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The order of the localization transition for a random copolymer

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Abstract

We use Monte Carlo methods and a scaling analysis to estimate the crossover exponent for a model of the localization transition for a random copolymer at the interface between two immiscible liquids. The model that we use is a directed walk in two dimensions. We find evidence that the nature of the phase transition is different in different regions of the phase diagram. This agrees with previous results for a self-avoiding walk model. We also use exact enumeration and series analysis methods to estimate the locations of the phase boundaries and compare our results to a rigorous bound obtained by partial annealing.

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1. Introduction

Random copolymers have a sequence of two or more co-monomers which is determined by some random process. Once the sequence is determined it is then fixed so the randomness is quenched.

Consider two immiscible liquids such as oil and water and a random copolymer with two types of monomers, one of which is lyophilic and one of which is hydrophilic. At low temperatures the polymer can localize at the interface between oil and water, crossing the interface frequently to ensure that most hydrophilic monomers are in the water phase and most lyophilic monomers are in the oil phase. At high temperatures the polymer will delocalize into one of the two bulk phases (to maximize the entropy). This phase transition has received considerable attention since the early work of Garel *et al* [1]. See for instance [2]. Various models have been used for the underlying configurational properties of the polymer including directed walks [3, 4], random walks [5] and self-avoiding walks [5–7]. In addition the details of the Hamiltonian vary somewhat between the different treatments.

We adopt the Hamiltonian used by Martin *et al* [6] in their treatment of a self-avoiding walk version of the problem. Consider a self-avoiding walk on the simple cubic lattice with vertices labelled $i = 0, 1, \ldots, n$ and with the first vertex at the origin. Vertices $i = 1, 2, \ldots, n$

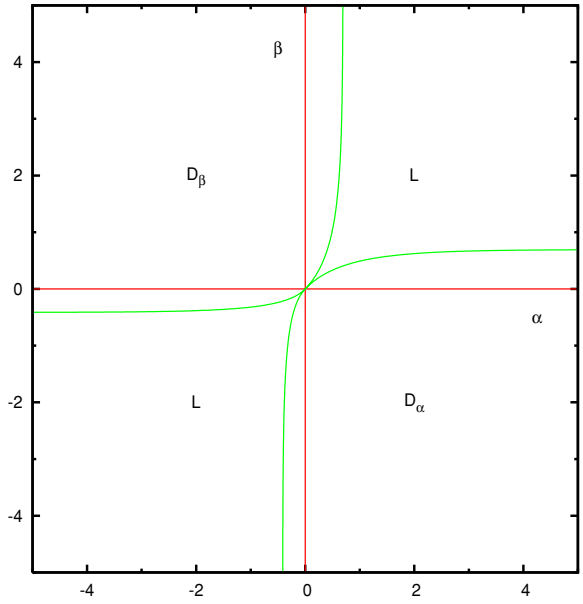

Figure 1. The localization/delocalization phase diagram for a bilateral Motzkin path model, calculated using the Morita approximation. The phase boundaries separate the localized phase L from two delocalized phases D_α and D_β.

(This figure is in colour only in the electronic version)

are independently coloured A or B with equal probability and we write $\chi_i = A$ if the ith vertex is A and $\chi_i = B$ if it is B. We write χ as a shorthand for $\{\chi_1, \chi_2, \ldots, \chi_n\}$. With a given fixed colouring χ let $c_n(v_A, v_B|\chi)$ be the number of n-edge self-avoiding walks, starting at the origin with v_A vertices coloured A with positive z-coordinate and with v_B vertices coloured B with negative z-coordinate. The partition function with a fixed colouring χ can be written as

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

and the finite n quenched average free energy is

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

where the angular brackets represent the expectation with respect to χ. The limiting quenched average free energy $\kappa(\alpha, \beta) = \lim_{n\to\infty} \kappa_n(\alpha, \beta)$ is known to exist [6] and a number of qualitative features of the phase diagram are understood rigorously [6, 7]. The phase diagram has the same qualitative form as that shown in figure 1 [7]. The order of the phase transition was investigated by Monte Carlo methods [8] and, surprisingly, the order seems to be different in the first and third quadrants. In quadrant 3 the crossover exponent $\phi \approx 0.5$ while in the first quadrant $\phi \approx 0.24$ for this model.

In this paper we return to this question and investigate the order of the phase transition for a different underlying configurational model, related to bilateral Motzkin paths. These are directed walks in two dimensions with steps with vectors $(1, \pm 1)$ and $(1, 0)$. If we number the vertices $i = 0, 1, 2, \ldots, n$ and write (x_i, y_i) for the coordinates of the ith vertex then the walks are restricted so that $y_0 = y_n = 0$. This model has several advantages. It is sufficiently simple that we can calculate the phase boundaries in both quadrants in the

Morita approximation [9], which is known [10] to give a bound on the locations of the phase boundaries for the quenched model. If we relax the condition that $y_n = 0$ we obtain another model with the same thermodynamics (in the $n \to \infty$ limit). For this less restrictive model the Monte Carlo calculations are somewhat easier than for self-avoiding walks and we have been able to obtain quite high quality data. (It is worth pointing out that it is not possible to solve the quenched version of this problem even for bilateral Motzkin paths. The simpler configurational model does not help since the essential difficulty is in taking the quenched average.) We also exactly enumerate the walks for small n and carry out the quench over all 2^n colourings to calculate the quenched average free energy exactly for small n. We then use series analysis techniques to estimate the location of the phase transition. We also examine a model where the monomer sequence is strictly alternating. This problem can be solved exactly by combinatorial techniques.

2. Monte Carlo approach

The Monte Carlo scheme which we use is to sample on a realization of a Markov chain defined on the set of all bilateral Motzkin paths without the restriction that the final vertex is in the line $y = 0$. (We shall call these paths *ballot paths*.) We define an underlying symmetric Markov chain with four types of elementary moves, as follows:

(i) Edge replacement: an edge of the walk is chosen at random and replaced by one of the two other possible edges, chosen at random.
(ii) Pivot move: a vertex (x^*, y^*) is chosen at random and the walk is disconnected into two subwalks at that vertex. The second subwalk is reflected about the line $y = y^*$ and the two walks are reconnected. The new walk is guaranteed to be a member of the required class of walks.
(iii) Local move: a vertex (other than the two end vertices) is chosen at random and the two edges incident on this vertex are permuted.
(iv) End move: delete the edge at one (randomly chosen) end of the walk and add this edge at the other end, then translate the walk so that the zeroth vertex is at the origin.

The edge replacement move guarantees ergodicity and the pivot move gives high mobility in the configuration space. A Markov chain is then defined using the usual metropolis scheme with this as the underlying symmetric Markov chain. The process is then implemented using multiple Markov chains to avoid quasi-ergodicity problems [11]. We calculated some thermodynamic and metric properties at two fixed values of α ($\alpha = \pm 3$) for various values of β to ensure that we collected data in both the localized and delocalized phases at those values of α.

We analysed the data (and, in particular, estimated ϕ) by fitting the results to a scaling form. Let $\langle v_B \rangle$ be the number of B vertices with negative y-coordinate. For $\alpha < 0$ it is easy to show that $\lim_{n\to\infty} \langle v_B \rangle / n = 1/2$ for values of β greater than the critical value $\beta_c(\alpha)$ so for finite n

$$u_B = \langle v_B \rangle - \frac{n}{2} = o(n). \tag{2.1}$$

For $\beta < \beta_c(\alpha) u_B$ should be linear in n (to leading order) and should be negative. Hence u_B is a suitable order parameter in this regime. We expect that

$$u_B \sim n^{\phi} f[(\beta - \beta_c(\alpha)) n^{\phi}] \tag{2.2}$$

for some function f, so that if we plot u_B/n^{ϕ} against $(\beta - \beta_c(\alpha))n^{\phi}$ we should see data collapse for suitably chosen values of ϕ and $\beta_c(\alpha)$.

3. The alternating case

To check the validity of this procedure we first applied it to the case where the colouring is alternating $ABAB\cdots$ or $BABA\cdots$. For this case the problem can be solved exactly by combinatorial methods. Let $G_{AA}(a, b, z)$ be the generating function for bilateral Motzkin paths starting and ending with an A vertex and with the colouring being strictly alternating. Define G_{AB}, G_{BA} and G_{BB} in a similar way. The variables a and b are conjugate to v_A, the number of vertices coloured A with positive y-coordinate, and to v_B, the number of vertices coloured B with negative y-coordinate, respectively, and z is conjugate to n. That is, $a = e^{\alpha}$ and $b = e^{\beta}$. Let $M_o(z)$ count Motzkin paths with an odd number of edges and let $M_e(z)$ count Motzkin paths with an even number of edges, so that

$$M_o = \frac{\sqrt{1+2z-3z^2} - \sqrt{1-2z-3z^2} - 2z}{4z^2} \tag{3.1}$$

and

$$M_e = \frac{2 - \sqrt{1-2z-3z^2} - \sqrt{1+2z-3z^2}}{4z^2}. \tag{3.2}$$

A factorization argument gives the following simultaneous equations:

$$\begin{aligned} G_{AA} = \frac{1}{1-z^2}\big[1 + z^2\big(&M^{(a)}_{BA}G_{BA} + M^{(a)}_{BB}G_{AA} + bM^{(b)}_{BA}G_{BA} + bM^{(b)}_{BB}G_{AA}\big) \\ &+ z^3\big(aM^{(a)}_{AA}G_{BA} + aM^{(a)}_{AB}G_{AA} + M^{(b)}_{AA}G_{BA} + M^{(b)}_{AB}G_{AA}\big)\big] \end{aligned} \tag{3.3}$$

and

$$\begin{aligned} G_{BA} = \frac{1}{1-z^2}\big[z\big(1 + z^2\big(&M^{(a)}_{BA}G_{BA} + M^{(a)}_{BB}G_{AA} + bM^{(b)}_{BA}G_{BA} + bM^{(b)}_{BB}G_{AA}\big)\big) \\ &+ z^2\big(aM^{(a)}_{AA}G_{BA} + aM^{(a)}_{AB}G_{AA} + M^{(b)}_{AA}G_{BA} + M^{(b)}_{AB}G_{AA}\big)\big], \end{aligned} \tag{3.4}$$

where

$$\begin{aligned} M^{(a)}_{AA} &= M^{(a)}_{BB} = M_e(z\sqrt{a}) & M^{(b)}_{AA} &= M^{(b)}_{BB} = M_e(z\sqrt{b}) \\ M^{(a)}_{AB} &= M_o(z\sqrt{a})/\sqrt{a} & M^{(b)}_{AB} &= \sqrt{b}M_o(z\sqrt{b}) \\ M^{(a)}_{BA} &= \sqrt{a}M_o(z\sqrt{a}) & M^{(b)}_{BA} &= M_o(z\sqrt{b})/\sqrt{b}. \end{aligned} \tag{3.5}$$

There is a similar pair of simultaneous equations relating G_{BB} and G_{AB}.

All four of the generating functions G_{AA}, G_{BB}, G_{AB} and G_{BA} have the same three physically relevant singularities $z_1 = 1/(3\sqrt{a}), z_2 = 1/(3\sqrt{b})$ and a third singularity, z_3 which is a complicated function of a and b. When z_1 is dominant the system is delocalized into the positive half-space and the free energy is $\log 3 + \alpha/2$. When z_2 is dominant the system is delocalized into the negative half-space and the free energy is $\log 3 + \beta/2$, while when z_3 is dominant the system is localized and the free energy is greater than $\max[\log 3 + \alpha/2, \log 3 + \beta/2]$. The phase boundaries between the localized and delocalized phases are the solutions of the equations $z_1 = z_3$ and $z_2 = z_3$. We have calculated the value of $\beta_c(\alpha)$ for $\alpha = -3$ as the appropriate solution of $z_2 = z_3$, and we find that $\beta_c(-3) = -0.556\ldots$. The crossover exponent for this transition is $1/2$. In figure 2 we show the scaling behaviour derived from our Monte Carlo data for this problem. The agreement with the exact values is excellent.

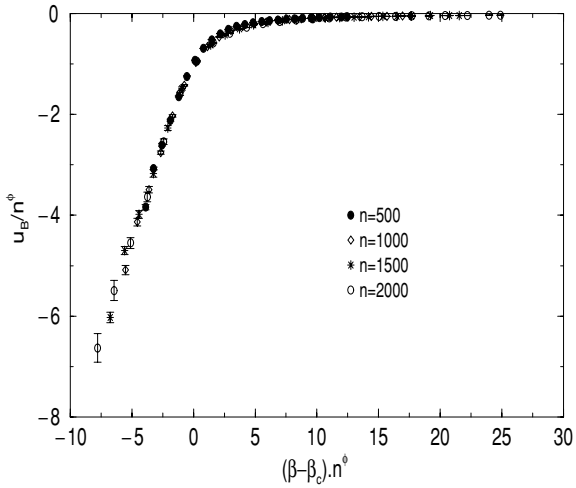

Figure 2. The behaviour of the scaled energy for the strictly alternating case when $\alpha = -3$, with $\phi = 1/2$ and $\beta_c = -0.556$.

4. The random case: third quadrant

We now turn to the random case, where we are interested in quenched averages. For this case we have estimated β_c by exactly enumerating the directed paths for $n \leqslant 20$, keeping track of which vertices have positive y-coordinate and which have negative y-coordinate. We carried out a complete quench (i.e., we computed the quenched average free energy exactly) for these values of n and used series analysis techniques to estimate the limiting ($n \to \infty$) quenched average free energy for various values of (α, β) in the third quadrant.

The quenched free energy κ_n is calculated for a fixed (α, β) point for $n \leqslant 20$. We assume that $e^{n\kappa_n} = An^{\gamma-1}\, e^{n\kappa}\left(1 + \frac{a}{n} + \frac{b}{n^2} + \cdots\right)$ where κ is the infinite n limit of the free energy, which implies that

$$\kappa_n = \frac{\log A}{n} + (\gamma - 1)\frac{\log n}{n} + \kappa + \frac{\log\left(1 + \frac{a}{n} + \frac{b}{n^2} + \cdots\right)}{n}. \tag{4.1}$$

Successive values of κ_n and κ_{n-1} are combined to give

$$L_n = \frac{n\kappa_n \log(n-1) - (n-1)\kappa_{n-1}\log n}{n\log(n-1) - (n-1)\log n} \tag{4.2}$$

and the assumption in (4.1) then gives

$$L_n = \kappa + \log A \left[\frac{\frac{1}{\log n} - \frac{1}{\log n - 1}}{\frac{n}{\log n} - \frac{n-1}{\log(n-1)}}\right] \tag{4.3}$$

plus higher order terms. Graphical analysis of L_n plotted against

$$\frac{\frac{1}{\log n} - \frac{1}{\log n - 1}}{\frac{n}{\log n} - \frac{n-1}{\log(n-1)}}$$

(the transformed n coordinate) allows for the estimation of κ and the easy comparison of the value of κ with the predicted value for the delocalized phase (e.g. $\log 3 + \beta/2$ for $\alpha < 0$).

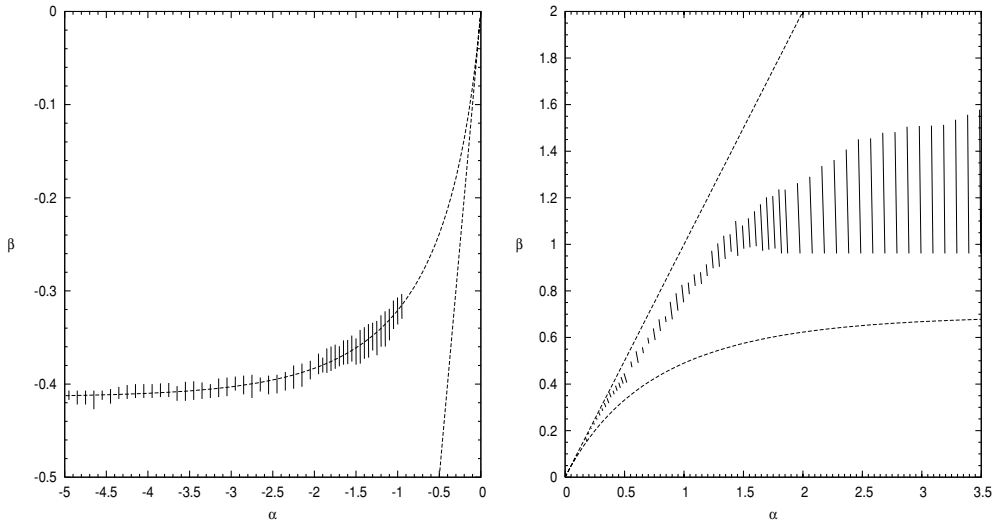

Figure 3. The locations of the phase boundaries as estimated by exact enumeration and series analysis. Note that the scales are different in the two quadrants. The dashed curves are the bounds obtained from a partial annealing argument. In each case the straight line is the line $\beta = \alpha$ which is also a bound on the phase boundary.

We used this approach to estimate $\beta_c(\alpha)$ for a variety of values of $\alpha < 0$, and specifically for $\beta_c(-3)$. We found that $-0.38 \geqslant \beta_c(-3) \geqslant -0.42$. The estimated phase boundary (in the fifth octant) is shown in figure 3, together with the upper bound on the phase boundary which results from the partial annealing treatment [10]. We do not give estimates of $\beta_c(\alpha)$ for α greater than about -1 because, although we can carry out the complete quench there, we are unable to obtain reliable estimates from the series analysis.

We repeated the Monte Carlo procedure for the quenched average case at $\alpha = -3$, and estimated the values of ϕ and β_c by examining the scaling of the Monte Carlo data. When we plot the fluctuation quantity $\langle v_B^2 \rangle - \langle v_B \rangle^2$ against β we see peaks which grow more rapidly than linearly as n increases. This strongly suggests a second order transition with $\phi \geqslant 1/2$. The results for the scaling form with the best values that we could find for β_c and ϕ are shown in figure 4. In the same figure we show the corresponding data for the y-component of the end point of the walk, y_{end}. In the delocalized phase $y_{\mathrm{end}} \sim n^{1/2}$ and we expect the scaling form to be

$$y_{\mathrm{end}} \sim n^{1/2} h[(\beta - \beta_c) n^{\phi}] \tag{4.4}$$

for some suitable function h. We also show the data plotted in this way in figure 4. We estimate that $\beta_c(-3) = -0.40 \pm 0.01$ and $\phi = 0.50 \pm 0.01$. This value of β_c is consistent with our series analysis estimate. Although we cannot calculate the value of β_c exactly we can get an upper bound on this value by a calculation using the Morita approximation [9, 10]. The value we obtained is $\beta_c(-3) \leqslant -0.403$ so the Morita bound is an excellent approximation to the value that we estimate for the quenched problem.

5. The random case: first quadrant

We have used series analysis techniques to estimate $\beta_c(3)$ using the exact values for the quenched average free energy for small n. The series analysis was similar to that described in

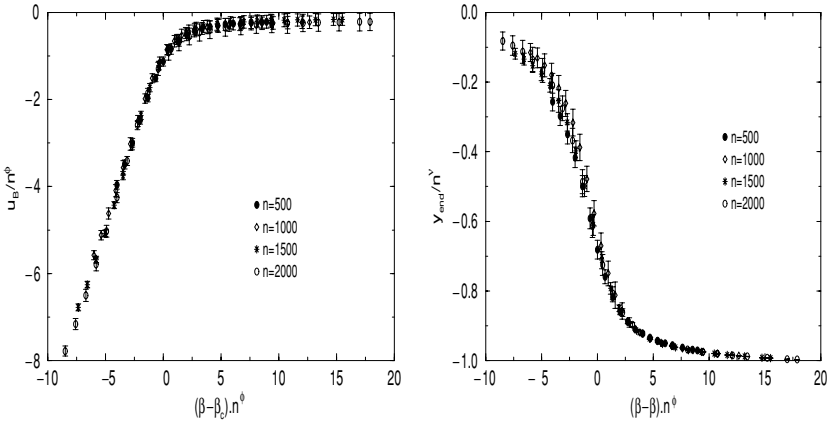

Figure 4. The scaled energy and the scaled y-component of the end point for the random case with $\alpha = -3$. The scaling is for $\phi = 0.5$ and $\beta_c = -0.4$.

the previous section. We show our estimates for the location of the phase boundary in the first octant in figure 3. Estimates of the upper bound on $\beta_c(\alpha)$ are generally easier to determine than lower bounds, but monotonicity of $\beta_c(\alpha)$ in α means that the lower bound (established with reasonable confidence), $\beta_c(1.82) \geqslant 0.96$, may be extended for all $\alpha > 1.82$. For $\alpha = 3$ we estimate that $0.96 \leqslant \beta_c(3) \leqslant 1.4$.

We have calculated the fluctuations in v_B for large values of n using the Monte Carlo approach described earlier. When we plot $\langle v_B^2 \rangle - \langle v_B \rangle^2$ against β at $\alpha = 3$, we see no evidence for peaks in the range $0 \leqslant \beta \leqslant 1.5$, suggesting that the transition is higher than second order. This is consistent with a value of $\phi < 1/2$.

When we try to carry out a scaling analysis on our Monte Carlo data for the first quadrant of the (α, β)-plane, the situation regarding the order parameter is slightly different because $\lim_{n\to\infty} \langle v_B \rangle / n = 0$ for $\beta < \beta_c(\alpha)$. Consequently we can use $u_B/n \equiv \langle v_B \rangle / n$ as an order parameter and we expect (2.2) to be an appropriate scaling form for this new definition of u_B.

We have tried to find values of ϕ and $\beta_c(3)$ which give the best agreement between (2.2) and our Monte Carlo data. This gives a rather large possible range of values, perhaps because of the large error bars at large values of β. For values in the range $0.35 \leqslant \phi \leqslant 0.45$ and $0.92 \leqslant \beta_c(3) \leqslant 1.0$ we obtain a χ^2 value (per degree of freedom) which is less than 0.5, so all these values give a reasonable fit to the data. In figure 5 we plot u_B/n^ϕ against $(\beta - \beta_c)n^\phi$ for the values of ϕ and $\beta_c(3)$ which give the best data collapse, i.e., $\phi = 0.42$ and $\beta_c(3) = 0.98$, and we show the scaling of the metric quantity $y_{\text{end}}/n^{1/2}$ in the same figure. The scaling of y_{end} is not especially good at large β and it is not clear if this is due to corrections to scaling which are important at these values of n, or to other factors. We estimate that $\phi = 0.42 \pm 0.04$ and $\beta_c(3) = 0.98 \pm 0.03$. The value of $\beta_c(3)$ estimated in this way agrees quite well with the value obtained by exact enumeration and series analysis. The bound obtained from a Morita calculation is $\beta_c(3) \geqslant 0.668$ and it is easy to see that $\beta_c(3) \leqslant 3$. While our estimate of $\beta_c(3)$ is consistent with these bounds, the Morita calculation does not give a good numerical estimate of the quenched critical point in this region.

6. Discussion

We have investigated a bilateral Motzkin path model of localization of a copolymer at an interface between two immiscible liquids. For the case where the sequence of co-monomers

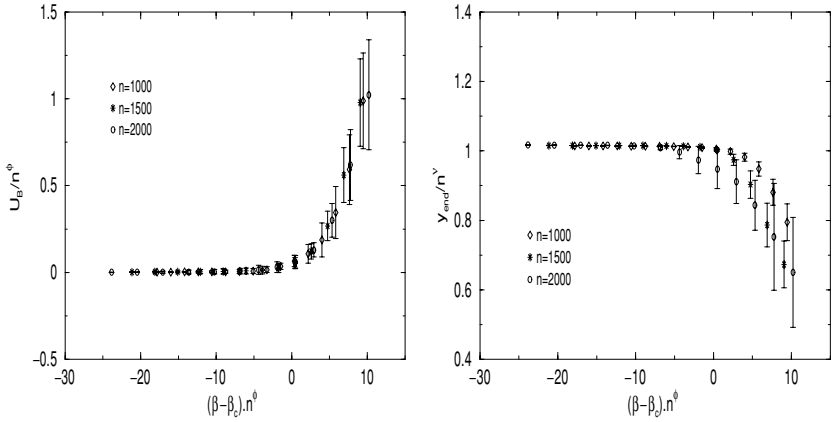

Figure 5. The scaled energy and the scaled y-component of the end point for the random case with $\alpha = 3$. The scaling is for $\nu = 0.5$, $\phi = 0.42$ and $\beta_c = 0.98$.

is strictly alternating ($ABABAB\cdots$) we have solved the model exactly using combinatorial techniques. For the quenched random case (where the probability of each monomer is equal) we have investigated the locations and shapes of the phase boundaries by exact enumeration methods with a complete quench over all monomer sequences. Series analysis methods yielded estimates of the phase boundaries, which can be compared with bounds on the locations of the phase boundaries obtained by partial annealing [9, 10]. We found that the bound is a close approximation to the actual phase boundary in the third quadrant but not in the first. We suspect that this is connected with the fact that in the first quadrant the bound is insensitive to the underlying configurational model, being identical to that for a self-avoiding walk model [7].

In order to investigate the order of the phase transition we have used Monte Carlo methods and fitted our data to a finite size scaling form. We checked this approach by comparing the exact values for the strictly alternating case. For the random case we found good agreement between the location of the phase boundary estimated by Monte Carlo and by exact enumeration with series analysis. We also estimated the crossover exponent ϕ and this seems to differ between the two quadrants. The phase transition seems to be of second order in the third quadrant but higher than the second order in the first quadrant, which agrees with earlier results for a self-avoiding walk model [8]. The difference in values of the crossover exponent may be due to the special role of the interface in the third quadrant where vertices are being pushed out of a phase. The interface is not unfavourable for either type of the vertex, and in this sense the problem resembles adsorption at a penetrable surface, for which the crossover exponent for bilateral Motzkin paths is $1/2$. Randomness plays a more decisive role in the first quadrant, which may lead to the different crossover exponent.

Acknowledgment

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