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Adsorption and collapse of self-avoiding walks at a defect plane

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Abstract. We consider self-avoiding walks and polygons on the simple cubic lattice with a vertex–vertex interaction (i.e. a contact interaction), which also interact with a defect plane, $z = 0$. The walks or polygons can undergo a collapse transition, and can also adsorb at the defect plane. For the polygon case we prove that the limiting free energy exists, and show that there is an adsorption transition for each finite value of the vertex–vertex interaction. We use Monte Carlo methods to investigate the form of the phase diagram for the walk problem.

1. Introduction

Surface effects in magnetic systems have been widely studied since the pioneering work of Binder and Hohenberg (1972) and Bray and Moore (1977). If one considers a magnetic system with a (ferromagnetic) interaction J between bulk spins and a different (ferromagnetic) interaction J_1 between surface spins there are two interesting cases. The first is when the surface is a boundary of the magnet, and the second is when it forms a defect plane within the magnet. Each problem has a polymer analogue.

Consider the simple cubic lattice Z^3 . In the first case, the analogous situation is a self-avoiding walk starting in the plane $z = 0$, confined to the half-space $z \geq 0$, and interacting with the surface plane. This is a model of polymer adsorption at a surface and has been the subject of considerable research for over 30 years. It is known (Hammersley *et al* 1982) that the model exhibits a phase transition corresponding to adsorption, and the location of the transition has been estimated by exact enumeration and Monte Carlo methods. For recent reviews see De’Bell and Lookman (1993) and Eisenriegler (1993).

In the second case, the self-avoiding walk interacts with the plane $z = 0$ but can cross the plane. This has been suggested as a possible model of polymer adsorption at a liquid–liquid interface. Again it is known that the model has a phase transition (Hammersley *et al* 1982) and the location of the transition is thought to be at ‘infinite temperature’ for any attractive interaction. The model has been studied by real-space renormalization group techniques (Nakanishi 1981) and by exact enumeration and series analysis (Ishinabe 1984, Zhao *et al* 1990).

Long linear polymers in dilute solution can also undergo a collapse transition from an open coil to a compact ball. The exponent (ν) characterizing the dependence of the mean square radius of gyration

$$\langle S_n^2 \rangle \sim n^{2\nu} \quad (1.1)$$

on the degree of polymerization (n) changes at this transition point. In the collapsed (low temperature) phase one expects that $\nu = 1/3$ in three dimensions, while in the expanded (high temperature) phase $\nu \approx 0.588$ (Li *et al* 1995). The experimental observation of a

dramatic change in the dimensions as a function of temperature or solvent quality has been reported by several groups (Nishio *et al* 1979, Sun *et al* 1980, 1990, Nakata 1995). The transition has been studied theoretically for a model in which a short range attractive force is associated with nearby pairs of vertices of a self-avoiding walk. Many results for this model have been obtained using Monte Carlo methods (Webman *et al* 1981, Meirovitch and Lim 1989, Grassberger and Hegger 1995, Tesi *et al* 1996a, Nidras and Brak 1997).

Polymer adsorption can occur from poor or good solvents and the special case of adsorption at the θ point has attracted particular attention. The values of various surface critical exponents have been estimated numerically (Vanderzande *et al* 1991, Foster *et al* 1992, Hegger and Grassberger 1994), and renormalization group arguments predict that the three-dimensional system will have random walk exponents but with novel non-power-law logarithmic corrections (Eisenriegler and Diehl 1988).

Several authors have considered the influence of the adsorption and collapse phenomena on one another. Foster (1990) and Foster and Yeomans (1991) have analysed the case of a *directed* polymer model in two dimensions. They observed three phases: a desorbed-expanded phase, a desorbed-collapsed phase and an adsorbed phase, and derived the form of the phase diagram. A similar phase diagram was reported (using exact enumeration and series analysis methods) for an undirected model in two dimensions by Foster *et al* (1992). We (Vrbová and Whittington 1996) derived some rigorous results about the form of the phase diagram in three dimensions where one expects two adsorbed phases, one expanded and one collapsed, and studied the nature of the phase diagram using Monte Carlo methods (Vrbová and Whittington 1998).

The aim of this paper is to investigate the form of the phase diagram in three dimensions when the polymer is interacting with a penetrable (rather than an impenetrable) surface, which corresponds to the defect plane model.

2. Some rigorous results

We consider the simple cubic lattice Z^3 whose vertices are the integer points in R^3 and whose edges connect pairs of vertices which are unit distance apart. A *self-avoiding walk* is an alternating sequence of vertices and edges such that all vertices are distinct. We shall normally consider self-avoiding walks with a vertex of degree one at the origin, and write c_n for the number of such walks with n edges.

A *contact* is an edge of the lattice which is incident on two vertices of the walk but is not an edge of the walk. A *visit* is a vertex of the walk in the plane $z = 0$. Let $c_n(v, k)$ be the number of self-avoiding walks with n edges, starting at the origin, having $v + 1$ visits and k contacts. We call such walks *attached walks*. Define the generating function

$$C_n(\alpha, \beta) = \sum_{v,k} c_n(v, k) e^{\alpha v + \beta k}. \quad (2.1)$$

Similarly, let $c_n^+(v, k)$ be the number of these walks with the added restriction that no vertex has negative z -coordinate. We call such walks *positive walks* and define their generating function to be

$$C_n^+(\alpha, \beta) = \sum_{v,k} c_n^+(v, k) e^{\alpha v + \beta k}. \quad (2.2)$$

Clearly $\sum_{v,k} c_n(v, k) = c_n$ and we write $\sum_{v,k} c_n^+(v, k) = c_n^+$ where c_n^+ is the total number of n -edge positive walks.

We call an embedding of the circle graph in Z^3 a *polygon*. The *bottom vertex* of a polygon is the vertex whose coordinates are lexicographically first. Let p_n be the number of

undirected n -edge polygons, with their bottom vertex at the origin. It is known (Hammersley 1961, Whittington 1975) that

$$0 < \lim_{n \rightarrow \infty} n^{-1} \log p_n = \lim_{n \rightarrow \infty} n^{-1} \log c_n = \lim_{n \rightarrow \infty} n^{-1} \log c_n^+ = \kappa < \infty. \quad (2.3)$$

We are interested in undirected polygons with at least one vertex in the plane $z = 0$. Among the vertices of the polygon with zero z -coordinate, one will have x - and y -coordinates which are lexicographically first. We call this vertex the *origin* of the polygon. If the origin of the polygon is $(0, 0, 0)$ we call the polygon an *attached polygon*. We call the subset of attached polygons which have no vertex with negative z -coordinate *positive polygons*. Let the number of n -edge attached polygons with $v + 2$ visits and k contacts be $p_n(v, k)$ and let the corresponding number of positive polygons be $p_n^+(v, k)$. Define their generating functions to be

$$P_n(\alpha, \beta) = \sum_{v,k} p_n(v, k) e^{\alpha v + \beta k} \quad (2.4)$$

and

$$P_n^+(\alpha, \beta) = \sum_{v,k} p_n^+(v, k) e^{\alpha v + \beta k}. \quad (2.5)$$

Using concatenation arguments similar to those in Vrbová and Whittington (1996) we can prove the following theorem.

Theorem 2.1. The limiting free energy of attached polygons

$$\kappa_0(\alpha, \beta) = \lim_{n \rightarrow \infty} n^{-1} \log P_n(\alpha, \beta) \quad (2.6)$$

exists for all finite values of α and β . In addition $\kappa_0(\alpha, \beta)$ is a doubly convex, monotone non-decreasing function of α and β .

Vrbová and Whittington (1996) proved the existence of the limiting free energy

$$\kappa_0^+(\alpha, \beta) = \lim_{n \rightarrow \infty} n^{-1} \log P_n^+(\alpha, \beta) \quad (2.7)$$

for all finite values of α and β , for positive polygons. Moreover they showed that

$$\lim_{n \rightarrow \infty} n^{-1} \log C_n^+(\alpha, \beta) = \kappa_0^+(\alpha, \beta) \quad (2.8)$$

for all $\beta \leq 0$, $\alpha < \infty$, and that

$$\kappa_0^+(\alpha, \beta) = \kappa_0^+(0, \beta) \quad (2.9)$$

for any $\alpha < 0$, for all finite β .

We next prove some similar results about $\kappa_0(\alpha, \beta)$. Our results are contained in the following theorem.

Theorem 2.2. The limiting free energies of positive and attached polygons are related by the inequality

$$\kappa_0^+(\alpha, \beta) \leq \kappa_0(\alpha, \beta) \quad (2.10)$$

for all finite α and β . Moreover,

$$\kappa_0(\alpha, \beta) = \kappa_0(0, \beta) = \kappa_0^+(0, \beta) \quad (2.11)$$

for all $\alpha < 0$, for all finite β , and

$$\max[\kappa_0(0, \beta), \kappa_2(\beta) + \alpha] \leq \kappa_0(\alpha, \beta) \leq \kappa_0(0, \beta) + \alpha \quad (2.12)$$

for $\alpha \geq 0$, for any finite β . $\kappa_2(\beta)$ is the limiting free energy for self-interacting polygons on the square lattice.

Proof. Since positive polygons are a subset of attached polygons, $p_n^+(v, k) \leq p_n(v, k)$, so that $P_n^+(\alpha, \beta) \leq P_n(\alpha, \beta)$ and (2.10) follows on taking logarithms, dividing by n and letting n tend to infinity. We note that any attached polygon is a translate of a positive polygon. In this translation the value of v might change but the value of k is fixed. This implies that

$$\sum_v p_n^+(v, k) \leq \sum_v p_n(v, k) \leq \frac{n}{2} \sum_v p_n^+(v, k) \quad (2.13)$$

from which it follows that

$$\kappa_0^+(0, \beta) = \kappa_0(0, \beta) \quad (2.14)$$

for any finite β . But $\kappa_0(\alpha, \beta)$ is a non-decreasing function of α at fixed β and, using (2.9) and (2.10), we have (2.11) for all $\alpha < 0$, for all finite β . To prove (2.12) we fix $\beta < \infty$ and take any $\alpha \geq 0$. Then

$$P_n(\alpha, \beta) \leq \sum_{v,k} p_n(v, k) e^{\alpha n + \beta k} = e^{\alpha n} P_n(0, \beta). \quad (2.15)$$

The upper bound in (2.12) follows on taking logarithms, dividing by n and letting $n \rightarrow \infty$. To obtain the lower bound we first note that $\kappa_0(\alpha, \beta)$ is non-decreasing in α so that $\kappa_0(\alpha, \beta) \geq \kappa_0(0, \beta)$ for any positive α . Then we bound the partition function by taking only a subset of the (non-negative) terms in the sum, giving

$$P_n(\alpha, \beta) \geq \sum_k p_n(n-2, k) e^{\alpha(n-2) + \beta k}. \quad (2.16)$$

Taking logarithms, dividing by n and letting n go to infinity gives

$$\kappa_0(\alpha, \beta) \geq \lim_{n \rightarrow \infty} n^{-1} \log \sum_k p_n(n-2, k) e^{\beta k} + \alpha \equiv \kappa_2(\beta) + \alpha. \quad (2.17)$$

Then (2.12) follows immediately. \square

Theorem 2.3. There is a phase boundary between desorbed and adsorbed phases and this phase boundary is at a non-negative α and is never above the corresponding phase boundary for the half-space problem.

Proof. Equations (2.11) and (2.12) imply that $\kappa_0(\alpha, \beta)$ is a non-analytic function of α for every finite β . This implies the existence of a phase boundary between the desorbed and adsorbed phases which we write as $\alpha = \alpha_c(\beta)$. From (2.11) and (2.12) it is clear that $\alpha_c(\beta) \geq 0$. Vrbová and Whittington (1996) showed the existence of a similar curve of singularities for positive polygons, which we write as $\alpha = \alpha_c^+(\beta)$. From (2.10) it follows that $\alpha_c^+(\beta) \geq \alpha_c(\beta)$. \square

We next state a theorem about the shape of the phase boundary between the desorbed-expanded and desorbed-compact phases.

Theorem 2.4. If attached polygons exhibit a collapse transition at $\beta = \beta_0$ for $\alpha = 0$ then there is a line, $\beta = \beta_0$, of collapse transitions between a desorbed-expanded and a desorbed-compact phase for attached polygons, for all $\alpha < \alpha_c(\beta_0)$.

Proof. The proof is essentially identical to the proof of theorem 3.4 in Vrbová and Whittington (1996). \square

In addition, positive polygons and attached polygons collapse at the same value of β . This follows at $\alpha = 0$ from the fact that every attached polygon is a translate of a positive polygon, and the number of contacts is not affected by the translation. This result extends to all values of $\alpha < \alpha_c(\beta_0)$, using theorem 2.4.

The next theorem connects the limiting free energies of attached walks and attached polygons.

Theorem 2.5. The limiting free energy

$$\kappa(\alpha, \beta) = \lim_{n \rightarrow \infty} n^{-1} \log C_n(\alpha, \beta) \quad (2.18)$$

exists for all $\beta \leq 0$ and all $\alpha < \infty$ and, under these conditions,

$$\kappa(\alpha, \beta) = \kappa_0(\alpha, \beta). \quad (2.19)$$

In addition, if the mean number of contacts in attached polygons is at least as large as the mean number of contacts in attached walks, for all $\alpha < \infty$ and for all positive β , for sufficiently large even n , then the limit defining $\kappa(\alpha, \beta)$ exists and (2.19) remains true for all finite β .

Proof. The proof is similar to the proof of theorem 2.10 in Vrbová and Whittington (1996) and theorem 2.8 in Tesi *et al* (1996b). \square

3. Monte Carlo method and results

The Monte Carlo method which we have used is very similar to that described in Vrbová and Whittington (1998), and we give only a very brief summary. The method is a Markov chain Monte Carlo scheme based on the pivot algorithm (Lal 1969, Madras and Sokal 1988) with additional local moves. To avoid the long autocorrelation times associated with the compact phases we implemented this using multiple Markov chains (Geyer 1991, Tesi *et al* 1996a) with swap probabilities chosen to make the limit distribution of the Markov chain equal to the product of the marginal distributions of the elementary Markov chains.

We first consider the case $\beta = 0$ corresponding to the pure adsorption problem. We expect that the limiting free energy will be singular at $\alpha = \alpha_c(0) \equiv \alpha_0$ and that close to this value it will behave as

$$|\kappa(\alpha, 0) - \kappa(\alpha_0, 0)| \sim |\alpha - \alpha_0|^{1/\phi} \quad (3.1)$$

where ϕ is the crossover exponent. At finite n there will be peaks in the second derivative of the free energy (the heat capacity) and the height of the peak at $\alpha = \alpha_0$ should scale as

$$h_n \sim n^{2\phi-1}. \quad (3.2)$$

For the case of an impenetrable plane ϕ is thought to be $\frac{1}{2}$ (Hegger and Grassberger 1994) or a little greater (Eisenriegler *et al* 1982, Meirovitch and Livne 1988) so that the heat capacity peaks should diverge as n increases, and their position should approach the value of α_0 . Hence the heat capacity peaks are a useful device for locating the adsorption transition. For the defect plane case $\phi = 1 - \nu$ (Bray and Moore 1977) which is less than $\frac{1}{2}$ in three dimensions, so that $2\phi - 1 < 0$ and the heat capacity peaks decrease in height as n increases. Peaks in the heat capacity at finite n may not reflect the singularity in $\kappa(\alpha, 0)$ but may come from the analytic background contribution. For this reason we chose to locate the adsorption transition using a different method. We expect a graph of $\langle v \rangle/n$ as a function of α to have

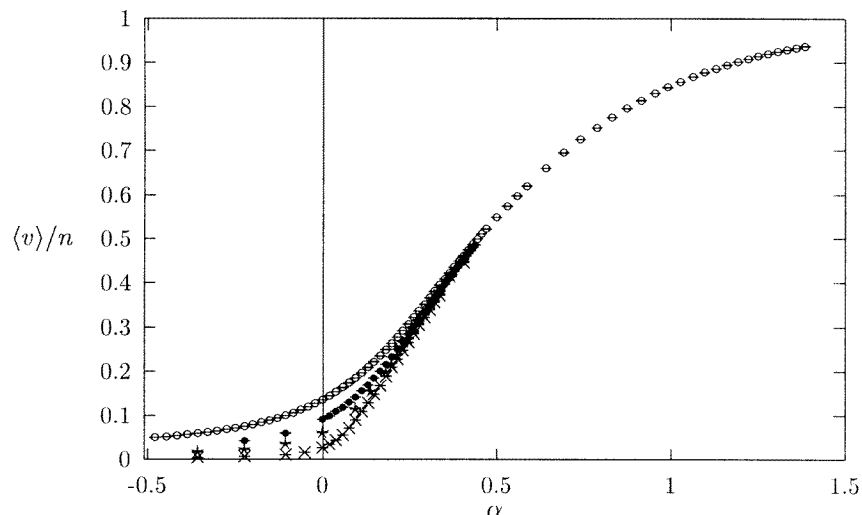


Figure 1. The mean number of visits per edge, $\langle v \rangle/n$, as a function of α at $\beta = 0$ for $n = 50$ (\circ), $n = 100$ (\bullet), $n = 200$ (\star) and $n = 800$ (\times).

an inflexion point at each value of n , and the tangent at this inflexion point should cut the α -axis at an n -dependent value, α_n . The sequence of α_n values should approach a value which is no smaller than α_0 , as $n \rightarrow \infty$. Since we know that $\alpha_0 \geq 0$ this gives a useful method for locating the transition. In figure 1 we show the α -dependence of $\langle v \rangle/n$ for several values of n at $\beta = 0$. The adsorption transition occurs at a value of α between $\alpha = 0$ and $\alpha = 0.05$.

In section 2 we argued that the location of the collapse transition occurs at a value of β which is independent of α for $\alpha \leq \alpha_c(\beta)$. To confirm this we examined $\partial^2 \kappa_n(0, \beta)/\partial \beta^2$ as a function of β for $n = 50$ and 100 . The location of the peak in $\partial^2 \kappa_n(0, \beta)/\partial \beta^2$ is very similar to the corresponding location for the impenetrable case, and moves to smaller values of β as n increases. We have carried out similar calculations for two negative values of α and the peak positions are essentially independent of the values of α , consistent with this phase boundary being a vertical line.

To locate the phase boundaries between the adsorbed-expanded and adsorbed-compact phases, and between the adsorbed-compact and desorbed-compact phases we carried out multiple Markov chain runs in which we began at $\alpha = \beta = 0$, increased α at $\beta = 0$ to a value above the adsorption transition, and then increased β at fixed α until we reached the desorbed-compact phase. Let

$$\kappa_n(\alpha, \beta) = n^{-1} \log C_n(\alpha, \beta). \quad (3.3)$$

In figure 2 we show the β -dependence of $\partial^2 \kappa_n(\alpha, \beta)/\partial \beta^2$ for $n = 100$ at three values of α . In each case we see two peaks in $\partial^2 \kappa_n(\alpha, \beta)/\partial \beta^2$. The peak at the lower value of β is roughly independent of the value of α while the second peak position moves to larger values of β as α increases. In figure 3 we show the β -dependence of $\langle v \rangle/n$ at the three values of α . In each case there is a rapid decrease in $\langle v \rangle/n$ at a value of β corresponding to the second peak in figure 2. Similarly the z -component of the radius of gyration increases rapidly around this value of β so we are confident that the second peak in figure 2 corresponds to desorption in the compact regime, while the first peak must be associated with collapse in the adsorbed regime. In figure 4 we compare the behaviour of $\partial^2 \kappa_n(\alpha, \beta)/\partial \beta^2$ at $\alpha = 1.39$

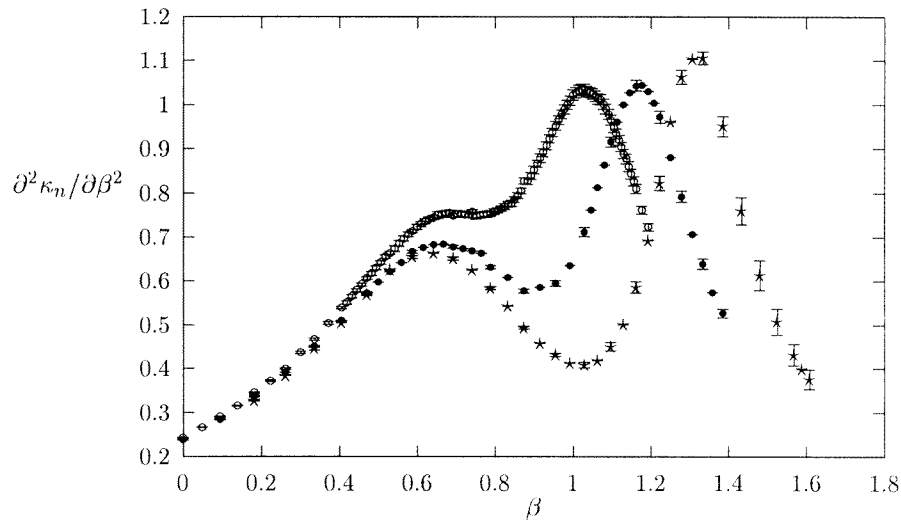


Figure 2. The β -dependence of $\partial^2 \kappa_n(\alpha, \beta) / \partial \beta^2$ for $n = 100$, at $\alpha = 1.25$ (\circ), $\alpha = 1.39$ (\bullet) and $\alpha = 1.50$ (\star).

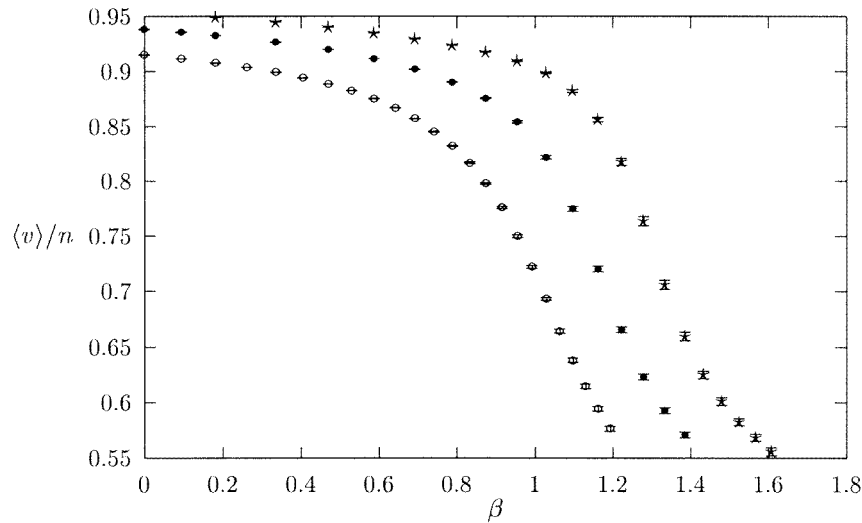


Figure 3. The mean number of visits per edge, $\langle v \rangle / n$, as a function of β at $\alpha = 1.25$ (\circ), $\alpha = 1.39$ (\bullet) and $\alpha = 1.50$ (\star).

for $n = 50$ and 100 . The peaks increase in height as n increases so that we have no reason to suspect that the peaks might disappear in the large n limit.

To confirm the location of the phase boundary between the adsorbed-collapsed and desorbed-collapsed phases we carried out multiple Markov chain runs beginning at $\alpha = \beta = 0$, first decreasing the value of α to $\alpha \approx -1$ (to make sure that we were in the desorbed-expanded phase), and then increasing β at this fixed value of α (to cross into the desorbed-collapsed regime). Then with β fixed (for instance at $\beta = 1.17$) we increased α to about $\alpha = 1.5$. In figure 5 we show the α -dependence of $\partial^2 \kappa_n(\alpha, \beta) / \partial \alpha^2$ at $\beta = 1.17$

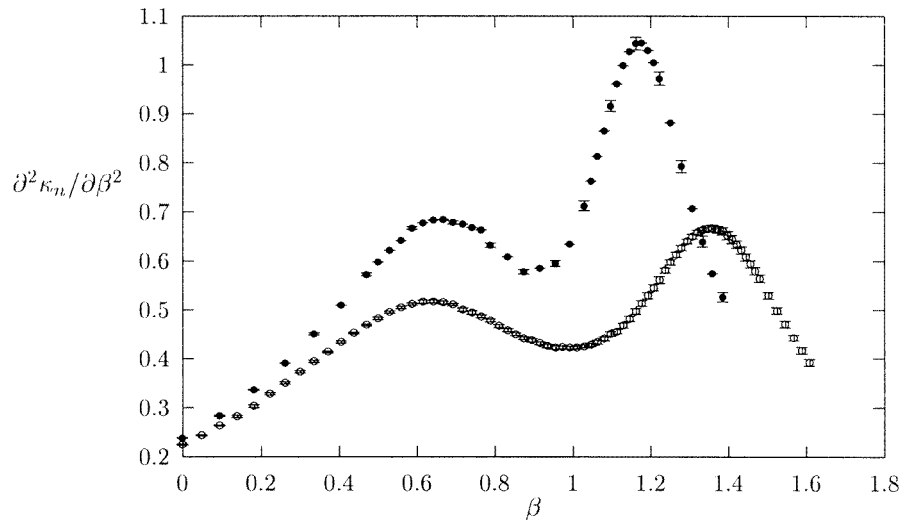


Figure 4. The β -dependence of $\partial^2 \kappa_n(\alpha, \beta) / \partial \beta^2$ at $\alpha = 1.39$, for $n = 50$ (\circ) and $n = 100$ (\bullet).

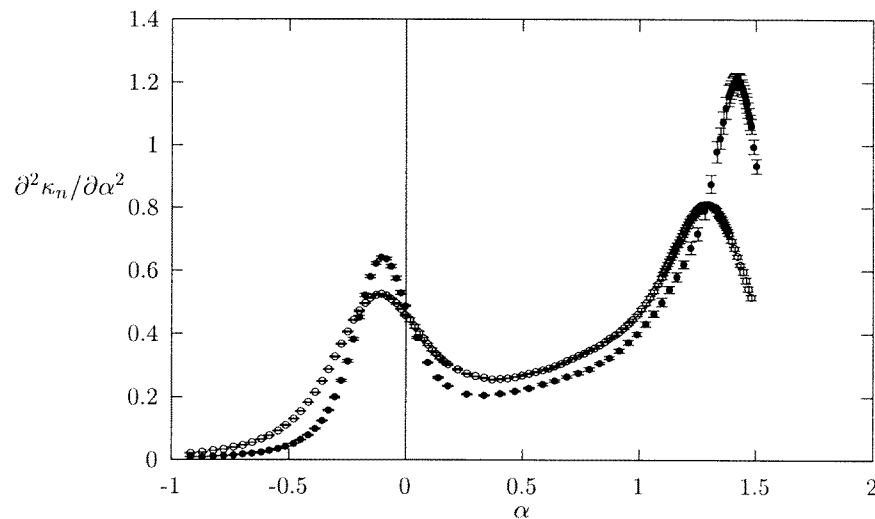


Figure 5. The α -dependence of $\partial^2 \kappa_n(\alpha, \beta) / \partial \alpha^2$ at $\beta = 1.17$, for $n = 50$ (\circ) and $n = 100$ (\bullet).

for $n = 50$ and 100 . The second peak in the figure increases in height as n increases and its location is close to the location of the phase boundary between the desorbed-compact and adsorbed-compact phases, as estimated from figure 2. However, the first peak at around $\alpha = -0.1$ also increases in height as n increases. To understand this we first note that

$$\frac{\partial \kappa(\alpha, \beta)}{\partial \alpha} = \lim_{n \rightarrow \infty} \frac{\langle v \rangle}{n} = 0 \quad (3.4)$$

everywhere in the desorbed phases, so that we expect that the first peak in $\partial^2 \kappa_n(\alpha, \beta) / \partial \alpha^2$ will disappear in the infinite n limit, provided that the second peak is associated with the adsorption transition. Our explanation for the existence of the first peak at finite n is as follows. At $\alpha = 0$ and $\beta > \beta_0$ the walk will be a compact object straddling the defect

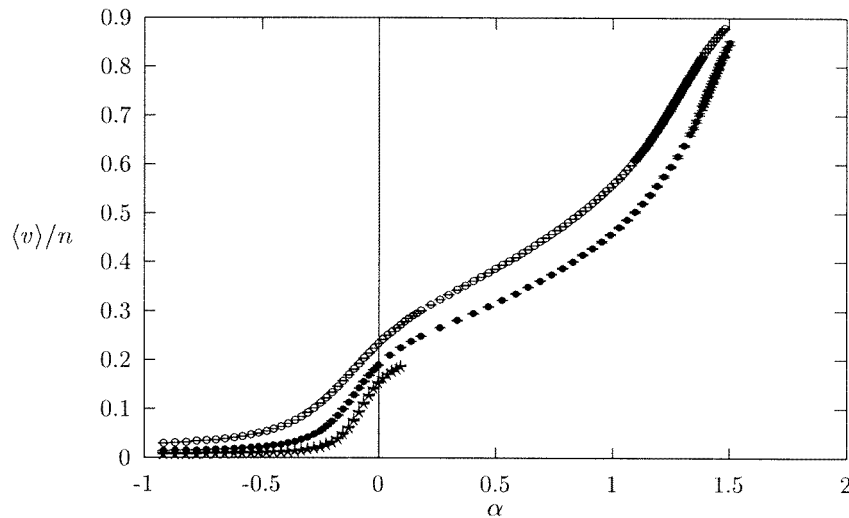


Figure 6. The α -dependence of $\langle v \rangle / n$ at $\beta = 1.17$, for $n = 50$ (\circ), $n = 100$ (\bullet) and $n = 200$ (\star).

plane so that $O(n^{2/3})$ vertices will be in the defect plane. For any $\alpha < 0$ there will be an energetic disadvantage to having vertices in the defect plane and the walk can reduce the number of visits by moving out of the defect plane while remaining compact, with a small entropic penalty (since a vertex of degree one must then be outside the compact region of the walk). This suggests that $\langle v \rangle / n$ will be $O(n^{-1})$ for $\alpha < 0$ and will increase to become $O(n^{-1/3})$ for α positive but less than $\alpha_c(\beta)$, and $O(1)$ for $\alpha > \alpha_c(\beta)$. In figure 6 we show the α -dependence of $\langle v \rangle / n$ at $\beta = 1.17$ for $n = 50, 100$ and 200 . The behaviour roughly coincides with our expectations.

In figure 7 we show an approximate phase diagram obtained from our Monte Carlo results. The points are all for $n = 100$ and, of course, their positions are expected to change in detail as n increases, so that the diagram is only suggestive of the general behaviour in the $n \rightarrow \infty$ limit. The points corresponding to the phase boundary between the desorbed-expanded and adsorbed-expanded phases come from the ‘tangent at the inflexion point’ construction described above, and the remaining points come from peaks in the ‘heat capacities’. A similar calculation at $n = 50$ shows only minor changes in the locations of the phase boundaries.

4. Discussion

We have discussed the adsorption and collapse behaviour of self-avoiding walks and polygons at a defect plane on the simple cubic lattice. We showed rigorously that, for polygons, there is an adsorption transition for any finite value of the vertex–vertex interaction parameter (β). This phase boundary is at a value of the vertex–surface interaction parameter (α) which is no larger than for polygons interacting with an impenetrable surface. We also showed that if polygons collapse in the absence of an interaction with the defect plane then there is a phase boundary between the desorbed-expanded and desorbed-compact phases which is a straight line.

We used a multiple Markov chain algorithm based on a mixture of pivot and local moves

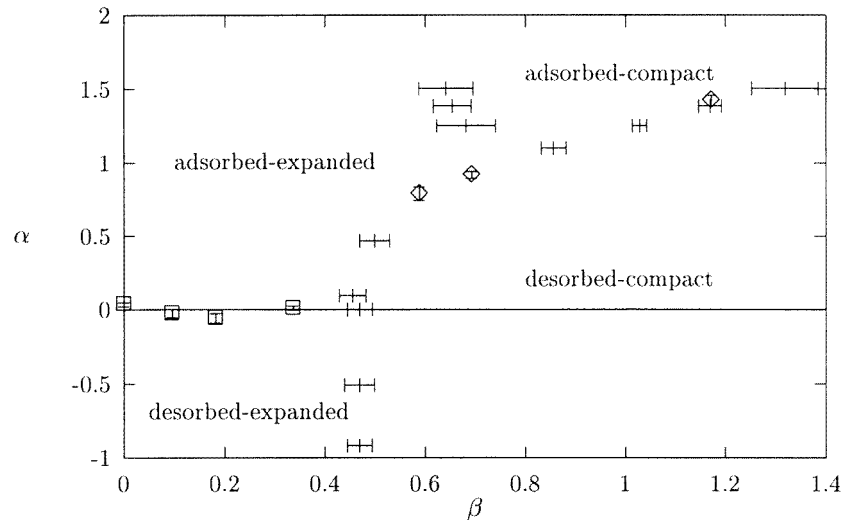


Figure 7. The locations of the ‘heat capacity’ peaks (for the transitions involving a collapsed phase) and the intersections of a tangent at the inflection point of $\langle v \rangle$ versus α with the x -axis (desorbed-expanded to adsorbed-expanded phase transition) for $n = 100$. The diamonds correspond to peaks in $\partial^2 \kappa_n(\alpha, \beta) / \partial \alpha^2$ at fixed β , the crosses correspond to peaks in $\partial^2 \kappa_n(\alpha, \beta) / \partial \beta^2$ at fixed α , and the squares correspond to the intersections of the tangent at the inflection point of $\langle v \rangle$ versus α with the x -axis.

to probe the details of the phase diagram. The method is highly effective at sampling in compact phases. Our results can be summarized by the phase diagram shown in figure 7. We clearly see four phases. The phase boundary between the desorbed-expanded and adsorbed-expanded phases seems to be close to the line $\alpha = 0$, which agrees with previous results for the special case of $\beta = 0$ (Hammersley *et al* 1982, Zhao *et al* 1990). The phase boundary between the desorbed-expanded and desorbed-collapsed phases seems to be a vertical line, in agreement with the results of section 2. For large β the phase boundary between the desorbed-collapsed and adsorbed-collapsed phases is very close to that for the half-space problem (Vrbová and Whittington 1998). The phase boundary between the adsorbed-expanded and adsorbed-collapsed phases is quite steep but our results are not sufficiently precise to decide on whether it has positive or negative slope. At the values of n for which we were able to sample efficiently we clearly see evidence for two triple points, so that there seems to be a phase boundary between the adsorbed-expanded and desorbed-collapsed phases.

We emphasize that our results are at modest values of n so that the quantitative details of the phase diagram are only approximate. Although we see no significant differences at the values of n which we used, further results at larger n values, and extrapolations to infinite n , would be very interesting.

Acknowledgments

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