 2$. We replace L_1 and L_2 by three new uniform finite-step walks L_1', L_2' and L_3' which are confined to $x_1 \geqslant 0$ and are defined such that they are disjointed except at the vertices $\boldsymbol{A} = (3, 0, \ldots, 0)$ and $\boldsymbol{x}(0)$, with the first step of L_1' being the edge $[\boldsymbol{A}, \boldsymbol{A} - \boldsymbol{e}_1]$, the first step of L_2' being the edge $[\boldsymbol{A}, \boldsymbol{A} + \boldsymbol{e}_d]$ and the first step of L_3' being the edge $[\boldsymbol{A}, \boldsymbol{A} + \boldsymbol{e}_1]$ (figure 9). We concatenate the walks in $\mathscr{B}_n^+$ with L_1', L_2' and L_3', and follow the same procedures for constructing the walks, watermelons and polygons. This will yield new walks, watermelons and polygons such that all of these new components have their $\boldsymbol{x}(S)$s and $\boldsymbol{x}(E)$s in the surface $x_1 = 3$. By using these new components and following the same procedure as that for the penetrable surface, but replacing $A(\omega)$ with $A^+(\omega)$ where necessary, we obtain that the reduced

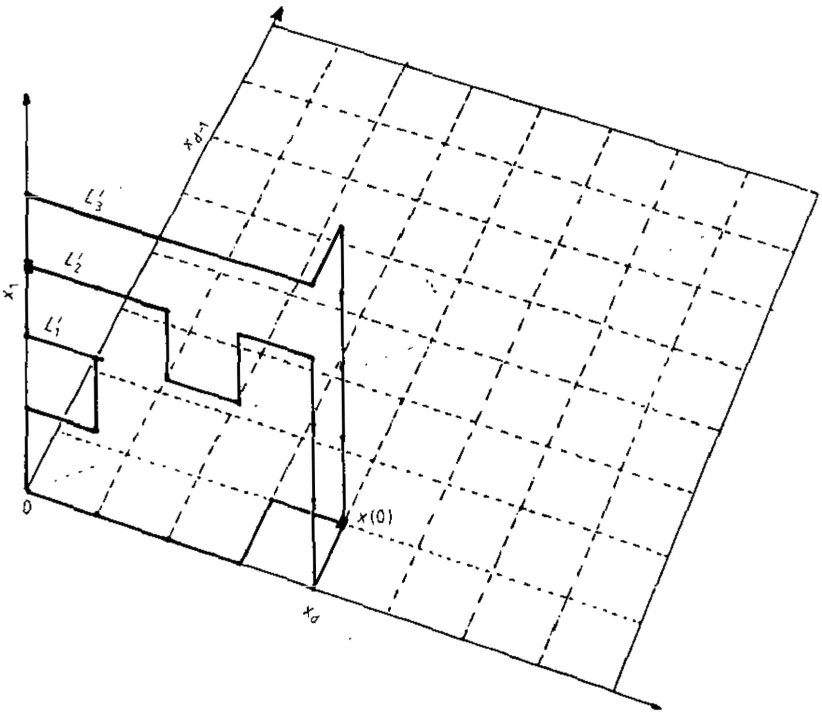

Figure 9. Three new defined finite walks L_1', L_2' and L_3'.

free energy for polymer networks interacting with an impenetrable surface is the same as that for SAWs.

3. Summary

We have considered the problem of the interaction between a surface and polymer networks with a specific topology defined by the values $\{c, n_3, n_4, \ldots, n_{2d}\}$. The values $\{c, n_3, n_4, \ldots, n_{2d}\}$ do not define a unique topology. We have established that such networks have the same reduced free energy (and hence critical point and crossover behaviour) as that for SAWs interacting with a surface. For $c \neq 0$, the definitions (1.1) and (1.2) allow a chain to have the same initial and terminal vertex, resulting in a loop or polygon that can only have an even number of monomers in a hypercubic lattice. Hence, for a uniform topology with $c \neq 0$, each chain is restricted to having an even number of monomers. For $c = 0$, each chain can have an even or odd number of monomers. We note that the trees obtained as precursors also give uniform brushes (combs), implying that our result also holds for brushes (combs).

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Note added in proof. Specified polymer topologies are also the subject of a recent preprint by C E Soteros.

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