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A self-avoiding walk model of copolymer adsorption

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Abstract. We discuss a self-avoiding walk model of the adsorption of a copolymer at a plane surface, where the copolymer contains two types of monomers. We concentrate on the case where one type of monomer (A) has a short-range interaction with the surface and the other (B) has no interaction with the surface. We show that the sequence distribution of the comonomers affects the location of the adsorption transition and that for some sequence distributions the adsorption transition occurs at the same place as for the homopolymer poly-A. Moreover, in some circumstances the crossover exponent is identical to that of poly-A.

1. Introduction

Self-avoiding walks on the simple cubic lattice Z^3, starting at the origin and confined to the half-space $z \geqslant 0$, are a useful model of polymer adsorption at a surface (De'Bell and Lookman 1993). If we include an attractive interaction with the surface (for each vertex of the walk in the plane $z = 0$) then Hammersley *et al* (1982) showed that the model has a phase transition corresponding to polymer adsorption. This transition has been studied by many different approaches and De'Bell and Lookman (1993) have given an excellent review of this field. The extension to the adsorption of nonlinear polymers has been investigated by Whittington and Soteros (1991) and Soteros (1992).

The aim of this paper is to present some rigorous results on a lattice model of copolymer adsorption and, to set the scene, we shall first briefly recall some results on adsorption of homopolymers. An n-edge *self-avoiding walk* on the simple cubic lattice Z^3 is a sequence of $n+1$ distinct vertices in Z^3 labelled $i = 0, 1, 2, \ldots, n$ with vertices i and $i+1$ unit distance apart. We add an edge between each such pair of adjacent vertices so that a walk with $n+1$ vertices has n edges. We write (x_i, y_i, z_i) for the coordinates of the ith vertex. If the walks start at the origin we write c_n for the number of distinct n-edge self-avoiding walks, so that $c_1 = 6$, $c_2 = 30$, etc. The *connective constant* (Hammersley 1957) of the lattice Z^3 is

$$\kappa_3 = \lim_{n\to\infty} n^{-1} \log c_n. \tag{1.1}$$

A self-avoiding walk is a *positive walk* if the walk starts at the origin and $z_i \geqslant 0$ for all values of i. We write c_n^+ for the number of n-edge positive walks and it is known (Whittington 1975) that

$$\lim_{n\to\infty} n^{-1} \log c_n^+ = \kappa_3. \tag{1.2}$$

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Let $c_n^+(v)$ be the number of n-edge positive walks with $v+1$ vertices in the plane $z=0$. We say that such a walk *visits* the surface $v+1$ times and has $v+1$ *visits*. Define the partition function

$$Z_n^+(\alpha) = \sum_v c_n^+(v)\, \mathrm{e}^{\alpha v}. \tag{1.3}$$

Hammersley *et al* (1982) have established the existence of the limit

$$\lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha) = \kappa^+(\alpha) \tag{1.4}$$

for all $\alpha < \infty$ and showed that $\kappa^+(\alpha)$ is continuous, convex and non-decreasing. Moreover,

$$\kappa^+(\alpha) = \kappa_3 \tag{1.5}$$

for all $\alpha \leqslant 0$ and

$$\max[\kappa_3, \kappa_2 + \alpha] \leqslant \kappa^+(\alpha) \leqslant \kappa_3 + \alpha \tag{1.6}$$

for $\alpha > 0$, where κ_2 is the connective constant of the square lattice, Z^2. This implies the existence of a singular point α_0, where $0 \leqslant \alpha_0 \leqslant \kappa_3 - \kappa_2$, corresponding to the adsorption transition. (In fact, the inequalities are known to be strict.) The mean fraction of vertices in the surface, $\lim_{n\to\infty}\langle v\rangle/n$, is zero for $\alpha \leqslant \alpha_0$ and non-zero for $\alpha > \alpha_0$, and

$$\lim_{\alpha\to\infty} \lim_{n\to\infty} \langle v\rangle/n = 1. \tag{1.7}$$

Although there are a number of recent papers on the theory of copolymer adsorption (Sommer and Daoud 1995, Sommer *et al* 1996) and some Monte Carlo results (Wang *et al* 1993), we know of no corresponding rigorous results for copolymer adsorption. In the next section we describe a self-avoiding walk model of copolymer adsorption, and report results for the special cases of block copolymers in section 3 and strictly alternating copolymers in section 4.

2. Copolymer adsorption

The idea of the model is to consider self-avoiding walks whose vertices are coloured A or B. The colouring (i.e. the sequence of A's and B's) is fixed throughout the calculation, so that the system is 'quenched'. A and B vertices have different interactions with the surface $z=0$. Consider n-edge self-avoiding walks with vertices labelled $i = 1, 2, \ldots, n$. Each walk has one vertex (say the kth) at the origin, and no vertex has negative z-coordinate. (If $k=0$ the walk is a positive walk.) Each vertex of the walk is coloured A or B and, once this colouring is chosen, it is fixed. If the ith vertex is coloured A we say that it is an A-vertex and set $\chi_i = 1$. If the ith vertex is coloured B we say that it is a B-vertex and set $\chi_i = 0$. For convenience we shall take $\chi_k = 1$ if the kth vertex is fixed at the origin.

Let $c_n^+(v_A, v_B|\chi)$ be the number of such walks with n edges, v_A+1 A-vertices in $z=0$ (or v_A+1 A-visits) and v_B B-vertices in $z=0$ (or v_B B-visits). We append the symbol χ to label the sequence of comonomers and the particular vertex which is fixed at the origin. Define the partition function

$$Z_n^+(\alpha_A, \alpha_B|\chi) = \sum_{v_A, v_B} c_n^+(v_A, v_B|\chi)\, \mathrm{e}^{\alpha_A v_A + \alpha_B v_B}. \tag{2.1}$$

In general, we are interested in the existence of the limit

$$\kappa^+(\alpha_A, \alpha_B|\chi) = \lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha_A, \alpha_B|\chi) \tag{2.2}$$

and in the singularities of $\kappa^+(\alpha_A, \alpha_B|\chi)$ in the (α_A, α_B)-plane. However, in this paper we shall confine our attention to the case $\alpha_A = \alpha$ and $\alpha_B = 0$. In the next two sections we investigate two interesting special cases.

3. Adsorption of block copolymers

In this section we investigate the case of a block copolymer where the sequence of comonomers is a set of two or more long blocks. The essential thing is that the block lengths increase linearly with the total degree of polymerization.

We need some definitions and two preliminary lemmas. We define a *loop* to be a positive walk which satisfies the following conditions:

$$0 = x_0 \leqslant x_i < x_n \qquad \forall i < n \tag{3.1}$$

and

$$0 = z_0 = z_n \leqslant z_i \qquad \forall i. \tag{3.2}$$

The first condition says that the walk should be unfolded in the x-direction, while the second condition says that the two vertices of unit degree should be in the plane $z = 0$. The point is that loops are easier to work with than walks. The first lemma says that we do not lose much by working with loops. Let $l_n(v)$ be the number of loops with n edges having $v + 1$ visits, and define the corresponding partition function

$$L_n(\alpha) = \sum_v l_n(v)\, \mathrm{e}^{\alpha v}. \tag{3.3}$$

Lemma 1 (Hammersley et al 1982). The limit

$$\kappa^L(\alpha) = \lim_{n\to\infty} n^{-1} \log L_n(\alpha) \tag{3.4}$$

exists for all finite values of α and $\kappa^L(\alpha) = \kappa^+(\alpha)$.

The second lemma connects walks interacting with a surface and positive walks interacting with a surface. Let $c_n^i(v)$ be the number of n-edge self-avoiding walks with no vertex having negative z-coordinate, $v + 1$ visits and the ith vertex in $z = 0$. Let $c_n^*(v)$ be the number of walks with n edges, no vertices with negative z-coordinate, $v + 1$ visits and $v \geqslant 0$ (so that at least one vertex must be in the plane $z = 0$). Define the corresponding partition functions

$$Z_n^i(\alpha) = \sum_v c_n^i(v)\, \mathrm{e}^{\alpha v} \tag{3.5}$$

and

$$Z_n^*(\alpha) = \sum_v c_n^*(v)\, \mathrm{e}^{\alpha v}. \tag{3.6}$$

Lemma 2. The limiting free energies

$$\kappa^i(\alpha) = \lim_{n\to\infty} n^{-1} \log Z_n^i(\alpha) \tag{3.7}$$

and

$$\kappa^*(\alpha) = \lim_{n\to\infty} n^{-1} \log Z_n^*(\alpha) \tag{3.8}$$

exist and are equal to $\kappa^+(\alpha)$ for all $i \leqslant n$ and for all finite values of α.

Proof. We obtain an upper bound on $Z_n^i(\alpha)$ by considering two independent positive walks, one of length i and the other of length $n-i$, both having their zeroth vertex at the origin. This gives the inequality

$$c_n^i(v) \leqslant \sum_w c_i^+(w)\, c_{n-i}^+(v-w) \tag{3.9}$$

where the sum over w comes from the total number of visits being distributed over the two independent positive walks. Then, by the convolution theorem,

$$Z_n^i(\alpha) \leqslant Z_i^+(\alpha)\, Z_{n-i}^+(\alpha) \tag{3.10}$$

and

$$\limsup_{n\to\infty} n^{-1} \log Z_n^i(\alpha) \leqslant \kappa^+(\alpha) \tag{3.11}$$

both when i is fixed (or $i = o(n)$) as n goes to infinity, and when $i = \gamma n$ for some fixed $0 < \gamma \leqslant 1$. To obtain a lower bound we consider the subset of these walks which are a concatenation of two loops, one of length i and the other of length $n-i$. We then have

$$c_n^i(v) \geqslant \sum_w l_i(w)\, l_{n-i}(v-w) \tag{3.12}$$

for $v \geqslant 4$. If $v < 4$ we simply take $c_n^i(v) \geqslant 0$. Multiplying by $e^{\alpha v}$ and summing over v gives

$$Z_n^i(\alpha) \geqslant L_i(\alpha)\, L_{n-i}(\alpha) \tag{3.13}$$

so that, using lemma 1, we obtain

$$\liminf_{n\to\infty} n^{-1} \log Z_n^i(\alpha) \geqslant \kappa^+(\alpha). \tag{3.14}$$

The first part of the lemma follows from (3.11) and (3.14). The second part then follows from the inequalities

$$c_n^+(v) \leqslant c_n^*(v) \leqslant (n+1) \max_i c_n^i(v) \tag{3.15}$$

thus completing the proof. □

Suppose we have a polymer with b blocks, the first having n_1 A-vertices, the second having n_2 B-vertices, and so on, so that $\sum_{i\leqslant b} n_i = n+1$, the total number of A-vertices is $n_1 + n_3 + \cdots$ and the total number of B-vertices is $n_2 + n_4 + \cdots$. Suppose that the zeroth vertex is in the plane $z = 0$. Let $a = (n_1 + n_3 + \cdots)/(n+1)$. As a shorthand we shall write $\chi = bl$ where bl is intended to label the general block copolymer described above.

Theorem 1. The limiting free energy $\lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha, 0|bl)$ exists and is equal to $a\kappa^+(\alpha) + (1-a)\kappa_3$.

Proof. To obtain an upper bound on $Z_n^+(\alpha, 0|bl)$ we consider each block to be embedded independently in Z^3 but connected to the previous block by an edge (whose direction can be chosen in at most five ways). The first block is a positive walk, the second can be embedded in at most c_{n_2-1} ways, with a similar expression for all B-blocks. Each A-block can either have no vertices in $z = 0$, in which case it can be embedded in at most c_{n_j-1} ways, or it can have at least one vertex in $z = 0$, in which case it can be embedded in at most $c^*_{n_j-1}(v_j)$ ways for some $v_j \geqslant 0$. This gives the inequality

$$Z_n^+(\alpha, 0|bl) \leqslant 5^b Z^+_{n_1-1}(\alpha) \prod_{p\geqslant 1} c_{n_{2p}-1} \prod_{p\geqslant 1} 2\max[c_{n_{2p+1}-1}, Z^*_{n_{2p+1}-1}(\alpha)]. \tag{3.16}$$

Writing $n_i = \gamma_i n$, taking logarithms, dividing by n and letting n go to infinity with γ_i fixed, gives

$$\limsup_{n\to\infty} n^{-1} \log Z_n^+(\alpha, 0|bl) \leqslant a\kappa^+(\alpha) + (1-a)\kappa_3 \tag{3.17}$$

where we have made use of lemma 2. To obtain a lower bound we consider the subset of the walks where each block is separately a loop, and where the loops are connected by additional edges in the surface $z = 0$. Since the loops can be embedded independently we obtain the inequality

$$Z_n^+(\alpha, 0|bl) \geqslant \prod_{p\geqslant 1} L_{n_{2p-1}-1}(\alpha)\, L_{n_{2p}-1}(0). \tag{3.18}$$

Again, setting $n_i = \gamma_i n$, taking logarithms, dividing by n and letting n go to infinity with γ_i fixed, we obtain

$$\liminf_{n\to\infty} n^{-1} \log Z_n^+(\alpha, 0|bl) \geqslant a\kappa^+(\alpha) + (1-a)\kappa_3. \tag{3.19}$$

The theorem follows from (3.17) and (3.19). □

This theorem implies that the free energy of this type of block copolymer (with $a > 0$) has a singular point at the same location as that of a homopolymer of A monomers, since the free energy is singular when $\kappa^+(\alpha)$ is singular; that is, the homopolymer and the block copolymer will adsorb at the same temperature. In the adsorbed phase, the fraction of monomers in the surface (for the block copolymer) will increase to an asymptotic value of $\lim_{n\to\infty}\langle v_A\rangle/n = a$, so that the loops of B units are expected to extend far into the bulk phase. (The Monte Carlo results of Wang *et al* (1993) also suggest this behaviour.) Since the shape of the free energy near the transition is controlled by the behaviour of $\kappa^+(\alpha)$ near the singular point, the crossover exponent ϕ will also be the same as for the homopolymer.

4. Adsorption of an alternating copolymer

In this section we examine a second special case, that of a strictly alternating copolymer. The model we use is a self-avoiding walk, starting at the origin and having no vertices with $z \leqslant 0$, and with the vertices coloured alternately A and B. We choose n to be odd so that there are equal numbers of A- and B-vertices.

Let $c_n^+(v_A, v_B|alt)$ be the number of n-edge positive walks with an alternating sequence of A- and B-vertices which have $v_A + 1$ A-visits and v_B B-visits. Define the corresponding partition function

$$Z_n^+(\alpha_A, \alpha_B|alt) = \sum_{n_A, n_B} c_n^+(v_A, v_B|alt)\, \mathrm{e}^{\alpha_A v_A + \alpha_B v_B}. \tag{4.1}$$

Lemma 3. The limiting free energy

$$\kappa^+(\alpha_A, \alpha_B|alt) = \lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha_A, \alpha_B|alt) \tag{4.2}$$

exists for all finite values of α_A and α_B and is a convex, continuous function of α_A and α_B.

Proof. The proof is a straightforward application of the methods of Hammersley *et al* (1982). One can show, using a concatenation argument, that the corresponding free energy for loops (with an alternating sequence) exists, and then that loops and walks have the same free energy. We omit the details. □

Lemma 4. The limiting free energy $\kappa^+(\alpha, 0|alt)$ is equal to κ_3 for $\alpha \leqslant 0$ and satisfies the following bounds for $\alpha \geqslant 0$:

$$\max[\kappa_3, \kappa_2 + \alpha/2] \leqslant \kappa^+(\alpha, 0|alt) \leqslant \kappa_3 + \alpha/2. \tag{4.3}$$

Proof. The proof is essentially the same as that given for the case of a homopolymer by Whittington (1975). The only difference comes from noticing that when the walk is entirely in the plane $z = 0$ the number of A-vertices is $(n+1)/2$. Again we omit further details. □

Lemma 4 establishes that there is an adsorption transition (at α_0^a, say) for an alternating copolymer, with $0 \leqslant \alpha_0^a \leqslant 2(\kappa_3 - \kappa_2)$. In the next theorem we establish some improved bounds on its location.

Theorem 2. If we write α_0^a for the location of the adsorption transition for a strictly alternating copolymer then

$$3\alpha_0/2 \leqslant \alpha_0^a \leqslant 3\alpha_0. \tag{4.4}$$

Proof. We call a sequence of vertices in $z = 0$ an *incursion*. If the incursion has an even number of vertices then the number of A-visits and the number of B-visits in the incursion must be the same. If the number of vertices in the incursion is odd and not equal to one, the number of A-visits (v_A^0) and the number of B-visits (v_B^0) in the incursion are related by the inequalities

$$v_A^0/2 \leqslant v_B^0 \leqslant 2v_A^0. \tag{4.5}$$

If the incursion has a single vertex it must be a vertex of degree one, and can be either an A-vertex or a B-vertex. By considering all possible combinations of incursions we then have the inequalities

$$\tfrac{1}{2}v_A \leqslant v_B \leqslant 2v_A + 2. \tag{4.6}$$

The partition function for a homopolymer can be written as

$$Z_n^+(\alpha) = \sum_{v_A, v_B} c_n^+(v_A, v_B|alt)\, \mathrm{e}^{\alpha(v_A+v_B)} \tag{4.7}$$

where the A- and B-vertices in the copolymer are treated as being identical. Using this expression and (4.6) we have, for $\alpha \geqslant 0$,

$$\begin{aligned} Z_n^+(\alpha) &\geqslant \sum_{v_A, v_B} c_n^+(v_A, v_B|alt)\, \mathrm{e}^{\alpha v_A + \alpha v_A/2} \\ &= \sum_{v_A, v_B} c_n^+(v_A, v_B|alt)\, \mathrm{e}^{3\alpha v_A/2} \\ &= Z_n^+(3\alpha/2, 0)|alt) \end{aligned} \tag{4.8}$$

and, hence,

$$\kappa^+(\alpha) \geqslant \kappa^+(3\alpha/2, 0|alt). \tag{4.9}$$

If $\alpha \leqslant \alpha_0$ then $\kappa^+(\alpha) = \kappa_3$ so, by (4.9), $\kappa^+(3\alpha/2, 0|alt) = \kappa_3$. Therefore $\alpha_0^a \geqslant 3\alpha_0/2$. Similarly, using the opposite inequality in (4.6) we have

$$Z_n^+(\alpha) \leqslant \mathrm{e}^{2\alpha} \sum_{v_A, v_B} c_n^+(v_A, v_B|alt)\, \mathrm{e}^{3\alpha v_A} = \mathrm{e}^{2\alpha} Z_n^+(3\alpha, 0|alt). \tag{4.10}$$

If $\alpha > \alpha_0$ then $\kappa^+(\alpha) > \kappa_3$ so $\kappa^+(3\alpha, 0|alt) > \kappa_3$, and hence $\alpha_0^a \leqslant 3\alpha_0$. □

This theorem establishes that a strictly alternating copolymer does not adsorb at the same temperature as a homopolymer and therefore (by theorem 1) does not adsorb at the same temperature as a block copolymer, even if the block copolymer contains equal amounts of the two comonomers.

Regular copolymers with the structure $AB_pAB_p\ldots$ where B_p means a block of p B-vertices, can be analysed using a similar argument. For each case where $p > 1$ we find that the location (α_0^p) of the transition satisfies the inequality $\alpha_0^p \geqslant 2\alpha_0$.

5. Discussion

We have described a simple self-avoiding walk model of the adsorption of a copolymer and have shown that, if one comonomer (A) is attracted to the surface and the other (B) does not interact with the surface, then the location of the adsorption transition for block copolymers with long blocks is the same as for the homopolymer poly-A. In contrast, strictly alternating copolymers have an adsorption transition but not at the same place as the homopolymer.

Apart from the intrinsic interest of copolymer adsorption, these results are interesting because of the current interest in phase transitions in quenched random systems. The theta transition in quenched random polymers has been the subject of considerable recent work (see, for instance, Kantor and Kardar 1994, Grassberger and Hegger 1995) and one can think of copolymer adsorption as a simpler analogue of this problem.

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