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Tereza Vrbová and Stuart G Whittington

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

Abstract. We consider self-avoiding walks on the simple cubic lattice, with a unit degree vertex at the origin and confined to the half-space $z \geqslant 0$. In addition the walks interact with the plane $z = 0$ and have a vertex–vertex interaction within the walk, so that the walk can adsorb at the surface $z = 0$ and also undergo collapse. We investigate the interaction between collapse and adsorption using Monte Carlo methods, and explore the form of the phase diagram.

1. Introduction

Self-avoiding walks have become the standard model of the equilibrium properties of linear polymer molecules in dilute solution in a good solvent (Madras and Slade 1993). Including a short-range attractive interaction with an impenetrable surface provides a model of polymer adsorption (for reviews see Whittington (1982), De'Bell and Lookman (1993) and Eisenriegler (1993)) and one version of this model is a self-avoiding walk on (say) the simple cubic lattice, with a unit degree vertex fixed at the origin and all vertices having non-negative z-coordinate. Each vertex with zero z-coordinate contributes an additional energy term. If this surface interaction term is attractive the system can exhibit an adsorption transition (Hammersley *et al* 1982) and the model has been extensively studied using Monte Carlo methods (Eisenriegler *et al* 1982, Meirovitch and Chang 1993, Hegger and Grassberger 1994, Grassberger and Hegger 1995a). The location of the transition is known quite accurately and the values of several critical exponents, including the crossover exponent ϕ, have been estimated.

The effect of solvent quality can be investigated by introducing a vertex–vertex interaction into the self-avoiding walk model. Although there is no proof of the existence of a collapse transition in this model, the numerical evidence for a transition is very strong. This problem has also been extensively studied by Monte Carlo methods (Mazur and McCrackin 1968, Kremer *et al* 1981, Webman *et al* 1981, Meirovitch and Lim 1989, Grassberger and Hegger 1995b, Tesi *et al* 1996a, Nidras and Brak 1997).

Of course, adsorption can occur from solvents of different quality and the interplay between the adsorption and collapse phenomena has been investigated by a number of authors. The special case of adsorption at the θ point has received considerable attention, and the values of the surface critical exponents have been estimated numerically (see for instance Vanderzande *et al* 1991, Foster *et al* 1992, Hegger and Grassberger 1994). Renormalization group arguments (Eisenriegler and Diehl 1988) predict that the three-dimensional system will have random walk exponents, but with interesting non-power-law logarithmic corrections.

For systems in which both the vertex–vertex interaction and the vertex–surface interaction can vary, the form of the phase diagram has been investigated by several approaches (Foster 1990, Foster and Yeomans 1991, Cattarinusi and Jug 1991, Foster *et al* 1992, Vrbová and Whittington 1996). In two dimensions a directed version of this problem has been studied using transfer matrix methods and its phase diagram is well understood (Foster 1990, Foster and Yeomans 1991). For the directed model in two dimensions there are three phases: desorbed-expanded, desorbed-compact and a single adsorbed phase, and one expects the same three phases for the undirected version in two dimensions (Foster *et al* 1992). In three dimensions one expects four phases since collapse can occur in the adsorbed phase. These are: desorbed-expanded (DE), desorbed-compact (DC), adsorbed-expanded (AE) and adsorbed-compact (AC). There are some rigorous results about the form of this phase diagram (Vrbová and Whittington 1996), but many questions still remain to be answered. The aim of this paper is to investigate these details for the three-dimensional problem using Monte Carlo methods.

2. Definition of the model

We consider self-avoiding walks on the simple cubic lattice, starting at the origin and with no vertex having negative z-coordinate. We call such walks *positive walks*. A *visit* is a vertex of the walk which is in the plane $z = 0$. A *contact* is a pair of vertices of the walk which are unit distance apart and which are not connected by an edge of the walk. Let $c_n^+(v, k)$ be the number of n-edge positive walks with $v + 1$ visits and k contacts. We define the partition function

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

and the corresponding free energy

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

The limit $\lim_{n\to\infty} \kappa_n^+(\alpha, \beta)$ has been proved to exist for all $\alpha < \infty$ when $\beta \leqslant 0$ (Vrbová and Whittington 1996), and the corresponding limiting free energy for polygons with adsorption and collapse terms has been proved to exist for all finite values of α and β. For the polygon case there is an adsorption transition for every value of β, so that there is a phase boundary $\alpha = \alpha_c(\beta)$ between the desorbed and adsorbed phases. For $\beta \geqslant 0$, $\alpha_c(\beta)$ satisfies the inequalities

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

where A is a certain positive constant. In addition, if there is a collapse transition for polygons at $\beta = \beta_o$ when $\alpha = 0$, then there is a collapse transition for polygons at the same value of β for all $\alpha < \alpha_c(\beta_o)$. One would expect exactly the same behaviour for walks as for polygons.

In this paper we shall concentrate on the adsorption and collapse of self-avoiding walks. We shall investigate the large n behaviour of $\kappa_n^+(\alpha, \beta)$, and especially $\partial^2\kappa_n^+(\alpha, \beta)/\partial\alpha^2$ and $\partial^2\kappa_n^+(\alpha, \beta)/\partial\beta^2$, using Monte Carlo methods, in order to obtain information about the phase diagram in the (α, β)-plane.

3. Monte Carlo approach

We are interested in investigating the complete phase diagram which involves sampling at points which include large positive values of both α and β. This suggests that a standard

Markov chain Monte Carlo approach is unlikely to be successful. This is because it is difficult to construct a Markov chain, defined on a set of positive walks with n fixed and reasonably large, which will be sufficiently mobile at large positive values of α and β. Instead we use a multiple Markov chain method (Geyer 1991) where one samples simultaneously at various values of α and β, including $\alpha = \beta = 0$ where convergence will be rapid. This method has been used successfully to investigate the collapse transition in walks (Tesi *et al* 1996a) and polygons (Tesi *et al* 1996b).

We first define an underlying symmetric Markov chain, with transition matrix elements q_{ij}, on the set of n-edge positive walks labelled $i = 1, 2, 3, \ldots$. The elementary moves of this Markov chain are the pivot moves (Madras and Slade 1993, section 9.4.3) together with local moves designed to reduce the autocorrelation time associated with local variables such as the number of contacts. See Tesi *et al* (1996a) for details. This Markov chain can be shown to be ergodic for positive walks by adapting the argument in section 9.7.3 of Madras and Slade (1993). We then define a Markov chain, at fixed α and β, with transition matrix elements

$$p_{ij} = q_{ij} \min[1, e^{\alpha(v_j - v_i) + \beta(k_j - k_i)}] \qquad j \neq i \qquad (3.1)$$

where v_i and k_i are the numbers of visits and contacts in the positive walk i. We next consider such Markov chains at a set of values of α and β, (α_l, β_l), $l = 1, 2, \ldots, M$, with corresponding transition matrices $\| p_{ij}(l) \|$. These Markov chains are evolved in parallel and, at fixed specified times, an adjacent pair of values l and $l + 1$ are chosen, and the configurations are swapped between the two Markov chains, with a probability chosen to make the limit distribution of this composite Markov chain the product of the limit distributions of the elementary Markov chains at (α_l, β_l). For details see Geyer (1991) and Tesi *et al* (1996a). Since the limit distribution is a product distribution the data at the different values of (α_l, β_l) can be analysed as if they had been obtained by separate runs. Although the method gives estimates at only a discrete set of values of the α-and β-parameters, these data can be reweighted to obtain estimates at intermediate values. Of course, the correlation between data at different (α_l, β_l)-values must be taken into account in the analysis.

The main practical problem in the implementation of the multiple Markov chain scheme is the choice of (α_l, β_l), $l = 1, 2, \ldots, M$. The pairs (α_l, β_l) and $(\alpha_{l+1}, \beta_{l+1})$ must be such that swaps between these values are sufficiently frequently accepted. We shall normally be interested in estimating thermodynamic and metric properties at a set of α-values at fixed β or at a set of β-values at fixed α. Consequently we usually choose $\alpha_1 = \beta_1 = 0$ (so that we have at least one pair of values at which convergence is rapid) and then a set of values along the α- or β-axis up to the value of α or β which is of interest. Finally we choose a set of values of β at fixed α, or α at fixed β, which probes the relevant region of the phase diagram, and crosses the phase boundary (or phase boundaries) in which we are interested. By carrying out preliminary runs, and keeping track of the frequency of accepted swaps, it is quite easy to construct the required set of (α_l, β_l) values.

4. Results

Our main aim was to locate approximately the phase boundaries between the expected phases: DE, AE, DC and AC. At finite n there are no singularities in the free energy but we expect peaks in the 'heat capacities' $\partial^2 \kappa_n^+(\alpha, \beta) / \partial \alpha^2$ and $\partial^2 \kappa_n^+(\alpha, \beta) / \partial \beta^2$ when we cross a phase boundary along a line of constant β or constant α. In addition we calculated the mean number of visits, the mean number of contacts, and the components of the radius
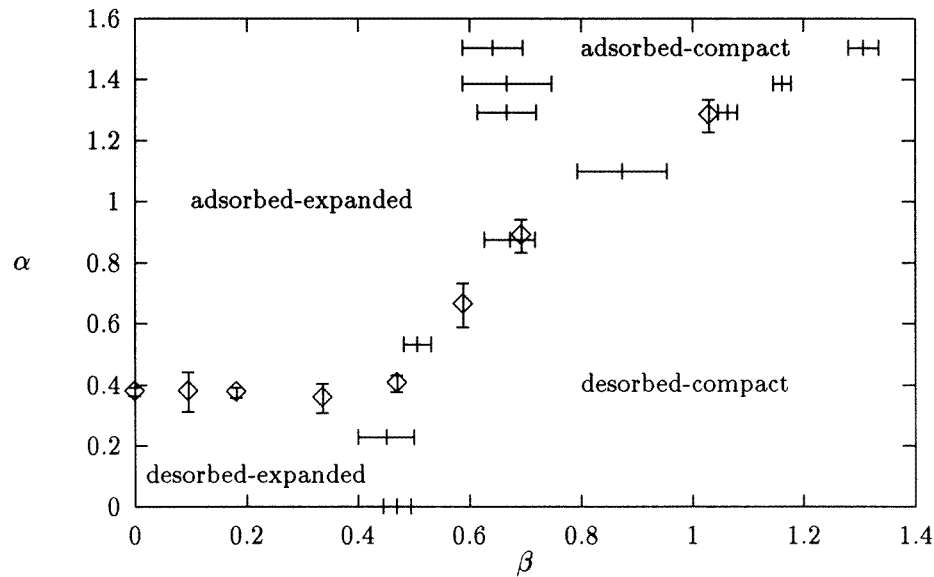
Figure 1. The locations of the heat capacity peaks for $n = 100$. The diamonds correspond to peaks in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\alpha^2$ at fixed β, and the crosses correspond to peaks in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ at fixed α.

of gyration parallel and perpendicular to the surface. These quantities were very useful in deciding which phase boundary was being crossed.

In figure 1 we show the locations of heat capacity peaks for $n = 100$. 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. There is a single peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\alpha^2$ as α is varied at small values of β, corresponding to crossing the phase boundary from DE to AE (see figure 2), and a single peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ as β is varied at small α, corresponding to crossing the phase boundary from DE to DC. In each case the peak heights increase as n increases. The location of the peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\alpha^2$ depends only weakly on β. Vrbová and Whittington (1996) showed that the phase boundary between the DE and DC phases is a vertical line and the peak position which we observe in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ at two values of α agree within the error bars even at this small value of n.

The situation becomes more complicated when we attempt to locate the phase boundaries between AE and AC, and between DC and AC. We used a set of (α_l, β_l) values which involved a set of α values along the α-axis, followed by a set of β values (up to $\beta = 1.6$) at fixed α, in an attempt to locate both phase boundaries in a single run. In figure 3 we show the β-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ for $n = 100$, at three values of α. Each curve shows two peaks. The location of the first peak depends only weakly on the value of α, while that of the second peak moves to larger β-values as α increases. We expect that the first peak is associated with collapse in the adsorbed phase, and the second with desorption in the collapsed phase. In figure 4 we show the mean number of visits per edge, $\langle v \rangle/n$, as a function of β at the same three values of α. In each case there is a rapid decrease in $\langle v \rangle/n$ close to the location of the second peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$, confirming that this peak is associated with desorption. In figure 5 we show the mean-square z-component of the radius of gyration as a function of β, at three values of α. In each case there is a marked increase, close to the location of the second peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$, again confirming that this peak
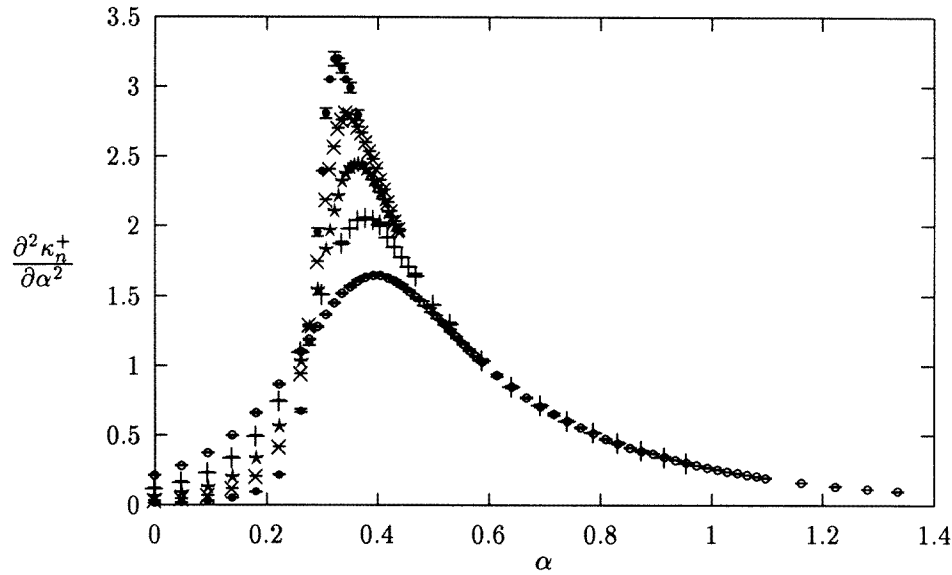
Figure 2. The α-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\alpha^2$ at $\beta = 0$ for 50 ($\bigcirc$), 100 (+), 200 ($\star$), 400 ($\times$) and 1000 ($\bullet$) edges.
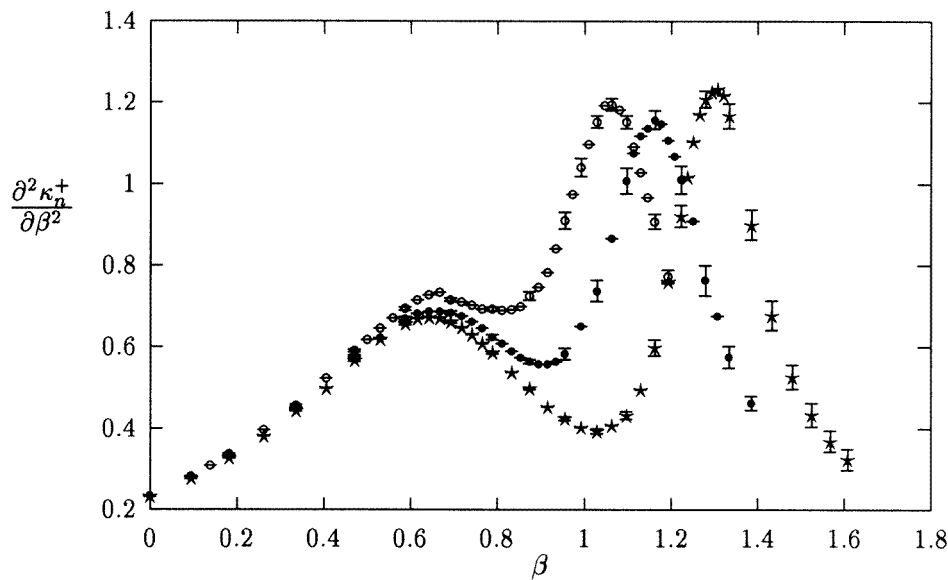

Figure 3. The β-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ for $n = 100$, at $\alpha = 1.29$ ($\bigcirc$), $\alpha = 1.39$ ($\bullet$) and $\alpha = 1.50$ ($\star$).

is associated with desorption. The mean-square x-component of the radius of gyration decreases monotonically with β, but the most rapid decrease is at small β, suggesting that the first peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ is associated with collapse in the adsorbed phase.

The obvious question is the n-dependence of these quantities. In figure 6 we show the β-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial\beta^2$ at $\alpha = 1.39$ for $n = 50, 100$ and 200. Both peaks
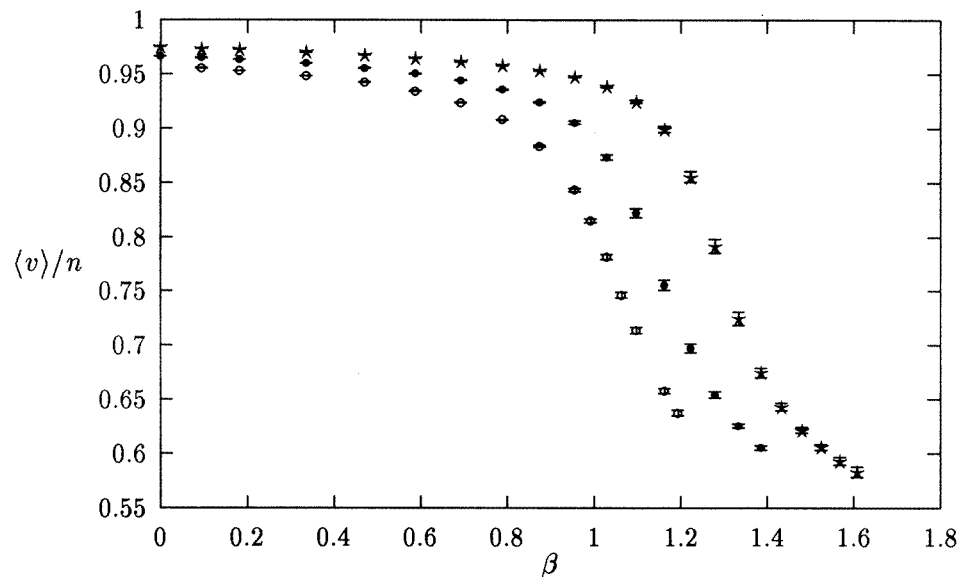
Figure 4. The mean-number of visits per edge, $\langle v \rangle / n$, for $n = 100$, as a function of β at $\alpha = 1.29$ ($\bigcirc$), $\alpha = 1.39$ ($\bullet$) and $\alpha = 1.50$ ($\star$).
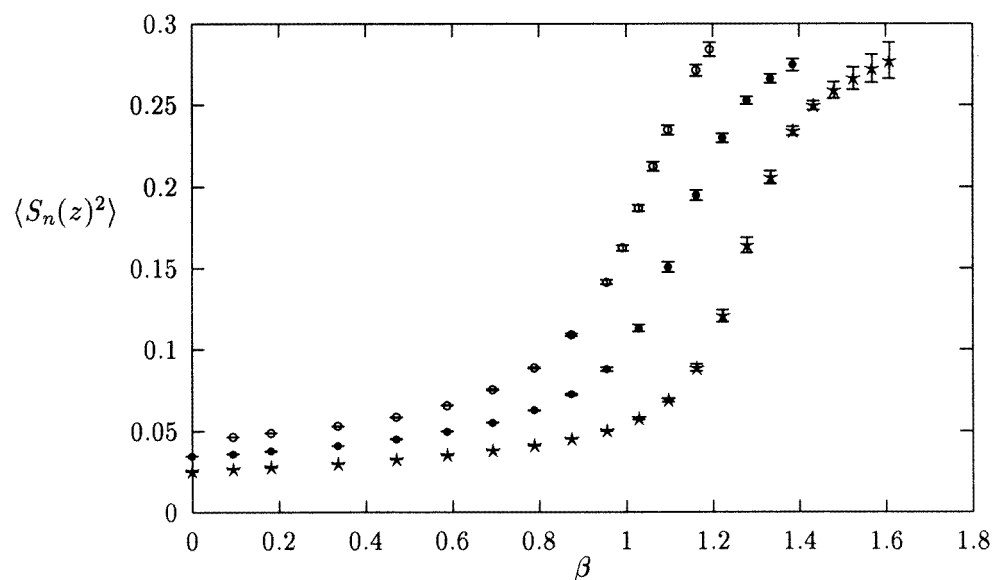

Figure 5. The mean square z-component of the radius of gyration as a function of β for $n = 100$, at $\alpha = 1.29$ ($\bigcirc$), $\alpha = 1.39$ ($\bullet$) and $\alpha = 1.50$ ($\star$).

increase in height as n increases though this is much more marked for the peak at higher values of β. This peak also sharpens considerably as n increases. The increase in height (and the sharpening) suggests that these peaks will remain in the infinite n limit and that they are indicative of the thermodynamic behaviour of the system. The peak at lower β moves somewhat towards larger values of β as n increases while the peak at larger β moves
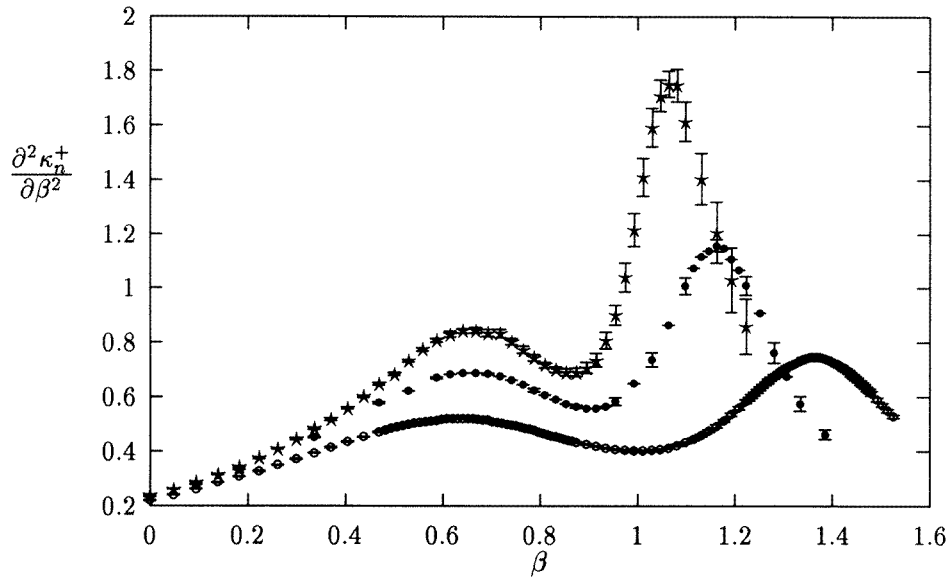
Figure 6. The dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \beta^2$ at $\alpha = 1.39$, for $n = 50$ ($\bigcirc$), $n = 100$ ($\bullet$) and $n = 200$ ($\star$).
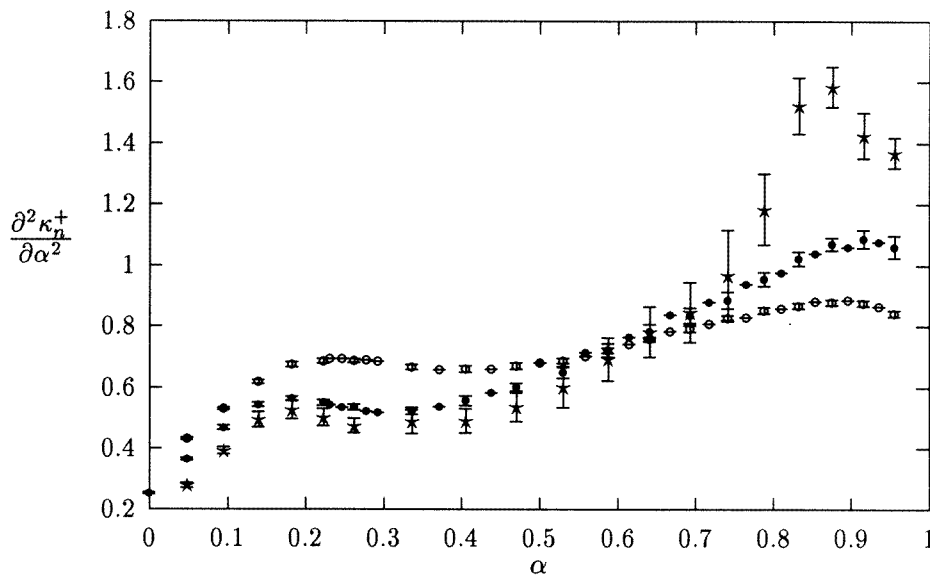

Figure 7. The α-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$ at $\beta = 0.693$, for $n = 100$ ($\bigcirc$), $n = 200$ ($\bullet$) and $n = 400$ ($\star$).

to smaller β-values with increasing n.

To confirm the location of the phase boundary between AC and DC we also carried out runs using a set of (α_l, β_l)-values with a set of β-values along the β-axis, to cross into the DC phase, followed by a set of α-values (up to $\alpha = 1.4$) at fixed β. In figure 7 we show the α-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$ at $\beta = 0.693$, for $n = 100$, 200 and 400. There are
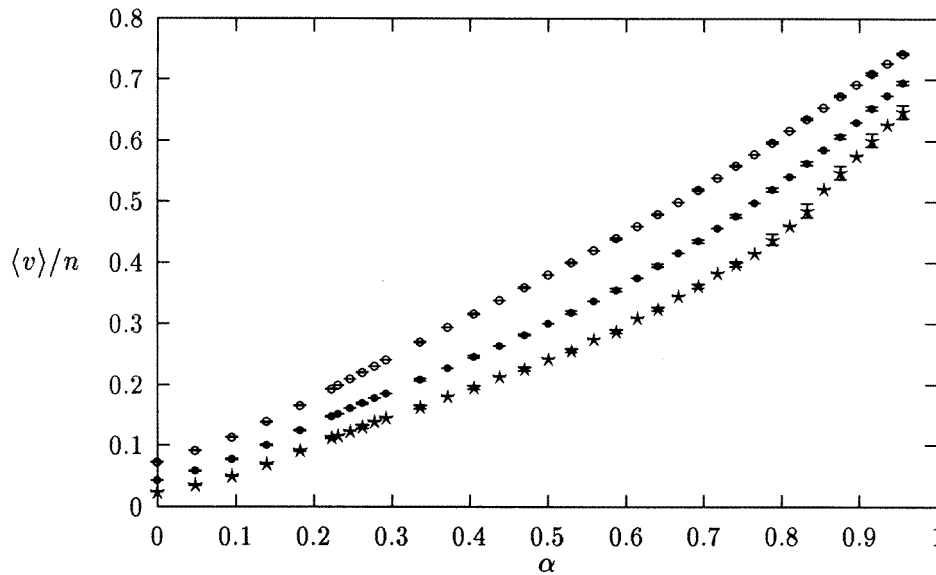
Figure 8. The α-dependence of $\langle v \rangle / n$ at $\beta = 0.693$, for $n = 100$ (O), $n = 200$ (●) and $n = 400$ (⋆).

two peaks, the first of which *decreases* in height as n increases. If, as we argue below, the second peak is associated with the adsorption transition, then we know rigorously, at least for polygons (Vrbová and Whittington 1996), that $\lim_{n\to\infty}\langle v \rangle / n$ is zero for $\alpha < \alpha_c(\beta)$ for any β, so there can be no peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$ in the $n \to \infty$ limit below the adsorption transition. A plot of $\langle v \rangle / n$ against α at $\beta = 0.693$, for $n = 100, 200$ and 400 (see figure 8) shows that $\langle v \rangle / n$ is a decreasing function of n (for these values of n) at least up to $\alpha = 0.9$, consistent with $\lim_{n\to\infty}\langle v \rangle / n$ being zero below the phase boundary. The question of why convergence to zero is so slow as n increases is an interesting one. In the DC phase one expects that the walk will be a compact object and, at small positive α, the walk can have $O(n^{2/3})$ vertices in the surface without substantial loss of entropy. Therefore one expects that $\langle v \rangle / n = O(n^{-1/3})$ for α positive but below the adsorption phase boundary, which converges slowly to zero as n goes to infinity.

The second peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$ increases in height as n increases and its position moves to slightly smaller values of α as n increases. We associate this peak with adsorption for the following reasons. The mean number of contacts at first increases slightly as α increases (presumably as the walk is pulled down towards the surface) and then undergoes a marked decrease as the walk expands in the x- and y-directions, and we associate this latter decrease with adsorption. The mean-square x-component of the radius of gyration increases rapidly at α values around the location of the second peak in $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$, corresponding to the walk spreading in the (x, y)-plane when adsorption occurs.

We have carried out a similar calculation at $n = 100$ and at $n = 200$, with $\beta = 1.03$, and the location of the adsorption transition estimated in this way agrees well with the estimate obtained by varying β at fixed α. See figure 9.

Our results for $n = 100$ are summarized in figure 1. We have repeated several of the runs for $n = 200$ and, although there are small shifts in the peak positions, the qualitative form of the phase diagram remains the same.
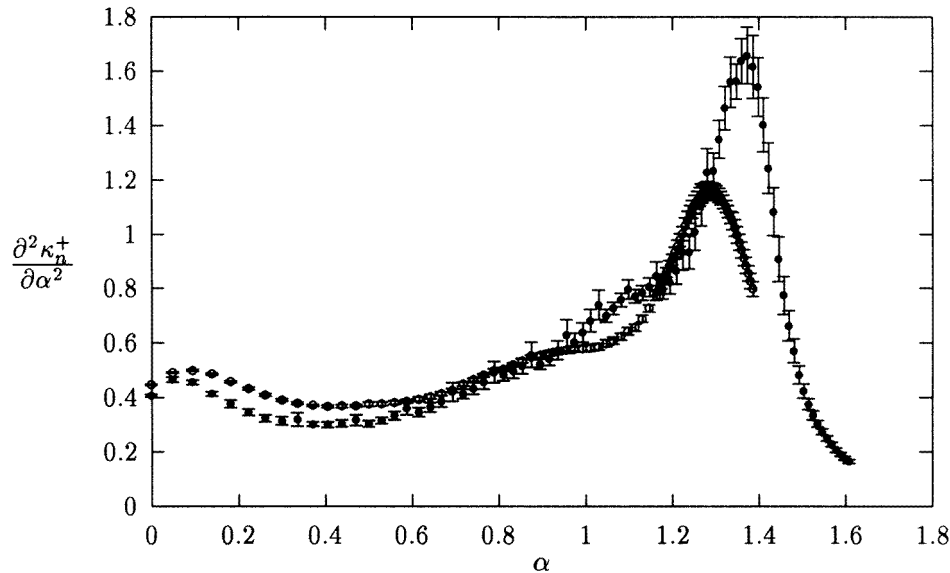
Figure 9. The α-dependence of $\partial^2 \kappa_n^+(\alpha, \beta)/\partial \alpha^2$ at $\beta = 1.030$ for 100 ($\bigcirc$) and 200 ($\bullet$) edges.

5. Discussion

The phase diagram suggested by figure 1 shows four phases, as expected. In addition, the shapes of the phase boundaries between the DE and DC phases, and between the DC and AC phases, are consistent with the rigorous arguments of Vrbová and Whittington (1996). The phase diagram has two triple points so that there is a phase boundary between the AE and DC phases. (We use *triple point* to mean a point in the phase diagram where three phases coexist, making no assertions about the orders of the phase transitions along the three phase boundaries.) Of course, the locations of the phase boundaries are determined by the infinite n behaviour, so the estimates from finite n data can only be regarded as approximations. Ideally one should use data at a range of values of n and extrapolate to infinite n, but that is beyond the scope of this paper. However, our results at $n = 100$ and 200 show that the qualitative features of the phase diagram are the same for these values of n.

There is very strong evidence that both the DE to AE transition (see for instance Eisenriegler *et al* 1982, Hegger and Grassberger 1994) and the DE to DC transition (see for instance Duplantier 1986, 1987, Maritan *et al* 1989, Meirovitch and Lim 1990) are second order. In addition the collapse transition for a self-avoiding walk in two dimensions (i.e. crossing the phase boundary from AE to AC at $\alpha = \infty$) is second order (see for instance Saleur 1986, Batchelor and Yung 1995), so that one would expect the AE to AC transition to be second order. Our results are consistent with these predictions although our data do not extend to sufficiently large values of n to make reliable estimates of the crossover exponents. The orders of the transitions from DC to AC and from DC to AE are less clear, though results on the directed model in two dimensions indicate that adsorption from the compact phase is a first-order transition (Foster 1990, Foster and Yeomans 1991).

This is the first time that evidence for these four phases has been obtained from a Monte Carlo calculation, and multiple Markov chain sampling is clearly a highly effective way of probing the behaviour in compact phases. An alternative approach would be to use umbrella

sampling (Torrie and Valleau 1977) and it would be very interesting to compare the relative effectiveness of the two methods for demanding problems of this type.

Acknowledgments

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