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Extent of self-averaging in the statistical mechanics of finite random copolymers

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Abstract

We investigate the extent of thermodynamic self-averaging in a coloured self-avoiding walk model of finite random copolymer adsorption. We derive a bound on the extent of self-averaging as a function of the length of the self-avoiding walk.

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1. Introduction

Quenched random systems such as dilute magnets and copolymers have been studied since the pioneering work of Brout (1959). An important question which arises is the extent to which properties of the system depend on the particular realization of the quenched random variables. For instance, in the case of random copolymers the sequence of monomers is determined by some random process but this sequence is then fixed in that molecule. To what extent do the properties of the molecule depend on the particular sequence of comonomers? If the polymer has n monomers, then the system is said to be *thermodynamically self-averaging* if the free energy is equal to the quenched average free energy for almost all comonomer sequences, in the infinite-n limit.

Thermodynamic self-averaging has been proved for a number of model systems including a random magnet with short-range (van Hemmen and Palmer 1982) and long-range interactions (van Enter and van Hemmen 1983), self-avoiding walk models of random copolymer adsorption (Orlandini *et al* 1999) and localization (Martin *et al* 2000), a lattice tree model of branched random copolymer adsorption (You and Janse van Rensburg 2000) and some simplified models of randomly self-interacting copolymers (Orlandini *et al* 2000, Janse van Rensburg *et al* 2001). However, it is known that correlation functions are not self-averaging in some random spin problems (Derrida and Hilhorst 1981, Sourlas 1987), so self-averaging is not a trivial property.

The methods which have been used to prove thermodynamic self-averaging say little about the extent of self-averaging for finite systems. For spin systems van Hemmen and Palmer (1982) gave a large deviation result for finite systems and, more recently, self-averaging in finite random copolymers has been investigated numerically by Chuang *et al* (2001) and by

Naidenov and Nechaev (2001). They examined the dependence of thermodynamic functions on the comonomer sequence, as a function of system size, and investigated the extent of self-averaging for small n. The purpose of this paper is to supply some rigorous results about the question. We shall work in the context of a self-avoiding walk model of random copolymer adsorption.

2. Definitions and statement of results

We shall focus on self-avoiding walks on the d-dimensional hypercubic lattice, $\mathbb{Z}^d$ and write $(x, y, \ldots, z)$ for the coordinates of a vertex of $\mathbb{Z}^d$. Let c_n be the number of distinct n-edge self-avoiding walks on $\mathbb{Z}^d$, starting at the origin. The *connective constant* κ_d of $\mathbb{Z}^d$ is given by

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

(Hammersley and Morton 1954), and it is known that $c_n = \mathrm{e}^{\kappa_d n + \mathrm{O}(\sqrt{n})}$ (Hammersley and Welsh 1962). We define a *positive walk* to be a self-avoiding walk with n edges on $\mathbb{Z}^d$, which starts at the origin and is confined to the half-space $z \geqslant 0$, but we shall often consider translates of a positive walk in the $z = 0$ plane. We write $(x_i, y_i, \ldots, z_i)$ for the coordinates of the ith vertex, $i = 0, 1, \ldots, n$, so that $z_0 = 0$ and $z_i \geqslant 0$ for all $i > 0$. The zeroth vertex is uncoloured and the remaining vertices of the walk are coloured independently and uniformly by a random variable belonging to a probability space Y. A sequence $\chi = \chi_1, \chi_2, \ldots, \chi_n$ of n colours can be sampled from the product space $X = Y \times Y \times \cdots \times Y$. In fact we shall consider colourings by only two colours A and B, but this can easily be generalized to cases with any finite number of colours.

Let $c_n^+(v|\chi)$ be the number of positive walks with n edges, with vertices $1, 2, \ldots, n$ coloured $\chi_1, \chi_2, \ldots, \chi_n \equiv \chi$, having v vertices coloured A in the surface $z = 0$. We define the partition function

$$Z_n^+(\alpha|\chi) = \sum_v c_n^+(v|\chi)\mathrm{e}^{\alpha v}, \tag{2.2}$$

and the reduced free energy

$$\kappa_n(\alpha|\chi) = n^{-1} \log Z_n^+(\alpha|\chi). \tag{2.3}$$

We define an n-edge *loop* to be a positive walk with n edges which satisfies the inequalities

$$0 = x_0 < x_i \leqslant x_n, \qquad 0 < i \leqslant n, \tag{2.4}$$

and the condition

$$0 = z_0 = z_n \leqslant z_i, \qquad 0 \leqslant i \leqslant n. \tag{2.5}$$

We write $l_n(v|\chi)$ for the number of loops with n edges and colouring χ, having v vertices coloured A in the plane $z = 0$. Define the partition function

$$L_n(\alpha|\chi) = \sum_v l_n(v|\chi)\mathrm{e}^{\alpha v}. \tag{2.6}$$

Let $c_n^h(v|\chi)$ be the number of n-edge self-avoiding walks, confined to the half-space $z \geqslant 0$, having initial vertex with coordinates $(0, 0, \ldots, 0, h)$ (i.e. with $z_0 = h$), having colouring χ and having v vertices coloured A in $z = 0$. Notice that $c_n^0(v|\chi) \equiv c_n^+(v|\chi)$. Define the corresponding partition function

$$Z_n^h(\alpha|\chi) = \sum_v c_n^h(v|\chi)\mathrm{e}^{\alpha v}, \tag{2.7}$$

and let

$$Z_n^*(\alpha|\chi) = \max_h Z_n^h(\alpha|\chi). \tag{2.8}$$

Orlandini *et al* (1999) proved the existence of the quenched average free energy

$$\lim_{n\to\infty} \langle \kappa_n(\alpha|\chi)\rangle \equiv \bar{\kappa}(\alpha), \tag{2.9}$$

where the angular brackets denote an average over colourings χ, and that

$$\lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha|\chi)\rangle = \lim_{n\to\infty} \langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle = \bar{\kappa}(\alpha). \tag{2.10}$$

Our main result is a bound on the width of the distribution of the free energy $\kappa_n(\alpha|\chi)$. We state this in the following theorem.

Theorem 1. *For any $\alpha < \infty$ there exists $K = K(\alpha, d) < \infty$, such that for any $\epsilon > 0$, the following inequality holds with probability exceeding $\left(1 - 2K/\lfloor\sqrt{n}\rfloor\right)$:*

$$|\kappa_n(\alpha|\chi) - \langle\kappa_n(\alpha|\chi)\rangle| \leqslant \mathrm{O}(n^{-\frac{1}{4}+\epsilon}). \tag{2.11}$$

The proof is by a series of lemmas, and is given in the next section.

3. Proof of results

The general approach is to divide an n-edge walk into a set of p subwalks each of length m and derive upper and lower bounds on $\log Z_n^+(\alpha|\chi)$ in terms of the averages of $\log L_m(\alpha|\chi)$ and $\log Z_m^*(\alpha|\chi)$, with correction terms coming from the distributions of $\log L_m(\alpha|\chi)$ and $\log Z_m^*(\alpha|\chi)$. The main tool is an application of Chebyshev's inequality (see for instance Moran 1968). The remaining problem is to relate the averages $\langle\log L_m(\alpha|\chi)\rangle$ and $\langle\log Z_m^*(\alpha|\chi)\rangle$ to $\langle\log Z_m^+(\alpha|\chi)\rangle$. We first prove several lemmas which address the second problem. The first lemma gives an upper bound on the quenched average free energy for loops.

Lemma 1. *For all $\alpha < \infty$ the quenched average free energy for loops is bounded above by the limiting quenched average free energy. I.e. for any $n > 0$,*

$$\langle n^{-1} \log L_n(\alpha|\chi)\rangle \leqslant \bar{\kappa}(\alpha). \tag{3.1}$$

Proof. Fix $\alpha < \infty$. Two loops can be concatenated to form a loop by identifying the last vertex of one loop with the first vertex of the other loop. Since the first vertex of a loop is not coloured, the common vertex inherits the colour of the last vertex of the first loop. This gives the inequality

$$L_{m+n}(\alpha|\chi) \geqslant L_m(\alpha|\chi_1) L_n(\alpha|\chi_2) \tag{3.2}$$

where the colouring χ is the concatenation of the two colourings χ_1 and χ_2. Taking logarithms and averaging over the colourings gives

$$\langle\log L_{m+n}(\alpha|\chi)\rangle \geqslant \langle\log L_m(\alpha|\chi_1)\rangle + \langle\log L_n(\alpha|\chi_2)\rangle \tag{3.3}$$

so that $\langle\log L_n(\alpha|\chi)\rangle$ is a superadditive function. Since

$$\langle n^{-1} \log L_n(\alpha|\chi)\rangle \leqslant \max[\log(2d), \log(2d) + \alpha] < \infty \tag{3.4}$$

we have (Hille 1948)

$$\sup_{n>0} \langle n^{-1} \log L_n(\alpha|\chi)\rangle = \lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha|\chi)\rangle \tag{3.5}$$

and this limit is known to be equal to $\bar{\kappa}(\alpha)$ (Orlandini *et al* 1999). □

Lemma 2. *For all $\alpha < \infty$ and for any $n > 0$,*

$$\langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle \geqslant \bar{\kappa}(\alpha). \tag{3.6}$$

Proof. Fix $\alpha < \infty$. By cutting walks with $m+n$ edges into two subwalks with m and n edges respectively we obtain the inequality

$$Z_{m+n}^*(\alpha|\chi) \leqslant Z_m^*(\alpha|\chi_1) Z_n^*(\alpha|\chi_2) \tag{3.7}$$

where the colourings χ_1 and χ_2 of the two subwalks are determined by the colouring χ. Taking logarithms and averaging over χ shows that $\langle \log Z_n^*(\alpha|\chi)\rangle$ is a subadditive function. Since

$$\langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle \geqslant \frac{\log d}{2} \tag{3.8}$$

for $n \geqslant 2$, it follows (Hille 1948) that

$$\inf_{n>0} \langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle = \lim_{n\to\infty} \langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle \tag{3.9}$$

and the result then follows since $\lim_{n\to\infty}\langle n^{-1} \log Z_n^*(\alpha|\chi)\rangle = \bar{\kappa}(\alpha)$ (Orlandini *et al* 1999). □

The next lemma is essentially a sharpened version of a result due to Orlandini *et al* (1999) and uses a construction similar to theirs.

Lemma 3. *For all $\alpha < 0$*

$$Z_n^*(\alpha|\chi) \leqslant c_n, \tag{3.10}$$

and for $0 \leqslant \alpha < \infty$

$$Z_n^*(\alpha|\chi) \leqslant L_{n+2k}(\alpha|\chi')\mathrm{e}^{\mathrm{O}(\sqrt{n})} \tag{3.11}$$

for some colouring χ' which is an extension of χ, and for some k which is independent of n, α and the colouring χ.

Proof. If $\alpha < 0$ the interaction with the surface is repulsive, and every walk contributing to $Z_n^h(\alpha|\chi)$ is a self-avoiding walk so that $Z_n^*(\alpha|\chi) \leqslant c_n$. Now suppose that $\alpha \geqslant 0$. Consider a walk confined to the half-space $z \geqslant 0$, with at least one vertex in $z = 0$. The strategy will be to operate on both ends of the walk to convert the walk into a loop.

First, treat the case when at least one of z_n or z_0 is zero. For each of these, x-unfold the walk and attach to the end or beginning of the resulting walk a new four-edge walk which lies in the plane $z = 0$, and is oriented in the x-direction in such a manner that the walk remains x-unfolded. Thus each end of the original walk lying in the plane $z = 0$ contributes an additional four edges and four vertices in the plane $z = 0$.

Second, we treat any end of the walk that does not lie in $z = 0$. It suffices to describe the construction for one end of the walk, since the procedure may then be repeated *mutatis mutandis*, at the other end, as necessary, to form the loop. We suppose that $z_n > 0$. Let m be the last vertex in the plane $z = 0$. Then vertex $m-1$ will also be in $z = 0$. This is true because either end of the walk lying in $z = 0$ has already been treated, above. Disconnect the walk into three subwalks, ω_1 from vertex 0 to vertex $m-1$, ω_2 being the single edge (in $z = 0$) from vertex $m-1$ to vertex m, and ω_3 from vertex m to vertex n. Unfold ω_1 in the x-direction to form a walk ω_4 with $m-1$ edges so that $x_{m-1} \geqslant x_i$ for all $i \leqslant m-1$. Reorient the single edge ω_2 to form an edge $\tilde{\omega}_2$ in the positive x-direction, lying in the $z = 0$ plane. Unfold ω_3 in the x-direction to form ω_5 with $x_m \leqslant x_j \leqslant x_n$ for all $m \leqslant j \leqslant n$. Unfold ω_5 in the z-direction to form ω_6 with $z_n \geqslant z_j \geqslant z_m = 0$ for all $m \leqslant j \leqslant n$. Define $z^* = 1 + z_n/2$ if z_n is even, and $z^* = (1+z_n)/2$ if z_n is odd. Let r be the last vertex in ω_6 in the plane $z = z^*$. Disconnect ω_6 at vertex r to form two walks, ω_7 from vertex m to vertex r and ω_8 from vertex r to vertex n.

Note that $\omega_8 = \emptyset$ if and only if $z_n \in \{1, 2\}$, in which case $r = n$. This does not affect the proof. Unfold ω_7 in the x-direction so that $x_r \geqslant x_j \geqslant x_m$, $m \leqslant j \leqslant r$, to form ω_9. Unfold ω_8 in the x-direction so that $x_r \leqslant x_j \leqslant x_n$, $r \leqslant j \leqslant n$, and then reflect this unfolded walk in the plane $z = z^*$ to form ω_{10}. We now reconnect these subwalks in the following order: ω_4, $\tilde{\omega_2}$, ω_9, a single edge in the positive x-direction at height $z = z^*$, and finally ω_{10} (empty or not). The z-coordinate of the final vertex of the resulting new walk is now equal to either 1 or 2. Now add one or two edges in the negative z-direction so that the final vertex is in the plane $z = 0$, and then add two or one edges in the positive x-direction. The total number of edges which has been added is four, and the total number of new vertices in the plane $z = 0$ is either three or two.

Once both ends of the walk have been treated in the manner and order described above, the resulting object is a loop with eight additional edges and at most eight extra vertices in $z = 0$. Now, relabel the vertices so that the relabelling χ' of the loop is any fixed labelling of the four vertices (numbered 1 to 4), followed by the labelling χ of the vertices numbered 5 to $n+4$, followed by any fixed labelling of vertices $n+5$ to $n+8$. We note that the unfolding operations only contribute a factor of $\mathrm{e}^{\mathrm{O}(\sqrt{n})}$. Also, because of the way χ has been shifted to obtain χ', we observe that the original energy contributions remain unchanged. Thus, since α is fixed and no more than eight new vertices may affect the energy contributions, these changes in energy can be incorporated into the $\mathrm{e}^{\mathrm{O}(\sqrt{n})}$ term. If the original walk has no vertices in $z = 0$ we have a contribution from self-avoiding walks, no bigger than c_n. But it follows from a result of Tesi *et al* (1996) that $c_n \leqslant L_n(\alpha|\chi)\mathrm{e}^{\mathrm{O}(\sqrt{n})} \leqslant L_{n+8}(\alpha|\chi')\mathrm{e}^{\mathrm{O}(\sqrt{n})}$ so that

$$Z_n^*(\alpha|\chi) \leqslant c_n + L_{n+8}(\alpha|\chi')\mathrm{e}^{\mathrm{O}(\sqrt{n})} \leqslant L_{n+8}(\alpha|\chi')\mathrm{e}^{\mathrm{O}(\sqrt{n})}. \tag{3.12}$$

This completes the proof, with $k = 4$. □

Lemma 4. *For all* $\alpha < \infty$

$$\langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle \leqslant \bar{\kappa}(\alpha) + \mathrm{O}(m^{-1/2}). \tag{3.13}$$

Proof. First consider $\alpha \geqslant 0$. Then by lemma 3 we have

$$Z_m^*(\alpha|\chi) \leqslant \mathrm{e}^{\mathrm{O}(\sqrt{m})} L_{m+2k}(\alpha|\chi'). \tag{3.14}$$

Taking logarithms, dividing by m and averaging over colourings gives

$$\begin{aligned}\langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle &\leqslant \frac{m+2k}{m}\langle (m+2k)^{-1} \log L_{m+2k}(\alpha|\chi')\rangle + \mathrm{O}(m^{-1/2}) \\ &\leqslant \bar{\kappa}(\alpha) + \mathrm{O}(m^{-1/2}),\end{aligned} \tag{3.15}$$

where we have made use of the fact that $\langle m^{-1} \log L_m(\alpha|\chi)\rangle$ is bounded above by $\bar{\kappa}(\alpha)$ (lemma 1). For $\alpha < 0$, $Z_m^*(\alpha|\chi) \leqslant c_m$, by lemma 3, and $c_m = \mathrm{e}^{\kappa_d m + \mathrm{O}(\sqrt{m})}$ (Hammersley and Welsh 1962) so that

$$\langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle \leqslant \kappa_d + \mathrm{O}(m^{-1/2}) = \bar{\kappa}(\alpha) + \mathrm{O}(m^{-1/2}), \tag{3.16}$$

since $\bar{\kappa}(\alpha) = \bar{\kappa}(0) = \kappa_d$ for all $\alpha \leqslant 0$ (Orlandini *et al* 1999). □

The next lemma gives a lower bound on the quenched average free energy for loops.

Lemma 5. *For all* $\alpha < \infty$

$$\langle m^{-1} \log L_m(\alpha|\chi)\rangle \geqslant \bar{\kappa}(\alpha) - \mathrm{O}(m^{-1/2}). \tag{3.17}$$

Proof. For $\alpha \leqslant 0$ the result is immediate since $L_m(\alpha|\chi) = c_m \mathrm{e}^{\mathrm{O}(\sqrt{m})}$ (Tesi *et al* 1996) and $\bar{\kappa}(\alpha) = \kappa_d$ (Orlandini *et al* 1999). For $\alpha \geqslant 0$, using lemma 3,

$$L_m(\alpha|\chi) \geqslant Z^*_{m-2k}(\alpha|\chi')\mathrm{e}^{\mathrm{O}(\sqrt{m})}, \tag{3.18}$$

where χ' is a suitable truncation of the colouring χ. Taking logarithms, dividing by m, averaging over the colourings and using lemma 2 gives the required result. $\square$

We now turn to the basic ingredient in the proof of theorem 1, which is an application of Chebyshev's inequality to upper and lower bounds on $n^{-1} \log Z^+_n(\alpha|\chi)$.

Lemma 6. *Suppose that $X_1, X_2, X_3, \ldots,$ is a sequence of independent, identically distributed random variables, with mean zero, such that $\forall j$ $|X_j| \leqslant \Lambda$, for some fixed constant $\Lambda < \infty$. Form the pth sum $S_p = \sum_{j=1}^{p} X_j$. Then there is a constant $K = K(\Lambda)$ depending only on Λ, such that*

$$\mathrm{Prob}\left\{\left|\frac{S_p}{p}\right| \geqslant \frac{\log p}{\sqrt{p}}\right\} \leqslant \frac{K}{p}. \tag{3.19}$$

Proof. Let $a_p = \sqrt{p}\log p$. Then, we wish to find an upper bound on the probability $\mathrm{Prob}\{|S_p| \geqslant a_p\}$. To do this, we first consider the following:

$$\mathrm{Prob}\{S_p \geqslant a_p\} = \mathrm{Prob}\left\{\sqrt{\mathrm{e}^{S_p/\sqrt{p}}} \geqslant \sqrt{\mathrm{e}^{a_p/\sqrt{p}}}\right\} \leqslant \frac{\langle \mathrm{e}^{S_p/\sqrt{p}}\rangle}{\mathrm{e}^{a_p/\sqrt{p}}} = \frac{\langle \mathrm{e}^{S_p/\sqrt{p}}\rangle}{p}, \tag{3.20}$$

where the upper bound has been obtained through an application of Chebyshev's inequality. By assumption, there is a $\Lambda < \infty$, so that $|X_j| \leqslant \Lambda$, for each j. Using this, and the fact that $X_1, X_2, \ldots,$ are i.i.d. with $\langle X_j\rangle = 0$, we obtain the following upper bound:

$$\begin{aligned}
\langle \mathrm{e}^{S_p/\sqrt{p}}\rangle &= \left\langle \mathrm{e}^{(1/\sqrt{p})\sum_{j=1}^{p} X_j}\right\rangle = \left\langle \prod_{j=1}^{p} \mathrm{e}^{X_j/\sqrt{p}} \right\rangle = \langle \mathrm{e}^{X_1/\sqrt{p}}\rangle^p \\
&= \left(1 + \frac{\langle X_1\rangle}{p^{1/2}} + \frac{\langle {X_1}^2\rangle}{2!\,p} + \frac{\langle {X_1}^3\rangle}{3!\,p^{3/2}} + \frac{\langle {X_1}^4\rangle}{4!\,p^2} + \cdots\right)^p \\
&= \left(1 + \frac{1}{p}\left(\frac{\langle {X_1}^2\rangle}{2!} + \frac{\langle {X_1}^3\rangle}{3!\,p^{1/2}} + \frac{\langle {X_1}^4\rangle}{4!\,p^1} + \cdots\right)\right)^p \\
&\leqslant \left(1 + \frac{1}{p}\left(\frac{\Lambda^2}{2!} + \frac{\Lambda^3}{3!} + \frac{\Lambda^4}{4!} + \cdots\right)\right)^p \\
&\leqslant \left(1 + \frac{B}{p}\right)^p \leqslant \mathrm{e}^B,
\end{aligned} \tag{3.21}$$

where $B = \mathrm{e}^{\Lambda}$ will do the job. By exactly the same argument, we obtain

$$\begin{aligned}
\mathrm{Prob}\{S_p \leqslant -a_p\} &= \mathrm{Prob}\{-S_p \geqslant a_p\} \\
&= \frac{\langle \mathrm{e}^{-S_p/\sqrt{p}}\rangle}{p} \leqslant \frac{\mathrm{e}^B}{p}.
\end{aligned} \tag{3.22}$$

Combining the results of equations (3.21) and (3.22), we have

$$\begin{aligned}
\mathrm{Prob}\{|S_p| \geqslant a_p\} &= \mathrm{Prob}\{S_p \geqslant a_p \text{ or } S_p \leqslant -a_p\} \\
&= \mathrm{Prob}\{S_p \geqslant a_p\} + \mathrm{Prob}\{S_p \leqslant -a_p\} \\
&\leqslant \frac{2\mathrm{e}^B}{p},
\end{aligned} \tag{3.23}$$

and the lemma is proved, with $K = 2\mathrm{e}^B$, where $B = \mathrm{e}^{\Lambda}$. $\square$

Lemma 7. *Fix $m \geqslant 4$ and write $n = mp + q$, $0 \leqslant q < m$. For all $\alpha < \infty$ there is a constant $K = K(\alpha, d) < \infty$, depending only on α and the dimension d, such that the following inequality holds with probability exceeding $1 - \frac{K}{p}$:*

$$n^{-1} \log Z_n^+(\alpha|\chi) \geqslant \frac{1}{1 + q/mp}\left[\langle m^{-1} \log L_m(\alpha|\chi)\rangle - \frac{\log p}{\sqrt{p}}\right] + \min[0, 3\alpha/n]. \tag{3.24}$$

Proof. Fix $m \geqslant 4$ and write $n = mp + q$, $0 \leqslant q < m$. Fix $\alpha < \infty$. By concatenating p loops each of length m together with an additional loop of length q we have the lower bound

$$Z_n^+(\alpha|\chi) \geqslant \left[\prod_{j=1}^{p} L_m(\alpha|\chi_j)\right] \times L_q(\alpha|\chi_{p+1}), \tag{3.25}$$

where we define $L_0 \equiv 1$ and where the colourings $\chi_1, \ldots, \chi_{p+1}$ of the $p + 1$ loops are determined by the colouring χ. Taking logarithms, dividing by n and using the fact that $L_q(\alpha|\chi) \geqslant \min[1, \mathrm{e}^{3\alpha}]$, we have

$$n^{-1} \log Z_n^+(\alpha|\chi) \geqslant \left(\frac{mp}{mp + q}\right) p^{-1} \sum_{j=1}^{p} m^{-1} \log L_m(\alpha|\chi_j) + \min[0, 3\alpha/n]. \tag{3.26}$$

Choosing the i.i.d., mean zero, random variables $X_1, X_2, \ldots,$ of lemma 6 to be defined by

$$X_j = m^{-1} \log L_m(\alpha|\chi_j) - \langle m^{-1} \log L_m(\alpha|\chi_j)\rangle, \tag{3.27}$$

we note that (for m big enough) $|X_j| \leqslant \Lambda = 2 \max[\log 2d, \alpha + \log 2d]$. Therefore, setting $K = 2\mathrm{e}^B$, with $B = \mathrm{e}^\Lambda$, lemma 6 yields

$$p^{-1} \sum_{j=1}^{p} m^{-1} \log L_m(\alpha|\chi_j) \geqslant \langle m^{-1} \log L_m(\alpha|\chi)\rangle - \frac{\log p}{\sqrt{p}}, \tag{3.28}$$

with probability exceeding $1 - \frac{K}{p}$, and the lemma then follows. □

Lemma 8. *Fix $m \geqslant 4$ and write $n = mp + q$ with $0 \leqslant q < m$. For all $\alpha < \infty$, there is a constant $K = K(\alpha, d) < \infty$, depending only on α and dimension d, such that the following inequality holds with probability exceeding $1 - \frac{K}{p}$:*

$$n^{-1} \log Z_n^+(\alpha|\chi) \leqslant \langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle + \frac{\log p}{\sqrt{p}} + \frac{m}{n} \max[\log 2d, \alpha + \log 2d]. \tag{3.29}$$

Proof. By dividing a walk of length n into p subwalks of length m and a final subwalk of length q, $0 \leqslant q < m$, we have the inequality

$$Z_n^+(\alpha|\chi) \leqslant \left[\prod_{j=1}^{p} Z_m^*(\alpha|\chi_j)\right] \times Z_q^*(\alpha|\chi_{p+1}) \tag{3.30}$$

where we define $Z_0^* \equiv 1$ and where the colourings $\chi_1, \ldots, \chi_{p+1}$ of the $p + 1$ subwalks are determined by the colouring χ. Taking logarithms, dividing by n and using the fact that $Z_q^*(\alpha|\chi_{p+1}) \leqslant \max[(2d)^m, (2d)^m \mathrm{e}^{\alpha m}]$, we obtain the bound

$$n^{-1} \log Z_n^+(\alpha|\chi) \leqslant p^{-1} \sum_{j=1}^{p} m^{-1} \log Z_m^*(\alpha|\chi_j) + mn^{-1} \max[\log 2d, \alpha + \log 2d]. \tag{3.31}$$

Again, we use lemma 6, this time choosing the i.i.d., mean zero random variables $X_1, X_2, \ldots$ to be defined by

$$X_j = m^{-1} \log Z_m^*(\alpha|\chi) - \langle m^{-1} \log Z_m^*(\alpha|\chi)\rangle, \tag{3.32}$$

and we note that $|X_j| \leqslant \Lambda = 2\max[\log 2d, \alpha + \log 2d]$. Therefore, setting $K = 2e^B$, with $B = e^\Lambda$, lemma 6 yields

$$n^{-1}\log Z_n^+(\alpha|\chi) \leqslant \langle m^{-1}\log Z_m^*(\alpha|\chi)\rangle + (m/n)\max[\log 2d, \alpha + \log 2d] + \frac{\log p}{\sqrt{p}} \tag{3.33}$$

with probability exceeding $1 - K/p$, which completes the proof. □

Lemma 9. *Fix $\alpha < \infty$. Then there is a constant $K = K(\alpha, d) < \infty$, such that $\forall\epsilon > 0$ the following inequality holds with probability exceeding $\left(1 - 2K/\lfloor\sqrt{n}\rfloor\right)$:*

$$|n^{-1}\log Z_n^+(\alpha|\chi) - \bar{\kappa}(\alpha)| \leqslant O(n^{-\frac{1}{4}+\epsilon}). \tag{3.34}$$

Proof. From lemmas 5 and 7, for sufficiently large m there is a constant $K = K(\alpha, d) < \infty$, such that for any $\epsilon > 0$ the following inequality holds with probability exceeding $1 - K/p$:

$$\begin{aligned} n^{-1}\log Z_n^+(\alpha|\chi) &\geqslant \frac{1}{1 + (q/mp)}\left[\bar{\kappa}(\alpha) - O(m^{-1/2}) - \frac{\log p}{\sqrt{p}}\right] + \min[0, 3\alpha/n] \\ &= (1 - O(p^{-1}))[\bar{\kappa}(\alpha) - O(m^{-1/2}) - O(p^{-\frac{1}{2}+2\epsilon})] + O(p^{-1}) \\ &= \bar{\kappa}(\alpha) - O(m^{-1/2}) - O(p^{-\frac{1}{2}+2\epsilon}). \end{aligned} \tag{3.35}$$

This is most effective when we let $p \sim m \sim \sqrt{n}$. We therefore take $m = \lfloor\sqrt{n}\rfloor$, so that $p \geqslant \lfloor\sqrt{n}\rfloor$ and we have the following inequality, with probability exceeding $\left(1 - K/\lfloor\sqrt{n}\rfloor\right)$:

$$n^{-1}\log Z_n^+(\alpha|\chi) \geqslant \bar{\kappa}(\alpha) - O(n^{-\frac{1}{4}+\epsilon}). \tag{3.36}$$

Combining lemmas 4 and 8 yields, for the same K, the following inequality, with probability exceeding $\left(1 - K/\lfloor\sqrt{n}\rfloor\right)$:

$$n^{-1}\log Z_n^+(\alpha|\chi) \leqslant \bar{\kappa}(\alpha) + O(n^{-\frac{1}{4}+\epsilon}). \tag{3.37}$$

The lemma is proved by combining equations (3.36) and (3.37). □

Finally we return to theorem 1. Because a loop is a positive walk, and a positive walk is a *-walk, it is not difficult to show that

$$\langle n^{-1}\log L_n(\alpha|\chi)\rangle \leqslant \langle n^{-1}\log Z_n^+(\alpha|\chi)\rangle \leqslant \langle n^{-1}\log Z_n^*(\alpha|\chi)\rangle. \tag{3.38}$$

In addition, lemmas 1 and 5 yield $\langle n^{-1}\log L_n(\alpha|\chi)\rangle = \bar{\kappa}(\alpha) - O(n^{-1/2})$, and lemmas 2 and 4 yield $\langle n^{-1}\log Z_n^*(\alpha|\chi)\rangle = \bar{\kappa}(\alpha) + O(n^{-1/2})$. Combining these last two equations with (3.38) gives

$$\bar{\kappa}(\alpha) - O(n^{-1/2}) \leqslant \langle n^{-1}\log Z_n^+(\alpha|\chi)\rangle \leqslant \bar{\kappa}(\alpha) + O(n^{-1/2}). \tag{3.39}$$

Theorem 1 follows from an application of the triangle inequality, using equation (3.34) of lemma 9, and equation (3.39).

4. Discussion

We have considered the extent of thermodynamic self-averaging in an n-edge self-avoiding walk model of random copolymer adsorption. Our main result (theorem 1) is that the free energy of the system with a randomly chosen colouring of the vertices differs from its expectation over colourings by no more than a term $O(n^{-1/4+\epsilon})$ with high probability. In addition we showed (lemma 9) that the free energy with n edges and a randomly chosen colourings differs from the limiting quenched average free energy by no more than $O(n^{-1/4+\epsilon})$ with high probability. The reason that these two error terms are of the same order is that the quenched average free energy converges to the limiting quenched average free energy even more rapidly, in fact at least as rapidly as $O(n^{-1/2})$.

These results are for large values of n but one might ask, from the physical point of view, how large does n have to be? In order for (3.24) and (3.29) to be useful, p must be large compared with K, and the bound which we give on K, i.e. $K < 2e^{e^{\Lambda}}$ is very weak. With a little more work this can be improved to $K < 2e^{\Lambda^2}$ provided that $p > 4e^{2\Lambda}/\Lambda^4$. When we insert reasonable values for α and d, this results in bounds which are more physically useful, and which could probably be improved still more.

Our arguments are for a specific problem but can be extended to other models such as self-averaging in a randomly coloured self-avoiding walk model of localization of a copolymer at an interface between two immiscible solvents (Martin *et al* 2000).

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