Size-Dependent Transitions in Grafted Polymer Brushes

Courtney Bosse
University of Texas at El Paso, cebosse@miners.utep.edu

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SIZE DEPENDENT TRANSITIONS IN GRAFTED POLYMER BRUSHES

Courtney Elizabeth Bosse

Department of Physics

Approved:

Marian Manciu, Ph.D.

Chunqiag Li, Ph.D

Emil Schwab, Ph.D

Benjamin C. Flores, Ph.D.
Dean of the Graduate School
SIZE DEPENDENT TRANSITIONS IN GRAFTED POLYMER BRUSHES

By

Courtney E Bosse

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1. Introduction

Polymers are long chains of molecules made by assembling a series of monomers, either of the same type (homopolymer) or a mixture (copolymer). The number of monomers linked in a chain can be very large, but the stress that occurs in long chains can cause them to break up. Polymers have many different properties that can be used for many things including protective coatings, artificial joints or even building materials [1].

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A grafted polymer brush is a layer of grafted polymers that have one end attached to a surface. My thesis concentrates on these types of polymers and, using probabilities, finds the most likely configuration the polymer will take.

Finding probabilities in order to find the most likely configuration of a grafted polymer chain is easily calculated by solving a random walk problem, starting form a given point (the surface). A random walk is defined as a stochastic process formed by successive steps, either away from the surface or toward the surface, with the probabilities p and q, respectively ( with p + q = 1) [2]. The random walk starts at the interface at n = 0. Every step after that leads away or towards this “wall.” If the wall is reflecting, it basically means that if the random walk moves back to the same position as where it was a n = 0, the next step reflects off the wall and goes back the opposite direction. Once the first step moves away from the wall, the random walk can never pass that wall in the opposite direction. The random walk can go on forever, but only on
one side of the reflecting interface. An adsorption, on the other hand, is when the \( n = 0 \) interface adsorbs the walk and the random walk ends. Again, all steps are on one side of the adsorption interface, but the random walk can be as short as two steps or as long as an infinity of steps. It can be show than in 1 D, the non-biased (e.g. \( p=q=1/2 \)) random walks will always return eventually to the interface. That means, the probability that a random walk will never return to the interface in the long run (\( n \to \infty \)) is vanishingly small. This is one of the earliest results of the theory of probability, known as Gambler Ruin, which implies that even when playing a fair game (when the probability of winning equal the probability of losing) against a Casino of infinite resources, the gambler will eventually lose all of its money.

A more complicated case is when the Gambler stops playing when is bankrupt (\( n=0 \)) or hit a certain sum of money (\( n=i \)). This case correspond to a grafted polymer between two "adsorbing" interfaces, one at \( n = 0 \) and the other at \( n = i \). This means that the random walk will stop once it either returns back to the grafting surface (\( n = 0 \)) or reaches the opposite interface (\( n = i \)).

The property of the random walk, in the absence of an opposite barrier (\( i = \infty \)), to always return to the grafting surface, can be used to describe the partition function of a polymer in terms of a sum over possible loops configurations, which will be shown later that simplifies tremendously the problem of calculating the partition function of the grafted polymer.

A non-interacting random walk is a random walk in which the step probabilities \( p \) and \( q \) does not depend on the history of the walk. This is not realistic for a real polymer; in this case it is very likely that the random walker will prefer to walk away from the regions with high concentrations of monomers, to avoid overlap with itself (e.g., volume fraction occupations larger than one). Whereas the problem of non-interacting random walk has been well studied in
the theory of the probability, the problem of self-interacting random walks cannot be solved exactly and various approximations have been suggested.

The real polymers interact with themselves and with the solvent, and therefore both the energy and the entropy are involved in the calculation of the partition function of the chain. Polymers tend to move in a way that gives a higher entropy, meaning there are more options of the possible configurations compatible with the final state. For example, it is unlikely to find a polymer chain completely stretched out in a line, which allows only one configuration. On the other hand, the configurations with high energy (such as those with a very high local monomer concentrations) are also unlikely.

Because finding any type of most likely configuration for the interacting random walk is extremely difficult and involved, for my thesis we have come up with a new way to solve this problem. Our idea was to take the easily solved equations that give the solutions for the non-interacting random walks and adding a new term with a specific given energy. Doing this allows us to find the probabilities of loop formation, and from there the most likely configuration, of interacting random walks. This method, written in a paper by Marian Manciu and Courtney Bosse of the Department of Physics at the University of Texas at El Paso and Dr. Eli Ruckensein from the Chemical and Biological Engineering Department at the State University of New York at Buffalo, has been accepted for publication [8].

A typical configuration of the polymer has been also calculated using Monte Carlo, a statistics procedure in which many random configurations have been generated randomly, based on the probability of loop formation. However, Monte Carlo procedures, in order to be accurate, need a lot of sampling points, which in turn need a lot of computer time. Practically, they are limited to chains with less than 1000 segments, which are not close to the phase transitions.
The search for an analytical approximation for a most likely configuration resulted from Monte Carlo calculations parallel a current thrust in Medical Physics Radiation Therapy research. It is well known that the most accurate treatment planning procedures are based on Monte-Carlo calculations, however their accuracy is limited by the computer time available. If better analytical approximations will be found for Monte-Carlo calculations, they will drastically decrease the computing time requirement, and hence, more accurate TPS (Treatment Planning Systems) would be available to the Medical Physics community.
2. The 1D Random Walk

2.1 The simple 1-D Random Walk

The random walk is the stochastic process formed by summation of independent, identically distributed random variables [2]. In laymen’s terms, the random walk has identical variables, “steps,” that are added together for a discrete, finite or infinite number of time or steps. The discussion in this chapter follows Reif [4].

The steps of equal length are taken with the probability \( p \) and \( q \ (p+q = 1) \) in forward and backward direction, respectively (or towards left and right, respectively). Basically, the one-dimensional random walk can be thought of as a binomial distribution of steps, which is defined as the distribution of the number of successes in a sequence of \( n \) independent yes/no experiments, where each experiment yields success with a probability \( p \). (and failure with the probability \( q=1-p \)).

A random walk is exactly a binomial distribution if four things happen:

1) The number of observations/steps \( N \) is known;

2) Each step is independent;

3) Each step represents one of two outcomes (step right or left), and

4) The probability, \( p \), of “success” (a step right) is the same for each step [3].

The random walk problem can be shown in its simplest form by considering a drunk trying to walk starting out at a lamppost located on a street [4]. The problem works with a drunk man because the direction of each step, whether right or left, needs to be completely independent of the preceding step, meaning there is the same probability that he will step right or left. We let
each step he takes be of equal length, \( l \), the probability of the step being to the right be \( p \), and the probability of the step being to the left be \( q = 1 - p \). The simplest case is when equal probability for a left or right step exists \( (p = q) \). We choose to set the lamppost at the origin, \( x = 0 \). We know, since each step is equal length \( l \), the position of the drunk on the x-axis is of the form \( x = ml \) where \( m \) is an integer. The random walk question we then need answered is what is the probability of the drunk being located at \( x = ml \) after he has taken \( N \) steps?

The above example is again one of the simplest forms of the random walk. Other, more related to physics examples include: 1) In magnetism, an atom has a spin of \( \frac{1}{2} \) and a magnetic moment \( \mu \). The spin can either point up or down, like the drunk can walk left or right. 2) For diffusion of a molecule in gas, a molecule can travel in three dimensions, as if the drunk could walk forward, with a mean distance of \( l \) between collisions. 3) Light intensity due to \( N \) incoherent light sources, the light amplitude is represented by a two-dimensional vector whose direction specifies the phase of the disturbance [4].

Now, let’s look at the random walk of a particle in one dimension and show how we go from \( x = ml \) to actually finding that probability. So, after a total of \( N \) steps of equal length \( l \), we have

\[
x = ml
\]

(2.1.1)

where \( m \) is an integer between:

\[-N \leq m \leq N\]

Now, we want to calculate the probability \( P_N(m) \) of finding the particle at the position \( x = ml \) after \( N \) steps. Let \( n_1 \) denote the number of steps to the right and \( n_2 \) the corresponding number of steps to the left. That means the total number of steps \( N \) is then
\[ N = n_1 + n_2 \]  \hspace{1cm} (2.1.2)

The total displacement is measured by units of a step length to the right and is given by:

\[ m = n_1 - n_2 \]  \hspace{1cm} (2.1.3)

Plugging in for steps taken to the right, we get

\[ m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N \]  \hspace{1cm} (2.1.4)

Since we assumed that each successive step is independent of another, we can use the multiplication rule of probability to find the \( p \) and \( q \) probabilities [5]. This rule states that when two events, \( A \) and \( B \), are independent, the probability of both occurring is \( P(A \text{ and } B) = P(A) \times P(B) \). This means, using our earlier definitions of \( p \) and \( q \), we can find the probability of any one given sequence of \( n_1 \) and \( n_2 \) steps by multiplying the respective probabilities

\[ pp \cdots pqq \cdots q = p^{(n_1)}q^{(n_2)} \]

This equation represents just one sequence, however, and is not enough to finish the problem because there are many different ways of taking \( N \) steps with \( n_1 \) and \( n_2 \) steps to the right and left, respectively. Basically, we need to count each of these different ways. Using probability rules, we find that in our case, the first sequence is occupied by any of the \( N \) objects, the second sequence is occupied by any of the \( (N-1) \) remaining objects, etcetera, and the \( N \)th sequence can only have the last object [4]. Therefore, all the available sequences can be added by a factorial

\[ N(N-1)(N-2)\cdots 1 = N! \]

The same occurs for all \( n_1 \) and \( n_2 \) permutations. By dividing the total number of \( N! \) arrangements by the \( n_1!n_2! \), we can obtain the total number of distinct ways \( N \) objects can be
arranged,

\[
\frac{(N!)}{(n_1!n_2!)}
\]

Putting these two equations together to find the probability, \( W_M(n_1) \), of taking \( n_1 \) steps to the right and \( n_2 \) steps to the left, we get

\[
W_N(n_1) = \frac{N!}{n_1!n_2!} p^{(n_1)} q^{(n_2)} \quad (2.1.5)
\]

This is where we see that the random walk is basically a binomial distribution. The above probability is just simplified from the binomial expansion

\[
(p + q)^N = \sum_{n=0}^{N} \left[ \frac{N!}{n!(N-n)!} \right] p^n q^{(N-n)} \quad (2.1.6)
\]

Earlier, we showed that knowing the \( n_1 \) steps to the right leads us to the net displacement, \( m \). This means that the probability \( P_N(m) \) that the particle is found at position \( m \) after \( N \) steps is the same as the probability of the random walk taking \( n_1 \) steps to the right, \( W_M(n_1) \),

\[
P_N(m) = W_M(n_1)
\]

Combining our \( N \) and \( m \) equations from the start of the example gives us

\[
n_1 = \frac{1}{2} (N + m) \quad , \quad n_2 = \frac{1}{2} (N - m) \quad (2.1.7)
\]

Substituting all of our equations together gives us the probability

\[
P_N(m) = \frac{\binom{N}{n_1}}{\binom{N+m}{(N+m)/2}\binom{N-m}{(N-m)/2}} p^{(N+m)/2} (1-p)^{(N-m)/2} \quad (2.1.8)
\]

In the special case where \( p = q = \frac{1}{2} \), the equation assumes the symmetrical form with the last part of the equation becoming \((\frac{1}{2})^N\). This corresponds to the symmetric binomial expansion that
when graphed gives a perfect Gaussian distribution [4].

Next, it is important to find how to calculate the mean value of the number of steps right for our random walk problem. The first thing to do is to verify that the \( W_N(n_1) \) probability is normalized, meaning the probability of making any number of right steps between 0 and \( N \) be unity,

\[
\sum_{n_1=0}^{N} W_N(n_1) = 1 \quad (2.1.9)
\]

This basically means that the probability of the particle going any number of right steps is always 1. If the random walk goes on for infinity, that number of right steps will eventually be taken. Only if there is some sort of restriction on the random walk would this not occur.

Substituting in \( W_N \) and using the fact that \( n_2 = N - n_1 \), we get

\[
\sum_{n_1=0}^{N} \left[ \frac{N!}{n_1!(N-n_1)!} p^{(n_1)} q^{(N-n_1)} \right] = (p + q)^N \quad (2.1.10)
\]

By substituting in \( q = 1 - p \) and then incorporating the binomial theorem, which states that the expansion of any power \((a + b)^m\) of a binomial \((a + b)\) as a certain sum of products \(a^j b^l\), such as

\((a + b)^2 = a^2 + 2ab + b^2\) we can verify the normalization

\[(p + q)^N = 1^N = 1 \quad (2.1.11)\]

The average of any function is defined by the sum of the probabilities of the function multiplied by the function and divided by the sum of the probabilities of the function. By using the normalization condition, this can be simplified to just the sum of the probabilities multiplied by the function,
\[
\overline{f(u)} = \sum_{i=1}^{M} P(u_i)f(u_i)
\]  \hspace{1cm} (2.1.12)

Using this simplification in our problem to find the mean number of \(n_1\) steps to the right using the \(W_N\) probabilities, we get the binomial expansion with an extra \(n_1\) term,

\[
n_1' = \sum_{n_1=0}^{N} W_N(n_1)n_1 = \sum_{n_1=0}^{N} \left[ \frac{N!}{n_1!(N-n_1)!} p^{(n_1)} q^{(N-n_1)} \right] n_1 \hspace{1cm} (2.1.13)
\]

Luckily, this equation can be simplified greatly by considering \(p\) and \(q\) as arbitrary parameters [4]. Using a differentiation of \(p\) and by interchanging the order of the summation and differentiation we can reduce the equation to

\[
n_1' = Np \hspace{1cm} (2.1.14)
\]

This also applies to the steps to the left giving us

\[
n_2' = Nq \hspace{1cm} (2.1.15)
\]

We can then find the average displacement by subtracting the two averages

\[
m = N(p - q) \hspace{1cm} (2.1.16)
\]

If \(p = q\), then the average displacement is 0, which makes sense. For example, if the particle takes 10 steps to the right and 10 steps to the left, then it would be back to where it started at 0.

Continuing along the same lines, we can find the dispersion, the degree of scatter of the data around an average value which is just calculating

\[
(\Delta n_1)^2
\]

The delta means we are finding the change between the average \(n_1\) and \(n_1, (n_1 - \bar{n_1})^2\). This
expands out to just $(\bar{n}_1)^2 - (\tilde{n}_1)^2$. The second term is just a square of our average, but we need to calculate the first term, the dispersion term.

\[
\bar{n}_1^2 = \sum_{n_1=0}^{N} W_N (n_1)n_1^2 = \sum_{n_1=0}^{N} \left[ \frac{N!}{n_1!(N-n_1)!} \right] p^{(n_1)}q^{(N-n_1)}n_1^2
\]

We can use the same differentiation and sign change trick as we did with to find the mean $n_1$ to simplify the dispersion to get

\[
(\Delta n_1)^2 = Npq 
\]

and using this to find the dispersion of the displacement $m$ gives us

\[
(\Delta m)^2 = N
\]
2.2 Analytical approximations for large N

So far, we have only been looking at probabilities when the total number of steps $N$ is not very large. Now, we can find the approximate expression for $W(n_1)$ that is valid when $N$ is sufficiently large. When this is the case, if we look at the binomial distribution, we notice that the average $n_1$ becomes a pronounced maximum and from there, the $n_1$ drops off rapidly on each side of the graph. This fact is what we use to find our $W$ values. We want to look at the region where both $N$ and $n_1$ are large. When this happens, the fractional change in $W$ when $n_1$ changes by one is relatively small [4].

$$\left| W(n + 1) - W(n_1) \right| \ll W(n_1)$$

The smaller the change in $W$, the easier it is to approximate $W$ as a continuous function with $n_1$ as a continuous variable. Having $n_1$ be continuous means we can take the integral values instead of having to add large numbers together. We can determine the location of the maximum of $W$, $n_1 = \bar{n}$, by the condition

$$\frac{dW}{dn_1} = 0 \text{ or equivalently } \frac{d\ln W}{dn_1} = 0$$

evaluating the derivatives for $n_1 = \bar{n}$. To investigate the behavior of $W_N(n_1)$ near its maximum, we can use for $n_1$

$$n_1 = \bar{n}_1 + \eta$$

and expand $\ln W(n_1)$ in a Taylor's series about $\bar{n}_1$. Expanding $\ln W$ is better than just expanding $W$ because the $\ln$ function varies much slower around $n_1$ so the power series expansion should converge more rapidly than the one for $W$.

Let’s use
\( B_k \equiv \frac{d^k \ln W}{d n_1^k} \)

as our \( k \)th derivative to simplify our expansion [4]. We end up with

\[
\ln W(n_1) = \ln W(\bar{n}_1) + B_1 \eta + \frac{1}{2} B_2 \eta^2 + \frac{1}{6} B_3 \eta^3 + \cdots \quad (2.2.2)
\]

There are two things we know right away since we are expanding about a maximum: 1) \( B_1 = 0 \) and

2) \( \frac{1}{2} B_2 \eta^2 \) must be negative, meaning, \( B_2 \) must be negative, \( B_2 = -|B_2| \).

Now, our \( \ln W \) equation yields, using \( \bar{W} = \bar{W}(\bar{n}_1) \),

\[
W(n_1) = \bar{W} e^{\frac{1}{2} B_2 \eta^2 + \frac{1}{6} B_3 \eta^3 + \cdots} = \bar{W} e^{-\frac{1}{2} B_2 \eta^2 + \frac{1}{6} B_3 \eta^3 + \cdots} \quad (20.3)
\]

We can neglect the higher-order terms since \( \eta \) is small and we obtain an expression of the simple form

\[
W(n_1) = \bar{W} e^{-\frac{1}{2} |B_2| \eta^2} \quad (2.2.4)
\]

Now let's investigate deeper into the expansion so we can find \( \bar{n}_1 \).

Going all the way back to equation (2.1.5)

\[
W_N(n_1) = \frac{N!}{n_1! (N-n_1)!} p^{(n_1)} q^{(N-n_1)},
\]

we take the \( \ln \) of both sides and get

\[
\ln W_N(n_1) = \ln N! - \ln n_1! - \ln (N - n_1)! + n_1 \ln p + (N - n_1) \ln q \quad (2.2.5)
\]

If \( n \) is very large, \( n >> 1 \), then \( \ln n! \) can be considered almost continuous, just like the \( n_1 \) from
before. Therefore, for \( n \gg 1 \)

\[
\frac{(dtnW)}{dn_1} = -ln n_1 + ln(N - n_1) + ln p - ln q \quad (2.2.6)
\]

We equate the first derivative to zero and find that the value of \( n_1 = \bar{n}_1 \) where \( W \) is maximum. Therefore,

\[
\bar{n}_1 = Np \quad (2.2.7)
\]

We can also find the value of the constant \( \bar{W} \) by using the normalization condition [4]. Since \( W \) and \( n_1 \) are thought of as quasicontinuous in our example, the sum over all values of \( n_1 \) can be approximately replaced by an integral yielding

\[
\sum_{n_1=0}^{N} W_N (n_1) \approx \int W_N (n_1) dn_1 = \int_{-\infty}^{\infty} W_N (\bar{n}_1 + \eta) d\eta = 1 \quad (2.2.8)
\]

Substituting our \( W_N \) equation in here gives us

\[
\bar{W} \int_{-\infty}^{\infty} e^{-\frac{1}{2} |\bar{\eta}|^2} d\eta = \bar{W} \sqrt{\frac{2\pi}{|\bar{\eta}|}} = 1 \quad (2.2.9)
\]

and from there our \( W_N \) equation becomes

\[
W_N (n_1) = \sqrt{\frac{|\bar{\eta}|}{2\pi}} e^{-\frac{1}{2} |\bar{\eta}| (n_1 - \bar{n}_1)^2} \quad (2.2.10)
\]

The reasoning behind both our \( W_N \) equations comes from the Gaussian distribution, which is very general in nature. This means that Gaussian distributions occur often in statistics when someone is dealing with very large numbers. It also means that these distributions are the easiest to work with. We, however, have been using the binomial distribution and through that with our Gaussian, our last equation becomes
\[ W_N(n_1) = (2\pi Npq)^{-\frac{1}{2}} \exp \left[ \frac{-(n_1-Np)^2}{2Npq} \right] \] (2.2.11)

Writing this in terms of our mean values of \( n_1 \) and our \( n_1 \) dispersion gives us

\[ W_N(n_1) = \left[ 2\pi (\Delta n_1)^2 \right]^{-\frac{1}{2}} \exp \left[ \frac{-(n_1-n_1')^2}{2(\Delta n_1^2)} \right] \] (2.2.12)

We can also use the Gaussian approximation we found above to find our probability \( P(m) \) for large number of \( N \) steps [4]. We already know that \( P(m) = W_N(n_1) \), using our \( n_1 = \frac{1}{2}(N + m) \), and playing with our \( n_1 \) and \( m \) equations, we rewrite the Gaussian as

\[ P(m) = W_N \left( \frac{N+m}{2} \right) = [2\pi Npq]^{-\frac{1}{2}} \exp \left[ \frac{-(m-N(p-q))^2}{8Npq} \right] \] (2.2.13)

This can also be expressed in the terms of our original equation \( x = ml \). If we let \( l \) be small compared to the smallest length of interest, it doesn't matter that \( x \) is not continuous. Just as above with our \( W_N(n_1) \), when \( N \) is large, the \( P(m) \) of displacement \( m \) does not change much from one possible value of \( m \) to another,

\[ |P(m+2) - P(m)| \ll P(m) \]

and can therefore be thought of as a continuous smooth function of \( x \). Since \( x \) is now regarded as a continuous variable, the probability that the particle is found after \( N \) steps is in the range between \( x \) and \( x + dx \). Displacement \( m \) only assumes integral values separated by \( \Delta m = 2 \), so the \( dx \) range contains \( dx/2l \) possible values of \( m \) which all occur with nearly the same probability. The probability of finding the particle in this range is obtained by simply summing \( P(m) \) over all values of \( m \) lying in \( dx \). This basically means we multiply \( P(m) \) by \( dx/2l \).

\[ \rho(x)dx = P(m) \frac{dx}{2l} \] (2.2.14)
By plugging in our \( P(m) \) equation, we get the standard form of the Gaussian probability distribution,

\[
\rho(x)dx = \frac{1}{\sqrt{2\pi} \sigma} e^{-\frac{(x-\mu)^2}{2\sigma^2}}
\]

(2.2.15)

letting

\[
\mu \equiv (p - q)Nl
\]

\[
\sigma \equiv 2\sqrt{Npq}l
\]

We can use this standard form to compute the mean values, \( \bar{x} \) and the dispersion \( \overline{(x - \bar{x})^2} \). All sums over possible intervals \( dx \) become integrations whose limits can be from negative infinity to infinity since the equation becomes negligibly small when \( |x| \) is very large.

Like usual, we first verify the normalization,

\[
\int_{-\infty}^{\infty} \rho(x)dx = \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx
\]

\[
= \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} e^{-y^2/2\sigma^2} dy
\]

\[
= \int_{-\infty}^{\infty} \rho(x)dx = \frac{1}{\sqrt{2\pi} \sigma} \sqrt{\pi 2\sigma^2}
\]

\[
= 1
\]

We plugged in \( y \) for \( x - \mu \) and evaluated the integral by using an appendix. From here, we can calculate the mean value of \( x \).
\[
\tilde{x} \equiv \int_{-\infty}^{\infty} x \rho(x) dx
\]

\[
\tilde{x} = \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} e^{-(x-\mu)^2/2\sigma^2} dx
\]

\[
\tilde{x} = \frac{1}{\sqrt{2\pi} \sigma} \left[ \int_{-\infty}^{\infty} ye^{-y^2/2\sigma^2} dy + \mu \int_{-\infty}^{\infty} e^{-y^2/2\sigma^2} dy \right] \tag{2.2.16}
\]

The first integral vanishes by symmetry because it is an odd function of \(y\). The second integral is the same as the one we normalized with an extra value of \(\mu\), so we get

\[
\tilde{x} = \mu \tag{2.2.17}
\]

which just means that the distribution is symmetric around the position \(x = \mu\) of its maximum [4].

The dispersion becomes

\[
(x - \mu)^2 \equiv \int_{-\infty}^{\infty} (x - \mu)^2 \rho(x) dx
\]

\[
= \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} y^2 e^{-y^2/2\sigma^2} dy
\]

\[
= \frac{1}{\sqrt{2\pi} \sigma} \left[ \frac{\sqrt{\pi}}{2} (2\sigma^2)^{3/2} \right]
\]

\[
= \sigma^2 \tag{2.2.18}
\]

Finally, using all our equations, we obtain the relations

\[
\tilde{x} = (p - q)Nl \tag{2.2.19}
\]

\[
(\Delta x)^2 = 4Npq l^2 \tag{2.2.20}
\]
for our random walk problem.

Next, we need to look at the random walk with a restricting interface and then finally, a random walk with two restricting interfaces.
2.3 1-D Random Walk in the presence of an adsorbing or reflecting interfaces

A random walk can go on for an infinite amount of time, which we have derived above. However, a random walk can also be limited by including a reflection or adsorption at one or two interfaces. When the random walk starts, at \( n=0 \), an interface can be located anywhere along the plane, even at \( n=0 \). Every step after that leads away or towards this “wall.” Putting the wall at 0, if the wall is reflecting, it basically means that if the random walk moves back to the same position as where it was at \( n=0 \), the next step reflects off the wall and the next step is back the opposite direction. Once the first step moves away from the wall, the random walk can never pass that wall in the opposite direction. The random walk can go on forever, but only on one side of the reflecting interface.

An adsorption, on the other hand, is when the \( n=0 \) interface adsorbs the walk and the random walk ends. Again, all steps are on one side of the adsorption interface, but the random walk can be as short as two steps or as long as infinite steps. Staying in one dimension, let’s first consider the case of the reflecting barrier. We will follow the proof presented by Chandrasekhar [6].

First, instead of having the reflecting wall at 0, we set the reflecting barrier at \( m = m_1 \). We want to keep the problem general, but we can still suppose that \( m_1 > 0 \). Having the reflecting barrier at \( m_1 \) simply means that when the particle gets to \( m_1 \), there is a 100% probability of the particle bouncing back to where it was at \( m_1 - 1 \) for its next step. Now, as is the case in any random walk problem, we want to find the probability \( W(m, N; m_1) \) that the particle will arrive at \( m \) (which is less than \( m_1 \)) after \( N \) steps.

Without the reflecting wall, we already know the equation to find the probability that the
particle arrives at $m$ after $N$ steps

$$W_N(m) = \frac{(N!)}{[(N+m)/2]![N-m)/2]} p^{(N+m)/2}(1 - p)^{(N-m)/2} \quad (2.1.5)$$

The addition of the reflecting wall, however, requires the above equation to be modified to take account of the fact that a path reaching $m$ after $n$ reflections must be counted $2^n$ times. This is because at each reflection it has a probability of 1, meaning this always happens, of retracing its step. To take these relevant factors into account, we have to add the probability $W_N(2m_1 - m)$ of arriving at the image point $(2m_1 - m)$ after $N$ steps to our $W_N(m)$

$$W(m, N; m_1) = W(m, N) + W(2m_1 - m, N) \quad (2.3.1)$$

To verify this, we need to use the figure below. Note that the displacement of the particle means that it moves upward one unit and lateral one unit.

![Diagram](Reviews of Modern Physics, S. Chandrasekhar)

Lets first consider the path $OED$ that has only had one reflection at $m_1$. We see that after the reflection, at point $D$, we get the image point $(2m_1 - m)$. Before we have $m_1$ be a reflecting surface, we see that it takes the same number of steps to get to $D$ as to get to $D'$, and there is a
different probability for each. When we add in \( m_1 \) as the reflecting surface, notice that because of symmetry, \( D \) and \( D' \) become the same point. Now, instead of having two completely separate probabilities, we have one probability of the particle reaching \( D \) that is a sum of the original probabilities for \( D \) and \( D' \) before the reflecting wall was added. Basically for every trajectory leading to the image point, having crossed the line through \( m_1 \) once, there is exactly one which leads to \( m \) after a single reflection. Therefore, instead of counting twice each trajectory that has been reflected once, we can add our uniquely defined trajectory leading to \((2m_1 - m)\).

If we now consider a longer path, \( OABCD \), we can see this has two reflections and therefore four trajectories that need to be counted. Without the reflecting barrier give exactly four trajectories leading to \( m \) or its image \((2m_1 - m)\). Just like above, when we add in the reflecting barrier, we can add all the probabilities together instead of counting each one separately.

If we look at the limit of large \( N \), our \( W(m, N; m_1) \) equation becomes

\[
W(m, N; m_1) = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \{\exp(-m^2/2N) + \exp[-(2m_1 - m)^2/2N]\} \quad (2.3.2)
\]

Now, let us consider the case when we have a perfectly adsorbing wall at \( m = m_1 \). As I described earlier, the addition of an adsorbing wall at \( m_1 \) means that whenever the particle arrives at \( m_1 \), it is unable to suffer and more displacements, basically it can't move anymore and the random walk ends. In this problem, there are two questions we want answered. The first is our normal what is the probability that the particle arrives at \( m \) after taking \( N \) steps? The other is more specific to this problem. It concerns the average rate at which the particle will get to the adsorbing wall, the higher the rate, the higher the probability of the particle getting adsorbed and vice versa.
In the reflecting wall scenario, we had to take into account the extra trajectories that got reflected off the wall. In this case however, there are forbidden trajectories that we have to exclude. These forbidden trajectories include any that have even a single arrival to \( m_1 \). On the other hand, each forbidden sequence does uniquely define another sequence leading to the image \((2m_1 - m)\) of \( m \) on the line \( m = m_1 \) in the plane. By reflecting about the line \( m = m_1 \) the part of a forbidden trajectory above its last point of contact with the adsorbing line before arriving at \( m \), we find a trajectory leading to the image point. Conversely, for every trajectory leading to \( 2m_1 - m \), we necessarily obtain by reflection a forbidden trajectory leading to \( m \). Therefore, we have to subtract the \( 2m_1 - m \) term from our \( W(m_1; N) \) equation

\[
W(m_1; N) = W(m, N) - W(2m_1 - m, N)
\]  

(2.3.3)

So for large \( N \), we now have

\[
W(m_1; N) = \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} \{ \exp(-m^2/2N) - \exp[-(2m_1 - m)^2/2N] \}
\]  

(2.3.4)

Moving on to our second question concerning rate, we first have to formulate a more specific problem. We ask simply what is the probability \( \alpha(m_1; N) \) that after taking \( N \) steps, the particle will arrive at \( m_1 \) without ever having touched the line \( m = m_1 \).

We will refer to the figure below for this problem

(Reviews of Modern Physics, S. Chandrasekhar)
We first notice that $N$ should have to be even or odd depending on whether $m_1$ is even or odd. We'll start by supposing that there is no adsorbing wall. Then, the arrival of the particle at $m_1$ after $(N - 1)$ steps must have been $(m_1 - 1)$ or $(m_1 + 1)$. But, every trajectory that hits $(m_1, N)$ from $(m_1 + 1, N - 1)$ is forbidden when we put in the adsorbing screen. However, not all trajectories arriving at $m_1$ from $(m_1 - 1, N - 1)$ are permitted ones. We see this by arguing that by reflection about the line $m = m_1$, we can uniquely derive $(m_1 - 1, N - 1)$, which has a forbidden character, from a trajectory leading to $(m_1 + 1, N - 1)$ and vice versa. Therefore, the number of permitted ways of arriving at $m_1$ for the first time after $N$ steps is equal to all the possible ways of arriving at $m_1$ after $N$ steps when there is not adsorbing wall minus two times the number of ways of arriving at $(m_1 + 1, N - 1)$, also when there is no adsorbing screen

\[
\frac{N!}{\left[\frac{1}{2}(N - m_1)\right]!\left[\frac{1}{2}(N + m_1)\right]!} - 2\frac{(N - 1)!}{\left[\frac{1}{2}(N + m_1)\right]!\left[\frac{1}{2}(N - m_1 - 2)\right]!} = \frac{N!}{\left[\frac{1}{2}(N - m_1)\right]!\left[\frac{1}{2}(N + m_1)\right]!} \left(1 - \frac{N - m_1}{N}\right)
\]

\[
= \frac{m_1}{N} \frac{N!}{\left[\frac{1}{2}(N - m_1)\right]!\left[\frac{1}{2}(N + m_1)\right]!}.
\]

(2.3.5)

Therefore, the required probability is

\[
\alpha(m_1, N) = \frac{m_1}{N} W(m_1, N)
\]

(2.3.6)

and for large $N$ we have
\[ \alpha(m_1, N) = \frac{m_1}{N} \left( \frac{2}{\pi N} \right)^{\frac{3}{2}} \exp(-m_1^2 / 2N) \] (2.3.7)
2. 4 Random Walk in the presence of two adsorbing interfaces

Finally, we can look at the random walk with two adsorbing interfaces. To do that, we first need to look at and understand characteristic functions.

If we have a real-valued random variable $X$, the function $\phi$ defined by

$$\phi(t) = E(e^{itX})$$  \hspace{1cm} (2.4.1)

is the characteristic function of $X$ [7]. We use characteristic functions to simplify summations of large amounts of numbers. They are also good because we can either start with a huge summation and make it into a characteristic function, or we can start with the characteristic function and use it to find the huge summation.

Let’s look at an example. Let $S = \{0, 1, 2, 3, \ldots\}, P(n) = e^{-\lambda}(\lambda^n/n!)$. We let $X(n) = n$ so $X$ is a Poisson random variable. Now we can compute the characteristic function of $X$.

$$\phi(t) = \sum_{n=0}^{\infty} e^{itX(n)} e^{-\lambda} \frac{\lambda^n}{n!} = \sum_{n=0}^{\infty} e^{int} e^{-\lambda} \frac{\lambda^n}{n!}$$

$$= e^{-\lambda} \sum_{n=0}^{\infty} \frac{(e^{it}\lambda)^n}{n!} = e^{-\lambda}e^{\lambda e^{it}} = e^{-\lambda(1-e^{it})}$$  \hspace{1cm} (2.4.2)

Now, let’s find the characteristic functions for our random walk problem.

We will look at a random walk where we find the probability that

a) The random walk returns to $x = 0$ for the first time at $t = 2n$

b) The random walk first reaches $x = 1$ at $t = 2n + 1$

c) The random walk first reaches $x = b$ at $t = n$ and never reaches $x = -a$ before $t
= n

Or, more specifically, we find the generating functions for \( p_{2n} \), \( v_{2n+1} \), and \( r_n(a, b) \) where

\[
p_{2n} = P(x_s(2n) = 0, x(t) \neq 0 \text{ for } 0 < t < 2n), n = 1, 2, 3
\]

\[
v_{2n+1} = P(x_s(2n + 1) = 1, x(t) < 1 \text{ for } 0 \leq t < 2n + 1), n = 0, 1, 2
\]

and for integers \( a, b \) with \( -a < 0 < b \)

\[
r_n(a, b) = P(x_s(n) = b, x(t) > -1 \text{ for } 0 \leq t \leq n), n = 1, 2, 3
\]

We find these generating functions to be

\[
\sum_{n=1}^{\infty} p_{2n} z^{2n}, \sum_{n=0}^{\infty} v_{2n+1} z^{2n+1}, \text{ and } \sum_{n=0}^{\infty} r_n(a, b)z^n \quad (2.4.3)
\]

To find what our first generating function is equal to, we start with the conditions that our random walk is controlled by independent tossing of a coin with \( P(H) = p, P(T) = q = 1 - p \), and \( x_0 = 0 \). We see then that \( p_2 = 2pq \) and we want to prove the theorem that

\[
p_{2n} = \frac{(\frac{1}{2})(\frac{3}{2})(\frac{5}{2}) \cdots (\frac{2n-1}{2})}{2(n!)^2} (4pq)^n, \quad n = 2, 3, 4, ...
\]

To prove this, we have to use two non-probabilistic lemmas,

1) If \( n \geq 1 \)

\[
(-\frac{1}{2})(-\frac{3}{2})(-\frac{5}{2}) \cdots [-\frac{1}{2} - (n - 1)](-4)^n = \frac{(2n)!}{n!}
\]

and

2) If \( w \) is a real number and \( |w| < \frac{1}{4} \) then
\[(1 - 4w)^{-1/2} = \sum_{n=0}^{\infty} \left(\frac{2n}{n}\right) w^n\]

Using these two lemmas, we find that

\[\sum_{n=1}^{\infty} p_{2n} y^n = 1 - (1 - 4pqy)^{1/2} \quad (2.4.4)\]

and

\[\sum_{n=1}^{\infty} p_{2n} z^{2n} = 1 - (1 - 4pqz^2)^{1/2} \quad (2.4.5)\]

Now, to find what our second generating function is equal to, we use our current hypotheses with \(P(H) = p\) and \(P(T) = q\) for \(n = 1, 2, 3, \ldots\) to prove the theorem

\[v_{2n+1} = \frac{1}{2q} p_{2n+2} = \frac{1}{4} \frac{13 \ldots (1/2+n-1)}{(n+1)!} 4^{n+1} p^{n+1} q^n\]

In proving this, we see that random walks which reach \(x = 1\) for the first time at \(t = 2n + 1\) are in one-to-one correspondence with the random walks which return to \(x = 0\) for the first time at \(t = 2n + 2\) but are always to the left of \(x = 0\) for \(0 < t < 2n + 2\). Each random walk which reaches \(x = 1\) for the first time at \(t = 2n + 1\) has the probability \(p_{n+1}q_n\) so

\[v_{2n+1} = \frac{1}{2q} \frac{13 \ldots (1/2+n-1)}{(n+1)!} 4^{n+1} p^{n+1} q^n\]

\[= \frac{1}{2q} \left[ \frac{135 \ldots (1/2+n-1)}{(n+1)!} (4pq)^{n+1} \right] = \frac{1}{2q} p_{2n+2}\]

If we take the corollary that says \(z \neq 0\) and \(|z| < 1\), we get

\[\sum_{n=0}^{\infty} v_{2n+1} z^{2n+1} = \frac{1}{2q} \left[ 1 - (1 - 4pqz^2)^{1/2} \right] \quad (2.4.6)\]
To find what the third generating function is equal to, we should look at the problem a bit differently. If we look at a gambler starting out with $c \geq 0$ dollars and plays so that he wins $1$ on a coin toss that lands on heads, $H$, and loses $1$ on a toss that lands on tails, $T$. The fortune he is winning from is $l \geq c$ dollars. We can see that the probability, $u_n(c)$, that the gambler's fortune reaches $l$ for the first time at $n$th turn and he does not go broke before this is

$$u_n(c) = r_n(c, l - c)$$

Looking closer, we study a random walk of independent tosses with $P(H) = p$, $P(T) = q = 1 - p$ and our current generating functions definitions. If we substitute $d(z) = \sqrt{1 - 4pqz^2}$, to keep our equation as simple as possible, and say $l \geq c \geq 0$ we find our probability to be

$$U(z, c) = \sum_{n=0}^{\infty} u_n(c)z^n = (2pz)^{l-c} \frac{[1+d(z)]^c - [1-d(z)]^c}{[1+d(z)]^l - [1-d(z)]^l} \quad (2.4.7)$$

Using this makes it easy to solve for our third generating function. Plugging in $r_n(a, b)$ in for $u_n(c)$, we get the equation

$$\sum_{n=0}^{\infty} r_n(a, b)z^n = (2pz)^b \frac{[1+d(z)]^a - [1-d(z)]^a}{[1+d(z)]^a+b - [1-d(z)]^a+b} \quad (2.4.8)$$

The above characteristic function can be expanded in Taylor series to extract the probabilities than a random walk started at the location $c$ end up at the location $l$ in the presence of the second adsorbing barrier located at the origin [7].
3. Analytical Approximation For Grafted Polymer Brushes

The below calculations and assumptions all come from the paper *Size-Dependent Transitions in Grafted Polymer Brushes*, written by Marian Manciu, Courtney Bosse and Eli Ruckenstein, accepted for publication in Journal of Physical Chemistry B [8].

3.1 The loop model for grafted polymer brushes

To derive a solution for grafted polymer brushes, we will use a simple approximation of the partition function that has been suggested recently [9]. This method involves its decomposition in simple configurations, meaning random walks that end at the distance $z$ from the surface, making the probabilities of occurrence easily calculated. The probabilities for a random walk that end at the distance $z$ from the surface involve an entropic term and an energy term $\exp\left(-\frac{U}{kT}\right)$ that is due to segment-segment and segment-solvent interactions. We simplify this equation even more by neglecting the higher energies because they provide negligible contributions and only using the minimum free energy, $U_{\text{min}}$. This model can predict both the step-like monomer density distribution for high grafting densities and/or good solvents and a parabolic distribution for low grafting densities and poor solvents.

We can also extend this approach to grafted adsorbing neutral polymers. We do this by decomposing each individual configuration of the chain in an ensemble of loops of various lengths, either short loops, called trains, where most monomers are confined to near the surface, or open loops, called tails [10]. These loops make calculating the probabilities of occurrence much easier.

For sufficiently high grafting densities and small adsorption energies of Kuhn segments
(which are the "steps" of the random walk describing the polymer), the loops unbind from the surface to form tails, but for sufficiently low grafting densities and large adsorption energies, configurations with many trains are more likely because they provide higher total adsorption energy.

This increase in short-range interactions between the segments and the surface leads to the collapse of the brush on the surface [10]. In Ref [10], a Monte-Carlo procedure was used to calculate the density distribution of monomers in the brush. In my project, we use an analytic approach that involves the search for the most likely configuration. We will show that for any non-zero interaction between segments and surface, a grafted polymer of infinite length leads either to a collapse or a stretched configuration. However, for a grafted polymer of finite length, the collapse or stretching transitions occurs when interactions exceed critical values, which depend on polymer length.
3.2 The approximate partition function in the absence of segment-segment and segment-solvent interactions

First, let’s look at the most likely configuration dependence for segment-surface interactions. We assume that the brush is homogeneous in the plane of the surface and each polymer chain has $N$ Kuhn segments, freely joined to each other. We can approximate the density distribution of the segments by a one-dimensional random walk normal to the surface. This provides an impenetrable barrier to the walk, just like the barrier I described earlier. If there are no interactions, a random walk that leaves the surface has the probability $P_i^\infty$ of first return to the surface after $2i$ steps:\(^1\)

$$P_i^\infty = \frac{1}{(2i-1)2^{2i}} \binom{2i}{i}$$  \hspace{1cm} (3.2.1)

which, for large values of $i$, can be approximated by:\(^6\)

$$P_i^\infty = \frac{1}{2i-1} \sqrt{\frac{2}{(2i-1)\pi}} \exp \left( - \frac{1}{2(2i-1)} \right)$$  \hspace{1cm} (3.2.2)

When the walk returns to the surface, it will bind to it forming a closed loop of $2i$ segments. Then, another random walk, independent of the first, will begin.

While random walks in 3 dimensions and larger there is a chance that it might not return to the origin, it was proven by Polya’ that in one and two dimensions, a random walk will always return to the origin \([11]\), \(\sum_i P_i^\infty = 1\). This implies that any infinite random walk is composed of only closed loops of various lengths occurring with the probabilities given by Eq.(3.2.1). Finite walks end after $N$ steps, the last loop forming a tail. Large loops can’t be formed when it is
restricted to $N$ steps so the probabilities of loop formation for finite walks differ from those in an infinite random walk. The probabilities of occurrence of a loop in a finite chain,

$$P_i = \frac{n_i}{n_S}, \quad (3.2.3a)$$

calculated as the fraction of loops of $2i$ segments, $n_i$, divided by the total number of loops $n_S$:

$$n_S = \sum_i n_i, \quad (3.2.3b)$$

are slightly different from the probabilities of loop formation in an infinite chain. When the walk reaches its maximum number of steps, it is returned to the surface and another walk starts. This means that for small $i$, $P_i$ for finite chains are larger than $P_i^\infty$ for infinite chains. This compensates for large values of $i$, for which $P_i=0$, whereas $P_i^\infty > 0$ (infinite chains).

If the chain is sufficiently long, however, its finite size does not really affect the probabilities of the short loops

$$\frac{P_i}{P_{i+1}} \approx \frac{P_i^\infty}{P_{i+1}^\infty}, \quad (3.2.4a)$$

which implies that:

$$P_i = \alpha P_i^\infty, \quad (3.2.4b)$$

The value of $\alpha$ for a finite chain of $N$ segments ($1 < i < N$) is determined by the normalization condition, Eqs. (3.2.3a) and (3.2.3b):

$$\alpha = \frac{1}{\sum_{i=1}^{N} P_i^\infty}, \quad (3.2.4c)$$
We can therefore write the partition function of a grafted polymer chain as a sum over all configurations of loop ensembles [10],

\[ Z = \sum_j \exp \left( - \frac{U_j}{kT} \right) = \sum_{[n_1, n_2, \ldots]} \exp \left( - \frac{U_{[n_1, n_2, \ldots]}}{kT} \right) \]

(3.2.5)

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( U \) the total energy of the configuration with \([n_1, n_2, \ldots]\) loops and with the summation performed over all possible configurations. We can assume that for each configuration \([n_1, n_2, \ldots]\), there is a corresponding value of the minimum energy of the configuration, \( U(n_1, n_2, \ldots) \). With that assumption, the partition function is simplified to

\[ Z = \sum_j \exp \left( - \frac{U_j}{kT} \right) = \sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} P_1^{n_1} P_2^{n_2} \ldots P_i^{n_i} \exp \left( - \frac{U(n_1, n_2, \ldots)}{kT} \right) \]

(3.2.6)

where \( n_s = \sum_i n_i \) is the total number of loops and \( P_i \) is the probability of formation of a loop of 2\( i \) segments in a finite chain.

Firstly, we assume that the only interaction in the system is between the Kuhn segments and the surface, with an adsorption energy \( A \) per segment adsorbed, which is negative for attraction and positive for repulsion.

If we neglect segment-segment and segment-solvent interaction, the energy associated to each \([n_1, n_2, \ldots]\) configuration depends only on the total number of loops \( n_s \), and the partition function becomes

\[ Z = \sum_j \exp \left( - \frac{U_j}{kT} \right) = \sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} P_1^{n_1} P_2^{n_2} \ldots \exp \left( - \frac{A n_s}{kT} \right) \]

(3.2.7)
The most likely configuration of the brush is provided by the maximum of

\[
\log\left(\frac{n_s!}{n_1!n_2!...}P_1^{n_1}P_2^{n_2}...\exp\left(-\frac{An_s}{kT}\right)\right)
\]

(3.2.8)

with respect to \(n_1, n_2\ ...,\) which, after employing Stirling's approximation, \(\log(n!) = n\log(n) - n\), reduces for an infinite chain to the system of equations:

\[
\sum \frac{n_i}{n_s} = \frac{n_i}{n_s}\exp\left(\log(P_i) - \frac{A}{kT}\right)
\]

\(1 < i < \infty\) \hspace{1cm} (3.2.9)

We already noted that an infinite 1D random walk will always return to origin. Therefore, the sum of all probabilities for the formation of loops of \(2i\) segments has to be unity:

\[
\sum P_i = 1
\]

\(1 < i < \infty\) \hspace{1cm} (3.2.10)

With no interactions between segments and surface \((A=0)\), the solution of the system of equations (3.2.9) is trivial,

\[
\frac{n_i}{n_s} = P_i
\]

(3.2.11)

This shows that the number of loops \(n_i\) of \(2i\) segments, in an infinite chain, is proportional to their probability of occurrence \(P_i\) \((n_i = P_i n_s)\). However, when \(A\) is non zero, the system of equations (3.2.9) does not have a physical solution, because for

\[
A>0,\ \ \frac{n_i}{n_s} < P_i
\]

for all \(i\) and consequently
\[
\sum_{i} \frac{n_i}{n_s} = 1 < \sum_{i} P_i = 1.
\]

Similarly, for

\[
A < 0, \quad \frac{n_i}{n_s} > P_i
\]

for all \(i\), which is also impossible. This means that the most probable configuration of an infinite chain composed of segments interacting with a surface is either collapsed on the surface (for \(A < 0\)) or stretched (for \(A > 0\)).

Now, let’s look at the more realistic case of a finite chain of \(N\) segments. The most probable configuration is constrained by

\[
2n_1 + 4n_2 + ... + 2in_i + ... = N
\]

(3.2.12a)

with an additional condition that

\[
n_i > 0.
\]

(3.2.12b)

The equations for an extremum in the presence of the constrain (3.2.12a)

\[
\frac{d}{dn_i} \left( \log \left( \frac{n_s!}{n_1!n_2!...} P_1^{n_1} P_2^{n_2} ... \exp \left( - \frac{An_s}{kT} \right) \right) - \lambda \left( N - \sum_i 2i n_i \right) \right) = 0
\]

(3.2.13)

lead to:

\[
n_i = n_s \exp \left( \log(P_i) - \frac{A}{kT} - 2i\lambda \right)
\]

(3.2.14)

\(1 < i < i_{max}\)
where \( \lambda \) is a Lagrange multiplier and \( i_{\text{max}} \) is the loop of maximum length compatible with Eqs. (3.2.12 a and b).

By summing over all values of \( n_i \) provided by Eqs.(3.2.14), one obtains:

\[
\sum_i n_i = \sum_i n_s \exp\left(\log(P_i) + \frac{A}{kT} - 2i\lambda\right) \quad (3.2.15)
\]

which, because \( n_s = \sum_i n_i \), reduces to:

\[
\sum_i \exp\left(\log(P_i) + \frac{A}{kT} - 2i\lambda\right) = 1 \quad (3.2.16)
\]

which can be solved for \( \lambda \). Once \( \lambda \) is known, \( n_s \) can be determined from the constrain equation 3.2.12a

\[
\sum_i 2i n_i = 2n_s \sum_i i \exp\left(\log(P_i) + \frac{A}{kT} - 2i\lambda\right) = N \quad (3.2.17)
\]

From now on, we will only use the assumption that any configuration of the grafted chain is composed of closed loops with \( 1 \leq i \leq N/2 \) and open loops with \( N/2 < i \leq i_{\text{max}} = N \). The small loops with \( i=1 \), which correspond to the closest possible approach of the segments to the surface, constitute the trains.

Figures 1a and b examine the effect of segment-surface interaction when \( N = 1000 \) and \( N = 100 \), respectively. The probabilities of formation of loops with \( 2i \) segments, \( \frac{n_i}{n_s} \), for various interactions \( A \), are plotted as a functions of \( i \). We can observe that the repulsion between
segments and surface only slightly affects the density distribution of segments. On the other hand, the attractive interaction strongly affects the distribution, especially for long chains. This is because when segment-surface interaction is attractive, the short loop formations lead to large ns values and therefore high adsorption.
Figures 1 a and b. Probabilities of loops occurrence in brushes of finite chains (Figure 1a: \(N=1000\); Figure 1b: \(N=100\)) as functions of loop number \(i\) for various segment-surface interactions \(A\). The change in probabilities (particularly for attractive interactions) is strongly dependent on the length of the polymer chains.

energies \((n_s A)\). When the absolute value of \(A\) is sufficiently large, the brush collapses. When the interaction between segments and surface is repulsive, however, the configurations with tails are more likely, meaning \(n_s\) is small and the energy \((n_s A)\) is small. Therefore its effect is much less significant.

Let us compare the above results to those provided by our previous Monte Carlo simulations. As suggested in Ref.[10], a trial chain configuration was generated as follows. Successive loops of \(j_1, j_2, \ldots\) segments have been generated randomly with probabilities \(P(i)\) provided by Eqs. (3.2.4) until the total number of segments exceeded \(N (j_1+ j_2+ \ldots > N)\), the last (incomplete) loop being
considered a tail. Once a configuration was obtained, a weighing factor due to the interaction energy

$$\exp\left(-\frac{(n_s - 1)A}{kT}\right),$$

was associated with that configuration and another trial was started.

Figure 2a shows that, in the absence of surface-segment interactions, a small number of trials \((t=1000)\) was sufficient to obtain good approximations for the probabilities of occurrence of loops in the brush, compared to those provided by the present treatment. When the number of trials was increased \((t=10^5)\), there is almost no difference between the two. However, even for a relatively short chain \((N=100)\) and a small attractive interaction \((A=-0.2\ kT)\), \(t=10^5\) Monte Carlo trials fails to reproduce the probability of occurrence of long loops in the brush, overestimating them drastically compared to the present method.
Figure 2a. The probabilities of loop occurrence in most likely configuration (continuous line) compared to Monte Carlo simulations, for $A = 0$ and $A = -0.2 \, kT$, $N=100$, as functions of loop number $i$.

The percentage differences between the Monte Carlo simulations and the present calculated probabilities of the loop occurrence in the most likely configuration (Eqs. (3.2.14)-(3.2.17)) are plotted in Figure 2b. For slightly larger adsorption interactions ($A = -0.5 \, kT$), even increasing the number of trials to $t=10^6$ does not improve much the accuracy. The reason for this behavior is that "train" configurations (with mostly short loops), which possess very large weight factors, are unlikely to be generated in a Monte Carlo trial; for example, a configuration of loops
with $i=2$ has the probability to be generated of only $\left(\frac{1}{2}\right)^{\frac{N}{2}}$, even so it has a large weight factor $\exp\left(-\frac{NA}{2kT}\right)$. For $N=100$ and $A=-0.5 \text{ kT}$, the probability is $\sim 10^{-15}$ and the weight factor is $\sim 10^{11}$.

The incapability of Monte-Carlo estimations to predict accurately the collapse of the brush was avoided in Ref.[10] by generating all possible configurations composed of short loops via the Young diagrams; however, the procedure becomes very time consuming for $N$ larger than about $\sim 100$ segments. The present method can be applied to practically any value of $N$ (it was employed here for up to $N=50\,000$).
Figure 2b. The relative error of the probability of loop occurrence between Monte Carlo simulations and most likely configurations, for various $A$ values.

The profile of the brush, meaning the density of segments as a function of the distance from the surface, is presented in Figure 3, for $N = 1000$. For large repulsive interactions between segments and surface, the distribution of segments is almost step-like, whereas for sufficiently large attractive interactions the distribution is exponential-like, with most segments confined to the vicinity of the surface.

Figure 3. Profile of the brush (the density of Kuhn segments as a function of the distance from the surface) for various segment-surface interactions $A$. 
The thickness of the brush, defined as the average distance between segments and surface, is plotted versus $A$ in Figures 4 for various chain lengths. Where Figure 2 shows a dramatic increase in the number of loops when $A$ is negative and large in value, Figure 4a shows that the thickness of the brush increases sharply when $A$ becomes positive and large, with critical values of $A$ dependent on the length of the chain. In Figure 4b, the ratio between the thickness of the brush and the thickness of the brush for $A = 0$, shows that the critical value of $A$ for the collapse of the brush depends on the length of the polymer.

**Figure 4a.** Thickness of the brush (calculated as the average distance between a Kuhn segment and the surface) vs $A$, for various chain lengths.
Figure 4b. Ratio between the thickness of the brush and the thickness of the brush for A=0 shows that the collapse of the brush on the surface is strongly dependent on the length of the polymer.

The probabilities for a segment to belong to a train \((i=1)\), a loop \((1 < i \leq N/2)\) or a tail \((N/2 < i \leq N)\) are plotted in Figure 5 as functions of \(A\), for \(N = 100\) and \(N = 1000\). Both the transition from loops to trains, collapse, and the transition from loops to tails, the stretching of the polymer, as functions of the segment-surface interaction parameter \(A\), are strongly dependent on the length of the polymer chain. For sufficiently long polymers, they behave like phase transitions.
Figure 5. Percentages of Kuhn segments belonging to trains, loops and tails for $N=100$ and $N=1000$ as functions of the segment-surface interaction $A$. 
3.3 The approximate partition function in the presence of segment-segment and segment-solvent interactions

To find the most likely configuration for segment-surface, segment-segment and segment-solvent interactions, we assume they can be described by the Flory-Huggins free energy density [13]

\[ F_{FH}(z) = \frac{kT}{a^3} \left( \frac{\phi}{N} \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right) \]

\[ \cong \frac{kT}{a^3} (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \]  

(3.3.1)

where \( a \) is the length of a Kuhn segment, \( \phi \) is the volume fraction of the polymer, and \( \chi \) is the Flory interaction parameter. The term containing \( N \) is negligible because \( N \) is very large.

If a polymer chain consisting of \( N \) Kuhn segments of length \( a \) and volume \( v \) occupies an area \( s^2 \) on the surface, the grafting density is \( D = \frac{N}{s^2} \). For a conformation composed of \( \frac{N}{2i} \) loops of \( 2i \) segments, each loop occupies an area

\[ \frac{s^2}{N/(2i)} = \frac{2is^2}{N} \text{.} \]

The total free energy associated with a loop is the integral of the free energy density over the volume of the loop. As a functional of \( \phi(\zeta) \), the total free energy is given by

\[ U(\phi) = \frac{2is^2}{N} \int_0^a F_{FH}(\phi) d\zeta = \frac{2is^2kT}{Na^3} \int_0^a ((1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)) d\zeta \]

(3.3.2a)
with the condition that the loop contains exactly $2i$ segments:

$$2i = \frac{2is^2}{Nv} \int_{0}^{\alpha} \phi(\zeta) d\zeta .$$

(3.3.2b)

The function $\phi(\zeta)$ which minimizes the functional (3.3.2a) with the constraint (3.3.2b) is provided by the extremum of the functional

$$\bar{N}(\phi(\zeta)) = \int_{0}^{\alpha} F(\phi(\zeta)) d\zeta \int_{0}^{\alpha} \left( (1 - \phi) \ln(1 - \phi) + \chi(1 - \phi) + \lambda' \phi(\zeta) \right) d\zeta$$

where $\lambda'$ is a Lagrange multiplier. The corresponding Euler-Lagrange equation:

$$\frac{\partial}{\partial \zeta} \left( \frac{\partial F}{\partial \phi} \right) - \frac{\partial F}{\partial \phi} = 0$$

(3.3.4)

leads to:

$$\ln(1 - \phi) - \chi(1 - 2\phi) = \lambda' - 1$$

(3.3.5)

Since the right hand member is independent of $\zeta$, so should be the left hand member of Eq. (3.3.5), which implies that $\phi(\zeta) =$ constant. The condition (3.3.2b) then leads to:

$$\phi(\zeta) = \frac{Nv}{s^2 i\alpha}$$

Subsequently, the minimum Flory-Huggins free energy associated with each loop of $2i$ segments is obtained by integrating over the volume of the loop:
\[
U_{FH}(i) = \frac{2i s^2 i a}{N} \int F_{FH}(\xi) d\xi = \frac{2i s^2 kT}{Na^2} \int ((1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)) d\xi = 
\]

\[
= \frac{2i s^2 kT}{Na^2} ((1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)) \tag{3.3.6}
\]

The total Flory-Huggins energy of the configuration with \([n_1, n_2, \ldots]\) loops is the sum:

\[
U_{FH} = \sum_i n_i U_{FH}(i) \tag{3.3.7}
\]

and the partition function (Eq. 3.2.6) becomes:

\[
Z = \sum_i \exp \left( -\frac{U_i}{kT} \right) = \sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} P_1^{n_1} P_2^{n_2} \ldots P_i^{n_i} \ldots \exp \left( -\frac{U(n_1, n_2, \ldots)}{kT} \right) = 
\]

\[
\sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} P_1^{n_1} P_2^{n_2} \ldots P_i^{n_i} \ldots \exp \left( -\frac{\sum n_i U_{FH}(i)}{kT} - \frac{n_s A}{kT} \right) \tag{3.3.8}
\]

The above expression can be rewritten as:

\[
Z = \sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} (P_1 \exp \left( -\frac{U_{FH}(1)}{kT} \right))^{n_1} \ldots (P_i \exp \left( -\frac{U_{FH}(i)}{kT} \right))^{n_i} \ldots \exp \left( -\frac{n_s A}{kT} \right) = 
\]

\[
\sum_{n_1, n_2, \ldots} \frac{n_s!}{n_1! n_2! \ldots} (P_1)^{n_1} (P_2)^{n_2} \ldots (P_i)^{n_i} \ldots \exp \left( -\frac{n_s A}{kT} \right) \tag{3.3.9}
\]

If we replace the probabilities of loop formation for a finite random walk by

\[
P_i^* = P_i \exp \left( -\frac{U_{FH}(i)}{kT} \right) \tag{3.3.10}
\]

We see that Eq.(3.3.9) is the same as the partition function of a chain that doesn’t have segment-segment and segment-solvent interactions Eq.(3.2.7).
When $\phi$ is large, the exclusion interactions prevent $\phi$ to reach unity. Instead of the maximum possible value of $\phi$, at close packing, depending on the shape of the segments, it will be simply assumed from now on that $\phi = \frac{Nv}{s^2ia} < \phi_{\text{max}} = 1$. We want to imply that the loops with a small number $2i$ of segments cannot be present in the brush, because in this case $U_{FH}(i)$ is divergently large, hence $P_i^* = 0$ in Eq.(3.3.10), which lead to a lower bound, $i_{\text{min}}$, for $i$:

$$\phi = \frac{Nv}{s^2ia} < 1 \quad i > i_{\text{min}} = \frac{Nv}{s^2a} \quad (3.3.11)$$

Consequently, when segment-segment and segment-solvent interactions are accounted for, the probability of loop formation $P_i^*$ becomes:

$$P_i^* = 0 \quad (3.3.12a)$$

$$P_i^* = P_i \exp \left( - \frac{2i^2 s^2}{Na^2} \left( (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \right) \right) \quad (3.3.13b)$$

where $\phi = \frac{Nv}{s^2ia}$, and $P_i$ is the probability of loop formation in the absence of segment-segment and segment-solvent interactions.

The effect of segment-segment and segment-solvent interactions, on the probabilities of loop formation $\frac{n_i}{n_s}$ is presented in Figure 6a, for a good ($\chi=0$), neutral ($\chi=0.5$), and bad ($\chi=1$) solvent, for $N = 1000$, $A = 0$ and a small grafting density $D = \frac{N}{s^2} = 0.2$ segments/Å$^2$. 
Figure 6a The probabilities of occurrence of loops of $2i$ segments in a brush, $\frac{n_i}{n_s}$, for a relatively low grafting density $D = 0.2$ segment/$Å^2$ for a good ($\chi=0$), neutral ($\chi=0.5$), and bad ($\chi=1$) solvent, compared to the same probabilities in the absence of segment-segment and segment-solvent interactions. The segment-surface interactions have been neglected ($A=0$).

Whereas at low grafting densities the effect is negligible, it becomes much stronger for large grafting densities ($D=1$ in Figure 6b). At very large grafting densities, the loop with small number of segments are forbidden because of exclusion effects, the probabilities of loops with intermediate values of $i$ are increased, and those of the loops with large values of $i$ are decreased (see Figure 6c).
Figure 6b The probabilities of occurrence of loops of 2i segments in a brush, $\frac{n_i}{n_s}$, for a relatively large grafting density $D = 1.0$ segment/Å$^2$ for a good ($\chi=0$), neutral ($\chi=0.5$), and bad ($\chi=1$) solvent, compared to the same probabilities in the absence of segment-segment and segment-solvent interactions. The segment-surface interactions have been neglected ($A=0$).
The thickness of the brush, as functions of the interaction between segments and surface ($A$), are shown in Figure 7 for good, neutral and bad solvents. The dependence of the brush thickness on $A$ is very similar the one in the absence of segment-segment and segment-solvent interactions, with bad solvents favoring the collapse of the brush on the interface and good solvent favoring the loop to tail transition.

![Figure 7](image)

**Figure 7** Thickness of the brush plotted against $A$, for $N=1000$ segments, $D=1$ segment/$Å^2$ for a good ($\chi=0$), neutral ($\chi=0.5$), and bad ($\chi=1$) solvent. All curves have a behavior similar to those obtained when segment-segment and segment-solvent interactions have been neglected.
4. Conclusions

We have seen that the possible grafted chain configurations, when segment-segment and segment-solvent interactions were neglected, can be described as ensembles of loops of $2i$ segments that have probabilities equal to those of first return of a random walk, and can be modified when the latter interactions were taken into account. The most likely configuration for an infinite chain with non-vanishing interactions between segments and surface with respect to the number of loops of $2i$ segments, $n_i$, provided a system of equations that does not have solution. However, for finite chains the system of equations has solution for any segment-surface interaction $A$. We concluded that the brush collapses on the surface when the attractive segment-surface interactions are sufficiently large, and the brush stretches when the repulsive segment-surface interactions are strong enough.

The critical values of $A$, at which the loops to trains and the loops to tails transitions start to occur, depend strongly on the number of Kuhn segments of the polymer as well as on the segment-segment and segment-solvent interactions and grafting density. Therefore, we concluded that for a selected adsorption interaction between segments and surface, it is possible to design a polymer brush of certain length and grafting density, whose thickness is strongly dependent to changes in the solvent properties.
5. References


6. Curriculum Vitae

Courtney Bosse

My most recent education was at the University of Texas at El Paso graduating with a Master’s in Medical physics with a final GPA of 3.78. The medical physics program at UTEP is geared more toward pure physics than typical Master’s program meaning the students are required to take 4 physics classes and 4 medical physics classes.

Also, all students in the UTEP physics department are required to take two seminar classes. These allow students to learn about projects in all different physics fields and see what might be of greatest interest to the student.

Students in the physics graduate school are all given Teaching Assistant jobs. I was assigned the General Physics labs each semester. It has been fun and rewarding teaching lab each semester, but I learned that teaching is not what I want to be doing the rest of my life.

Before finishing at UTEP, I was able to coauthor a paper with my advisor and another professor. The paper, Size-Dependent Transitions in Grafted Polymer Brushes, was written by Dr. Marian Manciu, Dr. Eli Ruckenstein and myself. The paper has been recently accepted for publication.

My undergraduate degree was earned at St. Bonaventure University. There, I majored in Engineering Physics, which is only one class different from majoring in Physics, which I took anyway. The classes were small, usually only 5 people, allowing me to learn better and have relationships with all my professors.

In order to graduate with any type of Physics degree, a student has to pass an oral final in which all the physics professors (there were five) take you into a room and ask you questions based on every physics class the student has taken over all four years. I finished at St. Bonaventure with a degree in Engineering physics and a minor in mathematics. My final GPA was 3.6. I made the Deans List each semester, was invited to join the Phi Eta Sigma Academic Honor Fraternity and the Pi Mu Epsilon Mathematics Fraternity, of which I was Vice President. I also was awarded the highest academic scholarship at St. Bonaventure, the Presidential Academic Scholarship and a full-tuition Athletic Scholarship.

My Private Jesuit high school in Indianapolis, Indiana was called Brebeuf Jesuit Preparatory School. It was rated the number one high school in Indiana in 2006. At Brebeuf, I played first chair viola in the symphony orchestra. Before my senior year, we traveled and performed throughout Germany and Eastern Europe for ten days.

My work experience includes many different teaching opportunities. I was a GRE Tutor from 2011 to 2012. This was a two-week course on teaching how to take the GRE to undergraduates. I was also a Lab Teaching Assistant at UTEP and St. Bonaventure, both times teaching General Physics labs. Along with teaching lab at St. Bonaventure, I was a Calculus tutor for a year.

In the summer between my junior and senior year at St. Bonaventure, I was accepted into a Research Education for Undergraduates program (REU) at Indiana University. There I used Mat Lab Programming to solve quantum mechanics physics problems and was able to tour the Fermi Labs in Chicago.
The summer before that, I was an intern at Sirius XM Radio. While there, I assisted soldering chips on circuit boards and helped make portable satellite reception testing boxes.

This August, I will be attending the University of Texas Health Science Center in San Antonio to pursue a Doctorate in Medical Physics (DMP) degree.