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Localization of a random copolymer at an interface: an untethered self-avoiding walk model

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Abstract

We consider two related n-step self-avoiding walk models of a copolymer at an interface between two bulk phases. In one case the walk is confined to start in the interface while in the other this condition is relaxed. We prove that both models have the same limiting free energy (in the $n \to \infty$ limit) and hence that their phase diagrams are identical. We also show that the limits $n \to \infty$ and certain energy parameters going to plus or minus infinity can be interchanged. These latter results are interesting from the viewpoint of numerical studies.

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1. Introduction

A random copolymer has at least two types of comonomers and the sequence of comonomers is determined by a random process. We shall be concerned with the situation where there are two monomers, A and B. We write $\chi_i = A$ or B according to whether the ith monomer is A or B, and we shall restrict ourselves to the case where the χ_i are independent and identically distributed random variables. We write χ as a shorthand for $\chi_1, \chi_2, \ldots, \chi_n$, the sequence of monomers on a polymer with n monomers. The sequence of monomers, once chosen, is fixed, so this is an example of a *quenched random system* (Brout 1959). We shall be interested in the situation where we have two immiscible liquids separated by the plane $z = 0$, in $\mathbb{Z}^d$. The half-space $z > 0$ corresponds to one liquid phase and $z < 0$ to the other. If it is energetically preferable for the A monomers to be in the half-space $z > 0$ and for the B monomers to be in the half-space $z < 0$ then at low temperatures we expect the polymer to cross the interfacial plane $z = 0$ frequently to optimize its energy. At high temperatures entropy will dominate and, provided that the temperature is finite, the polymer will be in the energetically most favourable of the two half-spaces and delocalize into that region. This is the phenomenon of localization and delocalization of a random copolymer at an interface.

Various models of the localization of random copolymers have been examined. They differ mainly in the details of the Hamiltonian chosen to represent the physical situation, and the model used for the configurational properties of the polymer molecule. Bolthausen and den Hollander (1997) considered a directed walk model in two dimensions and gave the first mathematically rigorous treatment of the problem in which the sequence of monomers was quenched. They proved the existence of a phase transition and derived qualitative properties of the phase diagram. Biskup and den Hollander (1999) extended this work to give results about path properties. Additional results on a directed walk model were derived by Orlandini *et al* (2002). A self-avoiding walk model was first considered by Maritan *et al* (1999) and further results about such models were derived by Martin *et al* (2000) and Madras and Whittington (2003).

The model which we shall consider is identical to that used by Madras and Whittington (2003), which in turn is a generalization of the model introduced by Martin *et al* (2000). The polymer molecule is modelled as a self-avoiding walk on the d-dimensional hypercubic lattice $\mathbb{Z}^d$. We write $(x, y, \ldots, z)$ for the coordinates of a vertex of the lattice and consider the hyperplane $z = 0$ to represent the dividing plane between two immiscible solvents corresponding to the two half-spaces $z > 0$ and $z < 0$. The vertices of the walk are numbered $i = 0, 1, 2, \ldots, n$ and we associate a colouring χ_i with the ith vertex $(i = 1, 2, \ldots, n)$ where χ_i is A or B. The zeroth vertex is uncoloured. With a given colouring χ suppose that $c_n(v_A, v_B, w|\chi)$ is the number of walks (starting at the origin) with v_A vertices coloured A having positive z-coordinate, v_B vertices coloured B with negative z-coordinate and w vertices (of either colour) in the plane $z = 0$. We call these tethered walks. We use α as a parameter associated with the energy of an A-vertex in the upper half-space, β for B-vertices in the lower half-space, and γ for vertices in the interfacial plane. The partition function of tethered walks is defined as

$$Z_n(\alpha, \beta, \gamma|\chi) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B + \gamma w} \tag{1.1}$$

and the corresponding free energy is defined as

$$\kappa_n(\alpha, \beta, \gamma|\chi) = n^{-1} \log Z_n(\alpha, \beta, \gamma|\chi). \tag{1.2}$$

For convenience, for any walk counted in $c_n(v_A, v_B, w|\chi)$ we refer to the exponent $\alpha v_A + \beta v_B + \gamma w$ as the *reduced energy* of the walk.

Madras and Whittington (2003) derived a number of properties of the phase diagram for this model, extending the earlier results of Martin *et al* (2000). (Martin *et al* studied the case where $\gamma = 0$ and $d = 3$.) These results are largely for the case of tethered walks where the walk is confined to start in the interfacial plane. Madras and Whittington pointed out that lemma 2.4 of Martin *et al*, suitably generalized to $\gamma \neq 0$, implies that the model where the walk is untethered, i.e. not required to start in the plane $z = 0$, has the same phase diagram as the tethered walk model. In particular, in the untethered walk model in the localized phase, the walk would find the interfacial plane and cross it frequently. Unfortunately there is a gap in the proof of lemma 2.4 of Martin *et al*. The main purpose of this paper is to repair this gap, and generalize the proof to $\gamma \neq 0$. The proof which we present is designed to handle cases where α, β and γ are not necessarily finite. As a biproduct we are able to prove some results about the interchange of certain limits in the model, which are useful in a forthcoming numerical study (James *et al* 2003).

2. Definitions and statement of results

We shall focus on self-avoiding walks on the d-dimensional hypercubic lattice, $\mathbb{Z}^d$. 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 (Hammersley 1957)

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

and it is known that $c_n = \mathrm{e}^{\kappa_d n + O(\sqrt{n})}$ (Hammersley and Welsh 1962). We consider n-edge self-avoiding walks on $\mathbb{Z}^d$, and number the vertices of each walk $i = 0, 1, \ldots, n$. We write $(x_i, y_i, \ldots, z_i)$ for the coordinates of the ith vertex, $i = 0, 1, \ldots, n$. 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 where, independently for each i, $\chi_i = A$ with probability p and $\chi_{\mathrm{i}} = B$ with probability $1 - p$.

We define a walk to be *x-unfolded* if it satisfies the condition

$$x_0 \leqslant x_i \leqslant x_n \qquad 0 \leqslant i \leqslant n. \tag{2.2}$$

If $c_n^\dagger$ is the number of x-unfolded walks starting at the origin then (Hammersley and Welsh 1962)

$$c_n \leqslant c_n^\dagger \, \mathrm{e}^{O(\sqrt{n})}. \tag{2.3}$$

We define an n-edge *loop* to be an x-unfolded walk with n edges which satisfies the additional conditions

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

and

$$0 = z_0 = z_n. \tag{2.5}$$

We write $l_n(v_A, v_B, w|\chi)$ for the number of loops starting at the origin with n edges and colouring χ, having v_A vertices coloured A above the plane $z = 0$, v_B vertices coloured B below $z = 0$, and w vertices in the surface $z = 0$. Define the partition function

$$L_n(\alpha, \beta, \gamma|\chi) = \sum_{v_A, v_B, w} l_n(v_A, v_B, w|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B + \gamma w}. \tag{2.6}$$

For any finite integer h, let $c_n^h(v_A, v_B, w|\chi)$ be the number of n-edge self-avoiding walks, having initial vertex with coordinates $(0, 0, \ldots, 0, h)$ (i.e. with $z_0 = h$), having colouring χ (as usual the first vertex is not coloured), and having v_A vertices coloured A in $z > 0$, v_B vertices coloured B below $z = 0$, and w vertices in the surface $z = 0$. Note that $c_n^0(v_A, v_B, w|\chi) = c_n(v_A, v_B, w|\chi)$. Define the corresponding partition function

$$Z_n^h(\alpha, \beta, \gamma|\chi) = \sum_{v_A, v_B, w} c_n^h(v_A, v_B, w|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B + \gamma w} \tag{2.7}$$

and let

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

which we refer to as the partition function of untethered walks. Note that it is sufficient to take the maximum on the right-hand side over all h such that $|h| \leqslant n + 1$.

We define the limiting quenched average free energy to be

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

where the angular brackets denote an average over colourings χ. Martin *et al* proved the existence of the limiting quenched average free energy for the case where $\gamma = 0$ and that

$$\lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha, \beta, 0|\chi)\rangle = \bar{\kappa}(\alpha, \beta, 0). \tag{2.10}$$

Madras and Whittington (2003) pointed out that these proofs also apply, *mutatis mutandis*, to the case when $\gamma \neq 0$, i.e. for all finite α, β, and γ we have that

$$\lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha, \beta, \gamma|\chi)\rangle = \bar{\kappa}(\alpha, \beta, \gamma). \tag{2.11}$$

Our primary goal is to prove that

$$\lim_{n\to\infty} \langle n^{-1} \log Z_n^*(\alpha, \beta, \gamma|\chi)\rangle = \bar{\kappa}(\alpha, \beta, \gamma). \tag{2.12}$$

The approach is a modification and extension of the argument given by Martin *et al*. The key intermediate result is that there exist finite constants C and l such that

$$Z_n^*(\alpha, \beta, \gamma|\chi) \leqslant \mathrm{e}^{C\sqrt{n}}\, \mathrm{e}^{\max\{0,-8\gamma\}} L_{n+2\ell}(\alpha, \beta, \gamma|\chi') \tag{2.13}$$

where χ' is a suitable extension of the colouring χ. This intermediate result also allows us, using ideas from James and Whittington (2002), to make statements about the rate at which $\langle \kappa_n(\alpha, \beta, \gamma|\chi)\rangle$ approaches $\bar{\kappa}(\alpha, \beta, \gamma)$ and about the limiting behaviour of $\bar{\kappa}(\alpha, \beta, \gamma)$ as $\beta \to -\infty$, or $\gamma \to -\infty$, or $\alpha \to +\infty$. Other limiting cases could be handled in a similar manner.

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

3. Results for finite energies

The main problem is to relate the averages $\langle \log L_n(\alpha, \beta, \gamma|\chi)\rangle$ and $\langle \log Z_n^*(\alpha, \beta, \gamma|\chi)\rangle$ to $\langle \log Z_n(\alpha, \beta, \gamma|\chi)\rangle$. We first prove several lemmas which address this problem. The first lemma gives an upper bound on the quenched average free energy for loops and the second establishes the existence of the limiting quenched average free energy, corresponding to the partition function $Z_n^*(\alpha, \beta, \gamma|\chi)$, and the direction from which it is approached. These are straightforward extensions of the $\gamma = 0$ results of Martin *et al* (2000).

Lemma 1. *For all finite α, β, γ the quenched average free energy for loops is bounded above by the limiting quenched average free energy, i.e. for any $n > 0$*

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

Proof. Fix α, β, γ finite. 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

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

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

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

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

$$\langle n^{-1} \log L_n(\alpha, \beta, \gamma|\chi)\rangle \leqslant \log(2d) + \max\{0, \alpha, \beta, \gamma\} < \infty \tag{3.4}$$

we have (Hille 1948)

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

and this is equal to $\bar{\kappa}(\alpha,\beta,\gamma)$, by equation (2.11). □

Lemma 2. *For all finite α, β, γ and for any $n > 0$,*

$$\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle \geqslant \lim_{n\to\infty}\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle. \tag{3.6}$$

Proof. Fix α, β, γ finite. By cutting a walk with $m+n$ edges into two subwalks with m and n edges respectively we obtain the following inequality for any h:

$$c_{m+n}^h(v_A, v_B, w|\chi) \leqslant \sum_{v'_A, v'_B, w', h'} c_m^{h,h'}(v'_A, v'_B, w'|\chi_1) c_n^{h'}(v_A - v'_A, v_B - v'_B, w - w'|\chi_2) \tag{3.7}$$

where χ_1 concatenated with χ_2 gives χ (here we use the fact that the first vertex is not coloured) and where $c_m^{h,h'}$ is the number of walks that start in $z = h$ and end in $z = h'$. Multiplying both sides of (3.7) by $\mathrm{e}^{\alpha v_A + \beta v_B + \gamma w}$ and summing, gives

$$\begin{aligned}
Z_{m+n}^h(\alpha,\beta,\gamma|\chi) &= \sum_{v_A, v_B, w} c_{m+n}^h(v_A, v_B, w|\chi)\,\mathrm{e}^{\alpha v_A + \beta v_B + \gamma w} \\
&\leqslant \sum_{v'_A, v'_B, w', h'} \Bigg\{ c_m^{h,h'}(v'_A, v'_B, w'|\chi_1)\,\mathrm{e}^{\alpha v'_A + \beta v'_B + \gamma w'} \\
&\quad \times \sum_{v_A, v_B, w} c_n^{h'}(v_A - v'_A, v_B - v'_B, w - w'|\chi_2)\,\mathrm{e}^{\alpha(v_A - v'_A) + \beta(v_B - v'_B) + \gamma(w - w')} \Bigg\}
\end{aligned} \tag{3.8}$$

where the final sum in equation (3.8) is equal to $Z_n^{h'}(\alpha,\beta,\gamma|\chi_2)$, which in turn is bounded above by $Z_n^*(\alpha,\beta,\gamma|\chi_2)$. Furthermore, since $\sum_{h'} c_m^{h,h'}(v'_A, v'_B, w'|\chi_1) = c_m^h(v'_A, v'_B, w'|\chi_1)$, equation (3.8) becomes

$$\begin{aligned}
Z_{m+n}^h(\alpha,\beta,\gamma|\chi) &\leqslant Z_m^h(\alpha,\beta,\gamma|\chi_1) Z_n^*(\alpha,\beta,\gamma|\chi_2) \\
&\leqslant Z_m^*(\alpha,\beta,\gamma|\chi_1) Z_n^*(\alpha,\beta,\gamma|\chi_2).
\end{aligned} \tag{3.9}$$

Hence, maximizing equation (3.9) over h yields

$$Z_{m+n}^*(\alpha,\beta,\gamma|\chi) \leqslant Z_m^*(\alpha,\beta,\gamma|\chi_1) Z_n^*(\alpha,\beta,\gamma|\chi_2). \tag{3.10}$$

Taking logarithms and averaging over χ shows that $\langle\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle$ is a subadditive function. Since

$$\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle \geqslant \frac{\log d}{2} + \frac{\max\{\alpha,\beta\}}{2} \tag{3.11}$$

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

$$\inf_{n>0}\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle = \lim_{n\to\infty}\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle \tag{3.12}$$

and the result then follows. □

The next lemma and the fact that $Z_n^*(\alpha,\beta,\gamma|\chi) \geqslant Z_n(\alpha,\beta,\gamma|\chi)$ will establish equation (2.12). The strategy of the proof is to convert, via unfolding and reflection as appropriate, an arbitrary walk starting at height h into a loop. Care is taken to ensure that, apart from the interfacial contribution, the reduced energy of the walk does not decrease at any step of the construction. This leads to a result which is also useful for studying the behaviour of $\bar{\kappa}(\alpha,\beta,\gamma)$ as, for instance, $\beta \to -\infty$.

Lemma 3. *There exist C and ℓ such that for any n and any finite α, β, γ*

$$Z_n^*(\alpha, \beta, \gamma|\chi) \leqslant \mathrm{e}^{C\sqrt{n}}\, \mathrm{e}^{\max\{0,-8\gamma\}} L_{n+2\ell}(\alpha, \beta, \gamma|\chi') \tag{3.13}$$

for every colouring χ' which is an arbitrary extension of χ in which ℓ colours are added to each end.

Proof. Fix $h, n, \alpha, \beta, \gamma$ and χ. Suppose we have a walk, Ω, that starts at height h and whose last vertex is located at an arbitrary height. The strategy will be to operate on both ends of the walk to convert the walk into a loop.

To facilitate the following discussion, define five special walks, $\bar{\omega}(k)$, ω_U, ω_D, $\omega_\Gamma(k+1)$, and $\omega_L(k+1)$ as follows. Let $\bar{\omega}(k)$ be the k-edge horizontal walk lying parallel to the x-axis such that $x_0 < x_1 < \cdots < x_k$, for $k \geqslant 1$. Let ω_U be the 'one-step-up' walk consisting of one edge, with $z_0 < z_1$. Similarly, the 'one-step-down' walk, ω_D, consists of one edge, with $z_0 > z_1$. Joining the top (bottom) vertex of ω_U (ω_D) to the left-most vertex of $\bar{\omega}(k)$ forms the $(k+1)$-edge walk, $\omega_\Gamma(k+1)$ ($\omega_L(k+1)$), in the shape of the letter 'Γ' (or 'L'), with height 1.

We shall employ (acting first on the end of Ω) the procedure given below, i.e. a fixed number of disconnecting and reconnecting surgeries, unfoldings, and reflections, to convert the n-edge Ω into a new $(n+3)$-edge x-unfolded walk, Ω', ending in the plane $z = 0$. We may then convert Ω' into a $(n+6)$-edge loop, by removing the first edge, with its uncoloured vertex, repeating *mutatis mutandis* the procedure given below (acting now on the start of Ω', i.e. think of the steps of Ω' as being reversed for the procedure below), and then attaching a new first edge in the plane $z = 0$, lying parallel to the x-axis, so that x-unfoldedness is maintained in the resulting loop. This will prevent the uncoloured vertex from making an undesired contribution to the energy either in the α- or β-phase. The construction will be performed in such a way as to limit the effect on the energy terms v_A, v_B, and w in the partition function.

If there is at least one vertex of Ω in the plane $z = 0$, let m be the last vertex in the plane $z = 0$ (i.e., $z_i \neq 0$ for all $i \geqslant m+1$) and disconnect Ω into two subwalks, ω_0 from vertex 0 to vertex m, and ω_1 from vertex m to n. If there are no vertices of Ω in $z = 0$ then set $m = 0$, take ω_0 to be a single vertex at the origin and $\omega_1 = \Omega$. Unfold ω_0 in the x-direction to form a walk $\tilde{\omega}_0$ with m edges so that $x_m \geqslant x_i$ for all $i \leqslant m$. (Note that if ω_0 is a single vertex then $\tilde{\omega}_0 = \omega_0$.) Without loss of generality, we assume that ω_1 is in the α-phase, except possibly for its initial vertex (that is, $z_i > 0$, for $i \geqslant m+1$), and note that the β-phase may be treated similarly, using a symmetrical argument through the plane $z = 0$. There are three cases depending on the number of edges, $E = n - m$, in ω_1: $E \in \{0, 2\}$, $E = 1$, or $E \geqslant 3$. If $E = 0$, then obtain Ω' by attaching to the end of $\tilde{\omega}_0$ the 3-edge walk $\bar{\omega}(3)$. If $E = 2$, then discard ω_1 and obtain Ω' by attaching to the end of $\tilde{\omega}_0$ the 2-edge walk $\omega_\Gamma(2)$ followed by the 3-edge walk $\omega_L(3)$. In either case, Ω' is an $(n+3)$-edge walk, which is x-unfolded, and we have neither deleted nor added any vertices to the α-phase (correspondingly, the β-phase), and we have added exactly three vertices to the interface ($z = 0$).

Next, consider the case when $E = 1$. In this case, discard ω_1 and obtain the $(n+3)$-edge walk, Ω', by attaching to the end of $\tilde{\omega}_0$ the 4-edge walk, $\omega_1'(\mathrm{sgn}(\alpha))$, depending on the sign of α as follows. If $\alpha < 0$, then set $\omega_1'(\mathrm{sgn}(\alpha)) = \bar{\omega}(4)$, lying in the plane $z = 0$. In this case, we have deleted i vertices ($i \in \{0, 1\}$) coloured by A from the α-phase, and we have added four vertices to the interface ($z = 0$). If $\alpha \geqslant 0$, then form $\omega_1'(\mathrm{sgn}(\alpha))$ by joining the last vertex of $\omega_\Gamma(2)$ to the first vertex of $\omega_L(2)$. In this case, we have added i' vertices ($i' \in \{0, 1\}$) coloured by A to the α-phase, and we have added two vertices to the interface ($z = 0$).

Otherwise, we are left with the case when $E \geqslant 3$. Disconnect ω_1 into two subwalks, the 3-edge subwalk ω_2, from vertex m to vertex $m+3$, and the $(n-m-3)$-edge subwalk, $\tilde{\omega}_1$ (possibly a single vertex), from vertex $m+3$ to vertex n. Unfold $\tilde{\omega}_1$ in the x-direction, to obtain ω_3, with $x_{m+3} \leqslant x_i \leqslant x_n$, for $m+3 \leqslant i \leqslant n$. Now, unfold ω_3 in the z-direction and translate, as necessary, to form $\tilde{\omega}_3$, with $1 = z_{m+3} \leqslant z_i \leqslant z_n$, for $m+3 \leqslant i \leqslant n$. Next, consider the height, $H = z_n - z_{m+3}$, of $\tilde{\omega}_3$. Form the $(n-m-2)$-edge walk, $\tilde{\tilde{\omega}}_3$, by attaching to the last vertex of $\tilde{\omega}_3$ the one-step walk, $\omega'(H)$, depending on H as follows: if H is even then let $\omega'(H)$ be the one-step-up walk, ω_U, and if H is odd then set $\omega'(H) = \bar{\omega}(1)$. Replace ω_2 with $\tilde{\omega}_2 = \omega_\Gamma(2)$, the 2-edge Γ-shaped walk, with initial vertex in the plane $z = 0$. Create ω_4, the $(n-m)$-edge walk, starting in the plane $z = 0$, by joining the last vertex of $\tilde{\omega}_2$ to the first vertex of $\tilde{\tilde{\omega}}_3$. Note that ω_4 is still both x- and z-unfolded, and its height, $H' = z_n - z_m = z_n$, is even, with $H' \geqslant 2$. Set $z^* = H'/2 \geqslant 1$. Let r be the last vertex in the plane $z = z^*$ (i.e. $z_i > z^*$, for $i \geqslant r+1$). Break ω_4 into three pieces, ω_5 from vertex m to vertex r, ω_6 the single edge from vertex r to vertex $r+1$, and ω_7 the subwalk (possibly a single vertex) from vertex $r+1$ to vertex n. Note that, if ω_7 is a single vertex then $z_n = z_{r+1}$, which makes $z^* = H'/2 = z_n - z_r = 1$. Unfold ω_5 in the x-direction to form $\tilde{\omega}_5$. Rotate ω_6 into the plane $z = z^*$ in the positive x-direction to form $\tilde{\omega}_6$. Translate ω_7 downwards one unit, unfold in the x-direction, to form $\tilde{\omega}_7$, the $(n-r-1)$-step walk, with $z^* = z_{r+1} \leqslant z_i \leqslant z_n = H' - 1$, for $r+1 \leqslant i \leqslant n$. Reflect $\tilde{\omega}_7$ through the plane $z = z^*$ and add to the end the three-step L-shaped walk, $\omega_L(3)$ to form the $(n-r+2)$-step walk, $\tilde{\tilde{\omega}}_7$, beginning in the plane $z = z^*$ and ending in the plane $z = 0$, and lying entirely in the α-phase, except for the three additional vertices from $\omega_L(3)$, which have been added to the plane $z = 0$. (If ω_7 is a single vertex, then set $\tilde{\tilde{\omega}}_7 = \omega_L(3)$, beginning in $z = z^* = 1$ and ending in $z = 0$.) We now reconnect these subwalks in the following order to form the $(n+3)$-edge walk, Ω': $\tilde{\omega}_0$, $\tilde{\omega}_5$, $\tilde{\omega}_6$, and $\tilde{\tilde{\omega}}_7$. In this case, we have neither added nor deleted any vertices from the α-phase, and we have added exactly three vertices to the interface.

Once both ends of Ω have been treated in the manner and order described above, the resulting object is an $(n+6)$-edge loop with i vertices coloured by A deleted (added) to the α-phase for $\alpha < 0$ ($\alpha \geqslant 0$), j vertices coloured by B deleted (added) to the β-phase for $\beta < 0$ ($\beta \geqslant 0$), and k vertices added to the interface ($z = 0$), where $i, j \in \{0, 1, 2\}$ and $k \in \{4, 5, 6, 7, 8\}$. Defining the function, $s(\alpha)$, as follows:

$$s(\alpha) = \begin{cases} 1 & \alpha \geqslant 0 \\ -1 & \alpha < 0 \end{cases}$$

we see that (using the Hammersley–Welsh argument which led to (2.3))

$$c_n^h(v_A, v_B, w|\chi) \leqslant \mathrm{e}^{O(\sqrt{n})} \sum_{i,j,k} l_{n+6}(v_A + s(\alpha)i, v_B + s(\beta)j, w + k|\chi') \tag{3.14}$$

where $i, j \in \{0, 1, 2\}$, and $k \in \{4, 5, 6, 7, 8\}$. Therefore

$$\begin{aligned} Z_n^h(\alpha, \beta, \gamma|\chi) &\leqslant \mathrm{e}^{O(\sqrt{n})} \sum_{i,j,k} \mathrm{e}^{-\alpha s(\alpha)i - \beta s(\beta)j - \gamma k} \\ &\quad \times \sum_{v_A, v_B, w} \{l_{n+6}(v_A + s(\alpha)i, v_B + s(\beta)j, w + k|\chi')\, \mathrm{e}^{\alpha(v_A + s(\alpha)i) + \beta(v_B + s(\beta)j) + \gamma(w+k)}\} \\ &\leqslant \mathrm{e}^{O(\sqrt{n})} \left(\sum_{i,j,k} \mathrm{e}^{-|\alpha|i - |\beta|j - \gamma k} \right) L_{n+6}(\alpha, \beta, \gamma|\chi') \\ &\leqslant \mathrm{e}^{O(\sqrt{n})} \left(\sum_{i,j,k} \mathrm{e}^{-\gamma k} \right) L_{n+6}(\alpha, \beta, \gamma|\chi') \\ &\leqslant \mathrm{e}^{O(\sqrt{n})}\, \mathrm{e}^{\max\{0, -8\gamma\}} L_{n+6}(\alpha, \beta, \gamma|\chi'). \end{aligned} \tag{3.15}$$

Maximizing over all h, we have the desired result, with $\ell = 3$. □

Lemma 4. *For $k = 3$, and for any finite α, β, γ, we have that*

$$\langle m^{-1} \log Z_m^*(\alpha, \beta, \gamma|\chi)\rangle \leqslant \left(1 + \frac{2k}{m}\right)\bar{\kappa}(\alpha, \beta, \gamma) + O(m^{-1/2}) + \max\{0, -8\gamma\}m^{-1} \tag{3.16}$$

where the term $O(m^{-1/2})$ is independent of α, β, and γ.

Proof. By lemma 3 we have, for $k = 3$,

$$Z_m^*(\alpha, \beta, \gamma|\chi) \leqslant \mathrm{e}^{O(\sqrt{m})}\,\mathrm{e}^{\max\{0,-8\gamma\}} L_{m+2k}(\alpha, \beta, \gamma|\chi') \tag{3.17}$$

where the $O(\sqrt{m})$ contribution in equation (3.17) comes purely from the unfolding argument of the proof of lemma 3, and is independent of the variables α, β, and γ. Taking logarithms, dividing by m, averaging over colourings, and applying lemma 1 we have

$$\begin{aligned}\langle m^{-1} \log Z_m^*(\alpha, \beta, \gamma|\chi)\rangle &\leqslant \frac{m+2k}{m}\langle (m+2k)^{-1} \log L_{m+2k}(\alpha, \beta, \gamma|\chi')\rangle \\ &\quad + O(m^{-1/2}) + \max\{0, -8\gamma\}m^{-1} \\ &\leqslant \left(1 + \frac{2k}{m}\right)\bar{\kappa}(\alpha, \beta, \gamma) + O(m^{-1/2}) + \max\{0, -8\gamma\}m^{-1}.\end{aligned} \tag{3.18}$$

□

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

Lemma 5. *For $k = 3$ and for any finite α, β, γ, we have that*

$$\langle m^{-1} \log L_m(\alpha, \beta, \gamma|\chi)\rangle \geqslant \left(1 - \frac{2k}{m}\right)\bar{\kappa}(\alpha, \beta, \gamma) - O(m^{-1/2}) - \max\{0, -8\gamma\}m^{-1} \tag{3.19}$$

where the term $O(m^{-1/2})$ is independent of α, β and γ.

Proof. Using lemma 3, we have for $k = 3$,

$$L_m(\alpha, \beta, \gamma|\chi) \geqslant \mathrm{e}^{-O(\sqrt{m})}\,\mathrm{e}^{-\max\{0,-8\gamma\}} Z_{m-2k}^*(\alpha, \beta, \gamma|\chi') \tag{3.20}$$

where χ' is a suitable truncation of the colouring χ, and where the term $-O(\sqrt{m})$ in equation (3.20) comes purely from the unfolding argument of lemma 3, and is independent of the variables α, β, and γ. Taking similar steps as in lemma 4, the desired result is achieved after taking logarithms, dividing by m, averaging over the colourings and using lemma 2. □

Note that for finite α, β, and γ, equation (3.16) in lemma 4 and equation (3.19) in lemma 5 imply that

$$\langle m^{-1} \log Z_m^*(\alpha, \beta, \gamma|\chi)\rangle \leqslant \bar{\kappa}(\alpha, \beta, \gamma) + O(m^{-1/2}) \tag{3.21}$$

and

$$\langle m^{-1} \log L_m(\alpha, \beta, \gamma|\chi)\rangle \geqslant \bar{\kappa}(\alpha, \beta, \gamma) - O(m^{-1/2}) \tag{3.22}$$

where, in general, the terms $O(m^{-1/2})$ in equations (3.21) and (3.22) depend on α, β, and γ. Also note that, by definition, $L_n(\alpha, \beta, \gamma|\chi) \leqslant Z_n(\alpha, \beta, \gamma|\chi) \leqslant Z_n^*(\alpha, \beta, \gamma|\chi)$, and thus equations (3.21) and (3.22) imply that for all finite α, β, γ,

$$\bar{\kappa}(\alpha, \beta, \gamma) - O(n^{-1/2}) \leqslant \bar{\kappa}_n(\alpha, \beta, \gamma) \leqslant \bar{\kappa}_n^*(\alpha, \beta, \gamma) \leqslant \bar{\kappa}(\alpha, \beta, \gamma) + O(n^{-1/2}) \tag{3.23}$$

where $\bar{\kappa}_n(\alpha, \beta, \gamma) \equiv \langle n^{-1} \log Z_n(\alpha, \beta, \gamma|\chi)\rangle$, $\bar{\kappa}_n^*(\alpha, \beta, \gamma) \equiv \langle n^{-1} \log Z_n^*(\alpha, \beta, \gamma|\chi)\rangle$, and each of the terms $O(n^{-1/2})$ depends, in general, on α, β, and γ. In particular, note that equation (3.23) implies that

$$\lim_{n\to\infty} \bar{\kappa}_n^*(\alpha, \beta, \gamma) = \lim_{n\to\infty} \bar{\kappa}_n(\alpha, \beta, \gamma) = \bar{\kappa}(\alpha, \beta, \gamma). \tag{3.24}$$

4. Behaviour when an energy parameter is infinite and $p = 1/2$

In this section we investigate the behaviour of the limiting quenched average free energy when one of the energy parameters α, β or γ is $\pm\infty$. This is motivated by a recent numerical study (James *et al* 2003) in which we map out the form of the phase diagram in α, β, γ space for the case $p = 1/2$. By symmetry, for $p = 1/2$ we can confine our attention to the case $\alpha \geqslant \beta$. In the numerical investigation, we are interested in the locations of the asymptotes of the phase boundaries as $\beta \to -\infty$ and $\alpha \to \infty$, and the behaviour as $\gamma \to -\infty$. From the numerical point of view, it is convenient to set one of the energy parameters equal to $-\infty$, for instance, before investigating the behaviour of the free energy as $n \to \infty$. This raises the question as to whether it is permissible to interchange the order of the limits $\beta \to -\infty, n \to \infty$, for instance. We address this question in this section.

4.1. The case $\beta \to -\infty$

$\bar{\kappa}_n(\alpha, \beta, \gamma)$ is bounded below by $\alpha/2 + n^{-1} \log c_n^+ \geqslant \alpha/2 + (\log d)/2$, where c_n^+ is the number of walks starting at the origin and otherwise confined to the half-space $z > 0$. Define $\bar{\kappa}_n(\alpha, -\infty, \gamma) \equiv \lim_{\beta\to-\infty} \bar{\kappa}_n(\alpha, \beta, \gamma)$, where the limit exists since $\bar{\kappa}_n(\alpha, \beta, \gamma)$ is non-decreasing in β and is bounded below. The walks contributing to $Z_n(\alpha, -\infty, \gamma|\chi)$ are precisely the walks which have no B-vertex with negative z coordinate.

Lemmas 1, 2, 3 apply *mutatis mutandis* to the case $\beta = -\infty$ (i.e. to the set of walks which have no B-vertex with negative z coordinate). Hence the limit $\bar{\kappa}(\alpha, -\infty, \gamma) \equiv \lim_{n\to\infty} \bar{\kappa}_n(\alpha, -\infty, \gamma)$, exists.

In the next lemma we prove that the order of the limits $\beta \to -\infty$ and $n \to \infty$ can be interchanged. Since we are confining our attention to the case $\beta \leqslant \alpha$ and because the function $\bar{\kappa}(\alpha, \beta, \gamma)$ is non-decreasing in each of its variables, equation (3.19) in lemma 5 implies

$$\begin{aligned} \bar{\kappa}_m(\alpha, \beta, \gamma) \geqslant \langle m^{-1} \log L_m(\alpha, \beta, \gamma|\chi)\rangle \geqslant \bar{\kappa}(\alpha, \beta, \gamma) \\ - \frac{2k}{m}\bar{\kappa}(\alpha, \alpha, \gamma) - O(m^{-1/2}) - \max\{0, -8\gamma\}m^{-1} \end{aligned} \tag{4.1}$$

where the first inequality follows by inclusion. The final inequality uses the fact that $\bar{\kappa}(\alpha, \beta, \gamma) \leqslant \bar{\kappa}(\alpha, \alpha, \gamma)$ for $\beta \leqslant \alpha$.

Lemma 6. *For any fixed $-\infty < \alpha, \gamma < \infty$,*

$$\begin{aligned} \bar{\kappa}(\alpha, -\infty, \gamma) &= \lim_{n\to\infty} \lim_{\beta\to-\infty} \bar{\kappa}_n(\alpha, \beta, \gamma) = \lim_{\beta\to-\infty} \lim_{n\to\infty} \bar{\kappa}_n(\alpha, \beta, \gamma) \\ &= \lim_{\beta\to-\infty} \bar{\kappa}(\alpha, \beta, \gamma). \end{aligned} \tag{4.2}$$

Proof. Given $\epsilon > 0$, choose n sufficiently large so that $\bar{\kappa}_n(\alpha, -\infty, \gamma) - \bar{\kappa}(\alpha, -\infty, \gamma) \leqslant \epsilon/3$ and so that $\bar{\kappa}(\alpha, \beta, \gamma) - \bar{\kappa}_n(\alpha, \beta, \gamma) \leqslant \epsilon/3$ for all $\beta \leqslant \alpha$. Note that the second statement is possible by equation (4.1) since α and γ are fixed. With n fixed, choose $M > 0$ such that for all $\beta^* < -M$, $\bar{\kappa}_n(\alpha, \beta^*, \gamma) - \bar{\kappa}_n(\alpha, -\infty, \gamma) < \epsilon/3$. Thus for all $\beta^* < \min\{\alpha, -M\}$

$$\begin{aligned} 0 \leqslant \bar{\kappa}(\alpha, \beta^*, \gamma) - \bar{\kappa}(\alpha, -\infty, \gamma) \leqslant \bar{\kappa}(\alpha, \beta^*, \gamma) - \bar{\kappa}_n(\alpha, \beta^*, \gamma) + \bar{\kappa}_n(\alpha, \beta^*, \gamma) \\ - \bar{\kappa}_n(\alpha, -\infty, \gamma) + \bar{\kappa}_n(\alpha, -\infty, \gamma) - \bar{\kappa}(\alpha, -\infty, \gamma) \leqslant \epsilon \end{aligned} \tag{4.3}$$

where the first inequality holds because the quenched average free energy is non-decreasing in β. □

4.2. The case $\gamma \to -\infty$

Define $\bar{\kappa}_n(\alpha, \beta, -\infty) \equiv \lim_{\gamma\to-\infty} \bar{\kappa}_n(\alpha, \beta, \gamma)$, where the limit is known to exist since $\bar{\kappa}_n(\alpha, \beta, \gamma)$ is non-decreasing in γ and is bounded below. The walks contributing to $Z_n(\alpha, \beta, -\infty|\chi)$ are precisely the walks which have no coloured vertices in the plane $z = 0$.

Note that $L_n(\alpha, \beta, -\infty|\chi) = 0$, since each loop necessarily has two coloured vertices in $z = 0$. Hence the approach that was used to prove the existence of the limiting quenched average free energy at $\beta = -\infty$ is not applicable here. In this case, however, we are able to establish the following instead. Let $\bar{\kappa}^*_n(\alpha, \beta, -\infty) \equiv \lim_{\gamma\to-\infty} \bar{\kappa}^*_n(\alpha, \beta, \gamma)$ where the limit is known to exist since $\bar{\kappa}^*_n(\alpha, \beta, \gamma)$ is non-decreasing in γ and is bounded below.

Lemma 7. *For any fixed finite α and any fixed $\beta < \infty$,*

$$\lim_{n\to\infty} \bar{\kappa}_n(\alpha, \beta, -\infty) = \lim_{n\to\infty} \bar{\kappa}^*_n(\alpha, \beta, -\infty) = \kappa_d + \max\{\alpha/2, \beta/2\}. \tag{4.4}$$

Proof. Consider any walk starting in the plane $z = h$ which never intersects the plane $z = 0$, except possibly at its first vertex (i.e. $h = 0$). For $|h| > n$, the number of such walks is c_n and otherwise it is bounded above by c_n. The maximum weight of such a walk is $\mathrm{e}^{\max\{\alpha A(\chi),\beta B(\chi)\}}$, where $A(\chi)$ and $B(\chi)$ are the number of A- and B-vertices in χ, respectively. Hence $Z_n(\alpha, \beta, -\infty|\chi) \leqslant Z^*_n(\alpha, \beta, -\infty|\chi) \leqslant c_n\, \mathrm{e}^{\max\{\alpha A(\chi),\beta B(\chi)\}}$. Then since $c^+_n\, \mathrm{e}^{\max\{\alpha A(\chi),\beta B(\chi)\}} \leqslant Z_n(\alpha, \beta, -\infty|\chi)$ and since

$$\lim_{n\to\infty} n^{-1} \log c^+_n = \kappa_d \tag{4.5}$$

the required result follows (Whittington 1975). □

The next lemma shows that it is possible to interchange the limits $n \to \infty, \gamma \to -\infty$ for $\bar{\kappa}^*_n(\alpha, \beta, \gamma)$.

Lemma 8. *For any fixed finite α and fixed $\beta < \infty$,*

$$\lim_{\gamma\to-\infty} \lim_{n\to\infty} \bar{\kappa}^*_n(\alpha, \beta, \gamma) = \lim_{n\to\infty} \lim_{\gamma\to-\infty} \bar{\kappa}^*_n(\alpha, \beta, \gamma) = \kappa_d + \max\{\alpha/2, \beta/2\}. \tag{4.6}$$

Proof. For any fixed finite α, γ and fixed $\beta < \infty$ we know from lemmas 1, 2 and 3 that

$$\bar{\kappa}^*_n(\alpha, \beta, \gamma) \geqslant \lim_{n\to\infty} \bar{\kappa}^*_n(\alpha, \beta, \gamma) = \bar{\kappa}(\alpha, \beta, \gamma). \tag{4.7}$$

From lemma 7 and since lemma 2 holds *mutatis mutandis* for $\bar{\kappa}^*_n(\alpha, \beta, -\infty)$ then

$$\bar{\kappa}^*_n(\alpha, \beta, -\infty) \geqslant \kappa_d + \max\{\alpha/2, \beta/2\}. \tag{4.8}$$

Then using an argument similar to that used in the proof of lemma 6, the required result is obtained as follows.

Given $\epsilon > 0$, choose n sufficiently large so that $0 \leqslant \bar{\kappa}^*_n(\alpha, \beta, -\infty) - \kappa_d - \max\{\alpha/2, \beta/2\} \leqslant \epsilon/2$. With n fixed, choose $M > 0$ such that for all $\gamma^* < -M$, $0 \leqslant \bar{\kappa}^*_n(\alpha, \beta, \gamma^*) - \bar{\kappa}^*_n(\alpha, \beta, -\infty) \leqslant \epsilon/2$. Then

$$\begin{aligned} 0 \leqslant \bar{\kappa}(\alpha, \beta, \gamma^*) - \kappa_\mathrm{d} - \max\{\alpha/2, \beta/2\} &\leqslant \bar{\kappa}(\alpha, \beta, \gamma^*) - \bar{\kappa}^*_n(\alpha, \beta, \gamma^*) + \bar{\kappa}^*_n(\alpha, \beta, \gamma^*) \\ &\quad - \bar{\kappa}^*_n(\alpha, \beta, -\infty) + \bar{\kappa}^*_n(\alpha, \beta, -\infty) - \kappa_\mathrm{d} - \max\{\alpha/2, \beta/2\} \leqslant \epsilon. \end{aligned} \tag{4.9}$$

Note that the first inequality holds by a monotonicity argument and for the third inequality we have used equation (4.7). □

Now, using the above lemmas, we show that it is possible to interchange the limits $n \to \infty, \gamma \to -\infty$ for $\bar{\kappa}_n(\alpha, \beta, \gamma)$.

Lemma 9. *For any fixed finite α and fixed $\beta < \infty$,*

$$\lim_{\gamma\to-\infty}\lim_{n\to\infty}\bar{\kappa}_n(\alpha,\beta,\gamma) = \lim_{n\to\infty}\lim_{\gamma\to-\infty}\bar{\kappa}_n(\alpha,\beta,\gamma) = \kappa_d + \max\{\alpha/2, \beta/2\}. \tag{4.10}$$

Proof. By lemma 7

$$\kappa_d + \max\{\alpha/2, \beta/2\} = \lim_{n\to\infty}\bar{\kappa}_n(\alpha,\beta,-\infty) \tag{4.11}$$

and by monotonicity in γ and since $Z_n(\alpha,\beta,\gamma|\chi) \leqslant Z_n^*(\alpha,\beta,\gamma|\chi)$

$$\lim_{n\to\infty}\bar{\kappa}_n(\alpha,\beta,-\infty) \leqslant \lim_{\gamma\to-\infty}\lim_{n\to\infty}\bar{\kappa}_n(\alpha,\beta,\gamma) \leqslant \lim_{\gamma\to-\infty}\lim_{n\to\infty}\bar{\kappa}_n^*(\alpha,\beta,\gamma). \tag{4.12}$$

Then using lemmas 7 and 8

$$\lim_{\gamma\to-\infty}\lim_{n\to\infty}\bar{\kappa}_n^*(\alpha,\beta,\gamma) = \lim_{n\to\infty}\bar{\kappa}_n^*(\alpha,\beta,-\infty) = \kappa_d + \max\left\{\frac{\alpha}{2}, \frac{\beta}{2}\right\} \tag{4.13}$$

and this gives the required result. □

4.3. The case $\alpha \to \infty$

We focus on the case that $\alpha > \beta$, with $\beta < \infty$ and γ finite. Define

$$Z_n'(\alpha,\beta,\gamma|\chi) \equiv \mathrm{e}^{-\alpha A(\chi)} Z_n(\alpha,\beta,\gamma|\chi) \tag{4.14}$$

and

$$\bar{\kappa'}_n(\alpha,\beta,\gamma) \equiv \langle n^{-1}\log Z_n'(\alpha,\beta,\gamma|\chi)\rangle = \bar{\kappa}_n(\alpha,\beta,\gamma) - \frac{\alpha}{2} \geqslant n^{-1}\log c_n^+ \geqslant \frac{\log d}{2}. \tag{4.15}$$

Then

$$\bar{\kappa'}(\alpha,\beta,\gamma) \equiv \lim_{n\to\infty}\bar{\kappa'}_n(\alpha,\beta,\gamma) = \bar{\kappa}(\alpha,\beta,\gamma) - \frac{\alpha}{2} \geqslant \kappa_d. \tag{4.16}$$

Note that $\bar{\kappa'}_n(\alpha,\beta,\gamma)$ and consequently $\bar{\kappa'}(\alpha,\beta,\gamma)$ are both non-increasing functions of α since

$$\bar{\kappa'}_n(\alpha,\beta,\gamma) = \left\langle n^{-1}\log\sum_{v_A,v_B,w} c_n(v_A,v_B,w|\chi)\,\mathrm{e}^{\alpha(v_A-A(\chi))+\beta v_B+\gamma w}\right\rangle \tag{4.17}$$

and $v_A \leqslant A(\chi)$.

Define $\bar{\kappa'}_n(\infty,\beta,\gamma) \equiv \lim_{\alpha\to\infty}\bar{\kappa'}_n(\alpha,\beta,\gamma)$, where the limit exists since $\bar{\kappa'}_n(\alpha,\beta,\gamma)$ is non-increasing in α and is bounded below. The walks contributing to $Z_n'(\infty,\beta,\gamma)$ are precisely the walks which have $v_A = A(\chi)$, i.e. there are no vertices coloured A either in the interface $z = 0$ or with negative z-coordinate ($z < 0$).

Next consider $L_n'(\alpha,\beta,\gamma|\chi)$ and $Z_n^{*'}(\alpha,\beta,\gamma|\chi)$ to be defined in analogy with equation (4.14). Note that $L_n'(\infty,\beta,\gamma|\chi) = 0$ for any χ whose first or last colour is an A. Hence we require an alternate definition of loops for this case, namely we consider $L_n^\dagger(\alpha,\beta,\gamma|\chi)$ to be the partition function (appropriately scaled as in equation (4.14)) for loops translated so that the initial vertex of the loop is in $z = 1$.

In order to prove that it is possible to interchange the limits $n \to \infty$ and $\alpha \to \infty$ for $\bar{\kappa}_n'(\alpha,\beta,\gamma)$ we use arguments similar to those of section 4.2. The key result needed is the analogue of lemma 3 for the case $\alpha = \infty$. Our proof of this involves modification of the proof of lemma 3 with the partition functions scaled as in equation (4.14) and the loops are translated so that they start and end in $z = 1$. The essential difference from the proof of lemma 3 is that all the A-vertices are required to be in the half-space $z > 0$.

Lemma 10. *There exist constants C and ℓ such that for any n, any $\beta < \infty$ and any finite γ*

$$Z_n^{*'}(\infty, \beta, \gamma|\chi) \leqslant \mathrm{e}^{C\sqrt{n}}\,\mathrm{e}^{f(\beta,\gamma)} L_{n+2\ell}^{\dagger}(\infty, \beta, \gamma|\chi') \tag{4.18}$$

for every colouring χ' which is an arbitrary extension of χ in which ℓ colours are added to each end and where $f(\beta, \gamma)$ is finite for $\beta < \infty$ and γ finite.

Proof. An outline of the proof is as follows. In general, we shall let the plane $z = 1$ play the role of the plane $z = 0$ and the point $(0, 0, \ldots, 0, 1)$ play the role of the origin in the lemma 3 proof. Let χ be any colouring of length n and let Ω be an arbitrary n-edge walk such that $v_A = A(\chi)$. As in the proof of lemma 3, we start by operating on the end of Ω, but now with the goal of creating an x-unfolded walk Ω' which ends in $z = 1$. For the operations on the end of Ω, if the last edge goes from $z = -1$ to $z = 0$, remove this last edge and name this new walk Ω and define $\delta = 1$; otherwise $\delta = 0$. Hence, Ω has $n - \delta$ edges. Note that in the case $\delta = 1$, a B-vertex gets removed from the plane $z = 0$, and this vertex will get replaced, in the formation of Ω', by a vertex in the plane $z = 1$. Define m such that the m'th vertex is the last vertex of the walk Ω in $z = 1$ (set $m = 0$ if there are no vertices of Ω in $z = 1$) and the definitions of the walks ω_0 and ω_1 remain unchanged from lemma 3, except that the origin is replaced by $(0, 0, \ldots, 0, 1)$, i.e. $\omega_0 = (0, 0, \ldots, 0, 1)$, if $m = 0$. In addition, we define $\tilde{m}, m \leqslant \tilde{m}$, to be the last vertex of ω_1 in $z = 0$ (set $\tilde{m} = m$ if there are no vertices of ω_1 in $z = 0$). Define ω_{12} to be the subwalk of Ω from vertex $\tilde{m}$ to its last vertex. It is then necessary to consider two cases separately.

Case 1. ω_{12} lies entirely in the half plane $z > 0$. In this case $\tilde{m}$ is necessarily equal to m and the $\alpha < 0$ case arguments of the lemma 3 proof can be used directly on ω_0 and ω_1 (with the general modifications described above, i.e. $z = 1$ plays the role of $z = 0$). This results in Ω' which is x-unfolded, ends in the plane $z = 1$, and has exactly three new consecutive vertices at the end of the walk, all of which are in the plane $z = 1$.

Case 2. ω_{12} lies entirely in $z \leqslant 0$. Let $E' = n - \delta - \tilde{m}$, the number of edges of ω_{12}. Next create $\tilde{\omega}_0$ by x-unfolding the subwalk of Ω from vertex 0 to vertex $\tilde{m}$. When $E' \leqslant 5$, the strategy will be to remove the last E' edges of Ω and then modify the walk to end in $z = 1$; three subcases are required. If $E' \leqslant 5$, and if $\tilde{m} > m + 1$, then since the last edge of Ω does not go from $z = -1$ to $z = 0$, the last edge of $\tilde{\omega}_0$ must lie in $z = 0$. Remove the last edge of $\tilde{\omega}_0$, x-unfold the resulting walk, and then create Ω' by adding (identifying last and first vertices) the sequence of walks $\bar{\omega}(1), \omega_U, \bar{\omega}(E' + 2 + \delta)$ to the end of this walk. If $E' \leqslant 5$, and if $\tilde{m} = m + 1$, form Ω' by x-unfolding ω_0 and identifying the last vertex of the resulting walk with the first vertex of $\bar{\omega}(E' + 4 + \delta)$ (this removes a B-vertex from $z = 0$ and it is ultimately moved to $z = 1$). If $E' \leqslant 5$, and if $\tilde{m} = m$, then necessarily $m = 0$, so form Ω' by identifying the vertex, ω_0, with the first vertex of $\bar{\omega}(E' + 3 + \delta)$. In all of the above cases, $E'B$-vertices have been removed from the β-phase and relocated in $z = 1$ and three new vertices have been added to $z = 1$. For $E' \geqslant 6$, if $\tilde{m} = m$, then necessarily $m = 0$ so in this case we redefine $\tilde{\omega}_0$ to be the single vertex $(0, 0, \ldots, 0, 0)$, namely the origin; otherwise the definition of $\tilde{\omega}_0$ remains unchanged. Now let $\tilde{\omega}_1$ be the $(n - \delta - \tilde{m} - 6)$-edge subwalk of Ω from vertex $\tilde{m} + 6$ to vertex $n - \delta$. Transform $\tilde{\omega}_1$ exactly as described for the $\tilde{\omega}_1$ of the proof of lemma 3, i.e. using the plane $z = 0$ and the β-phase case, to obtain the walks $\tilde{\omega}_5, \tilde{\omega}_6, \tilde{\tilde{\omega}}_7$, with a total of six more edges than in $\tilde{\omega}_1$, i.e. $n - \delta - \tilde{m}$ edges. The walk $\Omega^{\dagger} = \tilde{\omega}_0\tilde{\omega}_5\tilde{\omega}_6\tilde{\tilde{\omega}}_7$, which is obtained by joining these walks together (identifying last and first vertices), is an $(n - \delta)$-edge walk which ends in $z = 0$ and its last three steps are the same as $\omega_\Gamma(3)$. Ω' is then formed by identifying the last vertex of $\Omega^\dagger$ with the first vertex of $\omega_\Gamma(\delta+3)$. This results in three B-vertices being moved from the β-phase to $z=0$ and three new vertices being added to $z=1$.

Next the above procedures are applied to the start of Ω', modified slightly to take into account the uncoloured vertex, as discussed in the proof of lemma 3, to obtain the required loop (starting and ending in $z=1$). Let χ' be an arbitrary extension of χ in which $\ell\equiv 3$ colours are added to each end and colour the loop according to χ'. Hence the loop has all its A-vertices in $z>0$.

This gives the result

$$Z_n^{*'}(\infty,\beta,\gamma|\chi)\leqslant \mathrm{e}^{C\sqrt{n}}\,\mathrm{e}^{2\max\{0,2\gamma,5\beta,5\beta+2\gamma,3\beta-3\gamma,3\beta-2\gamma\}}L^\dagger_{n+2\ell}(\infty,\beta,\gamma|\chi') \tag{4.19}$$

and note that for $\beta<0$, $\max\{0,2\gamma,5\beta,5\beta+2\gamma,3\beta-3\gamma,3\beta-2\gamma\}\leqslant\max\{2\gamma,-3\gamma\}$. This gives the required result. □

Note also that if an edge from $z=0$ to $z=1$ is added to the start of any loop counted in $L_n^\dagger(\infty,\beta,\gamma|\chi)$, then the result is a unique walk that is counted in $Z'_{n+1}(\infty,\beta,\gamma|\chi'')$, where χ'' is an arbitrary extension of χ in which one colour is added to the start of χ. Thus

$$L_n^\dagger(\infty,\beta,\gamma|\chi)\leqslant Z'_{n+1}(\infty,\beta,\gamma|\chi'')\leqslant Z^{*'}_{n+1}(\infty,\beta,\gamma|\chi''). \tag{4.20}$$

The analogue of lemma 1 holds for $L_n^\dagger(\infty,\beta,\gamma|\chi)$ and hence the limit $\bar{\kappa}'(\infty,\beta,\gamma)\equiv\lim_{n\to\infty}\langle n^{-1}\log L_n^\dagger(\infty,\beta,\gamma|\chi)\rangle$ exists and using equations (4.19) and (4.20) gives

$$\bar{\kappa}'(\infty,\beta,\gamma)=\lim_{n\to\infty}\langle n^{-1}\log Z_n^{*'}(\infty,\beta,\gamma|\chi)\rangle=\lim_{n\to\infty}\langle n^{-1}\log Z'_n(\infty,\beta,\gamma|\chi)\rangle. \tag{4.21}$$

Thus we have a result analogous to lemma 7 from the $\gamma\to-\infty$ case. From the definition of $Z_n^{*'}(\alpha,\beta,\gamma|\chi)$ and lemma 2, we have that for $\beta<\infty$, finite α and γ, and any $n\geqslant 0$

$$\bar{\kappa}'^*_n(\alpha,\beta,\gamma)\equiv\langle n^{-1}\log Z_n^{*'}(\alpha,\beta,\gamma|\chi)\rangle\geqslant\bar{\kappa}'(\alpha,\beta,\gamma). \tag{4.22}$$

Following, *mutatis mutandis*, the proof of lemma 8 it can then be shown that it is possible to interchange the limits $n\to\infty$ and $\alpha\to\infty$ for $\bar{\kappa}'^*_n(\alpha,\beta,\gamma)$, and then consequently, in analogy with the proof of lemma 9, for $\bar{\kappa}'_n(\alpha,\beta,\gamma)$, i.e. for any $\beta<\infty$ and γ finite,

$$\lim_{\alpha\to\infty}\lim_{n\to\infty}\bar{\kappa}'_n(\alpha,\beta,\gamma)=\lim_{n\to\infty}\lim_{\alpha\to\infty}\bar{\kappa}'_n(\alpha,\beta,\gamma). \tag{4.23}$$

5. Discussion

Martin *et al* (2000) claimed that

$$\lim_{n\to\infty}\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle=\lim_{n\to\infty}\langle n^{-1}\log Z_n(\alpha,\beta,\gamma|\chi)\rangle \tag{5.1}$$

for $\gamma=0$ and for finite α,β, but their proof was incomplete. We have repaired the gap and extended the argument to $\gamma\neq 0$. This result implies that the untethered walk model (where the walk is not required to start in the plane $z=0$) has the same phase diagram as the tethered walk model (where the walk starts in $z=0$). In particular, for untethered walks in the localized phase, the walk finds the interfacial plane and crosses it frequently. The method of proof of equation (5.1) has also enabled us to obtain results about the rate at which the limit is approached. In particular, we have shown for finite α,β,γ that

$$\bar{\kappa}(\alpha,\beta,\gamma)-O(n^{-1/2})\leqslant\bar{\kappa}_n(\alpha,\beta,\gamma)\leqslant\bar{\kappa}_n^*(\alpha,\beta,\gamma)\leqslant\bar{\kappa}(\alpha,\beta,\gamma)+O(n^{-1/2}). \tag{5.2}$$

In addition we have proved equation (5.1) for several infinite values of the energy parameters: α,γ finite and $\beta=-\infty$; α finite, $\beta<\infty$ and $\gamma=-\infty$; $\beta<\infty$, γ finite and $\alpha=\infty$ (with the partition functions appropriately scaled). Combining these infinite cases with the fact that $\langle n^{-1}\log Z_n^*(\alpha,\beta,\gamma|\chi)\rangle$ is a subadditive function has allowed us to prove that it is possible to interchange the order of the limit $n \to \infty$ and various infinite energy parameter limits. These results will be applied to a numerical study which is in progress. In the numerical study, $\langle n^{-1} \log Z_n(\alpha, \beta, \gamma|\chi)\rangle$ is known for finite values of n and it is most convenient to let the energy parameters go to $\pm\infty$ first, and then extrapolate to $n \to \infty$.

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References

Biskup M and den Hollander F 1999 *Ann. Appl. Probab.* **9** 668–87
Bolthausen E and den Hollander F 1997 *Ann. Probab.* **25** 1334–66
Brout R 1959 *Phys. Rev.* **115** 824–35
Hammersley J M 1957 *Math. Proc. Camb. Phil. Soc.* **53** 642–45
Hammersley J M and Welsh D J A 1962 *Q. J. Math. Oxford* **13** 108–10
Hille E 1948 *Functional Analysis and Semi-Groups (Am. Math. Soc. Colloq. Publ. 31)* (New York: American Mathematical Society)
James E W, Soteros C E and Whittington S G 2003 at press
James E W and Whittington S G 2002 *J. Phys. A: Math. Gen.* **35** 3203–11
Madras N and Whittington S G 2003 *J. Phys. A: Math. Gen.* **36** 923–38
Maritan A, Riva M P and Trovato A 1999 *J. Phys. A: Math. Gen.* **32** L275–L280
Martin R, Causo M S and Whittington S G 2000 *J. Phys. A: Math. Gen.* **33** 7903–18
Orlandini E, Rechnitzer A and Whittington S G 2002 *J. Phys. A: Math. Gen.* **35** 7729–51
Whittington S G 1975 *J. Chem. Phys.* **63** 779–85