

A Monte Carlo study of polymer adsorption: random copolymers and random surfaces

Maria Sabaye Moghaddam and Stuart G Whittington

Department of Chemistry, University of Toronto, Toronto, Canada M5S 3H6

Received 26 September 2001

Published 21 December 2001

Online at stacks.iop.org/JPhysA/35/33

Abstract

We consider a model of random copolymer adsorption in which an n -edge self-avoiding walk in three dimensions interacts with a plane defining a half-space to which the walk is confined. Each vertex of the walk is randomly labelled A with probability p or B with probability $1 - p$, and only vertices labelled A are attracted to the surface plane. The system is quenched, i.e. the labelling is fixed and then the thermodynamic properties are computed. We use Monte Carlo methods to investigate the behaviour of this system. We observe self-averaging of the energy as n increases, and investigate the location of the adsorption transition for various values of p . In addition, we compare the behaviour of this system with that of a homopolymer adsorbing at a randomly heterogeneous surface consisting of two types of sites, only one of which interacts with the monomers of the polymer.

PACS numbers: 05.50.+q, 82.70.-y

1. Introduction

The adsorption of homopolymers at an impenetrable surface is a well-studied problem and one of the useful models is a self-avoiding walk on a lattice, confined to a half-space and interacting with the confining plane (see, e.g., Hammersley *et al* 1982, De'Bell and Lookman 1993, Hegger and Grassberger 1994). This model is known to have a phase transition (in the thermodynamic limit) corresponding to adsorption.

Much less is known about copolymer adsorption (in which only one of two comonomers interacts with the surface, say), although the problem has been studied by several groups (Cosgrove *et al* 1990, Wang *et al* 1993, Joanny 1994, Sommer and Daoud 1995, Sommer *et al* 1996, Whittington 1998, Moghaddam *et al* 2000). In the case where the copolymer is random the most interesting case is *quenched randomness* where the sequence of comonomers is fixed during the computation of thermodynamic quantities, and the logarithm of the partition function is averaged over the quenched comonomer sequences. Grossberg *et al* (1994) have considered periodic quenched randomness, and the case of non-periodic quenched randomness

has been studied by several groups using a variety of techniques (Garel *et al* 1989, Guttman and Chakraborty 1994, 1995, Bolthausen and den Hollander 1997, Biskup and den Hollander 1999, Sumithra and Baumgaertner 1998, 1999, Orlandini *et al* 1999). In particular, for the self-avoiding walk model of adsorption of a quenched random copolymer, Orlandini *et al* (1999) proved that the system has a phase transition, and is thermodynamically self-averaging.

In this paper we use multiple Markov chain Monte Carlo methods to investigate the adsorption of a random copolymer at a homogeneous surface (section 2) and compare this behaviour with that of a homopolymer adsorbing at a randomly heterogeneous surface consisting of two kinds of sites, only one of which interacts with the monomers of the homopolymer (section 3). In section 4 we compare the Monte Carlo results for the quenched random copolymer and the quenched random surface with results for an annealed model (in which the partition function is averaged before the logarithm is taken to construct the free energy). Finally, in section 5 we discuss our results and point out some open questions and possible directions for further research.

2. Adsorption of a random copolymer

The model which we consider in this section is a particular case of that studied by Orlandini *et al* (1999). We consider an n -edge self-avoiding walk on the simple cubic lattice Z^3 . The vertices of the walk are numbered $i = 0, 1, \dots, n$ and we fix the 0th vertex at the origin. All vertices are constrained to have non-negative z -coordinate, and the plane $z = 0$ is the plane at which adsorption can occur. The vertices $i = 1, 2, \dots, n$ are randomly and independently labelled A or B such that the probability of a vertex being labelled A is p . Let $c_n(v_A|\chi)$ be the number of n -edge walks with these constraints, having a labelling χ , and having v_A vertices labelled A in the plane $z = 0$. The partition function for a fixed labelling is

$$Z_n(\alpha|\chi) = \sum_{v_A} c_n(v_A|\chi) e^{\alpha v_A} \quad (2.1)$$

and the quenched average free energy $\bar{\kappa}(\alpha)$ is

$$\bar{\kappa}(\alpha) = \lim_{n \rightarrow \infty} \langle n^{-1} \log Z_n(\alpha|\chi) \rangle \quad (2.2)$$

where $\langle \dots \rangle$ represents an average over the labellings χ . Of course, $\bar{\kappa}(\alpha)$ depends on the parameter p but we shall normally suppress this dependence in our notation. Orlandini *et al* (1999) showed that the limit exists in (2.2) for all $\alpha < \infty$ and that, for all $\alpha \leq 0$, $\bar{\kappa}(\alpha)$ is equal to $\bar{\kappa}(0) \equiv \kappa_3$, the connective constant of the simple cubic lattice. Define α_q such that

$$\alpha_q = \max[\alpha | \bar{\kappa}(\alpha) = \bar{\kappa}(0)] \quad (2.3)$$

so that α_q is a singular point of $\bar{\kappa}(\alpha)$. The walk is desorbed for all $\alpha < \alpha_q$ and adsorbed for all $\alpha > \alpha_q$. Since α_q is at least as large as the corresponding critical value of α for homopolymer adsorption (all vertices coloured A) we know that α_q is strictly positive.

Although these results give interesting qualitative information about the temperature dependence of the free energy they say little about the location of the transition (and its dependence on composition) and nothing about the order of the transition. We have investigated these questions using Monte Carlo methods.

Since the system is strongly interacting we have used a multiple Markov chain approach in which one samples at a variety of different temperatures at the same time and ‘swaps’ configurations between different temperatures with swap probabilities chosen so that the limit distribution of the process is the product of the Boltzmann distributions at the individual temperatures. The method was originally invented by Geyer (1991) and was first used in

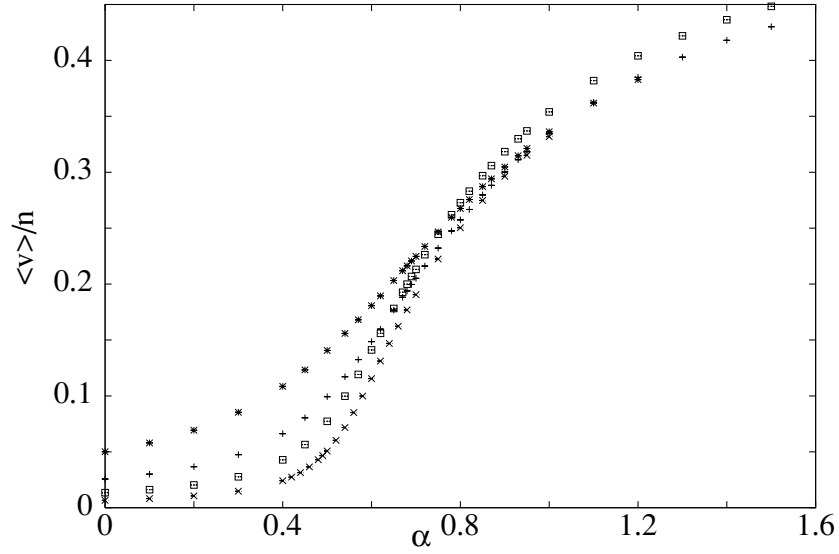


Figure 1. The mean number of A-vertices in the surface, per edge of the walk, for the random copolymer case, for $p = 1/2$, $n = 50$ (*), 100 (+), 200 (\square) and 400 (\times).

polymer statistical mechanics by Tesi *et al* (1996). Details can be found in those references. The underlying (symmetric) Markov chain used was a combination of the pivot algorithm (Lal 1969, Madras and Sokal 1988) and local moves (Verdier and Stockmayer 1962).

For any fixed value of p , $0 \leq p \leq 1$, the quenched average free energy for finite n , $\bar{\kappa}_n(\alpha)$, is given by

$$\bar{\kappa}_n(\alpha) = \sum_{j=1}^{2^n} p^{m_j} (1-p)^{n-m_j} n^{-1} \log Z_n(\alpha | \chi_j) \quad (2.4)$$

where χ_j is the j th labelling, m_j is the number of vertices labelled A in this labelling, and the sum is over the 2^n possible labellings. Differentiating with respect to α gives the quenched average energy per edge, i.e. the mean number of A vertices in the surface divided by n . That is

$$\frac{\partial \bar{\kappa}_n(\alpha)}{\partial \alpha} = \sum_{j=1}^{2^n} p^{m_j} (1-p)^{n-m_j} n^{-1} \left[\frac{\sum_{v_A} v_A c_n(v_A | \chi_j) e^{\alpha v_A}}{\sum_{v_A} c_n(v_A | \chi_j) e^{\alpha v_A}} \right] = \frac{\langle v_A(\alpha) \rangle}{n} \quad (2.5)$$

where the final angular brackets represent an average over configurations at fixed labelling, followed by an average over labellings.

We have calculated $\langle v_A(\alpha) \rangle / n$ and the corresponding quenched average heat capacity

$$C_n(\alpha) = \partial^2 \bar{\kappa}_n(\alpha) / \partial \alpha^2 \quad (2.6)$$

for various values of n and α . In each case the energy and heat capacity were calculated for a fixed labelling (monomer sequence) and then averaged over about 40 different labellings. At larger values of n , fewer labellings were required, consistent with the fact that the system is thermodynamically self-averaging in the $n \rightarrow \infty$ limit. In figure 1 we show the α -dependence of $\langle v_A(\alpha) \rangle / n$ when $p = 1/2$, for $n = 50, 100, 200$ and 400. For small α the values of $\langle v_A(\alpha) \rangle / n$ are small, and decrease as n increases. The curves rise sharply over a small range of α values and the rise becomes steeper as n increases. Figure 2 shows the corresponding behaviour for

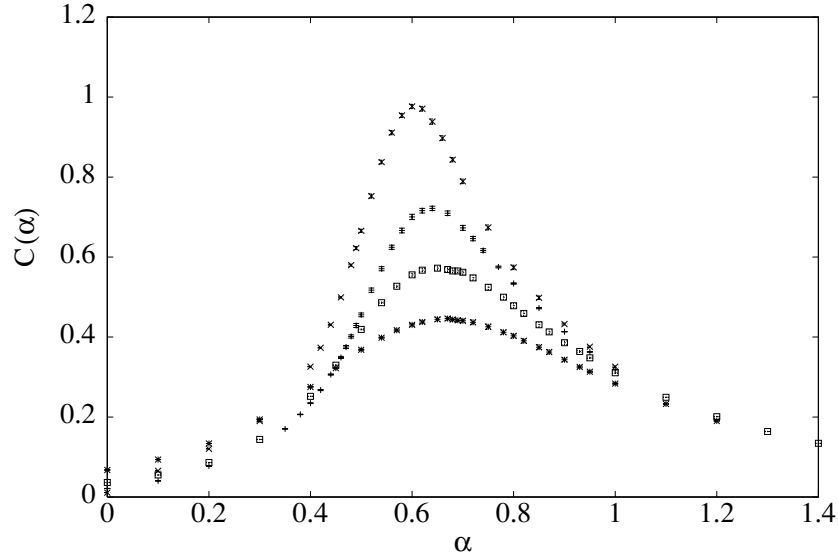


Figure 2. The heat capacity $C_n(\alpha)$ for the random copolymer case when $p = 1/2$, for $n = 50$ (*), 100 (\square), 200 (+) and 400 (\times).

$C_n(\alpha)$. The heat capacity peaks become higher and narrower as n increases, consistent with a second-order phase transition. We have checked this by examining histograms of the energy and see no evidence for a two-peaked distribution at any values of α . This is evidence that the adsorption transition is of second order as is believed to be the case for a homopolymer (De'Bell and Lookman 1993, Hegger and Grassberger 1994).

In figure 3 we show $\langle v_A(\alpha) \rangle / n$ at $n = 400$ for three values of p . As p increases the value of α at which $\langle v_A(\alpha) \rangle / n$ begins to increase rapidly (corresponding to a peak in the heat capacity) moves to smaller values of α as expected. $\langle v_A(\alpha) \rangle / n$ tends to p at large α , and so the height of the plateau increases as p increases.

We have plotted the locations of the heat capacity peaks, α_n , against $n^{-\phi}$ for various values of p and ϕ . For each value of p we obtain roughly linear behaviour for values of ϕ in the range $\phi = 0.5$ to 0.52 but we see no evidence that ϕ depends on p . It seems likely that ϕ retains the homopolymer value (about 0.5, Hegger and Grassberger (1994)) when randomness is introduced. However, our evidence for this is not very strong and further work on this question would be useful.

For this problem the free energy is known to be self-averaging in the $n \rightarrow \infty$ limit (Orlandini *et al* 1999), but this says little about the extent of self-averaging for finite values of n . To investigate this we have calculated the energy (averaged over conformations) at several fixed labellings. That is, we calculated

$$\langle v_A(\alpha|\chi) \rangle = \frac{\sum_{v_A} v_A c_n(v_A|\chi) e^{\alpha v_A}}{\sum_{v_A} c_n(v_A|\chi) e^{\alpha v_A}} \quad (2.7)$$

as a function of α and n for several fixed values of χ . With n and α fixed there will be a distribution of values of $\langle v_A(\alpha|\chi) \rangle$ and we can estimate the variance of this distribution as

$$V(\alpha, n) = (s-1)^{-1} \sum_{j=1}^s (\langle v_A(\alpha|\chi_j) \rangle - \overline{\langle v_A(\alpha|\chi_j) \rangle})^2 \quad (2.8)$$

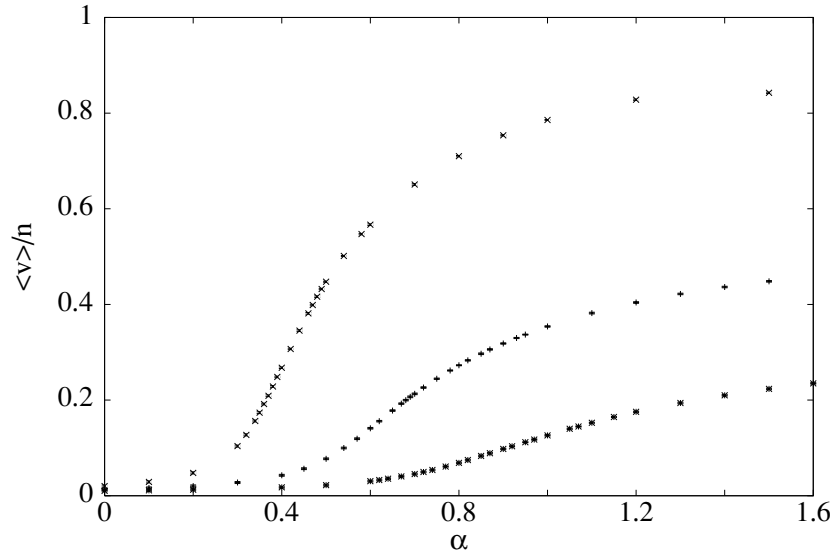


Figure 3. The α -dependence of $\langle v_A(\alpha) \rangle / n$ for the random copolymer case when $n = 400$ and $p = 0.3$ (*), 0.5 (+) and 0.9 (x).

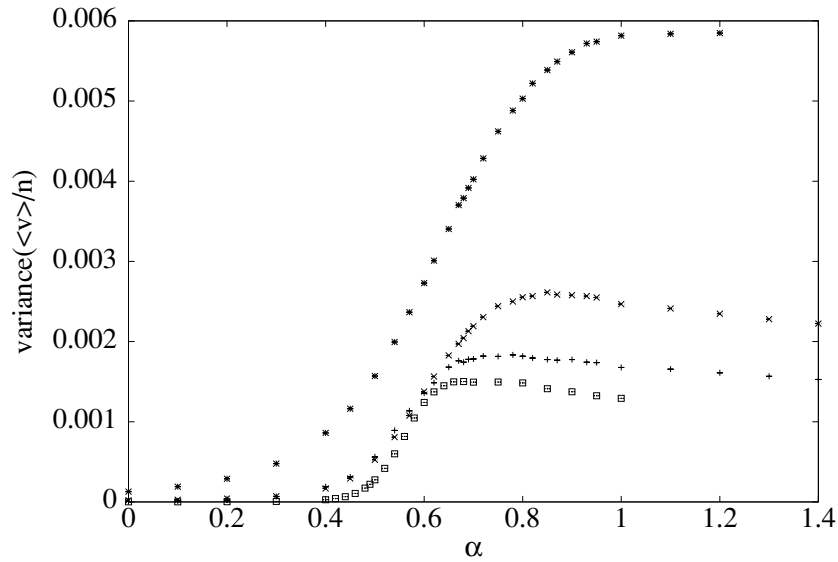


Figure 4. The α -dependence of the variance of $\langle v_A(\alpha|\chi) \rangle / n$ for the random copolymer for $n = 50$ (*), 100 (x), 200 (+) and 400 (\square).

where the sum runs over s randomly chosen labellings and the bar represents a sample average over labellings. In figure 4 we show the α -dependence of $V(\alpha, n)/n^2$, the estimated variance of $\langle v_A(\alpha|\chi) \rangle / n$, for various values of n . The self-averaging is rapid (i.e. the variance is small even for small values of n) at small values of α . At larger values of α , close to and beyond the adsorption transition, larger values of n are required before we see a reasonable degree of self-averaging.

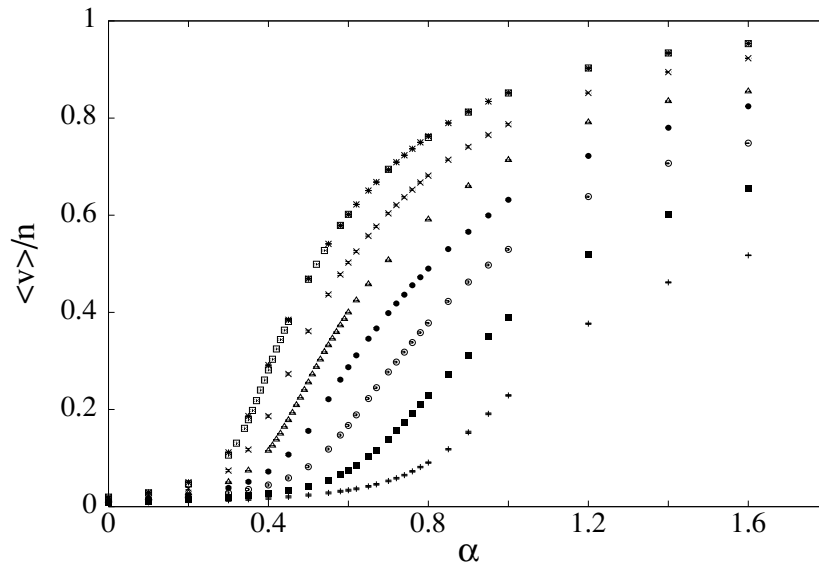


Figure 5. The α -dependence of $\langle v_A \rangle / n$ for the random surface case when $n = 200$ and $p = 0.3$ (+), 0.4 (■), 0.5 (○), 0.6 (●), 0.7 (△), 0.8 (×) and 0.9 (□ and *, two independent sets of data).

3. Adsorption of a polymer at a random surface

In this section we turn to the problem of adsorption of a homopolymer at a random surface. The sites of the surface are of two types, only one of which interacts with the monomers of the polymer. Once again the polymer is modelled as a self-avoiding walk on the simple cubic lattice, starting at the origin and confined to the half-space $z \geq 0$. The vertices of the surface plane ($z = 0$) are labelled A and B , uniformly and independently, and the vertices of the walk only interact with surface vertices labelled A . We write p for the probability that a surface vertex is labelled A and χ for a particular (random) labelling of the surface vertices. We shall label the origin as A and write $v_A + 1$ for the number of vertices of the walk at vertices of the surface labelled A . We call v_A the number of A -visits and write $c_n(v_A | \chi)$ for the number of self-avoiding walks (in the half-space defined above) with n edges and v_A A -visits, given a surface labelling χ . We have used Monte Carlo methods to estimate the energy (i.e. the expected value of v_A) and heat capacity (the variance of v_A) for given χ , and formed averages over χ to estimate the quenched average energy and heat capacity. The methods used were essentially identical to those described for the random copolymer in section 2.

In figure 5 we show the mean fraction of A -visits, $\langle v_A \rangle / n$, as a function of α , for $n = 200$, for various values of p between $p = 0.3$ and 0.9. The values of $\langle v_A \rangle / n$ increase as α increases, to values which are clearly larger than p (in contrast to the case for the random copolymer where the horizontal asymptote is p). This is because, in the random surface case for $p > p_c$, where p_c is the site percolation threshold for the square lattice, there is a positive probability that the origin is a member of an infinite cluster of A vertices and the walk can arrange itself on the lattice so as to follow A -vertices in this percolating cluster. For $p < p_c$ there is no infinite percolating cluster but the walk can still optimize the number of vertices in $z = 0$ which are A vertices, to optimize the energy. Thus the horizontal asymptote can still be larger than p .

Figure 6 shows the α -dependence of the quenched average heat capacity $C_n(\alpha) = n^{-1} [\langle v_A^2 \rangle - \langle v_A \rangle^2]$ for $n = 50, 100, 200$ and 400, for $p = 0.8$. As n increases the peaks

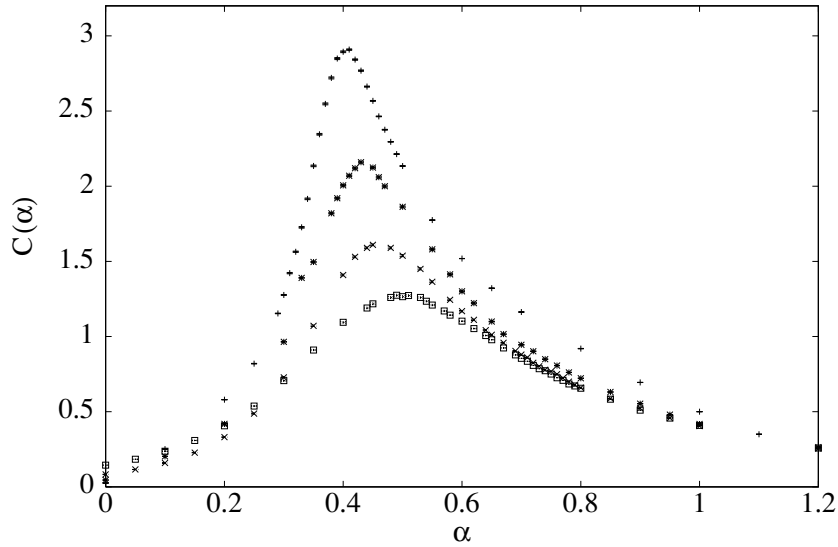


Figure 6. The α -dependence of the heat capacity $C_n(\alpha)$ for the random surface when $p = 0.8$, $n = 50$ (\square), 100 (\times), 200 ($*$) and 400 ($+$).

grow in height and become sharper, consistent with an adsorption transition. Similar trends are observed for other values of p . In figure 7 we show the α -dependence of $C_n(\alpha)$ for $n = 50$ for various values of p . The peak position moves to smaller values of α as p increases, so that adsorption occurs at smaller α as p increases. There appears to be an adsorption transition for every value of $p > 0$, including values for $p < p_c$. It is interesting to compare the random surface and random copolymer cases and we show heat capacities for the two cases in figure 8 for $p = 0.3, 0.5$ and 0.9 . The heat capacity peaks are considerably higher for the random surface case than for the random copolymer case. There is some evidence that the peak positions occur at slightly smaller values of α for the random surface case (than for the random copolymer) and this is more marked at lower values of p . Whether or not this persists in the infinite n limit is an open question.

Sumithra and Baumgaertner (1998) have reported evidence that the crossover exponent depends on p , at least for $p \geq 0.6$. However, our data can be reasonably represented by a value of ϕ around 0.5 or 0.52 , independent of p . If the crossover exponent is p -dependent then our data are not sufficiently precise to see this. Where we can compare our raw data with those of Sumithra and Baumgaertner, the agreement seems to be quite good.

4. The annealed case

In the annealed version of the problem the operations of taking the logarithm and averaging over labellings are reversed in computing the free energy. That is, the annealed free energy, $\kappa_n^a(\alpha)$, is given by

$$\kappa_n^a(\alpha) = n^{-1} \log \langle Z_n(\alpha | \chi) \rangle \quad (4.1)$$

where the angular brackets denote an average over the labellings χ . By the arithmetic mean–geometric mean inequality

$$\kappa_n^a(\alpha) \geq \bar{\kappa}_n(\alpha) \quad (4.2)$$

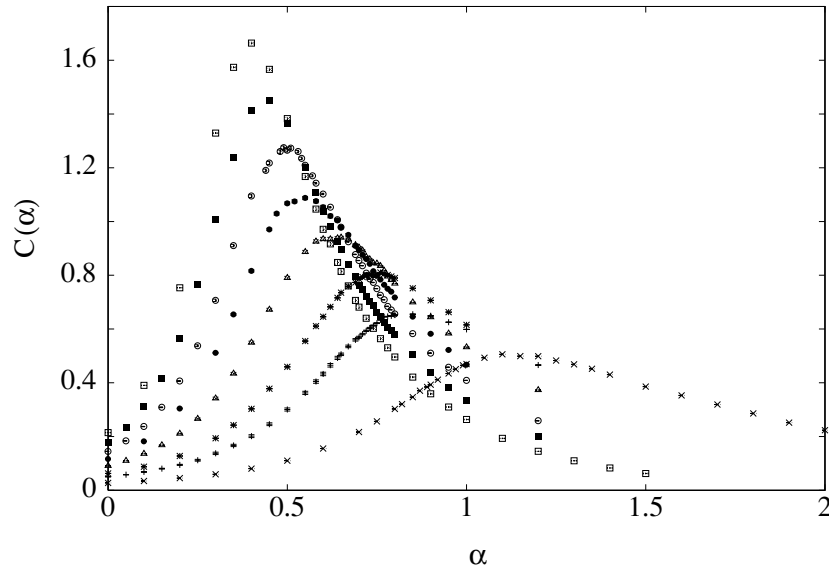


Figure 7. The α -dependence of the heat capacity $C_n(\alpha)$ for the random surface when $n = 50$, $p = 0.3$ (\times), 0.4 ($+$), 0.5 ($*$), 0.6 (\triangle), 0.7 (\bullet), 0.8 (\circ), 0.9 (\blacksquare) and 1.0 (\square).

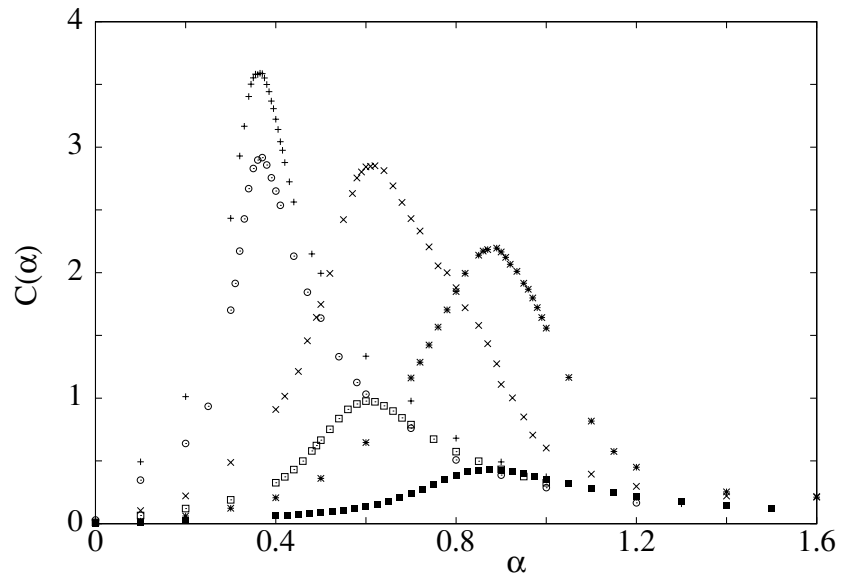


Figure 8. The heat capacity $C_n(\alpha)$ for $n = 400$ for various values of p . For $p = 0.3$, random copolymer (\blacksquare), and random surface ($*$). For $p = 0.5$, random copolymer (\square), and random surface (\times). For $p = 0.9$, random copolymer (\circ), and random surface ($+$).

so that the annealed version of the problem gives an upper bound to the quenched average free energy. For the two problems considered in this paper, the random copolymer and the random surface, the annealed version of the problem is identical. In the random copolymer problem annealing is a convenient mathematical approximation which yields an upper bound but in the

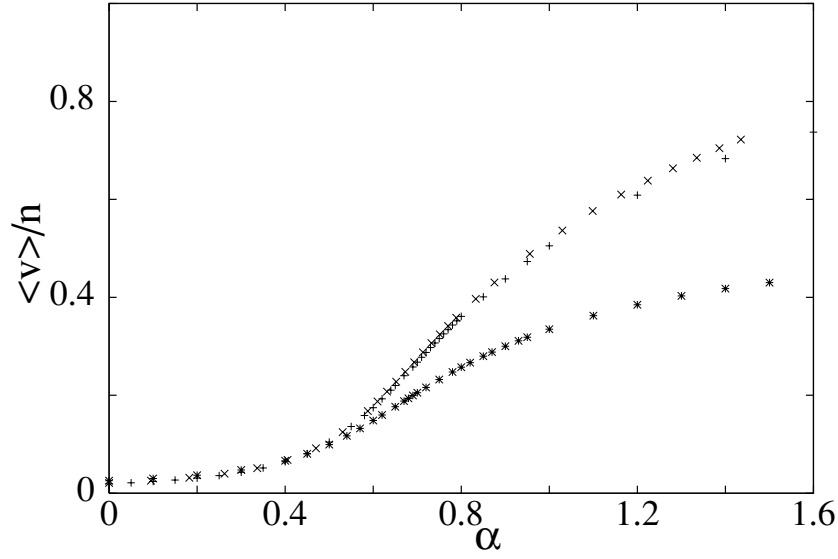


Figure 9. The α -dependence of $\langle v_A(\alpha) \rangle / n$ for $n = 100$, $p = 1/2$, for the annealed (\times), quenched random surface ($+$) and quenched random copolymer ($*$).

random surface problem there is a direct physical model whose free energy is the annealed free energy. Up to now we have considered the case where the surface, once randomly labelled, is fixed. However, it is possible to consider the case of a mobile or deformable surface where the labelling can change to accommodate the adsorption process. That is, the surface sites can rearrange to optimize their interaction with the adsorbing polymer.

The annealed case can be related to the homopolymer adsorption case as follows. Suppose that $c_n(v)$ is the number of walks (unlabelled) with n edges, having $v+1$ vertices in the surface. If vertices (of either the walk or surface) are randomly labelled to be of type A with probability p the average of the partition function can be written as

$$\langle Z_n(\alpha|\chi) \rangle = \sum_v \sum_{v_A} c_n(v) \binom{v}{v_A} e^{\alpha v_A} p^{v_A} (1-p)^{v-v_A}. \quad (4.3)$$

Performing the binomial summation gives

$$\langle Z_n(\alpha|\chi) \rangle = \sum_v c_n(v) [pe^\alpha + (1-p)]^v \quad (4.4)$$

which can be written as

$$\langle Z_n(\alpha|\chi) \rangle = \sum_v c_n(v) e^{\gamma v} \quad (4.5)$$

where $\gamma = \log[pe^\alpha + (1-p)]$. Hence the average of the partition function can be written as the partition function of a homopolymer interacting with a homogeneous surface with interaction parameter γ . The behaviour of the annealed case can be obtained from the pure homopolymer case by the transformation derived above. In figure 9 we show the α -dependence of the mean fraction of visits $\langle v_A \rangle / n$ for $n = 100$, $p = 1/2$, for the annealed case (top curve), the quenched random surface (centre curve) and the quenched random copolymer (lower curve). Note that the annealed values are higher than those of the two quenched cases, but much closer to the quenched random surface case.

5. Discussion

We have used Monte Carlo methods to investigate the adsorption at a homogeneous surface of a quenched random copolymer containing two comonomers A and B where only one of them (A , say) interacts with the surface. We have investigated the temperature dependence of the energy and heat capacity as a function of the proportion of A monomers, and have numerically investigated self-averaging of these properties as a function of temperature, and the length of the polymer. These results have been compared with corresponding results for a homopolymer adsorbing at a spatially heterogeneous surface, consisting of two types of sites, only one of which interacts with the monomers of the polymer. We have also compared our Monte Carlo results with those from an annealed model, which gives a bound on the free energies of both the quenched models studied.

The annealed model gives a lower bound on the location of the adsorption transition for both quenched models which we have studied. Our Monte Carlo results suggest that the locations are very similar for all the three models. Whether or not the locations of the transitions are identical remains an open question.

Acknowledgment

This research was supported, in part, by NSERC of Canada.

References

- Biskup M and den Hollander F 1999 *Ann. Appl. Prob.* **9** 668
Bolthausen E and den Hollander F 1997 *Ann. Prob.* **25** 1334
Cosgrove T, Finch N A and Webster J R P 1090 *Macromolecules* **23** 1334
De'Bell K and Lookman T 1993 *Rev. Mod. Phys.* **65** 87
Garel T, Huse D A, Leibler S and Orland H 1989 *Europhys. Lett.* **8** 9
Geyer C J 1991 Markov chain Monte Carlo maximum likelihood *Computing Science and Statistics: Proc. 23rd Symp. on the Interface* ed E M Keramidis (Fairfax Station: Interface Foundation) pp 156–63
Grosberg A, Izrailev S and Nechaev S 1994 *Phys. Rev. E* **50** 1912
Gutman L and Chakraborty A K 1994 *J. Chem. Phys.* **101** 10074
Gutman L and Chakraborty A K 1995 *J. Chem. Phys.* **103** 10733
Hammersley J M, Torrie G M and Whittington S G 1982 *J. Phys. A: Math. Gen.* **15** 539
Hegger R and Grassberger P 1994 *J. Phys. A: Math. Gen.* **27** 4069
Joanny J-F 1994 *J. Physique II* **4** 1281
Lal M 1969 *Mol. Phys.* **17** 57
Madras N and Sokal A 1988 *J. Stat. Phys.* **50** 109
Moghaddam M S, Vrbová T and Whittington S G 2000 *J. Phys. A: Math. Gen.* **33** 4573
Orlandini E, Tesi M C and Whittington S G 1999 *J. Phys. A: Math. Gen.* **32** 469
Sommer J U and Daoud M 1995 *Europhys. Lett.* **32** 407
Sommer J U, Peng G W and Blumen A 1996 *J. Physique II* **6** 1061
Sumithra K and Baumgaertner A 1998 *J. Chem. Phys.* **109** 1540
Sumithra K and Baumgaertner A 1999 *J. Chem. Phys.* **110** 2727
Tesi M C, Janse van Rensburg E J, Orlandini E and Whittington S G 1996 *J. Stat. Phys.* **82** 155
Verdier P and Stockmayer W H 1962 *J. Chem. Phys.* **36** 227
Wang W, Lin Z, Ebner C and Nikas Y 1993 *Phys. Rev. E* **48** 4622
Whittington S G 1998 *J. Phys. A: Math. Gen.* **31** 3769