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A directed-walk model of copolymer adsorption

S G Whittington
Department of Chemistry, University of Toronto, Toronto, Canada M5S 3H6

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Abstract. We consider a model of copolymer adsorption where the polymer is represented by a directed walk on the square lattice, interacting with a line defining a half-space to which the walk is confined. For the case of an alternating copolymer we determine exactly the location of the adsorption transition, and some associated critical exponents, and compare with the values for the corresponding model for homopolymer adsorption.

1. Introduction

The adsorption of polymers at surfaces is a well-studied problem. The standard model is a self-avoiding walk on a lattice, interacting with a line or plane which represents the surface at which adsorption occurs. This model has been investigated by many different techniques and the area has been reviewed by De'Bell and Lookman (1993). Most work has focused on the adsorption of homopolymers but, more recently, copolymer adsorption has received considerable attention; see, for instance, Whittington (1998) and references quoted therein. The emphasis has been on the location of the adsorption transition, and on the calculation of critical exponents (such as the crossover exponent ϕ which characterizes the behaviour of the free energy close to the transition). For the self-avoiding walk model of polymer adsorption such quantities can be calculated exactly only for a few problems (see, for instance, Duplantier and Saleur 1986, Cardy 1987, Vanderzande *et al* 1991, Batchelor and Yung 1995).

Privman *et al* (1988) introduced an exactly solvable model in which a homopolymer is modelled as a directed walk on a lattice, confined to a half-space and interacting with the line or plane defining the half-space. A particular example which they considered is a walk on the square lattice, confined to the half-space $y \geqslant 0$, and interacting with the line $y = 0$. The walk starts at the origin, is self-avoiding and is not allowed to take any steps in the negative x-direction. The weight of the walk is determined by the number of *steps* of the walk on the line $y = 0$. Privman *et al* (1988) solved this problem using transfer matrix techniques, located the adsorption transition and calculated the values of various critical exponents; see also Forgacs *et al* (1989). For the corresponding model of a directed walk interacting with a defect plane see Carvalho and Privman (1988).

The aim of this paper is to extend this type of model to copolymer adsorption. Specifically we shall describe and solve a directed model of the adsorption of an alternating copolymer, in which only one of the two monomers interacts with the surface. Our methods are quite different from those used by Privman *et al* and we first describe our approach in section 2, and apply it to three models of homopolymer adsorption (one of which was discussed by Privman *et al*). In section 3 we make the extension to copolymer adsorption and compare our results for the homopolymer and alternating copolymer problems.

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2. The homopolymer case

We consider self-avoiding walks on the square lattice Z^2 with two added restrictions:

(i) the walk has no steps in the negative x-direction, and
(ii) the walk starts at the origin, has its last vertex on the line $y = 0$ and has no vertices with negative y-coordinate.

Let $b_n(v)$ be the number of such walks with n edges having $v+1$ vertices on the line $y = 0$. Define

$$Z_n(x) = \sum_v b_n(v)\, x^v \tag{2.1}$$

and

$$G(x, y) = \sum_n Z_n(x)\, y^n = \sum_{v,n} b_n(v)\, x^v y^n. \tag{2.2}$$

It is easy to prove, using concatenation arguments, that the limit

$$\kappa(x) = \lim_{n\to\infty} n^{-1} \log Z_n(x) \tag{2.3}$$

exists for any finite x, and that $\kappa(x)$ is continuous and monotonically non-decreasing and is a convex function of $\log x$. At fixed x, $G(x, y)$ converges provided that $y < \mathrm{e}^{-\kappa(x)}$. The shape of this boundary of convergence determines the free energy $\kappa(x)$ and the location of a singularity on this boundary determines the location of the adsorption phase transition. Consequently, we focus on calculating $G(x, y)$ and determining its boundary of convergence.

We shall use a version of the *partial generating function* method introduced by Temperley (1956). The first step of the walk can be in the positive y-direction or the walk can make $j > 0$ steps in the positive x-direction before first leaving the line $y = 0$. We write $g_0(x, y)$ for the generating function of walks which immediately leave the line, and $g_j(x, y)$ for the generating function of walks which first leave the line after j steps on the line. For instance,

$$g_0(x, y) = 1 + xy^3 + xy^4 + x^2y^4 + \cdots \tag{2.4}$$

where the leading term represents a single point. Clearly

$$G(x, y) = \sum_{j\geqslant 0} g_j(x, y) \tag{2.5}$$

and

$$g_j(x, y) = x^j y^j\, g_0(x, y) \tag{2.6}$$

so that

$$G(x, y) = \frac{g_0(x, y)}{1 - xy} \tag{2.7}$$

provided that $|xy| < 1$.

We next define a *loop* to be a self-avoiding walk with no steps in the negative x-direction, having its first and last vertices on the line $y = 0$ and with the y-coordinate of all other vertices being positive, i.e. a loop has only its first and last vertices on the line $y = 0$. Write l_n for the number of loops with n steps and define the generating function

$$L(y) = \sum_n l_n y^n. \tag{2.8}$$

Lemma 2.1. The generating function for loops is given by

$$L(y) = \frac{1 - y - y^2 - y^3 - \sqrt{y^6 + 2y^5 - y^4 - y^2 - 2y + 1}}{2y}. \tag{2.9}$$

Proof. We first note that $L(y) = y^2[G(1, y) - 1]$ and we write $G(1, y) = S(y)$ for convenience. By inspection

$$S(y) = 1 + y + y^2 + 2y^3 + \cdots \tag{2.10}$$

where the leading term represents a single point. We can write down an equation determining $S(y)$ by noting that the walk has its first step in either the positive x-direction or the positive y-direction. The generating function for walks with their first step in the positive x-direction is $y\,S(y)$. If the first step is in the positive y-direction then the walk is either a loop, with generating function $y^2[S(y) - 1]$, or a loop followed by a walk with its first step in the positive x-direction. Hence

$$S(y) = 1 + y\,S(y) + y^2[S(y) - 1] + y^3 S(y)[S(y) - 1]. \tag{2.11}$$

This immediately gives

$$S(y) = \frac{1 - y - y^2 + y^3 - \sqrt{y^6 + 2y^5 - y^4 - y^2 - 2y + 1}}{2y^3} \tag{2.12}$$

and the lemma follows since $L(y) = y^2[S(y) - 1]$. □

When we expand in powers of y we obtain

$$L(y) = y^3 + y^4 + 2y^5 + 4y^6 + 8y^7 + 16y^8 + 33y^9 + 69y^{10} + \cdots \tag{2.13}$$

and it is easy to check the first few terms by direct enumeration. Lemma 2.1 implies that $l_n \sim n^{-3/2}(1 + \sqrt{2})^n \sim n^{\gamma_{11}-1}(1 + \sqrt{2})^n$ so that the exponent $\gamma_{11} = -\frac{1}{2}$.

We can express $G(x, y)$ in terms of $L(y)$ and we state this in the next lemma.

Lemma 2.2. The generating function $G(x, y)$ is given by

$$G(x, y) = \frac{1 + x\,L(y)}{1 - xy - x^2 y\,L(y)}. \tag{2.14}$$

Proof. We can write down an expression connecting g_0, G and L by noticing that g_0 can be a single point, a loop, or a loop followed by one or more steps in the surface and then possibly a walk which leaves the surface. Hence

$$g_0(x, y) = 1 + x\,L(y) + x\,L(y)[G(x, y) - g_0(x, y)]. \tag{2.15}$$

The lemma follows on solving the simultaneous equations (2.7) and (2.15) for G. □

$G(x, y)$ is singular if $L(y)$ is singular or if the denominator is zero. Hence the boundary of convergence $y = y_c(x)$ is given by the line $y = \sqrt{2} - 1$ for $x \leqslant x^*$ and by the solution of the equation

$$x = \frac{-1 + \sqrt{1 + 4L(y)/y}}{2L(y)} \tag{2.16}$$

for $x \geqslant x^*$. The boundary of convergence has a singular point where these two branches meet, i.e. at

$$(x^*, y^*) = \left(\frac{\sqrt{5} - 1}{2(\sqrt{2} - 1)}, \sqrt{2} - 1\right). \tag{2.17}$$

Translating into the canonical ensemble, the free energy $\kappa(x) = \log(1+\sqrt{2})$ for $x \leqslant x^*$, and $\kappa(x) = -\log y_c(x) > \log(1+\sqrt{2})$ for $x > x^*$. x^* gives the location of the adsorption transition. The crossover exponent describes the behaviour of $\kappa(x)$ as $x \to x^*+$

$$\kappa(x) - \kappa(x^*) \sim (x - x^*)^{1/\phi} \tag{2.18}$$

and an easy calculation shows that $\phi = \frac{1}{2}$. At x^* we expect that

$$Z_n(x^*) \sim n^{\gamma_{11}^s - 1}(\sqrt{2}+1)^n \tag{2.19}$$

so that

$$G(x^*, y) \sim \frac{1}{[1 - y(\sqrt{2}+1)]^{\gamma_{11}^s}} \tag{2.20}$$

as $y \to y^*-$. We can calculate γ_{11}^s by evaluating the limit

$$\gamma_{11}^s = -\lim_{y \to y^*} \frac{\log G(x^*, y)}{\log[1 - y(\sqrt{2}+1)]} = \frac{1}{2}. \tag{2.21}$$

One can treat the case of a walk with its first vertex fixed on the line $y = 0$, but with the last vertex not necessarily in $y = 0$, in a similar way. If we write $c_n(v)$ for the number of n-step self-avoiding walks with the first vertex at the origin, with no steps in the negative x-direction, no vertices with negative y-coordinate, and having $v+1$ vertices with zero y-coordinate, then we can define the generating function

$$C(x, y) = \sum_{v,n} c_n(v)\, x^v y^n. \tag{2.22}$$

A *directed tail* is a self-avoiding walk with no steps in the negative x-direction, which starts at $(0, 0)$ and with all other vertices having positive y-coordinate. Let t_n be the number of directed tails with n steps. Clearly $t_1 = 1$, $t_2 = 2$, $t_3 = 4$, etc. Let

$$T(y) = \sum_{n>0} t_n y^n. \tag{2.23}$$

We shall show that $C(x, y)$ is determined by $G(x, y)$ and $T(y)$. We first show that $T(y)$ can be obtained from $S(y)$.

Lemma 2.3. The generating function for directed tails is given by

$$T(y) = \frac{yS(y)}{1 - y - y^2 S(y)}. \tag{2.24}$$

Proof. We first note that $T(y) = y\,C(1, y)$ and we derive an equation for $C(1, y)$. These walks can be either a tail, or a sequence of loops, or a sequence of loops followed by a step in $y = 0$ and then followed by a tail. Therefore

$$C(1, y) = T(y) + S(y) + y\,S(y)\,T(y) \tag{2.25}$$

so that

$$T(y) = y\,T(y) + y\,S(y) + y^2\,S(y)\,T(y) \tag{2.26}$$

and the lemma follows on solving for $T(y)$. □

This implies that $t_n \sim n^{-1/2}(1+\sqrt{2})^n$ so that the critical exponent $\gamma_1 = \frac{1}{2}$.

Lemma 2.4. The generating function $C(x, y)$ is given by

$$C(x, y) = T(y) + G(x, y)[1 + xy\,T(y)]. \tag{2.27}$$

Proof. The walks counted by $C(x, y)$ are either tails or loops or sequences of loops followed by a step in $y = 0$ and then followed by a tail. Hence

$$C(x, y) = T(y) + G(x, y) + G(x, y)[xy\,T(y)] \tag{2.28}$$

from which the lemma follows immediately. □

Clearly $C(x, y)$ is singular when $T(y)$ is singular or when $G(x, y)$ is singular so the boundary of convergence of C is identical to the boundary of convergence of G. Translating to the canonical ensemble this means that the limiting free energies of walks with one or both ends on the line $y = 0$ are identical. Of course, this could have been proved, using the methods of Hammersley *et al* (1982), without calculating either quantity explicitly. We can calculate the exponent γ_1^s as

$$\gamma_1^s = -\lim_{y \to y^*} \frac{\log C(x^*, y)}{\log[1 - y(\sqrt{2} + 1)]} \tag{2.29}$$

giving $\gamma_1^s = 1$.

The models which we have just described differ from those of Privman *et al* (1988) in that we have counted vertices in the surface rather than steps in the surface. We can obtain results for one of Privman's models in exactly the same way. If we write G' for the generating function (corresponding to G) for this 'steps-in-the-surface' model, the only difference is that G' and L are related by

$$G'(x, y) = \frac{1 + L(y)}{1 - xy - xy\,L(y)}. \tag{2.30}$$

A similar argument then shows that the boundary of convergence of G' has a singular point at

$$(x^*, y^*) = ((2 + \sqrt{2})/2, \sqrt{2} - 1) \tag{2.31}$$

which agrees with the result given in Privman *et al* (1988).

3. Adsorption of an alternating copolymer

One can model the adsorption of an alternating copolymer in a very similar way. The underlying walk model is exactly as described in section 2 but the vertices $i = 0, 2, 4, 6, \ldots$ are coloured A and vertices $i = 1, 3, 5, \ldots$ are coloured B. Only A vertices interact with the surface. If $a_n(v)$ is the number of walks with n steps having $v + 1$ A vertices on the line $y = 0$ and $a_n^j(v)$ is the corresponding number of walks with the first j steps in the positive x-direction, then we define the partial generating functions

$$h_j(x, y) = \sum_{v,n} a_n^j(v)\, x^v y^n \tag{3.1}$$

and the generating function

$$H(x, y) = \sum_j h_j(x, y) = \sum_{v,n} a_n(v)\, x^v y^n. \tag{3.2}$$

By inspection, $h_0(x, y) = 1 + y^3 + 2xy^4 + \cdots$. If we consider $h_j(x, y)$ with j even, we note that when the walk first leaves the surface (after j steps) the last vertex in $y = 0$ is an A vertex. Therefore

$$h_{2p}(x, y) = x^p y^{2p}\, h_0(x, y) \tag{3.3}$$

and

$$\sum_{p\geqslant 0} h_{2p}(x, y) = h_0 + h_2 + \cdots = \frac{h_0(x, y)}{1 - xy^2} \tag{3.4}$$

is $|xy^2| < 1$. Similarly, if j is odd, after $j - 1$ steps in the surface the remainder of the walk starts with an A vertex and has one step in the surface before leaving the surface. Hence

$$h_{2p+1}(x, y) = x^p y^{2p} h_1(x, y) \tag{3.5}$$

and

$$\sum_{p\geqslant 0} h_{2p+1}(x, y) = \frac{h_1(x, y)}{1 - xy^2} \tag{3.6}$$

if $|xy^2| < 1$. Therefore

$$H(x, y) = \frac{h_0(x, y) + h_1(x, y)}{1 - xy^2}. \tag{3.7}$$

If we define

$$L_1(y) = l_1 y + l_3 y^3 + l_5 y^5 + \cdots = (L(y) - L(-y))/2 \tag{3.8}$$

and

$$L_2(y) = l_2 y^2 + l_4 y^4 + l_6 y^6 + \cdots = (L(y) + L(-y))/2 \tag{3.9}$$

then the relation between $H(x, y)$ and $L_1(y)$ and $L_2(y)$ is given by the following lemma.

Lemma 3.1. The generating function for the alternating copolymer case is given by

$$H(x, y) = \frac{1 + L_1 + x\,L_2 - xy\,L_1(1 + L_1 + x\,L_2) + y(1 + x\,L_2)(1 + x\,L_1 + L_2)}{(1 + x\,L_2)(1 - xy^2 - xy\,L_1 - xy^2\,L_2) - xy\,L_1 - x\,L_2 + x^2y^2\,L_1^2 + x^2y\,L_1L_2}. \tag{3.10}$$

Proof. We can write down an equation for $h_0(x, y)$ by noting that such walks are either

(i) a single vertex,
(ii) a loop with an odd number of steps, in which case the final vertex (which is on the line $y = 0$) is a B vertex,
(iii) a loop with an even number of steps, in which case the final vertex (which is on the line $y = 0$) is an A vertex,
(iv) a loop followed by one or more steps on the line $y = 0$, and the walk might then leave $y = 0$.

This gives

$$h_0(x, y) = 1 + L_1(y) + x\,L_2(y) + L_1(y)\,xy\,H(x, y) + x\,L_2(y)[H(x, y) - h_0(x, y)]. \tag{3.11}$$

A similar argument for h_1 gives

$$h_1(x, y) = y + xy\,L_1(y) + y\,L_2(y) + xy\,L_1(y)[H(x, y) - h_0(x, y)] + xy^2\,L_2(y)\,H(x, y). \tag{3.12}$$

The lemma then follows on solving the three simultaneous equations (3.7), (3.11) and (3.12). □

For small x the boundary of convergence of $H(x, y)$ is the line, $y = \sqrt{2} - 1$, while for large x it is given by the solution of the equation

$$(1 + x\,L_2(y))(1 - xy^2 - xy\,L_1(y) - xy^2\,L_2(y)) - xy\,L_1(y) - x\,L_2(y) + x^2y^2\,L_1(y)^2 + x^2y\,L_1(y)\,L_2(y) = 0. \tag{3.13}$$

These two branches meet at the singular point (x^*, y^*) on the boundary of convergence where $x^* = 2.194\,052\,87\ldots$ and $y^* = \sqrt{2} - 1$. Hence the free energy is singular at $x^* = 2.194\,052\,87\ldots$. Again the crossover exponent (ϕ) is $\frac{1}{2}$ and $\gamma^s_{11} = \frac{1}{2}$.

4. Discussion

We have described a directed-walk model of copolymer adsorption in two dimensions. We showed that Temperley's method of partial generating functions (Temperley 1956) can be used to solve both homopolymer and alternating copolymer models. We have determined the locations of the adsorption transitions exactly and have calculated the value of the crossover exponent ϕ. In each case $\phi = \frac{1}{2}$, as one might expect from universality considerations. The location of the adsorption transition for the alternating copolymer $x^*(\text{alt}) = 2.194\,05\ldots$ while that for the homopolymer is $x^*(\text{homo}) = (\sqrt{5} - 1)/[2(\sqrt{2} - 1)] = 1.492\,066\ldots$. Note that $x^*(\text{alt}) < x^*(\text{homo})^2$.

The method which we have used could also be applied to a directed model of other periodic copolymers.

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