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2000 J. Phys. A: Math. Gen. 33 7903

(http://iopscience.iop.org/0305-4470/33/44/305)

J. Phys. A: Math. Gen. **33** (2000) 7903–7918. Printed in the UK PII: S0305-4470(00)15847-0

Localization transition for a randomly coloured self-avoiding walk at an interface

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Received 26 July 2000

Abstract. We consider a lattice model of random heteropolymers at the interface between two immiscible solvents. One solvent is preferred by one comonomer, while the other solvent is preferred by the other comonomer. We investigate the phase diagram of the system and, in particular, the transition from localization at the interface to delocalization into one of the two phases. We prove some rigorous results concerning the system and, in particular, show that there is a phase change as the solvent qualities for the two comonomers are varied. We use Monte Carlo methods and exact enumeration and series analysis techniques to map out the form of the phase diagram.

1. Introduction

Random heteropolymers (i.e. copolymers with a random distribution of comonomers) can be modelled as self-avoiding walks whose vertices are randomly coloured. The adsorption of such polymers at an impenetrable surface has been studied and the system is known to exhibit a phase transition. Moreover, the system is thermodynamically self-averaging (Orlandini *et al* 1999). The situation which we shall investigate here is somewhat different, and what we have in mind is as follows: the polymer is anchored at the interface between two immiscible solvents which we call α and β. It is energetically favourable for one of the two comonomers (A say) to be in phase α and for the other comonomer (B) to be in phase β. We are interested in the localization of the polymer at the interface when the energetic advantage of having the two comonomers in their preferred phases overcomes the entropic term, and its delocalization when the entropic term dominates. The heteropolymer is modelled as a randomly coloured self-avoiding walk, with vertices coloured A with probability p_A and B with probability $p_B = 1 - p_A$, independently. We shall present some rigorous results on the behaviour of the quenched average free energy in section 2, and on the form of the phase diagram in section 3. In section 4 we present Monte Carlo and exact enumeration results for this model and investigate the detailed form of the phase diagram in the special case of $p_A = \frac{1}{2}$.

Similar models have been considered by several other groups including Bolthausen and den Hollander (1997), Biskup and den Hollander (1999) and Maritan *et al* (1999) (see also Garel *et al* 1990, Stepanow *et al* 1998). Bolthausen and den Hollander (1997) considered a two-dimensional model in which the walk was partially directed. The edges of the walk carry a randomly chosen 'charge' of $\omega_i = \pm 1$ and the reduced Hamiltonian is of the form

$$H = -\lambda \sum_{i=1}^{n} (\omega_i + h)\Delta_i \tag{1.1}$$

where the sum runs over the n edges of the walk. $\Delta_i = \pm 1$ depending on whether the edge is in one phase or the other, so that one type of monomer prefers one phase and the other type of monomer prefers the other phase. h is an asymmetry parameter which controls the relative affinity of the two types of monomers for the two phases. λ essentially plays the role of an inverse temperature. Bolthausen and den Hollander (1997) proved that a localization/delocalization transition exists in this model and that there is a curve in the (λ, h)-plane along which the transition takes place, and Biskup and den Hollander (1999) extended this work by deriving results concerning the path of the walk. Maritan *et al* (1999) considered both a random walk model and a self-avoiding walk model also with charges on the comonomers so that there was an energetic advantage for a particular monomer to be in one phase and a disadvantage for the monomer to be in the other phase. The charges were distributed independently according to a Gaussian distribution. They gave a non-rigorous argument that the system would always be localized when the polymer is neutral (i.e. where the overall charge is zero) and that there is a localization/delocalization transition when the polymer has a net charge.

2. Rigorous results concerning the quenched average free energy

We consider the cubic lattice Z^3 whose vertices are the integer points in R^3 and whose edges join adjacent pairs of vertices which are unit distance apart. We consider n-edge self-avoiding walks which start at the origin, and number the vertices of the walk $i = 0, 1, \ldots, n$. We write the coordinates of the ith vertex as $r_i = (x_i, y_i, z_i)$. The vertices of the walk are coloured randomly and independently, each being coloured A with probability p_A and B with probability $p_B = 1 - p_A$. We write $\chi_i = +1$ if vertex i is coloured A and -1 if vertex i is coloured B. Since vertex 0 is always in the plane $z = 0$ its colour is irrelevant and we write χ for the colouring $\chi_1, \chi_2, \ldots, \chi_n$. Let $c_n(v_A, v_B|\chi)$ be the number of self-avoiding walks with n edges and colouring χ which have v_A A-vertices with positive z-coordinate and v_B B-vertices with negative z-coordinate. We define the partition function

$$Z_n(\alpha, \beta|\chi) = \sum_{v_A, v_B} c_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B} \tag{2.1}$$

and the corresponding free energy

$$\kappa_n(\alpha, \beta|\chi) = n^{-1} \log Z_n(\alpha, \beta|\chi). \tag{2.2}$$

Note that neither vertices of type A nor of type B have an interaction with the interfacial plane $z = 0$.

We say that a walk is *x-unfolded* if $x_0 \leqslant x_i \leqslant x_n$ for all i and *z-unfolded* if $z_0 \leqslant z_i \leqslant z_n$ for all i. Walks can be x-unfolded (z-unfolded) by successive reflections in the planes containing the vertices with smallest and largest x-coordinate (z-coordinate) (Hammersley and Welsh 1962). We define a subclass of self-avoiding walks which we call *loops*. An *n-edge loop* is an n-edge self-avoiding walk with its zeroth vertex at the origin, its nth vertex in the plane $z = 0$ and satisfying the constraint that $0 = x_0 < x_i \leqslant x_n$ for all $i \neq 0, n$. (Loops are examples of x-unfolded walks, but not all x-unfolded walks are loops.) Loops can be coloured in a similar way to walks and we write $l_n(v_A, v_B|\chi)$ for the number of n-edge loops with v_A A-vertices with positive z-coordinate and v_B B-vertices with negative z-coordinate, given the colouring $\chi = \{\chi_1, \chi_2, \ldots, \chi_n\}$. We define the partition function

$$L_n(\alpha, \beta|\chi) = \sum_{v_a, v_b} l_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B}. \tag{2.3}$$

Lemma 2.1. *The quenched average limiting free energy for loops exists for all $\alpha, \beta < \infty$. That is, the limit*

$$\lim_{n\to\infty} \langle n^{-1} \log L_n(\alpha, \beta|\chi)\rangle \equiv \bar{\kappa}(\alpha, \beta) \tag{2.4}$$

where $\langle\cdots\rangle$ is the expectation over random colourings, exists for all $\alpha, \beta < \infty$.

Proof. Loops can be concatenated in pairs to form larger loops by identifying the last vertex of one loop with the first vertex of the other loop. This gives the inequality

$$l_{m+n}(v_A, v_B|\chi_1 + \chi_2) \geqslant \sum_{v_1, v_2} l_m(v_1, v_2|\chi_1) l_n(v_A - v_1, v_B - v_2|\chi_2) \tag{2.5}$$

where we have written $\chi_1 + \chi_2$ for the concatenation of the colourings χ_1 and χ_2. Multiplying both sides by $\mathrm{e}^{\alpha v_A + \beta v_B}$ and summing over v_A and v_B gives

$$L_{m+n}(\alpha, \beta|\chi_1 + \chi_2) \geqslant L_m(\alpha, \beta|\chi_1) L_n(\alpha, \beta|\chi_2). \tag{2.6}$$

Taking logarithms and averaging over the colourings χ_1 and χ_2 we obtain the functional inequality

$$\langle \log L_{m+n}(\alpha, \beta|\chi_1 + \chi_2)\rangle \geqslant \langle \log L_m(\alpha, \beta|\chi_1)\rangle + \langle \log L_n(\alpha, \beta|\chi_2)\rangle \tag{2.7}$$

where the angular brackets denote expectations with respect to colourings. Since the number of self-avoiding walks is exponentially bounded, so is $\langle L_n(\alpha, \beta|\chi)\rangle$ for $\alpha, \beta < \infty$ so the lemma follows from (2.7) upon application of a standard theorem on super-additive functions (Hille 1948). □

We next prove a lemma concerning convexity.

Lemma 2.2. *The quenched average free energy $\bar{\kappa}(\alpha, \beta)$ is a convex function of α and β for all $\alpha, \beta < \infty$. Moreover, $\bar{\kappa}(\alpha, \beta)$ is continuous and monotonically non-decreasing in both variables.*

Proof. From the definition it is clear that $L_n(\alpha, \beta|\chi)$ is a monotonically non-decreasing function of α and β and, for fixed n, is bounded in any fixed closed interval of values of α and β. Consequently, to establish that $\langle \log L_n(\alpha, \beta|\chi)\rangle$ is a convex function of α and β it is enough to prove that

$$\frac{\langle \log L_n(\alpha_1, \beta_1|\chi)\rangle + \langle \log L_n(\alpha_2, \beta_2|\chi)\rangle}{2} \geqslant \langle \log L_n((\alpha_1 + \alpha_2)/2, (\beta_1 + \beta_2)/2|\chi)\rangle \tag{2.8}$$

for all $\alpha, \beta \in \mathcal{R}$. Fix n and the colouring χ. By Cauchy's inequality

$$\begin{aligned} L_n(\alpha_1, \beta_1|\chi) L_n(\alpha_2, \beta_2|\chi) &= \sum_{v_A, v_B} l_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha_1 v_A + \beta_1 v_B} \sum_{v_A, v_B} l_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha_2 v_A + \beta_2 v_B} \\ &\geqslant \left(\sum_{v_A, v_B} l_n(v_A, v_B|\chi)\, \mathrm{e}^{(\alpha_1+\alpha_2)v_A/2 + (\beta_1+\beta_2)v_B/2} \right)^2 \\ &= L_n^2((\alpha_1 + \alpha_2)/2, (\beta_1 + \beta_2)/2|\chi). \end{aligned} \tag{2.9}$$

Taking logarithms in (2.9) and averaging over χ gives (2.8). If the limit of a sequence of convex functions exists, that limit is also a convex function, so that $\bar{\kappa}(\alpha, \beta)$ is convex, and hence continuous (since the function is monotonically non-decreasing and bounded in any fixed closed interval of values of α and β). □

Now we relate the free energy for loops to the free energy for walks.

Theorem 2.3. *The quenched average free energy for walks* $\lim_{n\to\infty}\langle n^{-1}\log Z_n(\alpha,\beta|\chi)\rangle$ *exists and is equal to* $\bar{\kappa}(\alpha,\beta)$.

Proof. Since $L_n(\alpha,\beta|\chi)\leqslant Z_n(\alpha,\beta|\chi)$ we see immediately that

$$\bar{\kappa}(\alpha,\beta)\leqslant\liminf_{n\to\infty}\langle n^{-1}\log Z_n(\alpha,\beta|\chi)\rangle. \tag{2.10}$$

To obtain a bound in the other direction we describe a construction for converting walks into loops. Consider an n-edge walk ω, with the first vertex at the origin, and let $m=\max[i|z_i=0]$. If $m=n$ the walk can be converted into a loop by unfolding in the x-direction, translating through unit distance in the positive x-direction, and adding an edge to join the first vertex to the origin. Otherwise $z_{m+1}=z_m\pm 1$ and we consider the case $z_{m+1}=z_m+1$. The other case can be handled by a similar argument. Disconnect the walk at vertex m into two subwalks, ω_1 and ω_2, with vertices $0,1,\ldots,m$ and $m,m+1,\ldots,n$. x-unfold ω_1 to form ω_3, x-unfold ω_2 and then z-unfold the resulting walk to form ω_4. Suppose that the final vertex of ω_4 has z-coordinate equal to h. If $h=1$ add an edge in the negative z-direction so that the final vertex is in the plane $z=0$, and reconnect this walk to ω_3, using an additional intermediate edge in the x-direction. Translate this walk in the x-direction and connect to the origin by adding an edge. The resulting walk is a loop. If $h>1$ we have two possibilities, h odd and h even. Suppose $h=2p+1$ and $m=\max[i|z_i=p+1]$, where the z_i are the z-coordinates of the vertices of ω_4. Disconnect ω_4 at vertex m to form two subwalks ω_5 and ω_6. x-unfold ω_5 to form ω_7 and ω_6 to form ω_8. Reflect ω_8 in the plane $z=p+1$ to form ω_9. Reconnect ω_3, ω_7 and ω_9, adding an additional edge in the x-direction at each rejoining position, and translate and add an additional edge to join the resulting walk to the origin. The walk can be converted to a loop by adding an edge joining the last vertex of the walk to a vertex in $z=0$. If $h=2p$ carry out a similar construction, but reflect in the plane $z=p+1$, adding two edges at the final stage. Different walks can give rise to the same loop by this procedure but the maximum degeneracy associated with each unfolding operation is $\mathrm{e}^{\mathrm{O}(\sqrt{n})}$. At most six edges are added to the original walk during this construction. Consequently,

$$L_n(\alpha,\beta|\chi)\leqslant Z_n(\alpha,\beta|\chi)\leqslant \mathrm{e}^{\mathrm{O}(\sqrt{n})}\mathrm{e}^{6\max[\alpha,\beta,0]}\max_{0\leqslant k\leqslant 6}L_{n+k}(\alpha,\beta|\chi') \tag{2.11}$$

where the labellings χ' are derived from χ by randomly labelling any additional vertices. Taking logarithms, dividing by n, taking expectations with respect to χ', and letting $n\to\infty$, we obtain

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

which proves the theorem. □

We next give a proof that the system is thermodynamically self-averaging. To do this we need an additional lemma. We define $c_n^h(v_A,v_B|\chi)$ to be the number of self-avoiding walks with n edges and colouring χ for which $z_0=h$ (note that h can be positive, zero or negative) and which have v_A A-vertices with positive z-coordinate and v_B B-vertices with negative z-coordinate. Clearly, $c_n^0(v_A,v_B|\chi)=c_n(v_A,v_B|\chi)$. Define the partition function

$$Z_n^h(\alpha,\beta|\chi)=\sum_{v_A,v_B}c_n^h(v_A,v_B|\chi)\,\mathrm{e}^{\alpha v_A+\beta v_B} \tag{2.13}$$

and let

$$Z_n^*(\alpha,\beta|\chi)=\max_h Z_n^h(\alpha,\beta|\chi). \tag{2.14}$$

Lemma 2.4. *For all* $\alpha, \beta < \infty$

$$\lim_{n\to\infty} \langle n^{-1} \log Z_n^*(\alpha, \beta|\chi)\rangle = \bar{\kappa}(\alpha, \beta). \tag{2.15}$$

Proof. Since the walks counted in the partition function $Z_n^*(\alpha, \beta|\chi)$ clearly include loops we have the inequality

$$Z_n^*(\alpha, \beta|\chi) \geqslant L_n(\alpha, \beta|\chi) \tag{2.16}$$

so that

$$\liminf_{n\to\infty} \langle n^{-1} \log Z_n^*(\alpha, \beta|\chi)\rangle \geqslant \bar{\kappa}(\alpha, \beta). \tag{2.17}$$

Fix h, n, α, β and χ. Walks with their first vertex having z-coordinate h either (I) have at least one vertex in $z = 0$ or (II) have no vertices in $z = 0$. We write the partition functions for walks in these two classes as $Z_n^I(\alpha, \beta|\chi)$ and $Z_n^{II}(\alpha, \beta|\chi)$, and note that

$$\begin{aligned} Z_n^I(\alpha, \beta|\chi) + Z_n^{II}(\alpha, \beta|\chi) &= Z_n^h(\alpha, \beta|\chi) \leqslant Z_n^*(\alpha, \beta|\chi) \\ &\leqslant 2 \max_h \max[Z_n^I(\alpha, \beta|\chi), Z_n^{II}(\alpha, \beta|\chi)]. \end{aligned} \tag{2.18}$$

If the walk is in the first class let m be the first vertex in $z = 0$. Divide the walk into two subwalks, one of length m and the other of length $n - m$. By reading one of these walks in the reverse direction these two walks each start in $z = 0$. Consequently, the partition function for walks in class I is bounded by

$$Z_n^I(\alpha, \beta|\chi) \leqslant \sum_m Z_m(\alpha, \beta|\bar{\chi}_1) Z_{n-m}(\alpha, \beta|\chi_2) \leqslant (n+1) \max_m Z_m(\alpha, \beta|\bar{\chi}_1) Z_{n-m}(\alpha, \beta|\chi_2) \tag{2.19}$$

where χ_1 and χ_2 are colourings whose concatenation is χ, and $\bar{\chi}_1$ is the colouring χ_1 read in reverse order. If the walk is in class II translate the walk in the z-direction towards the interface until at least one vertex is in $z = 1$ or -1 and no vertices are in $z = 0$. Whichever side of the plane $z = 0$ the walk was on before the translation, it is still on the same side after the translation, so there is no change in v_A or v_B. If there is a vertex of degree one at unit distance from $z = 0$ add a vertex in $z = 0$ and an edge joining it to the vertex of degree one. Otherwise consider the first vertex which is unit distance from $z = 0$ and suppose this is the mth vertex. Then vertex $m + 1$ will have the same z-coordinate. Delete the edge joining the mth and $(m + 1)$th vertices. Add two vertices a and b with the same x and y coordinates as the mth and $(m + 1)$th vertices but with zero z-coordinate. Add three edges joining the mth vertex to a, a to b and b to the $(m + 1)$th vertex. Divide the walk into two subwalks at vertex a to give two walks with $m + 1$ and $n - m + 1$ edges, respectively. By reading one of these walks in the reverse direction these two walks each start in $z = 0$. Consequently, the partition function for walks in class II is bounded by

$$Z_n^{II}(\alpha, \beta|\chi) \leqslant Z_{n+1}(\alpha, \beta|\chi_3) + Z_{n+1}(\alpha, \beta|\bar{\chi}_4) + \sum_m Z_{m+1}(\alpha, \beta|\bar{\chi}_5) Z_{n-m+1}(\alpha, \beta|\chi_6) \tag{2.20}$$

where χ_3 and χ_4 are one-point extensions of the colouring χ and $\bar{\chi}_4$ is χ_4 read in reverse. Similarly χ_5 and χ_6 are colourings which are derived from χ by adding two interior vertices, and $\bar{\chi}_5$ is the reverse of χ_5. Then

$$\begin{aligned} Z_n^{II}(\alpha, \beta|\chi) \leqslant 3 \max[&Z_{n+1}(\alpha, \beta|\chi_3), Z_{n+1}(\alpha, \beta|\bar{\chi}_4), \\ &(n+1) \max_m Z_{m+1}(\alpha, \beta|\bar{\chi}_5) Z_{n-m+1}(\alpha, \beta|\chi_6)]. \end{aligned} \tag{2.21}$$

The inequalities (2.19) and (2.21) together with theorem 2.3 then give

$$\langle n^{-1} \log Z_n^*(\alpha, \beta|\chi)\rangle \leqslant \bar{\kappa}(\alpha, \beta) + \mathrm{o}(1) \tag{2.22}$$

when we average over colourings. This completes the proof. □

Theorem 2.5. *The limit* $\lim_{n\to\infty} n^{-1} \log Z_n(\alpha, \beta|\chi_0)$ *exists and is equal to* $\bar{\kappa}(\alpha, \beta)$ *for almost all fixed quenches* χ_0.

Proof. For fixed $\alpha, \beta < \infty$ and fixed m let $n = mp+q$ with $0 \leqslant q < m$. We consider a subset of n-edge 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 ith loop, and χ_0 is the labelling of the concatenated loops, we have

$$Z_n(\alpha, \beta|\chi_0) \geqslant \left[\prod_{i=1}^{p} L_m(\alpha, \beta|\chi^{(i)})\right] L_q(\alpha, \beta|\chi^{(p+1)}). \tag{2.23}$$

Taking logarithms and dividing by n gives

$$n^{-1} \log Z_n(\alpha, \beta|\chi_0) \geqslant \left[\frac{1}{m(p+q/m)} \sum_{i=1}^{p} \log L_m(\alpha, \beta|\chi^{(i)})\right] + n^{-1} \log L_q(\alpha, \beta|\chi^{(p+1)}). \tag{2.24}$$

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

$$\begin{aligned}\liminf_{n\to\infty} n^{-1} \log Z_n(\alpha, \beta|\chi_0) &\geqslant \limsup_{p\to\infty} p^{-1} \sum_{i=1}^{p} m^{-1} \log L_m(\alpha, \beta|\chi^{(i)}) \\ &= \langle m^{-1} \log L_m(\alpha, \beta|\chi)\rangle \end{aligned} \tag{2.25}$$

almost surely, where the equality comes from application of the strong law of large numbers. To get a corresponding upper bound we concatenate a set of p walks, labelled $i = 1, 2, \ldots, p$, each with m edges, and a final walk with q edges, labelled $i = p + 1$, where the colouring on the ith subwalk is $\chi^{(i)}$ and $\chi^{(1)} + \cdots + \chi^{(p+1)}$. The z-coordinate of the first vertex in the $(i + 1)$th walk is chosen to match the z-coordinate of the last vertex in the ith walk. This concatenated set will contain all the corresponding self-avoiding walks (as well as the cases where the subwalks are self- but not mutually avoiding) and, since $Z_n^h(\alpha, \beta|\chi) \leqslant Z_n^*(\alpha, \beta|\chi)$ we have the inequality

$$Z_n(\alpha, \beta|\chi) \leqslant \left[\prod_{i=1}^{p} Z_m^*(\alpha, \beta|\chi^{(i)})\right] Z_q^*(\alpha, \beta|\chi^{(p+1)}). \tag{2.26}$$

Taking logarithms, dividing by n, and letting $p \to \infty$ with m fixed gives

$$\limsup_{n\to\infty} n^{-1} \log Z_n(\alpha, \beta|\chi_0) \leqslant \langle m^{-1} \log Z_m^*(\alpha, \beta|\chi)\rangle \tag{2.27}$$

almost surely, where we have again used the strong law of large numbers. Letting $m \to \infty$ in (2.25) and (2.27) and using lemma 2.4 gives

$$\lim_{n\to\infty} n^{-1} \log Z_n(\alpha, \beta|\chi_0) = \bar{\kappa}(\alpha, \beta) \tag{2.28}$$

for almost all colourings χ_0. □

3. The form of the phase diagram

In this section we prove some results concerning the α and β dependence of the quenched average free energy which enable us to make some predictions about the form of the phase diagram in the (α, β)-plane.

Lemma 3.1. *For fixed $\alpha \geqslant 0$ the limiting quenched average free energy $\bar{\kappa}(\alpha, \beta)$ is independent of β for $\beta \leqslant 0$.*

Proof. For fixed n and a fixed colouring χ let v_A^o and v_B^o be the number of vertices coloured A and B respectively. For $\alpha \geqslant 0$ and $\beta \leqslant 0$ we have

$$\begin{aligned} Z_n(\alpha, \beta|\chi) &= \sum_{v_A, v_B} c_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B} \\ &\leqslant \sum_{v_A, v_B} c_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A^o} \\ &= c_n \mathrm{e}^{\alpha v_A^o} \end{aligned} \tag{3.1}$$

where c_n is the number of n-edge self-avoiding walks. Similarly

$$\begin{aligned} Z_n(\alpha, \beta|\chi) &= \sum_{v_A, v_B} c_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B} \\ &\geqslant \sum_{v_A} c_n(v_A, 0|\chi)\, \mathrm{e}^{\alpha v_A} \\ &\geqslant c_n(v_A^o, 0|\chi)\, \mathrm{e}^{\alpha v_A^o} \\ &\geqslant c_{n-1}^+ \mathrm{e}^{\alpha v_A^o} \end{aligned} \tag{3.2}$$

where c_n^+ is the number of n edge self-avoiding walks with the first vertex at the origin and confined to the half-space $z \geqslant 0$. Since (Hammersley 1957, Whittington 1975)

$$\lim_{n\to\infty} n^{-1} \log c_n^+ = \lim_{n\to\infty} n^{-1} \log c_n \equiv \kappa < \infty \tag{3.3}$$

where κ is the connective constant of the simple cubic lattice, we have, from (3.1) and (3.2),

$$\lim_{n\to\infty} \langle n^{-1} \log Z_n(\alpha, \beta|\chi) \rangle = \kappa + \alpha \lim_{n\to\infty} [v_A^o/n] \equiv \kappa + \alpha p_A. \tag{3.4}$$

The right-hand side is independent of β which completes the proof. □

Of course, there is a similar result for the case of $\alpha \leqslant 0$ and $\beta \geqslant 0$. We next look at the first quadrant, $\alpha \geqslant 0$ and $\beta \geqslant 0$.

Lemma 3.2. *In the first quadrant, $\alpha, \beta \geqslant 0$, the free energy $\bar{\kappa}(\alpha, \beta)$ is singular along the curve $\alpha \mapsto \beta_c(\alpha)$ where $0 \leqslant \beta_c(\alpha) \leqslant \alpha p_A/(1 - p_A)$.*

Proof. From the previous lemma, and the monotonic non-decreasing nature of $\bar{\kappa}(\alpha, \beta)$ we see that

$$\bar{\kappa}(\alpha, \beta) \geqslant \kappa + \alpha p_A \tag{3.5}$$

for all β when $\alpha \geqslant 0$. A similar argument shows that

$$\bar{\kappa}(\alpha, \beta) \geqslant \kappa + \beta(1 - p_A) \tag{3.6}$$

for all α when $\beta \geqslant 0$. With α fixed at some positive value, take $\beta > \alpha p_A/(1-p_A)$. Then

$$\bar{\kappa}(\alpha,\beta) \geqslant \kappa + \beta(1-p_A) > \kappa + \alpha p_A. \tag{3.7}$$

Hence at fixed $\alpha > 0$ $\bar{\kappa}(\alpha,\beta)$ is a constant for $\beta \leqslant 0$ and greater than this constant for $\beta > \alpha p_A/(1-p_A)$. The function must therefore have a singularity at some value of β in the interval $0 \leqslant \beta \leqslant \alpha p_A/(1-p_A)$, which proves the theorem. □

Although this lemma establishes that the free energy is singular along a curve in the first quadrant, it does not answer the question about whether or not there is a non-trivial region in which the walk is localized at the boundary $z = 0$. The next theorem addresses this question.

Theorem 3.3. *In the region of the first quadrant,* $0 \leqslant \beta \leqslant \alpha p_A/(1-p_A)$*, the singularity in* $\bar{\kappa}(\alpha,\beta)$ *occurs for* β *less than some constant, uniformly in* α*. Similarly, in the region* $0 \leqslant \alpha \leqslant \beta(1-p_A)/p_A$*, the singularity occurs for* α *less than some constant, uniformly in* β*.*

Proof. Consider the fixed sequence of $k+6$ colours, $\eta = AAB_{k+2}AA$, $k \geqslant 2$, where the subscript indicates $k+2$ copies of B. For a set of n Bernoulli trials where the outcome is A with probability p_A and B with probability $1-p_A$, $0 < p_A < 1$, there exists a $\delta = \delta(k, p_A) > 0$, such that there are at least δn disjoint occurrences of η for all except exponentially few sequences of trials. For each such sequence of colours consider the walks in which, for each of the first δn occurrences of η, the first and last Bs are in $z = 0$ and the middle k Bs are in $z < 0$, and the rest of the walk is in $z > 0$. This ensures that all the A-vertices are in $z > 0$ and that δnk B-vertices are in $z < 0$. There is at least one such walk (e.g. in which the subwalks in the $z > 0$ and $z < 0$ half-spaces are just straight lines in the x-direction). For each such colouring χ the partition function satisfies the inequality

$$Z_n(\alpha,\beta|\chi) \geqslant \mathrm{e}^{v_A^o\alpha+\delta nk\beta}. \tag{3.8}$$

Then

$$\langle n^{-1}\log Z_n(\alpha,\beta|\chi)\rangle \geqslant 2^{-n}[2^n(1-\mathrm{e}^{-\gamma n})](p_A\alpha+\delta k\beta) \tag{3.9}$$

for some positive γ, and, letting $n \to \infty$,

$$\bar{\kappa}(\alpha,\beta) \geqslant p_A\alpha + \delta k\beta. \tag{3.10}$$

For fixed $\alpha > 0$ we know that $\bar{\kappa}(\alpha,\beta) = \kappa + \alpha p_A$ for $\beta < \beta_c(\alpha)$). Hence

$$\beta_c(\alpha) \leqslant \frac{\kappa}{\delta k}. \tag{3.11}$$

For α sufficiently large this is less than $\alpha p_A/(1-p_A)$ so that we have a non-trivial region in which localization occurs. Similarly, for fixed sufficiently large β there is a singularity in $\bar{\kappa}(\alpha,\beta)$ for some $\alpha \leqslant \kappa/\delta' k < \beta(1-p_A)/p_A$ where $\delta' > 0$. □

This implies that there is a region of the first quadrant where the walk is localized at the interface, in the sense that it has a positive density of vertices in $z = 0$.

We next examine the third quadrant, $\alpha \leqslant 0$, $\beta \leqslant 0$. We first consider $\alpha < 0$, $\beta > 0$ where $\bar{\kappa}(\alpha,\beta) = \kappa + (1-p_A)\beta$, independent of α. This result, combined with a lower bound on $\bar{\kappa}(\alpha,\beta)$ in the third quadrant, gives some information on the location of the phase boundary from the delocalized to the localized phase. The idea is to make a connection to the problem of adsorption at an impenetrable plane, which has been investigated for a random copolymer by Orlandini *et al* (1999). Let $b_n^+(w_A|\chi)$ be the number of n-edges self-avoiding walks with colouring χ, beginning at the origin and confined to the half-space $z \geqslant 0$, with exactly w_A A-vertices in the plane $z = 0$. Define the partition function

$$B_n^+(\omega|\chi) = \sum_{w_A} b_n^+(w_A|\chi)\,\mathrm{e}^{\omega w_A}. \tag{3.12}$$

It is known (Orlandini *et al* 1999) that the limiting quenched average free energy

$$B(\omega) = \lim_{n\to\infty} \langle n^{-1} \log B_n^+(\omega|\chi)\rangle \tag{3.13}$$

exists for all $\omega < \infty$ and that this free energy is singular at $\omega = \omega_c(p_A)$ where $0 < \omega_c(p_A) \leqslant (\kappa - \kappa')/p_A$, κ is the connective constant of the simple cubic lattice and κ' is the connective constant of the square lattice.

Theorem 3.4. *$\bar{\kappa}(\alpha, \beta)$ is singular in the third quadrant on a curve $\alpha \mapsto \beta_c(\alpha)$ where $\beta_c(\alpha) \geqslant -(\kappa - \kappa')/(1 - p_A)$.*

Proof. Fix $\alpha < 0$. We are interested in the behaviour of the free energy for $\beta < 0$. Clearly,

$$Z_n(\alpha, \beta|\chi) \geqslant \sum_{v_B} c_n(0, v_B|\chi)\,\mathrm{e}^{\beta v_B}. \tag{3.14}$$

If we confine the walk to the half-space $z \leqslant 0$ then the number of B-vertices in $z = 0$, w_B, is given by

$$w_B = v_B^o - v_B \tag{3.15}$$

so that $c_n(0, v_B|\chi) \geqslant b_n^+(w_B)$. Hence

$$\begin{aligned} Z_n(\alpha, \beta|\chi) &\geqslant \sum_{v_B} c_n(0, v_B|\chi)\,\mathrm{e}^{\beta v_B} \\ &\geqslant \sum_{w_B} b_n^+(w_B)\,\mathrm{e}^{\beta v_B^o - \beta w_B} \\ &= \mathrm{e}^{\beta v_B^o} \sum_{w_B} b_n^+(w_B)\,\mathrm{e}^{-\beta w_B} \\ &= \mathrm{e}^{\beta v_B^o} B_n^+(-\beta|\chi). \end{aligned} \tag{3.16}$$

Taking logarithms, dividing by n, averaging over χ and letting $n \to \infty$ gives

$$\bar{\kappa}(\alpha, \beta) \geqslant \beta(1 - p_A) + B(-\beta). \tag{3.17}$$

However, using the results of Orlandini *et al* (1999), $B(-\beta)$ is equal to κ for $\beta \geqslant \beta_c$ and greater than κ for $\beta < \beta_c$. Moreover, $0 < -\beta_c \leqslant (\kappa - \kappa')/(1 - p_A)$. Hence

$$\bar{\kappa}(\alpha, \beta) > \kappa + (1 - p_A)\beta \tag{3.18}$$

for $-\beta > (\kappa - \kappa')/(1 - p_A)$. □

In figure 1 we sketch a phase diagram which is consistent with the results of this section. Note that we have *not* proved that the phase boundaries pass through the origin.

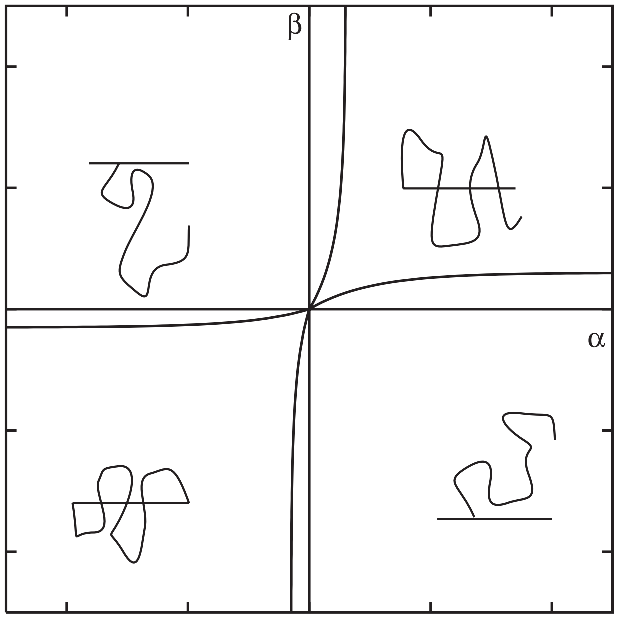

Figure 1. Sketch of the expected form of the phase diagram for $p_A = \frac{1}{2}$. This form is consistent with the rigorous results obtained in section 3.

4. Numerical results

In this section we present some exact enumeration and series analysis data which we use to investigate the details of the phase diagram in the special case $p_A = \frac{1}{2}$. We have enumerated self-avoiding walks with up to 20 edges on Z^3 keeping track of what we call the *touch map* of the walks. That is, with each walk we associate a string of n letters, each of which is a, b or s. An a in the ith position of the string means that vertex i has positive z-coordinate, while a b means that vertex i has negative z-coordinate and an s denotes a zero z-coordinate. For each such possible string we record the number of self-avoiding walks which correspond to that string. The set of strings and their corresponding counts constitute the touch map. The touch map is independent of the colouring χ but can be used with a particular colouring sequence to compute the partition function $Z_n(\alpha, \beta|\chi)$ for that colouring. We then compute $\kappa_n(\alpha, \beta|\chi) = n^{-1} \log Z_n(\alpha, \beta|\chi)$ and its average, $\langle \kappa_n(\alpha, \beta|\chi)\rangle$, over all 2^n colourings χ.

We expect that

$$Q_n(\alpha, \beta) = \mathrm{e}^{\langle \kappa_n(\alpha,\beta|\chi)\rangle n} \sim n^{\gamma_1 - 1} \mathrm{e}^{\bar{\kappa}(\alpha,\beta)n} \tag{4.1}$$

when the walks are in the delocalized phase, where γ_1 is the surface exponent analogous to the layer susceptibility exponent. In the localized phase (where the system has a two-dimensional quality in that the walks cross the plane $z = 0$ a positive density of times) we expect a similar expression but with γ_1 replaced by $\gamma_2 = \frac{43}{32}$, the exponent for self-avoiding walks in two dimensions (Nienhuis 1982). Since the transition is expected to be second order a third exponent associated with a tricritical behaviour is expected along the critical curve. From (4.1) we obtain

$$R_n(\alpha, \beta) = \sqrt{\frac{Q_n}{Q_{n-2}}} = \mathrm{e}^{\bar{\kappa}(\alpha,\beta)} \left(1 + \frac{\gamma_1 - 1}{n} + \mathrm{O}(n^{-2})\right). \tag{4.2}$$

Plotting $R_n(\alpha, \beta)$ against $1/n$ should produce an asymptotically linear curve with $e^{\bar{\kappa}(\alpha,\beta)}$ as the intercept. Since $\gamma_1 < 1$ in three dimensions (see, for instance, Hegger and Grassberger 1994) the intercept should be approached from below, while the system is in the delocalized phase. In the localized phase γ_1 is replaced by γ_2 (which is greater than 1) so the intercept should be approached from above. Of course the situation is complicated by crossover effects at small values of n.

Consider the behaviour in the first quadrant ($\alpha, \beta > 0$). If we fix $\alpha > 0$ and take a point in the fourth quadrant (where $\beta < 0$) we know, from section 3, that the intercept will be $e^{\kappa+\alpha/2}$, independent of β. As β is increased we should reach a critical value $\beta_c(\alpha)$ beyond which the intercept will be strictly greater than $e^{\kappa+\alpha/2}$. The point at which the intercept becomes dependent on β signals the phase boundary. This, together with the change in slope of the ratio plot (discussed in the previous paragraph), should allow us to locate the phase boundary approximately. We have computed $R_n(\alpha, \beta)$ as a function of n and β for various positive values of α and carried out the ratio analysis as indicated above.

Since we believe that the behaviour will be governed by the exponent γ_1 in the delocalized phase we can make use of the value of γ_1 to accelerate the convergence. If we define

$$R_n'(\alpha, \beta) = R_n(\alpha, \beta)\frac{n}{n + \gamma_1 - 1} \tag{4.3}$$

then, from (4.2), we see that

$$R_n'(\alpha, \beta) = e^{\bar{\kappa}(\alpha,\beta)}(1 + O(n^{-2})). \tag{4.4}$$

Plotting $R_n'(\alpha, \beta)$ against $1/n$ should produce a curve with asymptotically zero slope provided that we are in the delocalized phase. (Even if the value used for γ_1 is slightly incorrect the curve will still go to $e^{\bar{\kappa}(\alpha,\beta)}$ as $n \to \infty$ but not with asymptotically zero slope.) We have used our exact enumeration data (together with a recent estimate for κ due to MacDonald *et al* (2000)) to estimate γ_1 and we find $\gamma_1 = 0.680 \pm 0.004$ in good agreement with the Monte Carlo estimate (Hegger and Grassberger 1994) of 0.679 ± 0.002. We have used $\gamma_1 = 0.68$ in most of our analysis. Similarly, one expects that in the localized phase the behaviour will be governed by the exponent γ_2. In practice, this turns out to be true well inside the localized region, but with a slow crossover after the phase boundary is passed.

It is more convenient to look at

$$A_n(\alpha, \beta) = R_n'(\alpha, \beta)\, e^{-\bar{\kappa}(\alpha,0)} \tag{4.5}$$

since, at fixed α, A_n will be equal to unity for β values which correspond to the delocalized phase. In figure 2 we give four examples of ratio plots of A_n with two values of the exponent (γ_1 and γ_2) and the corresponding linear extrapolants $(nA_n - (n-2)A_{n-2})/2$, at different values of β, for $\alpha = 1.7$. For $\beta = 0$ and for $\beta = 0.4$ we see clear evidence that A_n (when the exponent being used is γ_1) is approaching unity with asymptotically zero slope. For $\beta = 1.2$ it is quite clear that the curves are approaching a value greater than unity so that the system is clearly in the localized phase. The curves for $\beta = 1.0$ suggest that the transition is somewhere in this region.

For some values of α, increasing β still further might give rise to a second transition, this time from the localized phase to a phase in which the walk is delocalized, but now into the region with $z < 0$. From the arguments given in the proof of lemma 3.2 we know that

$$\bar{\kappa}(\alpha, \beta) \geqslant \kappa + \beta/2 \tag{4.6}$$

and this inequality will be an equality in this delocalized phase. One can therefore examine the behaviour of R_n (or R_n' or A_n) at fixed α, and look for values of β beyond which the intercept is equal to $e^{\kappa+\beta/2}$.

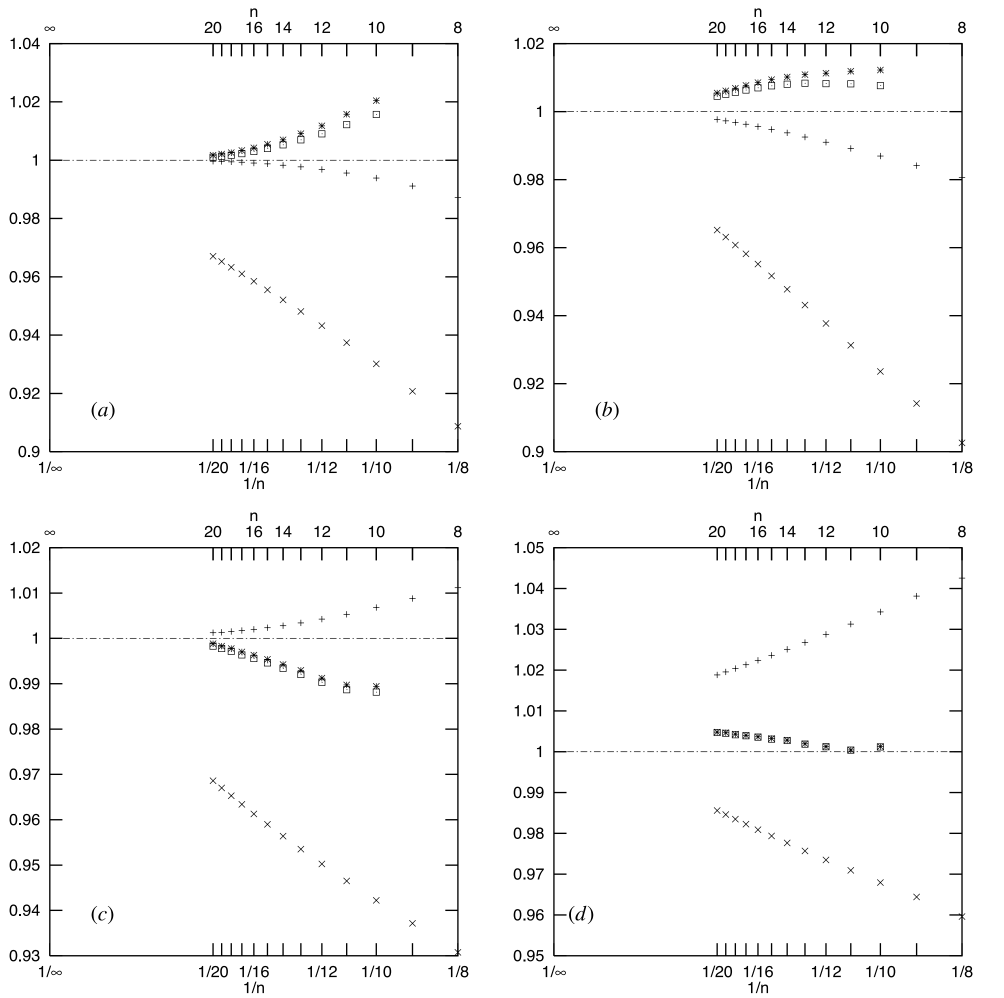

Figure 2. $A_n(\alpha, \beta)$ plotted against $1/n$ for $\alpha = 1.7$ and (*a*) $\beta = 0$, (*b*) $\beta = 0.4$, (*c*) $\beta = 1.0$ and (*d*) $\beta = 1.2$. A_n with $\gamma_1 = 0.68$ (+), and the corresponding linear extrapolant ($*$). A_n with $\gamma_2 = \frac{43}{32}$ ($\times$) and the corresponding linear extrapolant (□).

In the third quadrant the situation is quite similar. In this case we fix $\alpha < 0$ and calculate R_n as a function of n and β, starting with $\beta > 0$. In the second quadrant ($\alpha < 0$, $\beta > 0$) the intercept will be $e^{\kappa+\beta/2}$ and will change with β in this way as β is decreased, until we reach $\beta_c(\alpha)$ after which point the intercept will be strictly larger than this value. Again we expect a change in the sign of the slope of the ratio plots around the phase boundary, because the behaviour should be controlled by γ_1 in the delocalized phase and by γ_2 in the localized phase. We can make use of the fact that we know γ_2 and have an accurate estimate of γ_1, and form the function $R'_n(\alpha, \beta)$ as for the first quadrant. Again it is convenient to define a function analogous to that defined in (4.5) but now we define

$$A_n(\alpha, \beta) = R'_n(\alpha, \beta)\, e^{-\bar{\kappa}(0,\beta)}. \tag{4.7}$$

Figure 3 shows the behaviour of A_n and its linear extrapolants at four different values of β for $\alpha = -3.0$. Once again we are looking for the value of β at which the intercept ceases to

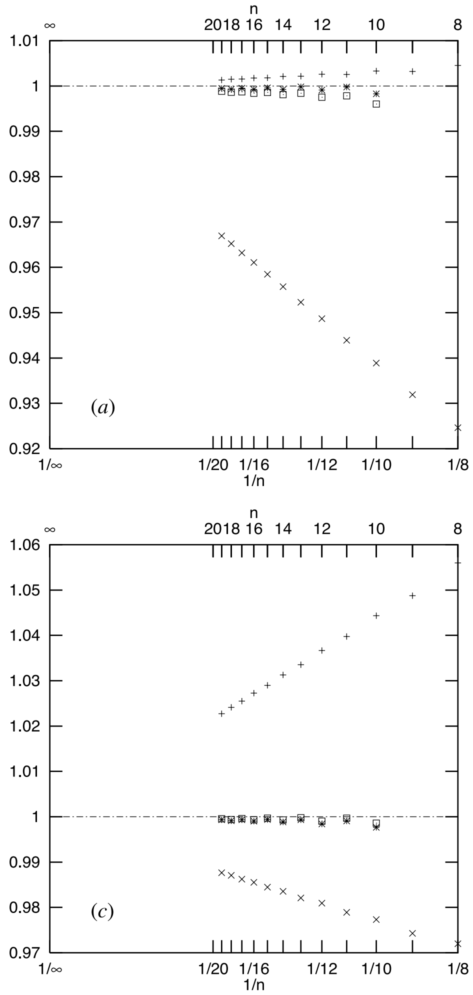

Figure 3. $A_n(\alpha, \beta)$ plotted against $1/n$ for $\alpha = -3.0$ and (*a*) $\beta = 0$, (*b*) $\beta = -0.2$, (*c*) $\beta = -0.4$ and (*d*) $\beta = -0.6$. A_n with $\gamma_1 = 0.68$ (+), and the corresponding linear extrapolant ($*$). A_n with $\gamma_2 = \frac{43}{32}$ ($\times$) and the corresponding linear extrapolant ($\square$).

be equal to unity. For $\beta = 0$ and -0.2 the graphs suggest that the intercept is unity, while it is certainly greater than unity when $\beta = -0.6$. It seems that the critical value of β is close to -0.4. Our final estimates of the locations of the phase boundaries in the first and third quadrants are given in figure 4.

We have also used Monte Carlo methods to investigate the localization behaviour. The Monte Carlo algorithm which we have used is a Markov chain algorithm. The underlying symmetric Markov chain uses a mixture of local and global moves in different proportions depending on the relative values of α and β. In the asymmetric regime ($\alpha/\beta \gg 1$) where the walk is largely confined to a half-space, pivot (Lal 1969, Madras and Sokal 1988) and cut-and-permute moves (Causo 2000) are used. These latter moves help to mitigate the quasi-ergodic problems which the pivot algorithm can display in a quasi-confined geometry. The elementary move in the cut-and-permute scheme is as follows. At a randomly chosen vertex of the walk, the walk is disconnected into two subwalks, w_1, attached to the surface at a vertex of degree one,

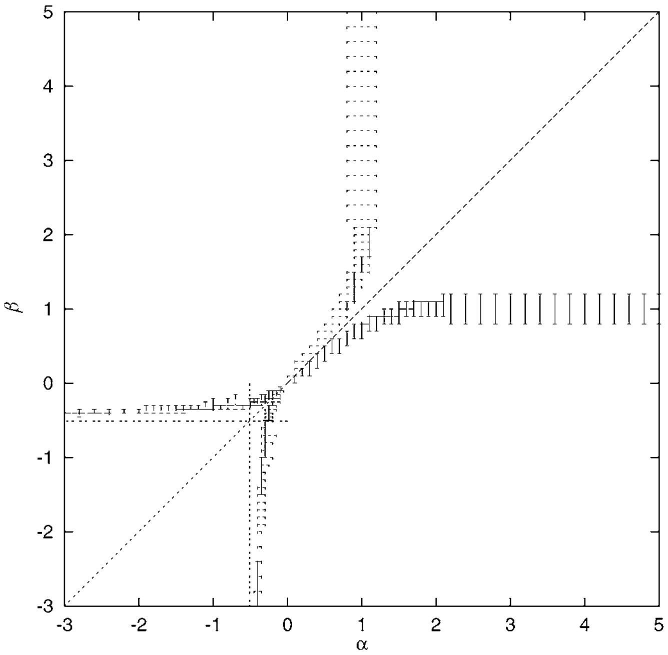

Figure 4. Estimated locations of the phase boundaries in the first and third quadrants. In the third quadrant we also include bounds obtained using theorem 3.4 and a numerical estimate of the location of the singularity in $B(-\beta)$. The diagonal line $\beta = \alpha$ is included as a guide to the eye.

and w_2. A randomly chosen lattice symmetry operation is applied to w_2, and the walk is rebuilt permuting the order of the two subwalks. For details see Causo (2000). In the region where $\beta \approx \alpha$ local moves (Verdier and Stockmayer 1962) are used with increased probability, while the cut-and-permute moves are used with lower probability. The whole process is implemented using a multiple Markov chain technique (Geyer 1991, Tesi *et al* 1996). We have estimated quantities such as $\langle v_A \rangle$, $\langle v_B \rangle$, $\langle v_A^2 \rangle - \langle v_A \rangle^2$ and $\langle v_B^2 \rangle - \langle v_B \rangle^2$ as a function of β at fixed α. In figure 5 we show the β dependence of $n^{-1}\langle v_B \rangle$ and $n^{-1}[\langle v_B^2 \rangle - \langle v_B \rangle^2]$ at $\alpha = -3$. The results are for $n = 1000$ and for an average over 12 random colourings of the walk. For β close to zero we see that the B-vertices are essentially all in the $z < 0$ phase, and the walk is delocalized. As β decreases the number of B-vertices in the $z < 0$ phase decreases and, in fact, these vertices primarily go into the interfacial plane $z = 0$, so that the walk becomes localized around the interface. The behaviour of the 'heat capacity' $n^{-1}[\langle v_B^2 \rangle - \langle v_B \rangle^2]$ is exactly what would be expected from theorem 3.4, and especially from (3.16). The heat capacity is close to zero until β reaches a sufficiently negative value, and then goes through a peak whose shape is characteristic of the asymmetric transition seen in adsorption problems.

5. Discussion

We have considered a coloured self-avoiding walk model of a random copolymer at an interface between two immiscible liquids. There are several different Hamiltonians which one could choose to model such systems and we have chosen to study the case in which there is an energetic advantage for one comonomer to be in one phase and for the other comonomer to be in the other phase. There is no energetic penalty if a monomer is in the other phase, and

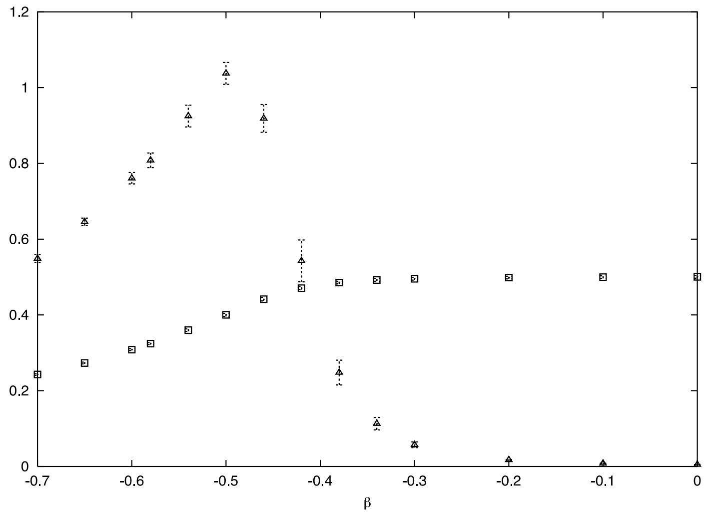

Figure 5. Monte Carlo estimates of $n^{-1}\langle v_B\rangle$ (□) and $n^{-1}[\langle v_B^2\rangle - \langle v_B\rangle^2]$ (△) as a function of β for $\alpha = -3$ and $n = 1000$.

there is no energetic advantage or penalty if a monomer is in the dividing surface between the two phases. For this case we have proved that the limiting quenched average free energy exists and that the system is thermodynamically self-averaging. In addition we have proved the existence of a phase transition from a delocalized phase to a localized phase, and derived bounds which give qualitative information concerning the shapes of the phase boundaries. In particular, these bounds are sufficient to establish that the localized region is a phase, and does not degenerate to a curve in the phase diagram.

We have used exact enumeration and series analysis data to map out details of the phase diagram, and to locate the phase boundaries, at least approximately. We have also reported Monte Carlo data which give information concerning the nature of the localization.

There is a related model which can, to some extent, be handled in a similar way. In this case the dividing surface between the two phases does not have the special property that there is no energetic advantage or disadvantage for a monomer in this plane. In this case we write v_A for the number of A-vertices with non-negative z-coordinate and v_B for the number of B-vertices with negative z-coordinate. If $d_n(v_A, v_B|\chi)$ is the corresponding number of n-edge walks with colouring χ and

$$D_n(\alpha, \beta|\chi) = \sum_{v_A, v_B} d_n(v_A, v_B|\chi)\,\mathrm{e}^{\alpha v_A + \beta v_B} \tag{5.1}$$

is the corresponding partition function, then the arguments in section 2 can be adapted to prove a similar set of results for this model. The results of section 3 concerning the behaviour of the free energy in the first, second and fourth quadrants all go over, with minor modifications, to this model. However, theorem 3.4 has no analogous version since there is no special plane into which the walk can retreat to avoid unfavourable interactions with the two solvents.

Let v_A^* be the number of A-monomers with negative z-coordinate and v_B^* be the number of B-monomers with non-negative z-coordinate. Then

$$v_A + v_A^* = v_A^o \tag{5.2}$$

and

$$v_B + v_B^* = v_B^o. \tag{5.3}$$

We note that

$$D_n(-\alpha, -\beta|\chi) = \mathrm{e}^{-\alpha v_A^o - \beta v_B^o} D_n(\alpha, \beta|\chi) \tag{5.4}$$

so that in this model there is a mapping of the free energy between the first and third quadrants.

This model is related to a model similar in spirit to those considered by Bolthausen and den Hollander (1997) and by Maritan *et al* (1999). Those authors considered models in which a monomer can be energetically favoured in one solvent but energetically penalized in the other solvent. We can construct a model which has an energetic penalty for a monomer to be in the unfavourable solvent by writing the partition function

$$Q_n(\alpha, \beta|\chi)) = \sum_{v_A, v_B} d_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B - \alpha v_A^* - \beta v_B^*}$$
$$= \mathrm{e}^{-\alpha v_A^o - \beta v_B^o} \sum_{v_A, v_B} d_n(v_A, v_B|\chi)\, \mathrm{e}^{2\alpha v_A + 2\beta v_B} \tag{5.5}$$

so that

$$\lim_{n\to\infty} \langle n^{-1} \log Q_n(\alpha, \beta|\chi)\rangle = -\alpha p_A - \beta(1 - p_A) + \lim_{n\to\infty} \langle n^{-1} \log D_n(2\alpha, 2\beta|\chi)\rangle. \tag{5.6}$$

Setting $\alpha = \beta$ reduces this to something like the model used by Maritan *et al* (but they used a Gaussian distribution of charges, instead of the two 'charges' appearing in our model). Their symmetric model (or neutral case) corresponds to $p_A = \frac{1}{2}$ and their more general model corresponds to $p_A \neq \frac{1}{2}$, but still with $\beta = \alpha$.

Acknowledgments

The authors would like to thank Frank den Hollander for many useful conversations, and NSERC of Canada for financial support.

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