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LETTER TO THE EDITOR

A Monte Carlo investigation of the localization transition in random copolymers at an interface

Maria Serena Causo[1] **and Stuart G Whittington**[2]

[1] Dipartimento di Fisica, Università di Roma 'La Sapienza', I-00185 Roma, Italy
[2] Department of Chemistry, University of Toronto, Toronto, Canada M5S 3H6

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Abstract

We have used Markov chain Monte Carlo methods to study the nature of the phase transition in a self-avoiding walk model of localization of a random copolymer at an interface between two immiscible solvents. We present evidence that the order of the phase transition is different in different regions of the phase diagram.

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Random copolymers are polymers with at least two kinds of monomer which are distributed at random along the polymer chain. We shall be concerned here with linear polymers having two kinds of monomer which we call A and B. For a polymer with n monomers we label the monomers $i = 1, 2, \ldots n$ and write $\chi_i = A$ if the ith monomer is of type A and $\chi_i = B$ if the ith monomer is of type B. The χ_i are independent random variables and we write p for the probability that $\chi_i = A$.

This system is an interesting example of a system with quenched randomness (Brout 1959) since the sequence of monomers in a particular polymer molecule is determined by a random process but, once chosen, the sequence is fixed. Suppose we have two immiscible solvents α and β and suppose that it is energetically favourable for A monomers to be in solvent α and for B monomers to be in solvent β. Then the system can show interesting localization behaviour (Sinai and Spohn 1996, Bolthausen and den Hollander 1997, Biskup and den Hollander 1999, Maritan *et al* 1999, Martin *et al* 2000). At high temperatures the polymer will pick the energetically most favourable solvent and delocalize into that phase. At low temperatures it will arrange itself at and near the interface to optimize the numbers of monomers in their prefered solvent.

The model which we shall discuss here was first introduced by Martin *et al* (2000). The polymer is modelled as an n-edge self-avoiding walk on the simple cubic lattice Z^3, starting at the origin. The vertices of the walk are numbered $i = 0, 1, 2, \ldots n$ and vertices $1, 2, \ldots n$ are randomly and independently coloured A or B. The region of the lattice with $z > 0$ corresponds to the α solvent, the region with $z < 0$ corresponds to the β solvent and the plane $z = 0$ is the interfacial plane. If a vertex coloured A has positive z-coordinate it contributes a reduced

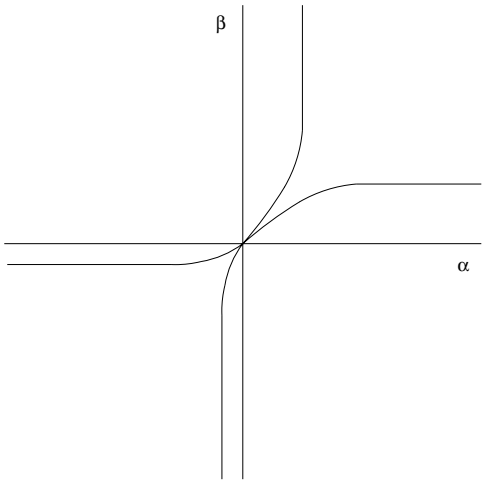

Figure 1. Sketch of phase diagram when $p = 1/2$. In the second and the fourth quadrants the polymer is delocalized into the β and α solvents, respectively. The full curves are phase boundaries corresponding to localization and the quenched average free energy is singular along these curves.

energy α and if a vertex coloured B has negative z-coordinate it contributes a reduced energy β. Vertices in the interfacial plane $z = 0$ make no contribution to the energy. Write χ as shorthand for $\{\chi_1, \chi_2, \ldots \chi_n\}$. Given the colouring χ suppose that $c_n(v_A, v_B|\chi)$ is the number of n-edge self-avoiding walks with v_A A-vertices having positive z-coordinate and v_B B-vertices having negative z-coordinate. Then the partition function is

$$Z_n(\alpha, \beta|\chi) = \sum_{v_A, v_B} c_n(v_A, v_B|\chi)\, \mathrm{e}^{\alpha v_A + \beta v_B} \tag{1}$$

and the associated free energy is

$$\kappa_n(\alpha, \beta|\chi) = n^{-1} \log Z_n(\alpha, \beta|\chi). \tag{2}$$

Martin *et al* (2000) proved the existence of the limiting quenched average free energy

$$\bar{\kappa}(\alpha, \beta) = \lim_{n\to\infty} \langle \kappa_n(\alpha, \beta|\chi)\rangle \tag{3}$$

where the angle brackets denote an average over colourings. They showed that in the second quadrant of the (α, β)-plane, $\alpha < 0, \beta > 0, \bar{\kappa}(\alpha, \beta) = \kappa_3 + (1 - p)\beta$ and in the fourth quadrant $\bar{\kappa}(\alpha, \beta) = \kappa_3 + p\alpha$, where p is the probability that a monomer is an A-monomer and κ_3 is the connective constant of the simple cubic lattice. These values correspond to the polymer being delocalized into the β and α phases, respectively, and show that the free energy is not differentiable at the origin along lines such as $\beta = -\alpha$. They also showed that the free energy is singular along certain curves in the first and third quadrants of the (α, β)-plane, corresponding to the localization transition, and that these phase boundaries have horizontal and vertical asymptotes. The locations of the phase boundaries were estimated by exact enumeration and series analysis methods. See figure 1 for a sketch of the expected phase diagram when $p = 1/2$.

Although we have quite a lot of qualitative information about the nature of the phase diagram, and a rough idea of the locations of the phase boundaries, nothing seems to be known about the nature of the phase transitions between the localized and delocalized phases. The purpose of this letter is to report a Monte Carlo investigation of the nature of these phase transitions.

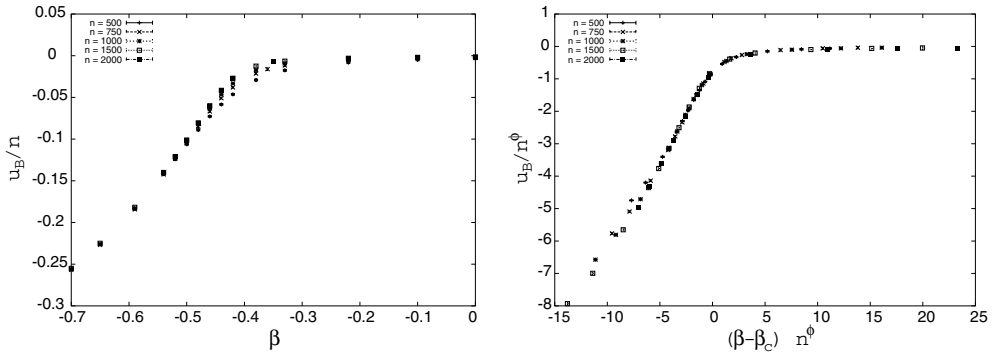

Figure 2. Dependence of u_B/n on β and n when $\alpha = -3$ (left) and collapse of data obtained for $\phi = 0.53$ and $\beta_c = -0.414$ (right).

The system is strongly interacting and, to mitigate quasi-ergodic problems, we have used a Monte Carlo scheme which samples at different values of the parameters α and β simultaneously, with swapping of configurations between different parameter values. This approach, originally invented by Geyer (1991), has been shown to be very effective in strongly interacting polymer problems (see, e.g., Tesi *et al* (1996)). One constructs a set of Markov chains, each operating at a particular pair of values of α and β, with limit distribution given by the appropriate Boltzmann factor, and designs swapping probabilities that ensure that the limit distribution of the process is the product of the limit distributions of the individual Markov chains: see Tesi *et al* (1996) for technical details. The individual Markov chains still need to be carefully designed and we used a mixture of non-local moves (Lal 1969, Madras and Sokal 1988, Causo 2002) and local moves (Verdier and Stockmayer 1962). The proportion of attempted local and non-local moves was varied in different parts of the (α, β)-plane to improve the convergence rate of the Markov chains.

We investigated the nature of the phase transition in the third quadrant ($\alpha, \beta < 0$) when $p = 1/2$ by fixing the value of $\alpha = -3$ and estimating the values of thermodynamic and metric quantities for $0 \geqslant \beta \geqslant -0.7$. This involved constructing a set of Markov chains including values from (0, 0) along the α-axis to $(-3, 0)$ and at a set of β values with α fixed at -3. Estimates were obtained for various values of n up to $n = 2000$. With n, α, β and χ fixed, let $v_B(\alpha, \beta|\chi)$ be the expectation (over the set of walks with fixed colouring) of the number of vertices coloured B which have negative z-coordinate. Let $B(\chi)$ be the total number of vertices coloured B. Define

$$u_B = \langle v_B(\alpha, \beta|\chi)\rangle - \langle B(\chi)\rangle \tag{4}$$

where $\langle\cdots\rangle$ denotes the average over χ. The observable u_B is defined in such a way that $u_B = o(n)$ when the walk is delocalized into the β solvent (and in particular when $\alpha < 0$ and $\beta > 0$). When the value of β is decreased to a value below the phase boundary, $\beta < \beta_c(\alpha)$, the number of B vertices with non-negative z-coordinate increases linearly with n while exactly on the phase boundary ($\beta = \beta_c(\alpha)$) we expect that $u_B \sim n^\phi$, with $\phi \leqslant 1$. One can look at u_B/n as the order parameter, which is non-vanishing (in the infinite n limit) only in the localized phase. The overall crossover scaling behaviour of the order parameter is expected to be

$$u_B/n \sim n^{\phi-1} f[(\beta - \beta_c)n^\phi] \tag{5}$$

where $f(x)$ is a scaling function such that $f(0) = \text{const} \neq 0$ and $f(x) \sim |x|^{-1+\frac{1}{\phi}}$ for $x \to -\infty$ and $f(x) \to 0$ for $x \to \infty$. Figure 2 (left) shows the β-dependence of u_B/n for

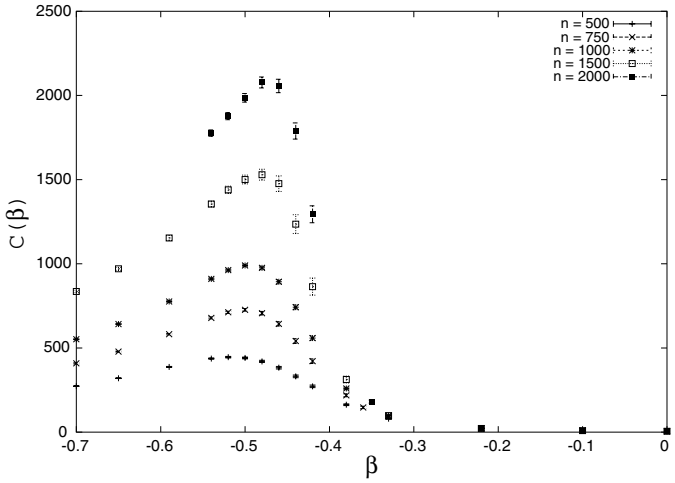

Figure 3. Dependence of the extensive heat capacity on β and n.

various values of n from $n = 500$ to $n = 2000$. There is clear evidence of strong corrections to scaling around $\beta = -0.4$, where the crossover between the localized and delocalized regimes takes place. For $\beta \gg -0.4$ the curve is close to 0, corresponding to delocalization into the β-solvent. Figure 2 (right) shows the best collapse on a single curve obtained by fitting all data with $n > 500$ and $-0.55 \leqslant \beta \leqslant -0.30$ to a polynomial of degree 4 in the scaling variable. The degree of the polynomial was chosen so that the results were compatible (within error bars) with those obtained by fitting to higher degree polynomials. We did not include data for $n = 500$ because they are subject to large corrections-to-scaling. Indeed, we found that our results from data with $n \geqslant n_{\min}$, for different values of $n_{\min}$, were compatible within error bars only for those $n_{\min} > 500$. We only considered β values less than or equal to -0.30 so as to focus on values where the order parameter is non-zero. We tried fitting with a variety of minimum values for β and eventually chose $\beta_{\min} = -0.55$ as the lowest value for which the results of the fits were compatible within error bars.

The best fit corresponds to $\phi = 0.53$ and $\beta_c = -0.414$. Defining the range of variability of ϕ (resp. β_c) as the interval including all ϕ (resp. β_c) values for which some value of β_c (resp. ϕ) was found for which data could be fitted with a χ^2 per degree of freedom less than 1, we estimate $0.52 \leqslant \phi \leqslant 0.56$ and $-0.42 \leqslant \beta_c \leqslant -0.41$. As we increased the minimum value of n considered, the best value obtained for ϕ decreased, reaching $\phi = 0.49$ when we included only $n = 1500$ and 2000, while the best estimate for β_c increased to $\beta_c = -0.39$. At the same time the range of variability broadened both for β_c and ϕ.

We would expect peaks in the extensive heat capacity which grow as $n^{2\phi}$ as n increases. Figure 3 shows the extensive heat capacity $C(\beta) = \frac{\partial u_B}{\partial \beta}$ as a function of β at $\alpha = -3$ for various values of n. We clearly see peaks whose positions shift and whose heights grow slightly faster than linearly as n increases. It is difficult to estimate ϕ from the scaling of the peak heights (when ϕ is close to $1/2$) but our best estimate is $\phi = 0.53 \pm 0.02$. Alternatively, assuming that $\phi = 1/2$, we have determined the location of the transition from the way the locations of the maxima change with n and estimated $\beta_c = -0.42 \pm 0.05$, consistent with our estimates from fitting to the assumed scaling form given above, but with much higher uncertainty. Changing the assumed value of the crossover exponent to $\phi = 0.53$ makes only a small difference (about one error bar) to the estimated value of β_c.

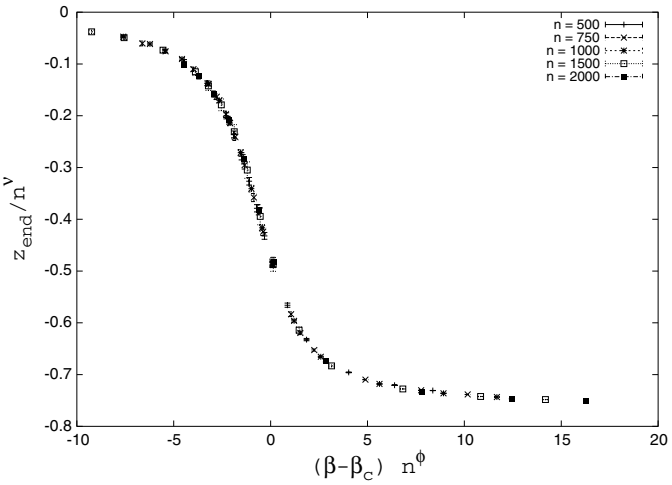

Figure 4. Collapse of data for z_{end} obtained with $\phi = 0.48$ and $\beta_c = -0.424$.

We have also estimated the expected value of the z-component of the end point of the walk, $z_{\text{end}}(n, \beta)$. By analogy with what is known about the scaling of metric properties at the special point (see, e.g., Diehl *et al* (1998)), we expect that

$$z_{\text{end}}(n, \beta) \sim n^{\nu} h[(\beta - \beta_c)n^{\phi}] \tag{6}$$

where $h(x)$ is a scaling function such that $h(0) = \text{const} \neq 0$, $h(x) \to 0$ for $x \to -\infty$, and $h(x) \to \text{const} \neq 0$ for $x \to \infty$. In order to find the best scaling form for our data, we have performed the same kind of analysis as for u_B and tried to fit our rescaled data to a sixth degree polynomial in the scaling variable. Results seem to be less sensitive to corrections-to-scaling, so that we could consider all data with $n \geqslant 500$ and $-0.60 \leqslant \beta \leqslant -0.29$. From the best fit we have obtained $\phi = 0.48$ and $\beta_c = -0.424$, but with a very large range of variability. Indeed, the range of variability was such that we estimate $0.45 \leqslant \phi \leqslant 0.55$ and $-0.43 \leqslant \beta_c \leqslant -0.40$. The best rescaling for all available n values is shown in figure 4. Our estimates for the exponent ϕ are close to the value found for adsorption at an impenetrable surface by Hegger *et al* (1994). This was not unexpected, since Martin *et al* (2000) showed that there is a connection between the localization problem in the third quadrant and adsorption at an impenetrable surface.

We now turn our attention to the phase boundary in the first quadrant. For $\alpha = 3$, we have estimated the values of several thermodynamic and metric quantities as a function of β and n, for $n = 500, 1000, 1500, 2000$ and $0 \leqslant \beta \leqslant 1.7$. From the work of Martin *et al* (2000) we know rigorously that there is a phase boundary in this quadrant (i.e. there is a curve in the quadrant where the quenched average free energy is singular) and Martin *et al* (2000) gave a rough estimate of the location of the phase boundary based on exact enumeration and series analysis techniques, and estimated that $\beta_c(3)$ is about 1. Surprisingly we found no evidence of peaks in the heat capacity for values of β between zero and 2, which suggested that the exponent ϕ could be less than $1/2$. In this region of the phase diagram, we can define as order parameter $u_B/n = \langle v_B(\alpha, \beta|\chi)\rangle/n$. It is a simple matter to see that, for $n \to \infty$, u_B/n is non-zero only in the localized phase. The scaling relations in equations (5) and (6) still hold, but the asymptotic behaviour is now 'reversed', $f(x) \sim |x|^{-1+\frac{1}{\phi}}$ for $x \to +\infty$ and $f(x) \to 0$ for $x \to -\infty$, $h(x) \to 0$ for $x \to +\infty$ and $h(x) \to \text{const}$ for $x \to -\infty$. Therefore, we were able to estimate β_c and ϕ by performing

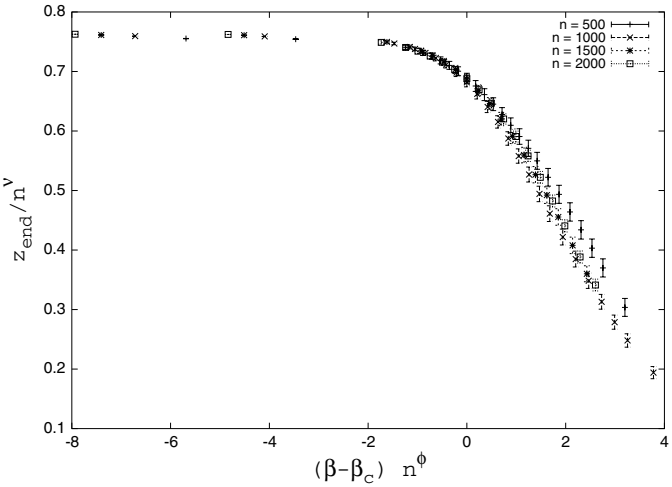

Figure 5. Data for $z_{\rm end}(n, \beta)$ at different values of n and β, rescaled as in equation (6) with $\beta_c = 1.28$ and $\phi = 0.24$.

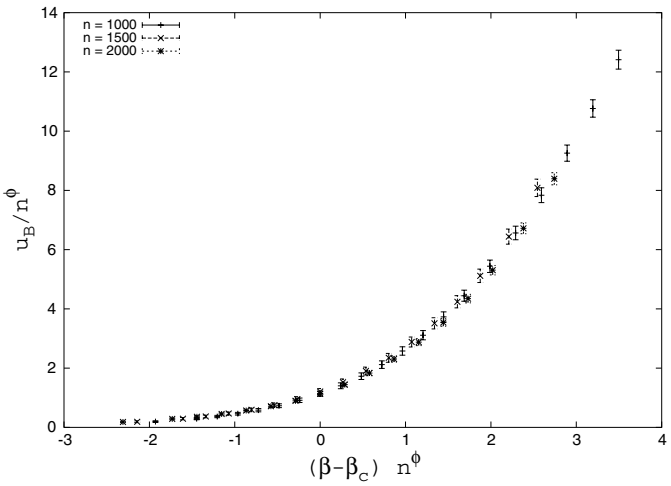

Figure 6. Data for $u_B = v_B$ at different values of n and β, rescaled as in equation (5) with $\beta_c = 1.32$ and $\phi = 0.26$.

the same kind of scaling analysis as for $\alpha = -3$. We fitted our data for the metric quantity $z_{\rm end}(n, \beta)$ to a polynomial of fourth degree in the scaling variable $(\beta - \beta_c)n^{\phi}$. Error bars on our data were larger than in the third quadrant. Therefore results were less sensitive to changes in β_c and ϕ and, including data for all n values, we estimate $1.24 \leqslant \beta_c \leqslant 1.32$ and $0.20 \leqslant \phi \leqslant 0.30$. Figure 5 shows the collapse of our data with the best estimates $\phi = 0.24$ and $\beta_c = 1.28$. We analysed our data for u_B in the same way. They seemed to be more affected by corrections to scaling, so that we did not find a fitting form with χ^2 per degree of freedom less than 1 including values for the lower value of n. Disregarding data for $n = 500$, we obtained as best estimates $\beta_c = 1.32$ and $\phi = 0.26$, with a range of variability $0.24 \leqslant \phi \leqslant 0.30$ and $1.28 \leqslant \beta_c \leqslant 1.4$. Figure 6 shows the best rescaling for $n \geqslant 1000$. From our analysis we can conclude that at $\alpha = 3$ the localization transition takes place for $1.24 \leqslant \beta_c \leqslant 1.4$ with

exponent $0.2 \leqslant \phi \leqslant 0.3$. Therefore our data indicate that the free energy is at least twice differentiable and the localization transition in the first quadrant is higher than second order. Although we have not attempted to find the location at which the transition switches from second to higher order, the origin seems to be a good candidate.

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