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Sampling Spaces of Thick Polygons

Abstract: Open and closed polygons provide an attractive coarse grained model for many molecular structures. The random selection of polygons of a specified thickness is, however, an objective that has not been achievable until very recently. Here, we give an elementary description of the distinct sampling strategies that have been employed, their limitations, and the new algorithms that now allow one to randomly sample the spaces of open and closed polygons with specified thickness. We observe that the introduction of even a very modest thickness has an immediate and profound effect on the shape, the size, and the type of knot formed.

1.1 Introduction

A polygon in three dimensional Euclidean space consists of a finite sequence of straight line segments, called edges, meeting only at the endpoints of adjacent edges, called vertices. Polygons are closed if they form a loop and are, otherwise, open. Analogous to the ball and rod molecular models, polygons have provided scientifically useful coarse grained models of locally linear molecular structures. These polygons have provided productive coarse grained models of a wide range of molecules: rubber, amber, polyethylene, or other polymer melts or individual DNA chains, or proteins. In some cases, the edge lengths are allowed to vary in length according to a given distribution and, in others, they are required to have a constant length, in some cases reflecting the monomers and bonds of the structure while, in others, reflecting the homogeneity of the persistence (or Kuhn) length of the modeled macromolecule. Similarly, the bending angles between adjacent edges reflect the curvature character of the molecule and a triple of adjacent edges can be used to measure the intrinsic torsion of the chain. Another facet of the modeling challenge is to capture the thickness of the macromolecule or, similarly, the excluded volume of the modeled chains. The notion of excluded volume, introduced by Kuhn [10], was employed by Paul Flory [6] to explain that certain fundamental aspects of polymer physics are a consequence of the fact that a portion of a long polymer can not occupy the same space as another portion of the same polymer. As a result, for example, circular polymer chains can not change their topological knot type, i.e. “crossings are forbidden,” and, furthermore, their properties are distinct from those of infintesimal mathematical polygonal rings.
The properties of excluded volume and thickness have proved to be a particularly challenging facet of the structure to simulate, even in a coarse grained manner, across a meaningful physical range of values.

Our focus will be on the available methods to sample the sets of open and closed polygons with which one may try to access structural information related to the thickness of the configuration. After an overview of how one may define the thickness of a polygon, we will describe these ways in sufficient detail that one may develop an algorithm to implement these methods. The first topic will be the ways in which one samples open and closed polygons without thickness constraints. These are subsequently sorted by thickness with the hope of generating a statistically robust sample for each range of thickness. Unfortunately, the rapid decay of sample size with increasing thickness limits the effectiveness of this method. We will next discuss two new methods that allow one to randomly sample collections of open and closed polygons having any desired thickness and, in conclusion, briefly describe some observations resulting from these new methods.

11.2 Classical Perspectives

The concept of excluded volume was introduced by Kuhn [10] and applied by Flory in the study of polymers [6, 21]. For example, the Kuhn length of polyethylene (PE) is 14 angstroms. Of coarse, the molecule has a cross-sectional molecular diameter as well as steric forces that give it an effective thickness that must be taken into consideration in a model. As noted, this has proved to be quite challenging due to the computational cost of a molecular model and the lack of a cruder, coarse grained, simulation method. If the effects of the excluded volume are neutralized in a given situation, described as being at the theta point, one ignores these interactions and employs the ideal chain model. These are defined as freely joined polygonal chains in which one ignores interactions between edges. We will now describe how one measures the thickness of polygonal chains, how such chains can be easily generated, and the character of the resulting thickness distribution.

11.2.1 Thickness of polygons

We employ the ideas of Rawdon [12, 20], to define the thickness of a polygon in 3-space (which Rawdon calls its injectivity radius). The underlying concept is that of a tubular neighborhood of a smooth curve consisting of the embedded family of discs of radius \( r \) at each point of the curve. The supremum of the radii of the embedded tubular neighborhoods is called the thickness of the curve. Rawdon extended this concept to polygons by taking the minimum, over all vertex angles, of a curvature constraint,
Fig. 11.1: Tubular neighborhoods of the unit equilateral triangle including one of maximal radius $\sqrt{\frac{7}{6}}$, and half the minimum distance between distant edges, taken over all pairs of distant edges, the distal distance constraint. Tubular neighborhoods of an equilateral triangle are illustrated in Figure 11.1 and, of random walks, in Figure 11.2.

11.2.2 Self-avoiding random walks

An embedded open chain with $n$ unit edge lengths and random vertex angles is a self-avoiding random walk, shown in Figure 11.2, is given by a sequence of vertices, $v_i$ with $i = 0, 1, ... n$ or, equivalently, a sequence of edge vectors, $e_j$ with $j = 1, ... n$. These are related by $v_0 = \{0, 0, 0\}$ and $v_i = \sum_{j=1}^{i} e_j$. To randomly generate an $n$ step random walk (or $n$ edge random open polygon) it is sufficient to individually generate the corresponding $n$ edge vectors as follows: select $\theta = 2 \pi \text{ randomreal}[0, 1]$ and $\varphi = \text{ArcCos}[2 \text{ randomreal}[0, 1] - 1]$ to define $e_j = (\sin(\theta) \sin(\varphi), \cos(\theta) \sin(\varphi), \cos(\varphi))$.

11.2.3 Closed polygons: fold algorithm

An embedded closed chain with $n$ unit edge lengths and random vertex angles is a self-avoiding polygon constrained by the requirement that the initial and terminal vertex are equal, i.e. the closure constraint. The satisfaction of the closure constraint is the critical feature of sampling algorithms. The fold method preserves the closure by randomly selecting a pair of non-adjacent vertices to define an axis dividing the polygon into two arcs. One of these arcs is rotated through a random angle and adjoined to the complementary arc to define, following confirmation that resulting configuration is embedded by directly checking for possible edge intersections between edge segments, a new polygon, see Figure 11.3. We also show the result of 100 random folds applied to the 10 edge regular polygon. While its randomness is an open question, the fold algorithm is known to be a transitive algorithm, i.e. one capable of taking any configuration to any other configuration, whose resulting statistics, for example those of
observed knot types or average radius of gyration, are consistent with being random [16, 17].

### 11.2.4 Closed polygons: crankshaft algorithm

The crankshaft method is a computationally attractive algorithm that has also been shown to be transitive and having statistics consistent with randomness [1]. This algorithm randomly selects a pair, larger subset if desired, of edge vectors of an equilat-

![Fig. 11.3: A regular 10 edge polygon, a first fold, and one created from the regular polygon using 100 random folds along axes such as the one indicated.](image)

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**Fig. 11.2**: A 20 step random walk: curvature constraint is 0.041 and the distal distance constraint is 0.071. The 100 step random walk has angle constraint of 0.054 and distal distance constraint 0.026.
Fig. 11.4: A regular 10 edge polygon, a first crankshaft, and one created from the regular polygon using 100 random crankshaft modifications.

eral polygon and defines a segment based at the origin using this ordered sequence of vectors. Following a random rotation about the axis defined by the origin and the endpoint of the segment, one replaces the originally selected edge vector by the corresponding one in the resulting segment. Since the sum of these edge vectors has not changed, the newly defined polygon is closed. If it is embedded, the result is the new polygon, see Figure 11.4. The fact that one only has to modify a small collection of edge vectors, in our case just two, makes the calculations fast as they are explicit as shown in the following formulae.

\[
e_i \mapsto \text{crank}(e_i, e_j, \theta) = \frac{e_i + e_j}{2} + \cos(\theta)\frac{e_i - e_j}{2} + \frac{\sin(\theta)}{|e_i + e_j|} e_i \times e_j
\]

(11.2.1)

\[
e_j \mapsto \text{crank}(e_j, e_i, \theta) = \frac{e_j + e_i}{2} + \cos(\theta)\frac{e_j - e_i}{2} + \frac{\sin(\theta)}{|e_j + e_i|} e_j \times e_i
\]

(11.2.2)

11.2.5 Quaternionic Perspective

Building upon a construction by Hausmann and Knutson [8], it is possible to describe a natural measure on open and closed polygons in 3-space [2, 3]. This is based on a map from the complex Stiefel manifold of 2-frames in n-space to the space of closed \( n \) edge polygons in 3-space of total length 2 whose construction employs the Hopf map on quaternions. In the setting of equilateral \( n \) edge polygons, this approach allows one to randomly sample these polygons by jointly sampling the polyhedron determined by a complete set of secants and \( n - 3 \) dihedral space angles between the triangles formed by the secants and the edges of the polygon, each with the uniform measure. Data generated from this approach is consistent with the data from the random fold and crankshaft methods and, therefore, provides evidence that both the fold and crankshaft algorithms sample the space of \( n \) edge equilateral polygons randomly.
11.3 Sampling Thick Polygons

A consequence of the desire to understand the geometric and topological consequences of excluded volume on the average character on \( n \) edged open and closed polygons, i.e. thick coarse grained models of polymers, one is led to use the methods we’ve discussed to acquire data that gives insight into the world of thick polygons. Unfortunately, the proportion of a random sample decays so rapidly that this approach means that generating sufficient data required to give robust estimates as thickness increases, see Figure 11.5, is unreasonable. This is especially true if one wishes to study the average properties of, for example, trefoil knots. In this section, we describe two new sampling algorithms that permit one to randomly sample the sets of open and closed polygons of a specified thickness. They were first presented in the the PhD dissertations of Laura Plunkett, for open polygons, and Kyle Chapman, for closed polygons [4, 19] at University of California, Santa Barbara. They are described below.

11.3.1 Primer on Probability Theory

Much of the value of the following algorithms comes from being able to use them to prove a Markov chain arising from the moves involved can be used to determine a probability measure on various sets. In order to motivate these algorithms, we start with some of the key definitions involved.

We consider a space of states, \( X \). We have a space of moves \( M \), which gives a map \( F : X \times M \rightarrow X \). If we choose a starting point \( x_0 \), then a random sequence in \( M \) gives a random sequence in \( X \). This is a Markov chain which gives a sequence of probability distributions \( P^n(x_0, A) \) on our space \( X \) defined by the probability of starting at \( x_0 \).
and landing in the Borel set $A$ after $n$ moves coming from $M$. The goal is to show that this sequence of probability distributions $P^n(x_0, A)$ converges to a limiting probability distribution $P(A)$.

The first step is knowing that there isn’t some lower dimensional subset we are restricted to. This is given by the notion of **Forward Accessible**, which means that independent of the choice of $x_0$ the orbit under $M$ has non-empty interior. While any single sequence only reaches a countable number of points, the set of all possible sequences can reach a full dimensional set.

The next step is knowing that the topology of the space is sufficiently well respected. We have the sequence of probability distributions $P^n$, so given any distribution on the natural numbers $a$, we get a new probability distribution $K_a(x, A) = \sum_{n=1}^{\infty} a(n) \cdot P^n(x, A)$. Our Markov chain is a **T-chain** if there is some measure $T$ on $X$ with $T(x, A) \leq K_a(x, A)$ for all $A$, $T(x, X) > 0$ for all $x$ and $T(x, A)$ lower semi-continuous in $x$ for all $A$. This is a complex and difficult to show directly, but having other properties, we use Lemma 11.3.1. (See below.) A Markov chain which is forward accessible and with $M$ having a lower semi-continuous probability density function is a T-chain. In our cases, moves from $M$ are being chosen uniformly, so it has the required PDF, and so we have a T-chain.

Having a reachable state $x_0$ for our space, and we having a T-chain allows us to assert that there is an invariant measure on $X$, but it may not be a probability measure. For example, if we consider a random walk on the line or in the plane, the sequence $P^n$ spreads steadily over the whole region, and the invariant measure is Lebesgue measure. The property which shows this issue does not happen and that the invariant measure $P$ is a probability measure is *bounded in probability on average*. This says that for every $\varepsilon$ there is a compact set $C$ with $\overline{P} = \frac{1}{n} \sum_{i=1}^{n} P^i$ satisfying $\lim \inf \overline{P}(C) \geq 1 - \varepsilon$. Essentially this amounts to showing that the probability of going to “$\infty$” is zero. We will be dealing with state spaces $X$ which are compact, so this issue is automatically resolved, and so the invariant measure $P$ is a probability distribution.

Finally, these can be combined to allow the use of the aperiodic ergodicity theorem to get the desired result. Letting $B(X)$ denote the Borel subsets of $X$,

$$\sup_{A \in B(X)} |P^n(x, A) - P(A)| \to 0.$$

### 11.3.2 Open polygons: Plunkett algorithm [18]

We would like to generate random elements from the set of walks with $n$ edges and thickness $t$. We will call the set of these walks $\mathcal{W}(n, t)$. To sample this space, we will start with a walk in the space, $W \in \mathcal{W}(n, t)$, and modify it, while ensuring we always have a thickness of at least $t$, until the resulting walk, $W'$, is independent of the original.
Our method is inspired by the pivot method, a Monte Carlo method proposed by Lal, and later implemented and proven to be ergodic by Madras and Sokal. The pivot method generates self-avoiding walks on the lattice by applying successive lattice symmetries at randomly selected vertices along the walk and accepting the new walk if it was not self-intersecting [13, 11]. Analogously, we perform reflections at vertices to portions of the walk.

- A single reflection will consist of selecting a random vertex and a random plane through that vertex. One portion of the walk will be reflected through the plane, and the other will remain fixed. If the new walk is still in $W(n, t)$, we accept the move and continue. If it is not, we return to the walk before our reflection and try again with a new vertex and a new plane.
- A double reflection will consist of selecting two random vertices and a random plane through each vertex. The reflections are performed successively, and if the end result is a walk in $W(n, t)$, we accept the change and continue. If it is not, we return to the walk before our reflections and try again.
- The acceptance probability of a reflection move varies with the thickness and length of walk. For example, for random walks of length 1000 and thickness of 1.00, the acceptance rate is 25.59% [18].

After a sufficient number of single and double reflections, we have a new walk, $W'$, independent of the starting walk $W$. What remains is to show that this method samples the space $W(n, t)$ ergodically [14]. Informally, this means that the Monte Carlo Markov Chain gives a sampling method that converges to the probability measure on, in this case, a continuous state space. The first requirement in showing that our method is ergodic is to show it is transitive. A transitive Monte Carlo method is capable of sampling (or visiting) every state in the state space. For our method, proving transitivity would require showing we can go from any walk, $W_0$, to any other, $W_1$, through a finite series of single and double reflections with each intermediate walk in $W(n, t)$. Because these reflections are reversible, this is equivalent to showing that we can get from any configuration, $W_0$, to the straight configuration, $W_s$, a straight rod of length $n$.

So suppose we start with a walk $W_0 \in W(n, t)$. We find a path to the straight configuration, $W_s$, by the following steps:

- we will perform single reflections on the outside of the convex hull of our walk until the ends of the walk determine the diameter of the convex hull, then
- we will use double reflections to remove critical points (maxima and minima) from the walk, and lastly
- we will perform more single reflections to straighten the configuration until we arrive at $W_s$. 
If we have a walk, \( W_i \), then we may perform any reflection through a vertex on the surface of the convex hull by a plane incident with only the surface of the convex hull. No reflection of this type will decrease the thickness of the resulting walk, as all pairs of edges either remain in the same position relative to each other, or the distance between them is sufficiently increased so as to never be less than \( 2t \). We will begin by reflecting in this way until both ends of the walk are on the surface of the convex hull and, further, that the two ends determine the diameter of the convex hull, as in Figure 11.6.

Fig. 11.6: Here we have three successive reflections through planes incident with points \( v_i \) on the convex hull. The end result is that the two ends of the chain have been moved to the surface of the convex hull, and determine the diameter of the convex hull. While the represented case is two dimensional, the application is in three dimensions.

Now we will remove pairs of maxima and minima (relative to the diameter of the convex hull, \( d^* \), from the last step) through a series of double reflections. If our walk \( W_i \) has no critical points, we may move on to the last step, the straightening. If there are critical points, each critical point (with respect to this diameter of the convex hull), is either at a vertex \( v_i \) or an edge \( s_i \). There is a plane through the critical point and perpendicular to the diameter, which we will call \( P_i \).
We will select our maximum and minimum very carefully. First, we select the highest local maximum, that is, the local maximum $m_i$ such that the distance between its plane $P_i$ and the plane $P_n$ containing the terminal and highest point is minimized, as in Figure 11.7. Between this maximum $m_i$ and the end of the walk $v_n$ there is at least one local minimum. We will select the local minimum $n_j$, $i < j < n$, such that the distance between the plane containing $n_j$, $P_j$, and the plane containing $v_i$, $P_i$, is greatest, as in Figure 11.7.

First, we will reflect the terminal end of the walk from $m_i$ to $v_n$ through the plane $P_i$. Then, we will reflect the terminal end of our modified chain, from $\hat{n}_j$ to $\hat{v}_n$ through the plane $\hat{P}_j$, the reflection of $P_j$. As in Figure 11.7, we have eliminated a pair of critical points. We now have three subsections of the walk to consider: from $v_0$ to $m_i$, $m_i$ to $\hat{n}_j$, and $\hat{n}_j$ to $\hat{v}_n$. Between $v_0$ to $m_i$ and $m_i$ to $\hat{n}_j$, we have performed a reflection similar to part 1, and no thickness reducing interactions have been introduced. Similarly for the interaction between $m_i$ to $\hat{n}_j$ and $\hat{n}_j$ to $\hat{v}_n$. For the interaction between the first and third segments, from $v_0$ to $m_i$ and $\hat{n}_j$ to $\hat{v}_n$, the third segment has been translated further away from the first segment. This increased distance is enough to verify that the thickness of the resulting walk has not been decreased.

Lastly, we will straighten this configuration by performing single reflections. Assume we have straightened the segments from $v_{j+1}$ to $v_n$ and we wish to straighten the next edge $s_j$ between $v_j$ and $v_{j+1}$. As in Figure 11.8, we perform a reflection so that the straight segment from $v_{j+1}$ to $v_n$ is in line with the edge $s_j$. We proceed until we have the straight configuration.

To prove that this method is ergodic, in addition to being transitive, we need the following lemmas about Markov chains.

**Lemma 11.3.1.** The Markov Chain $F$ being forward accessible and the state space $X$ having a probability density function implies that $F$ is a $T$-chain.

These are modifications of the arguments in Meyn and Tweedie [14]: Propositions 7.1.5 and 6.2.4.

**Lemma 11.3.2.** A $T$-chain with a reachable state is bounded in probability on average if and only if it is positive Harris recurrent.

This is proposition 18.3.2 in Meyn and Tweedie [14].

**Lemma 11.3.3.** $F$ is aperiodic.

**Sketch of Proof** Seeking a contradiction, suppose there exist $C_i$, subsets of the state space $X$ or in this case $W(n, t)$, such that $i \in \mathbb{Z}_n$, the cyclic group of order $n$, and they are a collection of disjoint non-empty closed sets with the probability of going from $C_i$ to $C_{i+1}$ is one. Let $w \in C_i$. In our context, if we apply a pair of reflections at the second
Fig. 11.7: Here we have a typical double reflection move for part two of the proof. First, we identify the local maximum, \( m_i \), and local minimum, \( m_j \), such that \( m_i \) is the highest maximum and \( n_j \) is the lowest minimum, relative to the axis selected at the beginning of this step. The first reflection through the plane \( P_i \) reflects the segments between \( m_i \) and \( v_n \). The reflection through \( \hat{P}_j \), the reflected image of \( P_j \), reflects the segments between \( \hat{n}_j \) and \( \hat{v}_n \). This gives us our new configuration, with two fewer critical points and with the same (or greater) thickness.
Fig. 11.8: In the previous step, we eliminated pairs of maxima and minima relative to $d^*$, the diameter of the convex hull in the first step. Now, via a single reflection, we straighten the segments $s_{j+1}, ..., s_n$ to be in line with $s_j$. 

to last vertex through planes containing the last edge, then $w$ is left fixed by this double reflection. Therefore there is a double reflection move $r$ with $r(w) = w \notin C_{i+1}$. Since $C_{i+1}$ is closed, there is an open neighborhood of $w$ which is not in $C_{i+1}$ so there is a positive probability of landing in this open neighborhood of $w$. This contradicts the requirements of periodicity. Thus, $F$ is aperiodic. 

**Theorem 11.3.1.** The Markov chain on walks in $\mathcal{W}(n, t)$, as described above, is ergodic.

**Proof.** From our work showing transitivity, we have that for any walk there is a sequence of finitely many single and double reflections which can transform this walk to the straight walk, and each single and double reflection in this sequence is on the interior of a smooth section of $F$. Then, by concatenating this sequence with the reverse of another such sequence, we can connect any two walks on the interior of $\mathcal{W}(n, t)$ with a sequence of reflections on the interior of a smooth section of $F$. Therefore $F$ creates a forward accessible Markov chain. Next, since our noise parameter $M$ has a probability density function, namely a constant, we can combine this with forward accessibility to get that the Markov chain is a T-chain. We get that any sequence of probability distributions is tight, so in particular our Markov chain $F$ is bounded in probability on average because our state space is compact. Because there is a sequence of reflections ensur-
Given Convex Projection
Made Planar
Made Regular

Fig. 11.9: An example of the three aspects being applied to a hexagon

ing that every walk can be modified to be within any neighborhood of the straight walk with positive probability, we conclude that $F$ has a reachable state. Therefore $F$, being a $T$-chain with a reachable state which is bounded in probability on average, must be positive Harris recurrent. Finally, since there is a fixed point at the interior of a smooth section, $F$ cannot be periodic and so the aperiodic ergodicity theorem [14] tells us that $F$ is ergodic.

\[ \square \]

### 11.3.3 Closed polygons: Chapman algorithm

We work in the space $\mathcal{R}(n, t)$ of polygonal rings with $n$ unit length edges and a thickness of greater than or equal to $t$. We show that any knot $K \in \mathcal{R}(n, t)$ has a sequence of polygonal folds which brings it to the regular planar polygon $P_n$, without having the thickness be less than $t$. Note that this algorithm unknots the polygon and, therefore, may not preserve the topological knot type of the polygon. The overall structure for making these choices has 3 aspects. The first aspect is being able to expand the knot until its orthogonal projection to the $x-y$ plane is a convex projection, without changing the number of minimal height vertices, with respect to the orthogonal projection. The second aspect is being able to take a knot with convex projection and increase the number of minimal height vertices, with respect to the orthogonal projection. These two actions are combined and alternated so as to allow one to make the knot planar and convex. The third aspect is to take a planar and convex polygon and make it regular.

A key piece for the first aspect, making the projection convex, is the fact that a reflection move across a plane which does not intersect the interior of the convex hull, does not increase the thickness. This is a special example of the fact that if no two vertices are made closer together, then the thickness in not increased. For making the projection convex, we utilize the argument of the Grünbaum-Zaks theorem [7]. To properly state this theorem we use need a weakened notion of convexity called exposed which
is shown in Figure 11.10. While a polygon in the plane is convex if it is an embedding onto the boundary of the convex hull, it is exposed if the image is the boundary of the convex hull and the pre-image of each vertex is connected. This means that the polygon might double back over an edge, but still cycles around the convex hull. The Grünbaum-Zaks theorem says that any polygon can be made exposed using a finite sequence of reflections across edges of the convex hull.

The Grünbaum-Zaks theorem allows us to make the projection exposed, so we need to make the projection convex. For that, we consider an edge of the convex hull which is not hit injectively. Taking the pre-image of that edge we get a strip, with an arc of the knot moving from one side of the strip to the other, as in Figure 11.11. Looking at the convex hull of this arc we can find a sub arc which has end points which share a bottom edge of that convex hull. This sub arc can be pushed out slightly using a rotation about the line labeled $l$ through a small angle, which can be done with a pair of reflections. This makes the projection more injective and so alternatimg with Grünbaum-Zaks theorem completes the first aspect.

The second aspect is much simpler. Since the knot is not planar, we can find a sub arc which is above the minimum height except at the endpoints which are minimal height vertices. This arc can be rotated down until another vertex has reached minimal height, as in Figure 11.12.

The final aspect uses a special move which consists of six reflections. Within the planar convex polygon, we choose an inscribed quadrilateral, which has two opposite corners which correspond to vertices at which the interior angles are smaller than the regular angle, and the complementary two corners correspond to vertices at which the interior angles are larger than regular the regular angle. Focusing on the inscribed quadrilateral, two reflections can give a new planar quadrilateral with different angles. This leaves four flaps in the form of the arcs connecting the vertices of the inscribed quadrilateral, and so an additional four reflections will make the whole knot planar. Intermediate value theorem allows this collection of six reflections to be chosen so one additional angle is regular.
Fig. 11.11: An example of the pre-image of an edge of the convex hull. $\alpha$ denotes a vertex which is strictly above another point in the arc. $\alpha_{\pm}$ denote the vertices in either direction which are on the bottom of the convex hull of the arc. $l$ is the boundary line of this convex hull shared by $\alpha_{\pm}$.

Fig. 11.12: An example of a rotation which increases the number of minimum height vertices, shown from a projection which is parallel to the axis of rotation.
We now let $F$ denote the Markov chain arising from applying sequences of 6 reflection moves at a time to a closed polygon $x$ in the state space $X = \mathcal{R}(n, t)$ of $n$ edge rings with thickness at least $t$.

**Lemma 11.3.4.** The Markov chain $F$ is ergodic

The algorithm we described shows that any point $x$ can be brought to the regular planar polygon with a finite sequence of moves, so by using this and its reverse, we can connect any two points in the state space. This means that we can utilize the same argument for $\mathcal{R}(n, t)$ as for $\mathcal{W}(n, t)$. The algorithm shows forward accessibility and a reachable point. This lets us claim that it is a $T$-chain. Since it is a compact state space we get an invariant probability measure. Finally, since there exists moves which take a point to itself, the Markov chain is aperiodic, so the aperiodic ergodicity theorem applies.

### 11.4 Discussion and Conclusions

Considering open polygons, we generated a data set consisting of 5000 samples for each of the following pairs of lengths and thicknesses:

- lengths, $N$: 100 to 1000 in steps of 100.
- thicknesses: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 (Note, these correspond to minimal interior angles of about $0^\circ$, $23^\circ$, $44^\circ$, $62^\circ$, $77^\circ$, $90^\circ$, $100^\circ$, $109^\circ$, $116^\circ$, $122^\circ$, and $127^\circ$.)

Even for the thickest and longest of these samples, the acceptance rate for a proposed reflection or double reflection was above 25%. From this data we examined...
squared radius of gyration, squared end to end distance, and for the length 300 samples, knotting in the open walks [15].

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{knot_probability.png}
\caption{Knot probability as a function of thickness for self avoiding walks of length 300. For each 0.1 thickness is increased, the probability of knot formation is cut by 50% or more, up to $t = 0.5$. For $t > 0.5$, the probability of knot formation is constant.}
\end{figure}

As we see in Figure 11.14, the probability of knot formation for walks with length 300 is quite high without the introduction of thickness, with more than half of samples having a dominant, nontrivial knot type, i.e. a specific knot type appearing more than half the time. For each 0.1 (to be compared to the length of each segment, 1,) that the thickness is increased, the probability of knot formation is cut in half until the thickness is at 0.5 after which this probability is constant. We conclude that the introduction of thickness has an immediate and profound effect on knot formation, and we expect that further studies will confirm that this effect persists to longer length scales and in both thicker and thinner walks.

We also analyzed the growth exponent for the thicknesses from 0.0 to 1.0 by finding the average radius of gyration squared, $R_g^2$, for each data set, and performing a linear regression with vertical offsets on the log of the data. Assuming that $R_g^2 \propto N^\nu$, this allowed us to solve for $\nu$ as a function of thickness.

For ideal chains it has been shown that $R_g^2 \propto N$, where $N$ is the number of segments. It is easy to verify that for $t = \infty$ we have the straight configuration and $R_g^2 \propto N^2$ [22]. Excluded volume has been classically characterized by the estimate $\nu = 1.2$ [5]. In wet experiments and numerical simulation for good solvent polymers, $\nu$ has been estimated between 1.1 and 1.2, with $2(0.588) = 1.18$ in walks on the simple, cubic lattice [5]. We can see that there is an immediate impact of thickness: the scal-
ing exponent increases to the [1.14, 1.17] interval almost immediately, as predicted by Vologodskii’s simulations of very thin walks and rings [9].

For comparison, we will refer to $\nu_t$ as the scaling exponent for the self avoiding walk with thickness $t$, and $\mu_t$ as the scaling exponent for the family of walks with only a bending constraint for adjacent edges, and no restrictions equivalent to excluded volume.

For those walks without long range or excluded volume interaction the growth exponent is, as expected, close to 1 as these walks should scale like ideal chains. The thick walks behave very differently. The growth exponents for families of walks with very small thicknesses immediately jumps to 1.16 where it was fairly stable ($\pm 0.01$) for thicknesses $t \in [0.2, 1.0]$. Therefore the effect of excluded volume is as immediate and profound on growth exponent as it is for knot formation: even the introduction of very modest thicknesses has a profound effect on shape, size and knotting.

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