

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.

1 Introduction

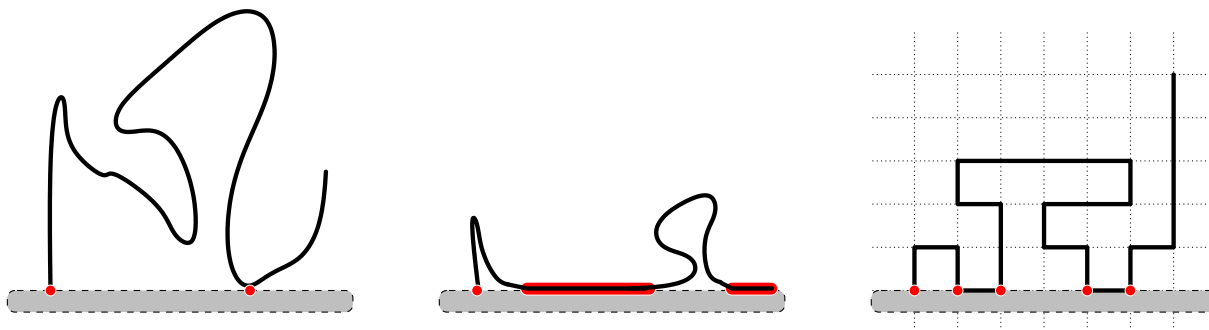


Figure 1: From left-to-right; a polymer in its desorbed or free phase, a polymer in the adsorbed phase, and a self-avoiding walk with vertex visits highlighted.

Consider a long chain polymer in solution close to the wall of the container (see figure 1). If there is an attractive force between the polymer and the wall, then the polymer may undergo a change in behaviour — If the attractive force is weak then the fraction of the polymer 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 the polymer 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*.

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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 [15, 25] in a half-space first defined in [15], in which configurations are weighted according to the number of vertices or edges lying in the boundary, being 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*.

Polymers are constructed from smaller molecules called *monomers*; the homopolymer case models polymers in which all the monomers are the same. Assigning different colours to the vertices or edges of a walk mimics a polymer made up of monomers with different properties. Such a polymer is called a *copolymer* and perhaps the best known example of a copolymer is DNA, which is constructed of four different monomers distinguished by their bases: adenine (A), guanine (G), cytosine (C), and thymine (T). By assigning different properties to vertices of different colours, one can model the effect of this inhomogeneity on the adsorption of the polymer.

Quite a lot is known rigorously about the adsorbing self-avoiding walk model: In particular, it is known that its phase diagram, which describes the behaviour of the model for different values of the interaction strength, includes a critical point which corresponds to an adsorption transition. The adsorption transition is driven by an interaction between visits in the walk and the plane, and takes place at a critical point at a critical strength of the interaction. For more details of this model, see references [17, 19, 31].

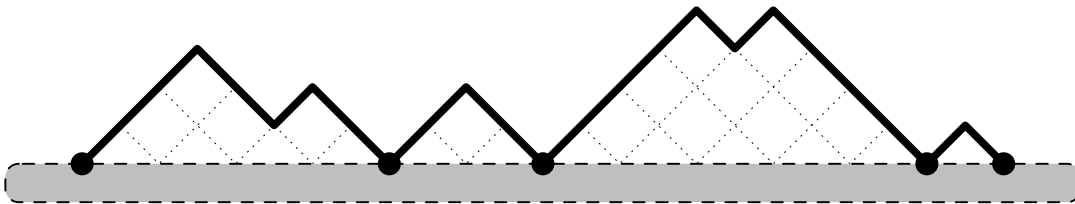


Figure 2: An example of a Dyck-path. The horizontal axis can be considered an adsorbing wall.

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 [25], and attention is instead often shifted to directed versions of the above problem [18], see also references [6, 8, 12, 28, 32]. The problem of adsorbing directed walks is equivalent to the problem of enumerating Dyck paths [12]. From the generating function of Dyck paths enumerated according to their length and number of vertex visits it is possible to extract details of the “physical” behaviour of the model. In this paper we only consider vertex visits and so we shall refer to them simply as “visits”.

The horizontal axis below Dyck paths can be considered to be an adsorbing wall (see figure 2) making this a natural model for an adsorbing directed polymer, as well as a simplification of the self-avoiding walk model. Dyck paths are, perhaps, one of the most studied and best understood objects in combinatorics. They are one of the many objects enumerated by the Catalan numbers [29] whose history dates back as far as Euler in the 18th century [21], and possibly even earlier [22, 24]. In spite of this long history, there still remain special challenges in the determination of the generating functions of models derived from the basic case. In this paper we shall consider a certain model of *vertex-coloured* Dyck paths, and our basic question would be to determine the generating function and the location of the adsorption transition as functions of this colouring. This problem has so far been generally intractable, but we shall solve it for an infinite family of periodic colourings (solutions exist for some particular cases in both the Dyck path model [19], and also in a related model of partially directed walks [32]).

Consider a set of k colours, let χ be a infinite sequence of these colours. We create a *vertex-coloured* Dyck

path, by assigning the i^{th} colour in χ to the $2i^{\text{th}}$ vertex of every Dyck path (since only even numbered vertices may be visited). In this paper we consider the problem of counting vertex-coloured Dyck paths according to their half-length and the number of visits of each colour. We refer to the $k = 1$ case as the *homopolymer* model and when $k > 1$ we refer to the *copolymer* model. If colours are assigned randomly then either a *quenched averaged* or *annealed* model is obtained (see [19] for more details). The annealed model is simply related to the homopolymer case. Quenched models are obtained when the colouring is fixed; these models are generally intractable, and in this paper we examine two families of fixed periodic colourings that are solvable.

In section 2 we review the generating functions associated with Dyck paths. These are found by methods which, broadly speaking, are one of the following types: a *factorisation* method or a *column-by-column* (or Temperley) method. In these models all visits are weighted identically; the models may be interpreted as models of homopolymer adsorption. We briefly consider the phase diagram of this model; it includes a critical point where an adsorption transition takes place, and it is in fact possible to write down the exact numerical value of the activity at this critical point. We also demonstrate how the Dyck path visit generating function can be derived using a technique we call an “*exchange relation*”.

In section 3 we examine the generating function of a model of adsorbing Dyck paths in which visits are not identically weighted — in particular visits are given one of two weights. This model is usually constructed by colouring the Dyck path with a sequence of two colours, A and B , from one endpoint, and assigning a weight to each visit according to its colour; these objects may be interpreted as models of directed copolymer adsorption. As in the case of a homopolymer model, there is a critical point in the phase diagrams of these models where an adsorption transition takes place; but the location of this point is a non-trivial function of the colouring. We explain why the standard techniques used to solve the homopolymer case break down for the copolymer case, and show how the exchange relation for Dyck paths may be used to write down an expression for the the generating function of Dyck paths coloured by the sequence $\{AB^{p-1}\}^*A$ for any p . We also determine the asymptotic form of the Dyck path generating function, and show how it may be used to write down an asymptotic expansion in p of the critical adsorption activity in this model .

2 Statistical mechanics of Adsorbing Dyck paths

Let c_n be the number of Dyck paths of half-length n ; it is well known that this number is simply the n^{th} Catalan number: $c_n = \frac{1}{n+1} \binom{2n}{n}$. Let $c_{n,m}$ be the number of Dyck paths of half-length n with m visits (*i.e.* having m vertices lying on the adsorbing line). The generating function of this model is defined to be

$$D(z, w) = \sum_{n,m} c_{n,m} w^m z^n \quad (1)$$

where z is the generating variable of the half-length of the paths. The number $c_{n,m}$ is known to be given by

$$c_{n,m+1} = \frac{m}{2n-m} \binom{2n-m}{n-m}. \quad (2)$$

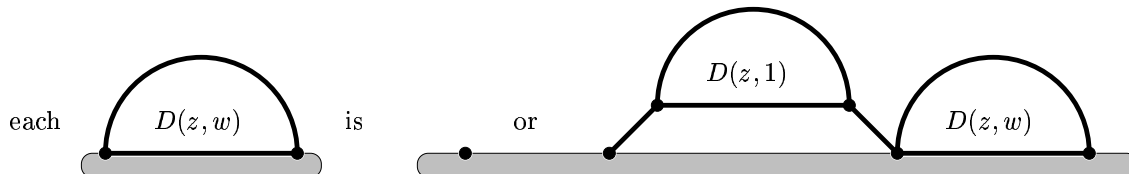
The generating variable w generates visits in the Dyck path, and is often called an *activity*. In the work that follows we shall refer to the paths enumerated by $D(z, w)$ as “adsorbing” or “weighted” Dyck paths, while those counted by $D(z, 1)$ as “unweighted” Dyck paths or just “Dyck paths” since visits are not considered. In statistical mechanics it is also not unusual to define $w = e^{J/kT} = e^\beta$ where J and k are some physical constants, T is temperature and β is proportional to the energy associated with each visit in the path¹. Under

¹If we write $w = e^\beta$, then in the language of statistical mechanics β can be called a *fugacity*, and w is an *activity*. In these models the activity is a parameter which controls the strength of interaction of the paths with the wall. We shall also often say that a visit is *weighted* by its generating variable, or its activity or fugacity [5]

this substitution, the generating function becomes the “*grand canonical partition function*” for the model, where z is related to a chemical potential [4]. This function is the central object in statistical mechanics, since it contains all the information required to determine the behaviour of the model. We now consider two methods for computing this generating function — factorisation and the Temperley method — and explain why their application to vertex-coloured Dyck paths is not practical.

2.1 Factorisation of adsorbing Dyck paths

The factorisation technique works by cutting Dyck paths recursively into smaller pieces where they return to the X -axis. A comprehensive study of Dyck paths can be found in reference [9]. An expression for $D(z, w)$ can be obtained by translating this construction into operations on the generating function. Namely



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).

Dyck paths with exactly two visits are sometimes called *excursions* [18, 19], or *primitive* Dyck paths; they have generating function $zD(z, 1)$. Putting all of this information together gives the following functional equation for $D(z, w)$:

$$D(z, w) = w + zwD(z, 1)D(z, w). \quad (3)$$

This is readily solved to give

$$D(z, w) = \frac{w}{1 - wzD(z, 1)} = \frac{w}{1 - \frac{w}{2}(1 - \sqrt{1 - 4z})}. \quad (4)$$

Alternatively, observe that $w[wzD(z, 1)]^m$ generates Dyck paths with m primitive components concatenated along the main diagonal, with each visit weighted by w . Hence $D(z, w) = \sum_{m=0}^{\infty} w[wzD(z, 1)]^m = w/(1 - wzD(z, 1))$ as seen above.

We note that if the vertices of the Dyck path are coloured, then this construction does not conserve the colouring. To overcome this one must take into account the colour of the first and second visit-vertices in this factorisation. In the case that the colouring is periodic with period p , then this leads to a system of p simultaneous equations in p generating functions — each one counting Dyck paths whose vertices are coloured starting from a different point in the period. For small p (up to 4 or 5, say) this system of equations may be solved by hand or computer (see [19, 32] for example), however for even moderate periods this quickly becomes impractical in terms of computer time and memory.

2.2 From generating functions to phase transitions

There is a close relation 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 the activity w in $D(z, w)$ 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:

$$D(z, w) = \sum_{n \geq 0} \left(\sum_{m \geq 1} c_{n,m} w^m \right) z^n = \sum_{n \geq 0} Z_n(w) z^n \quad (5)$$

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

$$\log z_c(w) = \left(\lim_{n \rightarrow \infty} \frac{1}{n} \log Z_n(w) \right)^{-1} = -\mathcal{F}(w), \quad (6)$$

where $z_c(w)$ is the radius of convergence, and $\mathcal{F}(w)$ is the *canonical limiting free-energy density*² [19]. This relation between $z_c(w)$ and $\mathcal{F}(w)$ explicitly connects the combinatorics and thermodynamics of the model. The change of phase, from desorbed to adsorbed, is signalled by a non-analyticity in $\mathcal{F}(w)$ and also in $z_c(w)$. Describing the location of this transition for vertex-coloured Dyck paths and the behaviour of the generating function close to it, are the major goals of this paper.

From equation (4) one sees that:

$$z_c(w) = \begin{cases} 1/4, & w \leq 2 \\ \frac{w-1}{w^2}, & w > 2 \end{cases}, \quad (7)$$

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

$$\mathcal{F}(w) = -\log z_c(w) = \begin{cases} 2 \log 2, & w \leq 2; \\ 2 \log w - \log(w-1), & w > 2. \end{cases} \quad (8)$$

Observe that for $w > 0$, the free energy is a continuous function of w , but that $\mathcal{F}(w)$ is non-analytic at $w = w_c = 2$. The non-analyticity is a phase transition in this model, and since the first derivative of $\mathcal{F}(w)$ to $\log w$ is also continuous, we call this phase transition a “*continuous transition*” (as opposed to a first order phase transition where the first derivative of $\mathcal{F}(w)$ is discontinuous; and where this is interpreted to signal the presence of a latent heat in the model).

Using singularity analysis, one can compute the mean number of visits in paths weighted by w^m as a function of the length of the path:

$$\text{mean number of visits}(n) \sim \begin{cases} \frac{2}{2-w} + o(1), & w < 2 \\ \sqrt{\pi} \sqrt{n} + O(1), & w = 2 \\ \frac{w-2}{w-1} n + O(\sqrt{n}), & w > 2 \end{cases} \quad (9)$$

This shows that that in the $n \rightarrow \infty$ 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 [19] for details)— If $w < 2$, then all the derivatives of the free energy, with respect to w , are zero; the expected 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 $w > 2$, 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 expected density of visits. Further analysis shows that the second derivative of $\mathcal{F}(w)$ with respect to $\log(w)$ (*i.e.* the specific heat) is:

$$\frac{d^2 \mathcal{F}(w)}{d(\log w)^2} = \begin{cases} 0, & w < 2; \\ \frac{w}{(w-1)^2}, & w > 2. \end{cases} \quad (10)$$

²We note that the derivative of the free energy to $\log(w)$ 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 $\log(w)$ is the *specific heat* which is a measure of the fluctuations in the density of visits.

This is a measure of the fluctuations in the number of visits and it is maximised at $w = w_c = 2$. We expect this to be the case, since when the model is away from the critical point, all members of the population 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 members of the population have widely different numbers of visits.

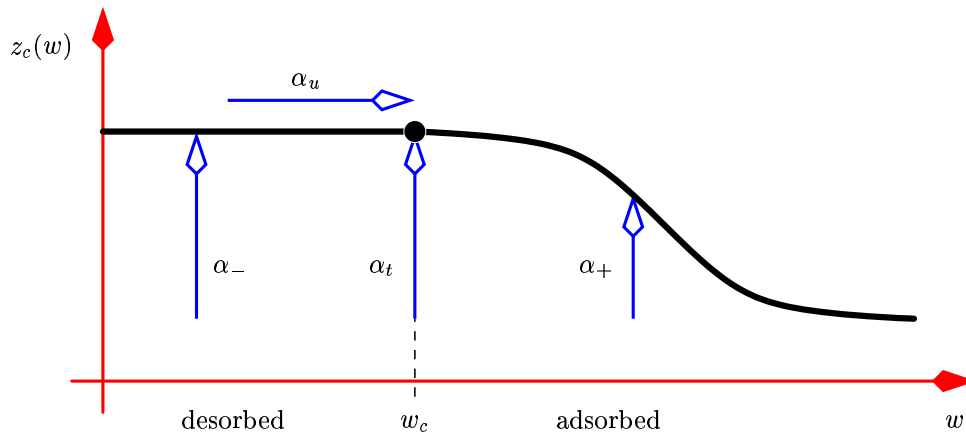


Figure 3: The radius of convergence and the definitions of various scaling exponents.

We are also interested in the behaviour of the generating function close to the critical point, w_c ; in this case $w_c = 2$. Physicists use critical exponents to describe and classify the nature of the phase transition; the square-root singularity in $D(z, w)$ is quite characteristic in models of this kind; and in particular it determines many of the critical exponents associated with the phase transition; for more details see reference [19]. In figure 3 we give a schematic plot of the radius of convergence of the adsorbing Dyck path generating function and indicate exponents associated with the behaviour of the generating function in regimes.

The part of the critical line $z_c(w) = 1/4$ with $w < w_c$ is usually called the τ -line. The critical curve $z_c(w)$ with $w > w_c$ is called the λ -line. The behaviour of the generating function as one approaches the τ -line with fixed $w < w_c$ defines the exponent α_- : $D(z, w) \sim (z_c(w) - z)^{2-\alpha_-}$, where the symbol \sim indicates the dominant singular behaviour of $D(z, w)$. Expanding $D(z, w)$ about $z = 1/4$ shows that

$$D(z, w) \sim \frac{2w}{2-w} - \frac{2w^2}{(2-w)^2} \sqrt{1-4z} + O(1-4z).$$

Thus, the dominant singular term in $1-4z$ is a square root, and $(2-\alpha_-) = +1/2$. A similar analysis at $w = w_c = 2$ gives the critical exponent $(2-\alpha_t) = -1/2$. Lastly, for $w > w_c$ the singularity is a simple pole and so $(2-\alpha_+) = -1$.

Since the generating function is convergent along the τ -line, but divergent at the adsorption transition, a further exponent $(2-\alpha_u)$ is introduced to describe the singularity in $D(z, w)$ as $w \rightarrow 2^-$ along the τ -line. In the situation here,

$$D(1/4, w) = \frac{2w}{2-w} \tag{11}$$

so that $(2-\alpha_u) = -1$. The general theory of tricritical points [19, 23, 27] defines a crossover exponent $\phi = (2-\alpha_t)/(2-\alpha_u) = 1/2$; remarkably, this exponent also describes the shape of the λ -line close to the critical point.

3 Vertex-coloured Dyck paths and critical points.

In this section we present our main results. We are particularly interested in the location of the critical adsorption point in Dyck path models of adsorbing copolymers. The location of this point is known for two models of adsorbing Dyck paths, one corresponding to an homopolymer model ($w_c = 2$) and the second to an alternating copolymer model ($w_c = 2 + \sqrt{2}$) [19]. The exact value of w_c is also known for some partially directed walk models of copolymers with short periodic colourings [26, 32], but there are no further general results in the literature. While we will be interested in values of w_c , we shall not be able to determine the exact value of w_c for any given colouring, but instead focus our energies on an infinite family of periodic copolymer models coloured by $\{AB^{p-1}\}^*A$. In this case we are able to calculate w_c exactly for small values of p , but more interestingly we are able to derive its asymptotic behaviour for large values of p .

We proceed by first determining a new functional relation related to equation (3). This relation establishes an exchange relation between $D(z, w)$ and $D(z, 1)$ with respect to $1 \longleftrightarrow w$. While this equation cannot be used to solve for $D(z, w)$ 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 activity.

3.1 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 w 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 3.1. 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 $D(z, w)$. The second half is an unweighted Dyck path, which may not be a single vertex since P is not empty, and so is enumerated by $D(z, 1) - 1$.

If the next visit in the path is now weighted then the lower half of figure 3.1 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 so is counted by $D(z, w) - w$. The unweighted half is shorter and so may 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 w .

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 $D(z, w)$ and $D(z, 1)$:

$$wD(z, w)(D(z, 1) - 1) = (D(z, w) - w)D(z, 1) \quad (12)$$

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

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

$$D(z, w) = \frac{wD(z, 1)}{w + (1 - w)D(z, 1)}. \quad (13)$$

This solution is not identical to the relation in equation (3), 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 $D(z, w)$ from equation (12); a solution for $D(z, 1)$ is needed as well and cannot be obtained by setting $w = 1$ in the above.

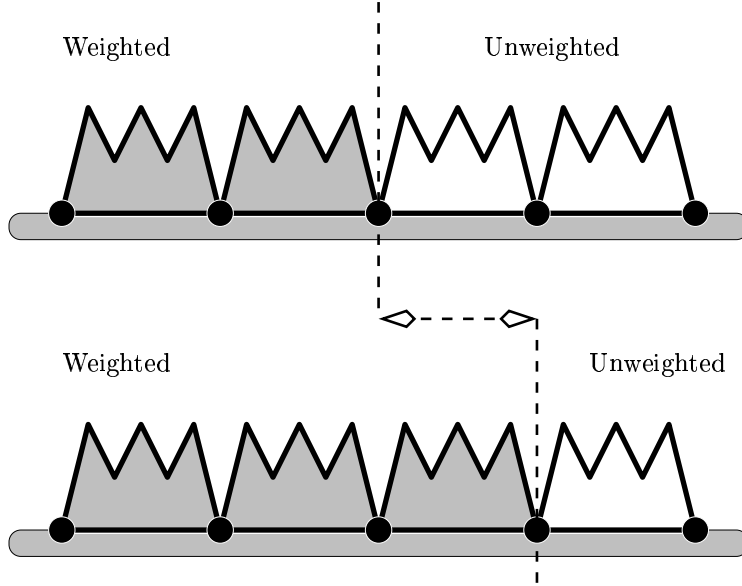


Figure 4: This is a schematic representation of a partially weighted Dyck path. Starting from the left and working towards the right, each visit is weighted w . At some point *before* the end of the path is reached the situation is as represented in the top half of the illustration. Proceeding on to the next visit gives the lower illustration. The correspondence between these two pictures gives equation (12).

This indicates that the exchange relation is not equivalent to equations (3), and at the same time, it does not appear to be particularly useful since $D(z, 1)$ must be computed by some other means.

An exchange relation for $D(z, w)$ may also be derived using a different approach.³ Let $P(z) = z^2 D(z, 1)$ be the generating function of an excursion. Then the generating function of Dyck paths may be decomposed uniquely into excursions so that $D(z, w) = w + w^2 P(z) + w^3 [P(z)]^2 + \dots$ from which it follows that

$$D(z, w) = \frac{w}{1 - wP(z)}. \quad (14)$$

This may also be seen by iterating equation (3). Solving for $P(z)$ shows that

$$P(z) = \frac{1}{w} - \frac{1}{D(z, w)} = \frac{1}{u} - \frac{1}{D(z, u)} \quad (15)$$

where $w \neq u$ in general. Solving this shows the exchange symmetry

$$u(D(z, w) - w) D(z, u) = wD(z, w) (D(z, u) - u) \quad (16)$$

under the exchange $w \leftrightarrow u$, a generalization of equation (12).

These exchange relations must be satisfied by $D(z, w)$, and also by the generating functions of certain vertex-coloured Dyck path models of copolymer adsorption; it will prove to be very useful in those models. It also appears to hold, in very similar forms, for other models of directed or partially directed paths [20].

³This was pointed out by an anonymous referee.

3.2 Generating Functions of $\{AB^{p-1}\}^*A$ and $\{BA^{p-1}\}^*B$.

The exchange relation in equation (12) can be applied to a Dyck path model of copolymers. In such models, the even vertices⁴ of the Dyck path are coloured with two colours A and B , where the A -visits are weighted by a and the B -visits by b . An assignment of colours in this way to a Dyck path will be called a “quench”; this term derives from polymer physics where a fixed sequence of comonomers along a linear polymer are said to be quenched. In this and subsequent sections we shall put $b = 1$ and a will be the only activity in the model.

The generating function of these models cannot be derived directly using the methods described in sections 2.1 and 2.2, with the exception of a couple of models with periodic quenches of very short period [19]. There are also some results along these lines for adsorbing partially directed walk models for copolymer adsorption [26, 32]. A good result would be to extend some of these results to other infinite families of quenches with, for example, arbitrarily long periods or even for aperiodic quenches; this still seems to be an intractable problem.

We shall instead focus on a quench given by the sequence $\{AB^{p-1}\}^*A$ of period p with activities a and $b = 1$, and determine an asymptotic expression for the critical value of $a = a_c$ as a function of p . The methods we develop here only apply to this particular quench, but we are also able to say something about its “complementary quench” $\{BA^{p-1}\}^*B$ where the activities are a and $b = 1$.

The correspondence which gave the exchange relation in equation (12) is also applicable to Dyck path models of periodic copolymers coloured by $\{AB^{p-1}\}^*A$. A weighted Dyck path is coloured, or “labelled”, starting from its leftmost vertex by putting a colour on every second vertex. Each A -vertex which is also a visit is given a weight a . The colouring is stopped at some A -visit, and the remaining part of the path is left uncoloured — notice that the coloured part of the path must have half-length congruent to $0 \pmod p$. 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. Hence we require that both parts of the path have half-length divisible by p .

Let us now define the following generating functions, half-length weighted by a , visits (coloured or otherwise) by w and A -visits by a :

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

- $U(z, w|p)$ is the generating function of all unlabelled Dyck paths of half-length $0 \pmod p$, with visits weighted by w , and defined by

$$U(z, w|p) = \sum_{n \geq 0} \sum_{m \geq 0} c_{np, m} w^m z^{np};$$

- $L(z, w, a|p)$ is the generating function of all Dyck paths coloured or labelled by $\chi = \{AB^{p-1}\}^*A$, with half-length congruent to $0 \pmod p$, and with visits weighted by w and A -visits weighted by a .

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

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

$$aL(z, w, a|p)(U(z, w|p) - w) = (L(z, w, a|p) - wa)U(z, w|p), \quad (17)$$

and therefore

$$L(z, w, a|p) = \frac{waU(z, w|p)}{wa + (1 - a)U(z, w|p)}. \quad (18)$$

⁴If the vertices along the path are labeled sequentially from the left by $0, 1, 2, 3, \dots$, then those with even labels are called “even vertices”. The remaining vertices are “odd” and cannot visit the adsorbing diagonal — hence they are not coloured.

□

Notice that $L(z, w, a|p)$ is not the generating function of all coloured Dyck paths of arbitrary half-length; but it is enough to describe the physics of the full model. The radius of convergence $z_c(w, a)$ of $L(z, w, a|p)$ can be seen to be equal to the radius of convergence of the full generating function for this model. To see this, consider the following definition and theorem 2.

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

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

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

$$F(z, w, a|p) = L(z, w, a|p)\overline{F}(z, w|p)/w. \quad (19)$$

Consequently

$$F(z, w, a|p) = L(z, w, a|p)D(z, w)/U(z, 1|p) = \frac{waD(z, w)}{wa + (1 - a)U(z, w|p)} \quad (20)$$

Proof. Any Dyck path coloured by $\{AB^{p-1}\}^*A$ may be uniquely factored into a Dyck path of length $0 \pmod p$ 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 $\overline{F}(z, w|p) = F(z, w, 1|p)/L(z, w, 1|p)$, and back-substitution gives the main result once we notice that $L(z, w, 1|p) = U(z, w|p)$ and $F(z, w, 1|p) = D(z, w)$. □

By setting $w = 1$ 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 $a \rightarrow 1/a$ and $w = a$ instead, then $F(z, a, 1/a|p)$ counts Dyck paths coloured with the “complementary” colouring $\chi = \{BA^{p-1}\}^*B$ with a the generating variable of 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 generates A -visits.

Remark. In the proof of Theorem 2 we made use of the generating function, $\overline{F}(z, w|p)$, that counts Dyck paths labeled $\{AB^{p-1}\}^*A$ in which all A -visits are forbidden, excepting the first. This generating function is obtained by starting with the generating function of all Dyck paths, $D(z, w)$, and then dividing by the generating function of those that end in an A -visit, $U(z, w|p)$.

It appears that this idea may be applicable to other periodic colourings, and it is certainly worthy of a more thorough investigation, particularly if it enables us to solve other copolymer adsorption models.

3.3 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 (4); and its radius of convergence $z_c(w)$ is given in equation (7). $z_c(w)$ is non-analytic at $w_c = 2$, and we have already argued that this corresponds to a critical adsorption point in this model. This point is also the intersection of a line of branch points in $D(z, w)$ along $z = 1/4$ and a line of simple poles along $z = (w - 1)/w^2$. The changeover from branch points to poles at the critical point is typical in a multi-critical phase diagram [19, 27], and indeed it is also apparent in these models of vertex-coloured Dyck paths.

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

$$F(z, 1, a|p) = \frac{aD(z, 1)}{a + (1 - a)U(z, 1|p)} \quad (21)$$

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

$$U(z, w|p) = \frac{1}{p} \sum_{j=0}^{p-1} D(\beta^j z, w), \quad \text{where } \beta = e^{2\pi i/p}. \quad (22)$$

This expression simplifies to give

$$U(z, 1|p) = \frac{-1}{p} \sum_{j=0}^{p-1} \frac{\sqrt{1 - 4z\beta^j}}{2z\beta^j}. \quad (23)$$

The generating function in equation (21) has two possible sources of singularities, namely the singularities of $U(z, 1|p)$ and the zero of the denominator, which is the solution of $a/(a - 1) = U(z, 1|p)$. We see from the expression for $U(z, 1|p)$ that dominant ‘‘physical’’ singularity (*i.e.* on the positive real axis) is the square root singularity at $z = 1/4$. These singularities determines the radius of convergence of $F(z, 1, a|p)$ — for small a this is given by $z = 1/4$, while for larger a it is determined by the simple pole encountered when the denominator in equation (21) vanishes. These singularities cross at the adsorption critical point, so that the critical value of a is given by the solution of

$$\frac{a_c}{a_c - 1} = U(1/4, 1|p), \quad \text{or} \quad a_c = \frac{U(1/4, 1|p)}{U(1/4, 1|p) - 1}. \quad (24)$$

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 [19]). 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

$$D(z, 1) = 1 + \sum_{n \geq 1} \binom{2n}{n} \frac{z^n}{n+1}, \quad \text{and so} \quad (25)$$

$$U(1/4, 1|p) = 1 + \sum_{n \geq 1} \binom{2np}{np} \frac{4^{-np}}{np+1}. \quad (26)$$

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. This gives the following lemma:

Lemma 4. *There exists $M \in [0, \infty)$ such that for sufficiently large n ,*

$$\left| \frac{1}{n+1} \binom{2n}{n} \frac{\sqrt{\pi n^3}}{4^n} - \left(1 - \frac{9}{8n} + \frac{145}{128n^2} \right) \right| < \frac{M}{n^3}. \quad (27)$$

Proof. This follows from Stirling's formula, but can also be obtained by following the method outlined in Theorem 5.2 in chapter 5 of Flajolet and Sedgewick [10]. The coefficient of z^n in $D(z, 1)$ may be evaluated from the following contour integral:

$$\frac{1}{2\pi i} \oint D(z, 1) \frac{dz}{z^{n+1}} = \frac{4^{n+1}}{2\pi i \sqrt{n^3}} \int_0^\infty \sqrt{-t} (1+t/n)^{-n-2} dt. \quad (28)$$

We expand $\sqrt{-t}(1+t/n)^{-n-2}$ asymptotically and uniformly in n :

$$\sqrt{-t}(1+t/n)^{-n-2} = i\sqrt{t}e^{-t} \left[1 + \frac{t^2 - 4t}{2n} + \frac{8t^2 - 32t^3 + 3t^4}{24n^2} + O(n^{-3}) \right]. \quad (29)$$

Integrating this term by term gives the lemma. \square

Next we use the above lemma to explore the asymptotic behaviour of $U(1/4, 1|p)$ for large p ; this will give 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 5. *The function $U(1/4, 1|p)$ is (as a function of p) asymptotic to:*

$$U(1/4, 1|p) \sim 1 + \frac{1}{\sqrt{p^3\pi}} \left(\zeta(3/2) - \frac{9\zeta(5/2)}{8p} + \frac{145\zeta(7/2)}{128p^2} + O(1/p^3) \right). \quad (30)$$

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

$$a_c(p) \sim \frac{\sqrt{\pi}}{\zeta(3/2)} p^{3/2} + \frac{9\sqrt{\pi}\zeta(5/2)}{8\zeta(3/2)^2} p^{1/2} + 1 + \frac{\sqrt{\pi} (162\zeta(5/2)^2 - 145\zeta(7/2)\zeta(3/2))}{128\zeta(3/2)^3} p^{-1/2} + O(p^{-3/2}) \quad (31)$$

Proof. By lemma 4 there exists $M \in [0, \infty)$ such that for sufficiently large p we have

$$\left| \frac{1}{p+1} \binom{2p}{p} 4^{-p} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{p^{3/2}} - \frac{9}{8p^{5/2}} + \frac{145}{128p^{7/2}} \right) \right| \leq M/p^{9/2}$$

Replace p by kp , and then sum over $k \geq 1$:

$$\left| \sum_{k \geq 1} \frac{1}{kp+1} \binom{2kp}{kp} 4^{-kp} - \sum_{k \geq 1} \frac{1}{\sqrt{\pi}} \left(\frac{1}{(kp)^{3/2}} - \frac{9}{8(kp)^{5/2}} + \frac{145}{128(kp)^{7/2}} \right) \right| \leq \sum_{k \geq 1} M/(kp)^{9/2}. \quad (32)$$

Since $\sum_{k \geq 1} (kp)^{-\gamma} = \zeta(\gamma)p^{-\gamma}$, we have

$$\left| \sum_{k \geq 1} \frac{1}{kp+1} \binom{2kp}{kp} 4^{-kp} - \frac{1}{\sqrt{\pi}} \left(\frac{\zeta(3/2)}{p^{3/2}} - \frac{9\zeta(5/2)}{8p^{5/2}} + \frac{145\zeta(7/2)}{128p^{7/2}} \right) \right| \leq M\zeta(9/2)/p^{9/2} \quad (33)$$

Since $U(1/4, 1|p) = 1 + \sum_{k \geq 1} \frac{1}{kp+1} \binom{2kp}{kp} 4^{-kp}$, the first equation follows. The second equation follows immediately from this. \square

We now consider the critical behaviour of these vertex-coloured Dyck paths, in particular the radius of convergence and the critical exponents describing the behaviour of the generating function. The critical curve $z_c(a)$ is divided into two parts, namely

$$z_c(a) = \begin{cases} 1/4 & a \leq a_c \\ U^{-1}(a/(a-1)|p) & a > a_c \end{cases}, \quad (34)$$

where $U^{-1}(x|p)$ denotes the inverse function of $U(z, 1|p)$.

Let us consider the sub-critical behaviour of the generating function; expanding $D(z, 1)$ and $U(z, 1|p)$ about $z = 1/4$ we find that

$$\begin{aligned} D(z, 1) &\sim 2 - 2\sqrt{1-4z} + O(1-4z); \\ U(z, 1|p) &\sim U(1/4, 1|p) - \frac{2\sqrt{1-4z}}{p} + O(1-4z). \end{aligned}$$

Substituting these into the expression for $F(z, 1, a|p)$ in Theorem 2 gives

$$\begin{aligned} F(z, 1, a|p) &\sim \frac{2a - 2a\sqrt{1-4z} + O(1-4z)}{a + (1-a)(U(1/4, 1|p) - \frac{2}{p}\sqrt{1-4z}) + O(1-4z)} \\ &\sim C_0(p, a) + C_1(p, a)\sqrt{1-4z}. \end{aligned} \quad (35)$$

Thus, the dominant singular term in $1-4z$ is a square root, and $(2 - \alpha_-) = +1/2$. A similar analysis at $a = a_c$ gives the critical exponent $(2 - \alpha_t) = -1/2$. Lastly, for $a > a_c$ the singularity is a simple pole and so $(2 - \alpha_+) = -1$.

Again we find that the generating function is convergent along the τ -line, but divergent at the adsorption transition, and so the exponent $(2 - \alpha_u)$ exists. Substituting $z = 1/4$ into the expression for F gives

$$F(1/4, 1, a|p) = \frac{D(1/4, 1)}{a + (1-a)U(1/4, 1|p)} \sim (a_c - a)^{-1}, \quad (36)$$

so that $(2 - \alpha_u) = -1$, and so the crossover exponent $\phi = (2 - \alpha_t)/(2 - \alpha_u) = 1/2$.

3.4 Analysis of $\{BA^{p-1}\}^*B$.

We have already shown that the generating function $F(z, a, 1/a|p)$ enumerates a copolymer model of adsorbing Dyck paths coloured $\{BA^{p-1}\}^*B$, where a generates A -visits. The explicit expression for this generating function is

$$F(z, a, 1/a|p) = \frac{D(z, a)}{1 + (1-1/a)U(z, a|p)}, \quad (37)$$

with $D(z, a)$ and $U(z, a|p)$ defined as above. As in the previous example, at $z = 1/4$ this generating function has square root singularities arising from $D(z, a)$ and $U(z, a|p)$. If $a > 2$, then both $D(z, a)$ and $U(z, a|p)$ have simple poles at $z = (a-1)/a^2$. In addition to these singularities, there is also a simple pole whenever the denominator is zero, *i.e.* when:

$$a + (a-1)U(z, a|p) = 0. \quad (38)$$

It is not hard to show (see below) that the simple poles arising in $D(z, a)$ and $U(z, a|p)$ cancel so that $F(z, a, 1/a|p)$ is not singular at the point $z = (a-1)/a^2$; this is contrary to what is observed for the homopolymer model in equation (4).

When a is sufficiently small (in the desorbed phase) the dominant singularity in $F(z, a, 1/a|p)$ will be a square root singularity at $z = 1/4$. To see this we note that $D(z, a)$ may be written as

$$D(z, a) = \frac{f(z, a)}{1 - \varphi z}, \quad \text{where } \varphi = a^2/(a - 1) \text{ and } f(z, a) = \frac{a(2 - a - a\sqrt{1 - 4z})}{2(1 - a)} \quad (39)$$

and using equation (22) we have

$$U(z, a|p) = \frac{1}{p} \sum_{j=0}^{p-1} \frac{f(z\beta^j, a)}{1 - \varphi z\beta^j}, \quad \text{where } \beta = e^{2\pi i/p}. \quad (40)$$

This allows us to write

$$\begin{aligned} F(z, a, 1/a|p) &= \left[\frac{af(z, a)}{1 - \varphi z} \right] \left[a + \frac{a - 1}{p} \sum_{j=0}^{p-1} \frac{f(z\beta^j, a)}{1 - \varphi z\beta^j} \right]^{-1} \\ &= \left[af(z, a) \right] \left[\frac{a - 1}{p} f(z, a) + (1 - \varphi z) \left(a + \frac{a - 1}{p} \sum_{j=1}^{p-1} \frac{f(z\beta^j, a)}{1 - \varphi z\beta^j} \right) \right]^{-1}. \end{aligned}$$

Let us now consider the potential singularities in this expression: Along the curve $(1 - \varphi z) = 0$ we see that $F(z, a, 1/a|p)$ is equal to $a(a - 1)/p$. Hence the simple pole in $D(z, a)$ cancels with a pole in $U(z, a|p)$ and neither gives rise to a singularity. The other poles in $U(z, a|p)$ are zeros of $F(z, a, 1/a|p)$ and consequently these do not give rise to singularities either, proving our claim. In the case that $z = 1/4$ and $1 - \varphi > 0$ (when a is small enough), then the square root singularities in $f(z, a)$ do not cancel and are thus present in $F(z, a, 1/a|p)$. Lastly, there is still a locus of simple poles in $F(z, a, 1/a|p)$ along the curve $a + (a - 1)U(z, a|p) = 0$. The intersection of this curve with $z = 1/4$ gives the location of the adsorption critical point in $F(z, a, 1/a|p)$.

The critical exponents for this model are, once again, the same as those of the homopolymer problem. In fact this value of the cross-over exponent seems to be the same for all models of adsorbing linear polymers in two dimensions and possibly three (though this is still the subject of some debate)[8, 13, 16, 19].

To parallel the former colourings, we would like to determine the asymptotic dependence of the adsorption critical point on p for this model. This is essentially determined by the asymptotic behaviour of the generating function $U(1/4, a|p)$. If the analysis [10] of section 3.3 is naively repeated on this problem (*i.e.* non-rigorously) then one obtains

$$U(1/4, a|p) \approx a + \frac{(a - 2)}{a} \left(\frac{\varphi^{p+1}}{4^p - \varphi^p} \right) + \frac{\zeta(3/2)}{\sqrt{\pi p^3}} \left(\frac{\varphi}{\varphi - 4} \right) + O(p^{-5/2}). \quad (41)$$

The second term in this expansion is due to the simple pole, while the branch point at $z = 1/4$ gives rise to the third (and higher) terms. This expansion breaks down when $a = 2$, since the simple pole and branch point coalesce, giving a different branch point at $z = 1/4$.

One might hope that this expansion is still adequate for a close to $a_c(p)$. However, when p is large almost all visits are A -visits and the model should behave much like the homopolymer model, and so we expect $a_c(p) \rightarrow 2^+$. For increasing p we find that this expansion is accurate on an increasing portion of the a -axis, however at the same time, $a_c(p)$ approaches 2^+ , precisely where the expansion of $U(1/4, a|p)$ is poor, due to the coalescing of the singularities in $D(z, a)$ as $a \rightarrow 2^+$. This is confirmed by numerical analysis — in figure 5 we plot both the exact value and asymptotic estimate of $U(1/4, a|50)$ against $\log_{10}(a - 2)$. It shows that the approximation is poor when a is close to $a_c(50) = 2.0215337\dots$

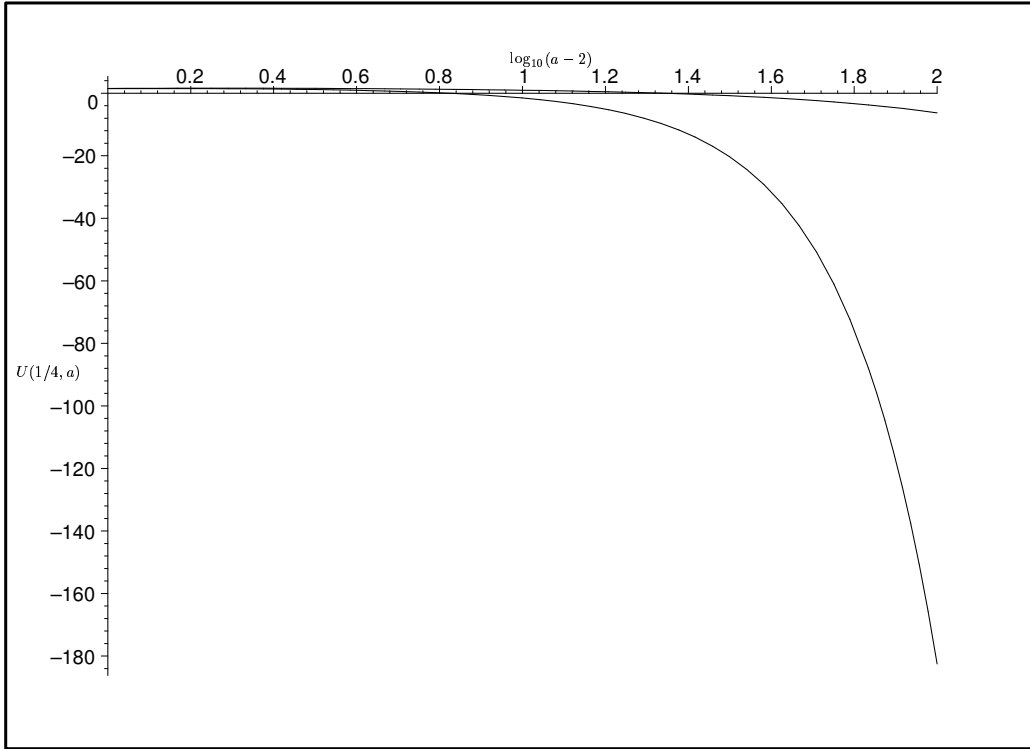


Figure 5: A plot of $U(1/4, a|50)$ (upper curve) and its approximation by equation (41) (lower curve). The horizontal axis is the negative logarithm of the distance from $a = 2$. The approximation appears to be good for $a > 2.1$, but then deteriorates rapidly. Unfortunately, $a_c(50) = 2.0215\dots$, and so cannot be computed from the asymptotic approximation of $U(1/4, a|p)$.

Since we were unable to proceed analytically, we hypothesised a scaling form using numerical data. Using the CLN⁵ library for c++, we computed $a_c(p)$ to 300 significant digits 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 [7, 14], we reached the following hypothesis for the asymptotic behaviour of $a_c(p)$:

$$a_c(p) \sim 2 + 1/p + c_1/p^{3/2} + c_2/p^2 + c_3/p^{5/2} + O(p^{-3}) \quad (42)$$

where

$$\begin{aligned} c_1 &= 0.41198 \pm 0.00002 \\ c_2 &= 0.792 \pm 0.002 \\ c_3 &= 0.83 \pm 0.02 \end{aligned}$$

The estimates of the constant in the p^{-1} term rapidly approach 1 as p increases, and it appears not to differ from 1 by more than 10^{-4} . In these circumstances, it is reasonable 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

⁵The 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>

suggestive that this leading asymptotic behaviour could perhaps be solved exactly — unfortunately we have not yet been able to do so. We also note here that a similar numerical analysis on $F(z, a, 1|p)$ agrees with the results of Theorem 5.

| Period p | $\{AB^{p-1}\}^*A$ | | $\{BA^{p-1}\}^*B$ | |
|---------------|-------------------|------------|-------------------|------------|
| | 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 (24), while for the complementary colouring, $\chi = \{BA^{p-1}\}^*B$, we have computed $a_c(p)$ by solving equation (38) 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 5 and equation (42).

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, and we are able to find all the critical exponents associated with the adsorption transition. 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.

Exchange relations have also been found in both vertex-coloured and edge-coloured Motzkin paths and partially directed walks and a paper is currently in preparation [20]. 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.

Appendix: Other Periodic Colourings.⁶

Consider the problem of enumerating Dyck paths of half length divisible by n , and coloured by the periodic sequence of colours $\{AC^{r-1}BC^{s-1}\}^*A$ on the even vertices of the path as before, and with $r + s = n$. An *excursion* (see section 2.1) is also a *primitive Dyck path*; and we generalise these objects by allowing them to start (have initial vertex) anywhere on the X -axis. Define the following *near-excursions* or *almost primitive* coloured Dyck paths, denoted $P_{AA}, P_{AB}, P_{BB}, P_{BA}$.

- Let P_{AA} be the set of Dyck paths coloured by $\{AC^{r-1}BC^{s-1}\}^*A$ with exactly two visits of colour A (the first and last vertices) at positions congruent to $0 \pmod{2n}$, and with no visits of colour B . There could be a number of visits of colour C . The lengths of the paths in P_{AA} are congruent to $0 \pmod{2n}$.
- Let P_{AB} be the set of Dyck paths with exactly one A -visit (its first vertex) at a position congruent to $0 \pmod{2n}$, and exactly one visit of colour B (which is also its last vertex) at position $2r \pmod{2n}$. There could be any number of C visits. The length of the paths are congruent to $2r \pmod{2n}$.
- Let P_{BA} be the set of Dyck paths with exactly one B -visit (its first vertex) at a position $2r \pmod{2n}$, and exactly one visit of colour A (which is also its last vertex) at position $0 \pmod{2n}$. There could be any number of C visits. The length of the paths are congruent to $2s \pmod{2n}$.
- Finally P_{BB} is the set of coloured Dyck paths of half length congruent to $0 \pmod{2n}$ with zero A -visits, and exactly two B visits at positions congruent to $2r \pmod{2n}$ (these are the first and last vertices).

The generating functions of the paths in the sets above may be denoted by $D_{AA}(z), D_{AB}, D_{BA}, D_{BB}(z)$ (respectively) where z is the weight of the half-length of the paths. The generating function of a Dyck path coloured by $\{AC^{r-1}BC^{s-1}\}^*A$ can be factored by cutting these paths at their penultimate A visit. This will factor the path into a (shorter) Dyck path coloured by $\{AC^{r-1}BC^{s-1}\}^*A$, and a path from the set P_{AA} . If the path is instead cut at its last B visit, then it is factored into a (shorter) Dyck path coloured by $\{AC^{r-1}BC^{s-1}\}^*AC^{r-1}B$ and a path from P_{BA} . Similarly, one may instead consider paths in the set P_{BB} coloured by $\{BC^{s-1}AC^{r-1}\}^*B$, and cut it at its last A visit, and at its last B visit. These factorisations can be conveniently described by a finite state automata with two states A (if the path ends in an A visit), and B (if the path ends in a B visit). To state A one may add paths from P_{AB} to end up in state B , or a paths from P_{AA} to remain in state A , and similarly for state B . These operations are denoted by the arcs in figure 6.

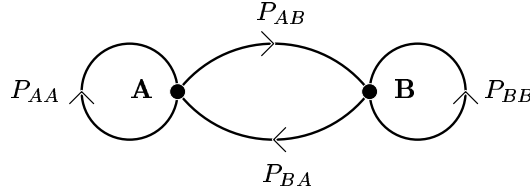


Figure 6: An automata that constructs Dyck paths coloured by $\{AC^{r-1}BC^{s-1}\}^*A$. The vertices A and B represent those Dyck paths ending in a vertex coloured A and B respectively. The edge-weights correspond to adding Dyck paths from the sets P_{AA}, P_{AB}, P_{BA} and P_{BB} .

⁶This appendix is due to an unknown referee who pointed out that the generating functions for more complicated periodic colourings of adsorbing Dyck path models of copolymers can be determined.

Since Catalan numbers c_n counts Dyck paths of half-length n , the matrix C

$$C = \begin{pmatrix} \sum_{n \geq 0} c_{nt} z^{nt} & \sum_{n \geq 0} c_{nt+r} z^{nt+r} \\ \sum_{n \geq 0} c_{nt+s} z^{nt+s} & \sum_{n \geq 0} c_{nt+r} z^{nt} \end{pmatrix} \quad (43)$$

has entries the generating functions of Dyck paths of half-lengths conjugate to $0 \pmod n$, to $r \pmod n$, and to $s \pmod n$. The generating functions of nearly primitive paths can similarly be put in matrix form:

$$D = \begin{pmatrix} D_{AA}(z) & D_{AB}(z) \\ D_{BA}(z) & D_{BB}(z) \end{pmatrix} \quad (44)$$

Since the paths in C can be decomposed into nearly primitive paths as described by the automaton in figure 6, it follows that

$$C = \sum_{n \geq 0} D^n = (I - D)^{-1}, \quad (45)$$

where I is the identity matrix. One may invert the matrices above to get an solution for D , so that the generating functions of nearly primitive Dyck paths are then known (provided that C can be computed). In this case, $D = I - C^{-1}$.

One may now slightly modify this to take into account the weights a and b associated with visits of colour A or colour B . By replacing the matrix D above by D_{ab} given by

$$D_{ab} = \begin{pmatrix} aD_{AA}(z) & bD_{AB}(z) \\ aD_{BA}(z) & bD_{BB}(z) \end{pmatrix}, \quad (46)$$

the generating function of Dyck paths coloured by $\{AC^{r-1}BC^{s-1}\}^*A$ with A visits weighted by a and B visits by b is given by the $(1, 1)$ element of the matrix $(I - \bar{D})^{-1}$.

Similar approaches can be implemented in cases of more complicated periodic sequences of coloured vertices.

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References

- [1] C. Banderier and P. Flajolet, 2001, Basic Analytic Combinatorics of Directed Lattice Paths. To appear in *Theo. Comp. Sci.*
- [2] M. Bousquet-Mélou, 1996, A Method for the Enumeration of Various Classes of Column-Convex Polygons, *Discrete Math.*, **154**, 1–25.
- [3] M. Bousquet-Mélou and M. Petkovšek, 2000, Linear Recurrences with Constant Coefficients: the Multivariate Case, *Discrete Math.*, **225**, 51–75.
- [4] R. Brak, A.J. Guttmann and S.G. Whittington, 1991, On the Behaviour of Collapsing Linear and Branched Polymers, *J. Math. Chem.* **8**, 255–68.
- [5] R. Brak, A.J. Guttmann and S.G. Whittington, 1992, A Collapse Transition in a Directed Walk Model, *J. Phys. A: Math Gen.* **25**, 2437–46.
- [6] R. Brak, J.M. Essam and A.L. Owczarek, 1998, New Results for Directed Vesicles and Chains near an Attractive Wall. *J. Stat. Phys.* **93**, 155–192.
- [7] A. R. Conway and A. J. Guttmann, 1996, Square Lattice Self-Avoiding Walks and Corrections to Scaling. *Phys. Rev. Lett.*, **77**, 5284–5287.
- [8] K. De’Bell and T. Lookman, 1993, Surface Phase Transitions in Polymer Systems. *Rev. Mod. Phys.* **65**, 87–114.
- [9] E. Deutsch, 1999, Dyck Path Enumeration. *Disc. Math.* **204**, 167–202.
- [10] P. Flajolet and R. Sedgewick, 2001, Analytic Combinatorics: Functional Equations, Rational and Algebraic Functions. *INRIA Rapport de Recherche No. 4103*, January 2001, chapter 5.
- [11] P. Flajolet and R. Sedgewick, 2001, Analytic Combinatorics: Functional Equations, Rational and Algebraic Functions. *INRIA Rapport de Recherche No. 4103*, January 2001, chapter 8.
- [12] I.M. Gessel, 1986, A Probabilistic Method for Lattice Path Enumeration. *J. Stat. Plan. and Infer.* **14**, 49–58.
- [13] I. Guim and T. W. Burkhardt, 1989, Transfer-Matrix Study of the Adsorption of a Flexible Self-Avoiding Polymer Chain in Two Dimensions. *J. Phys. A: Math. Gen.* **22**, 1131-1140.
- [14] A. J. Guttmann, I. Jensen, L. H. Wong and I. G. Enting, 2000, Punctured Polygons and Polyominoes on the Square Lattice. *J. Phys. A: Math. Gen.* **33**, 1735–1764.
- [15] J.M. Hammersley, G.M. Torrie and S.G. Whittington, 1982, Self-Avoiding Walks Interacting with a Surface. *J. Phys. A: Math. Gen.* **15**, 539–571.

- [16] R. Hegger and P. Grassberger, 1994, Chain Polymers Near an Adsorbing Surface. *J. Phys. A: Math. Gen.* **27**, 4069–4081.
- [17] E.J. Janse van Rensburg, 1998, Collapsing and Adsorbing Polygons. *J. Phys. A: Math. Gen.* **31**, 8295–8306.
- [18] E.J. Janse van Rensburg, 1999, Adsorbing Staircase Walks and Staircase Polygons. *Ann. Comb.* **3**, 451–473.
- [19] E.J. Janse van Rensburg, 2000, *The Statistical Mechanics of Interacting Walks, Polygons, Animals and Vesicles*. Oxford Lecture Series in Mathematics and its Applications **18** (OUP Inc., New York).
- [20] E.J. Janse van Rensburg and A. Rechnitzer, 2001, Exchange Symmetries in Partially and Fully Directed Models of Copolymer Adsorption. In preparation.
- [21] P. Larcombe and P. D. C. Wilson, 1998, On the trail of the Catalan sequence. *Mathematics Today* **34**, 114–117.
- [22] P. Larcombe, 1999, On the history of the Catalan numbers: a first record in China, *Mathematics Today* **35**, 89.
- [23] I.D. Lawrie and S. Sarlbach, 1984, Tricriticality. In *Phase Transitions and Critical Phenomena* **9**, 65–161. Eds.: C. Domb and J.L. Lebowitz (Academic Press, London).
- [24] J. J. Luo, 1993, Catalan numbers in the history of mathematics in China. In *Combinatorics and graph theory: proceedings of the spring school and international conference on combinatorics, Hefei, 6–27 April 1992*, 68–70. Eds.: H. P. Yap, T. H. Ku, E. K. Lloyd and Z. M. Wang (World Scientific).
- [25] N. Madras and G. Slade, 1992, *The Self-Avoiding Walk*. Probability and its Applications (Birkhäuser, Boston).
- [26] M.S. Moghaddam, T. Vrbova and S.G. Whittington, 2000, Adsorption of Periodic Copolymers at a Planar Interface. *J. Phys. A: Math. Gen.* **33**, 4573–4584.
- [27] A.L. Owczarek, T. Prellberg and R. Brak, 1993, New Scaling Form for the Collapsed Polymer Phase. *Phys. Rev. Lett.* **70**, 951–953; – 1993, The Tricritical Behaviour of Self-Interacting Partially Directed Walks. *J. Stat. Phys.* **72**, 737–772.
- [28] V. Privman, G. Forgacs and H.L. Frisch, 1988, New Solvable Models of Polymer Chain Adsorption near a Surface. *Phys. Rev.* **B37**, 9897–9900.
- [29] R. Stanley, 1999, *Enumerative Combinatorics Volume II*. Cambridge University Press.
- [30] H.N.V. Temperley, 1956, Combinatorial Problems suggested by the Statistical Mechanics of Domains and of Rubber-like Molecules. *Phys. Rev.* **103**, 1–16.
- [31] T. Vrbová and S.G. Whittington, 1996, Adsorption and Collapse of Self-Avoiding Walks and Polygons in Three Dimensions. *J. Phys. A: Math. Gen.* **29**, 6253–6264; — 1998, Adsorption and Collapse of Self-Avoiding Walks in Three Dimensions. *J. Phys. A: Math. Gen.* **31**, 3989–3998; — 1998, Adsorption and Collapse of of Self-Avoiding Walks at a Defect Plane. *J. Phys. A: Math. Gen.* **31**, 7031–7041.
- [32] S.G. Whittington, 1998, A Directed Walk Model of Copolymer Adsorption. *J. Phys. A: Math. Gen.* **31**, 8797–8803.