EXCHANGE RELATIONS, DYCK PATHS AND COPOLYMER ADSORPTION

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Abstract. We consider a lattice model of fully directed copolymer adsorption equivalent to the enumeration of vertex-coloured Dyck paths. For two infinite families of periodic colourings we are able to solve the model exactly using a type of symmetry we call an *exchange relation*. For one of these families we are able to find an asymptotic expression for the location of the critical adsorption point as a function of the period of the colouring. This expression describes the effect of a regular inhomogeneity in the polymer on the adsorption transition. We have found similar results for other directed path models.

Résumé. Nous considérons un modèle dirigé discret d'adsorption de polymères qui est équivalent à l'énumération de chemins de Dyck colorés aux sommets. Pour deux familles infinies de colorations périodiques, nous pouvons résoudre le modèle de manière exacte en utilisant un type de symétrie que nous appelons 'relation d'échange'. Pour une de ces familles, nous donnons une expression asymptotique pour le point critique d'adsorption comme fonction de la période de la coloration. Cette expression décrit l'effet d'une inhomogénéité régulière du polymère dans la transition d'adsorption. Nous avons obtenu des résultats semblables pour d'autres modèles de chemins dirigés.

1. Introduction

One of the most active areas of research at the interface of combinatorics and statistical mechanics has been the investigation of the physical properties of polymers in solution. The canonical model of this is the self-avoiding walk [14]. A self-avoiding walk is a path on a regular lattice that does not intersect itself. By considering additional properties and restrictions the self-avoiding walk model of polymers can be used to mimic a variety of physical situations. In this paper we consider *polymer adsorption*. In particular, the adsorption of polymers whose component molecules (which are called *monomers*) have different properties; such polymers are called *copolymers*.

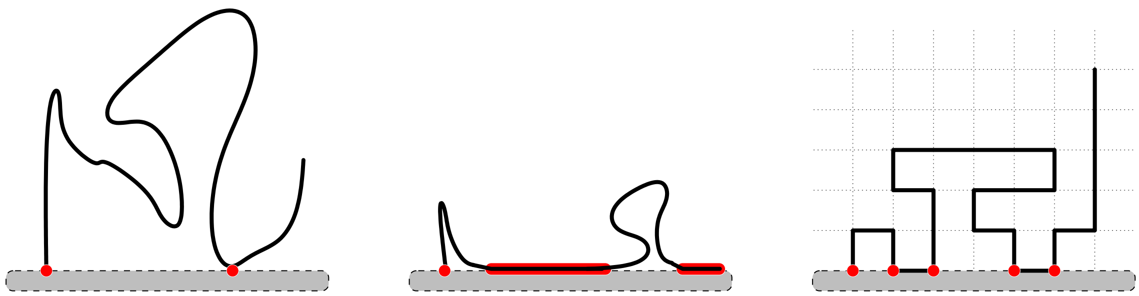


Figure 1. From left-to-right; a polymer in its desorbed or free phase, a polymer in the adsorbed phase, and a self-avoiding walk with vertex-visits highlighted.

1.1. **Polymers and Dyck paths.** Consider a long chain polymer in solution close to the wall of the container (see Figure 1). If there is a weak attractive force between the wall and the polymer, then the fraction of monomers in contact with the wall will be zero as the length of the polymer goes to infinity; in this case we say that the polymer is *desorbed* or *free*. If the attractive force is strong, then the limiting fraction of monomers in contact with the wall will be positive; we say that the polymer is *adsorbed*. Each of these distinct behaviours is called a *phase*, the change between the two phases is called a *phase transition*, and the point at which the transition occurs is called a *critical point*.

A variety of lattice models of polymer adsorption have received much attention in the literature over the last two decades. Perhaps the most well known model of this type is an adsorbing self-avoiding walk in a half-space first defined in [9]. In this model configurations are weighted according to the number of vertices or edges lying in the boundary (which is the X-axis in two dimensions and XY-plane in three dimensions). We refer to such vertices and edges as *vertex-visits* and *edge-visits*.

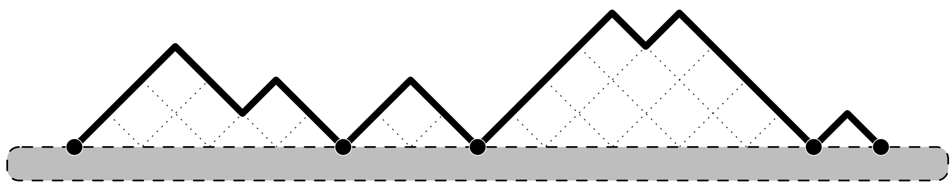


FIGURE 2. An example of a Dyck-path. The horizontal axis can be considered an adsorbing wall.

Underlying the "physical" properties of the adsorbing self-avoiding walk are its combinatorial properties. Unfortunately there are very few rigorous combinatorial results known for this model [14], and attention is instead focused on directed versions of the above problem [10], see also references [3, 5, 7, 15, 17]. The problem of adsorbing directed walks is equivalent to the problem of enumerating Dyck paths [7] according to their half-length and number of visits. The generating function of this model is given by

$$D(z,1) = \frac{1-\sqrt{1-4z}}{2z}, \tag{1}$$

$$D(z,v) = \frac{v}{1-\frac{v}{2}\left(1-\sqrt{1-4z}\right)}, \tag{2}$$

where z is conjugate to the half-length of the path, and v is conjugate to the number of vertex-visits.

This model of Dyck paths can be interpreted as a model of homopolymers since each vertex-visit is given the same weight. In nature one can find many examples of copolymers, such as DNA, whose monomers (potentially) have different physical and chemical properties. To study the effect of such inhomogeneity we consider a variation of the Dyck path model in which different vertex-visits may have different weights. In particular we consider a *fixed* colouring of the even vertices[1] of Dyck paths, and one wishes to enumerate the number of vertex-visits of each different colour. See Figure 3.

[1]If the vertices along the path are labeled sequentially from the left by $0, 1, 2, 3, \ldots$, then those with even labels are called "even vertices". The remaining vertices are "odd" and cannot visit the adsorbing diagonal — hence we can safely ignore their colour.

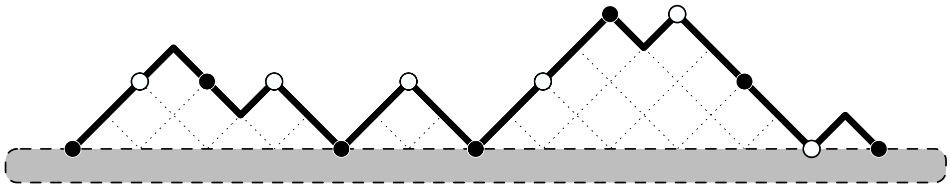


FIGURE 3. An example of a vertex-coloured Dyck-path. Every even vertex is coloured $A, B, A, B \ldots$. There are 4 A-visits and 1 B-visit.

1.2. **From generating functions to phase transitions.** There is a close relationship between the statistical mechanics and combinatorics in this model, and we describe its "physical" behaviour from the behaviour of the generating function. If the numerical value of v in $D(z, v)$ is increased, then paths with larger numbers of visits will contribute more to the generating function and, since they are in some sense "more important", determine the thermodynamic phase of the model — whether or not it is adsorbed or desorbed. Consider now the following:

$$D(z,v) = \sum_{n\geq 0} \left(\sum_{m\geq 1} c_{n,m} v^m \right) z^n = \sum_{n\geq 0} Z_n(v) z^n \tag{3}$$

where $Z_n(v)$ is the *partition function* of the model and is related to the radius of convergence of the model by

$$\log z_c(v) = \left(\lim_{n\to\infty} \frac{1}{n} \log Z_n(v) \right)^{-1} = -\mathcal{F}(v), \tag{4}$$

where $z_c(v)$ is the radius of convergence, and $\mathcal{F}(v)$ is the *limiting canonical free-energy density*[2] [11]. This relation between $z_c(v)$ and $\mathcal{F}(v)$ explicitly connects the combinatorics and thermodynamics of the model. The change of phase, from desorbed to adsorbed, is signalled by a non-analytic point in $\mathcal{F}(v)$ and hence also $z_c(v)$. Describing the location of this transition for vertex-coloured Dyck paths is one of the major goals of this paper.

From equation (2) one sees that:

$$z_c(v) = \begin{cases} 1/4, & v \leq 2 \\ (v-1)/v^2, & v > 2 \end{cases}, \tag{5}$$

from which the limiting free energy, $\mathcal{F}(v)$, can be explicitly computed:

$$\mathcal{F}(v) = -\log z_c(v) = \begin{cases} 2\log 2, & v \leq 2 \\ 2\log v - \log(v-1), & v > 2. \end{cases} \tag{6}$$

Observe that for $v > 0$, the free energy is a continuous function of v, but that $\mathcal{F}(v)$ is non-analytic at $v = v_c = 2$. The non-analytic point is interpreted a phase transition in this model; we refer to this value of v as the *critical adsorption point*, and denote it by v_c. Since the first derivative of $\mathcal{F}(v)$ to $\log v$ is also continuous, we call this phase transition a *continuous transition*. A phase transition is a *first order transition* if the first derivative of $\mathcal{F}(v)$ is discontinuous.

[2] We note that the derivative of the free energy to $\log(v)$ is the limiting density of visits, *i.e.* the limiting average number of visits per length. The second derivative of the limiting free energy to $\log(v)$ is the *specific heat* which is a measure of the fluctuations in the density of visits.

A singularity analysis of this generating function, allows one to compute the mean number of visits as a function of the length of the path:

$$\text{mean number of visits}(n) \sim \begin{cases} \frac{2}{2-v} & + o(1), & v < 2 \\ \sqrt{\pi}\,\sqrt{n} & + O(1), & v = v_c = 2 \\ \frac{v-2}{v-1}\, n & + O(\sqrt{n}), & v > 2 \end{cases} \tag{7}$$

This shows that that in the $n \to \infty$ limit, the density of visits is 0 in the desorbed phase and *at* the critical point, and is positive in the adsorbed phase. This can also be seen by an analysis of the free energy (see [11] for details). If $v < 2$, then all the derivatives of the free energy, with respect to v, are zero; the density of visits is zero, and the free energy is determined entirely by a class of Dyck paths which visits the adsorbing line with zero density. Whereas when $v > 2$, the first derivative of the free energy is positive and so the free energy is dominated by a class of Dyck paths which has a non-zero density of visits. Further analysis shows that the second derivative of $\mathcal{F}(v)$ with respect to $\log(v)$ (*i.e.* the specific heat) is:

$$\frac{\mathrm{d}^2\mathcal{F}(v)}{\mathrm{d}(\log v)^2} = \begin{cases} 0, & v \le 2; \\ \frac{v}{(v-1)^2}, & v > 2. \end{cases} \tag{8}$$

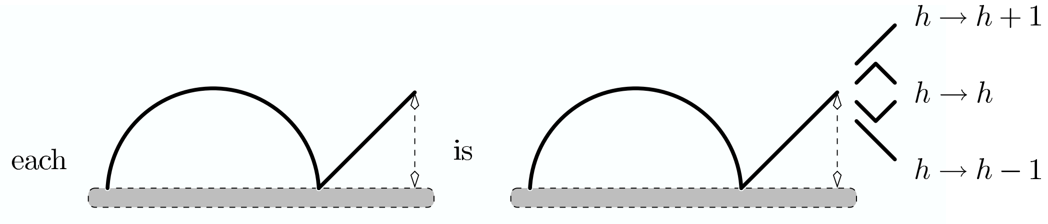
This is a measure of the fluctuations in the number of visits and it is maximised at $v = v_c = 2$. We expect this to be the case, since when the model is away from the critical point, typical configurations have roughly the same number of visits, however, when the model is close to the critical point and there is a change in the behaviour of the model, we expect that typical configurations will have widely different numbers of visits.

In the next section we describe two commonly used techniques for computing generating functions of lattice models and demonstrate why they are not practical for the enumeration of vertex-coloured Dyck paths. We introduce a type of symmetry that we call an exchange relation that allows us to find generating functions for two infinite families of vertex-coloured Dyck paths. These generating functions all have a similar form and for one of the two families we are able to use it to find an asymptotic expression for the location of the adsorption critical point. In Section 3 we find similar results for other directed models of copolymers.

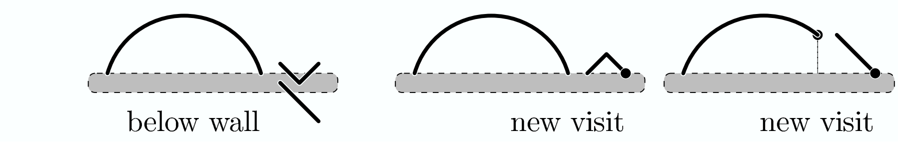
2. Exchange relations

Perhaps the two most successful techniques for the enumeration of lattice animals are the Temperley method and recursive constructions that are sometimes called "wasp-waist" factorisations. Both of these methods are readily applied to the enumeration of Dyck paths according to their length and number of visits. We shall quickly review these standard techniques in order to demonstrate that they are not well suited to the problem of vertex-coloured Dyck paths, and that one must, in fact, resort to other methods.

The Temperley method is based around the idea that many lattice-animals can be constructed column-by-column [2, 16]. One can apply this method to Dyck paths, by constructing left-factors of Dyck paths two steps at a time, while keeping track of the number of visits and the height of the last vertex:



but the following cases must be treated separately.

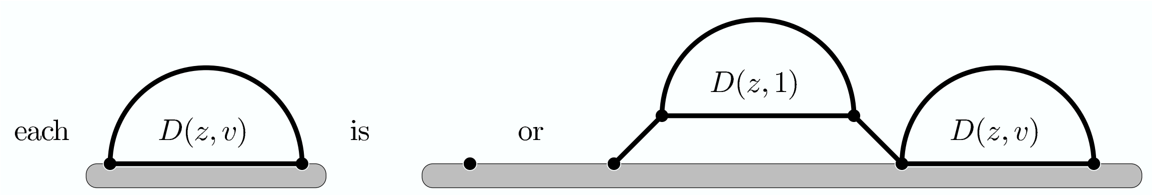


Let us write $D(s; z, v)$ as the generating function of left-factors of Dyck paths, where s, z and v are respectively conjugate to the height of the final vertex, the half-length of the path, and the number of visits. The above construction translates directly (see for example [2]) into a linear functional equation:

$$\begin{aligned} D(s; z, v) = v + {}& z(s + 2 + 1/s)D(s; z, v) + \\ & z(v - 2 - 1/s)D(0; z, v) + z(v - 1)\left(\frac{\partial D}{\partial s}\right)\Big|_{s=0}, \end{aligned} \tag{9}$$

This can then be solved (see [1, 2], for example) to give $D(0; z, v)$ which is the generating function of Dyck paths given above.

The wasp-waist factorisation, on the other hand, consists of cutting a Dyck path at an especially thin point into two smaller Dyck paths. More specifically



This factorisation shows that every adsorbing Dyck path is either a single visit, or has a prefactor which is a Dyck path with exactly two visits (its first and last vertices), and then followed by an arbitrary adsorbing Dyck path (which may consist of a single vertex). This gives:

$$D(z, v) = v + zvD(z, 1)D(z, v), \tag{10}$$

which can be solved to recover the Dyck path generating function.

Consider now the enumeration of vertex-coloured Dyck paths for some fixed periodic colouring with period p:

- To apply the Temperley method one must consider the colour of the vertex being added and this leads to a system of p equations involving p generating functions — one for each different half-length modulo p. These equations can be reduced to a single functional equation which may be interpreted as appending $2p$ edges to the end of a left-factor. As p increases, the equation contains higher and higher derivative order terms which make solving it increasingly difficult.

- The wasp-waist factorisation given above does not preserve the colouring and one must take into account the colour of the first and second visit-vertices in the factorisation. This leads to a system of p simultaneous equations in p generating functions — each one counts Dyck-paths whose vertices are coloured starting from a different point in the period.

For small periods (say up to 4 or 5) these equations may be solved by hand or computer (see [11, 17]), but beyond this the calculations quickly use up available human perseverance, as well as computer time and memory.

Though we have not investigated *all* the techniques that may been used to enumerate Dyck paths, we expect that similar problems will be encountered — though it would be interesting to see this problem tackled using other techniques in the literature.

In this paper we have succeeded in solving this problem for two infinite families of periodic colourings [12, 13]. The key to their solution is a type of symmetry that we call an *exchange relation.* This relation establishes a symmetry between $D(z, v)$ and $D(z, 1)$ with respect to $1 \longleftrightarrow v$. While this equation cannot be used to solve for $D(z, v)$ it does have the advantage that it also holds for certain vertex-colourings and enables us to find generating functions and asymptotic expressions for the adsorption critical point.

2.1. **Exchange relation in Adsorbing Dyck paths.** Let P be a non-empty and unweighted Dyck path. Start at the left-most vertex in P at the origin, and weight visits in P by v in sequence. After a certain arbitrary number of visits have been weighted, but not all, the situation is as depicted in the top half of Figure 2.1. This configuration factors into two halves: the left part is a weighted Dyck path, which may be a single vertex and so is enumerated by $D(z, v)$. The second half is an unweighted Dyck path, which may not be a single vertex (since the last vertex of P is not weighted), and so is enumerated by $\big(D(z, 1) - 1\big)$.

If the next visit in the path is now weighted then the lower half of Figure 2.1 is obtained. Again the walk factors into two halves — one weighted and one unweighted. The weighted part of the walk is longer than before and so cannot be a single vertex, and consequently is counted by $\big(D(z, v) - v\big)$. The unweighted half is shorter and may now possibly be a single vertex, and is counted by $D(z, 1)$. The statistics of this new configuration are the same as the starting configuration, except that there is exactly one more weighted visit, and so exactly one extra factor of v.

This construction creates a correspondence between pairs of weighted and unweighted Dyck paths, and applying it to all possible pairs of weighted and unweighted paths gives the following functional relation involving $D(z, v)$ and $D(z, 1)$:

$$vD(z, v)\Big(D(z, 1) - 1\Big) = \Big(D(z, v) - v\Big)D(z, 1) \tag{11}$$

This relation between $D(z, v)$ and $D(z, 1)$ exhibits an exchange symmetry which exchanges $v \longleftrightarrow 1$ between the generating functions of absorbing and free Dyck paths; notice the role reversal of the generating functions on both sides of the equation.

Solving this equation for $D(z, v)$ gives

$$D(z, v) = \frac{vD(z, 1)}{v + (1 - v)D(z, 1)}. \tag{12}$$

This solution is not identical to the relation in equation (10), but using the fact that $D(z, 1) = 1 + zD(z, 1)^2$, shows them to be equivalent. Further, it is not possible to solve for $D(z, v)$ from equation (11); a solution for $D(z, 1)$ is needed as well and cannot be obtained by setting $v = 1$ in the above. This indicates that the exchange relation is not equivalent to

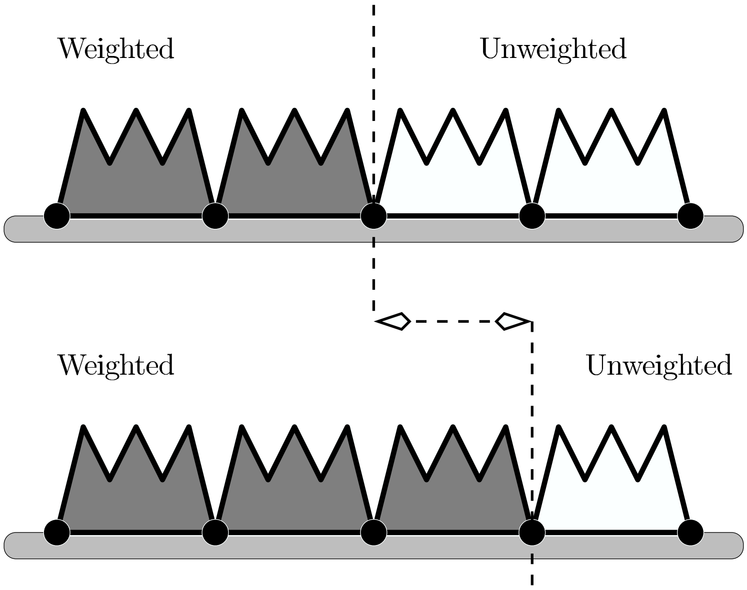


FIGURE 4. This is a schematic representation of a partially weighted Dyck path. Starting from the left and working towards the right, each visit is weighted v. At some point *before* the end of the path is reached the situation is as represented in the top half of the illustration. Proceeding on to the next visit gives the lower illustration. The correspondence between these two pictures gives equation (11).

equations (10) and (9), and at the same time, it does not appear to be particularly useful since $D(z,1)$ must be computed by some other means.

On the other hand, it establishes a relation which must be satisfied by the generating functions of certain vertex-coloured Dyck path models, where it proves to be very useful. It also appears to hold, in very similar forms, for other models (see Section 3).

2.2. **Generating Functions of paths coloured by $\{AB^{p-1}\}^*A$ and $\{BA^{p-1}\}^*B$.** The exchange relation in equation (11) can be applied to certain models of vertex-coloured Dyck paths. We consider a model in which the vertices of the Dyck path are coloured with two colours A and B, and A-visits are weighted by v_a and B-visits by v_b. In this and subsequent sections we shall put $v_b = 1$ and $v_a = a$.

As described above, applying the Temperley or factorisation methods to this model is not practical excepting for very short periodic colourings (and we believe that other techniques in the literature will encounter similar difficulties). The exchange relation we have defined above does not provide us with results for general colourings, however it proves extremely useful for two families of periodic colourings; in particular it enables us to find solutions in the case of walks coloured by the periodic sequence $\{AB^{p-1}\}^*A$ and the "complementary" colouring $\{BA^{p-1}\}^*B$ (for a given fixed period p). Other colourings seem not to be amenable to the treatment here.

We proceed in much the same manner as above. Consider a weighted Dyck path (all visits are weighted v), and start colouring its even vertices by the sequence $\chi = \{AB^{p-1}\}^*A$. Each A-vertex which is also a visit is given a weight a, while B vertices are ignored. Let us stop colouring the Dyck path at some A-visit, leaving the remaining part of the path uncoloured. This configuration factors into two Dyck paths, one part is coloured and has half-length equal to 0 (mod p), while the other is uncoloured.

If the path is then labelled up to and including the next A-visit, then the half-length of the coloured part of the path is increased by a multiple of p again, while the unweighted part of the path decreases in half-length by the same amount — and again the configuration factors into a coloured path of half-length 0 (mod p) and an uncoloured path. This construction forms the exchange relation — and to underline this symmetry we require that both the coloured and uncoloured parts of the walk have half-length 0 (mod p).

Let us now define the following generating functions, in which z is conjugate to the half-length, v is conjugate to the total number of visits (coloured or otherwise) and a is conjugate to the number of A-visits:

Definition 1. *Fix p, the period of the colouring. Then:*

- *$U(z,v|p)$ is the generating function of all* uncoloured *Dyck paths of half-length 0 (mod p), with visits generated by v;*
- *$L(z,v,a|p)$ is the generating function of all Dyck paths* coloured *or* labelled *by $\chi = \{AB^{p-1}\}^*A$, with half-length 0 (mod p), with visits generated by v and A-visits generated by a.*

The exchange relation obtained in the construction above can be written in terms of $U(z,v|p)$ and $L(z,v,a|p)$:

Theorem 1. *For any fixed p, the generating functions U and L satisfy*

$$aL(z,v,a|p)\big(U(z,v|p)-v\big) = \big(L(z,v,a|p)-va\big)U(z,v|p), \tag{13}$$

and therefore

$$L(z,v,a|p) = \frac{vaU(z,v|p)}{va+(1-a)U(z,v|p)}. \tag{14}$$

□

Notice that $L(z,v,a|p)$ is not the generating function of all coloured Dyck paths of arbitrary half-length; only those paths of half-length 0 (mod p) are counted. This is somewhat disappointing from the combinatorial point of view, but it is nevertheless enough to describe the physics of the model. In particular the radius of convergence $z_c(v,a)$ of $L(z,v,a|p)$ is equal to the radius of convergence of the full generating function. Fortunately we are able to find the full generating function, but first we require two more definitions.

Definition 2. *Let $F(z,v,a|p)$ be the full generating function of Dyck paths coloured by $\chi = \{AB^{p-1}\}^*A$. Further, let $\overline{F}(z,v|p) = \lim_{a\to 0}(F(z,v,a|p)/a)$, which is the generating function of these coloured Dyck paths, such that all but the first A-visit are forbidden.*

Notice that $L(z,v,a|p)$ is obtained by taking every p-th coefficient of $F(z,v,a|p)$, and that $\overline{F}(z,v|p)$ is also the coefficient of a^1 in $F(z,v,a|p)$.

Theorem 2. *The generating functions $F(z,v,a|p)$ and $\overline{F}(z,v|p)$ are related by*

$$F(z,v,a|p) = L(z,v,a|p)\overline{F}(z,v|p)/v. \tag{15}$$

Consequently

$$F(z,v,a|p) = L(z,v,a|p)D(z,v)/U(z,1|p) = \frac{vaD(z,v)}{va+(1-a)U(z,v|p)} \tag{16}$$

Proof. Any Dyck path coloured by $\{AB^{p-1}\}^*A$ may be uniquely factored into a Dyck path of length 0 (mod p) and a Dyck path with no subsequent A-visits, by cutting it at the rightmost A-visit. This proves the first equality.

Setting $a = 1$ gives $\overline{F}(z, v|p) = F(z, v, 1|p)/L(z, v, 1|p)$, and back-substitution gives the main result once we notice that $L(z, v, 1|p) = U(z, v|p)$ and $F(z, v, 1|p) = D(z, v)$. □

By setting $v = 1$ in the above, $F(z, 1, a|p)$ is obtained. This is the generating function of Dyck paths coloured by $\chi = \{AB^{p-1}\}^*A$ where A-visits are counted by a. On the other hand, if we let $a \to 1/a$ and $v = a$ instead, then $F(z, a, 1/a|p)$ counts Dyck paths coloured with the "complementary" colouring $\chi = \{BA^{p-1}\}^*B$ with a conjugate to the number of A-visits. This gives the following corollary to Theorem 2:

Corollary 3. *The generating function of a Dyck path model of adsorbing copolymers coloured by $\{AB^{p-1}\}^*A$ is given by $F(z, 1, a|p)$, and of adsorbing copolymers coloured by $\{BA^{p-1}\}^*B$ is given by $F(z, a, 1/a|p)$, where a is conjugate to the number of A-visits.*

2.3. **The Location of the Adsorption Critical Point.** Let us first consider the homopolymer case. The generating function of adsorbing Dyck paths is given by equation (2); and its radius of convergence $z_c(w)$ is given in equation (5). $z_c(w)$ is non-analytic at $w_c = 2$. This point is the intersection of a line of branch points in $D(z, w)$ along $z = 1/4$ and a line of simple poles along $z = (w-1)/w^2$. This may also be interpreted as the location of the adsorption transition; one can show that the density of average visit vertices in walks of half-length n is $O(1)$ below this point, $O(\sqrt{n})$ at this point and and $O(n)$ above this point.

Let us now consider Dyck paths coloured by $\chi = \{AB^{p-1}\}^*A$. The generating function is given by

$$F(z, 1, a|p) = \frac{aD(z, 1)}{a + (1-a)U(z, 1|p)} \tag{17}$$

where $U(z, v|p)$ the generating function of Dyck paths of length 0 (mod p), and can be explicitly expressed as

$$U(z, v|p) = \frac{1}{p}\sum_{j=0}^{p-1} D(\beta^j z, v), \qquad \text{where } \beta = e^{2\pi i/p}. \tag{18}$$

This expression simplifies to give

$$U(z, 1|p) = \frac{-1}{p}\sum_{j=0}^{p-1} \frac{\sqrt{1-4z\beta^j}}{2z\beta^j}. \tag{19}$$

One can show that the radius of convergence of $F(z, 1, a|p)$ is very similar to that of $D(z, v)$ — for small a it is given by $z = 1/4$, while for larger a it is determined by the simple pole encountered when the denominator in equation (17) vanishes. These singularities cross at the adsorption critical point, so that the critical value of a is given by the solution of

$$\frac{a_c}{a_c - 1} = U(1/4, 1|p), \qquad \text{or} \qquad a_c = \frac{U(1/4, 1|p)}{U(1/4, 1|p) - 1}. \tag{20}$$

For short periods (small values of p) it is possible to evaluate $U(1/4, 1|p)$, and hence a_c, exactly (this was done for alternating coloured paths in reference [11]). For larger values of p this is no longer the case, and instead we explore the asymptotic behaviour of a_c as a function of p.

In order to find an asymptotic form for $U(1/4, 1|p)$ and a_c, we find a uniform asymptotic estimate of the summands of $U(z, 1|p)$ and then sum them together. The starting point for this is to note that

$$D(z,1) = 1+\sum_{n\geq 1}\binom{2n}{n}\frac{z^n}{n+1}, \qquad \text{and so} \tag{21}$$

$$U(1/4,1|p) = 1+\sum_{n\geq 1}\binom{2np}{np}\frac{4^{-np}}{np+1}. \tag{22}$$

The uniform asymptotics of the summands of $U(1/4,1|p)$ may be found from the asymptotics of the coefficients of $D(z,1)$, and may be calculated by evaluating the contour integral $\frac{1}{2\pi i}\oint[D(z,1)/z^{n+1}]dz$, with a contour which circles the origin (see [6] for example). This gives the following lemma:

Lemma 1. *There exists $M \in [0,\infty)$ such that for sufficiently large n,*

$$\left|\frac{1}{n+1}\binom{2n}{n}\frac{\sqrt{\pi n^3}}{4^n} - \left(1-\frac{9}{8n}+\frac{145}{128n^2}\right)\right| < \frac{M}{n^3}. \tag{23}$$

By replacing the summands in the above expression for $U(1/4,1|p)$ with their uniform asymptotic expansions given by the above lemma, we are able to obtain the asymptotic behaviour of $U(1/4,1|p)$ for large p, and this in turn gives an asymptotic expression for the location of a_c, the adsorption critical point. This expression gives an idea of how the adsorption transition is affected by a regular inhomogeneity in the polymer.

Theorem 4. *The function $U(1/4,1|p)$ is (as a function of p) asymptotic to:*

$$U(1/4,1|p) \sim 1+\frac{1}{\sqrt{p^3\pi}}\left(\zeta(3/2)-\frac{9\zeta(5/2)}{8p}+\frac{145\zeta(7/2)}{128p^2}+O(1/p^3)\right). \tag{24}$$

Thus the adsorption critical point $a_c(p) = \frac{U(1/4,1|p)}{U(1/4,1|p)-1}$ is asymptotic to

(25)

$$a_c(p) \sim \frac{\sqrt{\pi}}{\zeta(3/2)}p^{3/2}+\frac{9\sqrt{\pi}\zeta(5/2)}{8\zeta(3/2)^2}p^{1/2}+1+\frac{\sqrt{\pi}\left(162\zeta(5/2)^2-145\zeta(7/2)\zeta(3/2)\right)}{128\zeta(3/2)^3}p^{-1/2}+O(p^{-3/2})$$

Unfortunately when we attempt to apply the above ideas to the analysis of complementary colouring, $\chi = \{BA^{p-1}\}^*B$, we encounter some problems. We are able to show that the radius of convergence has the same general form, but we are unable to find a similar asymptotic expression for the location of critical point.

We have already shown that the generating function for this model is given by $F(z,a,1/a|p)$, which is given more explicitly by:

$$F(z,a,1/a|p) = \frac{D(z,a)}{1+(1-1/a)U(z,a|p)}, \tag{26}$$

with $D(z,a)$ and $U(z,a|p)$ defined as above. The location of the critical point is given (as was the case above) by the zero of denominator when $z=1/4$:

$$a+(a-1)U(1/4,a|p) = 0. \tag{27}$$

We have been unable to find an asymptotic expression for the solution to this non-linear equation.

Since we were unable to proceed analytically, we hypothesised a scaling form using numerical data. Using the CLN[3] library for c++, we computed $a_c(p)$ to 300 significant digits

[3] The CLN package provides, amongst many other things, arbitrary precision complex number arithmetic functions for c++. At the time of writing, it was available from `http://clisp.cons.org/~haible/packages-cln.html`

for p from 10 to 400, and then to 1000 digits for p from 1000 to 1100. Plotting this data and using the techniques described in [4, 8], we reached the following hypothesis for the asymptotic behaviour of $a_c(p)$:

$$a_c(p) \sim 2 + 1/p + c_1/p^{3/2} + c_2/p^2 + c_3/p^{5/2} + O(p^{-3}) \tag{28}$$

where

$$\begin{aligned} c_1 &= 0.41198(2) \\ c_2 &= 0.792(2) \\ c_3 &= 0.83(2) \end{aligned}$$

The estimates of the constant in the p^{-1} term rapidly approach 1 as p is increases, and it appears not to differ from 1 by more than 10^{-4}. In these circumstances, it is not unreasonable to hypothesise that it is equal to 1. That the first coefficient in the asymptotic expansion of $a_c(p)$ is so close to 1 (if not exactly equal to 1) is quite suggestive that this leading asymptotic behaviour could perhaps be solved exactly. We also note here that a similar numerical analysis on $F(z, a, 1|p)$ agrees with the results of Theorem 4.

Period	$\{AB^{p-1}\}^*A$		$\{BA^{p-1}\}^*B$	
p	actual	asymptotic	actual	asymptotic
1	2	1.965	No transition	
2	$2+\sqrt{2}$	3.399	$2+\sqrt{2}$	5.03
3	5.152712190	5.144	2.631303464	2.99
4	7.165355763	7.159	2.403090211	2.55
5	9.419630950	9.415	2.295052084	2.38
10	23.66348531	23.6618	2.124630022	2.1236
20	63.41544315	63.4148	2.057152564	2.0571
30	114.6142480	114.614	2.036915291	2.0369
40	175.1068722	175.107	2.027215547	2.0272
50	243.6370630	243.637	2.021533738	2.0215
1000	21468.92712	21468.927	2.001013847	2.00101
∞	No transition		2	2

TABLE 1. A table of the critical adsorption points for vertex-coloured Dyck paths. For $\chi = \{AB^{p-1}\}^*A$ we have computed $a_c(p)$ using equation (20), while for the complementary colouring, $\chi = \{BA^{p-1}\}^*B$, we have computed $a_c(p)$ by solving equation (27) numerically using the CLN high-precision numerics library for c++. For the sake of comparison, we have also included estimates using the asymptotic expressions in Theorem 4 and equation (28).

3. Extensions to Motzkin paths and bargraphs

A natural extension of this work is to search for similar relations in other coloured path models. We have found such relations in a number of different models based on Motzkin paths and bargraphs (see Figure 5). Motzkin paths are a generalisation of Dyck paths, in which the path is also allowed to step east. Bargraphs are partially directed self-avoiding walks that lie on or above the horizontal axis. In these two models both edges and vertices may lie on the axis, and so one may also consider edge-coloured paths as well; i.e. in which one considers the number of edge-visits rather than vertex-visits.

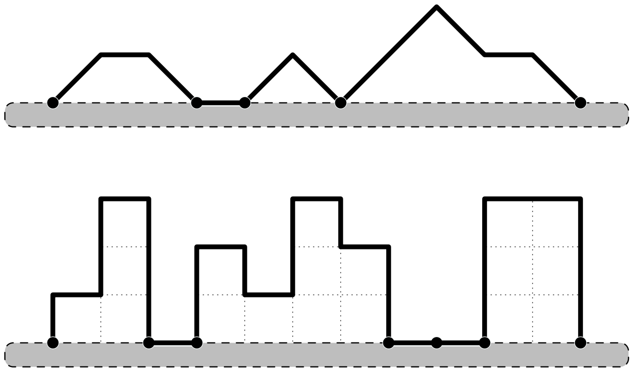


FIGURE 5. (top): a Motzkin path with 5 vertex-visits and 1 edge-visit. (bottom): a bargraph with 7 vertex-visits and 3 edge-visits.

In the following theorems we have fixed the colouring $\chi = \{AB^{p-1}\}^*A$, and all the generating functions are for paths of length 0 (mod p). We have found the following exchange relations:

Vertex-coloured Motzkin paths behave extremely similarly to vertex-coloured Dyck paths:

Theorem 5. *The generating function of vertex-coloured Motzkin paths, $M(z,v,a|p)$, satisfies the following exchange relation:*

$$\alpha M(z,v,a|p)(M(z,v,1|p) - v) = (M(z,v,a|p) - va)M(z,v,1|p). \tag{29}$$

We find that the critical point is given by

$$a_c(p) = \frac{2\sqrt{3\pi}}{9\zeta(3/2)}p^{3/2} + \frac{13\sqrt{3\pi}\zeta(5/2)}{24\zeta(3/2)^2}p^{1/2} + 1 + O(p^{-1/2}) \tag{30}$$

On the other hand, the edge-colouring problem is more complicated:

Theorem 6. *The generating function of edge-coloured Motzkin paths, $M(z,w,\alpha|p)$, satisfies the the exchange relation*

$$\begin{aligned}\alpha M(z,w,\alpha|p)H(z,w,1|p) - &\Big(M(z,w,\alpha|p) - M(z,w,0|p)\Big) \\ &= \Big(M(z,w,\alpha|p) - M(z,w,0|p)\Big)H(z,w,1|p)\end{aligned} \tag{31}$$

where α is conjugate to the number of A-edge-visits and $H(z,w,1|p)$ is the generating function of Motzkin paths that end in a horizontal step.

The asymptotic position of the adsorption critical point is given by:

$$\alpha_c(p) \sim \frac{2\sqrt{3\pi}}{3\zeta(3/2)}p^{3/2} + \frac{5\zeta(5/2)\sqrt{3\pi}}{8\zeta(3/2)^2}p^{1/2} + 1 + O(p^{-1/2}). \tag{32}$$

Notice that $\lim_{p\to\infty} \alpha_c(p)/a_c(p) = 3$. We do not, as yet, have a simple explanation of why this is so.

The edge-coloured bargraph and Motzkin path models behave very similarly and we find that the exchange relations are the same:

Theorem 7. *The generating function of edge-coloured bargraphs, $B(z, w, \alpha|p)$, satisfies the following exchange relation:*

$$\begin{aligned}\alpha B(z,w,\alpha|p)C(z,w,1|p) - \Big(B(z,w,\alpha|p) - B(z,w,0|p)\Big) \\ = \Big(B(z,w,\alpha|p) - B(z,w,0|p)\Big)C(z,w,1|p)\end{aligned} \tag{33}$$

where $C(z, w, 1|p)$ is the generating function of edge-coloured bargraphs that end in a horizontal step.

The asymptotic position of the critical point is given by

$$\alpha_c(p) \sim \frac{\sqrt{\varphi\pi}}{\zeta(3/2)}p^{3/2} + \frac{3\zeta(5/2)(71\sqrt{2}-100)\sqrt{\pi}}{16\sqrt{\varphi^7}\zeta(3/2)^2}p^{1/2} + 1 + O(p^{-1/2}) \tag{34}$$

where $\varphi = \sqrt{2} - 1$.

In the case of vertex-coloured bargraphs the exchange relation is complicated by the presence of two unknown generating functions — one for bargraphs that end in a horizontal step, $X(z, v, a|p)$, and one for bargraphs that end in a vertical step, $Y(z, v, a|p)$. This complication does not effect the edge-visit problem since if a bargraph ends in an edge-visit, then it must end in a horizontal step.

Theorem 8. *The generating functions $X(z, v, a|p)$ and $Y(z, v, a|p)$ satisfy the following exchange relation:*

$$\begin{aligned}\alpha\Big(X(a)\big(X(1)-v\big) + X(a)Y(1) + Y(a)\big(X(1)-v\big)\Big) = \\ \big(X(a)-va\big)X(1) + \big(X(a)-va\big)Y(1) + Y(a)X(1),\end{aligned} \tag{35}$$

where we have used $X(a)$ and $Y(a)$ as shorthand for $X(z, v, a|p)$ and $Y(z, v, a|p)$.

Since we have been unable to find an additional relation between these two unknown generating functions we are unable to proceed on to find an expression for the location of the critical point.

4. Conclusions

We have found a type of symmetry relation that we call an *exchange relation*. This relation allows us to solve two infinite families of vertex-coloured Dyck paths. These can be interpreted as models of fully directed copolymer adsorption. If the period of the colouring is short, then we are able to find exact expressions for the location of the adsorption transition, while for moderately long periods we are able to compute it numerically (see Table 1). For one of the two families we are also able to find an exact asymptotic expression for the critical point in terms of the period of the colouring. This expression gives an idea of the effect of a regular inhomogeneity on the adsorption transition. Unfortunately for the other family, we are only able to hypothesise an asymptotic form based on numerical estimates.

Exchange relations have also been found for infinite families of vertex-coloured and edge-coloured Motzkin paths and bargraphs. Unfortunately, it is not clear that the exchange-relation technique may be applied to more general colourings, however these models are certainly worthy of further investigation.

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