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Adsorption of self-avoiding walks at an impenetrable plane in the expanded phase: a Monte Carlo study

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Abstract. We consider self-avoiding walks on the simple cubic lattice, confined to the half-space $z \geqslant 0$. In addition, the walks interact with the plane $z = 0$ and have a vertex–vertex interaction. The walks can adsorb at the plane $z = 0$. The location of the adsorption phase transition depends, in general, on the contact interaction. We use Monte Carlo methods to investigate the form of the adsorption phase boundary in the expanded phase region.

1. Introduction

Self-avoiding walks on a lattice are a good model of linear polymer molecules in dilute solution in a good solvent (Madras and Slade 1993). If a short-range interaction between the vertices of the walk is included, we obtain a model in which the solvent quality is recognized. Then the walk is thought to undergo a transition in the infinite n limit (n stands for the length of the walk) from the expanded phase to the collapsed phase. Although there is no direct rigorous proof of the existence of this transition, the numerical results strongly support it. This problem has been extensively studied by Monte Carlo methods (Mazur and McCrackin 1968, Kremer *et al* 1981, Meirovitch and Lim 1989, Grassberger and Hegger 1995a, Tesi *et al* 1996, Nidras and Brak 1997).

Self-avoiding walks are also used as a model of polymer adsorption at a solid surface from dilute solutions. In this case one includes a short-range interaction of the walk with an impenetrable surface. A version of this model is a self-avoiding walk on the simple cubic lattice, with the first vertex of the walk at the origin, and no vertex of the walk with a negative z-coordinate. In addition, each vertex in the plane $z = 0$ contributes an energy term. Such a walk can be adsorbed into the plane $z = 0$, if this energy is attractive (Hammersley *et al* 1982). Similar models in two and three dimensions have been extensively studied using Monte Carlo methods (Meirovitch and Livne 1988, Meirovitch and Chang 1993, Hegger and Grassberger 1994, Grassberger and Hegger 1995b, Zhao *et al* 1990), and the location of the phase transition and values of several critical exponents have been estimated.

As polymer adsorption can occur from solvents of different quality, one is interested in the interplay between the adsorption and collapse phenomena. As a model, one considers a self-avoiding walk, restricted to a non-negative z half-space, with an internal (vertex–vertex) interaction and also a vertex–plane interaction, so that it can exhibit both a collapse transition

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and an adsorption transition. A Monte Carlo study on collapse of self-avoiding walks near a linear wall in two dimensions has appeared (Chang and Meirowitch 1993), and there is an exact enumeration study in two dimensions which investigates the form of the phase diagram (Foster *et al* 1992). Vrbová and Whittington (1996) derived some rigorous results about the form of the phase diagram in three dimensions, and studied the nature of the phase diagram using Monte Carlo methods (Vrbová and Whittington 1998). They suggested a phase diagram that shows four phases: (i) desorbed–expanded, (ii) desorbed–collapsed, (iii) adsorbed–expanded and (iv) adsorbed–collapsed. Since the estimates of the location of the phase boundaries were obtained at modest values of n, they are only approximations to the infinite n behaviour, and this effect might hide some features of the phase diagram.

One of the ambiguous results from the small n calculations was the correct shape of the phase boundary between the desorbed–expanded and adsorbed–expanded phases. The aim of this paper is to investigate the form of the adsorption phase boundary in the expanded phase in three dimensions to answer the question whether the solvent quality, in the good-solvent regime, influences the location of the adsorption phase transition.

2. The model

We consider self-avoiding walks on the simple cubic lattice, confined to the half-space $z \geqslant 0$ and interacting with the plane $z = 0$. A *visit* is a vertex of the walk with zero z-coordinate. In addition, there is a short-range vertex–vertex interaction and a *contact* is a pair of vertices of the walk, unit distance apart, which are not connected by an edge of the walk. We define the partition function

$$Z_n(\alpha, \beta) = \sum_{v,k} c_n(v, k) \mathrm{e}^{\alpha v + \beta k} \tag{2.1}$$

where $c_n(v, k)$ is the number of n-edge walks with $v + 1$ visits and k contacts, α is the vertex–plane interaction parameter and β is the vertex–vertex interaction parameter. The corresponding free energy is defined

$$\kappa_n(\alpha, \beta) = n^{-1} \log Z_n(\alpha, \beta). \tag{2.2}$$

The limit $\lim_{n\to\infty} \kappa_n(\alpha, \beta)$ is proved to exist for all finite values of α for $\beta \leqslant 0$ and the corresponding limiting free energy for polygons exists for all finite values of α and β (Vrbová and Whittington 1996). There is an adsorption phase transition for any value of β for the polygon case, and the location of this phase transition is bounded for $\beta \geqslant 0$ as

$$0 \leqslant \alpha_c(\beta) \leqslant A + 2\beta \tag{2.3}$$

where A is a positive constant. We believe that walks show the same behaviour as polygons.

The method is a Markov chain Monte Carlo scheme based on a combination of the pivot algorithm (Lal 1969, Madras and Sokal 1988) and the 'local moves' algorithm (Madras and Slade 1993). To avoid the long autocorrelation times associated with similar calculations involving compact phases we implemented this using the multiple Markov chain method (Geyer 1991, Tesi *et al* 1996). For the details of the implementation see Vrbová and Whittington (1998).

3. Results and discussion

Our main aim was to investigate adsorption of self-avoiding walks restricted to the half-space $z \geqslant 0$, having both vertex–vertex and vertex–plane interactions. In particular, we were

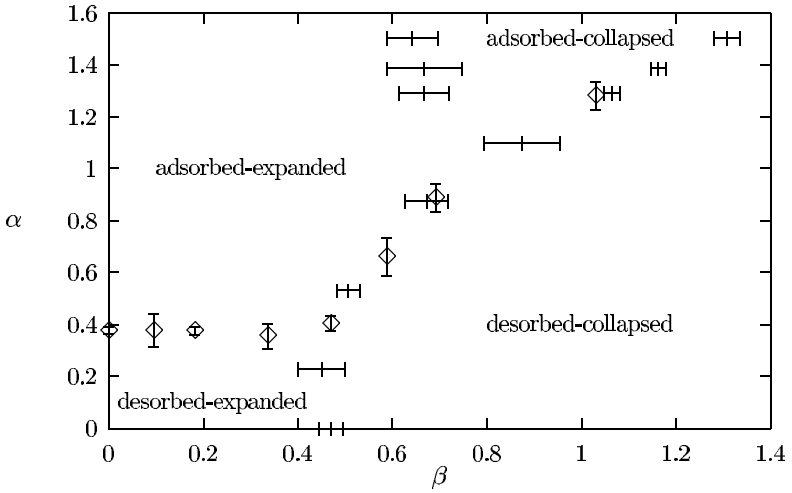

Figure 1. The locations of the heat capacity peaks for $n = 100$, adopted from Vrbová and Whittington (1996). The diamonds correspond to peaks in $\partial^2\kappa_n(\alpha, \beta)/\partial\alpha^2$ at fixed β, and the crosses correspond to peaks in $\partial^2\kappa_n(\alpha, \beta)/\partial\beta^2$ at fixed α.

interested in the shape of the corresponding phase boundary. Vrbová and Whittington (1998) investigated this system using moderate lengths of the walks. They estimated locations of the phase transitions using peaks in the heat capacities. Their results for $n = 100$ are shown in figure 1. The peak positions depend on n and finite n estimates are only approximations of the phase transition locations. With increasing n, the peak positions move towards the real locations of the phase transitions. Looking at figure 1, we see that the slope of the phase boundary between the desorbed–collapsed and adsorbed–collapsed phases is clearly positive. The authors compared $n = 100$ and $n = 200$ data and the shifts in the peak positions were small, therefore it is reasonable to assume that the slope remains positive even in the infinite n limit. Interpretation of the results for the phase transition between the desorbed–expanded and adsorbed–expanded phases is more difficult. The phase transition estimates lie almost on a horizontal line, and one is not able to predict the infinite n behaviour of the system from the small n data, since even small shifts in the peak positions with increasing n can change the final slope of the phase boundary. Results for much longer walks are therefore needed, together with extrapolation to the infinite n limit, to obtain the correct shape of the phase boundary.

We decided to perform an extensive Monte Carlo calculation for walks of up to 1600 edges, for several values of the vertex–vertex interaction parameter, and to extrapolate the estimates of the location of the phase transition to the infinite n limit. By comparing the resulting estimates for several values of β we should be able to obtain the correct shape of the corresponding phase boundary. Such simulation is very demanding on computer time and, after several preliminary runs, we decided to use only three values of β, although four or even more values would be probably more convincing. The first value of β used is negative. We chose $\beta = -0.51$ since this value is, in our opinion, small enough to capture any difference in the location of the transition as compared with the location of the phase transition at $\beta = 0$, and it is not too small to make the simulation impossible to perform with sufficient accuracy, which applies especially for the large values of n. The second value of β is, understandably, chosen to be zero. The third value of β is positive. For $n = 100$, position of the peak in $\partial^2\kappa_n(\alpha, \beta)/\partial\beta^2$ is around $\beta = 0.46$, and the value decreases with n. A current estimate of

the location of the collapse transition, without the presence of the solid surface, is 0.275 (Tesi *et al* 1996), and it is believed that the collapse phase transition occurs at the same β value for the half-space problem in the expanded phase. Thus, we have to use β smaller then 0.275. We chose $\beta = 0.18$, a value small enough to be sure that we sample in the expanded phase and that the vicinity of the collapse phase transition does not influence our results.

We estimated the location of the adsorption transition for these values of β, for several values of n, and then extrapolated the data to the infinite n limit. Typically, we used a set of eight or ten values of α, at fixed β and n, in a single multiple Markov chain run. These data were reweighted to obtain estimates at intermediate values of α.

There are no phase transitions and no singularities in the free energy at finite n. However, there are estimators of the phase boundary locations for finite n that approach the infinite n limit as n increases. For finite n, we expect a peak in the 'heat capacity' $\partial^2\kappa_n(\alpha, \beta)/\partial\alpha^2$ when we cross a phase boundary and we use the location of this peak as an estimator of the location of the phase transition. We estimate the location of the peak for various values of n and extrapolate to the infinite n limit. Another method of estimating the location of the phase transition takes advantage of the fact that $\langle v\rangle/n$ is zero, in the infinite n limit, for all $\alpha \leqslant \alpha_c$ and non-zero otherwise, and we use the intercept of the tangent at the inflection point of $\langle v\rangle/n$ and the α-axis, $\alpha_c(n)$, as an estimator of the upper bound on the phase transition location. As $n \to \infty$, the estimator $\alpha_c(n)$ approaches a value which is not smaller than α_c. In addition, we calculated the radius of gyration and the components of the radius of gyration parallel and perpendicular to the surface. These quantities are other indicators of the location of the phase boundary.

To locate the phase boundary between the desorbed–expanded and adsorbed–expanded phases, we carried out multiple Markov chain runs starting at $\alpha = 0$ and increased α to a value above the adsorption transition, keeping the β value fixed. In figure 2 we show the α-dependence of $\partial^2\kappa_n(\alpha, \beta)/\partial\alpha^2$ for $n = 50, 100, 200, 400, 800, 1000$ and 1600 for $\beta = 0$. There is a single peak as α is varied, corresponding to the adsorption phase transition. The peak increases in height and sharpens as n increases, which suggests that the peak will remain in the infinite n limit. The peak moves towards smaller values of α as n increases. In figure 3

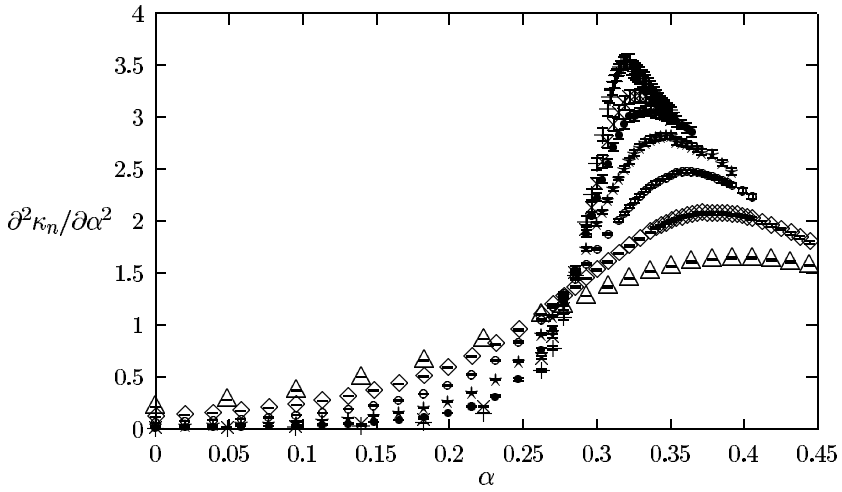

Figure 2. The α-dependence of $\partial^2\kappa_n(\alpha, \beta)/\partial\alpha^2$ for $n = 50$ ($\triangle$), $n = 100$ ($\diamond$), $n = 200$ ($\bigcirc$), $n = 400$ ($\star$), $n = 800$ ($\bullet$), $n = 1000$ ($\times$) and $n = 1600$ (+) for $\beta = 0$.

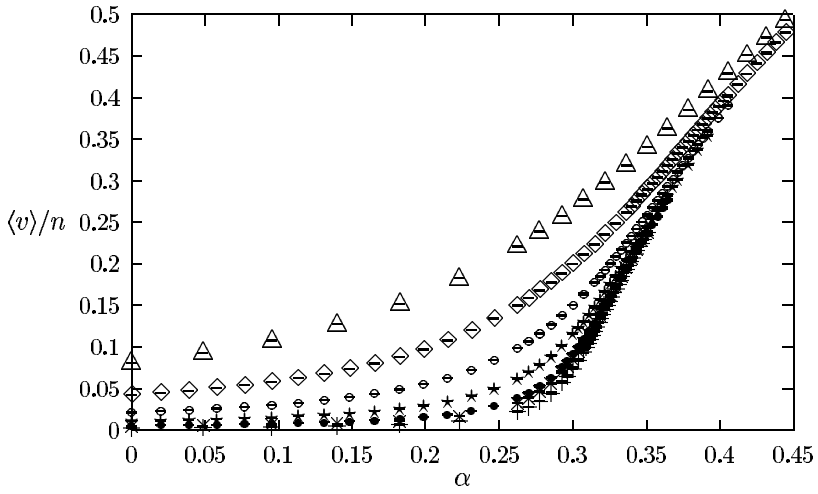

Figure 3. The mean number of visits per edge, $\langle v\rangle/n$, as a function of α at $\beta = 0$ for $n = 50$ (△), $n = 100$ (◇), $n = 200$ (○), $n = 400$ (⋆), $n = 800$ (●), $n = 1000$ (×) and $n = 1600$ (+).

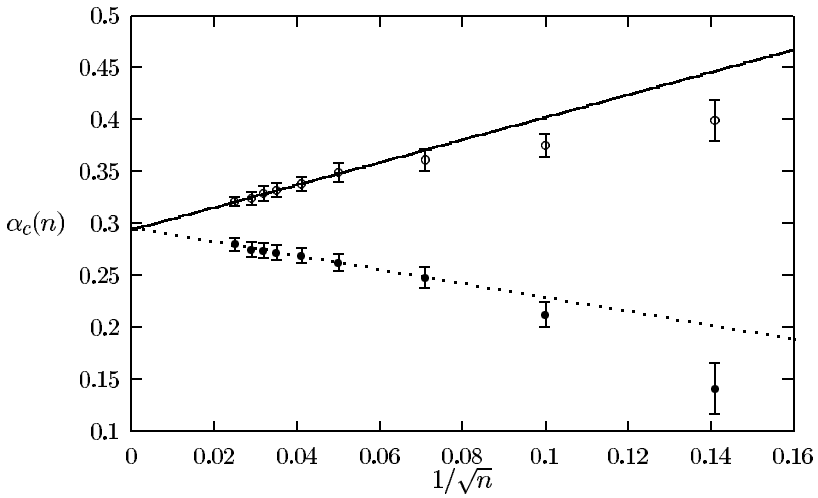

Figure 4. Estimates of $\alpha_c(n)$ for $\beta = 0$ using the location of the heat capacity peak maxima (upper line) and the intercept construction (lower line) for $n = 50, 100, 200, 400, 600, 800, 1000, 1200, 1600$, and the corresponding least squares fits to the data for $n \geqslant 600$.

we show the mean number of visits per edge, $\langle v\rangle/n$, as a function of α for the same values of n. We see a large increase in $\langle v\rangle/n$ corresponding to the phase transition. Our estimates of the phase transition location for $\beta = 0$ plotted against $1/\sqrt{n}$ (we use the value of the cross-over exponent obtained by Hegger and Grassberger (1995b) $\phi = 0.5$) are shown in figure 4. The graph is linear for large n values, and we have computed least squares fits to the data in the linear regime, with weights proportional to the inverse of the variances. In table 1 we give our estimates of α_c for three different values of β, $\beta = -0.51$, 0.0 and 0.18

Table 1. Estimated location of the adsorption transition from the heat capacity peak maxima, $\alpha_c^I(\beta)$, and from the tangent intercept of $\langle v\rangle/n$, $\alpha_c^{II}(\beta)$ for three values of β.

β	α_c^I	α_c^{II}
-0.51	0.295 ± 0.027	0.297 ± 0.021
0.0	0.294 ± 0.014	0.296 ± 0.018
0.18	0.290 ± 0.020	0.290 ± 0.021

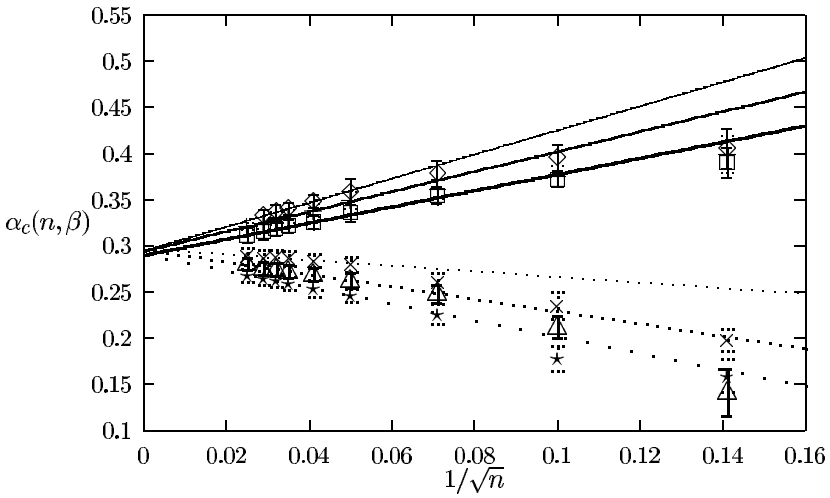

Figure 5. Estimates of $\alpha_c(n,\beta)$ using the location of the heat capacity peak maxima (full lines) for $\beta = -0.51$ ($\diamondsuit$), 0.0 (+) and 0.18 ($\square$), and the intercept construction (dotted lines) for $\beta = -0.51$ ($\times$), 0.0 ($\triangle$) and 0.18 ($\star$), together with the corresponding least squares fits to the data for $n \geqslant 600$.

4. Conclusion

We have investigated the shape of the phase boundary between the desorbed–expanded and adsorbed–expanded phases of self-avoiding walks at an impenetrable plane on the simple cubic lattice. We used the multiple Markov chain algorithm, based on a mixture of pivot and local moves, to estimate the location of the phase transition. We have estimated the locations of the heat capacity peak maxima for various values on n and extrapolated the data to obtain the estimates of $\alpha_c(\beta)$ for three different values of β in the expanded regime. We have also estimated $\alpha_c(\beta)$ extrapolating the estimates of $\alpha_c(n)$ obtained through the intercept method.

For the values of n used, $\alpha_c(n)$ depends on β, but this feature goes away with increasing n, and we believe that, at the thermodynamic limit, α_c does not depend on β in the expanded regime. This is nicely illustrated in figure 5, where the estimates of $\alpha_c(n)$ versus $1/\sqrt{n}$ are shown, together with the least squares fits to the large n data. The estimated values of $\alpha_c(\beta)$ all lie within the error bars for the three different values of β.

Finally, we would like to note that even though this study is an extension of previous work (Vrbová and Whittington 1996, Vrbová and Whittington 1998), there are still some interesting features of the phase diagram not fully explained. These are, for example, the existence of a phase transition between the adsorbed–expanded and desorbed–collapsed phases, and the way in which the location of the collapsed phase boundary in the adsorbed region approaches the infinite vertex–plane attraction limit.

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