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A Monte Carlo study of adsorption of random copolymers on random surfaces

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Abstract

We study the adsorption problem of a random copolymer on a random surface in which a 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_p or B with probability $1 - p_p$, and only vertices labelled A are attracted to the surface plane. Each lattice site on the plane is also labelled either A with probability p_s or B with probability $1 - p_s$, and only lattice sites labelled A interact with the walk. We study two variations of this model: in the first case the A -vertices of the walk interact only with the A -sites on the surface. In the second case the constraint of selective binding is removed; that is, any contact between the walk and the surface that involves an A -labelling, either from the surface or from the walk, is counted as a visit to the surface. The system is quenched in both cases, i.e. the labellings of the walk and of the surface are fixed as thermodynamic properties are computed. We present Monte Carlo simulation results which provide evidence for second-order transitions in both cases. We observe that in both cases the adsorption location depends on both p_s and p_p , the dilution of the interactive sites on the surface and the walk. We compare critical properties for the two cases and find that the adsorption location varies for different models while the crossover exponent is independent of the details of the models.

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1. Introduction

The adsorption of polymers at an impenetrable surface is an important problem both in terms of practical applications and statistical physics of polymers. Adsorption of homopolymers at an impenetrable surface is a well-studied problem dating back about half a century (for a review see De'Bell and Lookman (1993)). There have also been studies regarding heteropolymer adsorption, and in particular copolymer adsorption (in which one of the two comonomers interacts with the surface) has been studied by a number of experimental (Cosgrove *et al* 1990),

theoretical (Sommer and Daoud 1995, Whittington 1998) and computational methods (Moghaddam *et al* (2000) and reference cited therein).

The study of random polymers and random surfaces has also received a great deal of attention. Random copolymers are made up of two different monomer units that are distributed along the backbone in a random sequence. The disorder contained in these molecules is quenched; that is, the sequence distribution does not alter in response to prevailing conditions. They are important models for biological molecules and their adsorption on a homogeneous surface has been studied by a variety of theoretical and experimental techniques. Some studies have focused on effects of solvency and coverage (Cosgrove *et al* 1990), on the effect of architecture of the polymer on the structure of the adsorbed layer (Balazs and Gempe 1991) and on the effect of polymer sequence on its statistical behaviour (Denesyuk and Erukhimovich 2000) while others have focused more on the thermodynamic properties of the random copolymers. In particular, Sumithra and Baumgaertner (1999) used Monte Carlo methods and scaling arguments to study the critical behaviour of a random copolymer interacting with an impenetrable surface while Orlandini *et al* (1999) proved that the system has a phase transition and is thermodynamically self-averaging. Grosberg and Shakhnovich (1986) applied advanced renormalization group methods to random chains with a disordered sequence of links and obtained important information about the thermodynamic properties of an ideal polymer chain near the transition point. Interesting results have also been obtained for a phase transition in solid-on-solid models with quenched impurities using perturbation theory as the basis for a mathematical formulation of the problem (Forgas *et al* 1991). Other studies include Garel *et al* (1990), Moghaddam and Whittington (2002), Gutman and Chakraborty (1994) and Stepanow and Chudnovskiy (2002) and references cited therein.

These studies deal with the case of a random polymer interacting with a homogeneous surface. Most surfaces in practice are not homogeneous and include physical/chemical heterogeneities. The effect of surface roughness on the adsorption problem of polymers has been studied by various analytical, numerical and experimental methods. These works followed the pioneering work of Edwards and Muthukumar (1988) who examined the size of a polymer in a random medium. Baumgaertner and Muthukumar (1991) studied the effect of physical and chemical roughness by both scaling arguments and Monte Carlo simulations of a random walk model of the polymer, Gutman and Chakraborty (1995) analysed the phase diagram of a random heteropolymer near a solid surface by a field theory argument, Derrida *et al* (1992) studied the adsorption near a random wall in the context of wetting in two dimensions using transfer matrix methods and Sumithra and Baumgaertner (1998) examined the critical properties of a single polymer adsorption onto a random surface by Monte Carlo simulations and scaling arguments. Other studies include those by Thurtell and Thurtell (1988), Zajac and Chakrabarti (1997), Baumgaertner (1998) and references cited therein.

The behaviour of random copolymers in random media has been studied in the context of problems of interest in biology as well as in statistical physics of polymers. In particular, the adsorption of a random polymer onto a random surface is relevant to the study of behaviour of proteins near surfaces such as lipid bilayers of the cell membrane (Creighton 1992) and pattern recognition by macromolecules (Muthukumar 1988). Studies regarding random polymers in random media include those by Chakraborty *et al* (1995) who discussed the phase behaviour of a self-interacting random copolymer in random media, Bratko *et al* (1997) who studied the thermodynamics and structural behaviour of random heteropolymers immersed in a disordered medium, Srebnik (2000) who examined the role of segment interactions in pattern recognition between random heteropolymers and disordered surfaces and Chakraborty and Bratko (1998) who studied the recognition between random heteropolymers and disordered surfaces by Monte Carlo simulations and a nonreplica theory.

In this work, we study the adsorption problem for random copolymers interacting with random surfaces via multiple Markov chain Monte Carlo method (MMCMC). This is a problem of interest in the context of many biological problems such as pattern recognition by macromolecules. Proteins, for example, bind to certain substrates or surfaces and not others. The large molecule such as a protein can be modelled by a random copolymer and the heterogeneous surface of a cell membrane or surface can be modelled by a random surface. It is of interest to examine which parameters are important in this process. This is also a problem of interest from the point of view of statistical physics of polymers. Which parameters and to what extent do they influence the critical properties of the random systems? The critical exponents are known to be dependent on the dimension of the model. Are they affected by the details of the model as well? Very little is known about these aspects of the adsorption of random polymers on random surfaces.

In this work, we consider two variations of a self-avoiding walk model of adsorption of a random copolymer onto a random surface. We examine the existence of a phase transition and investigate factors affecting the adsorption location. We also examine the effect of constraint in the model on critical properties such as the crossover exponent. We comment on the dependence of these properties on p_s and p_p , the dilution of interactive sites on the surface and the vertices of the walk, respectively.

The paper is organized as follows: first we give a description of the model and the technique. Then we present the results for cases 1 and 2 and compare them. We summarize our findings in the conclusion section.

2. Model and the simulation technique

The model which we consider 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 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 $i = 1, 2, \dots, n$ of the self-avoiding walk are randomly and independently labelled with probability p_p as A or with probability $1 - p_p$ as B . The sites on the plane (Z^2) are numbered (i, j) , $i = -n, -n + 1, \dots, n$, $j = -n, -n + 1, \dots, n$ and are randomly and independently labelled as A with probability p_s or as B with probability $1 - p_s$.

We study two variations of this model: in the first case (which we shall refer to as case 1) we examine the adsorption behaviour of a random copolymer whose A -monomers interact with only the A -lattice sites on the surface. Let $c_n(v_{AA}|\chi_1, \chi_2)$ be the number of n -edge walks with these constraints, having a labelling χ_1 , and having v_{AA} vertices labelled A in the A -lattice sites of the plane $z = 0$ with the labelling, χ_2 . The partition function for a fixed labelling is

$$Z_n(\alpha|\chi_1, \chi_2) = \sum_{v_{AA}} c_n(v_{AA}|\chi_1, \chi_2) e^{\alpha v_{AA}} \quad (2.1)$$

where v_{AA} counts A -monomers that have hit an A -lattice site on the surface, and $\alpha = -\epsilon/k_B T$ with T as the temperature, $\epsilon (< 0)$ as the interaction energy of the self-avoiding walk with the surface and k_B as the Boltzmann constant. The quenched average free energy, $\bar{k}(\alpha)$, is

$$\bar{k}(\alpha) = \lim_{n \rightarrow \infty} \langle n^{-1} \log Z_n(\alpha|\chi_1, \chi_2) \rangle \quad (2.2)$$

where $\langle \dots \rangle$ represents an average over the labellings χ_1 and χ_2 . To the author's knowledge, there are no rigorous proofs regarding the existence of this limit or the temperature dependence

of free energy. To investigate the possibility of an adsorption transition for this problem, we have fixed the labelling of the walk and the surface and calculated the energy (the first derivative of the free energy) at several fixed labellings. That is, we calculated

$$\langle v_{AA}(\alpha|\chi_1, \chi_2) \rangle = \left\langle \frac{\sum_{v_{AA}} v_{AA} c_n(v_{AA}|\chi_1, \chi_2) e^{\alpha v_{AA}}}{\sum_{v_{AA}} c_n(v_{AA}|\chi_1, \chi_2) e^{\alpha v_{AA}}} \right\rangle \quad (2.3)$$

as a function of α and n for several fixed values of χ_1 and χ_2 . We write $\langle v_{AA}(\chi_1, \chi_2) \rangle/n$ for the mean fraction of A -vertices in the A -lattice sites of the surface averaged over all labellings of the walk and the surface.

For the second case (which we shall refer to as case 2) we examine the adsorption behaviour of a random copolymer whose A -monomers interact with the surface sites in a non-preferential way, and the A -sites on the surface interact indiscriminantly with monomers of the copolymer. Similar quantities are calculated in this case and then compared with case 1. For example, the energy is calculated as

$$\langle v_A(\alpha|\chi_1, \chi_2) \rangle = \left\langle \frac{\sum_{v_A} v_A c_n(v_A|\chi_1, \chi_2) e^{\alpha v_A}}{\sum_{v_A} c_n(v_A|\chi_1, \chi_2) e^{\alpha v_A}} \right\rangle \quad (2.4)$$

as a function of α and n for several fixed values of χ_1 and χ_2 where v_A represents a visit to the surface that involves an ‘ A ’-labelling either from the walk or from the surface. We write $\langle v_A(\chi_1, \chi_2) \rangle/n$ for the mean fraction of visits of the walk to the surface, which involve an A -labelling either from the walk or from the surface, averaged over all labellings of the walk and the surface.

The thermodynamic quantities in this study are calculated via multiple Markov chain Monte Carlo methods (see Geyer (1991)), together with the pivot algorithm (see Lal (1969)), to estimate the energy as a function of n and α and the heat capacity as a function of n and α . In a typical multiple Markov chain simulation 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 calculations are carried out for several (typically 20–40) different labellings of the walk and the surface. We have investigated values of n up to 400.

Throughout the calculations, the labellings of the surface and of the walk are fixed. The calculated quantities are averaged three times: once upon all conformations of the walk, then over all labellings of the walk (χ_1), and then over all labellings of the surface (χ_2).

3. Results and discussion

In this section, we present the multiple Markov chain Monte Carlo (MMCMC) calculations of thermodynamic functions of random copolymers interacting with random surfaces. The main goals are to investigate the existence of a phase transition and to examine the effect of dilution of interactive sites of the walk and of the surface on adsorption properties. We also examine the effect of the details of the model (selective binding versus non-preferential binding) on critical behaviour of random systems by comparing the properties such as the adsorption location and the crossover exponent. Two distinct cases are considered: in the first case (case 1), the A -vertices of the walk interact only with A -lattice sites on the surface. In the second case (case 2), the A -vertices of the walk are interacting with the surface, and the A -sites on the surface interact with the vertices of the walk. The second case may be more difficult to realize experimentally but its comparison with case 1 offers insight into the possible

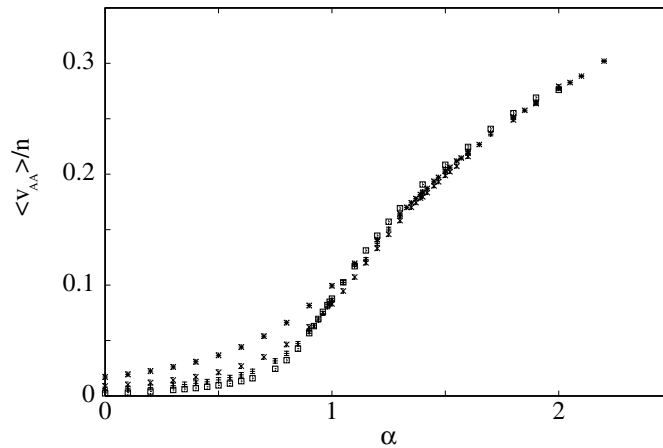


Figure 1. The mean fraction of visits as a function of α for a random copolymer ($p_p = p_s = 0.5$) of 50 (*), 100 (\times), 200 (+) and 400 (\square) edges interacting with a random surface.

dependence of critical properties such as transition location and the crossover exponent on the details of the model.

3.1. Adsorption of a random copolymer in a random surface: case 1

Figure 1 shows the α -dependence of the mean fraction of A-monomers that are visiting the A-lattice sites on the surface, $\frac{\langle v_{AA}(\alpha) \rangle}{n}$, when $p_p = p_s = 0.5$, for different values of n . For small α , the values of $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ are small and decrease as n increases. The curves rise over a small range of α values and the rise becomes sharper as n increases. The asymptotic value seems to be less than $p_p = p_s = 0.5$.

A similar trend is observed when $p_p = p_s = 0.6$, a value slightly higher than the percolation threshold of the surface. This is the value of p ($=0.583$ for a square lattice) at which an infinite cluster of active sites flow from one side of the surface to the other (Stauffer and Aharony 1994) thus accommodating the adsorption of the whole length of the active sites on the polymer. For this reason we expect that for $p \geq p_c$, the asymptotic value of $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ tends to unity in the case of adsorption of a homopolymer on a random surface. The walks seem to be going from a desorbed state to an adsorbed state as α increases.

Figure 2 shows the corresponding behaviour for the heat capacity or $C(\alpha)$. 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 . A similar trend is observed when $p_p = p_s = 0.6$ with larger peaks (in heights) and smaller locations for peak maxima. There are no rigorous proofs regarding the existence of a phase transition in this case. These results provide numerical evidence for an adsorption transition.

Figure 3 shows the α -dependence of $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ for $n = 50$ for fixed $p_s = 0.6$ ($>p_c$, where p_c is the percolation threshold of the surface) and various values of $p_p = 0.5, 0.6, 0.7$ and 1.0 . As p_p increases, the value of α at which $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ begins to increase rapidly (corresponding to a peak in the heat capacity) grows smaller as expected. $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ increases as p_p increases, but it tends to values smaller than p_p or p_s except for the case $p_p = 1$ where the height of the plateau tends to unity for larger values of α . Similar results are obtained when p_p is fixed and

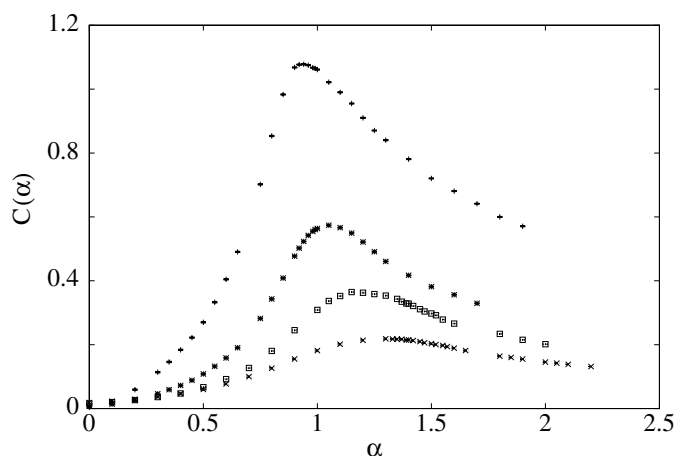


Figure 2. The heat capacity $C(\alpha)$ versus α (case 2) for $p_p = p_s = 0.5$ for different values of n , namely, 50 (\times), 100 (\square), 200 ($*$) and 400 ($+$).

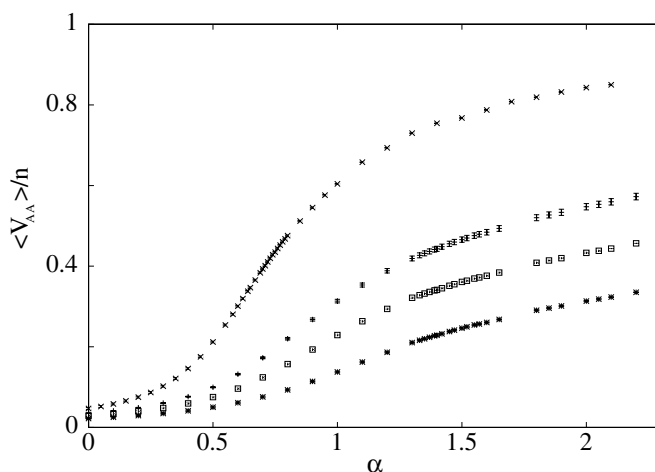


Figure 3. The mean fraction of visits as a function of α for a random copolymer of 50 edges interacting with a random surface when ($p_p = 0.5$ and $p_s = 0.6$) ($*$), ($p_p = p_s = 0.6$) (\square), ($p_p = 0.7$ and $p_s = 0.6$) ($+$) and ($p_p = 1.0$ and $p_s = 0.6$) (\times).

p_s increases. This is interesting for two reasons: first it shows that $\frac{\langle v_{AA}(\alpha) \rangle}{n}$ depends on two parameters (p_p and p_s). Secondly it exhibits the effect of the constraint of selective binding on $\frac{\langle v_{AA}(\alpha) \rangle}{n}$. This effect can be more carefully examined by removal of the constraint, which is done in the next case (2).

Before we present thermodynamic results for case 2 and compare them with those of case 1, we present a metric property of the model in this case, namely the root mean square of the z -component of the walk (Z). This is a measure of how far from the surface the walk lies. If Z is large, the walk is far from (off) the surface; if Z is small, the walk must be mainly lying on the surface. In figure 4, α -dependence of Z is shown for different values of p_s and p_p . In all cases, the walk seems to be going from the desorbed phase to an adsorbed phase. It can

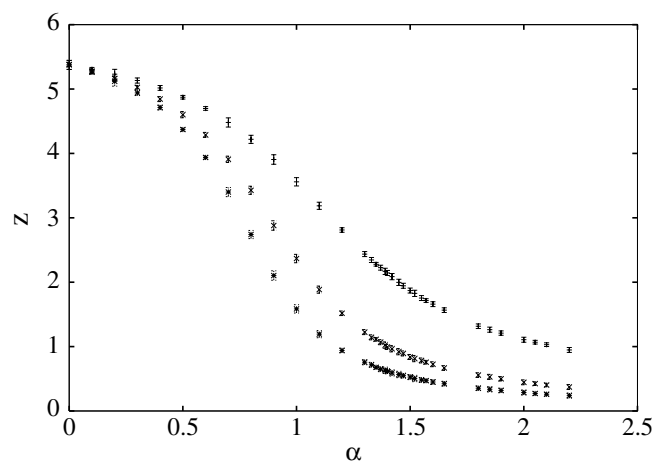


Figure 4. α -dependence of the root mean square of the z -component of the walk (Z) in case 1 for $(p_p = 0.7$ and $p_s = 0.6)$ (*), $(p_p = p_s = 0.6)$ (\times) and $(p_p = p_s = 0.5)$ (+) for $n = 50$.

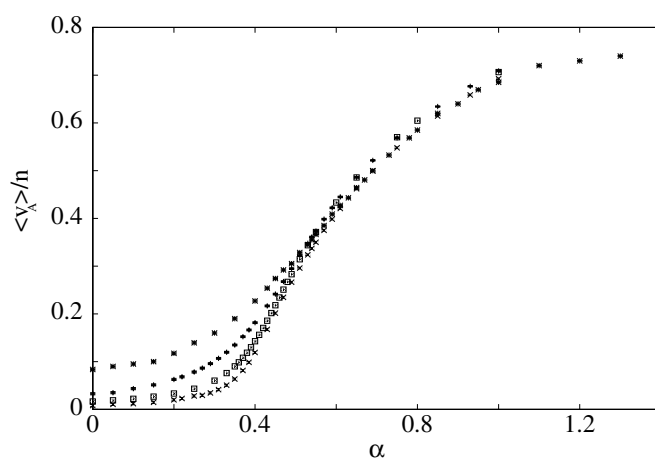


Figure 5. The mean fraction of visits (case 2) as a function of α for $p = 0.5$ for different values of n , namely, 50 (*), 100 (+), 200 (\square) and 400 (\times).

also be seen that in the case where $p_p = p_s = 0.5$, even for larger values of α , Z lies well above the corresponding quantities for the cases with larger p_p and p_s values.

3.2. Adsorption of a random copolymer in a random surface: case 2

We now examine the effect of removal of constraint by discussing the thermodynamic properties for the second model (case 2). Figure 5 shows the α -dependence of $\frac{\langle v_A(\alpha) \rangle}{n}$ when $p_s = p_p = 0.5$ for different values of n . For small α the values of $\frac{\langle v_A(\alpha) \rangle}{n}$ are small and decrease as n increases. The curves rise sharply over a small range of α values and the rise becomes sharper as n increases. The asymptotic value is considerably larger compared to that in the previous case (figure 1). This clearly exhibits the effect of constraint on the fraction of adsorbed vertices. Since $p_s < p_c$, one does not expect this value to tend to unity.

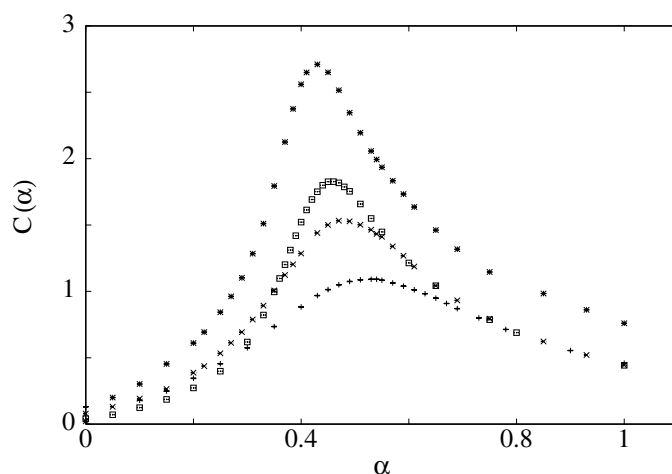


Figure 6. The heat capacity $C(\alpha)$ versus α for $p = 0.5$ for different values of n , namely, 50 (+), 100 (\times), 200 (\square) and 400 ($*$).

A similar trend is observed when $p_p = p_s = 0.6$, a value slightly larger than the percolation threshold of the surface. The walk seems to be going from a desorbed state to an adsorbed state as temperature decreases. The asymptotic value of $\frac{\langle v_A(\alpha) \rangle}{n}$ tends to unity as α increases. Once again, this is in sharp contrast with the corresponding results obtained in case 1 (figure 3).

Figure 6 shows the α -dependence of the heat capacity when $p_p = p_s = 0.5$, for different values of n . 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 . A similar trend is observed when $p_p = p_s = 0.6$, a value slightly higher than the percolation threshold of the surface. The location of maxima of the peaks tend to smaller values of α as $p_p (=p_s)$ increases indicating that the adsorption location depends on the dilution of the interactive sites of the walk and of the surface.

In figure 7 we compare the heat capacity for the two cases (1 and 2) for $p_s = 0.6$ and $p_p = 0.5$ and 0.6. Once again two factors seem to be affecting the adsorption location and the magnitude of fluctuations. The first one is the combination of the two parameters (p_p and p_s), and the second one is the role of the constraint. It can be seen that the adsorption location (α_c) depends on p_p ; as p_p increases, α_c decreases in both cases. Similar results are obtained by fixing p_p and increasing p_s . An increase in p_s shifts α_c to smaller values. It seems, from a comparison of the results for the two cases, that α_c is also affected by the constraint of selective binding; once it is removed, α_c shifts to smaller values.

The heights of the peaks are also considerably different. The fluctuations in $\frac{\langle v_A(\alpha) \rangle}{n}$ seem to be suppressed by the constraint of A -vertices interacting with A -sites. While for an infinite size system both these peaks should diverge; the comparison of results for finite size systems helps in understanding the effect of constraint on the properties of models of random systems.

To examine the effect of the selective binding constraint on the crossover exponent, ϕ , the locations of the heat capacity peaks, α_n have been plotted against $n^{-\phi}$ for various values of n for the two cases in figure 8. The three plots present data for ($p_p = p_s = 0.5$) obtained for cases 1 and 2 as well as the case of $p_p = 1$ while $p_s = 0.5$. This is the case of a homopolymer interacting with a random surface and is included as a reference. There are not

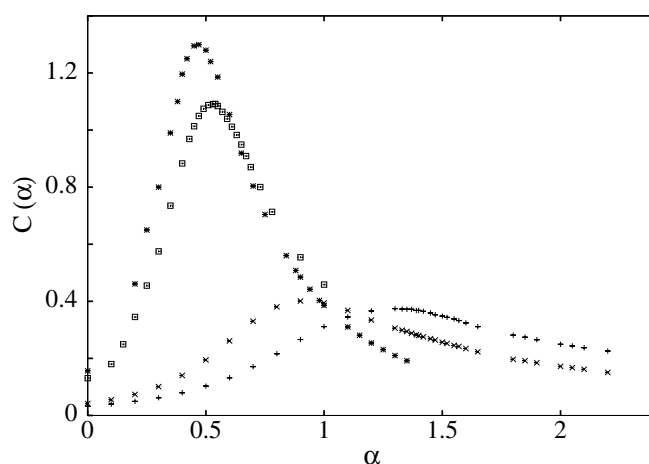


Figure 7. The heat capacity as a function of α for cases 1 (+ for $p_c = 0.5$ and \times for $p_c = 0.6$) and 2 (\square for $p_c = 0.5$ and $*$ for $p_c = 0.6$). For all these cases the data for $p_s = 0.6$ and $n = 50$ are shown.

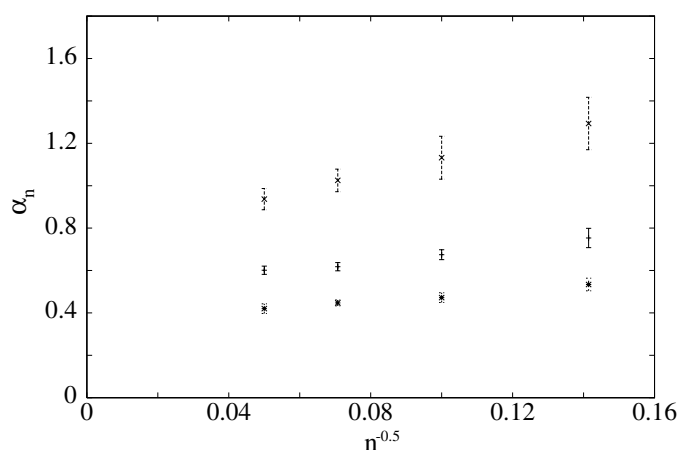


Figure 8. The locations of the heat capacity peaks plotted against $n^{-0.5}$ for $p_s = p_p = 0.5$ for case 1 (*), case 2 (+) and for case 2 when $p_p = 0.5$ and $p_s = 1$ (\times).

enough data points to make an independent estimate of ϕ ; therefore, we considered a value of $\phi = 0.5$ (Hegger and Grassberger 1994) similar to the case of adsorption of homopolymers and periodic copolymers. A linear behaviour is observed in all cases providing support for ϕ being about 0.5–0.52. It seems that the constraint in the model does not change the value of ϕ to an easily discernible degree. Similar results are obtained for $p_s = p_p = 0.6$; so ϕ does not seem to depend on the dilution of interactive sites either. This is similar to the results we obtained for models where either the walk or the surface contained interactive sites (Moghaddam and Whilington 2002) and where ϕ seemed to be independent of p . At that point, we performed the calculations for many values of p and examined the possibility of p -dependence of the crossover exponent. Our results then did not provide evidence for p -dependence of the crossover exponent as Sumithra and Baumgartner (1998) reported in their work on adsorption of a homopolymer on a random surface (for $p \geq 0.6$). Also in this

study, we do not observe any evidence for p -dependence of ϕ though we have performed the calculations for only two values of p in close vicinity of the percolation threshold. If the crossover exponent indeed depends on p , our data may not be precise enough to see this.

The self-avoiding walk model of adsorption of a random polymer onto a random surface where selective binding is imposed (case 1) is a basic model for pattern recognition by macromolecules. Adsorption implies that A -monomers 'find' A -lattice sites on the surface and bind to them strongly. The results obtained in this work suggest that the parameters of importance are the dilution of the interactive sites on the surface and the polymer as well as the strength of interaction between the interactive site. These results also indicate a strong dependence of adsorption location on the dilution of the interactive sites of the polymer and on the surface or p_p and p_s . As p_p and p_s increase, adsorption occurs at smaller α (related to the strength of the interaction energy). This can be of significance in designing polymers (surfaces) capable of 'recognizing' patterns on surfaces (polymers) and binding to them strongly.

Comparison of the results for the two variants of the model suggests that certain critical properties such as adsorption location depend on the details of the model such as the presence of a constraint. Other properties, however, do not follow the same rule. For example, these results provide support for ϕ being independent of the details of the model and for value of ϕ being about 0.5 in the case of random copolymers interacting with a random surface. This is in agreement with the findings of Hegger and Grassberger (1992) who performed extensive computational studies to determine ϕ for the adsorption of a homopolymer and suggested the notion of superuniversality of ϕ .

4. Conclusions

We have used Monte Carlo methods to investigate the thermodynamic properties of a self-avoiding walk model of the adsorption of a random copolymer interacting with a random surface. Two cases are considered: in the first case a random copolymer interacts selectively with interactive sites on the random surface while in the second case the random copolymer (the surface) interacts non-preferentially with sites on the random surface (monomers of the random copolymer). We have observed second-order phase transitions in both cases. The adsorption location depends on the dilution of the interactive sites or p_p and p_s in both models.

We have examined the effect of selective binding constraint on critical properties such as adsorption location and the crossover exponent by comparing the results from the two models we studied. Adsorption location changes as a result of implementing a constraint. The crossover exponent seems to be independent of the details of the model as well as of the dilution of the interactive sites of the walk and of the surface.

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