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# A self-avoiding walk model of random copolymer adsorption

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**Abstract.** We consider a model of random copolymer adsorption in which a self-avoiding walk interacts with a hypersurface defining a half-space to which the walk is confined. Each vertex of the walk is randomly labelled with a real variable which determines the strength of the interaction of that vertex with the hypersurface. We show that the thermodynamic limit of the quenched average free energy exists and is equal to the thermodynamic limit of the free energy for almost all fixed labellings, so the system is self-averaging. In addition we show that the system exibits a phase transition and we discuss the connection between the annealed and quenched versions of the problem.

## 1. Introduction

Self-avoiding walk models of polymer adsorption have been studied for a number of years. For the homopolymer case the standard model is a self-avoiding walk on a lattice where the walk starts at the origin, is confined to a half-space defined by a plane containing the origin, and where there is an energy associated with vertices of the walk which are in this plane. This model has been shown to exhibit a phase transition (Hammersley *et al* 1982).

More recently there have been a number of studies of the statistical mechanics of copolymer adsorption (see for instance, Cosgrove *et al* 1990, Wang *et al* 1993, Joanny 1994, Sommer and Daoud 1995, Sommer *et al* 1996, Whittington 1998). When the copolymer is random one must distinguish between the *annealed* case (where the partition function is averaged before taking the logarithm to obtain the free energy) and the *quenched* case (where the logarithm of the partition function is averaged). The case of *periodic quenched randomness* has been examined by Grossberg *et al* (1994). The non-periodic case of quenched randomness has been studied by Garel *et al* (1989) and by Gutman and Chakraborty (1994, 1995) using the replica trick, and by Bolthausen and den Hollander (1997) and Biskup and den Hollander (1998) using rigorous arguments for a partially directed random walk model. In this paper we shall be concerned primarily with non-periodic quenched randomness.

Recently there has been considerable interest in the problem of *collapse* of a copolymer with quenched randomness (see for instance, Kantor and Kardar 1994, Grassberger and Hegger 1995, Golding and Kantor 1997) and any progress which can be made in the study of the adsorption of quenched random copolymers might produce useful techniques in the study of the corresponding collapse problem.

In this paper we investigate a self-avoiding walk model of the adsorption of quenched random copolymers. Our main result is that the system is thermodynamically self-averaging. That is, we prove that the limiting quenched average free energy exists and is equal to the

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limiting free energy for a fixed quench for almost all quenches. In addition we show that the system has a phase transition and we derive bounds on the behaviour of the quenched average free energy. Finally we explore the connection between the annealed and quenched cases.

## 2. Definitions and statement of results

We consider the hypercubic lattice $Z^d$, with coordinate system $(x, y, \ldots, z)$. An *$n$-edge self-avoiding walk* is an ordered sequence of $n + 1$ vertices, $i = 0, 1, 2, \ldots, n$ such that the zeroth vertex is at the origin, neighbouring pairs of vertices in the sequence are unit distance apart, and all vertices are distinct. Neighbouring pairs of vertices in the sequence are connected by edges. We write $c_n$ for the number of distinct $n$-edge self-avoiding walks. We call a self-avoiding walk a *positive walk* if no vertex has $z$-coordinate less than zero, and we write $c_n^+$ for the number of $n$-edge positive walks. Hammersley (1957) proved that the limit

$$0 < \lim_{n\to\infty} n^{-1} \log c_n \equiv \kappa_d < \infty \tag{2.1}$$

exists, and Whittington (1975) showed that

$$\lim_{n\to\infty} n^{-1} \log c_n^+ = \kappa_d. \tag{2.2}$$

A convenient model of polymer adsorption is to consider a positive walk which interacts with the hyperplane $z = 0$. We write $c_n^+(v)$ for the number of $n$-edge positive walks with $v + 1$ vertices in the hyperplane $z = 0$ and define the partition function

$$Z_n^+(\alpha) = \sum_v c_n^+(v) \mathrm{e}^{\alpha v}. \tag{2.3}$$

Hammersley *et al* (1982) have established the existence of the limit

$$\kappa^+(\alpha) = \lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha) \tag{2.4}$$

for all $\alpha < \infty$ and they showed that $\kappa^+(\alpha)$ is a continuous, convex, monotone non-decreasing function of $\alpha$ with a singularity at $\alpha_c > 0$. For $\alpha \leqslant \alpha_c$, $\kappa^+(\alpha) = \kappa_d$.

We consider a general model of copolymer adsorption in which the $i$th vertex ($i = 1, 2, \ldots, n$) of the walk is assigned a real number $\chi_i$, $0 \leqslant \chi_i \leqslant M < \infty$, chosen independently from a (normalized) probability distribution $\Xi$, such that the mean value of $\chi_i$ is positive. For a given walk $w$ we write $\Delta_i(w) = 1$ if the $i$th vertex is in the hyperplane $z = 0$, and zero otherwise. The zeroth vertex is required to be in $z = 0$, since we consider positive walks. We write $\chi$ for the sequence $\chi_1, \chi_2, \ldots, \chi_n$, and define the partition function

$$Z_n^+(\alpha|\chi) = \sum \mathrm{e}^{\alpha \sum_{i=1}^n \chi_i \Delta_i(w)} \tag{2.5}$$

where the first sum is over all $n$-edge positive walks. Since $\chi_i \geqslant 0$, a positive value of $\alpha$ means that vertices either have no interaction with the surface ($\chi_i = 0$), or are attracted to the surface ($\chi_i > 0$). Similarly, a negative value of $\alpha$ means that vertices either have no interaction with the surface or are repelled by the surface. For a given walk $w$ we can relabel the vertices $i \geqslant 1$ with $\Delta_i(w) = 1$ as $i_1, i_2, \ldots$ and define $c_n^+(i_1, i_2, \ldots)$ to be the number of $n$-edge positive walks with only the vertices $0, i_1, i_2, \ldots$ in $z = 0$. Then we can rewrite equation (2.5) as

$$Z_n^+(\alpha|\chi) = \sum_{\{i_1, i_2 \ldots\}} c_n^+(i_1, i_2, \ldots) \mathrm{e}^{\alpha \sum_j \chi_{i_j}}. \tag{2.6}$$

This formulation is quite general and includes several models which have previously appeared in the literature. For instance if $\chi_i = 0$ or 1 then we obtain a copolymer with two types of vertices, only one of which interacts with the surface (Whittington 1998). If $\Xi$ is a truncated Gaussian the model is related to the work of Srebnik *et al* (1996).

Our main result is that the free energy of the system is self-averaging, and we state this in the following theorem.

**Theorem 2.1.** *Let $\langle \ldots \rangle$ represent an average with respect to the distribution $\Xi$. The limit*

$$\lim_{n\to\infty} \langle n^{-1} \log Z_n^+(\alpha|\chi)\rangle \equiv \bar{\kappa}(\alpha) \tag{2.7}$$

*exists for all $\alpha < \infty$. Moreover, the limit*

$$\lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha|\chi) \equiv \kappa(\alpha|\chi) \tag{2.8}$$

*exists and*

$$\kappa(\alpha|\chi) = \bar{\kappa}(\alpha) \tag{2.9}$$

*for all $\alpha < \infty$ for almost all sequences $\chi$, where the $\chi_i$ are chosen independently from $\Xi$.*

We call $\bar{\kappa}(\alpha)$ the *quenched average free energy* of the system. We also show that $\bar{\kappa}(\alpha)$ is a non-analytic function of $\alpha$ so that the system exibits a phase transition associated with adsorption.

## 3. Proof of results

In this section we first introduce unfolded walks and loops, which play a role in the proof of theorem 2.1. We then prove several lemmas about the quenched average free energies of loops and positive walks and derive upper and lower bounds on the partition function $Z_n^+(\alpha|\chi)$ which lead to the proof of theorem 2.1.

We say that an $n$-edge positive walk is *$x$-unfolded* if

$$0 = x_0 < x_i \leqslant x_n \tag{3.1}$$

for all $i > 0$. Similarly, we say that a positive walk is *$z$-unfolded* if

$$0 = z_0 \leqslant z_i < z_n \tag{3.2}$$

for all $i < n$. We write $c_n^\ddagger$ for the number of $n$-edge $x$-unfolded walks and $c_n^\ddagger(i_1, i_2, \ldots)$ for the number of $n$-edge $x$-unfolded walks with vertices $0, 1, i_1, i_2, \ldots$ in the hyperplane $z = 0$. Clearly

$$c_n^\ddagger(i_1, i_2, \ldots) \leqslant c_n^+(1, i_1, i_2, \ldots). \tag{3.3}$$

To every positive walk there corresponds a unique $x$-unfolded walk with one additional edge, obtained by successive reflections in hyperplanes, as described in Hammersley and Welsh (1962), followed by translation by unit distance in the positive $x$-direction and the addition of an edge from $(0, 0, \ldots, 0)$ to $(1, 0, \ldots, 0)$. This operation increases the number of vertices in $z = 0$ by one. The unfolding transformation is not bijective but, using the arguments of Hammersley and Welsh (1962)

$$c_n^+(i_1, i_2, \ldots) \leqslant \mathrm{e}^{\mathrm{O}(\sqrt{n})} c_{n+1}^\ddagger(i_1, i_2, \ldots). \tag{3.4}$$

We define a *loop* to be a positive walk which satisfies the inequalities in (3.1) and the following condition:

$$0 = z_0 = z_n \leqslant z_i \qquad \forall i. \tag{3.5}$$

We write $l_n$ for the number of $n$-edge loops and $l_n(i_1, i_2, \ldots)$ for the number of $n$-edge loops with vertices $0, 1, i_1, i_2, \ldots$ in $z = 0$.

For a given sequence $\chi \equiv \chi_1, \chi_2, \ldots, \chi_n$ we write the partition functions of unfolded walks and loops as

$$Z_n^\ddagger(\alpha|\chi) = \sum_{\{i_1, i_2, \ldots\}} c_n^\ddagger(i_1, i_2, \ldots) \mathrm{e}^{\alpha \sum_j \chi_{i_j}} \tag{3.6}$$

and

$$L_n(\alpha|\chi) = \sum_{\{i_1,i_2,\ldots\}} l_n(i_1, i_2, \ldots)\mathrm{e}^{\alpha\sum_j \chi_{i_j}}. \tag{3.7}$$

In the first lemma we prove the existence of an average free energy for loops.

**Lemma 3.1.** *The following limit exists for all* $\alpha < \infty$

$$\lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha|\chi)\rangle \equiv \bar{\kappa}(\alpha). \tag{3.8}$$

**Proof.** Consider an $m$-edge loop and an $n$-edge loop and translate the $n$-edge loop so that its zeroth vertex is coincident with the $m$th vertex of the $m$-edge loop. The resulting object is a loop with $m + n$ edges so that we have the inequality

$$l_m(i_1, i_2, \ldots)l_n(j_1, j_2, \ldots) \leqslant l_{m+n}(i_1, i_2, \ldots, m + 1, m + j_1, m + j_2, \ldots). \tag{3.9}$$

Let $\chi^{(m)} \equiv \{\chi_i^{(m)}\}$ be the sequence of $\chi$ values associated with the $m$-loop and $\chi^{(n)} \equiv \{\chi_i^{(n)}\}$ be the sequence of $\chi$ values associated with the $n$-loop. We write $\chi^{(m)+(n)}$ for the corresponding sequence associated with the concatenation of the two sequences. Multiplying both sides of (3.9) by $\mathrm{e}^{\alpha(\sum_k \chi_{i_k}^{(m)} + \sum_k \chi_{j_k}^{(n)})}$, and summing over appropriate indices we obtain the inequality

$$L_m(\alpha|\chi^{(m)})L_n(\alpha|\chi^{(n)}) \leqslant \max[1, \mathrm{e}^{-M\alpha}]L_{m+n}(\alpha|\chi^{(m)+(n)}). \tag{3.10}$$

Taking logarithms and averaging (3.10) over the random sequences $\chi^{(m)}$ and $\chi^{(n)}$ we obtain

$$\langle \log L_m(\alpha|\chi^{(m)})\rangle + \langle \log L_n(\alpha|\chi^{(n)})\rangle \leqslant \log(\max[1, \mathrm{e}^{-M\alpha}]) + \langle \log L_{m+n}(\alpha|\chi^{(m+n)})\rangle. \tag{3.11}$$

Since $L_n(\alpha|\chi^{(n)}) \leqslant \max[(2d)^n, (2d)^n \mathrm{e}^{\alpha M n}]$, the super-additive inequality (3.11) implies (Hille 1948) the existence of the limit in equation (3.8) for all $\alpha < \infty$. □

In the next lemma we establish a relation between the quenched average free energies of loops and positive walks. The general idea is to notice that loops are a subset of positive walks, and to construct loops by an operation on suitably unfolded walks.

**Lemma 3.2.** *The quenched average free energy of positive walks exists and is equal to that of loops.*

**Proof.** Inclusion implies the inequalities

$$L_n(\alpha|\chi) \leqslant Z_n^{\ddagger}(\alpha|\chi) \leqslant Z_n^{+}(\alpha|\chi). \tag{3.12}$$

To obtain a bound in the other direction we use a process of successive unfolding and reflection. Consider an $n$-edge positive walk $\omega$. Let $m = \max[i|\Delta_i = 1]$. If $m = n$ the positive walk starts and ends in $z = 0$ and is either a loop or can be converted to a loop by $x$-unfolding and adding an edge. This would increase the number of vertices in $z = 0$ by one. If $m \neq n$, disconnect the walk $\omega$ at the $m$th vertex to form two subwalks $\omega_1$ and $\omega_2$. $x$-unfold both subwalks and reconnect them. This operation can add up to two additional vertices in the hyperplane $z = 0$ but otherwise does not change which vertices are in $z = 0$. Let $z_n$ be the $z$-coordinate of the final vertex of the walk. Consider the following cases:

(1) If $z_n$=1, add an edge so that the $(n + 1)$th vertex is in $z = 0$.
(2) Otherwise unfold the subwalk from the $m$th to the $n$th vertex in the $z$-direction, to satisfy the condition (3.2). Let $z_n$ be the new $z$-coordinate of the $n$th vertex. If $z_n$ is even, let $m'$ be the vertex where the walk last crosses the hyperplane $z = z_n/2$. Disconnect the walk at this vertex, to form two subwalks $\omega_3$ and $\omega_4$, $x$-unfold the two subwalks to form $\omega_3'$ and $\omega_4'$, reflect the final subwalk $\omega_4'$ in the plane $z = z_n/2$ and reconnect the subwalks. This walk has its final vertex in $z = 0$.

(3) If in (2) $z_n$ is odd, let $m'$ be the last vertex where the walk crosses the plane $(z_n+1)/2$. Disconnect the walk at this vertex, $x$-unfold the two subwalks, reflect the final subwalk in the plane $z=(z_n+1)/2$ and reconnect the two subwalks. This walk will have its final vertex in $z=1$. Add an edge so that the new final vertex is in the plane $z=0$.

These operations involve at most five unfolding operations and the addition of at most five edges and three vertices in the plane $z=0$. Hence

$$Z_n^+(\alpha|\chi) \leqslant \mathrm{e}^{\mathrm{O}(\sqrt{n})}\max[1,\mathrm{e}^{3\alpha M}]\max[L_n(\alpha|\chi), L_{n+1}(\alpha|\chi'),\ldots L_{n+5}(\alpha|\chi'')] \tag{3.13}$$

where $\chi',\ldots,\chi''$ represent augmentations of the labelling $\chi$. Taking logarithms, dividing by $n$ and averaging over the labellings in equations (3.12) and (3.13) gives

$$\lim_{n\to\infty}\langle n^{-1}\log Z_n^+(\alpha|\chi)\rangle = \bar{\kappa}(\alpha). \tag{3.14}$$

□

In the next lemma we derive a result about the $\alpha$-dependence of $Z_n^+(\alpha|\chi)$ for $\alpha\leqslant 0$.

**Lemma 3.3.** *For $\alpha\leqslant 0$*

$$\lim_{n\to\infty} n^{-1}\log Z_n^+(\alpha|\chi) = \kappa_d \tag{3.15}$$

*for every labelling $\chi$.*

**Proof.** Clearly $Z_n^+(\alpha|\chi)$ is a monotone non-decreasing function of $\alpha$ so

$$Z_n^+(\alpha|\chi) \leqslant Z_n^+(0|\chi) \tag{3.16}$$

for every $\alpha\leqslant 0$, and $Z_n^+(0|\chi)=c_n^+$, independent of $\chi$, so that

$$\limsup_{n\to\infty} n^{-1}\log Z_n^+(\alpha|\chi) \leqslant \kappa_d \tag{3.17}$$

for all $\alpha\leqslant 0$. Each $(n-1)$-edge positive walk can be converted into an $n$-edge positive walk with only one vertex in the hyperplane $z=0$ by translating the walk through unit distance in the positive $z$ direction, and adding an additional edge joining $(0,0,\ldots,0)$ to $(0,0,\ldots,1)$, and this transformation is a bijection. The partition function $Z_n^+(\alpha|\chi)$ can be bounded below by the number of $n$-edge positive walks with only the zeroth vertex in $z=0$ which, by the above argument is equal to $c_{n-1}^+$. Hence

$$\liminf_{n\to\infty} n^{-1}\log Z_n^+(\alpha|\chi) \geqslant \lim_{n\to\infty} n^{-1}\log c_{n-1}^+ = \kappa_d \tag{3.18}$$

and the lemma follows from (3.17) and (3.18). □

Let $c_n^h(i_1,i_2,\ldots)$ be the number of $n$-edge walks with $z_0=h$, no vertices with negative $z$-coordinate, and vertices $i_1,i_2,\ldots$ in $z=0$. We define the partition function

$$Z_n^h(\alpha|\chi) = \sum_{\{i_1,i_2,\ldots\}} c_n^h(i_1,i_2,\ldots)\mathrm{e}^{\alpha\sum_j \chi_{i_j}} \tag{3.19}$$

and, for fixed $\alpha$, we define

$$Z_n^*(\alpha|\chi) = \max_h Z_n^h(\alpha|\chi). \tag{3.20}$$

**Lemma 3.4.** *The following equality holds:*

$$\lim_{n\to\infty}\langle n^{-1}\log Z_n^*(\alpha|\chi)\rangle = \lim_{n\to\infty}\langle n^{-1}\log Z_n^+(\alpha|\chi)\rangle. \tag{3.21}$$

**Proof.** Clearly $Z_n^*(\alpha|\chi) \geqslant Z_n^+(\alpha|\chi)$. Let $h_0$ be the value of $h$ which maximizes $Z_n^h(\alpha|\chi)$ so that $Z_n^*(\alpha|\chi) = Z_n^{h_0}(\alpha|\chi)$. Notice that $h_0$ will in general depend on $n, \alpha$ and $\chi$. If $h_0 = 0$ then $Z_n^*(\alpha|\chi) = Z_n^+(\alpha|\chi)$. Suppose that $h_0 \neq 0$. Then each walk either has no vertices in $z = 0$ or $i_1 \geqslant 1$. To derive an upper bound we can disconnect the walk at $i_1$ into two subwalks. Suppose that the two labellings of the two subwalks are $\chi^{(1)}$ and $\chi^{(2)}$. Both subwalks are positive walks so we have

$$\begin{aligned} Z_n^{h_0}(\alpha|\chi) &\leqslant c_n + \sum_{i_1 \geqslant 1} \sum_{i_2, i_3, \ldots} c_n^{h_0}(i_1, i_2, \ldots) \mathrm{e}^{\alpha \sum_j \chi_{i_j}} \\ &\leqslant c_n + \sum_{i_1 \geqslant 1} \max[\mathrm{e}^{\alpha M}, 1] Z_{i_1}^+(0|\bar{\chi}^{(1)}) Z_{n-i_1}^+(\alpha|\chi^{(2)}) \\ &\leqslant \mathrm{e}^{\kappa_d n + \mathrm{o}(n)} + \mathrm{e}^{\mathrm{o}(n)} \max_m [Z_m^+(0|\bar{\chi}^{(1)}) Z_{n-m}^+(\alpha|\chi^{(2)})] \end{aligned} \tag{3.22}$$

where the bar on $\bar{\chi}^{(1)}$ indicates that the labelling is being read in reverse order. If $\alpha \leqslant 0$ $Z_{n-m}^+(\alpha|\chi^{(2)})$ is bounded above by $Z_{n-m}^+(0|\chi^{(2)})$ so that (3.21) is an immediate consequence, when we make use of lemma 3.3. For $\alpha \geqslant 0$, $Z_m^+(0|\chi^{(2)}) \leqslant Z_m^+(\alpha|\chi^{(2)})$. Let $m^*$ be the value of $m$ which maximizes the final term in (3.22). Then, taking logarithms, dividing by $n$ and averaging over labellings, we have the bound

$$\begin{aligned} \langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle &\leqslant \max[\kappa_d, \langle n^{-1} \log Z_{m^*}^+(\alpha|\chi)\rangle + \langle n^{-1} \log Z_{n-m^*}^+(\alpha|\chi)\rangle] + \mathrm{o}(1) \\ &= \max\left[\kappa_d, \frac{m^* + (n-m^*)}{n} \bar{\kappa}(\alpha)\right] + \mathrm{o}(1) \\ &= \bar{\kappa}(\alpha) + \mathrm{o}(1) \end{aligned} \tag{3.23}$$

where we have used lemma 3.2 and the fact that $\bar{\kappa}(\alpha)$ is a non-decreasing function of $\alpha$. The result follows on letting $n$ go to infinity. □

The next lemma gives a lower bound on the free energy of a system with a given fixed quench.

**Lemma 3.5.**

$$\bar{\kappa}(\alpha) \leqslant \liminf_{n\to\infty} n^{-1} \log Z_n^+(\alpha|\chi_0) \tag{3.24}$$

*for any $\alpha < \infty$ and for almost all fixed quenches $\chi_0$.*

**Proof.** For fixed $\alpha < \infty$ and fixed $m$ let $n = mp + q$ with $0 \leqslant q < m$. We consider a subset of $n$-edge positive walks made up of a concatenation of $p$ $m$-edge loops, labelled $i = 1, 2, \ldots, p$ and a final $q$-edge loop, labelled $p + 1$. Writing $\chi_0 = \chi^{(1)} + \chi^{(2)} + \cdots + \chi^{(p+1)}$, where $\chi^{(i)}$ is the labelling of the $i$th loop, and $\chi_0$ is the labelling of the concatenated loops, we have

$$Z_n^+(\alpha|\chi_0)) \geqslant \left[\prod_{i=1}^p L_m(\alpha|\chi^{(i)})\right] L_q(\alpha|\chi^{(p+1)}). \tag{3.25}$$

Taking logarithms and dividing by $n$ we obtain

$$n^{-1} \log Z_n^+(\alpha|\chi_0) \geqslant \left[\frac{1}{m(p+q/m)} \sum_{i=1}^p \log L_m(\alpha|\chi^{(i)})\right] + n^{-1} \log L_q(\alpha|\chi^{(p+1)}). \tag{3.26}$$

Letting $p \to \infty$ with $m$ fixed we obtain

$$\liminf_{n\to\infty} n^{-1} \log Z_n^+(\alpha|\chi_0) \geqslant \limsup_{p\to\infty} p^{-1} \sum_{i=1}^p m^{-1} \log L_m(\alpha|\chi^{(i)}) = \langle m^{-1} \log L_m(\alpha|\chi)\rangle \tag{3.27}$$

almost surely, where the equality comes from application of the strong law of large numbers. Letting $m \to \infty$ and using lemma 3.2 gives (3.24). $\square$

In the next lemma we give a corresponding upper bound.

**Lemma 3.6.**

$$\bar{\kappa}(\alpha) \geqslant \limsup_{n\to\infty} n^{-1} \log Z_n^+(\alpha|\chi_0) \tag{3.28}$$

*for any $\alpha < \infty$ and for almost all fixed quenches $\chi_0$.*

**Proof.** For fixed $\alpha < \infty$ and fixed $m$ we write $n = mp + q$ with $0 \leqslant q < m$. We divide an $n$-edge positive walk into $p$ subwalks of length $m$ and a final subwalk of length $q$. Again we write $\chi_0 = \chi^{(1)} + \chi^{(2)} + \cdots + \chi^{(p+1)}$, where $\chi^{(i)}$ is the labelling of the $i$th subwalk, and $\chi_0$ is the labelling of the $n$-edge positive walk. The subdivision gives the inequality

$$Z_n^+(\alpha|\chi_0) \leqslant Z_m^+(\alpha|\chi^{(1)}) \left[ \prod_{i=2}^{p} Z_m^*(\alpha|\chi^{(i)}) \right] Z_q^*(\alpha|\chi^{(p+1)}). \tag{3.29}$$

Bounding the last term, taking logarithms, and dividing by $n$ gives

$$\frac{\log Z_n^+(\alpha|\chi_0)}{n} \leqslant \frac{\sum_{i=1}^{p} m^{-1} \log Z_m^*(\alpha|\chi^{(i)})}{p + q/m} + \frac{\max[q \log(2d), q \log(2d) + \alpha M q]}{m(p + q/m)} \tag{3.30}$$

where we have used the fact that $Z_m^+ \leqslant Z_m^*$. Letting $p \to \infty$ with $m$ fixed we have

$$\limsup_{n\to\infty} n^{-1} \log Z_n^+(\alpha|\chi_0) \leqslant \liminf_{p\to\infty} p^{-1} \sum_{i=1}^{p} m^{-1} \log Z_m^*(\alpha|\chi_i) = \langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle \tag{3.31}$$

almost surely, where the last equality comes from an application of the strong law of large numbers. Letting $m \to \infty$ and using lemma 3.4 gives (3.28). $\square$

Lemmas 3.5 and 3.6 together prove theorem 2.1.

We now turn to a discussion of the adsorption transition in such random systems. Theorem 2.1 tells us that the limit defining $\bar{\kappa}(\alpha)$ exists and we now derive bounds on its behaviour.

**Lemma 3.7.** *For $\alpha \geqslant 0$*

$$\bar{\kappa}(\alpha) \geqslant \max[\kappa_d, \kappa_{d-1} + \alpha\mu] \tag{3.32}$$

*where $\mu$ is the expected value of $\chi_i$.*

**Proof.** Consider an $n$-edge walk labelled with a sequence $\chi = \chi_1, \chi_2, \ldots$. Since $Z_n^+(\alpha|\chi)$ is monotone non-decreasing we have $Z_n^+(\alpha|\chi) \geqslant Z_n^+(0|\chi)$ for all $\alpha \geqslant 0$. In addition $Z_n^+(\alpha|\chi) \geqslant c_n^+(1, 2, \ldots, n)\mathrm{e}^{\alpha \sum_{i=1}^{n} \chi_i}$, corresponding to all vertices being in $z = 0$. Taking logarithms, dividing by $n$ and letting $n$ go to infinity we obtain

$$\kappa(\alpha|\chi) \geqslant \max\left[\kappa_d, \lim_{n\to\infty}\left(n^{-1} \log c_n^+(1, 2, \ldots, n) + \alpha n^{-1} \sum_{i=1}^{n} \chi_i\right)\right] \tag{3.33}$$

for any labelling $\chi$ which satisfies equation (2.9). Then using (2.9) we have (3.32). $\square$

Note that the restrictions placed on $\Xi$ ensure that $\mu > 0$. Since $\bar{\kappa}(\alpha)$ is constant for $\alpha \leqslant 0$ (from lemma 3.3) but not for $\alpha > (\kappa_d - \kappa_{d-1})/\mu$, $\bar{\kappa}(\alpha)$ is a non-analytic function of $\alpha$ and the system exibits a phase transition at $\alpha_q$ where $0 \leqslant \alpha_q \leqslant (\kappa_d - \kappa_{d-1})/\mu$. Since $\bar{\kappa}(\alpha) \leqslant \kappa^+(\alpha)$ (since $\chi_i \geqslant 0$) we have the improved lower bound $0 < \alpha_c \leqslant \alpha_q$.

Finally we discuss the relation between the annealed and quenched cases. The annealed free energy is defined as

$$\kappa_a(\alpha) = \lim_{n\to\infty} n^{-1} \log\langle Z_n^+(\alpha|\chi)\rangle \tag{3.34}$$

where the limit can be shown to exist by a suitable modification of the methods used to prove lemmas 3.1, 3.2 and 3.4, where the averaging is inserted at a suitable stage, and where one makes use of the independence of the labelling of subwalks. From lemma 3.3 it is clear that $\kappa_a(\alpha) = \bar{\kappa}(\alpha)$ for $\alpha \leqslant 0$. In addition, by the arithmetic mean—geometric mean inequality, $\kappa_a(\alpha) \geqslant \bar{\kappa}(\alpha)$ for all $\alpha$. (Recall our choice of sign in our definition of the free energy.) Hence $\kappa_a(\alpha)$ is a non-analytic function of $\alpha$ and has a singularity at $\alpha_a$ satisfying $0 < \alpha_c \leqslant \alpha_a \leqslant \alpha_q$, where we have made use of the obvious inequality $Z_n^+(\alpha|\chi) \leqslant Z_n^+(\alpha)$ for any positive $\alpha$. Clearly $\kappa_a(\alpha) = \bar{\kappa}(\alpha)$ for all $\alpha \leqslant \alpha_a$.

## 4. Discussion

We have investigated a self-avoiding walk model of random copolymer adsorption and have shown that the limiting quenched average free energy exists. Moreover the system is thermodynamically self-averaging in that the limiting quenched average free energy is equal to the limiting free energy for almost all comonomer sequences. Although our proof of self-averaging is for the case of independently labelled vertices, it could be extended to other labelling schemes for which the strong law of large numbers applies. These results have some practical importance in that they show that one has some hope of studying the system by Monte Carlo calculations on a randomly chosen set of comonomer sequences.

The limiting quenched average free energy is non-analytic so the system exhibits a phase transition. We have also considered the annealed case and we have shown that the limiting annealed and quenched average free energies are identical at high temperatures (i.e. in the desorbed phase).

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