A lattice tree model of branched copolymer adsorption

2000 J. Phys. A: Math. Gen. 33 1171

(http://iopscience.iop.org/0305-4470/33/6/306)

J. Phys. A: Math. Gen. **33** (2000) 1171–1186. Printed in the UK PII: S0305-4470(00)06948-1

A lattice tree model of branched copolymer adsorption

S You† and E J Janse van Rensburg‡

† Department of Physics and Astronomy, York University Toronto, Ontario, Canada M3J 1P3
‡ Department of Mathematics and Statistics, York University Toronto, Ontario, Canada M3J 1P3

Received 18 August 1999, in final form 12 November 1999

Abstract. Lattice models of adsorbing branched copolymers are examined. In particular, the existence of limiting free energies and the occurance of adsorption transitions are proven. The location of the adsorption critical points in quenched and annealed models of lattice branched copolymers are related and compared with the adsorption of branched homopolymers. Finally, we show that a certain quenched model of adsorbing branched copolymers is self-averaging.

1. Introduction

A lattice model of linear homopolymer adsorption was introduced in 1982 [13]. Since that paper, the adsorption problem for walk models of linear polymers has received considerable attention in the literature. For example, directed models of adsorbing walks have received attention [4, 10, 20, 25], and the adsorption problem for the self-avoiding walk has also been considered [2, 3, 9, 23]. More recently, the adsorption problem for linear copolymers has been examined [5, 16, 18, 21, 22, 24, 26]. Related problems of self-interacting linear copolymers with quenched randomness were examined by Kantor and Kardar [17], Grassberger and Hegger [12], and by Golding and Kantor [11].

Lattice tree models of adsorbing branched polymers were introduced in [6, 7] and [8]. In this paper we consider a variety of lattice tree models of branched copolymer adsorption. We first consider a model of an alternating branched copolymer. The existence of a limiting free energy in this model is shown, and it is demonstrated that there is an adsorption transition in this model. Next, we examine a model of a block branched copolymer, and show that it adsorbs at the same critical value of the fugacity as a branched homopolymer model. The existence of a limiting free energy in a particular model of quenched branched copolymers is examined in section 4, where we also show that this model is self-averaging.

A good starting point for the discussion is a brief review of the adsorption problem in a lattice model of branched homopolymers. Let t_n be the number of lattice trees with n edges, counted modulo translation. The coordinates of a vertex v in the lattice will be denoted by $(X(v), Y(v), \ldots, Z(v))$ in d dimensions, where X is the first coordinate, and Z is always the last (or dth) coordinate. The adsorption plane is the hyperplane defined by $\{v \in \mathcal{Z}^d | Z(v) = 0\}$, that is, all those vertices with Z-coordinate equal to zero. A lattice tree is *attached* if it has a vertex v with Z-coordinate in the set $\{1, 0, -1\}$ (that is, it is close to the adsorbing plane). A *positive tree* is an attached tree with Z-coordinates of all its vertices non-negative. The number of attached trees will be denoted by t_n, and the number of positive trees by t_n^+. A model of adsorbing branched polymers is obtained by counting attached and positive trees with respect to the number of vertices they have in the adsorbing plane (these are called *visits*). The basic quantities are then $t_n(v)$ and $t_n^+(v)$; where $t_n(v)$ is the number of attached trees with v visits, and $t_n^+(v)$ is the number of positive trees with v visits. The interaction with the adsorbing plane is modelled by introducing a *visit-fugacity* α, with α conjugate to the number of visits in the tree. It is known that there is an adsorption transition in these models at a critical value of the visit-fugacity [15]. The partition function for positive attached trees is

$$Z_n^+(\alpha) = \sum_{v \geqslant 0} t_n^+(v) \mathrm{e}^{\alpha v} \tag{1}$$

and the partition function of attached trees are similarly defined. At negative values of the parameter α the trees are desorbed. Increasing α should lead through an adsorption transition into an adsorbed phase. The limiting free energies of these models are the thermodymic limits of $\log Z_n(\alpha)$ and $\log Z_n^+(\alpha)$ per edge; these are known to exist [15], and in the case of positive trees are defined by

$$\mathcal{F}_d^+(\alpha) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha) \tag{2}$$

for all $\alpha < \infty$. The limiting free energy of attached trees $\mathcal{F}_d(\alpha)$ is similarly defined. Moreover, $\mathcal{F}_d(\alpha)$ and $\mathcal{F}_d^+(\alpha)$ are convex functions, and are non-decreasing, continuous, and differentiable almost everywhere [15]. Furthermore, it is known that the limiting free energy $\mathcal{F}_d^+(\alpha)$ is independent of α for all $\alpha \leqslant 0$ (that is, $\mathcal{F}_d^+(\alpha) = \mathcal{F}_d(0)$ for all $\alpha \leqslant 0$), and $\max\{\mathcal{F}_d(0), \mathcal{F}_{d-1}(0)+\alpha\} \leqslant \mathcal{F}_d^+(\alpha) \leqslant \mathcal{F}_d(0)+\alpha$ for $\alpha > 0$. These bounds imply the existence of a non-analyticity at a critical value α_c^h in the free energy of positive trees, and this corresponds to the adsorption transition of a homopolymer on a solid adsorbing plane. The critical value of the fugacity may be defined by

$$\alpha_c^h = \sup\{\alpha | \mathcal{F}_d^+(\alpha) = \mathcal{F}_d(0)\} \tag{3}$$

and it is known that $\alpha_c^h > 0$ [15].

A lattice model of a branched copolymer can be defined by colouring the vertices in a lattice tree. Each colour corresponds to a different type of monomer. There are a variety of ways of defining the models, depending on a rule for assigning colours to vertices. A simple model of a branched copolymer can be defined by colouring vertices in a tree with two colours, say red and blue, in an alternating fashion. That is, colour a vertex (say the bottom vertex) of a tree red, and then continue by colouring all nearest-neighbour vertices of red vertices blue, and all nearest neighbours of blue vertices red. Since the tree is a bipartite graph, this colouring can always be completed. Observe that there are two possible colourings for each tree, and that both are included in the ensemble. The adsorption of such an alternating branched copolymer model is examined in section 2. Block copolymers are also considered in section 3.

A different model is obtained if the tree is coloured in a random fashion. For example, let χ be a (random) sequence of colours. The colours in χ can be assigned to vertices in a tree by colouring the vertices in the tree in lexicographic order, we shall refer to this as a *lexicographic colouring* by χ. This model is a simplification of more realistic colourings, where the ordering is determined by the underlying graph (of the tree), and not by the embedding. In this model it is possible to take the average over all possible colourings. If the partition function is averaged over χ then an *annealed model* is found. If the free energy is averaged, the *averaged quenched model* is the result. The model is *lexicographic quenched* if the colouring is fixed.

Let $t_n^+(v_R, v_B|\chi)$ be the number of positive trees with n edges, with vertices coloured lexicographically by the random sequence χ, with $v_R + v_B$ visits, of which v_R are red visits (or R-visits) and v_B blue visits (or B-visits). The partition function of this model is

$$Z_n^+(\alpha_R, \alpha_B|\chi) = \sum_{v_R, v_B} t_n^+(v_R, v_B|\chi) \mathrm{e}^{\alpha_R v_R + \alpha_B v_B} \tag{4}$$

where α_R and α_B are visit-fugacities associated with red and with blue visits, respectively. In general one would be interested in the existence of the limiting free energy of a particular quenched, an annealed averaged ensemble and quenched averaged ensembles, with respect to the lexicographic colouring of the vertices by χ. These are defined, respectively, by

$$\mathcal{F}_d^+(\alpha_R, \alpha_B|\chi) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) \tag{5}$$

$$\mathcal{F}_d^a(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n} \log\langle Z_n^+(\alpha_R, \alpha_B|\chi)\rangle_\chi \tag{6}$$

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n} \langle\log Z_n^+(\alpha_R, \alpha_B|\chi)\rangle_\chi. \tag{7}$$

Adsorption transitions in these models will be signalled by non-analyticities at critical values of the fugacities α_R or α_B.

2. Alternating copolymer adsorption

As a simple model we discuss alternating branched copolymers. This is an example of a model of quenched branched copolymers adsorbing in the plane $Z = 0$. A lattice tree T can be coloured alternately with two colours red (R) and blue (B) by first colouring the bottom vertex (lexicographic least vertex) of T with (say) R. Continue then by colouring all nearest neighbours of R-vertices by B, and all nearest-neighbour vertices of B-vertices by R. Since T is bipartitite, the colouring will always be completed, and it will be alternating since all pairs of adjacent vertices will be of opposite colours. Notice that there are two distinct colourings for every T. Let $t_n^+(v_R, v_B|\mathrm{al})$ be the number of positive trees of n edges, coloured alternating R and B, and with v_R red visits and v_B blue visits. The partition function of this model is

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) = \sum_{v_R, v_B} t_n^+(v_R, v_B|\mathrm{al}) \mathrm{e}^{\alpha_R v_R + \alpha_B v_B}. \tag{8}$$

The existence of a limiting free energy in this model is shown by using concatenation and a theorem on supermultiplicative functions. In this case a new result, related to a theorem of Wilker and Whittington [27], is needed. In general, a supermultiplicative inequality of the type $b_n b_m \leqslant b_{n+m+o(n+m)}$ will be obtained. Taking logarithms, and defining a function $f_{n,m} = m + o(n + m)$, and defining $a_n = -\log b_n$, the result is a submultiplicative inequality $a_n + a_m \geqslant a_{n+f_{n,m}}$, where $f_{n,m}$ is restricted by its definition. In general, the restrictions on $f_{n,m}$ can be somewhat relaxed, while it is still possible to show that the limit $\lim_{n\to\infty}[a_n/n]$ exists. This is done in theorem 1.

Theorem 1. *Suppose that a_n is a function from the natural numbers into integers, such that $a_n - a_{n-1} = u_n$ where $u_n = \mathrm{o}(n)$, and suppose that a_n satisfies the generalized subadditivity relation*

$$a_n + a_m \geqslant a_{n+f_{n,m}}$$

where $f_{n,m}$ is a function with the properties that there are functions ϕ_m and a constant ϕ defined by

$$\sup_{n>0}\{f_{n,m}\} = \phi_m \qquad \sup_{m>0}\{\phi_m/m\} = \phi < \infty$$

and a function ψ_m defined by

$$\inf_{n>0}\{f_{n,m}\} = \psi_m \qquad \textit{where} \quad \lim_{m\to\infty}[\psi_m/m] = 1$$

exists. Suppose furthermore that $\inf_{n>0}\{a_n/n\} \geqslant C_0$*, where* C_0 *is a constant. Then the limit*

$$\lim_{n\to\infty} [a_n/n] = \nu$$

exists, and is finite. Moreover, $a_n \geqslant \psi_n \nu$*.*

Proof. Fix a (large) integer $m > 0$ and recursively define $m_0 = m$, $m_p = m_{p-1} + f_{m_{p-1},m_0}$ for $p = 1, 2, \ldots$. Then

$$a_{m_p} = a_{m_{p-1}+f_{m_{p-1},m_0}} \leqslant a_{m_{p-1}} + a_{m_0} \leqslant \cdots \leqslant p a_{m_0}.$$

Choose an n, and let p be the largest integer such that $n \geqslant m_p$, say $n = m_p + r$. Then $r \leqslant f_{m_p,m_0} \leqslant \phi_{m_0}$. Since $a_n - a_{n-1} = \mathrm{o}(n)$, it also follows that $a_n = a_{n-r} + v_n$ with $v_n = \mathrm{o}(n) m_0 \phi$ (notice that $r \leqslant m_0 \phi$). Thus,

$$a_n = a_{n-r} + v_n = a_{m_p} + v_n \leqslant p a_{m_0} + v_n.$$

Observe that $m_p = \sum_{i=0}^{p-1} f_{m_i,m_0} \geqslant p\psi_{m_0}$. Divide the previous inequality by n, and use this lower bound on m_p. This gives

$$\frac{a_n}{n} \leqslant \frac{a_{m_0}}{\psi_{m_0}} + \frac{v_n}{p\psi_{m_0}}.$$

Now take the lim sup as $n \to \infty$ with m_0 fixed. Then $p \to \infty$, and since $m_p \leqslant p\phi_{m_0}$, the p-dependence of v_n is $\mathrm{o}(n) m_0 \phi = \mathrm{o}(m_p) = \mathrm{o}(p)$, so that $v_n = \mathrm{o}(p)$. Thus

$$\limsup_{n\to\infty} \frac{a_n}{n} \leqslant \frac{a_{m_0}}{\psi_{m_0}}.$$

Now take the lim inf as $m_0 \to \infty$ on the right-hand side to show that the limit exists as claimed. Next, the last equation shows that $a_m \geqslant \psi_m \nu$, and the finiteness of ν follows from the bound $\inf_{n>0}\{a_n/n\} \geqslant C_0$. □

The existence of a limiting free energy in this model can be shown, by applying the result in theorem 1 to a supermultiplicative inequality obtained by concatenating trees. Concatenation of two trees are usually conveniently done by defining in each a lexicographic most vertex (the *top vertex*), and a lexicographic least vertex (the *bottom vertex*). If the trees are translated so that the top vertex of the first tree is one lattice edge in the first direction from the bottom edge of the second, then the trees can be concatenated by inserting an edge between these vertices. This gives the inequality $t_n t_m \leqslant t_{n+m+1}$. Two trees can also be concatenated by translating one until there is a pair of vertices a unit distance apart, and then inserting an edge to concatenate them. In general this situation is more difficult to analyse, but for attached trees the situation is not complicated. This is done in the proof of theorem 2.

Theorem 2. *The limiting free energy*

$$\mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al}) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\mathrm{al})$$

exists for all finite values of α_R *and* α_B*.*

Proof. Let T_1 and T_2 be two positive trees counted by $t_n^+(v_{1R}, v_{1B}|\mathrm{al})$ and $t_m^+(v_R - v_{1R}, v_B - v_{1B}|\mathrm{al})$ respectively. Translate T_2 parallel to the $Z = 0$ hyperplane until its bottom vertex has the same coordinates as the top vertex of T_1, except for the X- and Z-coordinates. Translate T_2 in the X-direction until the X-coordinate of its bottom vertex is two steps bigger than the X-coordinate of the top vertex of T_1. Next we translate T_2 in the negative X-direction, until there is a vertex in T_2 which is within a distance of two steps from a vertex in T_1. Let w_1 in

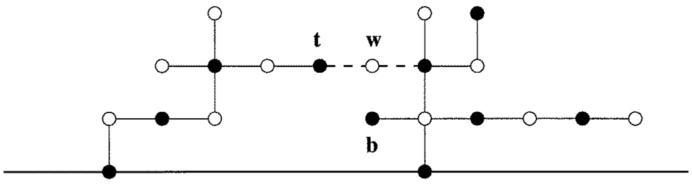

Figure 1. Concatenation of two alternating trees. Full circles (red vertices) and open circles (blue vertices) represent different types of vertices. t is the top vertex of T_1 and b is the bottom vertex of T_2. We concatenate T_1 and T_2 by adding a blue vertex (w) and two edges (dashed lines).

T_1 and w_2 in T_2 be two vertices which are exactly two steps apart. If they are both R-vertices (or B-vertices) we concatenate T_1 and T_2 by adding one B-vertex (or R-vertex) and two edges between w_1 and w_2. If they are coloured differently, then we translate T_2 one more step in the negative X-direction and concatenate T_1 and T_2 by adding one edge between w_1 and w_2. Since T_1 has size n, this construction can always be undone by finding that edge in the concatenated tree whose deletion will give a subtree of size n (see figure 1). Moreover, each distinct pair of trees will give a different outcome, thus

$$\sum_{v_{1R}=0}^{v_R}\sum_{v_{1B}=0}^{v_B} t_n^+(v_{1R}, v_{1B}|\mathrm{al}) t_m^+(v_R - v_{1R}, v_B - v_{1B}|\mathrm{al}) \leqslant \sum_{k=1}^{2}\sum_{i,j=0}^{1} t_{n+m+k}^+(v_R + i, v_B + j|\mathrm{al}).$$

Multiply this equation by $\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}$, and sum over v_R and v_B. This gives

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) Z_m^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant (1 + \mathrm{e}^{-\alpha_R})(1 + \mathrm{e}^{-\alpha_B}) \sum_{k=1}^{2} Z_{n+m+k}^+(\alpha_R, \alpha_B|\mathrm{al}).$$

Define $r_{n,m}$ as that value of k which maximizes the right-hand side. Then

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) Z_m^+(\alpha_R, \alpha_B 0|\mathrm{al}) \leqslant 2(1 + \mathrm{e}^{-\alpha_R})(1 + \mathrm{e}^{-\alpha_B}) Z_{n+m+r_{m,n}}^+(\alpha_R, \alpha_B|\mathrm{al}) \qquad (9)$$

where $|r_{m,n}| \leqslant 2$, and notice that $n^{-1}\log Z_n^+(\alpha_R, \alpha_B|\mathrm{al})$ is bounded above since

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant t_n^+(\mathrm{al})\mathrm{e}^{(n+1)\max\{1, \alpha_R + \alpha_B\}}.$$

Take the logarithms of equation (9) and multiply the result by negative one. The resulting subadditive inequality is of the form discussed in theorem 1. Thus, the limiting free energy exists for all finite α_R and α_B, and moreover, since $|r_{m,n}| \leqslant 2$, it follows that $Z_m^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant \mathrm{e}^{(m+2)\mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al})}$ for every m. □

The existence of an adsorption transition in this model is shown using the same techniques as in the case of a homopolymer model. In particular, bounds on the limiting free energy can be derived to show that it is constant for negative values of the fugacity α, and non-constant for some positive values of α. This model is also easily related to an adsorbing branched homopolymer by identifying R-vertices and B-vertices; note also that $t_n^+(al) = 2t_n^+$ so that from equation (1) the homopolymer partition function is given by

$$Z_n^+(\alpha) = \tfrac{1}{2}\sum_{v_R, v_B} t_n^+(v_R, v_B|\mathrm{al})\mathrm{e}^{\alpha(v_R + v_B)}. \qquad (10)$$

The existence of a limiting free energy $\mathcal{F}_d^+(\alpha)$ in this model is known [15], and is given by equation (2). Moreover, the critical fugacity is α_c^h given by equation (3), and that it is strictly positive was shown in [15]. It is also possible to show that there is an adsorption transition in this model of branched alternating copolymers.

Theorem 3. *The limiting free energy* $\mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al})$ *is independent of* α_R *and* α_B *for all* $\alpha_R \leqslant \alpha_c^h$ *and* $\alpha_B \leqslant \alpha_c^h$ *(that is,* $\mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al}) = \mathcal{F}_d(0)$ *for* $\alpha_R \leqslant \alpha_c^h$ *and* $\alpha_B \leqslant \alpha_c^h$*). On the other hand, if either* $\alpha_R > \alpha_c^h$*, or* $\alpha_B > \alpha_c^h$*, or both, then*

$$\max\{\mathcal{F}_d(0), \mathcal{F}_{d-1}(0) + (\alpha_R + \alpha_B)/2\} \leqslant \mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant \mathcal{F}_d(0) + \max\{\alpha_R, \alpha_B\}.$$

Proof. Suppose that $\alpha_R \leqslant \alpha_c^h$ and that $\alpha_B \leqslant \alpha_c^h$. Then from equation (10),

$$Z_n^+(\min\{\alpha_R, \alpha_B\}) \leqslant Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant Z_n^+(\alpha_c^h, \alpha_c^h|\mathrm{al}) = 2Z_n^+(\alpha_c^h)$$

where α_c^h is defined in equation (3). This shows that $\mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al}) = \mathcal{F}_d(0)$ whenever $\alpha_R \leqslant \alpha_c^h$ and $\alpha_B \leqslant \alpha_c^h$.

Next, suppose that either $\alpha_R > \alpha_c^h$ or $\alpha_B > \alpha_c^h$ or both. Consider that subclass of trees with every vertex a visit. This shows that

$$t_n^{(d-1)} \mathrm{e}^{\lfloor n/2 \rfloor \alpha_R + \lceil n/2 \rceil \alpha_B} \leqslant Z_n^+(\alpha_R, \alpha_B|\mathrm{al})$$

and so

$$\mathcal{F}_{d-1}(0) + (\alpha_R + \alpha_B)/2 \leqslant \mathcal{F}_d^+(\alpha_R, \alpha_B|\mathrm{al}).$$

Lastly, by equation (10),

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant 2Z_n^+(\max\{\alpha_R, \alpha_B\}) \leqslant 2t_n^+ \mathrm{e}^{\max\{\alpha_R, \alpha_B\}(n+1)}.$$

Thus, $\mathcal{F}_d^+(\alpha_R, \alpha_B) \leqslant \mathcal{F}_d^+(\max\{\alpha_R, \alpha_B\}) \leqslant \mathcal{F}_d^+(0) + \max\{\alpha_R, \alpha_B\}$. This completes the proof. □

The results in theorem 3 imply that there is a non-analyticity in $\mathcal{F}_d^+(\alpha_B, \alpha_R)$ which corresponds to an adsorption transition in this model. Notice that

$$Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) \leqslant 2Z_n^+(\max\{\alpha_R, \alpha_B\})$$

which implies that if $\max\{\alpha_R, \alpha_B\} \leqslant \alpha_c^h$ then the tree is desorbed. Next, $Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) \geqslant Z_n^+(\min\{\alpha_R, \alpha_B\})$ so that if $\min\{\alpha_R, \alpha_B\} \geqslant \alpha_c^h$ then the adsorbed phase must be found. This can be strengthened by noting that $Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) = Z_n^+(\alpha_B, \alpha_R|\mathrm{al})$ so that

$$\begin{aligned} 2Z_n^+(\alpha_R, \alpha_B|\mathrm{al}) &= \sum_{v_A, v_B} t_n^+(v_A, v_B|\mathrm{al})[\mathrm{e}^{\alpha_R v_R + \alpha_B v_B} + \mathrm{e}^{\alpha_R v_B + \alpha_B v_R}] \\ &\geqslant 2 \sum_{v_A, v_B} t_n^+(v_A, v_B|\mathrm{al})[\mathrm{e}^{(\alpha_R + \alpha_B)(v_A + v_B)/2}] \\ &= 2Z_n^+\left(\frac{\alpha_R + \alpha_B}{2}, \frac{\alpha_R + \alpha_B}{2}\middle|\, \mathrm{al}\right) \geqslant 2Z_n^+\left(\frac{\alpha_R + \alpha_B}{2}\right) \end{aligned} \tag{11}$$

if convexity of the exponential is used. This shows that if $\alpha_R + \alpha_B \geqslant 2\alpha_c^h$ then the adsorbed phase must be found. Thus, the adsorption transitions in the (α_R, α_B)-plane lie on the region defined by (see figure 2)

$$\begin{aligned} &\alpha_R + \alpha_B \leqslant 2\alpha_c^h \\ &\max\{\alpha_R, \alpha_B\} \geqslant \alpha_c^h. \end{aligned} \tag{12}$$

The limiting free energy, and bounds on it (similar to those in theorems 2 and 3) of a self-avoiding walk model of adsorbing alternating linear copolymers is also known to exist [25].

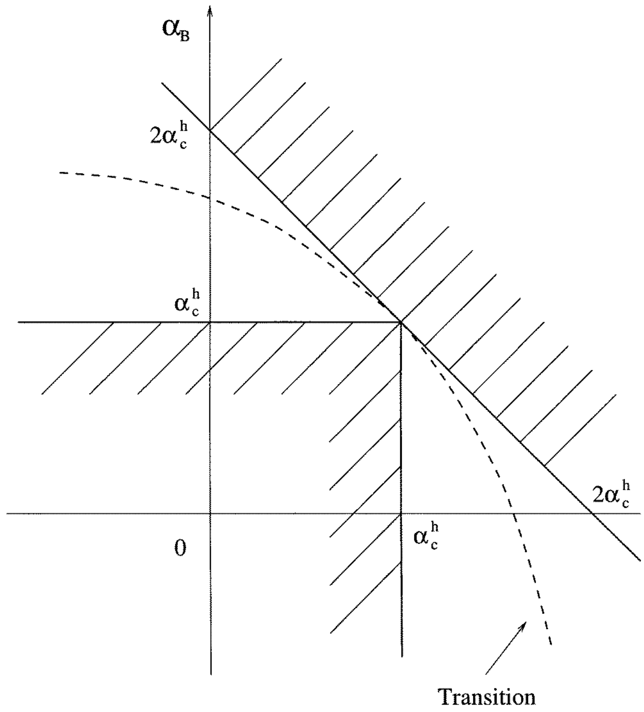

Figure 2. The adsorption transitions of alternating branched copolymers in the (α_R, α_B)-plane is located along the dashed curve.

3. Adsorption of a branched block copolymer

A copolymer T with red (R) and blue (B) vertices is a *block-copolymer* if there is an edge e in T so that $T - \mathrm{e} = U \cup V$ with U a red homopolymer and V a blue homopolymer. Let $t^+_{n_1,n_2}(v_R, v_B|\mathrm{bl})$ be the number of lattice trees with $n_1 + n_2 - 1 = n$ edges, n_1 R-vertices with v_R R-visits and n_2 B-vertices with v_B B-visits. A model of an adsorbing block copolymer is defined through the partition function

$$Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl}) = \sum_{v_R,v_B} t^+_{n_1,n_2}(v_R, v_B|\mathrm{bl})\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}. \tag{13}$$

We will limit the discussion to a model where n_1 (and n_2) are functions of n (the number of edges) such that

$$\lim_{n\to\infty} \frac{n_1}{n+1} = a \tag{14}$$

where a is a real number in the interval [0, 1].

Theorem 4. *The limiting free energy* $\lim_{n\to\infty} n^{-1} \log Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl})$ *exists and is equal to* $a\mathcal{F}^+_d(\alpha_R) + (1-a)\mathcal{F}^+_d(\alpha_B)$.

Proof. Let $t^+_n(v)$ be the number of positive trees with n edges and v visits. Let T be a tree counted by $t^+_{n_1,n_2}(v_R, v_B|\mathrm{bl})$, and let $a_n = n_1/(n+1)$. Then $\lim_{n\to\infty} a_n = a$, by equation (14). There is also an edge e in T so that $T - e$ is composed of two monochromatically coloured trees: an R-tree counted by $t^+_{n_1-1}(v_R)$ and a B-tree counted by $t^+_{n_2-1}(v_B)$. These trees can be reconnected in at most $(n_1n_2)^{2d}$ ways to recover T. This shows that

$$t^+_{n_1,n_2}(v_R, v_B|\mathrm{bl}) \leqslant (n_1n_2)^{2d} t^+_{n_1-1}(v_R) t^+_{n_2-1}(v_B).$$

Multiply this equation by $\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}$ and sum over both v_R and v_B. By equations (1) and (13) the outcome is the generalized submultiplicative inequality

$$Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl}) \leqslant (n_1n_2)^{2d} Z^+_{n_1-1}(\alpha_R) Z^+_{n_2-1}(\alpha_B). \tag{15}$$

Take the logarithm of this inequality, divide by n and let $n \to \infty$. This takes n_1 to infinity through $n_1 = (n+1)a_n$, and $n_2 = n + 1 - n_1$. The result is that

$$\limsup_{n\to\infty} \frac{1}{n} \log Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl}) \leqslant a\mathcal{F}^+_d(\alpha_R) + (1-a)\mathcal{F}^+_d(\alpha_B). \tag{16}$$

Next, concatenate a tree counted by $t^+_{n_1-1}(v_R)$ with a tree counted by $t^+_{n_2-1}(v_B)$, using the construction in figure 1. The result is

$$t^+_{n_1-1}(v_R) t^+_{n_2-1}(v_B) \leqslant t^+_{n_1,n_2}(v_R, v_B|\mathrm{bl}).$$

Multiplying this equation by $\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}$, and summing over v_R and v_B gives

$$Z^+_{n_1}(\alpha_R) Z^+_{n_2}(\alpha_B) \leqslant Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl}).$$

Taking the logarithm, dividing by n, and letting $n \to \infty$ gives

$$\liminf_{n\to\infty} \frac{1}{n} \log Z^+_{n_1,n_2}(\alpha_R, \alpha_B|\mathrm{bl}) \geqslant a\mathcal{F}^+_d(\alpha_R) + (1-a)\mathcal{F}^+_d(\alpha_B).$$

Comparison with equation (16) then finishes the proof. □

The corollary to theorem 4 is that a block copolymer adsorbs at the same critical value of the fugacity as a homopolymer. Indeed, the critical values of α_R and α_B is defined by

$$\max\{\alpha_R, \alpha_B\} = \alpha^h_c. \tag{17}$$

Observe that this equation is only true if there is a non-zero density of visits of a given colour.

The model above also generalizes to block copolymers with more than two blocks. In particular, define $t^+_{n_1,n_2,\ldots,n_k}(v_1, v_2, \ldots, v_k|\mathrm{bl})$ to be number of positive trees T with $(n_1, n_2, \ldots, n_k)$ vertices and $(v_1, v_2, \ldots, v_k)$ visits of colours $(1, 2, \ldots, k)$, such that there are $(k-1)$ edges $\{e_1, e_2, \ldots, e_{k-1}\}$ so that $T - \{e_1, e_2, \ldots, e_{k-1}\} = \cup^k_{i=1} V_i$ where V_i is a monochromatic homopolymer of colour i. The construction leading to equation (15) then shows that

$$t^+_{n_1,n_2,\ldots,n_k}(v_1, v_2, \ldots, v_k|\mathrm{bl}) \leqslant n^{4dk} \prod_{i=1}^k t^+_{n_i-1}(v_i) \tag{18}$$

where $n = \sum^k_{i=1} n_i - 1$ and concatenating k trees gives

$$t^+_{n_1,n_2,\ldots,n_k}(v_1, v_2, \ldots, v_k|\mathrm{bl}) \geqslant \prod_{i=1}^k t^+_{n_i-1}(v_i). \tag{19}$$

Multiplication by $\mathrm{e}^{\sum^k_{i=1} \alpha_i v_i}$, and summing over the v_i gives corresponding inequalities which leads to a limiting free energy in this model in terms of linear combinations of $\mathcal{F}^+_d(\alpha_i)$. The block copolymer adsorbs whenever any of the $\alpha_i = \alpha^h_c$.

4. Random branched copolymer adsorption

In the previous sections we have considered the adsorption of two models of quenched branched polymers. In this section we turn our attention to models of quenched and random branched copolymers. The focus will again be on copolymers composed of only two types of monomers (red and blue), but the techniques here may be applied to models with more than two types of monomers. Random linear copolymers in interacting models in both the annealed and quenched ensembles have been examined in [18, 19] and [26]. In the next paragraph we show that an averaged annealed model is similar to a model of homopolymers.

An annealed model of random branched copolymers is obtained if each vertex in a positive lattice tree is assigned a random colour, say R with probability p, and otherwise B. Then the probability that w vertices in a tree with $n+1$ vertices will be coloured R, and the rest B, is given by the binomial distribution $\binom{n+1}{w}p^w(1-p)^{n+1-w}$. Let $t_n^+(v)$ be the number of trees with n edges and v visits. Then the partition function of adsorbing branched copolymers in an annealed ensemble is given by

$$Z_n^{+,a}(\alpha_R, \alpha_B, p) = \sum_{v=0}^{n+1} t_n^+(v) \sum_{w=0}^{v} \binom{v}{w} p^w (1-p)^{v-w} \mathrm{e}^{\alpha_R w + \alpha_B (v-w)}. \tag{20}$$

Executing the sum over w above gives

$$Z_n^{+,a}(\alpha_R, \alpha_B, p) = \sum_{v=0}^{n+1} t_n^+(v)(\mathrm{e}^{\alpha_R} p + (1-p)\mathrm{e}^{\alpha_B})^v = Z_n^+(\mathrm{e}^{\alpha_R} p + (1-p)\mathrm{e}^{\alpha_B}) \tag{21}$$

where $Z_n^+(\alpha)$ is defined in equation (1), and so $\mathcal{F}_d^a(\alpha_R, \alpha_B | p) = \mathcal{F}_d^+(\log(\mathrm{e}^{\alpha_R} p + \mathrm{e}^{\alpha_B}(1-p)))$. Thus, the critical adsorption fugacity in the annealed ensemble can be computed in terms of the critical adsorption fugacity of homopolymers. In the (α_R, α_B) parameter space, the critical curve is defined by the curve

$$\mathrm{e}^{\alpha_R} p + (1-p)\mathrm{e}^{\alpha_B} = \mathrm{e}^{\alpha_c^h}. \tag{22}$$

This can be seen from equation (21), and it defines a desorbed and an adsorbed phase. Equation (21) also shows that the annealed model of random branched copolymer adsorption is equivalent to homopolymer adsorption, and no more need be said about that model. Observe that the argument here is very general, and applies also to other annealed models, such as linear copolymers, and self-interacting copolymers [19].

A more interesting situation arises when the self-averaging of models of adsorbing random branched copolymers are considered. In the case of branched copolymers an immediate issue is the colouring of vertices. There are two parts to colouring the vertices of a tree. The first is a sequence of colours $\chi = (\chi_1, \chi_2, \ldots,)$, and the second is a rule for assigning colour χ_i to a vertex in the tree. A random sequence of colours is generated as follows. Let $\chi_i \in Y$, where Y is a probability space. Then $\chi \in X = Y \times Y \times Y \times \cdots$. Thus, a random sequence χ of identically distributed and independent colours can be selected. Next, these colours must be assigned to vertices to define a 'quenched model' of an adsorbing copolymer. The basic recipe is to label the vertices in a lattice tree by integers $(1, 2, \ldots)$, and then to assign colour χ_j to vertex j. In this paper we will use the following lexicographic rule.

Lexicographic quenched branched copolymers. Order the vertices in a lattice tree lexicographically. Assign colours in lexicographic increasing order to the vertices. It is important to note in this case that the colouring of the tree is dependent on its particular conformation in the lattice.

In section 4.1 we first consider a model of lexicographic quenched branched polymers with χ an alternating sequence. A simple concatenation such as in figure 1 is not enough to show existence of a limiting free energy, instead, concatenation combined with a most popular class argument is needed. In section 4.2 we consider the limiting free energy in an averaged quenched model of branched copolymers, and in section 4.3 the issue of self-averaging in this model is considered.

4.1. Adsorption of an alternating lexicographic quenched branched copolymer

Let ξ be the alternating sequence $\{R, B, R, B, \ldots\}$, and let $t_n^+(v_R, v_B|\xi)$ be the number of positive trees, coloured lexicographically by ξ, and with n edges, v_R R-visits and v_B B-visits. Define the partition function

$$Z_n^+(\alpha_R, \alpha_B|\xi) = \sum_{v_R, v_B=0}^{n+1} t_n^+(v_R, v_B|\xi)\mathrm{e}^{\alpha_R v_R+\alpha_B v_B}. \tag{23}$$

The existence of a limiting free energy in this model can be shown using a most popular argument. The *bottom vertex* of a positive tree is its lexicographic least vertex, and the *top vertex* of a positive tree is its lexicographic most vertex. Let the number of positive trees with bottom vertex a height h_b, and top vertex a height h_t, above the adsorbing plane $Z = 0$ be $t_n^+(v_R, v_B|\xi|[h_b, h_t])$, and let the partition function in this model be $Z_n^+(\alpha_R, \alpha_B|\xi|[h_b, h_t])$. Notice that $t_n^+(v_R, v_B|\xi|[h_b, h_t]) = t_n^+(v_R, v_B|\xi|[h_t, h_b])$ by symmetry. In addition, the heights $[h_b, h_t]$ can only assume at most $(n+1)^2$ values, and there is a most popular pair of heights, say $[h_b^*, h_t^*]$, which contributes at least as much as any other pair to the partition function. Thus

$$Z_n^+(\alpha_R, \alpha_B|\xi|[h_b^*, h_t^*]) \leqslant Z_n^+(\alpha_R, \alpha_B|\xi) \leqslant n^2 Z_n^+(\alpha_R, \alpha_B|\xi|[h_b^*, h_t^*]) \tag{24}$$

and so we only have to consider the partition function of trees with most popular heights. With these definitions the existence of the limiting free energy can be proven.

Theorem 5. *The limiting free energy*

$$\mathcal{F}_d^q(\alpha_R, \alpha_B|\xi) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\xi)$$

exists for all finite values of α_R and α_B in the alternating lexicographically quenched model of branched copolymer adsorption.

Proof. Consider a tree T_1 counted by $t_n^+(v_R - v_{1R}, v_B - v_{1B}|\xi|[hh])$ and a tree T_2 counted by $t_m^+(v_{1R}, v_{1B}|\xi|[hh])$. Translate T_1 and T_2 along the adsorbing plane until the top vertex t_1 of T_1 is two steps removed in the X-direction from the bottom vertex b_2 of T_2 (since these have the same heights, this is always possible). If t_1 and b_2 have the same colours (say blue), then insert an extra red vertex between them, and two edges, to join the trees into a single tree. This tree is surely coloured in a lexicographically alternating fashion, since every vertex of T_1 is lexigraphically less than any vertex in T_2. If t_1 and b_2 have different colours, then translate T_2 until t_1 is one step in the x-direction from b_2, and add a single edge to obtain a new tree, also coloured in a lexicographically alternating fashion. The number of edges may change by 1 or by 2, and the new vertex may also be a visit (and either be blue or be red). This shows that

$$\sum_{v_{1R}, v_{1B}} t_n^+(v_R - v_{1R}, v_B - v_{1B}|\xi|[hh])t_m^+(v_{1R}, v_{1B}|\xi|[hh])$$
$$\leqslant \sum_{k=1}^{2} \sum_{i,j=0}^{1} t_{n+m+k}^+(v_R + i, v_B + j|\xi|[hh]).$$

Multiply this by $e^{\alpha_R v_R + \alpha_B v_B}$ and sum over both v_R and v_B. The result is that

$$Z_n^+(\alpha_R, \alpha_B|\xi|[hh])Z_m^+(\alpha_R, \alpha_B|\xi|[hh]) \leqslant (1 + e^{-\alpha_R})(1 + e^{-\alpha_B}) \sum_{k=1}^{2} Z_{n+m+k}(\alpha_R, \alpha_B|\xi|[hh]).$$

Choose $k = r(n, m)$ to be that value of k which maximizes the right-hand side of the equation. Then

$$Z_n^+(\alpha_R, \alpha_B|\xi|[hh])Z_m^+(\alpha_R, \alpha_B|\xi|[hh]) \leqslant 2(1 + e^{-\alpha_R})(1 + e^{-\alpha_B})Z_{n+m+r(n,m)}(\alpha_R, \alpha_B|\xi|[hh])$$

and since $|r(n, m)| \leqslant 2$ we can use theorem 1 to show that the limit

$$\lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\xi|[hh]) = \mathcal{F}_d^+(\alpha_R, \alpha_B|\xi)$$

exists. Next, notice that there are most popular choices for $[hh]$ in $Z_n^+(\alpha_R, \alpha_B|\xi|[hh])$, say $[h^*h^*]$. Note also that

$$(Z_n^+(\alpha_R, \alpha_B|\xi|[h^*h^*]))^2 \leqslant (Z_n^+(\alpha_R, \alpha_B|\xi|[h_b^*h_t^*]))^2 \leqslant (1 + e^{-\alpha_R})(1 + e^{-\alpha_B}) \sum_{k=1}^{2} Z_{2n+k}(\alpha_R, \alpha_B|\xi|[h_b^*h_b^*])$$

by exploiting the fact that $t_n^+(v_R, v_B|\xi|[h_b, h_t]) = t_n^+(v_R, v_B|\xi|[h_t, h_b])$. In other words, from these inequalities and equation (24), it follows that

$$\mathcal{F}_d^q(\alpha_R, \alpha_B|\xi) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\xi).$$

This completes the proof. □

The existence of an adsorption transition in this model follows by using the same techniques used in theorem 3. The limiting free energy $\mathcal{F}_d^q(\alpha_R, \alpha_B|\xi)$ is independent of α_R and α_B for all $\alpha_R \leqslant \alpha_c^h$ and $\alpha_B \leqslant \alpha_c^h$ (that is, $\mathcal{F}_d^q(\alpha_R, \alpha_B|\xi) = \mathcal{F}_d(0)$ for $\alpha_R \leqslant \alpha_c^h$ and $\alpha_B \leqslant \alpha_c^h$). Next, notice that $\mathcal{F}_d^q(\alpha_R, \alpha_B|\xi) = \mathcal{F}_d^q(\alpha_B, \alpha_R|\xi)$ and argue as in section 2 to see that if $\alpha_R + \alpha_B \geqslant 2\alpha_c^h$ then the tree is adsorbed (see figure 2).

4.2. Branched copolymer adsorption in the averaged lexicographic quenched ensemble

Let $Z_n^+(\alpha_R, \alpha_B|\chi)$ be defined as before (equation (23)). The averaged lexicographic quenched limiting free energy is defined by $\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n}\langle \log Z_n^+(\alpha_R, \alpha_B|\chi)\rangle_\chi$, where the average is over all colourings χ in the space X. That this limit exists is seen in the next theorem, and it too relies on the use of a most popular class argument.

Theorem 6. *There exists a limiting free energy in the averaged lexicographic quenched ensemble:*

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n} \langle \log Z_n^+(\alpha_R, \alpha_B|\chi)\rangle_\chi$$

where the average $\langle\cdot\rangle_\chi$ *is over all sequences of two colours.*

Proof. Let $t_n^+(v_R, v_B|\chi|[h_b h_t])$ be the number of positive trees coloured lexicographically by the sequence χ of two colours (say red and blue), with v_R R-visits and v_B B-visits, and with its bottom vertex with z-coordinate h_b, and top vertex with z-coordinate h_t. A tree counted by $t_n^+(v_R - w_R, v_B - w_B|\chi_0|[hh])$ can be concatenated with a tree counted by $t_m^+(w_R, w_B|\chi_1|[hh])$

(by translating the second tree until its bottom vertex is one step in the x-direction from the top vertex of the first tree, and then joining them by adding a single edge). The resulting tree is coloured by a sequence $\chi' = \chi_0\chi_1$ composed of all the colours in $\chi_0\chi_1$, and which is uniquely determined by $\chi_0\chi_1$ for each pair of trees (that is, given χ' and the concatenated tree, one can uniquely recover $\chi_0\chi_1$). Thus

$$\sum_{w_R,w_B=0}^{n+1} t_n^+(v_R - w_R, v_B - w_B|\chi_0|[hh])t_m^+(w_R, w_B|\chi_1|[hh]) \leqslant t_{n+m+1}^+(v_R, v_B|\chi_0\chi_1|[hh]).$$

Multiply this by $e^{\alpha_R v_R + \alpha_B v_B}$ and sum over v_R and v_B. The result is

$$Z_n^+(\alpha_R, \alpha_B|\chi_0|[hh])Z_m^+(\alpha_R, \alpha_B|\chi_1|[hh]) \leqslant Z_{n+m+1}^+(\alpha_R, \alpha_B|\chi_0\chi_1|[hh]).$$

Take logarithms, and average over all possible sequences $\chi_0\chi_1$ of colours:

$$\langle \log Z_n^+(\alpha_R, \alpha_B|\chi|[hh])\rangle_\chi + \langle \log Z_m^+(\alpha_R, \alpha_B|\chi|[hh])\rangle_\chi \leqslant \langle \log Z_{n+m}^+(\alpha_R, \alpha_B|\chi|[hh])\rangle_\chi.$$

Thus, $\langle \log Z_n^+(\alpha_R, \alpha_B|\chi|[hh])\rangle_\chi$ is a super-additive function, and by the fundamental theorem of superadditive functions [14] the limit

$$\mathcal{F}_d^q(\alpha_R, \alpha_B|\chi|[hh]) = \lim_{n\to\infty} \frac{1}{n}\langle \log Z_n^+(\alpha_R, \alpha_B|\chi|[hh])\rangle_\chi$$

exists. There is a most popular value of h, say h^*, so define

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n}\langle \log Z_n^+(\alpha_R, \alpha_B|\chi|[h^*h^*])\rangle_\chi. \tag{25}$$

Next, consider the partition function $Z_n^+(\alpha_R, \alpha_B|\chi|[h_bh_t])$, and let $[h_b^*h_t^*]$ be the most popular choice for $[h_bh_t]$. Then the following is true. In the first place,

$$Z_n^+(\alpha_R, \alpha_B|\chi|[h^*h^*]) \leqslant Z_n^+(\alpha_R, \alpha_B|\chi|[h_b^*h_t^*])$$

and secondly,

$$[Z_n^+(\alpha_R, \alpha_B|\chi|[h_b^*h_t^*])]^2 \leqslant Z_{2n+1}^+(\alpha_R, \alpha_B|\chi|[h_b^*h_b^*]) \leqslant Z_{2n+1}^+(\alpha_R, \alpha_B|\chi|[h^*h^*])$$

and the first inequality in the last expressions is found by taking two trees counted by $Z_n^+(\alpha_R, \alpha_B|\chi|[h_b^*h_t^*])$, reflecting one through the hyperplane $x = 0$, and then concatenating them. Comparing this with equation (25) shows that the limiting free energy in the averaged quenched ensemble exists as claimed. □

That there is an adsorption transition in this model is seen as follows: First of all, each tree counted by $t_n^+(v_R, v_B|\chi)$ can be translated one step in the Z-direction to show that $t_n^+(v_R, v_B|\chi) \leqslant t_n^+(0, 0|\chi)$. Thus, notice that $t_n^+(0, 0|\chi) \leqslant Z_n^+(\alpha_R, \alpha_B|\chi)$, and for $\alpha_R \leqslant 0$ and $\alpha_B \leqslant 0$, $Z_n^+(\alpha_R, \alpha_B|\chi) \leqslant \sum_{v_R,v_B} t_n^+(0, 0|\chi)\mathrm{e}^{\alpha_R v_R + \alpha_B v_B} \leqslant (n+1)t_n^+(0, 0|\chi)$. Take logarithms and the average of χ to obtain

$$\langle \log t_n^+(0, 0|\chi)\rangle_\chi \leqslant \langle \log Z_n^+(\alpha_R, \alpha_B|\chi)\rangle_\chi \leqslant \langle \log((n+1)t_n^+(0, 0|\chi))\rangle_\chi. \tag{26}$$

If this is divided by n, and $n \to \infty$, then the result is that

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \mathcal{F}_d^q(0, 0) \qquad \forall \alpha_R \leqslant 0 \qquad \forall \alpha_B \leqslant 0. \tag{27}$$

On the other hand, notice that the average number (over all colourings) of v_R and v_B is $(n+1)/2$. Find a lower bound on the partition function by only taking trees with $v_R + v_B = n + 1$; this gives

$$\sum_{v_R,v_B} t_n^+(v_R, v_B|\chi)\mathrm{e}^{\alpha_R v_R + \alpha_B v_B} \geqslant \sum_{v_R,v_B} t_n^+(v_R, v_B|\chi)\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}\delta_{v_R+v_B=(n+1)}. \tag{28}$$

The second term corresponds to all those trees which have every vertex a visit, and there is at least one such tree. Thus if $v_R(\chi)$ and $v_B(\chi)$ are the numbers of R- and B-vertices in the colouring by χ, then equation (28) shows that

$$\sum_{v_R, v_B} t_n^+(v_R, v_B|\chi)\mathrm{e}^{\alpha_R v_R + \alpha_B v_B} \geqslant \mathrm{e}^{\alpha_R v_R(\chi) + \alpha_B v_B(\chi)}. \tag{29}$$

Take logarithms, and average over χ to obtain

$$\langle \log \sum_{v_R, v_B} t_n^+(v_R, v_B|\chi)\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}\rangle_\chi \geqslant (\alpha_R + \alpha_B)(n+1)/2 \tag{30}$$

and if this is divided by n, and $n \to \infty$, then

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) \geqslant (\alpha_R + \alpha_B)/2. \tag{31}$$

Thus, comparison with equation (27) proves that there is a non-analyticity in $\mathcal{F}_d^q(\alpha_R, \alpha_B)$ at critical values of α_R and α_B, and that these correspond to adsorption transitions.

4.3. Self-averaging of adsorbing lexicographic quenched branched copolymers

The existence of the limiting free energy in the averaged lexicographic quenched ensemble indicates that the self-averaging of adsorbing branched copolymers might be an interesting question. The key result which will show that this model is self-averaging is presented in lemma 1.

Lemma 1. *Let χ_0 be a fixed random sequence of independent identically distributed colours. Then*

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi_0) \geqslant \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

almost surely.

Proof. Let $n = Nm + r$, and decompose the sequence χ_0 into m parts χ_i, each of length N, so that $\chi_0 = \prod_{i=1}^{\infty} \chi_i$, where the product is taken as concatenation.

Consider trees counted by $t_{N-1}^+(v_i, w_i|\chi_i|[hh])$, and concatenate them from $i = 1$ to $i = m$, using the same construction as in theorem 6. Lastly, concatenate a tree counted by $t_r^+(v_r, w_r|\chi_r|[hh])$ onto this as well, where χ_r is the first r colours in the sequence χ_{m+1}. This shows that

$$t_n^+(v_R, v_B|\chi_0|[hh]) \geqslant \sum_{\{v_i\},\{w_i\}} \left[\prod_{i=1}^m t_{N-1}^+(v_i, w_i|\chi_i|[hh])\right] t_r^+(v_r, w_r|\chi_r|[hh])\delta_{v_R - \sum v_i}\delta_{v_B - \sum w_i}.$$

Multiply this by $\mathrm{e}^{\alpha_R v_R + \alpha_B v_B}$, and sum over $\{v_i, w_i\}$. Then

$$Z_n^+(\alpha_R, \alpha_B|\chi_0|[hh]) \geqslant \left[\prod_{i=1}^m Z_{N-1}^+(\alpha_R, \alpha_B|\chi_i|[hh])\right] Z_r^+(\alpha_R, \alpha_B|\chi_r|[hh]).$$

Take logarithms, and divide by n, and take the lim inf of the left-hand side.

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n(\alpha_R, \alpha_B|\chi_0|[hh]) \geqslant \liminf_{m\to\infty} \frac{1}{m} \sum_{i=1}^m \frac{1}{N} \log Z_{N-1}^+(\alpha_R, \alpha_B|\chi_i|[hh]).$$

This is true for any choice of $[hh]$, and in particular, one may choose the most popular values, and use equation (25) in the proof of theorem 6. Moreover, since $Z_n(\alpha_R, \alpha_B|\chi_0|[h^*h^*]) \leqslant Z_n(\alpha_R, \alpha_B|\chi_0) \leqslant n^2 Z_n(\alpha_R, \alpha_B|\chi_0|[h^*h^*])$, it follows that

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n(\alpha_R, \alpha_B|\chi_0) \geqslant \left\langle \frac{1}{N} \log Z_{N-1}^+(\alpha_R, \alpha_B|\chi|[h^*h^*])\right\rangle_\chi \to \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

for almost all colourings χ_0, by the law of large numbers. □

Consider a random sequence of colours $\chi = (\chi_1, \chi_2, \ldots)$ where $\chi_i \in Y$, Y a probability distribution, and $\chi \in X = Y \times Y \times \cdots$. Then X is a probability space with uniform measure $\mu(X) = 1$. Moreover, theorem 6 implies that

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \frac{1}{n} \int_X \mathrm{d}\chi \, \log Z_n^+(\alpha_R, \alpha_B|\chi) \tag{32}$$

while lemma 1 shows that

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) \leqslant \liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi_0) \tag{33}$$

for almost every $\chi_0 \in X$. Next we show that this model is self-averaging; see also Orlandini *et al* [19] for similar arguments leading to self-averaging in models of polymer collapse.

Theorem 7. *For almost every* $\chi_0 \in X$,

$$\lim_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi_0) = \mathcal{F}_d^q(\alpha_R, \alpha_B).$$

Proof. Apply Fatou's lemma to equation (32). This shows that

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \lim_{n\to\infty} \int_X \mathrm{d}\chi \, \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) \geqslant \int_X \mathrm{d}\chi \, \liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi). \tag{34}$$

Define the decomposition $X = X_- \cup X_0 \cup X_+$ of X into disjoint sets by

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) = \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

for all $\chi \in X_0$,

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) < \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

for all $\chi \in X_-$ and

$$\liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) > \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

for all $\chi \in X_+$. By equation (33), $\mu(X_-) = 0$. Suppose that $\mu(X_+) = a > 0$, so that $\mu(X_0) = 1 - a$. Then

$$\int_X \mathrm{d}\chi \, \liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) > a\mathcal{F}_d^q(\alpha_R, \alpha_B) + (1-a)\mathcal{F}_d^q(\alpha_R, \alpha_B) = \mathcal{F}_d^q(\alpha_R, \alpha_B).$$

This is in contradiction with equation (34), unless $a = 0$. Thus $\mu(X_+) = 0$, and consequently,

$$\mathcal{F}_d^q(\alpha_R, \alpha_B) = \liminf_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi_0)$$

for almost every $\chi_0 \in X$. Next, suppose that

$$\limsup_{n\to\infty} \frac{1}{n} \log Z_n^+(\alpha_R, \alpha_B|\chi) > \mathcal{F}_d^q(\alpha_R, \alpha_B)$$

for all $\chi \in U$, where $\mu(U) > 0$. Then there is an $\epsilon_\chi > 0$ and an infinite set of integers $\{n_i\}$, such that for each n_i.

$$\frac{1}{n_i} \log Z_{n_i}^+(\alpha_R, \alpha_B|\chi) > \mathcal{F}_d^q(\alpha_R, \alpha_B) + \epsilon_\chi/2.$$

Define $T_n = \frac{1}{n_{i+1}} \log Z^+_{n_{i+1}}(\alpha_R, \alpha_B|\chi)$ for $n_i < n \leqslant n_{i+1}$. Then for all $n \geqslant n_1$,

$$T_n > \mathcal{F}^q_d(\alpha_R, \alpha_B) + \epsilon_\chi/2.$$

Since T_n is measurable on X, it follows by the Lebesgue dominated convergence theorem that

$$\int_X \mathrm{d}\chi \lim_{n\to\infty} T_n = \lim_{n\to\infty} \int_X \mathrm{d}\chi\, T_n = \lim_{i\to\infty} \int_X \mathrm{d}\chi \frac{1}{n_i} \log Z^+_{n_i}(\alpha_R, \alpha_B|\chi).$$

Thus, by theorem 6 the consequence is that

$$\lim_{n\to\infty} \int_X \mathrm{d}\chi \frac{1}{n} \log Z^+_n(\alpha_R, \alpha_B|\chi) \geqslant \mathcal{F}^q_d(\alpha_R, \alpha_B) + \frac{1}{2}\int_U \mathrm{d}\chi\, \epsilon_\chi > \mathcal{F}^q_d(\alpha_R, \alpha_B).$$

This is in contradiction with equation (32), unless $\mu(U) = 0$. In other words,

$$\lim_{n\to\infty} \frac{1}{n} \log Z^+_n(\alpha_R, \alpha_B|\chi_0) = \mathcal{F}^q_d(\alpha_R, \alpha_B)$$

for almost every $\chi_0 \in X$. □

This completes a proof of self-averaging in this model. The existence of the limit $\lim_{n\to\infty}[\log Z^+_n(\alpha_R, \alpha_B|\chi_0)/n]$ is also a consequence of the local super-additive ergodic theorem of Akcoglu and Krengel [1]. Notice that the proof above is independent of the Akcoglu and Krengel local ergodic theorem; it is indeed possible to give a second proof of theorem 7 using the Akcoglu and Krengel local ergodic theorem, if it is first demonstrated that $\log Z^+_n(\alpha_R, \alpha_B|\chi_0)$ is a discrete super-additive process (for details, see [19]).

5. Conclusion

In this paper we considered several lattice models of branched copolymer adsorption. In particular, we paid attention to the existence of limiting free energies and the occurance of adsorption transitions. Questions similar to those in this paper had been studied for a self-avoiding walk model of adsorbing linear copolymers. In particular, the existence of a limiting free energy in the adsorption of block copolymers and strictly alternating copolymers, as well as the presence of adsorption critical points in their phase diagrams had been studied [26]. The same questions were considered for adsorbing random copolymers in the quenched average and annealed average ensembles [18]. Moreover, it is also known that this model is self-averaging [18], and this has been studied in the context of the Akcoglu and Krengel local ergodic theorem for collapsing random copolymers as well [19].

As examples of models of quenched branched coploymers we discussed in this paper branched alternating copolymers and branched block copolymers. We showed that there exist limiting free energies and non-analyticities in these free energies which correspond to adsorption transitions in the models. The location of the adsorption transiton critical points are related and compared to the adsorption of branched homopolymers: we proved that alternating copolymer cannot adsorb onto the hyperplane before a homopolymer and that a block copolymer adsorbs at the same critical value of the fugacity as a homopolymer (this is also known for a linear block copolymer [26]).

In the last section we studied the models of quenched and random branched copolymers. We showed that the annealed model of random branched copolymer adsorption is equivalent to homopolymer adsorption. As a simple model, we also studied alternating lexicographic quenched branched copolymers. Similar to the case of quenched alternating branched copolymers, this model cannot adsorb onto the hyperplane before a homopolymer. Moreover, the limiting averaged quenched free energy exists and it is non-analytic so that the system exhibits a adsorption transition. Lastly, the lexicographic quenched model of adsorbing branched copolymers is self-averaging: the limiting averaged quenched free energy is equal to the limiting free energy for almost all sequences of colours.

Acknowledgment

EJJvR is supported by an operating grant from NSERC (Canada).

References

[1] Akcoglu M A and Krengel U 1981 *J. Reine Angew. Math.* **323** 53
[2] Batchelor M T and Yung C M 1995 *Phys. Rev. Lett.* **74** 2026
[3] Cardy J L 1987 *Phase Transitions and Critical Phenomena* vol 11, ed C Domb and J L Lebowitz (London: Academic) p 55
[4] Carvalho M C T P and Privman V 1988 *J. Phys. A: Math. Gen.* **21** L1033
[5] Cosgrove T, Finch N A and Webster J R P 1990 *Macromolecules* **23** 3353
[6] De'Bell K and Lookman T 1985 *J. Phys. A: Math. Gen.* **18** L931
[7] De'Bell K and Lookman T 1993 *Rev. Mod. Phys.* **65** 87
[8] De'Bell K, Lookman T and Zhao D 1991 *Phys. Rev.* A **44** 1390
[9] Duplantier B and Saleur H 1986 *Phys. Rev. Lett.* **57** 3179
[10] Forgacs G, Privman V and Frisch H L 1989 *J. Chem. Phys.* **90** 3339
[11] Golding I and Kantor Y 1997 *Phys. Rev.* E **56** R1318
[12] Grassberger P and Hegger R 1995 *Europhys. Lett.* **31** 351
[13] Hammersley J M, Torrie G M and Whittington S G 1982 *J. Phys. A: Math. Gen.* **15** 539
[14] Hille E 1948 *Functional Analysis and Semi-Groups (AMS Coll. Publ. vol 31)* (Providence, RI: American Mathematical Society)
[15] Janse van Rensburg E J and You S 1998 *J. Phys. A: Math. Gen.* **31** 8635
[16] Joanny J-F 1994 *J. Physique* II **4** 1281
[17] Kantor Y and Kardar M 1994 *Europhys. Lett.* **28** 169
[18] Orlandini E, Tesi M C and Whittington S G 1999a *J. Phys. A: Math. Gen.* **32** 469
[19] Orlandini E, Tesi M C and Whittington S G 1999b *Preprint*
[20] Privman V, Forgacs G and Frisch H L 1988 *Phys. Rev.* B **37** 9897
[21] Sommer J U and Daoud M 1995 *Europhys. Lett.* **32** 407
[22] Sommer J U, Peng G W and Blumen A 1996. *J. Physique* II **6** 1061
[23] Vanderzande C, Stella A L and Seno F 1991 *Phys. Rev. Lett.* **67** 2757
[24] Wang W, Lin Z, Ebner C and Nikas Y 1993 *Phys. Rev.* E **48** 4622
[25] Whittington S G 1998 *J. Phys. A: Math. Gen.* **31** 3769
[26] Whittington S G 1999 *J. Phys. A: Math. Gen.* **32** 469
[27] Wilker J B and Whittington S G 1979 *J. Phys. A: Math. Gen.* **12** L245