Enumeration of Polymer Partially Directed Walks on a 2D Lattice using a Generating Function Approach

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Introduction

A polymer is compromised of many interconnected subunits called monomers.

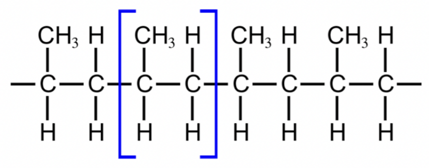


Figure 1. section of propylenepolymer

Long chain polymer structures can be modelled as directed, self avoiding walks embedded into a discretized 2D lattice, where each carbon-carbon bond forms a edge of the walk. We enumerate the number of configurations in a polymer of length n for the propagation of walks both above the wall and within a strip of a lattice

Intramolecular forces lead to attractive and repulsive interactions between the wall and the polymer, which we model with the wall interaction parameter a. We refer to polymers attracted to the wall as the adsorbed phase and those experiencing repulsion as the desorbed phase. Similarly, intermolecular and intramolecular forces influence molecular stiffness and packing, modelled by p

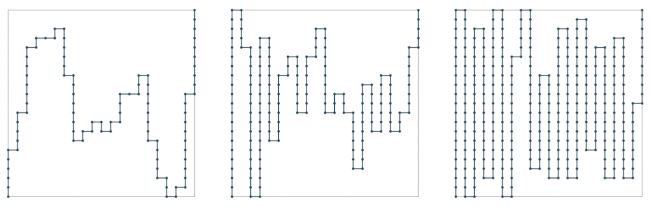


Figure 2. Effects of increasing the vertical stiffness parameter for walk in a strip

Background

Kernel Method: Generating functions are computed through the kernel method. Growth rate is extracted from the singularities. We follow a similar approach to Wong's 2015 paper.

Theorems

Multivariate Ordinary Generating Function For the combinatorial class $\mathscr{A}$, the multi-dimensional parameter ($\chi = \chi_1, \chi_2 \dots \chi_d$) on $\mathscr{A}$ maps the class to $\mathbb{N}^d$ of d-tuples of natural numbers.

$$A_{\{n,k_1 \dots k_d\}} \text{ where } |a| = n, \chi_1(a) = k_1, \chi_2(a) = k_2 \dots \chi_d(a) = d_1 \tag{1}$$

For the sequence $\{A_{n,\mathbf{k}}\}$ is the formal power series

$$A(z, \mathbf{u}) = \sum_{n,\mathbf{k}} A_{n,\mathbf{k}} \mathbf{u}^{\mathbf{k}} z^n \tag{2}$$

Pringsheim's Theorem(Flajolet and Sedgewick) [23], page 240. If $f(z)$ is representable at the origin by a series expansion that has non-negative coefficients and radius of convergence Rz , then the point $z_c = R_z$ is a singularity of $f(z)$ For a ordinary generating function f(z), if f(z) is analytic at 0 then radius of convergence R_z is the modulus of the dominant singularity. The co-efficent $f_n = [z_n]f(z)$ satisfies

$$f_n \bowtie \left(\frac{1}{R_z}\right)^n \tag{3}$$

Methodology

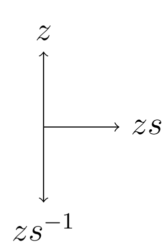
To reduce the complexity, let $H(z, s; a, b, p)$ represent the generating function of walks ending with a horizontal step, $D(z, s; a, b, p)$ all walks ending with a upstep and $U(z, s; a, b, p)$ represent all walks ending with a upstep. We define the variables:

Variable	Interpretation
z	length
s	height (final vertex)
w	strip width

Parameter	Interpretation
a	bottom wall interactions
a	top wall interactions
p	vertical stiffness

By definition, we construct these generating functions by taking an extension of all valid steps from the existing set of walks, and subtracting all invalid steps. For the case of walks in a strip there is the additional subtraction of invalid walks that cross over the upper wall and therefore the functional equation for walks above a wall are a subset of walks in a strip.

Step Set



Functional Equations

$$H(z,s;a,p) = \frac{1}{1-z} + \frac{z}{1-z}(U+D) + \frac{z}{1-z}(a-1)(H_0 + D_0 + s^w H_w + s^w D_w)$$
$$U(z,s;a,p) = H\frac{zs}{1-zsp} + (H_w + pU_w)\frac{zs^{w+1}}{1-zsp}$$
$$D(z,s;a,p) = U\frac{z}{s-zp} - (H_0 + pD_0)\frac{z}{s-zp}$$

Recursive Relations

$$H_0(z;a,p) = 1 + za\left(H_0(z;a,p) + D_0(z;a,p)\right)$$
$$H_w(z;a,p) = za\left(H_w(z;a,p) + D_w(z;a,p)\right)$$

note the trivial walk 1 belongs in neither equation, so it is arbitrarily added into $H(z, s; a, b, p)$

Methodology

Kernel

The kernel $k(z, s; a, p)$ is independent to wall interaction parameters. Computing for when $k(z, s; a, p) = 0$, the roots are quadratic in s

$$K(z,s;p) = 1 - z - \left(\frac{z^2 s}{1-zsp}\right) - \left(\frac{z^2}{s-zp}\right)$$

We find a symmetry relation between s_+ and s_- s.t the roots are inverse proportional. $s_- = \frac{1}{s_+}$

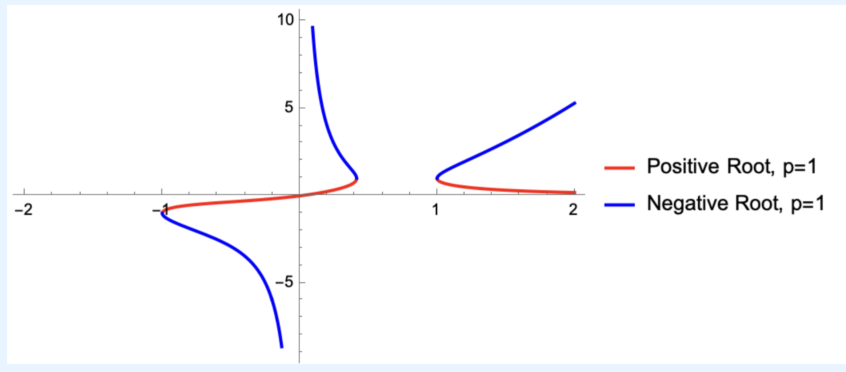


Figure 5. Symmetry of roots

$$s_\pm(z;p) = \left(\frac{1 - z + p^2 z^2 + 2pz^3 -^p 2z^3 \pm \sqrt{-4(pz + z^2 - pz^2)^2 + (1 - z + p^2 z^2 + 2pz^3 - p^2 z^3)^2}}{2(pz + z^2 - z^2)}\right)$$

We need to check if $s_\pm$ are valid by checking that generating functions are convergent. For a walk in a strip of length k, the height is at most k, therefore the polynomial $P_k(z) = [z^k]H(z, s)$ is maximally degree k. Substituting a finite polynomial into a power series will produce trivial convergence. So we only need to verify the above the wall case that is analogous to $w \mapsto \infty$,

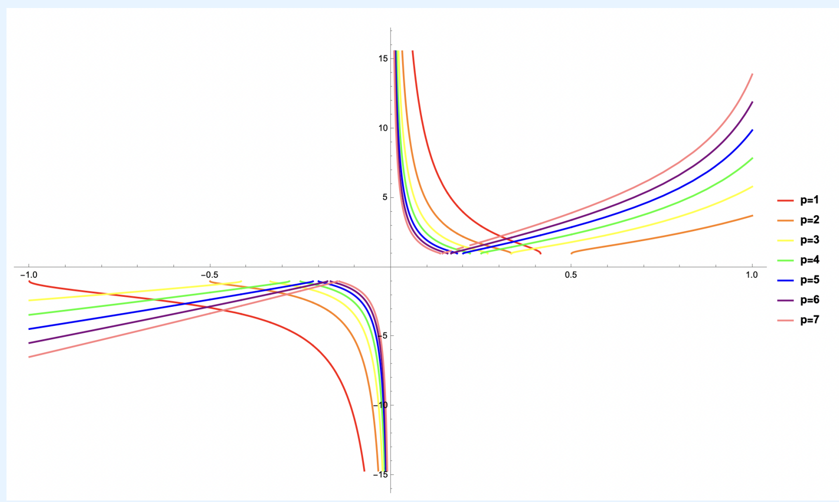


Figure 6. $s_-(z; a, p)$ for varying p against z

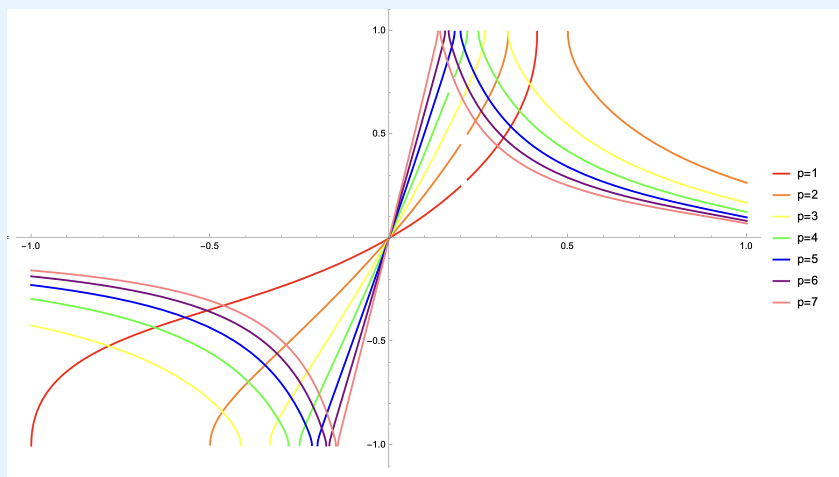


Figure 7. $s_+(z; a, p)$ for varying p against z

Taking a expansion of s with respects to z in our generating function

$$H(z, s_+; a, p) = \sum z^k P_k(s_+)\left(pz + z^2 + O(z^3)\right) = \sum O(z^{2k})$$
$$H(z, s_-; a, p) = \sum z^k P_k(s_-)\left(\frac{1}{bz} - \frac{1}{b^2} + O(z)\right) = \sum O(constant)$$

Therefore, only s_+ is defined by walks above a wall

Results

Generating Functions

To reduce complexity, we analyze the singularities in the subset of walks ending in a horizontal step along the bottom wall $s = 0$. The growth rate ought to remain consistent across all walks in the set and hence consistent across all subsets.

Walks Above Wall Coefficient:

$$H_0(z,s;a,p) = \left(\frac{(s - pz)(1 + zsp - z^2p^2)}{-\hat{s} + a\hat{s} - abz - az^2 + abz^2}\right)$$

Walks in a Strip Coefficient:

$$H_0(z,s;a,p) = \frac{\frac{1}{a^2 s^w}(1 + \frac{zp}{s-zp})(a - 1 - \frac{z(za+p(1-za))}{s-pz}) +}{-\frac{1}{a^2 s^w}(a - 1 - \frac{z(za+p(1-za)}{s-zp})^2 + \frac{s^w}{a^2}(a - 1 - \frac{zs(za+p(1-za))}{1-zsp})^2} \frac{+\frac{s^w}{a^2}(1 + \frac{zp}{\frac{1}{s}-pz})(a - 1 - \frac{zs(za+p(1-za))}{(1-zsp)})}{-\frac{1}{a^2 s^w}(a - 1 - \frac{z(za+p(1-za)}{s-zp})^2 + \frac{s^w}{a^2}(a - 1 - \frac{zs(za+p(1-za))}{1-zsp})^2}$$

Results

Singularities for Walks Above a Wall

There are two sources of singularities: square root and denominator. An exact equation was obtained between a and p where both singularities from the square root and denominator coincide.

$$(a-1)(p-2)^2 = a(5 - \sqrt{9 - 2p + p^2}) + b(2\sqrt{9 - 2p + p^2} - 7)$$

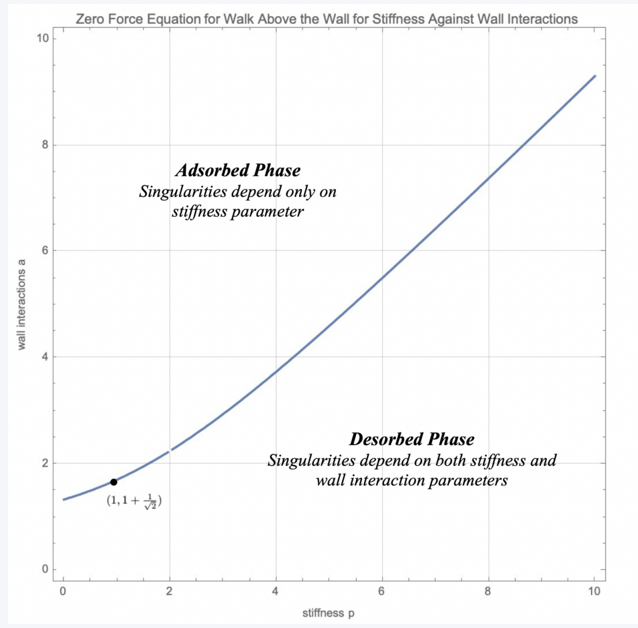


Figure 8. Zero Force Curve for Stifness against Wall Interactions Parameters

region	z_c
absorbed	$z = \left(\frac{1+b-\sqrt{9-2b+b^2}}{2(b-2)}\right)$
desorbed	$-\hat{s} + a\hat{s} - abz - az^2 + abz^2 = 0$

Singularities for Walks in a Strip

The extracted coefficient is rational, given that the associated transfer matrix comprises solely polynomials. With only pole-type singularities present, its dependency is strictly on the denominator.

$$\hat{a}_c(p) = \frac{1}{4}\left(2\sqrt{p^2 - 2p + 9} - \frac{\sqrt{p^2 - 2p + 9}}{p} + 2p + \frac{3}{p} - 1\right)$$

Employing the relationship between a and p as seen in walks above the wall, an exact solution for the zero-force curve was achieved. This curve signifies a point of width independence, where no force is applied to the walls.

$$F(w) = \frac{\partial k(w)}{\partial w}$$
$$F(w) = 0 \iff z_c(w) = z_c(w+1)$$

Equation for the dominant singularity z_c indpendent to both w and a

$$z_c(p) = 1 - \frac{-18 + 18p + 6\sqrt{9 - 2p + p^2} - 6p\sqrt{9 - 2p + p^2}}{2(2 - 3p + p^2)^2} + \frac{5 + 9p - 3\sqrt{9 - 2p + p^2} - 2p\sqrt{9 - 2p + p^2}}{2(2 - 3p + p^2)}$$

The free energy is given by:

$$\mathcal{K} = \log\left(\frac{1}{z_c(p)}\right) \tag{4}$$

Conclusion

The growth rate and free energy exhibit width independence as consequence of the the zero-force curve. This relationship establishes that growth rates for walks in a strip are analogous to walks above a wall, as the dominant singularities coincide.

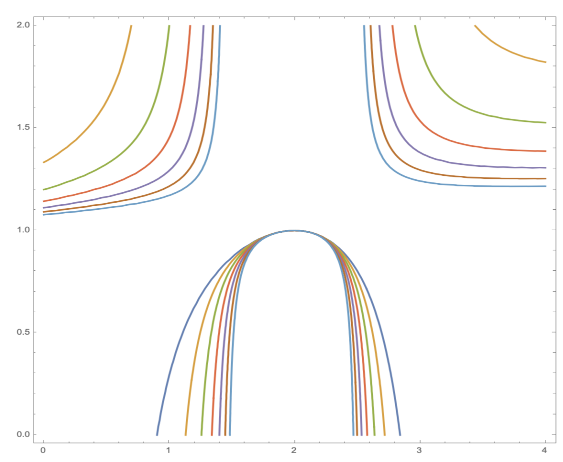


Figure 9. Co-efficent of Generating Function $H(z, s, \hat{a}_c(p), p)$ for varying p

References

[1] Nicholas R Beaton and Aleksander L. Owczarek. Exact solution of weighted partially directed walks crossing a square. *Phy. A: Math. Theor*, pages 1–21, 2023.

[2] Aleksander L. Owczarek. Exact solution for semi-flexible partially directed walks at an adsorbing wall. *J. Stat. Mech*, pages 1–17, 2009.

[3] Thomas Wong. Enumeration problems in directed walk models. *The University of British Coloumbia (Vancouver)*, pages 1–211, 2015.

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