

Adsorption of periodic copolymers at a planar interface

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Abstract. We use Monte Carlo methods to study a self-avoiding walk model of copolymers, with a periodic sequence of comonomers, adsorbing at a planar surface. The monomers are of two types, A and B , and only A monomers interact with the surface. We investigate how the location of the adsorption transition depends on the comonomer sequence and make comparisons with some rigorous results. We also investigate a directed-walk model (in two dimensions) and show that this model can be used to give insight into the behaviour of the more natural self-avoiding-walk model.

1. Introduction

The statistical mechanics of polymer adsorption is an important problem, both because of the practical importance of the phenomenon and because of interest in the nature of the adsorption transition. One of the standard models of homopolymer adsorption is a self-avoiding walk on a lattice (such as the simple cubic lattice, Z^3) which begins at the origin, is confined to the half-space $z \geq 0$ and where the vertices of the walk have a short-range attractive interaction with the surface $z = 0$. Hammersley *et al* (1982) showed that the model has a phase transition, and the location and nature of the transition have been studied by many different methods. For a review see De’Bell and Lookman (1993).

Recently, there has been considerable interest in the adsorption of both random and periodic copolymers. There are several recent papers on the theory of copolymer adsorption (see, for instance, Sommer and Daoud 1995, Sommer *et al* 1996, Whittington 1998a) and also some Monte Carlo results (Wang *et al* 1993). In the self-avoiding-walk model of copolymer adsorption the vertices of an n -step self-avoiding walk are numbered $i = 0, 1, 2, \dots, n$ and vertices are coloured A or B to represent two different types of comonomer. Only one comonomer (A , say) has an attractive interaction with the surface and vertex 0 is coloured A . Given a sequence χ of comonomers (i.e. a particular colouring of the vertices of the walk) one can ask for the number $c_n^+(v_A|\chi)$ of n -edge walks with $v_A + 1$ A -vertices in the plane $z = 0$, and define the partition function

$$Z_n(\alpha|\chi) = \sum_{v_A} c_n^+(v_A|\chi) e^{\alpha v_A}. \quad (1.1)$$

The free energy is

$$\kappa_n(\alpha|\chi) = n^{-1} \log Z_n(\alpha|\chi). \quad (1.2)$$

If the sequence χ is random one is interested in the existence and behaviour of the limit $\lim_{n \rightarrow \infty} \langle \kappa_n(\alpha|\chi) \rangle$, where the average $\langle \dots \rangle$ is taken over all random sequences χ from the appropriate probability distribution (Garel *et al* 1989, Gutman and Chakraborty 1994,

Bolthausen and den Hollander 1997, Orlandini *et al* 1999). If the sequence χ is periodic (e.g. an alternating copolymer) then one is concerned with the behaviour of the limit

$$\kappa(\alpha|\chi) = \lim_{n \rightarrow \infty} \kappa_n(\alpha|\chi). \quad (1.3)$$

This limiting free energy will be singular for some $\alpha_c(\chi) > 0$ and we are interested in the χ dependence of this adsorption threshold. We shall write the repeating sequence as a shorthand for χ . For instance, we shall write AAB as a shorthand for the sequence $AABAABAAB \dots$ and AB as a shorthand for the strictly alternating sequence $ABABAB \dots$. We shall number the vertices of the walk $i = 0, 1, 2, \dots, n$ and normally regard vertex 0 as being an A -vertex. For the case of the simple cubic lattice let the location of the adsorption transition for the homopolymer, poly- A , be α_0 . Then it is known rigorously (Whittington 1998a) that

$$3\alpha_0/2 \leq \alpha_c(AB) \leq 3\alpha_0 \quad (1.4)$$

and

$$\alpha_c(AB_p) \geq 2\alpha_0 \quad (1.5)$$

for all $p \geq 2$. Nothing is known rigorously about the location of the transition for AAB or $AABB$ (except the rather obvious result that α_c is at least as large as α_0). In the next section we present Monte Carlo estimates of α_c for AB , AAB , ABB , $AAAB$ and $ABBB$. In addition, we argue that the crossover exponent ϕ is close to $\frac{1}{2}$ for each of these cases, as it is for the homopolymer (Hegger and Grassberger 1994).

In section 3 we present corresponding results for a directed-walk model of adsorption in two dimensions. We consider walks on the square lattice, confined to the half-space $y \geq 0$ with no steps in the negative x -direction. This model was first discussed in the context of homopolymer adsorption by Privman *et al* (1988), and solved using transfer matrices. Whittington (1998b) gave a combinatorial solution and extended this to the alternating copolymer AB . We further extend this approach to handle the sequences AAB , ABB , $AABB$, $AAAB$ and $ABBB$. For each of these cases it is possible to derive the location of the transition exactly, and we discuss the trends in these values, and compare with our Monte Carlo estimates for the self-avoiding-walk problem.

2. Monte Carlo approach and results

In this section we present a Monte Carlo study of the adsorption of the periodic copolymers $AAAB$, AAB , AB , ABB and $ABBB$, modelled as coloured self-avoiding walks on the simple cubic lattice, and compare our results with those for the homopolymer and for block copolymers in which half of the polymer is composed of A units and half is composed of B units. In each case we consider self-avoiding walks on the simple cubic lattice Z^3 , starting at the origin and confined to the half space $z \geq 0$. We generate a correlated sample of walks using a Metropolis sampling scheme, with the trial moves being proposed by a pivot algorithm coupled with local moves. To speed up convergence we use a multiple Markov chain scheme (Geyer 1991) in which we run a set of Markov chains in parallel at different values of α with swapping of configurations between adjacent values of α . For details see Geyer (1991) and Tesi *et al* (1996). This method requires that convergence should be rapid at one of the α values, and we achieved this by always including $\alpha = 0$ in the multiple Markov chain runs.

For each of the five cases which we have investigated we have calculated the mean number of A -vertices in the surface, normalized by the number of edges in the walk,

$$\frac{\langle v_A \rangle}{n} = \frac{\partial \kappa_n(\alpha|\chi)}{\partial \alpha} \quad (2.1)$$

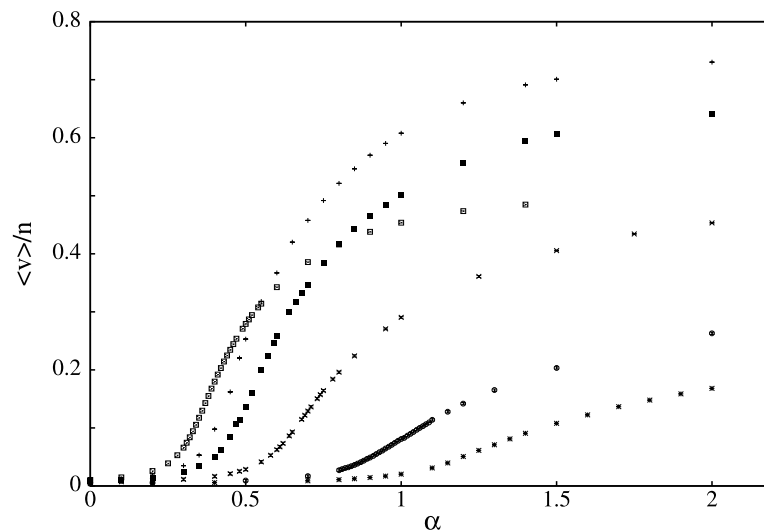


Figure 1. The mean number of vertices of type *A* in the plane, per edge, as a function of α , for $n = 400$. $A_{n/2}B_{n/2}$ (\square), $AAAB$ (+), AAB (\blacksquare), AB (\times), ABB (\circ) and $ABBB$ (*).

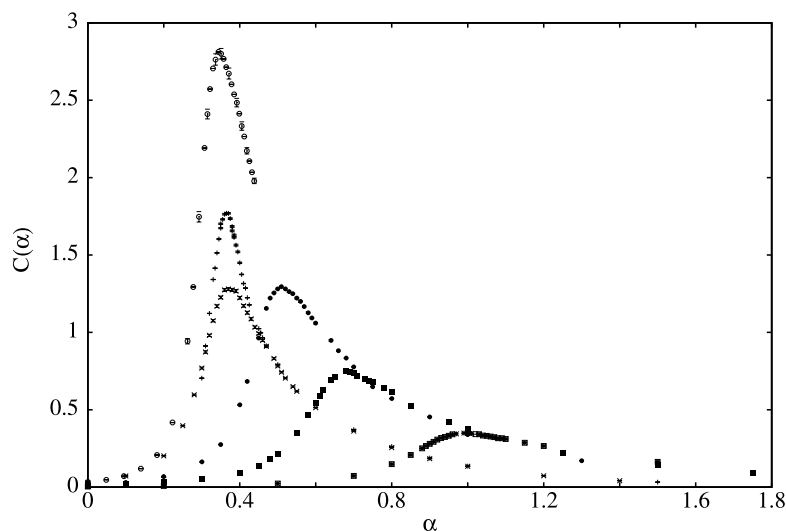


Figure 2. The α dependence of the reduced heat capacity $C_n(\alpha|\chi)$ for $n = 400$. The homopolymer *A* (\circ), the block copolymers $B_{n/2}A_{n/2}$ (+) and $A_{n/2}B_{n/2}$ (\times), and the periodic cases AAB (\bullet), AB (\blacksquare) and ABB (\square).

the ‘heat capacity’ $C_n(\alpha|\chi) = [\langle v_A^2 \rangle - \langle v_A \rangle^2] / n$ and metric properties such as the mean z -component of the vertices of the walk. These are all estimated for a range of values of α from $\alpha = 0$ to values far inside the adsorbed regime and for a number of values of n .

In figure 1 we show the α dependence of $\langle v_A \rangle / n$ for the diblock copolymer $A_{n/2}B_{n/2}$, and the periodic cases $AAAB$, AAB , AB , ABB and $ABBB$ for $n = 400$. At large values of α the values of $\langle v_A \rangle / n$ are ordered as one would expect from the relative proportions of *A* and *B* units. This remains true at small α except that the values for the block copolymer increase

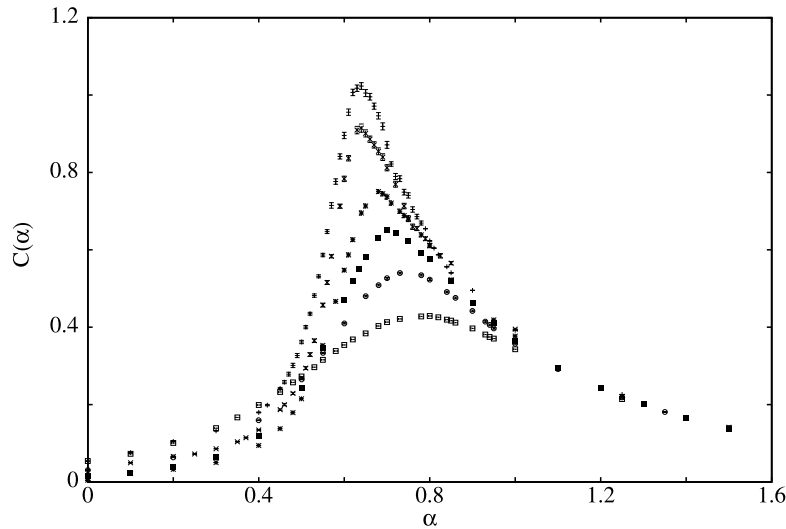


Figure 3. The α dependence of $C_n(\alpha|AB)$ for $n = 50, 100, 200, 400, 800$ and 1000 .

much more rapidly than those of AB (although they have the same proportion of A units) and the curve for the block copolymer is above the curves for other sequences, including those that have a larger fraction of A units. This is consistent with the rigorously known result that the critical value of α for the block copolymer is the same as for the homopolymer, and therefore less than that for the AB case (Whittington 1998a) and, as we shall see, for other periodic cases. In figure 2 we show the α dependence of $C_n(\alpha|\chi)$ for the homopolymer, the block copolymers $A_{n/2}B_{n/2}$ and $B_{n/2}A_{n/2}$, and for the three periodic cases AAB , AB and ABB , for $n = 400$. The locations of the heat capacity peaks indicate that the block copolymers adsorb at the lowest value of α , followed by AAB , AB and ABB in that order. Of course, the peak positions vary with n and, in figure 3, we show the α dependence of $C_n(\alpha|AB)$ for a range of n values. The peaks increase in height and decrease in width as n increases. In addition, the peaks are asymmetric, rising more rapidly than they fall, consistent with the rigorous result (Whittington 1998a) that the free energy $\lim_{n \rightarrow \infty} \kappa_n(\alpha|AB)$ is independent of α for values of α below the adsorption transition.

We examined the distribution of values of $\langle v_A/n \rangle$ as a function of α and found no evidence for a first-order transition. We therefore conclude that the transition is second order, as is thought to be the case for homopolymer adsorption. The way in which the peak positions approach the location of the adsorption transition (as $n \rightarrow \infty$) is controlled by the crossover exponent ϕ . For the homopolymer, numerical estimates of ϕ range from about 0.5 to 0.59 (see De'Bell and Lookman (1993) for a review, and Hegger and Grassberger (1994) for a more recent study). In fact, Hegger and Grassberger (1994) have suggested that the value might be exactly $\frac{1}{2}$. We have attempted to estimate the value of ϕ from our homopolymer data by fitting the heights, h_n , of the heat capacity peaks at various values of n to the functional form

$$h_n = An^{2\phi-1}(1 + B/\sqrt{n}). \quad (2.2)$$

We estimate that ϕ is roughly equal to 0.55, but emphasize that this is only a rough estimate. Certainly our data do not rule out a value as low as 0.5, especially in view of the uncertainty in the correction term in (2.2). It is natural to expect that the crossover exponent will have the same value for these copolymer models as for the homopolymer and, to test this, we

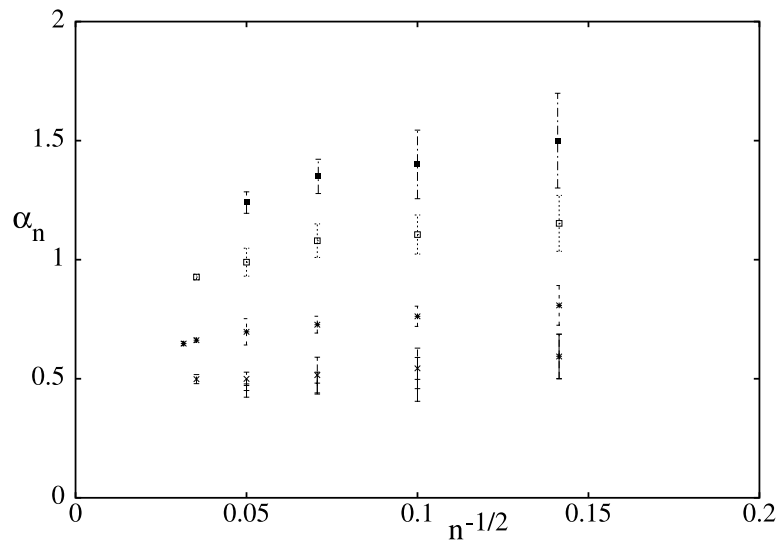


Figure 4. The locations of the heat capacity peaks plotted against $1/\sqrt{n}$ for AAAB (■), AAB (□), AB (*), ABB (×) and ABBB (+).

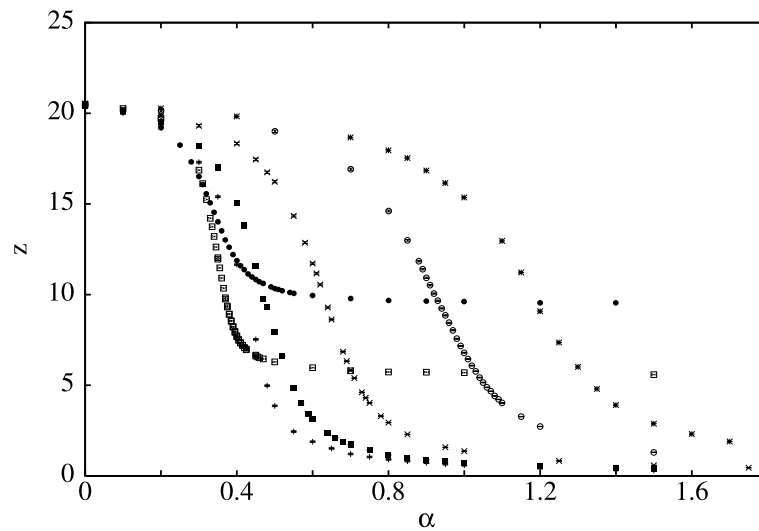


Figure 5. The α dependence of the mean z -coordinate of vertices of the walk for $n = 400$. $A_{n/2}B_{n/2}$ (●), $B_{n/2}A_{n/2}$ (□), AAAB (+), AAB (■), AB (×), ABB (○) and ABBB (*).

have plotted the location of the heat capacity peak $\alpha_c(n|\chi)$ for AAAB, AAB, AB, ABB and ABBB against $n^{-1/2}$ (implicitly assuming that $\phi = \frac{1}{2}$) in figure 4. The values for the homopolymer are also given for comparison. Changing the assumed value of ϕ by a small amount does not materially alter the general nature of this figure, and our results are not sufficiently precise to enable us to make an accurate estimate of ϕ , but the linearity in this figure suggests that ϕ is close to $\frac{1}{2}$ for all these models. Assuming this value of ϕ we can make a rough estimate of the location of the adsorption transition for these five cases. Our

estimates are $\alpha_c(AAAB) = 0.39 \pm 0.02$, $\alpha_c(AAB) = 0.475 \pm 0.02$, $\alpha_c(AB) = 0.57 \pm 0.05$, $\alpha_c(ABB) = 0.8 \pm 0.04$ and $\alpha_c(ABBB) = 1.0 \pm 0.07$.

In figure 5 we compare the α dependence of $\langle z \rangle$, the mean z -coordinate of the vertices of the walk, for several periodic copolymers and for the two-diblock copolymers $A_{n/2}B_{n/2}$ and $B_{n/2}A_{n/2}$, for $n = 400$. In each case the value of $\langle z \rangle$ drops dramatically as α is increased and, for the periodic cases, the decrease occurs at larger values of α as the proportion of B units increases. This is consistent with our results for locations of the heat capacity peaks. The decrease occurs at a smaller value of α for the two block copolymers, consistent with the adsorption transition being at the same location as that of the homopolymer (Whittington 1998a). The value of $\langle z \rangle$ at large α becomes very small for the periodic cases, but seems to be asymptotic to values well away from zero for the block copolymers. In the case of the block copolymers the B units extend well away from the surface, into the solution, even at large α . This asymptotic value is larger for $A_{n/2}B_{n/2}$ than for $B_{n/2}A_{n/2}$ since the first vertex is fixed in the surface and the B units can only form a loop in the latter case, whereas they can form a tail in the former case.

3. A directed-walk model

In this section we consider self-avoiding walks on the square lattice Z^2 which start at the origin, are confined to the half-space $y \geq 0$ and have no steps in the negative x -direction. In fact, we concentrate on the subset of these walks which also have their last vertex in the line $y = 0$. One can show (by the methods of Hammersley *et al* (1982)) that fixing the last vertex in $y = 0$ does not affect the limiting free energy and, in particular, that the location of the adsorption transition is the same for these walks as for walks where the last vertex is not constrained to have zero y -coordinate.

For a given (periodic) colouring χ let $a_n(v|\chi)$ be the number of such walks having n edges and $v + 1$ vertices of type A in the line $y = 0$. (Recall that the zeroth vertex is always of type A .) Let $a_n^j(v|\chi)$ be the corresponding number of walks with the first j steps in the positive x -direction and which either have exactly j steps (the case $j = n$) or which have the $(j + 1)$ th step in the positive y -direction (the case $j < n$). Define the generating function

$$H(x, y|\chi) = \sum_{v,n} a_n(v|\chi) x^v y^n \quad (3.1)$$

where $x = e^\alpha$, and the partial generating functions

$$h_j(x, y|\chi) = \sum_{v,n} a_n^j(v|\chi) x^v y^n. \quad (3.2)$$

The strategy is to derive equations relating H and the partial generating functions h_j and to solve these to find H . The thermodynamics of the system can then be derived from the shape of the boundary of convergence, $y = y_c(x)$, of H . For small x the boundary of convergence is always the line $y = \sqrt{2} - 1$, but at larger x the boundary depends on the model. The point (x^*, y^*) at which these two branches of the boundary of convergence meet gives the singular point in the free energy, and hence the location of the adsorption transition. The details of the calculations are given in the appendix.

We summarize the locations of the transition for various copolymers in table 1. The fact that $x^*(A) < x^*(AAAB) < x^*(AAB) < \dots$, increasing as the proportion of B units increases, is not surprising. We expect that $x^*(A_p B)$ will decrease as p increases, and $x^*(AB_p)$ will increase as p increases, and it would be interesting to establish these results for arbitrary integral p . We note that $x^*(AAAB) < x^*(A)^{4/3}$, $x^*(AAB) < x^*(A)^{3/2}$, etc, so the locations of

Table 1. Location of the adsorption transition for the directed model.

Repeat	x^*	α_c
A	1.492...	0.400...
AAAB	1.687...	0.522...
AAB	1.802...	0.589...
AABB	2.101...	0.742...
AB	2.194...	0.785...
ABB	3.078...	1.124...
ABBB	4.007...	1.388...

the adsorption transition for these copolymers are related to the location for the homopolymer in non-trivial ways. Similarly, $x^*(AABB) < x^*(AB)$. One would expect that $x^*(A_p B_p)$, would decrease as p increases, though this has not been established. Of course, if $p = \lfloor \epsilon n \rfloor$, for any positive value of ϵ , the copolymer is a block copolymer and x^* will be equal to $x^*(A)$, the value for the homopolymer.

In principle, it should be possible to extract exact values of critical exponents such as ϕ and γ_{11}^s from our results for these models. The exponent γ_{11}^s can be defined as the limit

$$\gamma_{11}^s = - \lim_{y \rightarrow y^* -} \frac{\log H(x^*, y)}{\log(y^* - y)} \quad (3.3)$$

and the crossover exponent can be computed as

$$1/\phi = \lim_{x \rightarrow x^* +} \frac{\log \log(y_c(x^*)/y_c(x))}{\log \log(x/x^*)}. \quad (3.4)$$

In practice, it is difficult to compute the necessary limits analytically, even with the help of Maple. Instead we have investigated the behaviour of the free energy as x approaches x^* along the critical curve, and we estimate that ϕ is between 0.499 and 0.5 for the *ABBB* case. Similarly, it seems clear that γ_{11}^s differs from $\frac{1}{2}$ by no more than one part in 5000 for the *ABBB* case. We have also estimated ϕ for the other periodic copolymers and in every case ϕ seems to differ from $\frac{1}{2}$ by no more than one part in 500. We regard this as excellent evidence that both ϕ and γ_{11}^s are exactly $\frac{1}{2}$, as is the case for the homopolymer and alternating copolymer cases (Whittington 1998b).

4. Discussion

We have used multiple-Markov-chain Monte Carlo methods to investigate a self-avoiding walk model of the adsorption of periodic copolymers of two comonomers. Only one of the two comonomers (monomer A) is attracted to the surface. For each of the periodic sequences investigated we have calculated the mean number of A monomers in the surface, and its variance (i.e. the heat capacity) as a function of the strength of the interaction with the surface and the length of the polymer. We have also calculated metric properties such as the mean distance of the monomers from the surface. We have compared the behaviour of these quantities for different periodic sequences, and also compared with the behaviour of the homopolymer and two-diblock copolymers.

In addition we considered a directed-walk model in two dimensions. For a variety of comonomer sequences this model is exactly solvable and we have identified the location of

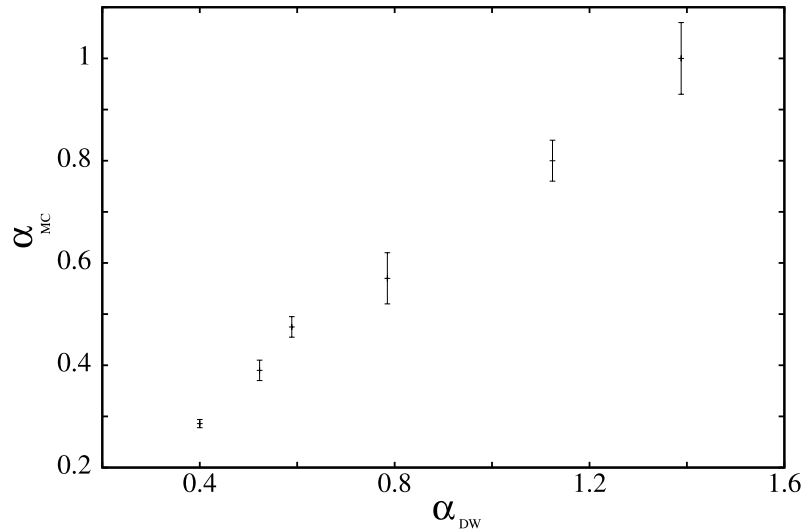


Figure 6. Estimates of the value of $\alpha_c(\chi)$ for the self-avoiding-walk model plotted against the corresponding values for the directed-walk model, for various periodic copolymers.

the adsorption transition for several comonomer sequences. We would expect that there would be a strong positive correlation between the locations of the adsorption transition in the two models and we plot $\alpha_c(\chi)$ for the self-avoiding-walk model against $\alpha_c(\chi)$ for the directed-walk model, for various periodic copolymers, in figure 6. The correlation is very strong, suggesting that calculations on the directed-walk model for other periodic copolymers, together with this graph, would give a good indication of the value of $\alpha_c(\chi)$ for the corresponding self-avoiding-walk model.

Acknowledgments

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Appendix

In this appendix we give details of the calculations for the directed-walk model on the square lattice. The calculations are somewhat different depending on the length of the repeat unit and we consider repeat units of length 3 and 4 separately.

Repeat units of length 3

We consider the *AAB* case in some detail and then write down the corresponding equations for *ABB*. We drop the dependence on χ when this is obvious. Since $h_{j+3}(x, y|AAB) = x^2y^3h_j(x, y|AAB)$ we have

$$\begin{aligned}
 H(x, y|AAB) &= h_0 + h_1 + h_2 + x^2y^3h_0 + x^2y^3h_1 + \dots \\
 &= (h_0 + h_1 + h_2)(1 + x^2y^3 + x^4y^6 + \dots) \\
 &= (h_0 + h_1 + h_2)/(1 - x^2y^3)
 \end{aligned}
 \tag{A.1}$$

provided that $|x^2y^3| < 1$. If we consider the terms contributing to $h_0(x, y|AAB)$ we see that we have a point, a set of loops (i.e. walks which start and end in $y = 0$ but have no intermediate vertices in this line) and configurations which begin with a loop and then continue in some way. If we write l_n for the number of n -edge loops then the generating function $L(y) = \sum_n l_n y^n$ is given by (Whittington 1998b)

$$L(y) = \frac{1 - y - y^2 - y^3 - \sqrt{y^6 + 2y^5 - y^4 - y^2 - 2y + 1}}{2y}. \quad (\text{A.2})$$

However, because of the three-fold periodicity loops with different values of n have different contributions depending on whether n is divisible by 3 or leaves a remainder of 1 or 2 when divided by 3. Define

$$\mathcal{L}_m(y) = \sum_{k \geq 0} l_{m+3k} y^{m+3k} \quad (\text{A.3})$$

for $m = 1, 2$ and 3 (remembering that $l_1 = l_2 = 0$). We can calculate \mathcal{L}_m as follows. Let

$$\omega = -\frac{1}{2} + \frac{1}{2}i\sqrt{3} \quad (\text{A.4})$$

then

$$\mathcal{L}_1(y) = \frac{(1 + \omega)L(\omega^2 y) - L(\omega y) - \omega L(y)}{(1 - \omega)^2} \quad (\text{A.5})$$

$$\mathcal{L}_2(y) = \mathcal{L}_1(y) - \left[\frac{L(\omega y) - L(\omega^2 y)}{\omega(1 - \omega)} \right] \quad (\text{A.6})$$

and

$$\mathcal{L}_3(y) = L(y) - \mathcal{L}_1(y) - \mathcal{L}_2(y). \quad (\text{A.7})$$

We can write $h_0(x, y|AAB)$ as

$$h_0 = 1 + x\mathcal{L}_1 + \mathcal{L}_2 + x\mathcal{L}_3 + x\mathcal{L}_3(H - h_0) + \mathcal{L}_1(H - h_0 - h_1)/y + xy\mathcal{L}_2H. \quad (\text{A.8})$$

In a similar way we obtain the relations

$$h_1 = xy(1 + \mathcal{L}_1 + x\mathcal{L}_2 + x\mathcal{L}_3) + x\mathcal{L}_3(H - h_0 - h_1) + x^2y^2\mathcal{L}_1H + x^2y\mathcal{L}_2(H - h_0) \quad (\text{A.9})$$

and

$$h_2 = xy^2(1 + x\mathcal{L}_1 + x\mathcal{L}_2 + \mathcal{L}_3) + x^2y^2\mathcal{L}_1(H - h_0) + x^2y^3\mathcal{L}_3H + xy\mathcal{L}_2(H - h_0 - h_1). \quad (\text{A.10})$$

On solving these four simultaneous equations for $H(x, y|AAB)$ we see that H can be written as $H = H_1/H_2$, where H_1 and H_2 are both polynomials in x , the coefficients of which are functions of y . H_1 is of degree three and H_2 is of degree four. H is singular when H_1 is singular and when $H_2 = 0$. For small x the boundary of convergence is determined by the behaviour of H_1 and is given by the line $y = \sqrt{2} - 1$. For larger x it is determined by the real positive zero of H_2 (which depends on y) and the boundary of convergence has a singularity at (x^*, y^*) where $x^* = 1.802\dots$ and $y^* = \sqrt{2} - 1$.

The case of ABB can be treated in an exactly similar way. In this case

$$H = \frac{h_0 + h_1 + h_2}{1 - xy^3} \quad (\text{A.11})$$

if $|xy^3| < 1$,

$$h_0 = 1 + \mathcal{L}_1 + \mathcal{L}_2 + x\mathcal{L}_3 + x\mathcal{L}_3(H - h_0) + \mathcal{L}_1(H - h_0 - h_1)/y + xy\mathcal{L}_2H \tag{A.12}$$

$$h_1 = y(1 + \mathcal{L}_1 + x\mathcal{L}_2 + \mathcal{L}_3) + \mathcal{L}_3(H - h_0 - h_1) + xy^2\mathcal{L}_1H + xy\mathcal{L}_2(H - h_0) \tag{A.13}$$

and

$$h_2 = y^2(1 + x\mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3) + xy^3\mathcal{L}_3H + xy^2\mathcal{L}_1(H - h_0) + y\mathcal{L}_2(H - h_0 - h_1). \tag{A.14}$$

The solution is very similar except that the numerator H_1 is a linear function of x and the denominator H_2 is a quadratic function of x . The phase boundary has a singular point at $x^* = 3.078 \dots$, $y^* = \sqrt{2} - 1$.

Repeat units of length 4

In this section we consider the repeat units $AABB$, $AAAB$ and $ABBB$ all of which have repeat units of length 4. In this case we need to count loops separately for n divisible by 4, and having a remainder of 1, 2 or 3 when divided by 4. Define

$$L_m(y) = \sum_{k \geq 0} l_{m+4k} y^{m+4k} \tag{A.15}$$

for $m = 1, \dots, 4$. It is easy to see that

$$L_1(y) = [L(y) - L(-y) - iL(iy) + iL(-iy)]/4 \tag{A.16}$$

$$L_2(y) = [L(y) + L(-y) - iL(iy) - L(-iy)]/4 \tag{A.17}$$

$$L_3(y) = [L(y) - L(-y) + iL(iy) - iL(-iy)]/4 \tag{A.18}$$

and

$$L_4(y) = [L(y) + L(-y) + L(iy) + L(-iy)]/4. \tag{A.19}$$

We can now set up equations relating $H(x, y|AABB)$ and the partial generating functions $h_0(x, y|AABB)$, $h_1(x, y|AABB)$, $h_2(x, y|AABB)$ and $h_3(x, y|AABB)$, giving

$$H = \frac{h_0 + h_1 + h_2 + h_3}{1 - x^2y^4} \tag{A.20}$$

if $|x^2y^4| < 1$,

$$h_0 = 1 + x(L_1 + L_4) + L_2 + L_3 + xyL_3H + xL_4(H - h_0) + L_1(H - h_0 - h_1)/y + L_2(H - h_0 - h_1 - h_2)/xy^2 \tag{A.21}$$

$$h_1 = xy(1 + L_1 + L_2 + xL_3 + xL_4) + x^2y^2L_2H + x^2yL_3(H - h_0) + xL_4(H - h_0 - h_1) + L_1(H - h_0 - h_1 - h_2)/y \tag{A.22}$$

$$h_2 = xy^2(1 + L_1 + L_4 + xL_2 + xL_3) + x^2y^3L_1H + x^2y^2L_2(H - h_0) + xyL_3(H - h_0 - h_1) + L_4(H - h_0 - h_1 - h_2) \tag{A.23}$$

and

$$h_3 = xy^3(1 + L_3 + L_4 + xL_1 + xL_2) + x^2y^4L_4H + x^2y^3L_1(H - h_0) + xy^2L_2(H - h_0 - h_1) + yL_3(H - h_0 - h_1 - h_2). \tag{A.24}$$

Solving these simultaneous equations we can again express H as a ratio of two polynomials in x (whose coefficients are functions of y), the numerator being of degree three and the denominator of degree four. To locate the singular point on the phase boundary we set $y = \sqrt{2} - 1$ and set the denominator equal to zero. The singular point is at $x^* = 2.101 \dots$, $y^* = \sqrt{2} - 1$.

The repeating patterns $AAAB$ and $ABBB$ can be handled in a similar way. For $AAAB$ the equations for the partial generating functions are

$$H = \frac{h_0 + h_1 + h_2 + h_3}{1 - x^3 y^4} \quad (\text{A.25})$$

and

$$h_0 = 1 + L_3 + x(L_1 + L_2 + L_4) + xyL_3H + xL_4(H - h_0) \\ + L_1(H - h_0 - h_1)/y + L_2(H - h_0 - h_1 - h_2)/xy^2 \quad (\text{A.26})$$

$$h_1 = xy + xyL_2 + x^2y(L_1 + L_3 + L_4) + x^2y^2L_2H + x^2yL_3(H - h_0) \\ + xL_4(H - h_0 - h_1) + L_1(H - h_0 - h_1 - h_2)/y \quad (\text{A.27})$$

$$h_2 = x^2y^2(1 + L_1 + xL_2 + xL_3 + xL_4) + x^3y^3L_1H + x^3y^2L_2(H - h_0) \\ + x^2yL_3(H - h_0 - h_1) + xL_4(H - h_0 - h_1 - h_2) \quad (\text{A.28})$$

$$h_3 = x^2y^3(1 + xL_1 + xL_2 + xL_3 + L_4) + x^3y^4L_4H + x^3y^3L_1(H - h_0) \\ + x^2y^2L_2(H - h_0 - h_1) + xyL_3(H - h_0 - h_1 - h_2). \quad (\text{A.29})$$

The singular point is at $x^* = 1.687 \dots$, $y = \sqrt{2} - 1$. For the $ABBB$ pattern we have

$$H = \frac{h_0 + h_1 + h_2 + h_3}{1 - xy^4} \quad (\text{A.30})$$

and

$$h_0 = 1 + L_1 + L_2 + L_3 + xL_4 + xyL_3H + xL_4(H - h_0) \\ + L_1(H - h_0 - h_1)/y + L_2(H - h_0 - h_1 - h_2)/y^2 \quad (\text{A.31})$$

$$h_1 = y + xyL_3 + y(L_1 + L_2 + L_4) + xy^2L_2H + xyL_3(H - h_0) \\ + L_4(H - h_0 - h_1) + L_1(H - h_0 - h_1 - h_2)/y \quad (\text{A.32})$$

$$h_2 = y^2(1 + L_1 + xL_2 + L_3 + L_4) + xy^3L_1H + xy^2L_2(H - h_0) \\ + yL_3(H - h_0 - h_1) + L_4(H - h_0 - h_1 - h_2) \quad (\text{A.33})$$

$$h_3 = y^3(1 + xL_1 + L_2 + L_3 + L_4) + xy^4L_4H + xy^3L_1(H - h_0) \\ + y^2L_2(H - h_0 - h_1) + yL_3(H - h_0 - h_1 - h_2). \quad (\text{A.34})$$

The singularity is at $x^* = 4.00775 \dots$, $y^* = \sqrt{2} - 1$.

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