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Multiple Markov chain Monte Carlo study of adsorbing self-avoiding walks in two and in three dimensions

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Abstract

A self-avoiding walk adsorbing on a line in the square lattice, and on a plane in the cubic lattice, is studied numerically as a model of an adsorbing polymer in dilute solution. The walk is simulated by a multiple Markov chain Monte Carlo implementation of the pivot algorithm for self-avoiding walks. Vertices in the walk that are visits in the adsorbing line or plane are weighted by e^β . The critical value of β , where the walk adsorbs on the adsorbing line or adsorbing plane, is determined by considering energy ratios and approximations to the free energy. We determine that the critical values of β are

$$\beta_c = \begin{cases} 0.565 \pm 0.010 & \text{in the square lattice} \\ 0.288 \pm 0.020 & \text{in the cubic lattice.} \end{cases}$$

In addition, the value of the crossover exponent is determined:

$$\phi = \begin{cases} 0.501 \pm 0.015 & \text{in the square lattice} \\ 0.5005 \pm 0.0036 & \text{in the cubic lattice.} \end{cases}$$

Metric quantities, including the mean square radius of gyration, are also considered, as well as rescaling of the specific heat and free energy, as the critical point is approached.

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1. Introduction

The interacting self-avoiding walk in the square and cubic lattice is a standard model of interacting polymers [7, 11, 12]. Polymer collapse has been modelled by walks with a

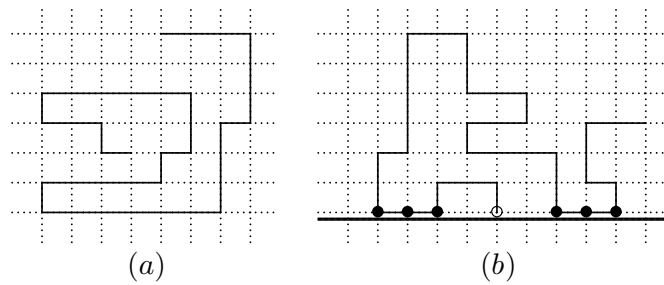


Figure 1. (a) A square lattice self-avoiding walk. (b) An adsorbing self-avoiding walk with seven vertices (visits) in the line $y = 0$. Six visits are denoted by \bullet while the first vertex is always a visit (denoted by \circ).

two-body interaction between vertices [5], while adsorbing polymers are modelled by walks with a one-body interaction: vertices in such a walk interact independently with an adsorbing interface [6]. The scaling theory of these thermodynamic phenomena has also been considered [7], and it is rather well understood. A brief description, relevant to this paper, is presented in section 2.

A polymer confined to one side of an interface can be modelled in two dimensions by a self-avoiding walk in the square lattice above the line $y = 0$. We may extend the model to include an adsorption interaction by fixing the first vertex of the walk to be at the origin of the lattice and then weighing the conformation according to the number of vertices in the line $y = 0$. See figure 1.

In this discrete lattice model, the most important quantity is $c_n(v)$; the number of walks from the origin, confined to the half-space $y \geq 0$, and with v vertices in the *adsorbing line* $y = 0$. This model generalizes to three dimensions by replacing the square lattice with the cubic lattice and the adsorbing line by the plane $z = 0$; the walks start at the origin and are confined to the half-space $z \geq 0$.

Lattice models of polymers are combinatorial in nature, all questions could be answered if $c_n(v)$ could be determined (that is, by counting all such walks of length n with v visits). In that event, the model can be solved and this will provide information on the polymer adsorption problem. Unfortunately, the non-Markovian character of these models means that most standard combinatorial tools are not applicable and, despite a great deal of effort, they remain unsolved. Some progress has been made in two and in three dimensions in [15]. Further results were obtained in [18] for an ensemble of collapsing and adsorbing walks; see also [38, 39]. Numerical studies of these models have been performed [17, 40] as well. Of primary interest in all these studies are the location of the adsorption critical point, and the values of (thermodynamic) critical exponents associated with the adsorption phase transition. In particular, numerical efforts to determine the *crossover exponent* ϕ in these models can be found in the literature [17] (this exponent describes rescaling in the model as the critical point is approached).

The thermodynamic description of adsorbing walks is based on the *partition function* defined by

$$Z_n(\beta) = \sum_{v=1}^n c_n(v) e^{\beta v}. \quad (1)$$

The usual definition of the free energy is

$$F_n(\beta) = \log Z_n(\beta). \quad (2)$$

The function $Z_n(\beta)$ is a polynomial in e^β and is analytic, so that $F_n(\beta)$ is also analytic. The model is interesting in the $n \rightarrow \infty$ limit, where the existence of the (normalized) *limiting free energy*

$$\mathcal{F}(\beta) = \lim_{n \rightarrow \infty} \frac{1}{n} \log Z_n(\beta) \quad (3)$$

can be demonstrated using techniques due to Hammersley *et al* [15]. It is known that $\mathcal{F}(\beta)$ is a convex function and is differentiable almost everywhere. In addition, there is a constant μ_d such that

$$\mathcal{F}(\beta) \begin{cases} = \log \mu_d & \text{if } \beta \leq \beta_c \\ > \log \mu_d & \text{if } \beta > \beta_c. \end{cases} \quad (4)$$

Hence, $\mathcal{F}(\beta)$ is non-analytic at the point β_c .

The *growth constant* of self-avoiding walks on the d -dimensional hyper-cubic lattice is μ_d [13]. It has been determined to high accuracy by Monte Carlo and series analysis in two and three dimensions [20, 25, 35]. The best estimates are due to series enumeration studies

$$\begin{aligned} \mu_2 &= 2.638\,158\,529\,27(1) \quad \text{see [20]} \\ \mu_3 &= 4.684\,04(9) \quad \text{see [25]}. \end{aligned} \quad (5)$$

Since the density of visits (or the *energy*) is the derivative of $\mathcal{F}(\beta)$, it follows that β_c is the critical adsorption point: for $\beta < \beta_c$, the density of visits is zero; for $\beta > \beta_c$, it is strictly positive.

It is known that $\beta_c > 1$ [15], and this bound has been improved to

$$2 \log \mu_2 \geq \beta_c \geq \log \sqrt{1 + \mu_2^{-2}} \quad \text{in two dimensions [18]}. \quad (6)$$

This shows that

$$1.940\,162\dots \geq \beta_c \geq 0.067\,125\dots \quad \text{in two dimensions} \quad (7)$$

and these are the best mathematically rigorous bounds in two dimensions. Otherwise, it is known that

$$\log(\mu_d/\mu_{d-1}) \geq \beta_c \geq \log \sqrt{1 + \mu_d^{-2}} \quad \text{in } d \text{ dimensions [18]}. \quad (8)$$

Numerically, this gives the bounds

$$0.574\,079\dots \geq \beta_c \geq 0.022\,285\dots \quad \text{in three dimensions}. \quad (9)$$

The critical point β_c has been determined ‘exactly’ in the honeycomb lattice ($\beta_c = \log \sqrt{1 + \sqrt{2}}$), but this is not a rigorous result [1].

In this paper we examine adsorbing walks in the square and cubic lattices numerically. Recent insights in models of walks produced a method for determining estimates of the free energy of interacting models of walks and trees using canonical Monte Carlo techniques [35]. We use this technique to study the free energy of adsorbing walks, and then to estimate the location of the critical point and to examine thermodynamic rescaling as the critical point is approached.

In section 2 we give a brief review of the essential statistical mechanics and thermodynamics of adsorbing walks in terms of tricritical scaling theory [23]. In particular, we introduce scaling assumptions for the free energy and discuss the role of critical exponents in rescaling the model as the critical point is approached. The hypothesis that the critical point in the (general grand canonical) phase diagram is of a tricritical nature has certain consequences; for example, it implies the existence of a *crossover exponent*, ϕ , that describes how the model rescales as the critical point is approached from different directions.

In section 3 we describe the numerical techniques used to generate and analyse data. We then investigate the scaling of the free energy and the specific heat under the tricritical scaling hypothesis in two and three dimensions in sections 3.1 and 3.3. The crossover exponent is best determined from energy ratios. Our best estimates are

$$\phi = 0.501 \pm 0.015 \quad \text{in two dimensions} \quad (10)$$

$$\phi = 0.5005 \pm 0.0036 \quad \text{in three dimensions.} \quad (11)$$

The error bars are 95% statistical confidence intervals. These results strongly support the notion that $\phi = 1/2$ in two and three dimensions in the polymer adsorption problem. The critical adsorption points are best determined by analysing energy ratios, the free energy and the specific heat. These analyses give our best estimates for the critical value of β :

$$\beta_c = 0.565 \pm 0.010 \quad \text{in two dimensions} \quad (12)$$

$$\beta_c = 0.288 \pm 0.020 \quad \text{in three dimensions} \quad (13)$$

with stated 95% statistical confidence intervals. These results are consistent with the bounds stated above, and also with estimates of β_c from quantities such as the specific heat and metric data (such as mean square radius of gyration).

Observe that these estimates are in particular for the model in this paper, where *vertices* interact with the adsorbing plane. A slightly different model has edges that interact with the adsorbing plane, forming *edge-visits* when they adsorb. The location of the critical points in that model is expected to be different from the estimates above, but one would expect to find the same values for the thermodynamic exponents, including ϕ .

As a by-product we also determined the growth constant for walks in two and three dimensions, consistent with the results in [35]

$$\mu_2 = 2.635 \pm 0.002 \quad (14)$$

$$\mu_3 = 4.670 \pm 0.014. \quad (15)$$

These estimates were obtained by analysing the limiting free energy estimates directly, and is consistent with estimates in the literature, as we observe elsewhere in this paper. These estimates are not of high accuracy, but it is interesting that they were made by using a canonical Monte Carlo simulation, exploiting the techniques developed in [35].

Finally, we examined the effect of the adsorption transition on metric quantities of the model. We analyse the mean square radius of gyration and mean span (the *span* is the average side length of the smallest box containing the walk) to determine the metric exponent ν as a function of β . In both the two- and three-dimensional models the results are consistent with a transition at $\beta = \beta_c$, as indicated by the thermodynamic properties. We conclude the paper with comments in section 4.

2. Thermodynamics of adsorbing walks

The thermodynamic properties of adsorbing walks are described by making general assumptions that the free energy and partition function of the model are described by tricritical scaling [23] in the vicinity of the critical adsorption point. In particular, define $\tau = \beta - \beta_c$, then the (finite) size free energy is a function of the rescaled variable $n^\phi \tau$, where ϕ is the crossover exponent which determines the crossover in rescaling as $n \rightarrow \infty$.

The phase transition at $\tau = 0$ is the *adsorption transition*, and it corresponds to a non-analytic point in $\mathcal{F}(\beta)$. The behaviour close to this point is described by the *specific heat exponent* α . It is thought that

$$\mathcal{F}(\beta) \sim \tau^{2-\alpha} \quad \text{as } \beta \rightarrow \beta_c^+. \quad (16)$$

Thus, the finite size free energy is assumed to scale as

$$F_n(\beta) \begin{cases} \sim C_0 & \text{if } \beta \leq \beta_c \\ \sim C_0 \tau^{2-\alpha} f(n^\phi \tau) & \text{if } \beta > \beta_c \end{cases} \quad (17)$$

where C_0 is a constant. It is known that $F_n(0) \rightarrow \log \mu$ as $n \rightarrow \infty$, where μ is the growth constant (see, for example, Madras and Slade [28]). Thus, one may put $C_0 = \log \mu_d$ in the above. Taking two derivatives of $F_n(\beta)$ with respect to τ shows that the specific heat should scale as

$$C_n(\beta) = \frac{d^2}{d\tau^2} F_n(\beta) \sim \tau^{-\alpha} g(n^\phi \tau) \quad \text{for } \tau > 0 \quad (18)$$

for some unknown scaling function $g(x)$. Thus α describes the singularity in the specific heat at the critical point when approached from the adsorbed phase.

For $\tau > 0$ the expression for $F_n(\beta)$ can be written as

$$F_n(\beta) \sim C_0 n^{-\phi(2-\alpha)} (n^\phi \tau)^{2-\alpha} f(n^\phi \tau) = n^{-\phi(2-\alpha)} h(n^\phi \tau) \quad (19)$$

where $h(x)$ is some unknown scaling function. Thus, $F_n(\beta) = [\log Z_n(\beta)]/n$ is a product of a power of n , and a function $h(n^\phi \tau)$ of the rescaled variable $n^\phi \tau$. More general scaling arguments (see, for example, [8]) can now be used to show that the crossover exponent ϕ , and the specific heat exponent α , are related by a hyperscaling relation

$$2 - \alpha = \frac{1}{\phi}. \quad (20)$$

Hence, the finite size free energy has the scaling form

$$F_n(\beta) \sim n^{-\phi(2-\alpha)} h(n^\phi \tau) \sim n^{-1} h(n^\phi \tau) \quad (21)$$

for some unknown scaling function $h(x)$.

In a previous paper [35] a statistic on self-avoiding walks called the *atmosphere* was defined. The atmosphere of a walk with first vertex at the origin is composed of the edges that can be added to its last vertex to increase its length by one step. This concept is abused by calling the *number* of such atmospheric edges also the atmosphere of the walk. For example, the walk in figure 1(a) has atmosphere of size two edges, and the walk in figure 1(b) has atmosphere of size three edges.

If the number of walks of n steps from the origin in the hypercubic lattice is c_n , then it can be shown that the mean size of atmospheres of walks of length n is equal to c_{n+1}/c_n [35]. It is not known that the limit $\lim_{n \rightarrow \infty} [c_{n+1}/c_n]$ exists, but the Kesten pattern theorem has been used to prove that $\lim_{n \rightarrow \infty} [c_{n+2}/c_n] = \mu_d^2$ [21, 22]. Together with the numerical evidence in [35], this strongly suggests that $\lim_{n \rightarrow \infty} [c_{n+1}/c_n] = \mu_d$. In other words, that the mean atmosphere converges with increasing n to the growth constant.

In this paper we generalize these notions to the model of adsorbing walks. The atmosphere of a walk attached to an adsorbing line or plane at its first vertex is the weighted sum over the edges that may be added to the last vertex to increase with length of the walk by one step. The additional edge is weighted by β if its addition generates one more visits, otherwise it carries weight 1. The mean atmosphere is the average over the atmospheres of all possible walks, and is denoted by $\mathcal{A}_n(\beta)$. In this case $\mathcal{A}_n(\beta)$ is a linear function of β . One may consider instead the mean (extended) atmospheres by adding two, or three, or more, edges appropriately weighted to walks. Denote $\mathcal{A}_n(\beta; i)$ to be the extended atmosphere if i weighted edges are appended to the walk. It is not difficult to show that

$$\mathcal{A}_n(\beta; i) = \frac{Z_{n+i}(\beta)}{Z_n(\beta)}. \quad (22)$$

As with the ratio c_{n+i}/c_n it is not generally known that the limit $\lim_{n \rightarrow \infty} \mathcal{A}_n(\beta; i)$ exists. Generalization of the techniques used for c_{n+2}/c_n for example do give some partial results, at least for $i = 2$ and for $\beta < \beta_c$.

The scaling of the atmospheric statistic $\mathcal{A}_n(\beta; i)$ can be examined by considering the scaling of the partition function. It is generally believed that

$$Z_n(\beta) = B \mu_\beta^{n\tau^{1/\phi}} n^{\alpha_t - 3} \lambda(n\tau^{1/\phi})^{\alpha_+ - \alpha_t} \quad (23)$$

where α_t and α_+ are critical exponents (and α is the specific heat exponent), and where $\lambda(x)$ is an unknown function. The function μ_β is directly related to the limiting free energy; for example, if we take the logarithm of equation (23), divide by n and then taking $n \rightarrow \infty$, then

$$\mathcal{F}(\beta) = \lim_{n \rightarrow \infty} \frac{1}{n} \log Z_n(\beta) = \tau^{1/\phi} \log \mu_\beta \quad \text{if } \tau > 0. \quad (24)$$

This should be compared with equation (17) via the hyperscaling relation in equation (20).

Consider the ratio of the scaling expression in equation (23) for $n+i$ and for n . If reasonable assumptions are made for the exponents α_+ and α_t , and if it is assumed that the function $\lambda(x)$ is dominated by the exponential growth of $\mu_\beta^{n\tau^{1/\phi}}$, then as $n \rightarrow \infty$, one obtains

$$\log \mathcal{A}_n(\beta; i) \sim i\tau^{1/\phi} \log \mu_\beta + (\alpha_t - 3) \log[(n+i)/n] + (\alpha_+ - \alpha_t) \log \left[\frac{\lambda((n+i)\tau^{1/\phi})}{\lambda(n\tau^{1/\phi})} \right]. \quad (25)$$

Taking $n \rightarrow \infty$ while considering equation (24) then indicates that the following limit:

$$\lim_{n \rightarrow \infty} \log \mathcal{A}_n(\beta; i) = i\mathcal{F}(\beta) \quad (26)$$

may exist. In other words, by considering the atmosphere statistic one may estimate the free energy directly as $n \rightarrow \infty$.

Therefore, one may define the functions

$$f_n(\beta) = \log \mathcal{A}_n(\beta) \quad (27)$$

as approximations to $\mathcal{F}(\beta)$. Moreover, by considering the results and assumptions in equations (17) and (24), the behaviour of $f_n(\beta)$ should be approximated by

$$f_n(\beta) \approx \log \mu_d + C\theta(\beta - \beta_n) |\beta - \beta_n|^{1/\phi} + D_n\beta^\Delta \quad (28)$$

where $\theta(t) = 1$ if $t > 0$ and $\theta(t) = 0$ otherwise, and where $D_n\beta^\Delta$ is an unknown background correction term that should become insignificant as $n \rightarrow \infty$. The number β_n is an estimate of β_c , and one would expect that $\beta_n \rightarrow \beta_c$ as $n \rightarrow \infty$.

3. Numerical results

We generated adsorbing self-avoiding walks on the square and cubic lattices. In both cases the walks started at the origin and were confined to the positive half-lattice bounded by the adsorbing line in two dimensions (the x -axis) and the adsorbing plane in three dimensions (the xy -plane). The walks were sampled along a Markov chain by a Metropolis implementation [14] of the pivot algorithm for self-avoiding walks [29]. A multiple Markov chain Monte Carlo technique ([9], see also [36]) was used to sample along 10 chains spaced in the adsorption activity β . In two dimensions, the activity β of the chains was spaced in the interval $[0, 1]$ and in three dimensions it was spaced in $[0, 0.6]$.

The adjacent chains in the simulation were switched by attempting a swap between two randomly selected chain once every 250 attempted elementary Monte Carlo iterations of the underlying pivot algorithm. Each chain was then iterated for $500\,000 \times 250$ times while

Table 1. Intersections of energy ratios in two dimensions.

Ratio 1	Ratio 2	β_c	ϕ
70/40	20/10	0.5735	0.5021
80/40	30/20	0.5705	0.4965
90/30	40/20	0.5745	0.5044
90/50	50/30	0.5690	0.4890
100/50	60/30	0.5770	0.5118

data were collected every 250 attempted iterations for a total of 500 000 data points for every chain.

The data were analysed by computing weighted averages to interpolate between adjacent chains, and confidence intervals were estimated by computing autocorrelation times of the resulting time series; for details, see Beretti and Sokal [2]. Data were collected in two dimensions for walks of lengths $n = 10$ to $n = 100$, but the simulations did not converge well for walks of lengths greater than 100. In three dimensions data were collected for walks of lengths $n = 10$ to $n = 120$, first in steps of 10 to $n = 100$, and thereafter for $n = 120$. Overall, the algorithms performed better in three dimensions; it is a feature of the pivot algorithm that it is more efficient in higher dimensions as the self-avoiding constraint has a smaller effect on the walks.

The main objective of the numerical work is to estimate the location of the critical point and the value of the crossover exponent, ϕ . It is widely thought that $\phi = 1/2$, and this will be verified for walks in two and three dimensions. Attempts to estimate ϕ from the estimated values of $f_n(\beta)$ and from estimated specific heats were not very successful. However, the ratios of energies (the average number of visits) produce very accurate estimates of both β_c and of ϕ , this technique was first developed in [41].

3.1. Adsorbing walks in two dimensions

Energy. The mean number of visits, or *energy*, is given by the first derivative of the free energy to β (or equivalently, to τ). If it is assumed that the hyperscaling relation in equation (20) is valid, then it follows from equation (21) that

$$\langle V_n \rangle = n \frac{\partial F_n(\tau)}{\partial \tau} \sim n^{1+\phi+\phi(\alpha-2)} h'(n^\phi \tau) \sim n^\phi h'(n^\phi \tau) \quad (29)$$

where $\langle V_n \rangle$ is the mean number of visits (or the total *energy* of the walk). At $\beta = \beta_c$, this shows that

$$\langle V_n \rangle|_{\tau=0} = n^\phi g'(0). \quad (30)$$

Of significance are the ratios

$$\frac{\langle V_m \rangle}{\langle V_n \rangle} = \left(\frac{m}{n} \right)^\phi \quad \text{where } \tau = 0. \quad (31)$$

If one chooses values for m and n , then at $\beta = \beta_c$ the energy ratios are all equal to $(m/n)^\phi$. Thus, both the crossover exponent ϕ and the critical adsorbing activity β_c may be determined by plotting (for example) $\log(\langle V_m \rangle / \langle V_n \rangle) / \log(m/n)$ against β . All the curves should intersect at the point (β_c, ϕ) .

In figure 2 the energy ratios are plotted for (m, n) equal to (100, 50), (80, 40), (60, 30) and (40, 20). The data can be interpolated to curves that all mutually intersect close to (0.57, 0.50). Including other ratios in our analysis gives the results in table 1.

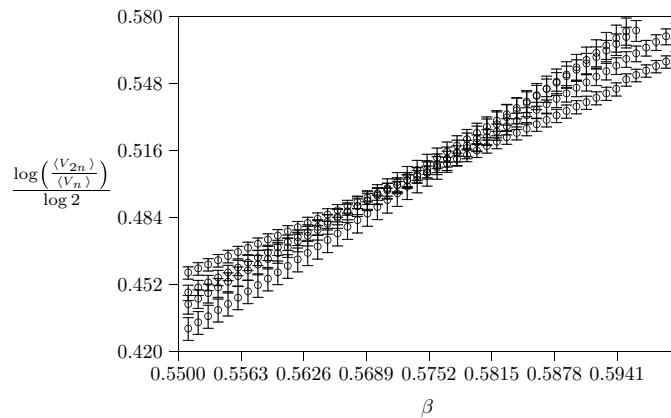


Figure 2. Plots of $\log(\frac{\langle V_{2n} \rangle}{\langle V_n \rangle}) / \log 2$ against β . These data can be interpolated to intersect close to $(0.57, 0.5)$, and best estimates for (β_c, ϕ) can be determined by analysing the intersections. In this graph, the values of (m, n) were chosen as $(100, 50)$, $(80, 40)$, $(60, 30)$ and $(40, 20)$. More data were not shown for clarity.

There appears to be no dependence of β_c and ϕ in table 1 with increasing n or m . If we treat simulations at different values of n as independent, then we can take averages of the results to determine our best estimates for β_c and ϕ . This gives

$$\beta_c = 0.5729 \pm 0.0058 \quad (32)$$

$$\phi = 0.501 \pm 0.015 \quad (33)$$

where the error bars are 95% statistical confidence intervals. This measurement only determines ϕ up to assuming hyperscaling, but β_c is determined to great accuracy. The estimates in table 1 also appear to be independent of or insensitive to n , and this indicates that corrections to scaling have largely been cancelled in the ratio of the energies.

Specific heat. The traditional methods for determining ϕ and β_c from Monte Carlo data involve the numerical analysis of the specific heat data [30, 41]. The location and height of the peak in the specific heat are known to contain information about ϕ and β_c , and by extrapolating the height and location of the peak, estimates for ϕ and β_c can be obtained.

The specific heat $C_n(\beta)$ of adsorbing walks is plotted in figure 3 for adsorbing walks in two dimensions. The error bars in these data are comparable to the size of the plotted points. These curves should converge as $n \rightarrow \infty$ to a limiting specific heat at a rate determined by the crossover exponent ϕ . By taking derivatives of the free energy in equation (17), it is expected that for each n

$$C_n(\beta) \sim n^{\alpha\phi} f''(n^\phi \tau). \quad (34)$$

In this model, our results in equation (33) suggest that $\phi = 1/2$, and hyperscaling relation (20) then suggests that $\alpha = 0$. Thus, if corrections to scaling are ignored, then the peaks in the specific heat may approach a cusp, or grow slowly with n (slower than a powerlaw).

The common point of intersection between the specific heat curves in figure 3 is an estimate of β_c . For values of $\beta < \beta_c$, $C_n(\beta) \rightarrow 0$ as $n \rightarrow \infty$. Subtracting the curves gives estimates of the points of intersection. These estimates increase from 0.41 for $n = 10$ and $n = 20$. If curves with $n < 50$ are ignored, and the smallest bounding box containing the points of intersection is considered, then

$$\beta_c = 0.56 \pm 0.01 \quad (35)$$

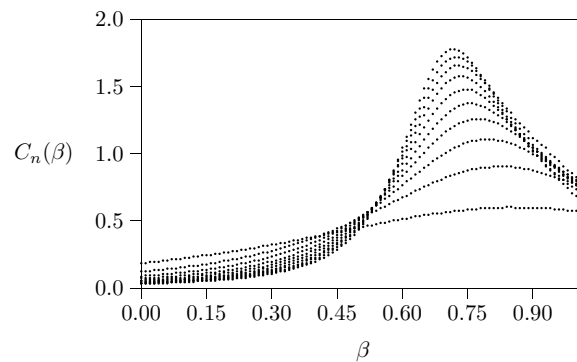


Figure 3. The specific heat for adsorbing walks in two dimensions. Error bars have been left away for clarity. The lengths of the paths increase in steps of 10 from $n = 10$ to $n = 100$. If the data at smaller n are ignored, then all these curves intersect close to $\beta = 0.56$. Plotting the points of intersection and bounding them within a smallest box gives the estimate $\beta_c = 0.56 \pm 0.01$ for the adsorption critical point. For values of β less than β_c , the specific heat decreases to zero, for values larger than β_c it increases with n . This estimate is consistent with the results in equation (33).

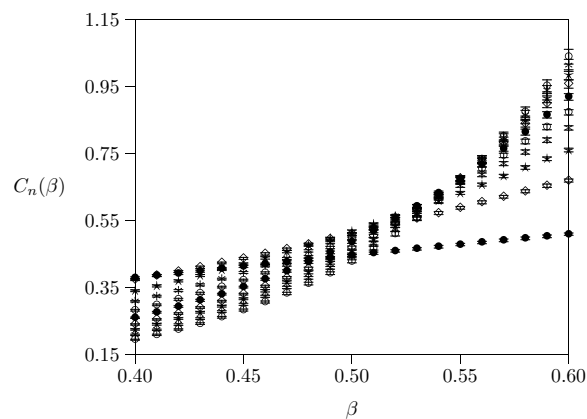


Figure 4. The area of intersections of the specific heats. If the data corresponding to $n < 50$ are ignored, then a bounding box of the intersections can be used to estimate the location of the critical adsorption point β_c as in equation (35). Data corresponding to $n = 10$ are denoted by \bullet in the lowest data points for $\beta > 0.50$, while data corresponding to $n = 100$ are the highest points for β approaching 0.60 and denoted by \circ . Other values of n are represented by points between these values.

where the error bar is the half-width of the bounding box. This compares well with the results in equation (33). The area of intersections is magnified in figure 4.

The curves $C_n(\beta)$ are all functions of the scaled variable $n^\phi \tau$, and if plotted against this, and scaled to have height 1, they should all collapse to a single curve. In figure 5 we present such a plot with $\beta_c = 0.57$ and $\phi = 1/2$.

In the past, the location and height of the peak in the specific heat data were tracked in order to estimate β_c and ϕ [30, 41]. This method gives values for ϕ considerably larger than $1/2$ [30]. This observation is confirmed by our data, a least squares fit with $n_{\min} = 20$ to the heights of the peaks in the specific heats gives $\alpha\phi = 0.45 \pm 0.025$ with least square error acceptable at the 95% level and a 95% statistical confidence interval. If one assumes

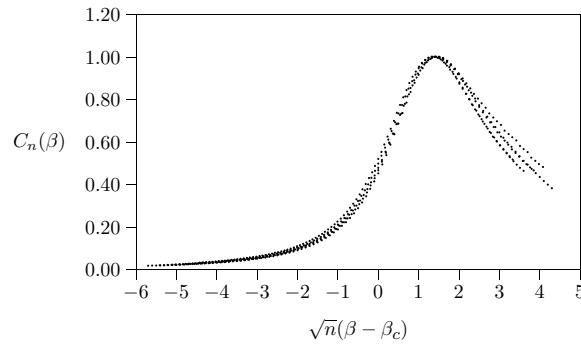


Figure 5. The specific heat normalized to height 1 and plotted against the combined variable $n^{1/2}(\beta - \beta_c)$, where $\beta_c = 0.57$, and for $n = 60, 70, 80, 90$ and 100 . All the curves collapse, with increasing n , to a common curve. This can be interpreted as a strong evidence that $\phi = 1/2$.

hyperscaling, then this implies that $\phi \approx 0.72$, significantly larger than $1/2$. In this model, the traditional method for analysing the specific heat to obtain the crossover exponent clearly gives an erroneous estimate. The notion that $\phi = 1/2$ is also further strengthened by results from conformal invariance that suggest $\phi = 1/2$ [3], further putting the result suggested by analysing the specific heat in doubt.

The value of the critical point β_c has also been traditionally determined by tracking the location of the peaks in the specific heat in figure 3. The location should converge to β_c at a rate proportional to $n^{-\phi}$. If one assumes that $\phi = 1/2$ then a least squares analysis with $n_{\min} = 20$ gives

$$\beta_c = 0.63 \pm 0.11 \quad (36)$$

where the error bar is a 95% statistical confidence interval. This result is consistent with equation (33), but it is a poor quality estimate of β_c . Increase in n_{\min} does not move the result outside the confidence interval above, and we settle for this value.

Free energy. The approximations $f_n(\beta)$ to the free energy $\mathcal{F}(\beta)$ defined in equation (28) are plotted in figure 6. Ideally, these data should be analysed using a least square analysis and the assumed functional form in equation (28). The parameter β_n should converge with increasing n to β_c , the critical adsorption point in this model. We analysed the data using a numerical procedure for minimizing the least squares fit to our data. In this analysis the standard numerical procedures were unstable. Therefore, we first minimized the error using a Monte Carlo scheme before switching to numerical derivatives and Newton's method minimizing the error. The χ^2 -statistic of the fit was tracked to determine goodness-of-fit. The fits in this analysis all failed at the 95% level³, and we adjusted the error bars on our parameters accordingly (the fit is repeated with error bars inflated to give an acceptable fit at the 95% level). In practice, this scales up the confidence intervals on the computed parameters by $\sqrt{\chi_{\text{obs}}^2 / \chi_{95}^2}$, where χ_{obs}^2 is the observed least squares error, and χ_{95}^2 the χ^2 -statistic expected at the 95% level. The results of these fits are listed in table 2. This analysis works reasonably well if one chooses $\Delta = 2$. Putting $\Delta = 1$ gave very poor numerical results, and we did not further pursue this possibility.

³ A fit is deemed acceptable if the least square error, which is distributed as a χ^2 statistic, is acceptable at the 95% level. Generally, data at the lowest values of n will be the most affected by correction terms, and will be discarded while the least square error is tracked until an acceptable fit is obtained.

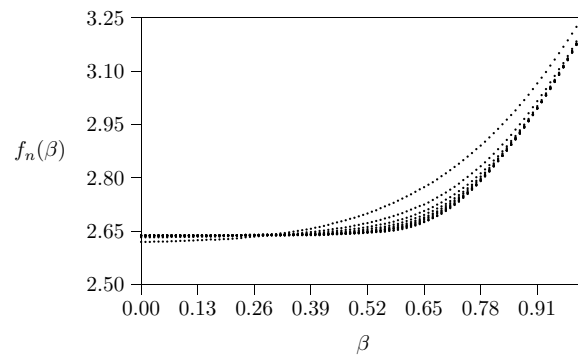


Figure 6. Estimates of the limiting free energy densities for adsorbing walks in two dimensions for lengths $n = 10$ to $n = 100$ in increments of 10. The curves converge quickly to a limiting free energy. There is no explanation for the apparent mutual intersections of the curves at $\beta \approx 0.30$. At this point, it appears that scaling corrections are largely cancelled by the interaction with the adsorbing line, and one should be able to take numerical advantage of this to determine the growth constant for self-avoiding walks to high accuracy.

Table 2. Free energy parameters.

n	μ	ϕ^{-1}	β_n
10	2.618 558(62)	3.326(18)	0.1659(53)
20	2.630 55(15)	3.122(17)	0.2914(43)
30	2.633 04(15)	2.717(23)	0.4061(46)
40	2.633 52(14)	2.464(19)	0.4591(36)
50	2.635 13(14)	2.239(17)	0.4983(31)
60	2.634 85(13)	2.145(14)	0.5165(25)
70	2.635 00(13)	2.044(13)	0.5378(23)
80	2.635 86(13)	1.930(12)	0.5547(20)
90	2.634 85(13)	1.906(11)	0.5596(19)
100	2.635 20(13)	1.911(11)	0.5595(18)

The data in table 2 for μ converge quickly with increasing n , and by $n = 50$ seem to have settled down. Taking the result at $n = 100$ as our best estimate, and taking as a systematic error the largest absolute difference amongst the estimates at $n \geq 50$, the result is that

$$\mu = 2.635\ 20 \pm 0.000\ 26 \pm 0.001\ 01 \quad (37)$$

where the format is *best estimate* \pm *95% statistical confidence interval* \pm *systematic error*. This result compares well with $\mu = 2.638\ 158\dots$, which is the value of μ obtained by other means in the literature, see, for example, [2, 10, 19, 20, 35]. Adding the 95% statistical confidence interval in equation (37) to the systematic error, and rounding the resulting error bar up gives $\mu = 2.635 \pm 0.002$, and this barely excludes the acceptable values of μ .

The points β_n increased with n , but stabilized at $n = 80$ to a value close to 0.56. The estimate did not move further with increasing n ; the estimates at $n = 90$ and $n = 100$ are barely excluded from the 95% statistical confidence interval obtained at $n = 80$. Taking the average of the results at $n = 80, 90$ and 100 as our best result, with the maximum difference between these estimates as a systematic error then gives

$$\beta_c = 0.5580 \pm 0.0040 \pm 0.0049 \quad (38)$$

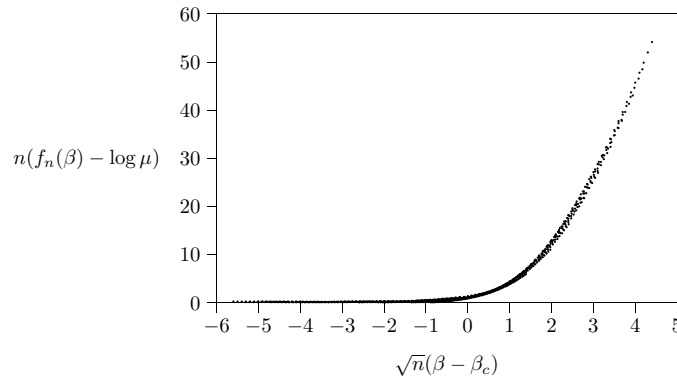


Figure 7. Estimates of $f_n(\beta)$ plotted against the rescaled variable $n^\phi \tau$. Error bars are omitted to produce a clearer graph. In this graph, $\phi = 0.5$ and $\beta_c = 0.56$. The curves should converge to a limiting curve, for these small values of n there are still corrections to scaling present.

where the format is *best estimate* \pm *95% statistical confidence interval* \pm *estimated systematic error*. This result is in close agreement with the estimate for β_c obtained from the energy ratios in equation (33). Lastly, the estimates for ϕ seem to approach a value close to 0.52 when $n = 100$. In this case the attempted fit is over the entire range of β , and corrections to scaling away from the critical point affect the estimate of ϕ . Thus, we consider the estimates in table 2 to be effective values of ϕ , unlike the estimate made from energy ratios above.

Rescaling may also be studied using our data. Observe that $f_n(\beta)$ in equation (27) is an approximation to the free energy. The scaling of $\log \mathcal{A}_n(\beta, 1)$ in equation (25) and of $F_n(\beta)$ in equation (21) then suggests that $f_n(\beta)$ should be a function of the combined variable $n^\phi \tau$ [23, 33]. If the fact that $f_n(\beta) \rightarrow \log \mu$ if $\beta < \beta_c$ and $n \rightarrow \infty$ is taken in account, then one might suppose that

$$f_n(\beta) - \log \mu \sim n^{-1} h(n^\phi \tau) + \text{corrections.} \quad (39)$$

Plotting $n(f_n(\beta) - \log \mu)$ against the rescaled variables $n^\phi \tau$ should collapse all these approximations to a single curve, up to finite size effects. These are plotted in figure 7.

Metric data. The adsorption of a walk is accompanied by a change in the average geometry of the walk from an object that explores conformations in two-dimensional bulk (on average it wanders away from the adsorbing plane) to an object that is attached to the adsorbing surface (in the sense that there is a non-zero density of vertices along the walk that are visits). This change in geometry characterizes the adsorption transition, and can be explored by studying the mean square radius of gyration of the walk, or the mean span, or a quantity such as the height (from the adsorbing plane) of the last vertex in the walk.

It is generally accepted (and known in more than four dimensions [16]), that the scaling properties of metric quantities are determined by the metric exponent ν . For example, if n is the length of the walk, then the mean square radius of gyration would scale as

$$\langle R_n^2(\beta) \rangle \approx A_\beta n^{2\nu} (1 + \dots). \quad (40)$$

Additive corrections to scaling are indicated, and can be important for small values of n . Generally, these corrections are dominated by $n^{2\nu}$ for large values of n . A_β is an *amplitude*. Similarly, the scaling of the mean span is expected to be

$$\langle s_n(\beta) \rangle \approx B_\beta n^\nu (1 + \dots). \quad (41)$$

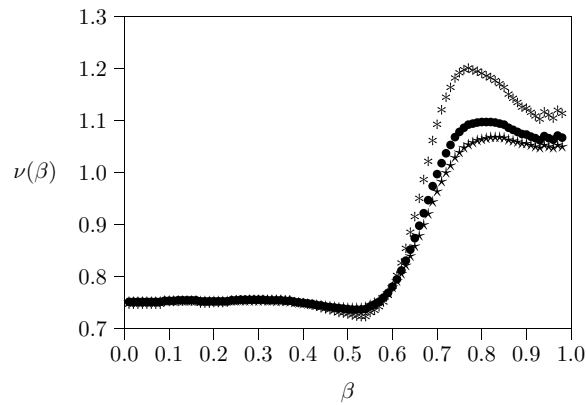


Figure 8. The metric exponent ν against β as determined by analysing mean square radius of gyration data of adsorbing walks in two dimensions. Linear least squares fits of the model $\log A + 2\nu \log n + B/n^\Delta$ with $n \geq n_{\min} = 30$. The exponent Δ was fixed at $\Delta = 0.5$ (*), $\Delta = 1.0$ (●) and $\Delta = 1.5$ (★).

The same exponent, ν , appears in both expressions and is believed to govern the scaling of any quantity with units of length.

The adsorption transition should be characterized as a discontinuous change in ν as a function of β . This means that the thermodynamic phase transition is associated with a rearrangement of the vertices in the walk: in the desorbed phase the walk has two-dimensional statistics, and its scaling exponents are given by those of the two-dimensional self-avoiding walk. In this case, Coulomb gas arguments (as well as numerical and other arguments) indicate that $\nu = 3/4$ [32]. In the adsorbed phase the walk revisits the adsorbing line repeatedly, and so must cover a distance proportional to n along the adsorbing line. Thus, $\nu = 1$ in that phase. The changeover from $3/4$ to 1 occurs at the critical point β_c . Hence, ν is a step-function of β :

$$\nu = \begin{cases} 3/4 & \text{if } \beta < \beta_c \\ 1 & \text{if } \beta > \beta_c. \end{cases} \quad (42)$$

Estimates of ν at fixed β can be made by linear least squares fits of the data (after taking logarithms) to $\log A + 2\nu \log n + B/n^\Delta$, where the term B/n^Δ is included to account for corrections to scaling. The exponent Δ represents an effective confluent correction to scaling, and it was fixed in our analysis to 0.5, 1.0 and 1.5. A comparison of the results would then give an idea of the uncertainty in the estimated value of ν due to inadequacies in the model.

The fits were performed by discarding data at values of $n < n_{\min}$, where n_{\min} was taken equal to 10, 20 and 30 to examine the effects of corrections to scaling on the estimates of ν . The resulting estimates are plotted in figure 8, where error bars are comparable to the size of the points plotted (and have been left away for clarity). Within a small error, ν is constant for $\beta < \beta_c$, but it increases quickly to $\nu = 1$ if $\beta > \beta_c$.

Closer scrutiny of the data for $\Delta = 1$ in figure 8 indicates that $|\nu - 3/4| \leq 0.01$ for all $\beta \leq 0.56$, but that $|\nu - 3/4| = 0.0117, \dots$, if $\beta = 0.57$, and $|\nu - 3/4| = 0.0163, \dots$, if $\beta = 0.58$. For $\beta = 0.59$ one obtains $|\nu - 3/4| = 0.0217, \dots$, and thereafter this difference increases very quickly with increasing β . Thus, the location of the critical point from this mean square radius of gyration is consistent with the estimate obtained from the thermodynamic data above.

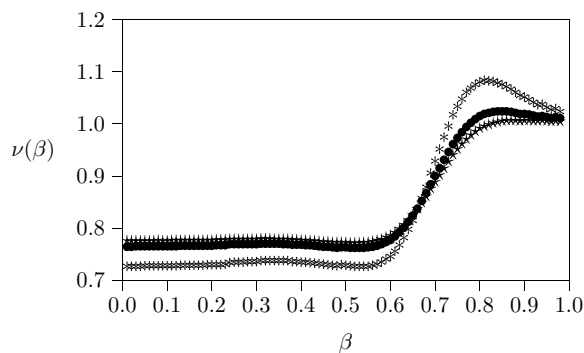


Figure 9. The metric exponent ν against β as determined by analysing mean span data of adsorbing walks in two dimensions. Linear least squares fits of the model $\log A + 2\nu \log n + B/n^\Delta$ with $n \geq n_{\min} = 70$. The exponent Δ was fixed at $\Delta = 0.5$ (*), $\Delta = 1.0$ (●) and $\Delta = 1.5$ (★).

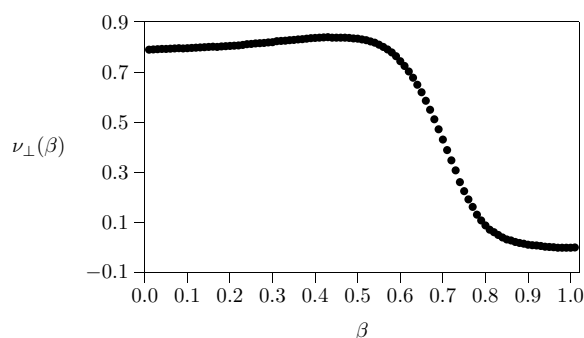


Figure 10. The metric exponent ν_\perp against β as determined by analysing the mean height of the last vertex of adsorbing walks in two dimensions. Linear least square fits with $n_{\min} = 60$ were performed to determine ν_\perp as a function of β .

Further metric support can be found by analysing the mean span data. In this case it appears that the corrections to scaling are more serious than for the mean square radius of gyration data, and our estimates were only marginally acceptable, even for fits with $n_{\min} = 70$. In that case $\nu \approx 0.78$ in the desorbed phase, slightly bigger than the accepted value of $3/4$. Our results are plotted in figure 9, and analysing ν as for the mean square radius of gyration data again indicates that $\beta_c \approx 0.57$.

Lastly, the height of the last vertex above the adsorbing plane can be analysed. In the desorbed phase ($\beta < \beta_c$), the height should scale with n as n^{ν_\perp} where $\nu_\perp = \nu$ for all $\beta < \beta_c$, but since a positive density of vertices are adsorbed if $\beta > \beta_c$, the last vertex is a constant average distance from the last visit, and so remains close to the adsorbing line. In that case, one would expect that $\nu_\perp = 0$ if $\beta > \beta_c$.

Thus, the height of the last vertex does not increase with n in this phase. The dependence of ν_\perp on β , calculated this time from the height of the last vertex is in figure 10. In this case, the location of the critical point is again $\beta_c \approx 0.57$, consistent with the results obtained above. The data for the mean height were analysed with $n_{\min} = 60$ to obtain fits acceptable at the 95% level. At $\beta = 0$, one obtains $\nu_\perp = 0.7865 \pm 0.0013$ with least squares error $E^2 = 3.12$ on three degrees of freedom, acceptable at the 63% level. This result excludes $3/4$ in its statistical confidence interval, but we made no allowance for a systematic error due

to corrections to scaling present in the data; the model was the two parameter model $C_0 n^{\nu_{\perp}}$ and ν_{\perp} was determined from a linear least squares log–log fit. For $\beta = 1.0$, the results are $\nu_{\perp} = -0.0038 \pm 0.0046$ with $E^2 = 4.86$ acceptable at the 82% level.

3.2. Discussion of two-dimensional adsorbing walks

The crossover exponent of adsorbing walks have been estimated using a number of different approaches. Conformal invariance approaches show that $\phi = 1/2$ [3]. Monte Carlo studies tended to produce a slightly larger value than this, for example,

$$\phi = 0.562 \pm 0.020 \quad \text{see [30].} \quad (43)$$

Our results confirm the conformal invariance calculations, showing that ϕ is indeed most likely equal to $1/2$ for the polymer adsorption problem in two dimensions. The best estimate for ϕ is given in equation (33)

$$\phi = 0.501 \pm 0.015 \quad (44)$$

where the error bar is a 95% statistical confidence interval.

The location of the critical point has been determined for a model of adsorbing walks in the honeycomb lattice [1]. Our calculations have now produced a good estimate for the critical point in two dimensions, namely $\beta_c = 0.573 \pm 0.006$ in equation (33), by analysing energy ratios. This result is supported by analysing the specific heat and atmosphere estimates of the free energy instead. A comparison of the results in equations (33), (35) and (38) produces our best estimate

$$\beta_c = 0.565 \pm 0.010 \quad \text{in two dimensions} \quad (45)$$

and where we took the average of the three estimates and rounded up the largest 95% statistical confidence interval to determine the error bar. This result is inconsistent with the estimate

$$\beta_c = 0.722 \pm 0.004 \quad \text{in [30]} \quad (46)$$

it excludes it well outside the stated confidence interval.

The simulation in this paper was not optimized to estimate the metric exponent ν . Instead, we attempted to compute ν as a function of β , but without considering corrections to scaling effects in the data. Our results show that $\nu \approx 3/4$ in the desorbed phase, and that its value increases quickly to one as the critical point β_c is approached. We also analysed the mean height of the last vertex in the walk above the adsorbing plane, and determined an exponent ν_{\perp} that measures the length scale in that direction. We found that $\nu_{\perp} \approx \nu$ if $\beta < \beta_c$, and $\nu_{\perp} = 0$ if $\beta > \beta_c$, as one would expect if there is a positive density of visits in the adsorbing line in the adsorbed phase.

3.3. Adsorbing walks in three dimensions

Energy. The energy ratios in equation (31) of the energies of adsorbing walks were also calculated in three dimensions, and the curves $\log(V_m/V_n)/\log(m/n)$ were plotted against β . In the two-dimensional model, all these curves seemed to intersect at the same point, as predicted by equation (31) and in figure 2 and allowing us to determine the crossover exponent ϕ and the critical point β_c .

In three dimensions the locations of intersections remained dependent on the choices of n and m , and instead we considered intersections between the curve $\log(V_{120}/V_{100})/\log(120/100)$ and the curves $\log(V_m/V_n)/\log(m/n)$ for (m, n) increasing from (20, 10) to (100, 60). The results are listed in table 3. Observe that the location of

Table 3. Intersections of energy ratios in three dimensions.

Ratio 1	Ratio 2	β_c	ϕ
120/100	20/10	0.299(6)	0.5737(22)
120/100	30/20	0.292(9)	0.5470(42)
120/100	40/20	0.292(9)	0.5468(26)
120/100	50/30	0.292(11)	0.5445(37)
120/100	60/30	0.291(11)	0.5417(28)
120/100	70/40	0.287(16)	0.5191(36)
120/100	80/40	0.287(16)	0.5213(30)
120/100	90/50	0.286(25)	0.5164(38)
120/100	100/50	0.285(28)	0.5116(36)
120/100	100/60	0.283(36)	0.5018(49)

the critical point β_c stabilizes quickly to $\beta_c \approx 0.28$, but that the estimate of the crossover exponent, while approaching $1/2$ with increasing (m, n) , depends on (m, n) .

A least squares extrapolation of the data for β_c in table 3 against $1/(n+m)$, where (n, m) are the sizes of the trees in ratio 2, is acceptable at the 95% level. This shows that

$$\beta_c = 0.284 \pm 0.017 \quad (47)$$

with 95% statistical confidence intervals. As a further check, assume instead that convergence of β_c is at a rate proportional to $1/\sqrt{n+m}$. In that case, a least squares analysis of the data in table 3 gives $\beta_c = 0.276 \pm 0.029$, within the confidence interval of the result above. Thus, we can accept the estimates in equation (47) for β_c . This estimate is consistent with most of the estimates in table 3; a simple average over these results also gives an estimate within the error bars of equation (47).

The estimates of ϕ in table 3 seem to approach $1/2$. However, an acceptable least squares extrapolation could not be found. Instead, the location of the critical point at $\beta_c = 0.284 \pm 0.017$ was used to estimate ϕ . The curve $\log(V_m/V_n)/\log(m/n)$ should pass through the point (β_c, ϕ) . Fixing $\beta = \beta_c = 0.284$, and then reading ϕ from

$$\frac{\log\left(\frac{V_m}{V_n}\right)}{\log(m/n)} = \phi \quad \text{at} \quad \beta = \beta_c \quad (48)$$

should give good estimates for ϕ . These estimates are listed in table 4 below. The confidence intervals in ϕ were calculated by repeating the analysis by taking values of β_c and of V_n at the limits of their confidence intervals in our data and in equation (47).

A least squares extrapolation of ϕ against $1/(n+m)$ gives an acceptable fit to all the data in table 4. In that case, the result for ϕ is

$$\phi = 0.5005 \pm 0.0036 \quad (49)$$

where the weighted least squares error is $E^2 = 6.83$ on 13 degrees of freedom, acceptable at the 10% level, and the error bar is a 95% statistical confidence interval.

Specific heat. The specific heat $C_n(\beta)$ is plotted in figure 11 for adsorbing walks in three dimensions. The intersections between these curves can again be used to estimate the value of the critical point, and the area surrounding the intersections is magnified in figure 12. Assuming that the specific heat scales with n as in equation (34), where $\phi = 1/2$, one may guess that the location of the intersections between the curves converges to the critical point at the rate $n^{-\phi}$. Determining the intersections, and extrapolating by using a least squares analysis, then shows that $\beta_c = 0.340 \pm 0.008$ if $n_{\min} = 10$ with least squares error $E^2 = 4.8$

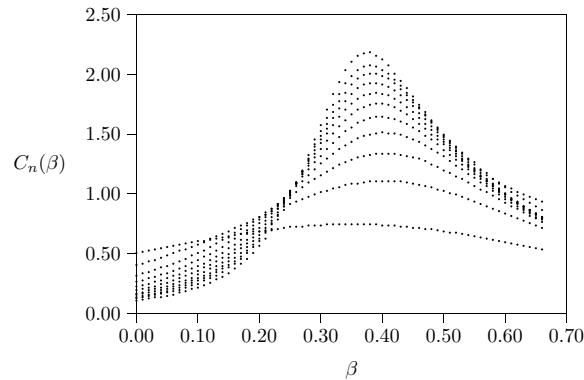


Figure 11. The specific heat for adsorbing walks in three dimensions. Error bars have not been shown for clarity. The lengths of the paths increase from the lowest peak at $n = 10$ in steps of 10 to $n = 100$, and then to $n = 120$. In this model the points of intersection between the curves increase with increasing n . Extrapolating the intersections against $n^{-\phi}$ with $\phi = 1/2$ gives $\beta_c = 0.33 \pm 0.02$. This is in contrast to the case of two-dimensional adsorbing walks, where the intersections quickly become stationary, and one may estimate the critical point by bounding them in a smallest box. For values of $\beta < \beta_c$ the curves decrease to zero, and for $\beta > \beta_c$, the peaks increase at the rate of $n^{\alpha\phi}$ to a limiting specific heat.

Table 4. Estimates of ϕ from energy ratios.

(m, n) in equation (48)	ϕ
(20,10)	0.5486(23)
(30,20)	0.5288(42)
(40,20)	0.5268(26)
(50,30)	0.5231(37)
(60,30)	0.5204(28)
(70,40)	0.5109(36)
(80,40)	0.5107(30)
(90,50)	0.5088(36)
(100,50)	0.5078(36)
(100,60)	0.5060(49)
(100,80)	0.513(12)
(120,70)	0.5100(52)
(120,80)	0.5100(71)
(120,90)	0.505(11)
(120,100)	0.507(18)

on nine degrees of freedom. This estimate changes to $\beta_c = 0.326 \pm 0.011$ if $n_{\min} = 20$ with least squares error $E^2 = 2.0$ on eight degrees of freedom. Subsequent increases in n_{\min} does not change the estimate outside its error bars. This estimate is higher than obtained in equation (47) above.

Assuming instead that convergence of β_c is at a rate proportional to n^{-1} gives $\beta_c = 0.284 \pm 0.009$ if $n_{\min} = 10$ with least square error $E^2 = 2.12$ on nine degrees of freedom. If $n_{\min} = 20$ in this case, then the analysis gives $\beta_c = 0.286 \pm 0.007$ with $E^2 = 2.0$ on eight degrees of freedom. In this case the estimate did not move with increasing n_{\min} .

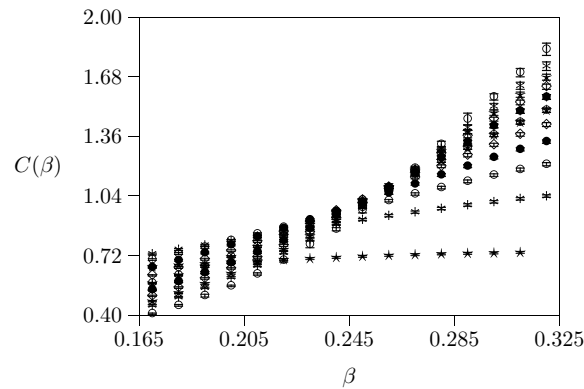


Figure 12. The intersections of specific heat data magnified. Extrapolating the intersections against $n^{-\phi}$ gives the estimate $\beta_c = 0.33 \pm 0.02$ for the critical point. Unlike the case for two-dimensional adsorbing walks, a box bounding the intersection does not give a credible estimate of β_c .

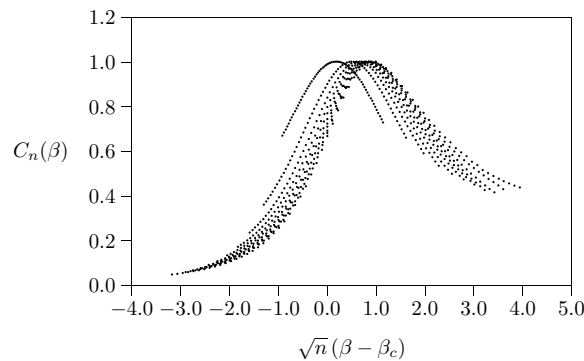


Figure 13. The specific heat of adsorbing walks in three dimensions normalized to height 1 and plotted against the scaled variable $n^\phi(\beta - \beta_c)$, where $\phi = 1/2$ and $\beta_c = 0.33$. All these curves should collapse with increasing n to a single universal curve, however, such convergence appears to be very slow. Lowering β_c to its best value in equation (47) does not improve the result. It appears that corrections to scaling in the specific heat disappear only slowly with increasing n .

These results suggest that there is a large systematic error present in estimates of β_c from the specific heat data. In particular, one can plot the specific heat, normalized to height 1, against $n^\phi(\beta - \beta_c)$; the data should collapse to a single underlying universal curve. Choosing $\beta_c = 0.33$ produces figure 13; smaller values of β_c (say around 0.29) produce curves that are even further apart. We independently verified this observation by repeating our runs using a flat histogram version of the pruned enriched Rosenbluth method [34]; we obtained an identical graph. This larger value of β_c is more consistent with the specific heat data, rather than the smaller estimate obtained in equation (47) from energy ratios. We conclude that poor estimates of β_c and ϕ are obtained by analysing specific heat data in this model.

Further analysis can be done by considering the location of peaks in the specific heat data. The locations of these peaks should converge with increasing n to β_c at a rate determined by $n^{-\phi}$. However, our data indicate that over the range of values of n considered, the positions of the peaks did not move significantly. At $n = 10$, the peak was located at $\beta = 0.35$, and

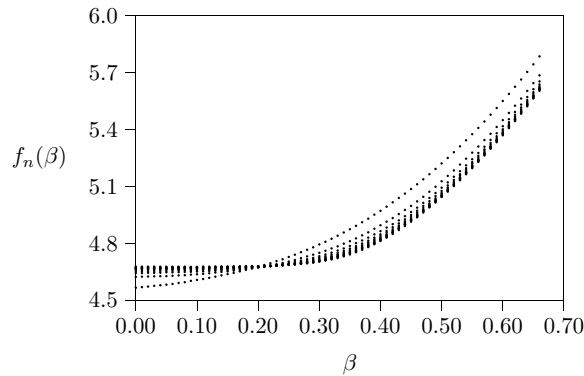


Figure 14. Estimates of $f_n(\beta)$ for adsorbing walks in three dimensions for lengths $n = 10$ to $n = 100$ in increments of 10, and for $n = 120$. The curves converge quickly to a limiting shape, and all seem to intersect close to $\beta = 0.21$. At this point, it appears that scaling corrections are largely cancelled by the interaction with the adsorbing line, and one should be able to take numerical advantage of this to determine the growth constant for self-avoiding walks to high accuracy. However, numerical analysis shows that the critical point for adsorption is likely larger than this.

Table 5. Free energy parameters in $3d$.

n	μ	ϕ^{-1}	β_n
10	4.560 76(24)	2.4978(64)	0.032 91(23)
20	4.615 44(33)	2.494(12)	0.1018(28)
30	4.635 51(30)	2.356(11)	0.1531(22)
40	4.644 51(27)	2.2060(97)	0.1932(18)
50	4.652 82(27)	2.1673(91)	0.2037(16)
60	4.656 32(26)	2.0886(85)	0.2230(14)
70	4.660 37(26)	2.0555(87)	0.2312(14)
80	4.661 64(25)	2.0020(76)	0.2408(13)
90	4.664 37(24)	1.9757(76)	0.2458(12)
100	4.666 72(25)	1.9461(75)	0.2495(12)
120	4.669 94(24)	1.8975(68)	0.2560(10)

$n = 20$ at $\beta = 0.40$, and at $n = 120$ at $\beta = 0.38$. Convergence to β_c is very slow, and extrapolating from specific heat data to β_c may be problematic in this model.

An attempt to analyse the peak heights in $C_n(\beta)$ to estimate $\alpha\phi$ in equation (34) was equally unsuccessful. Since we expect that $\alpha = 0$ in this model, the heights of the peaks may increase at a rate inconsistent with a power-law, and so assuming such a form may well lead to wrong estimates of ϕ .

Free energy. The free energies of adsorbing walks in three dimensions can be approximated by $f_n(\beta)$ using atmospheric data as in equation (27). These approximations are plotted in figure 14. As in two dimensions, one may assume that equation (28) be fitted to data in order to estimate μ , β_c and an effective value for ϕ . Acceptable fits could be performed when taking $N = 2$ in equation (28), similar to the analysis in two dimensions. In this analysis the weighted least squares error was first minimized by a Monte Carlo implementation of simulated annealing, and then by applying Newton's method using numerical derivatives when convergence has taken us close to the minimum. The results are listed in table 5.

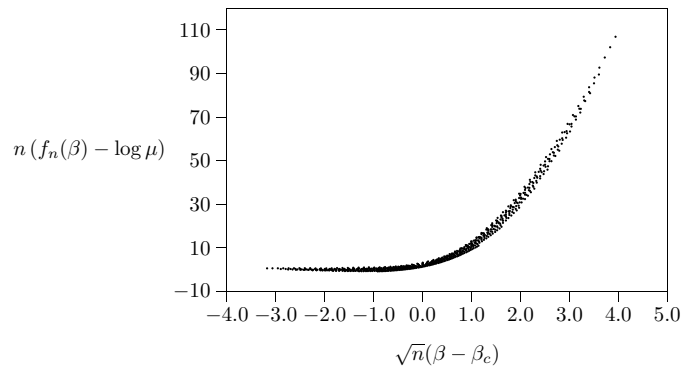


Figure 15. Rescaled estimates of $f_n(\beta)$ plotted against $n^\phi(\beta - \beta_c)$. Error bars were omitted to produce a better graph. In this graph, $\phi = 0.5$ and $\beta_c = 0.29$. The curves should converge to a limiting curve; for the small values of n there are still corrections to scaling present.

The estimates of μ in table 5 appears to have converged to at least two decimal places by $n = 120$. Choosing that value at $n = 120$ as our best estimate, and considering absolute differences for $n \geq 60$ as an indication of a systematic error, we obtain the estimate

$$\mu = 4.670 \pm 0.0006 \pm 0.013 \quad (50)$$

where the format is *best estimate* \pm *95% statistical confidence interval* \pm *estimated systematic error*.

Assuming that $\beta_n = \beta_c + Cn^{-1}$, and performing weighted least squares fits to the data in the last column of table 5 give an acceptable fit if $n_{\min} = 50$, in which case

$$\beta_c = 0.293 \pm 0.004 \pm 0.005 \quad (51)$$

and the least square error is acceptable at the 88% level, and with a stated 95% statistical confidence interval and a systematic error estimated by repeating the least squares analysis with $n_{\min} = 60$. Assuming the model $\beta_n = \beta_c + Cn^{-1/2}$ does not give an acceptable fit at $n_{\min} = 50$, and also produces the larger value of $\beta_c \approx 0.35$.

The estimate in equation (51) agrees with the estimate obtained from the energy ratios in (47), but excludes the values of ϕ determined by analysing specific heat data, and can be seen by extrapolating ϕ^{-1} in table 5.

In figure 15 the rescaled free energies $n(f_n(\beta) - \mu)$ are plotted against $\sqrt{n}(\beta - \beta_c)$ with $\beta_c = 0.29$. The curves collapse to a single curve, and rescaling with $\phi = 1/2$ and $\beta_c = 0.29$ underscores the results obtained in equations (48) and (51).

Metric data. In three dimensions the adsorption of the walk onto an adsorbing plane should be accompanied by a change in the averaged metric properties of the walk. Since there is a density of visits in the adsorbing plane if $\beta > \beta_c$, and a repulsion between these due to self-exclusion, one expects the walk to acquire the statistics of a two-dimensional self-avoiding walk. Hence, in the adsorbed phase, the metric exponent should take its two-dimensional self-avoiding walk value: $\nu = 3/4$. In the desorbed phase the walk will have the statistics of three-dimensional self-avoiding walks in bulk, and so $\nu = 0.578 \dots$ [4, 24]. In other words, in this model it is expected that

$$\nu = \begin{cases} 0.578 \dots & \text{if } \beta \leq \beta_c \\ 3/4 & \text{if } \beta > \beta_c. \end{cases} \quad (52)$$

We assumed the model $\log \langle R^2 \rangle = C_0 + 2\nu \log n + \alpha n^{-\Delta}$ describes the mean square radius of gyration data. The confluent correction exponent Δ was assumed to take values $\Delta = 0.5, 1.0$

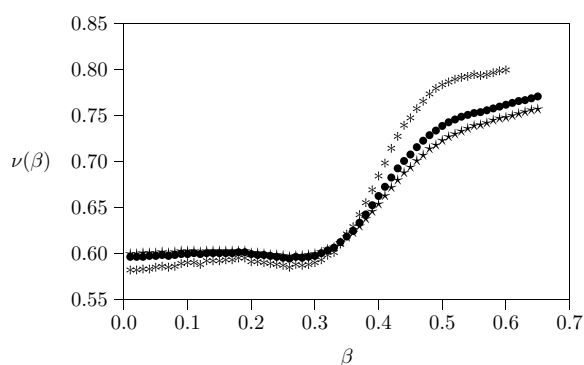


Figure 16. The metric exponent ν against β as determined by analysing mean square radius of gyration data of adsorbing walks in three dimensions. Linear least squares fits with $n_{\min} = 30$ were performed to determine ν as a function of β . The quality of the fits deteriorated at large values of β . The analysis was done by assuming that the confluent correction to scaling exponent takes values $\Delta = 0.5$ (\star), 1.0 (\bullet) and 1.5 ($*$).

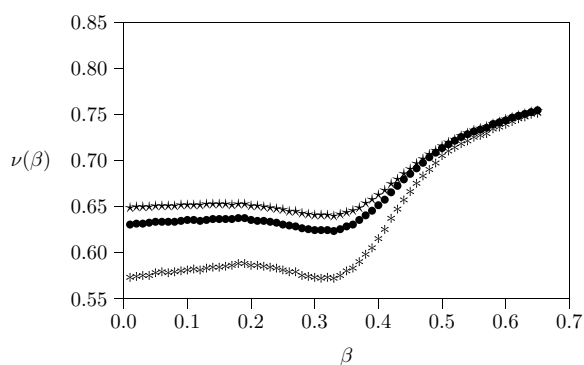


Figure 17. The metric exponent ν against β as determined by analysing mean span data of adsorbing walks in two dimensions. Linear least squares fits with $n_{\min} = 30$ were performed to determine ν as a function of β . The quality of the fits were generally not good. The analysis was done by assuming that the confluent correction to scaling exponent takes values $\Delta = 0.5$ (\star), 1.0 (\bullet) and 1.5 ($*$).

and 1.5, respectively; the difference in the three sets of results is an indication of a systematic error due to uncertainties in the model. We plot our results in figure 16.

Closer scrutiny of the data in figure 16 indicates that $|\nu - 0.58| \leq 0.02$ for all $\beta \leq 0.3$, but this increases quickly for larger β . Thus, the location of the critical point from this mean square radius of gyration is close to the estimate obtained above from the thermodynamic data.

Further metric support for the location of β_c can be found by analysing the mean span data (see figure 17). The model was again $\log\langle s_n \rangle = C_0 + \nu \log n + \alpha n^{-\Delta}$, including a confluent correction to scaling, and where we take $\Delta = 0.5, 1.0$ and 1.5 in three attempts to find good fits to our data. In this case it appears that the corrections to scaling are more serious than for the mean square radius of gyration data, and our estimates were only marginally acceptable, even for fits with $n_{\min} = 30$. In that case $\nu \approx 0.60$ in the desorbed phase when $\Delta = 1.0$, slightly larger than the accepted value of 0.58. Reading of the critical point gives $\beta_c \approx 0.3$, as before.

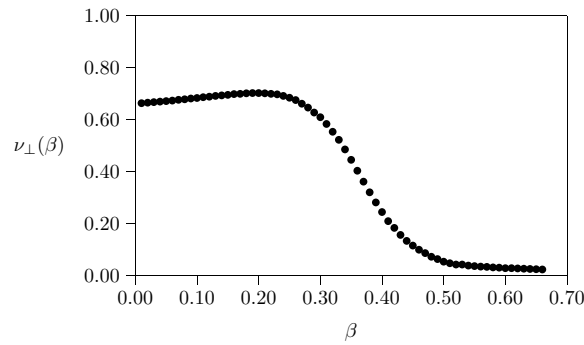


Figure 18. The metric exponent ν_{\perp} against β as determined by analysing the mean height of the last vertex of adsorbing walks in two dimensions. Linear least square fits with $n_{\min} = 70$ were performed to determine ν_{\perp} as a function of β .

One may similarly analyse the height above the adsorbing plane of the last vertex in the walk. Similar to two dimensions, one expects that the height to increase proportional to $n^{\nu_{\perp}}$ where $\nu_{\perp} = \nu$ in the desorbed phase with $\beta < \beta_c$, and $\nu_{\perp} = 0$ in the adsorbed phase (when $\beta > \beta_c$). We show our results in figure 18; these fits did not control for corrections to scaling. Instead, we took $n_{\min} = 70$ and used a two-parameter linear model fitting the logarithm of the height of the last vertex to $C_0 + \nu_{\perp} \log n$.

3.4. Discussion of three-dimensional adsorbing walks

Estimates of the crossover exponent ϕ for adsorbing walks in the three-dimensional cubic lattice can be found in [8, 17, 31]. In particular, estimates are as follows:

$$\begin{aligned} \phi &= 0.58 \pm 0.03 && \text{in [8]} \\ \phi &= 0.530 \pm 0.007 && \text{in [31]} \\ \phi &= 0.496 \pm 0.004 && \text{in [17].} \end{aligned} \tag{53}$$

In this paper we improved on these estimates by determining ϕ from energy ratios obtained by multiple Markov sampling. Our best value for ϕ is

$$\phi = 0.5005 \pm 0.0036 \tag{54}$$

comparable in accuracy to the result of Hegger and Grassberger in [17], and consistent with the belief that $\phi = 1/2$. This result barely excludes the Hegger and Grassberger value outside its 95% statistical confidence interval. However, the results by Eisenriegler *et al* ($\phi = 0.58 \pm 0.03$, [8]) and by Meirovitch and Livne ($\phi = 0.530 \pm 0.007$ [31]) are ruled out by this result. The much larger values obtained in earlier studies are consistent with our observations that analysis of the specific heat gives unreliable estimates of ϕ and β_c . These results strongly suggest that ϕ is indeed most likely equal to $1/2$ for the polymer adsorption problem in three dimensions.

Our calculations have now produced a good estimate for the critical point in three dimensions. Estimates from energy ratios in equation (47) and by directly analysing the free energy (see equation (51)), agree within error bars, and we take their average as our best estimate for β_c

$$\beta_c = 0.288 \pm 0.020 \quad \text{in three dimensions.} \tag{55}$$

The error was determined by rounding up the largest error bar of two estimates. This result compares well with other estimates of β_c in the literature. In particular,

$$\begin{aligned}
\beta_c &= 0.291 \pm 0.001 \quad \text{in [31]} \\
\beta_c &= 0.294 \pm 0.014 \quad \text{in [37]} \\
\beta_c &= 0.296 \pm 0.016 \quad \text{in [37]}.
\end{aligned}
\tag{56}$$

The results by Vrbová and Procházka ([37]) are consistent with our estimate, but our result is outside the confidence interval of the results in [31], indicating that the confidence interval in this study may have been underestimated.

The simulation in this paper was not optimized to estimate the metric exponent ν . Instead, we attempted to compute ν as a function of β , but without considering corrections to scaling effects in the data. Our results show that $\nu \approx 0.60$ in the desorbed phase, and that its value increases quickly to 0.75 in the adsorbed phase. We also analysed the mean height of the last vertex in the walk above the adsorbing plane, and determined an exponent ν_\perp that measures the length scale in that direction. We found that $\nu_\perp \approx \nu$ if $\beta < \beta_c$, and $\nu_\perp = 0$ if $\beta > \beta_c$, as one would expect if there is a positive density of visits in the adsorbing line in the adsorbed phase.

4. Conclusions

It can be shown that there is a (thermodynamic) adsorption transition of walks in a d -dimensional half-space onto a $(d - 1)$ -dimensional hyperplane [15]. The crossover exponent in all models of adsorbing polymers is believed to be equal to $1/2$. In this paper we examined this using a model of self-avoiding walks in two and in three dimensions. In these low dimensions the transition is accompanied by a change in the metric statistics of the walks: the metric exponent ν changes through the transition to a new value. In high dimensions $d > 4$ there is still an adsorption transition, but since self-avoiding walks are now described by a mean field theory, it is the case that $\nu = 1/2$ in both the adsorbed and desorbed phases.

In this paper we have examined in particular the thermodynamic nature of the adsorption transition. We estimated crossover exponents and locations of the critical adsorption point of adsorbing self-avoiding walks in two and in three dimensions, and our best estimates are listed in equations (33), (45), (49) and (55). Generally, thermodynamic quantities should also rescale along the β -axis with increasing length n of the walk proportional to n^ϕ . In two dimensions we demonstrated this rescaling for both the atmospheric approximations to the free energy and for the specific heat in figures 5 and 7. In three dimensions the rescaling is also demonstrated for the free energy in figure 15, but strong corrections to scaling in the specific heat complicates the picture in that case (figure 13). These results strongly support the tricritical hypothesis in describing the adsorption transition in this model. Our data also suggest that analysis of the specific heat data in three dimensions are fraught with difficulty.

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