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A numerical study of self-averaging in adsorption of random copolymers and random surfaces

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Received 17 May 2002, in final form 8 October 2002

Published 4 December 2002

Online at stacks.iop.org/JPhysA/35/10721

Abstract

Numerical studies involving random copolymers and random surfaces assume self-averaging of thermodynamic and metric properties of the systems to calculate different properties. For the problem of adsorption of a random copolymer, rigorous proofs regarding self-averaging of some properties such as free energy in the thermodynamic limit ($n \rightarrow \infty$) exist. This says little about the extent of self-averaging for finite size systems used in numerical studies. For the problem of adsorption of a homopolymer on a random surface, no analytical proofs regarding self-averaging exist. In this work assumptions of self-averaging of thermodynamic and metric properties of a self-avoiding walk model of random copolymer adsorption are tested via multiple Markov chain Monte Carlo method. Numerical evidence is provided in support of self-averaging of energy, heat capacity and the z -component of the self-avoiding walk in different temperature intervals. Self-averaging in energy of a homopolymer interacting with a random surface is also examined.

PACS numbers: 82.35.Jk, 05.10.Ln

1. Introduction

In recent years, the study of random systems such as random polymers and random surfaces has received a great deal of attention (Moghaddam *et al* (2002) and references therein). In numerical studies of random systems, a measurement of a thermodynamic property such as free energy, specific heat or internal energy, or a metric property of the system such as radius of gyration yields a different value for the exact average of every sample. Most numerical studies assume self-averaging of the properties and calculate only the ensemble averages (see for example, Sumithra and Baumgaertner (1999) and Moghaddam *et al* (2002)). This assumption implies that the properties of the system do not depend on the particular realization of the random variables. In most cases, these assumptions have not been verified although there have been a large number of studies investigating self-averaging of different properties in various random systems. Examples include works by van Hemmen and Palmer (1982) who

proved thermodynamic self-averaging for a random magnet with short range interactions, van Enter and van Hemmen (1983) who proved the same for a random magnet with large range interactions, Wiseman and Domany (1998a, 1998b) who discussed lack of self-averaging in critical disordered Ising models in three dimensions, Derrida and Hilhorst (1981) who proved the absence of self-averaging in correlation functions of random magnets, Buffet and Pule (1997) who found that the free energy of a model of continuous polymer with random charges does not self-average and Aharony and Harris (1996) who studied the absence of self-averaging in random systems near critical points.

With regard to random polymers, Chuang *et al* (2001) examined self-averaging of free energy in self-interacting random heteropolymers by exact enumeration, and Orlandini *et al* (1999) proved that the free energy of the self-avoiding walk model of adsorption of a quenched random copolymer self-averages. They have also examined the self-averaging of heat capacity, $C_n(\alpha)$, which is related to the second derivative of free energy with respect to temperature for the self-avoiding walk model of random copolymer adsorption (Orlandini *et al* (2002)). They proved the existence and finiteness of the limit of $C_n(\alpha)$. They also proved that under certain conditions such as boundedness and the approach to the limit from one side (below or above), $C_n(\alpha)$ self-averages far from the critical point for second and higher order transitions. By self-averaging it is meant that in the thermodynamic limit (as $n \rightarrow \infty$), with regard to some property, $P_n(\chi)$, which depends on the size (n) and the particular realization (χ), 'most' realizations of the randomness have the same value of that property. By a *quenched random* copolymer it is meant that the sequence of comonomers is fixed during the computation of thermodynamic and metric quantities.

This work in part deals with a numerical investigation of self-averaging in energy, heat capacity and a metric property of a self-avoiding walk model of adsorption of a quenched random copolymer by multiple Markov chain Monte Carlo (MMCMC) method. Investigating self-averaging in thermodynamic and metric properties of random copolymer adsorption is of interest for the following reasons. First, the rigorous proofs regarding self-averaging such as the one by Orlandini *et al* (1999) are done in the thermodynamic limit ($n \rightarrow \infty$). It is not clear whether self-averaging proved in the $n \rightarrow \infty$ limit (macroscopic) will apply to random copolymers of a few hundred monomers (mesoscopic); yet, these results have not been verified in numerical studies which involve only finite size samples.

Secondly, analytical proofs regarding self-averaging (Orlandini *et al* (1999)) usually prove self-averaging of a property but say little about the extent of self-averaging in a finite size system. This is to address the questions of to what extent the properties of a molecule depend on a particular realization of the quenched random variable for a finite size system. James and Whittington (2002) have examined the thermodynamic self-averaging of free energy in a coloured self-avoiding walk model of finite random copolymer adsorption and derived a bound on the extent of self-averaging as a function of the length of the self-avoiding walk. They obtained a power-law n -dependence of the free energy and defined an exponent for this relation. In this work, the extent of self-averaging in the energy of the random copolymer adsorption problem is examined by speculating a power-law dependence for energy and looking at the trends observed in a qualitative way. A proof of this relationship or an estimate of the exponent is beyond the scope of this work. The nature of the investigation is important as a first step in enhancing our understanding of an area where little work has been done so far.

Thirdly, many experimental studies involving random polymers are concerned with measurements of the mean fraction of visits or some metric property such as radius of gyration or the end-to-end distance. If these properties self-average, in practice, a measurement on a single very long polymer can represent the property of the ensemble. If it does not self-average, the measurement of a property of a single sample does not give a meaningful result

regardless of the sample size, and measurements have to be repeated on many samples. Thus self-averaging of the metric properties is not trivial; yet, there has not been an analytical or a numerical investigation of self-averaging in terms of metric properties of random copolymers interacting with a surface. There have been some studies examining self-averaging in metric properties of random systems. For example, lack of self-averaging of metric properties of random systems such as correlation functions in random magnets has also been studied by Derrida and Hilhorst (1981). This study examines self-averaging of the root mean square of the z -component of the vertices of the walk.

For the case of adsorption of a homopolymer interacting with a random surface, there has been no analytical proof of self-averaging of various properties. Numerical studies usually assume self-averaging of thermodynamic properties and evaluate the ensemble averages of energy and heat capacity. There has been no numerical verification of this assumption. In this work, self-averaging of energy of a homopolymer interacting with a random surface is also examined by MMCMC calculations.

2. Method

The model for the random copolymer in this study is a particular case of that studied by Orlandini *et al* (1999). An n -edge self-avoiding walk on the simple cubic lattice Z^3 is considered. The vertices of the walk are numbered $i = 0, 1, \dots, n$, and the 0th vertex is fixed 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. In the case of a random copolymer interacting with a surface, the vertices of the self-avoiding walk $i = 1, 2, \dots, n$ 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

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

where $\alpha = -\epsilon/k_B T$ with T as the temperature, $\epsilon (< 0)$ as the attractive interaction energy of the self-avoiding walk with the surface and k_B as the Boltzmann constant. 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 . $\bar{\kappa}(\alpha)$ depends on the parameter p but this dependence will normally be suppressed in the notation. Orlandini *et al* (1999) showed that the limit in (2.2) exists 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_c such that

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

so that α_c is a singular point of $\bar{\kappa}(\alpha)$ in the $\infty - n$ limit. The walk is desorbed for all $\alpha < \alpha_c$ and adsorbed for all $\alpha > \alpha_c$.

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.

This system is strongly interacting; therefore a multiple Markov chain approach is used. In this approach 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 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).

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

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

are calculated for various values of n and α for the specific case of $p = 1/2$. In each case the energy and heat capacity are calculated for a fixed labelling (monomer sequence) and then averaged over about 40–120 different labellings. It was found that at larger values of n fewer labellings were required; this provides some evidence for the thermodynamic self-averaging of the system in the $n \rightarrow \infty$ limit.

In order to verify self-averaging for finite values of n , the energy (averaged over conformations) at several fixed labellings has been calculated. That is,

$$\frac{\langle v_A(\alpha|\chi) \rangle}{n} = \frac{1}{n} \frac{\sum_{v_A} v_A c_n(v_A|\chi) e^{\alpha v_A}}{\sum_{v_A} c_n(v_A|\chi) e^{\alpha v_A}} \quad (2.7)$$

as a function of α and n for several fixed values of χ was calculated. With n and α fixed there will be a distribution of values of $\frac{\langle v_A(\alpha|\chi) \rangle}{n}$ and the variance of this distribution was estimated as

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

where the sum runs over s randomly chosen labellings and the bar represents a sample average over labellings. The same quantity for $C_n(\alpha)$ of the walks was calculated in a similar way.

Self-averaging of a metric property of the random copolymers interacting with a surface is also examined numerically in the following way. For different random realizations of the self-avoiding walk, the mean z -coordinate of the vertices of the walk (z) is calculated for various α and n values and then averaged over the realizations. That is, the variance of the mean of the distribution ($V_z(\alpha, n)$) is calculated and divided by the square of the expectation of z since z is an unscaled variable as follows:

$$V_z(\alpha, n) / \overline{z(\alpha|\chi_j)}^2 = (s-1)^{-1} \sum_{j=1}^s (z(\alpha|\chi_j) - \overline{z(\alpha|\chi_j)})^2 / \overline{z(\alpha|\chi_j)}^2 \quad (2.9)$$

where the sum runs over s randomly chosen labellings and the bar represents a sample average over labellings.

To investigate the validity of the assumption of self-averaging of energy for the adsorption a homopolymer in a random surface, MMCMC calculations are performed over 40–120

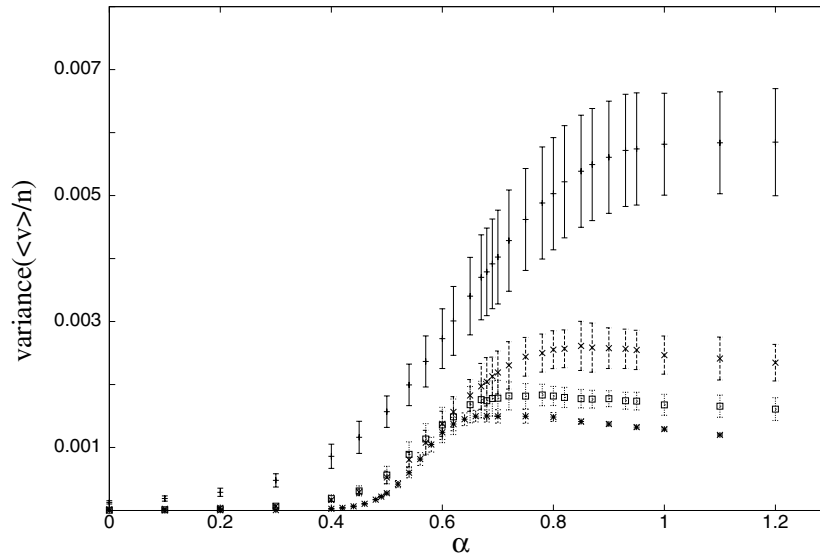


Figure 1. The variance of the $\langle v \rangle/n$ as a function of α for a random copolymer interacting with a homogeneous surface for $p = 1/2$, $n = 50(+)$, $100(\times)$, $200(\square)$ and $400(*)$. The error bars indicate the estimated sampling errors. The results indicate self-averaging of energy away from the critical point.

realizations of the surface for various sizes of homopolymers. 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 sites of the surface, plane ($z = 0$), are of two types, only one of which interacts with the monomers of the polymer. These sites are labelled A with probability p or B with probability $1 - p$, uniformly and independently. The rest of the procedure is basically the same as the one in the case of the adsorption of the random copolymer except that in this case the averaging is performed over the realizations of the surface.

3. Results and discussion

Figure 1 shows the α -dependence of $V(\alpha, n)$, the estimated variance of $\langle v_A(\alpha|\chi) \rangle/n$, for different values of n . The error bars are the estimated sampling errors in each case. It can be seen that the variance curve grows slowly for some values of α ($< \alpha_c$); rises sharply in the neighbourhood of α_c and then decreases very slowly for $\alpha \gg \alpha_c$ for all values of n . An estimate of α_c is obtained by taking the location of maxima in $C_n(\alpha)$ peaks at various values of n and using finite size scaling arguments (for details see Moghaddam *et al* (2000)). In general, $V(\alpha, n)$ decreases as n increases for values of α far from α_c . This indicates self-averaging of $\langle v_A(\alpha) \rangle/n$ in intervals of α both below and above α_c . In the region where $\alpha \approx \alpha_c$ it is difficult to establish a definite trend due to the presence of strong fluctuations.

It can also be seen (figure 1) that the extent of self-averaging is not the same for all values of α . That is, the rate of convergence of the energy of sequences to the mean value of energy is not the same at different values of α . There is no analytical proof of the existence of a power-law n -dependence for the energy in the adsorption of a random copolymer; however, the plot of the logarithm of variance of $\langle v_A(\alpha) \rangle/n$ as a function of $\log(n)$ at different values

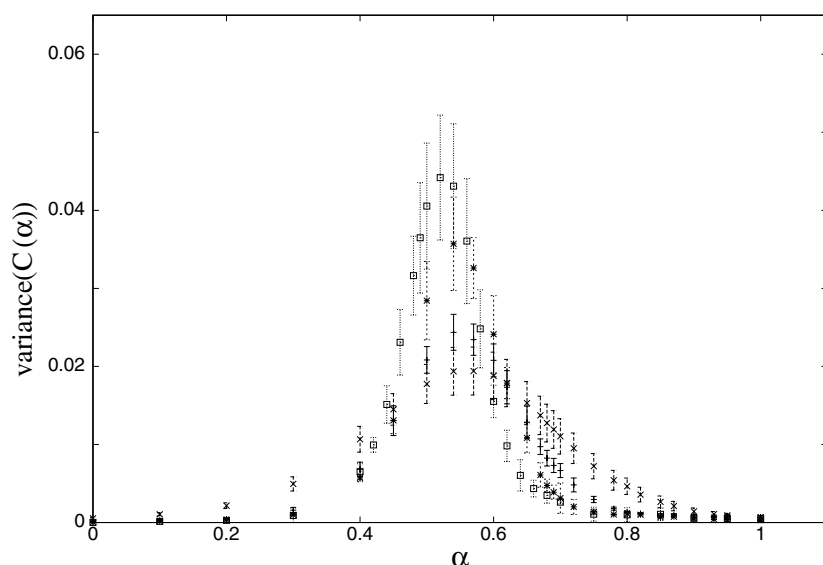


Figure 2. The variance of the heat capacity $C_n(\alpha)$, $(V_c(\alpha, n))$, as a function of α for the quenched random copolymer interacting with a surface when $p = 1/2$, for $n = 50(\times)$, $100(+)$, $200(*)$ and $400(\square)$. The error bars indicate the estimated sampling errors. The results indicate self-averaging of heat capacity away from the critical point.

of α exhibits a linear relationship. The slope of this line can be related to the exponent of n , if one speculates a power-law n -dependence of the energy. The value of this exponent is found to be the largest for $\alpha < \alpha_c$, the smallest for $\alpha \approx \alpha_c$ and at an intermediate value for $\alpha > \alpha_c$. These values suggest that there should be different regimes for the convergence of the energy of the labellings to the mean energy. For $\alpha < \alpha_c$, the value of the exponent is very large indicating a very fast convergence in contrast with the case $\alpha \approx \alpha_c$ where the value of the exponent is at a minimum indicating a very slow convergence. For $\alpha > \alpha_c$, the value of the exponent is between those for $\alpha \approx \alpha_c$ and $\alpha < \alpha_c$. This suggests that the rate of convergence at values of $\alpha > \alpha_c$ is an intermediate value between the rate of convergence near the critical point and the rate for $\alpha < \alpha_c$ interval. These results are obtained for n up to 400 and are not sufficient to allow for a quantitative estimate of this exponent. However, they suggest that the difference between the energy of the system with a randomly chosen colouring and its expectation over colourings may follow a power-law dependence.

Figure 2 shows the α -dependence of the variance of $C_n(\alpha)$, $(V_c(\alpha, n))$, for different values of n . Once again, the variance of the mean of the distribution of the labellings for each value of n slowly rises with a sharp increase in the vicinity of α_c followed by a decrease for values of $\alpha > \alpha_c$. Similar to the case in figure 1, three distinct α regimes are recognized. For $\alpha < \alpha_c$, the variance of $C_n(\alpha)$ decreases as n increases indicating the self-averaging of $C_n(\alpha)$ in this region. A similar trend is observed for $\alpha > \alpha_c$ providing evidence for self-averaging of $C_n(\alpha)$ in this interval. For $\alpha \approx \alpha_c$, however, the trend is reversed: as n grows larger, the variance of $C_n(\alpha)$ grows larger. Based on these results, $C_n(\alpha)$ does not self-average at the critical point.

Figure 3 shows the quenched average $C_n(\alpha)$ over all labellings for different values of n . The increase in height of $C_n(\alpha)$ peaks with an increase in n provides evidence that the adsorption transition of the self-avoiding walk model of a quenched random copolymer is a second-order one. It can also be seen that for $\alpha < \alpha_c$, $C_n(\alpha)$ values decrease as n increases.

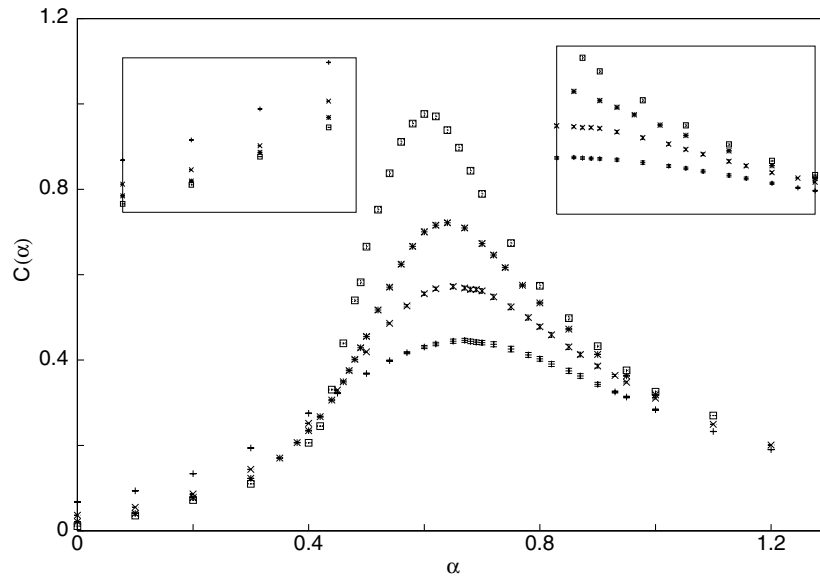


Figure 3. Quenched average $C_n(\alpha)$ as a function of α for $n = 50(+)$, $100(\times)$, $200(*)$ and $400(\square)$. The insets zoom on α intervals below α_c (left) and above α_c (right). Provided that the limiting $C_n(\alpha)$ is finite, as indicated by the numerical data, these results meet the conditions proposed by Orlandini *et al* (2002) for self-averaging of $C_n(\alpha)$ below and above the critical point.

Since the limiting $C_n(\alpha)$ is non-negative, $C_n(\alpha)$ values at different values of n have to approach this limiting value from above. For $\alpha > \alpha_c$, $C_n(\alpha)$ values increase as n increases. In this case, $C_n(\alpha)$ is bounded from below. Provided that the limiting $C_n(\alpha)$ is finite, as indicated by the numerical data, these results meet the conditions proposed by Orlandini *et al* (2002) for self-averaging of $C_n(\alpha)$ below and above the critical point.

Figure 4 shows the variance of z as a function of α for self-avoiding walks of 50, 100, 200 and 400 edges modelling the random copolymer of corresponding sizes interacting with a surface. Once again, the variance is increasing as α increases for various values of n . There are three distinct regimes of $\alpha < \alpha_c$, $\alpha \approx \alpha_c$ and $\alpha > \alpha_c$ over each of which the variance of mean z -coordinate of the walk behaves in different ways. For values of α far from α_c the variance decreases as n increases providing evidence for self-averaging. In the vicinity of α_c the variance, it is hard to establish a trend since the fluctuations are too strong.

Figure 5 shows the variance of $\langle v_A(\alpha|\chi) \rangle / n$, $V(\alpha, n)$, as a function of α for self-avoiding walks of 50, 100, 200 and 400 edges modelling the homopolymer of corresponding sizes interacting with a random surface. The results are for the case where the probability of a site on the surface being A , p , is 0.6. The variance is increasing as α increases for different values of n . There are three distinct regimes of $\alpha < \alpha_c$, $\alpha \approx \alpha_c$ and $\alpha > \alpha_c$ over each of which the variance of $\langle v_A(\alpha|\chi) \rangle / n$ behaves differently. For values of α far from α_c the variance decreases as n increases. This indicates that the energy of any particular sequence becomes closer to that of the expectation over labellings as n increases. In the vicinity of α_c a definite conclusion cannot be drawn due to large fluctuations in the data. The results for values of p below the percolation threshold of the surface, such as the case when $p = 0.5$ exhibit the same trend. The main result in this section is that energy self-averages below and above the critical point for a homopolymer interacting with a random surface. That is to say, far

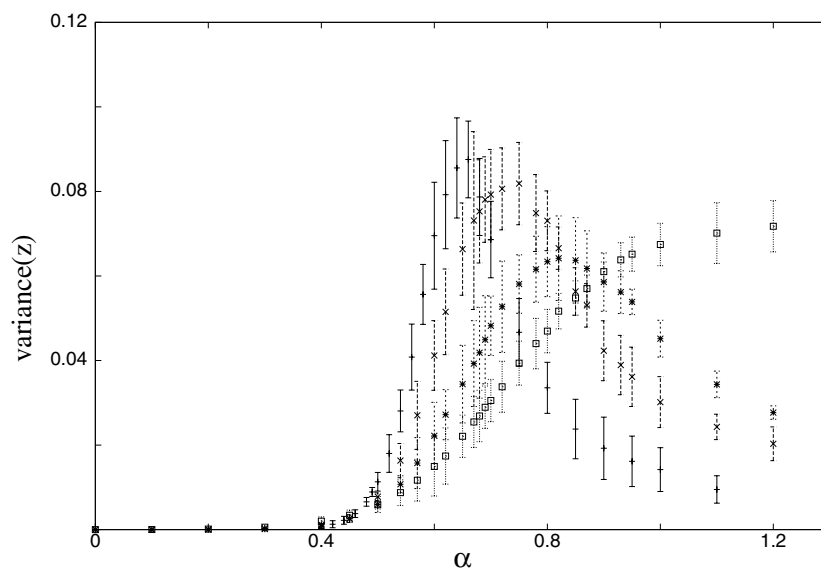


Figure 4. The variance of the mean z -coordinate of the walk, $(V_z(\alpha, n))$, for the random copolymer interacting with a homogeneous surface for $p = 1/2$, $n = 50(\square)$, $100(*)$, $200(\times)$ and $400(+)$. The error bars indicate the estimated sampling errors. Self-averaging of the mean z -coordinate of the walk is clearly indicated far from the critical point.

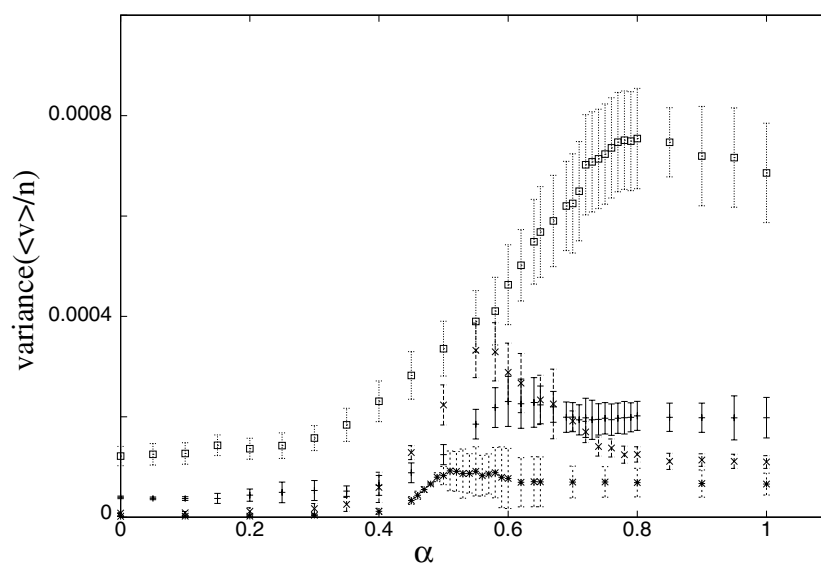


Figure 5. The variance of the $\langle v \rangle/n$ as a function of α for a homopolymer interacting with a random surface for $p = 0.6$, $n = 50(\square)$, $100(+)$, $200(\times)$ and $400(*)$. The error bars indicate the estimated sampling errors. The results indicate self-averaging of energy away from the critical point.

from the critical point, energy values for any particular sequence approach the expectation of energy over many labellings as n increases.

4. Conclusion

Monte Carlo methods are used to investigate self-averaging in thermodynamic and metric properties of the self-avoiding walk model of a quenched random copolymer interacting with a homogeneous surface. In this case an analytical proof of self-averaging of the free energy in the thermodynamic limit exists; however for metric properties no such proof exists. The temperature dependence of the variance of energy, heat capacity and the mean z -coordinate of the vertices of the walk is investigated numerically. The evidence provided in this work supports the assumption that these properties self-average in certain temperature intervals far from the critical point. At the critical point these results are not conclusive. These results verify the assumption of self-averaging made in calculating thermodynamic and metric properties in the case of the adsorption of a finite size random copolymer onto a surface. The extent of self-averaging in energy is also examined and commented upon.

MMCMC is also used to investigate self-averaging in the energy of a homopolymer interacting with a quenched random surface. For this problem there is no analytical proof of self-averaging even in the thermodynamic limit. Far from the critical point, self-averaging in energy is observed. In the vicinity of the critical point, no definite conclusions can be drawn. These results verify the assumption of self-averaging made in the case of the adsorption of a homopolymer onto a random surface.

Acknowledgments

Useful discussions with Professor S G Whittington are greatly appreciated. This research was supported, in part, by NSERC of Canada.

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