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Generating function approach to a directed walk model for polymer propagation

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Abstract

The physical behaviour of polymers such as DNA, proteins, and hydrocarbons, is of significant interest in many sciences. A self-avoiding walk on a lattice is a classic model for long polymer chains, and in this report, we will use 'directed walk' models to investigate the propagation of a semi-flexible polymer in a slit with sticky walls. Physical charactieristics of the system are captured by equipping our polymer with various types of interaction energy. Key results established in this report are the derivation of closed form expressions for generating functions that enumerate the number and type of walks, as well as the analytic verification of conjectured 'zero force curves' on which no push or pull is exerted on the walls of the slit by the polymer.

1 Introduction

A polymer is a long molecule composed of connected subcomponents called monomers. Mathematically, we can consider polymers as being embedded into a discretised space in order to i) obtain integer answers to questions like 'how many configurations of the polymer are there?', and ii) bring to bear a range of combinatorial tools. To reduce the complexity of the problem, we can ignore the detailed internal structure of the polymer, and just focus on its overall shape and connectivity. These ideas lead to models of polymers as discretised random walks, which were first studied by chemists like Flory [1] and have since become classic.

In this project we investigate the 2D propagation of a single polymer in a slit using directed walks on the square lattice - broadly speaking, walks that must move forward along the x axis at each step. These combinatorial objects naturally lend themselves to being studied with generating functions, which double as the partition functions of statistical mechanics, leading to some results regarding the physics of the system.

Three models are considered in this report. They are distinguished by the types of interactions they are equipped with, and are ordered by increasing complexity. In fact, each model subsumes the previous models - that is, each earlier model is one of the later models with restrictions on the interaction parameters. This does not turn out to be redundant, since in analysing later models, the simpler earlier models will often need to be dealt with as a separate case. The overall analysis of each of the models follows broadly the same steps, similar to work done by Owczarek et al [2] and Wong et al [3], although the complexity of the problem naturally increases each time.

2 Background

We present key concepts and results that will be used in this report. This is a truncated version of the presentation in my supervisor's PhD thesis [4], with many theorems and definitions drawn from Flajolet and Sedgewick [5].

2.1 Combinatorics

Definition 1 *Let $\mathcal{S}$ be a finite set of vectors in $\mathbb{Z}^2$. A general walk ϕ on $\mathbb{Z}^2$ is a sequence of lattice points $\phi = v_0 v_1 \dots v_n$, $v_i \in \mathbb{Z}^2$, where each step $v_{i+1} - v_i \in \mathcal{S}$. We call $\mathcal{S}$ the step set for this walk.*

The length of the walk n is denoted by $|\phi|$. We adopt the convention that $v_0 = (0, 0)$, and refer to walks generated from the step set $\mathcal{S} = \{(1, -1), (1, 1)\}$ as *directed walks*. This step set causes the walk to propagate in the positive x direction, and automatically makes the walk 'self-avoiding', i.e. $v_i \neq v_j$ for $i \neq j$.

To represent a polymer propagating down a slit, we fix $w \in \mathbb{N}$ and restrict the allowed vertices of the directed walk to the region

$$\{(x, y) \in \mathbb{Z}^2 \mid 0 \leq y \leq w\}.$$

We call w the width of the slit.

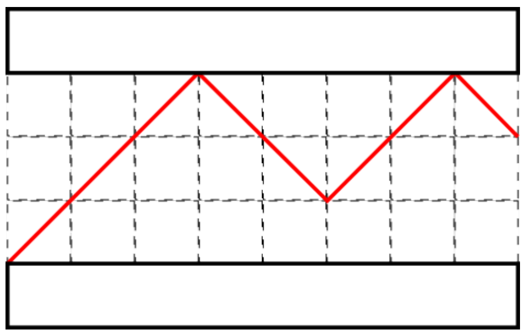


Figure 1: A directed walk of length 8 confined to a slit of width 3

Definition 2 *A combinatorial class $\mathcal{A}$ is a finite or countable set with a size function $|\,.\,| : \mathcal{A} \to \mathbb{Z}_{\geq 0}$ such that the number of elements of $\mathcal{A}$ of any given size is finite.*

We denote the number of elements in $\mathcal{A}$ of size n by A_n. Then the second condition above is that A_n is finite for all nonnegative integers n.

In this report, our combinatorial class $\mathcal{W}$ is the set of directed walks in the slit. Then W_n will be the number of walks in $\mathcal{W}$ with length n, i.e. the number of walks terminating on an x-coordinate of n. Note that there are no duplicate copies of the same walk in $\mathcal{W}$.

Definition 3 *Given a combinatorial class $\mathcal{A}$, its ordinary generating function is the formal power series*

$$A(z) = \sum_{n=0}^{\infty} A_n z^n.$$

A generating function is a way of encoding a sequence (a_n) of numbers by treating them as the coefficients of a power series. They are a central tool in combinatorics, and in particular are useful for solving recurrence relations.

For a formal power series $f(z) = \sum f_n z^n$, we will use the notation $[z^n]f(z)$ to refer to f_n, the z^n coefficient of $f(z)$. In particular, we have $[z^0]f(z) = f(0)$ - the constant coefficient can be extracted by evaluating $f(z)$ at $z = 0$.

For our purposes we will need to make our generating functions multivariate. First, we introduce notation for functions on $\mathcal{W}$ that can capture aspects other than just walk length.

Definition 4 *For a combinatorial class $\mathcal{A}$, a multidimensional parameter $\chi = (\chi_1, \chi_2, \ldots, \chi_d)$ on the class is a function $\mathcal{A} \to \mathbb{Z}^d_{\geq 0}$. The counting sequence of $\mathcal{A}$ with respect to the size and χ parameters is the multi-index sequence*

$$A_{n,k_1,k_2,\ldots,k_d} = |\{a \in \mathcal{A} \mid |a| = n, \chi_i(a) = k_i \ \forall\ 1 \leq i \leq d\}|$$

To illustrate, we frequently use the function $\chi : \mathcal{W} \to \mathbb{Z}_{\geq 0}$ such that $\chi(\phi)$ gives the y-coordinate of the terminating vertex v_n of ϕ (we will later restrict walks to the region $y \geq 0$). Then $W_{n,h}$ would be the number of walks that end on (n, h).

Below we use the notation $\mathbf{u} = (u_1, \ldots, u_d)$, $\mathbf{k} = (k_1, \ldots, k_d)$, and $\mathbf{u}^{\mathbf{k}} = u_1^{k_1} \ldots u_d^{k_d}$.

Definition 5 *Given a counting sequence $(A_{n,\boldsymbol{k}})$, its multivariate ordinary generating function is the formal power series*

$$A(z, \boldsymbol{u}) = \sum_{n,\boldsymbol{k}} A_{n,\boldsymbol{k}} \boldsymbol{u}^{\boldsymbol{k}} z^n$$

This generating function can be equivalently expressed as a summation over elements in the combinatorial class

$$A(z, \mathbf{u}) = \sum_{a \in \mathcal{A}} \mathbf{u}^{\chi(a)} z^{|a|}.$$

2.2 Statistical mechanics

Statistical mechanics is a field of physics which studies microscopic systems with a large number of degrees of freedom, and connects these microscopic behaviours with bulk macroscopic properties. The large number of degrees of freedom involved, such as in our model for the propagation of a long polymer, means a probabilistic treatment is needed.

We take the statistical ensemble of our physical system to be precisely $\mathcal{W}$ - in other words, the set of walks in the slit are taken to represent all possible physical configurations of our polymer, with each walk corresponding to one possible microstate.

Definition 6 *For a statistical ensemble consisting of the set of walks $\mathcal{W}$, the grand canonical generating function is*

$$S(z, \boldsymbol{u}) = \sum_{\phi \in \mathcal{W}} \boldsymbol{u}^{\chi(\phi)} z^{|\phi|}.$$

Definition 7 *Let $\mathcal{W}_n \subset \mathcal{W}$ be the set of walks of size n. The canonical partition function is defined*

$$Z_n(\boldsymbol{u}) = \sum_{\phi \in \mathcal{W}_n} \boldsymbol{u}^{\chi(\phi)}$$

The grand partition function is the same as our multivariate generating function, where each walk in $\mathcal{W}$ represents one microstate. Physically, the grand partition function is an algebraic representation of all microstates within the ensemble. The canonical partition function represents the sum of the 'weights' given to microstates of a certain length n. So we have the relation

$$S(z, \mathbf{u}) = \sum_{n \geq 0} Z_n(\mathbf{u}) z^n,$$

and therefore

$$[z^n] S(z, \mathbf{u}) = Z_n(\mathbf{u}).$$

The weight of a certain microstate is the relative probability that the system is in this microstate at any given time. In classical Boltzmann statistics, a state ϕ that has an associated energy of E_ϕ is given the weight $\exp\left(-\frac{E_\phi}{k_B T}\right)$, where k_B is the Boltzmann constant and T is the temperature. So we have

$$Z_n = \sum_{\phi \in \mathcal{W}_n} \exp\left(\frac{-E_\phi}{k_B T}\right) = \sum_{\phi \in \mathcal{W}_n} \prod_{i=1}^{d} u_i^{\chi_i(\phi)}.$$

Hence our variables $\mathbf{u} = u_1 \ldots u_d$ have a thermodynamic interpretation as the Boltzmann weight associated with one physical interaction of a particular type: $u_i = \exp\left(-\frac{\epsilon_i}{k_B T}\right)$, where ϵ_i is the interaction energy. The exponent of u_i, $\chi_i(\phi)$, represents the number of times this particular interaction occurs for the microstate ϕ. The total energy associated with microstate ϕ is $E_\phi = \sum_{i=1}^{d} \epsilon_i \chi_i(\phi)$. Note that this interpretation requires that our interaction parameters u_i are always positive.

Definition 8 *For a physical model with grand canonical partition function $S(z, \boldsymbol{u}) = \sum_{n\geq 0} Z_n(\boldsymbol{u}) z^n$, the (limiting) free energy of the system is defined as* [1]

$$\kappa(\boldsymbol{u}) = \limsup_{n\to\infty} \frac{1}{n} \log(Z_n(\boldsymbol{u})).$$

The limiting free energy of the system is an example of a macroscopic property that can be derived from analysis of the microstates.

Definition 9 *Given a model in a slit of width w with free energy $\kappa(w)$, the effective force on the walls due to the polymer is*

$$\mathcal{F}(w) = \frac{\partial \kappa(w)}{\partial w}.$$

Another macroscopic property of the system is the push or pull exerted on the walls. In particular, we are interested in finding 'zero force curves' - an equation relating the various interaction parameters in $\mathbf{u}$, such that when it is satisfied, we have $\mathcal{F}(w) = 0$, and no force is exerted on the walls. In practice w is always integral, so we will 'discretise' this derivative.

2.3 Analytic properties

The following theorems allow us to express the free energy in a much more convenient form, relating the free energy to analytic properties of the generating functions.

Theorem 1 (Pringsheim's Theorem) *If f(z) is representable at the origin by a series expansion that has non-negative coefficients and a radius of convergence R_z, then the point $z_c = R_z$ is a singularity of $f(z)$.*

This theorem holds for all ordinary generating functions. The point z_c is known as a *dominant singularity* of $f(z)$ - it is a singularity of the smallest magnitude. In this report we are only concerned with this dominant singularity on the positive x axis, so we will refer to it as *the* dominant singularity.

Definition 10 *A sequence of numbers (a_n) is said to be of exponential order K^n for some real number K if $\limsup_{n\to\infty} |a_n|^{1/n} = K$. We denote this by $a_n \bowtie K^n$.*

[1] Strictly speaking the definition should be $\kappa(\mathbf{u}) = \lim_{n\to\infty} \frac{1}{n}\log(Z_n(\mathbf{u}))$ - defining it the way we have allows us to ignore some details about convergence.

In this case, for any $\epsilon > 0$, the number $|a_n|$ exceeds $(K-\epsilon)^n$ infinitely often, and $(K+\epsilon)^n$ finitely often. K is called the growth rate of the sequence.

Theorem 2 (Flajolet and Sedgewick, page 240) *If $f(z)$ is analytic at 0, and R_z is the modulus of the singularity closest to the origin, then the coefficient $f_n = [z^n]f(z)$ satisfies*

$$f_n \bowtie \left(\frac{1}{R_z}\right)^n.$$

An important general principle in analytic combinatorics is that the location of a function's singularities dictates the growth of its coefficients.

So now let $z_c(\mathbf{u})$ be the dominant singularity of the grand partition function $S(z, \mathbf{u})$ - the existence of which is guaranteed by Pringsheim's theorem. By Theorem 2 above, $Z_n(\mathbf{u}) \bowtie \left(\frac{1}{z_c(\mathbf{u})}\right)^n$. So now we may write the free energy in terms of the dominant singularity:

$$\kappa(\mathbf{u}) = -\log(z_c(\mathbf{u})).$$

Some final remarks on generating functions and their singularities: the problem of propagating directed walks can be alternatively formulated using a transfer matrix method. My project partner employed this approach, and its specifics will be discussed in the Appendix. Two results relevant to our generating function approach arise conveniently from the transfer matrix perspective, and are summarised below. The first result guarantees that all of the generating functions we deal with are going to be *rational* functions - ratios of polynomials in z. We will later use this fact to argue that we can ignore any apparent square root type singularities in the generating function.

The second result is that for each slit width, the generating functions we deal with will have the same radius of convergence, and hence the same dominant singularity z_c. More specifically, instead of finding the dominant singularity of the overall grand partition function of all walks $S(z, \mathbf{u})$, we can just as well look for the dominant singularity of the generating function of walks that end at some specific height $y = h$. In fact, this proves to be simpler - in the following work, we will always be searching for the dominant singularity of $D_0(z)$ - the generating function of walks terminating back on $y = 0$.

3 Walk with stiffness parameter

We begin our investigation with a simple model with only one interaction type to illustrate the general process that will be used. For this model, set $\mathbf{u} := (c, s)$. $\chi_1(\phi)$, the exponent of c, is the number of consecutive pairs of up or down steps in ϕ. We call this a stiffness interaction. $\chi_2(\phi)$, the exponent of s, we set equal to the y-coordinate of the terminating vertex of ϕ. We are only interested in the former as a physical interaction - the latter is used as a mathematical tool akin to z rather than as a Boltzmann weight.

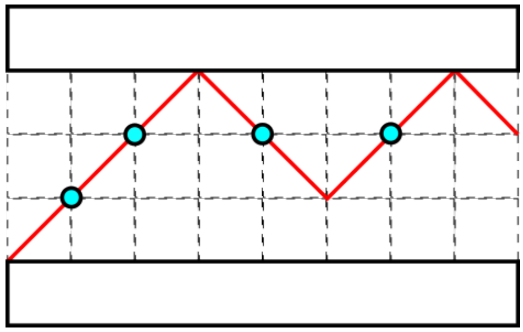


Figure 2: This walk has 4 stiffness points, and contributes the term $+c^4s^2z^8$

3.1 Generating function

Let $\mathcal{W}$ to be the set of all walks for this model. By convention they all originate at $(0,0)$, but no restrictions are imposed their terminating lattice point. Within $\mathcal{W}$ we have the set of walks such that the final step is an up step, which we will call $\mathcal{U}$, and the set of walks such that the final step is a down step, which we call $\mathcal{D}$. Note that the trivial 0-length walk consisting of the single vertex $(0,0)$ is included in neither of these sets. For our purposes it is consistent to place it into the $\mathcal{D}$ set, since all other walks ending on $y = 0$ must be in $\mathcal{D}$.

Let $U(z, s; c)$ be the grand partition function for $\mathcal{U}$, and $D(z, s; c)$ be the grand partition function for $\mathcal{D}$. Then we have the relations

$$U(z, s; c) = zsD(z, s; c) + zscU(z, s; c) - zs^{w+1}c[s^w]U(z, s; c) \tag{1}$$

$$D(z, s; c) = 1 + \frac{zc}{s}D(z, s; c) + \frac{z}{s}U(z, s; c) - \frac{zc}{s}[s^0]D(z, s; c). \tag{2}$$

These come from a column by column construction. With regard to equation (1), every $\mathcal{U}$ walk is made by appending an up step to an existing walk in $\mathcal{U}$ or $\mathcal{D}$, contributing $zscU(z, s; c)$ and $zsD(z, s; c)$ respectively. Finally, appending an up step to a $\mathcal{U}$ walk terminating on $y = w$ will take it outside the slit, so we need to cancel this contribution via $-zs^{w+1}c[s^w]U(z, s; c)$. $D(z, s; c)$ is constructed analogously, except the trivial 0-walk cannot be constructed by appending a step to a prior walk, and so is added separately as $+1$.

Let us write $D_0(z;c)$ for $[s^0]D(z,s;c)$, and analogously for general powers of s, as well as $U_h(z;c) = [s^h]U(z,s;c)$. The aim is to isolate $D_0(z;c)$ to obtain an explicit, closed form expression. From (2) we get

$$D(z,s;c) = \frac{1}{s-zc}\left(s + zU(z,s;c) - zcD_0(z;c)\right), \tag{3}$$

and substituting into (1) gives

$$\left(1 - zsc - \frac{z^2 s}{s-zc}\right)U(z,s;c) = \frac{zs^2}{s-zc} - \frac{z^2 sc}{s-zc}D_0(z;c) - zs^{w+1}cU_w(z;c). \tag{4}$$

The expression $K(z,s;c) = \left(1 - zsc - \frac{z^2 s}{s-zc}\right)$ is called the *kernel*, and we now use the *kernel method* to turn this one equation with three unknown functions into two equations with two unknown functions. The kernel is quadratic in s, and we find distinct roots

$$\hat{s}_{\pm}(z;c) = \frac{1 - z^2 + z^2c^2 \pm \sqrt{-4z^2c^2 + (-1 + z^2 - z^2c^2)^2}}{2zc} \tag{5}$$

such that $K(z,\hat{s};c) = 0$.

Now, if these expressions for $\hat{s}$ result in $U(z,\hat{s};c)$ converging as a power series in z, then this substitution is valid and eliminates the left hand side from equation (4). Indeed this is the case for both $\hat{s}_{\pm}$. We have $\hat{s}_- = cz + O(z^3)$ and $\hat{s}_+ = \frac{1}{cz} - \frac{z}{c} + O(z^3)$. Let $[z^k]U(z,s;c) = P_k(s;c)$. The height of a length k walk is at most k, and so $P_k(s;c)$ is a polynomial in s of degree (at most) $\min\{k,w\}$. Note when $k > w$ and k and w have opposite parity, the degree will be $w-1$, since a length k walk will not be able to end at height w. Hence

$$z^k P_k(\hat{s}_-) = O(z^k) \tag{6}$$

$$z^k P_k(\hat{s}_+) = \begin{cases} O(1) & k \le w \\ O(z^{k-w}) & k > w. \end{cases} \tag{7}$$

Then $U(z,\hat{s}_-;c) = \sum_{k=0}^{\infty} P_k(\hat{s}_-)z^k$ and $U(z,\hat{s}_+;c) = \sum_{k=0}^{\infty} P_k(\hat{s}_+)z^k$ both produce convergent power series in z, as their coefficients $[z^n]U(z,\hat{s}_{\pm};c)$ come from a sum of finitely many terms $z^k P_k(\hat{s})$.

There is a symmetry between the two solutions, $\hat{s}_+ = \frac{1}{\hat{s}_-}$. So without loss of generality we substitute in the two solutions $\hat{s}$ and $\frac{1}{\hat{s}}$ into (4) to eliminate the left hand side and get

$$0 = 1 - \frac{zc}{\hat{s}}D_0(z;c) - \hat{s}^w c\left(1 - \frac{zc}{\hat{s}}\right)U_w(z;c) \tag{8}$$

$$0 = 1 - z\hat{s}cD_0(z;c) - \frac{c}{\hat{s}^w}\left(1 - zc\hat{s}\right)U_w(z;c). \tag{9}$$

$U_w(z;c)$ can now be eliminated to obtain

$$D_0(z;c) = \frac{\hat{s}^{2w}(\hat{s}-cz)+\hat{s}(c\hat{s}z-1)}{cz(\hat{s}^{2w+1}(\hat{s}-cz)+(c\hat{s}z-1))}. \tag{10}$$

Note that in this process we could have replaced $U(z,s;c)$ instead of $D(z,s;c)$. This would have lead to

$$\left(1-\frac{zc}{s}-\frac{z^2}{1-zsc}\right)D(z,s;c) = 1-\frac{z^2s^wc}{1-zsc}U_w(z;c)-\frac{zc}{s}D_0(z;c). \tag{11}$$

This kernel has the same roots $\hat{s}$ as the previous one. The two kernels are related by the transformation $s \to \frac{1}{s}$. Applying the kernel method yields the same D_0 as above. Heuristically, this symmetry in s arises due to the fact that in the large limit, our system is invariant with respect to flipping the slit upside-down - a transformation that requires taking s^h to s^{w-h}.

3.2 Discussion

We can plug in the explicit form of $\hat{s}$ into the above equation to obtain the generating function. This gives a rather complicated expression:

$$-\frac{-\frac{\left((c^2-1)z^2-\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1\right)^w}{-(c^2-1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1}-\frac{\left((c^2-1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1\right)^w}{(c^2-1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}-1}}{c^2z^2\left(\frac{\left((c^2-1)z^2-\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1\right)^w}{-(c^2+1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1}+\frac{\left((c^2-1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}+1\right)^w}{(c^2+1)z^2+\sqrt{(c^2-1)^2z^4-2(c^2+1)z^2+1}-1}\right)}. \tag{12}$$

With this formula, for any given value of w, can take power series and calculate arbitrarily many terms, to know exactly how many different walks there are of each type of any given length.

The problem of finding the singularities analytically looks to be difficult. In particular, from later results we know that this model contains has no points where there is zero force, which means we do not get a nice width independent dominant singularity at any point. In order for a zero force curve to exist, there must be some 'incentive' for the walls to remain close together. No such incentive exists in this model, but in later models, wall interaction parameters with value > 1 will do the trick. Without the promise of nice algebraic simplification here, we move on from this model.

4 Stiffness parameter and wall interaction

Let us add an extra interaction to the model above. Let $\mathbf{u} := (a,c,s)$. The extra parameter a represents the interaction of the polymer with the wall. The exponent of a counts the number of times the walk touches either the $y=0$ or the $y=w$ wall. Note the initial contact at $(0,0)$ is not counted.

4.1 Generating function

The recurrence relation from the previous model gains a few extra boundary terms - specifically, the terms with functions subscripted with $w-1$ and 1.

$$\begin{aligned} U(z,s;a,c) &= zs(D(z,s;a,c)+cU(z,s;a,c)) + zs^w(a-1)D_{w-1}(z;a,c) \\ &\quad + zs^w c(a-1)U_{w-1}(z;a,c) - zs^{w+1}cU_w(z;a,c) \qquad (13) \\ D(z,s;a,c) &= 1+\frac{z}{s}(cD(z,s;a,c)+U(z,s;a,c)) + zc(a-1)D_1(z;a,c) \\ &\quad + z(a-1)U_1(z;a,c) - \frac{zc}{s}D_0(z;a,c) \qquad (14) \end{aligned}$$

For instance, in the first equation, we need to add an a factor every time the up walk touches $y=w$. So we replace $zs^wD_{w-1}(z;a,c)$ with $zs^waD_{w-1}(z;a,c)$, and $zs^wcU_{w-1}(z;a,c)$ with $zs^wacU_{w-1}(z;a,c)$.

There are eight unknown functions here. We can obtain additional relations by taking the $[s^0]$ and the $[s^w]$ coefficients of the above:

$$U_w(z;a,c) = z(D_{w-1}(z;a,c)+cU_{w-1}(z;a,c)) + z(a-1)D_{w-1}(z;a,c) + zc(a-1)U_{w-1}(z;a,c) \qquad (15)$$

$$D_0(z;a,c) = 1 + z(cD_1(z;a,c)+U_1(z;a,c)) + zc(a-1)D_1(z;a,c) + z(a-1)U_1(z;a,c). \qquad (16)$$

Rearrangement gives

$$cD_1(z;a,c)+U_1(z;a,c) = \frac{D_0(z;a,c)-1}{za} \qquad (17)$$

$$cU_{w-1}(z;a,c)+D_{w-1}(z;a,c) = \frac{U_w(z;a,c)}{za}. \qquad (18)$$

We can now eliminate four of the unknowns $D_1, U_1, D_{w-1}, U_{w-1}$ from the original equations.

$$D(z,s;a,c) = \frac{1}{a} + \frac{z}{s}(cD(z,s;a,c)+U(z,s;a,c)) + \left(1-\frac{1}{a}-\frac{zc}{s}\right)D_0(z;a,c) \qquad (19)$$

$$U(z,s;a,c) = zs(cU(z,s;a,c)+D(z,s;a,c)) + s^w\left(1-\frac{1}{a}-zsc\right)U_w(z,s;a,c) \qquad (20)$$

Now we proceed as in the previous model, by eliminating one of U or D, and then isolating the kernel

$$\begin{aligned} \left(1-zsc-\frac{z^2s}{s-zc}\right)U(z,s;a,c) &= \frac{zs^2}{a(s-zc)} + \frac{zs^2}{s-zc}\left(1-\frac{1}{a}-\frac{zc}{s}\right)D_0(z;a,c) \\ &\quad + s^w\left(1-\frac{1}{a}-zsc\right)U_w(z;a,c). \qquad (21) \end{aligned}$$

Note the kernel is the same as before, so we obtain the same roots $\hat{s}$. This is because the kernel captures the 'bulk' behaviour inside the slit, which is unchanged, whereas added boundary terms end up on the equation right hand side. Once again, use the two roots $\hat{s}$ and $\frac{1}{\hat{s}}$ to get two equations, and solve for D_0:

$$D_0(z;a,c) = \frac{\hat{s}^{2w-1}(\hat{s}-cz)(1+a(c\hat{s}z-1)) - \hat{s}((a-1)\hat{s}-acz)(c\hat{s}z-1)}{\hat{s}^{2w-1}(\hat{s}-cz)(1+a(c\hat{s}z-1))^2 + ((a-1)\hat{s}-acz)^2(c\hat{s}z-1)}. \tag{22}$$

It is easily verified that substituting $a = 1$ recovers equation (10).

4.2 Zero force curve

From numerical results obtained by my project partner [6], we expect a zero force curve $c = a - 1$. That is, for values (a, c) on this line, we have

$$\begin{aligned} \mathcal{F}(w) &= \frac{\partial \kappa(w)}{\partial w} \\ &\approx \kappa(w+1) - \kappa(w) \\ &= \log(z_c(w)) - \log(z_c(w+1)) \\ \mathcal{F}(w) = 0 &\iff z_c(w) = z_c(w+1) \end{aligned}$$

a width independent dominant singularity. We would like to verify this analytically. In the simplest case $w = 1$, the generating function is

$$D_0(z;a,c) = \frac{1}{1-a^2z^2}. \tag{23}$$

There are no c's since no stiffness points are possible. In this case the dominant singularity is the only positive real singularity $z_c = \frac{1}{a}$. In the case $w = 2$, we have

$$D_0(z;a,c) = \frac{az^2-1}{a^2(c^2-1)z^4 + 2az^2 - 1}. \tag{24}$$

Working now on the zero force curve, replacing c with $a - 1$ gives

$$D_{zfc}(z;a) := D_0(z;a,a-1) = \frac{az^2-1}{(a^4-2a^3)z^4 + 2az^2 - 1}. \tag{25}$$

The denominator has zeros $\pm\frac{1}{a}$, $\pm\frac{1}{\sqrt{2a-a^2}}$. For $a > 1$, a condition imposed by $c = a - 1 > 0$, we get $\frac{1}{a} < \frac{1}{\sqrt{2a-a^2}}$, so $\frac{1}{a}$ is again the dominant singularity. What we want to show is that for arbitrary w, $\frac{1}{a}$ is a singularity, and is also the smallest positive real singularity.

Similar models treated in the papers mentioned in the introduction suggest the best approach is to work in terms of $\hat{s}$ rather than z. Without loss of generality, in equation (22), let us take $\hat{s}$ to be

$$\hat{s}_- = \frac{1 - z^2 + z^2c^2 - \sqrt{-4z^2c^2 + (-1+z^2-z^2c^2)^2}}{2zc}, \tag{26}$$

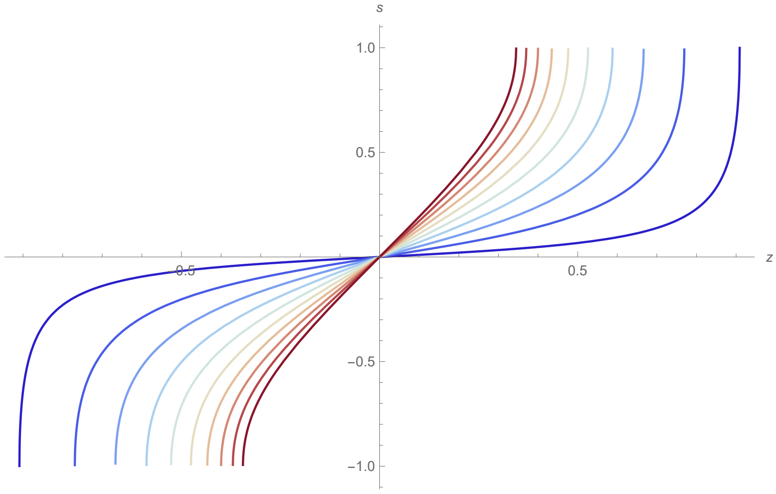
which becomes

$$\frac{1-2az^2+a^2z^2-\sqrt{1-2(2-2a+a^2)z^2+(a-2)^2a^2z^4}}{2(a-1)z} \tag{27}$$

when c is replaced with a.

A plot of $\hat{s}$ as a function of z for various $a > 1$ is given below. In particular, we can see that it is strictly increasing on the domain $z \in [-\frac{1}{a}, \frac{1}{a}]$, with range $\hat{s} \in [-1, 1]$. So on this restricted z domain

Figure 3: $\hat{s}$ vs z for various a



there is an inverse function, and we can replace z with a function in $\hat{s}$. Inverting equation (27) gives two solutions, and it is easily verified that

$$z = \frac{-1+a+(a-1)\hat{s}^2-\sqrt{-4(a-2)a\hat{s}^2+(1-a-(a-1)\hat{s}^2)^2}}{2(a-2)a\hat{s}} \tag{28}$$

is the right expression, with $\hat{s} \in [-1, 1]$. Equation (22) can now be expressed in one variable:

$$\frac{a\left(s^w-s^{2-w}\right)\left(-s\left(c^2z^2+1\right)+cs^2z+cz\right)+s^{3-w}(csz-1)-czs^w+s^{w+1}}{a^2\left(-s\left(c^2z^2+1\right)+cs^2z+cz\right)\left(s^{1-w}(s-cz)+czs^{w+1}-s^w\right)+2a\left(s^w-s^{2-w}\right)\left(-s\left(c^2z^2+1\right)+cs^2z+cz\right)+s^{3-w}(csz-1)-czs^w+s^{w+1}}. \tag{29}$$

First examine the denominator. The $(\hat{s}^{2w}-1)$ term contributes one factor of $(\hat{s}-1)(\hat{s}+1)$ as well as other complex roots of unity. We can ignore complex values since on the domain $z \in [-\frac{1}{a}, \frac{1}{a}]$, we have real $\hat{s}$. The rest of the denominator is a large w independent section - let's call it $T(\hat{s}; a)$. It looks deceptively complicated - solving $T(\hat{s}; a) = 0$ gives $\hat{s} = -1, 0, 1$. These correspond to zeros at $z = \pm\frac{1}{a}, 0$. So in all, the denominator has a term $(\hat{s}-1)$, along with $T(1; a) = 0$. A plot of $T(\hat{s}; a)$ for various $a > 1$ is included below (Fig. 4).

For completeness we could show that $z = 0$ is removable, but we can know this from the fact that a $z = 0$ singularity would cause our counting series coefficients to grow too fast. Another point is

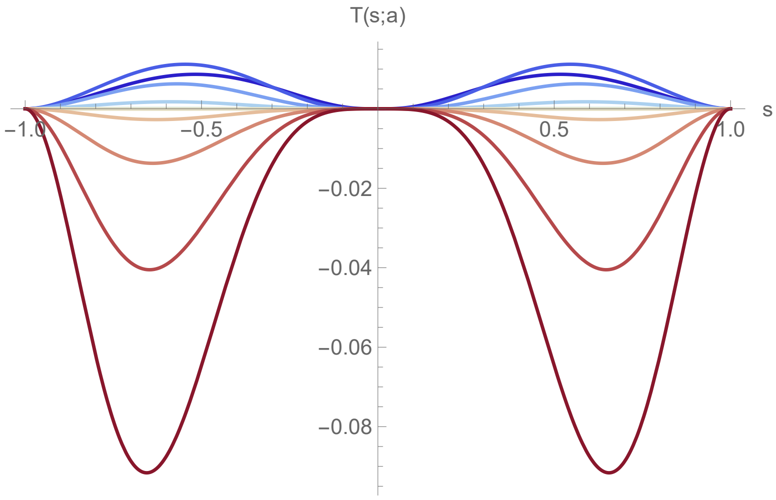


Figure 4: $T(\hat{s};a)$ term on $\hat{s} \in [-1,1]$

there could be square-root type singularities we need to consider - due to square root terms in $T(\hat{s};a)$ and also due to the fact $\hat{s}$ contains square-roots of z. However, as noted in the background, we know that our generating function is rational in z and contains only pole type singularities, so we can ignore these.

Hence, on $z \in [-\frac{1}{a}, \frac{1}{a}]$ the only possibly non removable singularities are $\pm\frac{1}{a}$. The final step is showing that $\frac{1}{a}$ is not removable. The numerator $N(\hat{s};a)$ does have a zero at $\hat{s} = 1$ since $\lim_{\hat{s}\to 1} N(\hat{s};a) = 0$ - however, $\lim_{\hat{s}\to 1} \frac{N(\hat{s})}{\hat{s}-1} = -4(a-2)^3$. So for $a \neq 2$, we are done. The special point $(a,c) = (2,1)$ corresponds to no stiffness parameter. We could deal with this case separately here - however, the model without stiffness has already been dealt with [2], and in this case we have $z_c = \frac{1}{2} = \frac{1}{a}$ as required.

5 Stiffness parameter and different wall interactions

We now differentiate the two wall interactions. Let $\mathbf{u} := (a,b,c,s)$. The a parameter is now the weight of interaction with the bottom wall, and its exponent counts the number of times the walk touches $y = 0$, whereas the b parameter is the weight of interaction with the top wall, and its exponent counts the number of $y = w$ contacts. Again the initial contact at $(0,0)$ is not counted.

5.1 Generating function

Equations (13) and (14) remain largely unchanged - only the a's in (13) are replaced with b's:

$$\begin{aligned} U(z,s;a,b,c) &= zs(D(z,s;a,b,c)+cU(z,s;a,b,c)) + zs^w(b-1)D_{w-1}(z;a,b,c) \\ &\quad + zs^w c(b-1)U_{w-1}(z;a,b,c) - zs^{w+1}cU_w(z;a,b,c) \qquad (30) \\ D(z,s;a,b,c) &= 1 + \frac{z}{s}(cD(z,s;a,b,c)+U(z,s;a,b,c)) + zc(a-1)D_1(z;a,b,c) \\ &\quad + z(a-1)U_1(z;a,b,c) - \frac{zc}{s}D_0(z;a,b,c). \qquad (31) \end{aligned}$$

The derivation then follows the previous section exactly, and we arrive at

$$\begin{aligned} \left(1 - zsc - \frac{z^2 s}{s-zc}\right)U(z,s;a,b,c) &= \frac{zs^2}{a(s-zc)} + \frac{zs^2}{s-zc}\left(1-\frac{1}{a}-\frac{zc}{s}\right)D_0(z;a,b,c) \\ &\quad + s^w\left(1-\frac{1}{b}-zsc\right)U_w(z;a,b,c). \qquad (32) \end{aligned}$$

Applying the kernel method again, we arrive at

$$D_0(z;a,b,c) = \frac{\hat{s}^{2w}(\hat{s}-cz)(1-b+bc\hat{s}z) + \hat{s}^2(c\hat{s}z-1)((1-b)\hat{s}+bcz)}{\hat{s}^{2w}(\hat{s}-cz)(1-a+ac\hat{s}z)(1-b+bc\hat{s}z) + \hat{s}(c\hat{s}z-1)((1-a)\hat{s}+acz)((1-b)\hat{s}+bcz)}. \qquad (33)$$

5.2 Zero force curve

Again, numerical work done by my partner [6] suggests a zero force curve $ab-a-b+1-c^2=0$ for $a,b>1$. The validity of this curve is supported by the fact that it correctly reduces to known curves when setting $a=b$ ($c=a-1$) and $c=1$ ($ab-a-b=0$ [2]). The process of proving of this formula is essentially the same as the previous section, modulo some complications. Again, we begin by plugging in some small w values to see what the dominant singularity is likely to be.

Working on the (hypothesised) zero force curve, we replace b with $1+\frac{c^2}{a-1}$. Define $D_{zfc}(z;a,c) = D_0(z;a,1+\frac{c^2}{a-1},c)$. As before, investigating small values of w suggests the dominant singularity of $D_{zfc}(z;a,c)$ is $z=\frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}}$.

We now prove this. Recall that $\hat{s}_-$ is strictly increasing and hence invertible on $z\in[-\frac{1}{c+1},\frac{1}{c+1}]$. The fact that $\frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}} < \frac{1}{c+1}$ means that our hypothesised dominant singularity, along with any smaller positive real singularities (if they exist), would be contained within the region where we can map z to $\hat{s}$ bijectively. Hence, it will suffice again to replace z with an expression valid on $-\frac{1}{c+1}\le z\le\frac{1}{c+1}$, or $-1\le\hat{s}\le 1$, and look for singularities in $\hat{s}$. The expression is

$$z = \frac{c+c\hat{s}^2-\sqrt{c^2+4\hat{s}^2-2c^2\hat{s}^2+c^2\hat{s}^4}}{2\hat{s}(c^2-1)}, \qquad (34)$$

which is used to obtain $D_{zfc}(z;a,c)$ purely in terms of $\hat{s}$:

$$\frac{bz\left(s^{2w}\left(\frac{1}{b(csz-1)}+1\right)+\frac{s^2(bcz-bs+s)}{b(s-cz)}\right)}{\frac{zs^{2w}(a(csz-1)+1)(b(csz-1)+1)}{csz-1}+\frac{sz((a-1)s-acz)((b-1)s-bcz)}{s-cz}}. \tag{35}$$

Again, the denominator factors very nicely into a w dependent roots of unity term $(\hat{s}^{2w}-1)$ and a w independent term we call $T(\hat{s};a,c)$. The roots of unity term gives the positive real valued zero $z=\frac{1}{c+1}$, which is larger than $\frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}}$. Solving $T(\hat{s};a,c)=0$ yields

$$\hat{s}_1 = 0, \tag{36}$$

$$\hat{s}_2 = \frac{\sqrt{a-1}\sqrt{c^2+a-1}}{\sqrt{a}c}, \tag{37}$$

$$\hat{s}_3 = -\frac{\sqrt{a-1}\sqrt{c^2+a-1}}{\sqrt{a}c}, \tag{38}$$

$$\hat{s}_4 = \frac{\sqrt{a}c}{\sqrt{a-1}\sqrt{c^2+a-1}}, \tag{39}$$

$$\hat{s}_5 = -\frac{\sqrt{a}c}{\sqrt{a-1}\sqrt{c^2+a-1}}. \tag{40}$$

Again $\hat{s}_1$ corresponds to $z=0$, which we assume is removable. Note that the other singularities are reciprocal to each other. Specifically, of the two positive singularities, one will always be in the region $0<\hat{s}\leq 1$ while the other is in $\hat{s}\geq 1$, and analogously for the two negative singularities.

When we map these map to z under (34), we find the corresponding singularities in z

$$z_2 = z_4 = \frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}}, \tag{41}$$

$$z_3 = z_5 = -\frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}}. \tag{42}$$

Since we know at least one of $\hat{s}_2, \hat{s}_4$ is on the invertible domain $-1\leq\hat{s}\leq 1$, then the map back to z is a valid move and $\pm\frac{\sqrt{a-1}}{\sqrt{a}\sqrt{c^2+a-1}}$ will always be a singularity (although possibly removable).

As stated prior, we can be sure the above two are a superset of non removable singularities on the domain $z\in[-\frac{1}{c+1},\frac{1}{c+1}]$. It remains to show they are not removable. This is done by plugging $\hat{s}_2$ and $\hat{s}_4$ into the numerator of (35) and verifying that the numerator is nonzero.

In the case of $\hat{s}_2$, the numerator becomes

$$\frac{2(a-1)^{w+2}(1-2a+a^2-c^2)(c^2-1)^3(c^2+a-1)^w}{a^{w+2}c^{2w+3}}. \tag{43}$$

The first and last term in the numerator is always nonzero in our domain of interest. Exceptions will occur when $c=a-1$ (due to the second term) and when $c=1$ (due to third term). But these reduce to previously completed simpler models where $b=a$ or where there is no stiffness.

In the case of $\hat{s}_4$, the numerator becomes

$$-\frac{2ac^3(1-2a+a^2-c^2)(c^2-1)^3}{(a-1)(c^2+a-1)^3}. \tag{44}$$

The denominator is always nonzero on our domain, and again the only exceptions are when $c = a-1$ or $c = 1$. So we are done - the hypothesised dominant singularity has been validated and $ab - a - b + 1 - c^2 = 0$ is the zero force curve for this model.

6 Conclusion

The two zero force curves ($c = a - 1$, $ab - a - b + 1 - c^2 = 0$) that were found numerically were not only correct, but within reach of analytic verification. In particular, working in the $\hat{s}$ variable instead of z was crucial to finding the right factorisations and simplifications, as was the case in [2].

More work will be conducted to further flesh out the second and third models. In particular, we will investigate the free energy κ on regions other than the zero force curve, employing asymptotic analysis to identify the regions in which certain physical behaviours occur.

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Appendix A Transfer matrix method

In this section we will show how the transfer matrix perspective leads to the two results claimed in Section 2.3. Again we borrow definitions and theorems from Flajolet and Sedgewick [5], and the presentation in [4].

Definition 11 *A directed graph (or digraph) G is a pair (V, E), where V is its vertex set and $E \subset V \times V$ is its edge set.*

We take $V = \{1, 2, \ldots, n\}$ and allow self-loops (edges of the form (e, e)).

Given a digraph $G = (V, E)$, a weighting for its edges can be given by a weight function $w : E \to \mathbb{R}_{>0}$. We can also define a *size function* $\sigma : E \to \mathbb{N}$. For a graph with a size function and a weight function, we can associate a transfer matrix $T(z)$ with components defined

$$T(z)[i,j] = \sum_{e \in Edge(i,j)} w(e) z^{\sigma(e)}$$

where $Edge(i, j)$ is the set of edges from i to j.

As an example, the following digraph with weights and sizes as indicated yields the following transfer matrix:

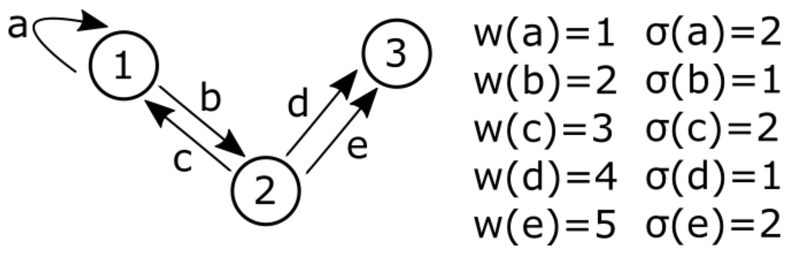

Figure 5: Weighted and sized digraph

$$T(z) = \begin{bmatrix} z^2 & 2z & 0 \\ 3z^2 & 0 & 4z + 5z^2 \\ 0 & 0 & 0 \end{bmatrix}.$$

Now for our system of directed walks in a slit of width w, we let each of the possible $2w$ steps be a node. That is, the set of states is defined by the last step taken. The edges of the graph will represent transitions between these steps. Our size function will be relatively boring - $\sigma(e) = 1$ for every edge - since each step increases the power of z by 1. Our weight function will be given by the additional Boltzmann weight parameters contributed by each step.

This is best understood with an illustration. Take $w = 3$. Then we have 6 nodes, corresponding to steps as indicated. Let us add in a stiffness parameter c and wall interaction a. Then the transfer

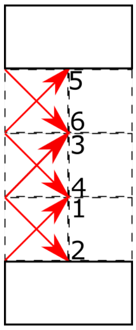

Figure 6: 6 allowed steps

matrix will be

$$T(z) = \begin{bmatrix} 0 & az & cz & 0 & 0 & 0 \\ z & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & z & acz & 0 \\ 0 & acz & z & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & z \\ 0 & 0 & 0 & cz & az & 0 \end{bmatrix}.$$

The transfer matrix captures the ‘change’ in the generating function of a walk when another step is added on. More specifically, $T(z)[i,j]$ are the extra terms multiplied to the generating function of a walk with a final step i when it has a step j appended to the end. Therefore, if $W_n(z)$ is a matrix such that $W_n(z)[i,j]$ is the generating function of all walks of length n with first step i and last step j, we would have

$$W_{n+1}(z) = W_n(z)\ T(z),$$

since $W_{n+1}(z)[i,j] = \sum_k W_n(z)[i,k]\ T(z)[k,j]$ - or in other words, we take the length n path beginning with an i step and ending with a k step, and add on whatever terms that appending a j step to a k step would contribute.

Consider $W_1(z)$, the matrix encoding walks of length 1. It would be very nearly an identity matrix

$$W_1(z) = \begin{bmatrix} z & 0 & 0 & 0 & 0 & 0 \\ 0 & az & 0 & 0 & 0 & 0 \\ 0 & 0 & z & 0 & 0 & 0 \\ 0 & 0 & 0 & z & 0 & 0 \\ 0 & 0 & 0 & 0 & az & 0 \\ 0 & 0 & 0 & 0 & 0 & z \end{bmatrix}.$$

Then the matrix capturing walks of all lengths (ignoring 0-length walks) would be

$$\sum_{n=1}^{\infty} W_n(z) = W_1(z) + W_1(z)T(z) + W_1(z)T(z)^2 + W_1(z)T(z)^3 + \dots \quad (45)$$

$$= W_1(z)(I + T(z) + T(z)^2 + T(z)^3 + \dots). \quad (46)$$

Naively, $I + T(z) + T(z)^2 + T(z)^3 + \dots \to 1/(I - T(z))$ - the following theorem tells us this is in fact true.

Theorem 3 (Flajolet and Sedgewick, page 357) *Given a sized graph with associated transfer matrix $T(z)$, the ordinary generating function $F^{<i,j>}(z)$ of the set of paths from i to j, where z counts the size, is the i, j entry of the matrix $(I - T(z))^{-1}$. That is,*

$$F^{<i,j>}(z) = (I - T(z))^{-1}[i, j].$$

In our case, the generating function of the set of paths on the graph is slightly different to the generating function of the set of walks in the slit, but only by a difference of a factor of z or az due to $W_1(z)$ and adding in some 1's to account for 0-length walks.

So for instance, our $D_0(z)$ will be related to $F^{<1,2>}(z)$ via $D_0(z) = (W_1(z)F(z))[1, 2] + 1 = zF(z)[1, 2] + 1$, and U_w where our $w = 3$ will be $(W_1(z)F(z))[1, 5] = zF(z)[1, 5]$, where we have let $F(z) = (I - T(z))^{-1}$. From this we know that $D_h(z)$, $U_h(z)$, and indeed $D(z)$, $U(z)$, and $S(z) = D(z) + U(z)$ are all rational functions with respect to z. This is because the entries of $T(z)$ are always polynomials, and in inverting a matrix, we never perform any operations that will cause us to lose this property.

Definition 12 *A non-negative square matrix A is called irreducible if its associated graph is strongly connected. That is, there exists a directed path between any two vertices.*

Clearly our $T(z)$ is irreducible.

Theorem 4 (Flajolet and Sedgewick, page 343) *Let $T(z)$ be an irreducible transfer matrix. Then all entries*

$$F^{<i,j>}(z) = (I - T(z))^{-1}[i, j]$$

have the same radius of convergence in z, R_z.

From this, we have that of the generating functions we mentioned above also have the same radius of convergence. Multiplication by z or az, or having $+1$ added, will not affect the convergence. By Pringsheim's theorem, they will then also all have a singularity at $z = R_z$, which will be the smallest singularity on the positive x axis. Hence, we are justified in looking for the dominant singularity of $D_0(z)$ rather than that of the grand partition function. Essentially what this is saying is in the large limit for walk length, the height we choose for the start and end of our walks does not affect the growth rate of the coefficients.