ABSTRACT

ANALYTIC MODELS OF REGULARLY BRANCHED POLYMER BRUSHES USING THE SELF-CONSISTENT MEAN FIELD THEORY

By

Daniel LeSher

May 2015

Polymer brushes consist of multiple monomers connected together with one of the polymer chain's ends attached to a surface. Polymer brushes have shown great promise for a wide variety of applications including drug delivery dendrimer systems and as tunable brushes that can change their shape and physical properties in response to changes in their environment. Regularly branched polymer brushes which are structured as a function of their chemical indices are investigated here using the self-consistent mean field theory for electrically neutral polymers. The brushes were described using weighting functions, $f(n)$, were n was the fewest number of monomers from a specified location to a free end. Brushes with weighting functions of the form $f(n) \quad n^b$, $f(n) \quad e^{bn}$, as well as $f(n) \quad d^{an}$ when $d \quad 2$ and $a \quad 2$ were found to match the parabolic free chain end profile expected, while it was determined that polymer brushes described using $f(n) \quad n^b$ must be very small in order to remain in equilibrium. However, brushes described by $f(n) \quad 2^{\frac{G(N \quad n)}{N}}$ and $f(n) \quad 2^n$ were found to be unstable for real, positive values of the potential of the system.

ANALYTIC MODELS OF REGULARLY BRANCHED POLYMER BRUSHES USING THE SELF-CONSISTENT MEAN FIELD THEORY

A THESIS

Presented to the Department of Department of Physics and Astronomy

California State University, Long Beach

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Applied Physics

Committee Members:

Galen Pickett, Ph.D. (Chair)
Thomas Gredig, Ph.D.
Michael Peterson, Ph.D.

College Designee:

Chuhee Kwon, Ph.D.

By Daniel LeSher

B.S., 2012, California State University, Chico

May 2015

ACKNOWLEDGEMENTS

My thesis advisor Dr. Galen Pickett has been very helpful throughout the process of writing this thesis by providing specific advice over the past year. The other members of my thesis committee, Dr. Michael Peterson and Dr. Thomas Gredig, have always assisted me when I asked. I would also like to thank Dr. Chuhee Kwon for helping me through the research process and for her work setting up the Student Summer Research Award which funded this project. Special thanks goes to Irene Howard for helping me navigate the complexities of the paperwork required to set up, finance, and complete this thesis. I would also like to thank my parents, Dana and Carol, my brother Michael, my sister Kelly, and Dira Putri. Without them I would not have been able to complete this thesis.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE Page

FIGURE Page

CHAPTER 1

INTRODUCTION

Polymer brushes are defined as an assortment of macromolecule chains with one end of the chain attached to a surface [1]. In the following sections the polymer brushes will be described with several distinguishable features, such as a maximum height above the surface that the brush extends to (denoted by h) and the monomer's location in terms of the number of flexible polymer spacers (denoted by n) from the end that is not attached. An example of such a polymer brush attached to a linear surface with regular branching points is shown in FIGURE 1.

Various methods have been developed in order to study polymers, including: the integral equation theory, density functional theory, and the self-consistent mean field theory (also known as the self-consistent field theory) [2]. The study of polymers through these methods is of great importance to the development of current and new potential polymer applications. Throughout the years, the importance of computational methods able to describe polymers using the self-consistent field theory has been recognized [3]. Polymer brushes have great potential for various applications in various fields including: physics, medicine, chemistry, and biology. A brief overview and history of polymer brushes and their applications is provided in the following pages.

Polymer Brushes in Physics

The foundation for the theory of polymer brushes was firmly established in part from the e orts of de Gennes and Alexander [1]. Interest in research of polymer brushes in physics has recently increased as various possible future applications have become apparent [4]. A current area of research for polymer brushes is their properties when they

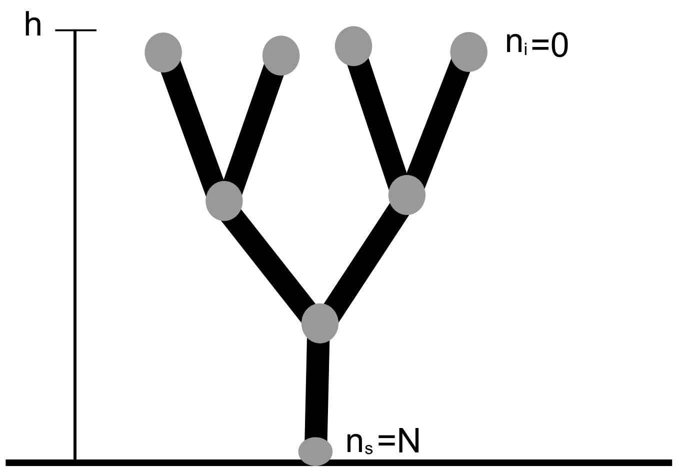

FIGURE 1. An example of a regularly branched polymer brush with a maximum possible height above the surface of h and a total number of flexible polymer spacers N (the polymer spacers are shown as the gray circles at each branching point). The location on the polymer is given by the integer value n corresponding to the flexible polymer spacers. The value of n is at a maximum value of N for the spacer attached to the substrate's surface (n_s) and at a minimum value of zero at the spacer at the free end of the brush (n_i). The position of a given n value above the surface substrate is defined by the function $z(n)$.

are attached to di erent surface configurations. Although polymer brushes attached to flat surfaces have been studied extensively, the properties of polymer brushes attached to various curved surfaces have not been su ciently studied. An example of polymer brushes on a curved surface that have been studied are star polymers, consisting of multiple polymer brushes attached to a spherical surface [5]. An example of a star polymer with four ”arms” attached to a common flexible polymer spacer is shown in FIGURE 2.

These star polymer systems present new opportunities in various fields including physics due to their structures and interactions with various surfaces and particles [5, 6, 7]. Another interesting topic of polymer brush research is how they respond to external

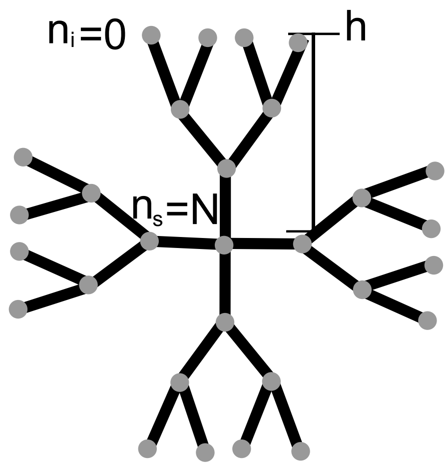

FIGURE 2. An example of a regularly branched star polymer brush with a maximum possible height above of h from a common flexible spacer and a total number of flexible polymer spacers N (the polymer spacers are shown as the gray circles at each branching point). The location on the polymer is given by the integer value n corresponding to the flexible polymer spacers. The value of n is at a maximum value of N for the common spacer for each "arm" (n_s) and at a minimum value of zero at the spacer at the free end of the brush (n_i). The position of a given n value from the common spacer is defined by the function $z(n)$.

stimulus. Over the past decade it has been observed that changes in the structure of certain polymer brushes will occur when the temperature of the surrounding environment is altered. Polymers such as poly(N-isopropylacrylamide) (PNIPAAM) have been observed to collapse into a denser formation above the lower critical solution temperature when the molecular weight and grafting density is su ciently large [8, 9]. Various other environmental changes have also been shown to alter the structure and properties of polymer brushes. Examples of some of these conditions are described in the following sections.

Biological Applications of Polymer Brushes

Polymer brushes show significant promise to be used in biotechnology with applications ranging from biosensing, molecule recognition, and engineered tissue sca olds [10]. Polymer brushes show great promise as biosensors for various reasons. In addition to being smaller than conventional biosensing equipment and relatively inexpensive compared to older analytical techniques, polymer brushes can be altered when they come in contact with specific biological materials. Contact with these materials can either produce a current in the brush or alter the electrical charge of the brush, this change in the system can then be detected through various conventional means in order to determine if specific biological elements are present [11]. In addition to their applicability in the field of biosensing, polymer brushes have also been used to prevent the adhesion of cells to various substrates. In 2008 Mizutani, et al. showed that cellular adhesion of bovine carotid artery endothelial cells to a surface decreased when the length of Poly(N-isopropylacrylamide) polymer brushes increased [12]. The ability of polymer brushes to prevent cellular adhesion to various surfaces is also of great interest due to its potential applications in medicine.

Medical Applications of Polymer Brushes

Specific polymer brushes also have the potential to be grafted onto medical devices in order to prevent damage to the medical device as well as preventing serious health risks to patients [13]. Leckband et al., described how polyethylene glycol polymer brushes can be used to prevent microbial adhesion to surfaces in 1999. By grafting polyethylene glycol polymers to a surface, several e ects will be produced to inhibit microbial adhesion. First, overcrowding due to the polymer brush creates an osmotic penalty which eliminates the adsorption free energy of a microbial protein. Secondly, any microbe that attempts to contact the surface must first overcome the potential barrier created due to induced overcrowding of the polymer brushes. Thirdly, the addition of the polymer brushes increases the effective viscosity on any proteins, this slows down the adsorption rate of the protein. Finally, the polymer brushes can form an incompressible layer which can prevent any proteins from ever reaching the surface [14].

Applications of Polymer Brushes in Chemistry and Materials Science

As high-tech and consumer devices increase in their complexity and the demand for more efficient products increases, new materials and fabrication methods must be developed. Frictional forces between solid surfaces have been shown to reduce when these surfaces have polymer brushes attached to them [15]. In 2003 Raviv, et. al. showed that charged polymer brushes in particular can severely reduce the frictional forces between solid surfaces [16]. This reduction in frictional forces can be used to increase the efficiency of various devices.

Another interesting application of polymer brushes is their use in creating thin polymer films. By detaching the polymer brushes from their substrate, polymer brushes can provide a way to tune the thin film to the desired specifications for microelectronics and precise filtering of various systems [17]. These are just some of the many present and future applications that polymer brushes may be used for.

CHAPTER 2

THEORY

In the following pages I will examine various polymer brush systems using the self-consistent field theory for polymers. Each polymer brush is assumed to be comprised of flexible polymer spacers which are composed of N spheres with an assumed diameter of $a = 1$, G number of generations (a generation is defined here as a group of statistically equivalent monomers), and the number of attached monomers at a given point is described by a weighting function $f(n)$ [18]. All of the polymer brush chains were assumed to be electrically neutral, similar to the method used by de Gennes in 1980 [19]. In order for these polymers to be effective polymer brushes they must remain mechanically stable. In order to ensure mechanical stability of a polymer brush, the free energy of a single chain, described as a function of the position above the substrate $z(n)$,

$$S_{tot}[z(n)] = \int_0^{GN} f(n)\left[\frac{1}{2}\left(\frac{dz}{dn}\right)^2 - P(z(n))\right] dn \tag{2.1}$$

must be minimized [20].

Since the kinetic energy can be written as $KE = \frac{f(n)}{2}\left(\frac{dz}{dn}\right)^2$ and the potential of the polymer is expressed as $P(z(n)) = P_0\left(1 - \frac{z(n)^2}{h^2}\right)$ where h is the height of the polymer, the single chain free energy can be written in terms of the polymer brush's Lagrangian

$$S_{tot} = \int_0^{GN} dn\, \mathcal{L}(z(n), \frac{dz}{dn}) \tag{2.2}$$

where

$$\frac{f(n)}{2} \frac{dz}{dn}^{2} \quad f(n)P(z(n)) \tag{2.3}$$

is the Lagrangian [21]. Later results can be simplified by converting the system to one dependent on a dimensionless variable $\quad \frac{n}{N}$ [18]. Therefore the single chain free energy will be minimized when the polymer's Euler-Lagrange equation

$$\frac{d}{d} \quad \frac{}{\dot{z}} \quad \frac{}{dz} \quad 0 \tag{2.4}$$

is solved.

Since the polymer brushes are static at the substrate, mechanical equilibrium requires that

$$\frac{dz}{d} \quad {}_{1} \quad 0 \tag{2.5}$$

and

$$\frac{d}{d} \quad f(\quad)\frac{dz}{d} \quad f(\quad) \quad P(z) \quad 0 \tag{2.6}$$

when $\quad$ 1 in order to determine the value of P_0.

Once the position of the polymer with respect to the dimensionless variable $\quad$ is obtained, the number of free chain ends ( ) with a position greater than a given value of z

$$1 \quad \int_{z}^{h} \frac{d \quad (z_0)}{dz_0} \frac{d}{dz} dz_o \tag{2.7}$$

can be found as a function of the location of the free chain end (z_0) [22]. Since there will be no free ends at a height grater than h, $\quad (h) \quad 0$ and therefore this equation can be reduced to

$$(z) \quad \frac{dz}{d} \tag{2.8}$$

provided that $\frac{d}{dz}$ is independent of z_0 for the polymer brush. Using this method it is anticipated that the number of free chain ends will be have a parabolic profile similar to the self-consistent field simulations created by Murat and Grest in 1989 [23]. Any value obtained equal to $10^{\ 7}$ was determined to be the minimum limit for the methods used, any values below this limit were unable to be modeled using the self-consistent mean field theory.

CHAPTER 3

ANALYSIS AND RESULTS

<u>$f(n) \quad n^b$</u>

For polymer brushes with a weighting function of $f(n) \quad n^b$, a Lagrangian of

$$\frac{n^b}{2}\frac{dz}{dn}^2 \quad n^b P_0 \; 1 \quad \frac{z(n)^2}{h^2} \tag{3.1}$$

is obtained.

In terms of $\quad \frac{n}{N}$ the Lagrangian is expressed as

$$\frac{(N \;)^b}{2}\frac{dz}{dn}^2 \quad (N \;)^b P_0 \; 1 \quad \frac{z(n)^2}{h^2} \tag{3.2}$$

since the weighting function is now described as $f(\;) \quad (N \;)^b$. Eq. 3.2 was then applied to the Euler-Lagrange equation to produce

$$\ddot{z}(\;) \quad \frac{b}{}\dot{z}(\;) \quad \frac{2P_0 z(\;)}{h^2} \quad 0 \tag{3.3}$$

In the following sections this equation was analyzed for various values of b.

<u>Case when $b \quad 0$</u>

When $b \quad 0$ the weighting function is reduced to a value of 1 regardless of the position on the polymer brush. An example of a brush with a weighting function of $f(n) \quad 1$ is shown in FIGURE 3.

The Lagrangian of this system can be expressed as

$$\frac{1}{2}\frac{dz}{d}^2 \quad P_0 \; 1 \quad \frac{z(\;)^2}{h^2} \tag{3.4}$$

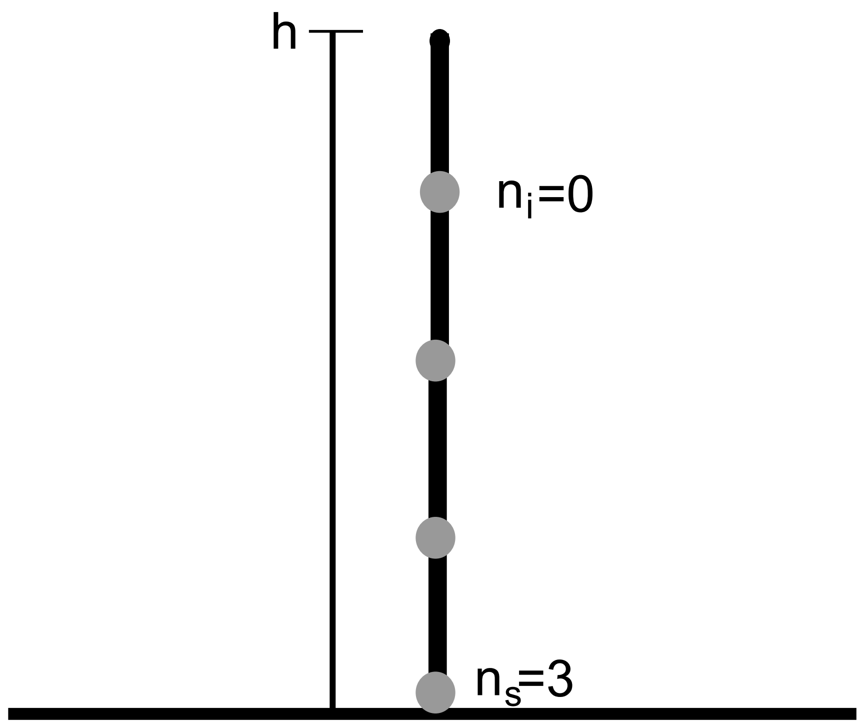

FIGURE 3. A polymer brush attached to a flat surface with a weighting function of $f(n)\quad 1$, a value of $N\quad 3$, and a maximum height of h.

which was then used in Eq. 2.4 to produce the equation of motion

$$\ddot{z}(\ )\quad \frac{2P_0 z(\ )}{h^2}\quad 0 \tag{3.5}$$

in order to produce an equation that accurately describes the structure of polymer brush as a function of . The structure of this polymer is described by Eq. 3.6.

$$z(\ )\qquad h\csc\ \frac{\overline{2P_0}}{h}\ \sin\ \frac{\overline{2P_0(\qquad 1)}}{h} \tag{3.6}$$

Differentiating Eq. 3.6 with respect to obtains

$$\frac{dz}{d} \quad \sqrt{2P_0}\cos\left(\frac{\sqrt{2P_0}(\quad 1)}{h}\right)\csc\left(\frac{\sqrt{2P_0}}{h}\right) \tag{3.7}$$

which was used with Eq. 2.8 to determine the number of free chain ends throughout the polymer brush as a function of its position. The equation for the number of free chain ends is expressed in Eq. 3.8.

$$(z[\quad]) \quad \sqrt{2P_0}\cos\left(\frac{\sqrt{2P_0}(\quad 1)}{h}\right)\csc\left(\frac{\sqrt{2P_0}}{h}\right) \tag{3.8}$$

Evaluation of Eq. 3.7 at 0 produces

$$\frac{dz}{d}_{\quad 0} \quad \sqrt{2P_0}\cot\frac{\sqrt{2P_0}}{h} \tag{3.9}$$

which will be approximately zero when $\frac{\sqrt{2P_0}}{h} \quad \frac{}{2}$. Therefore the position of the polymer brush and the number of free chain ends can be expressed as a function of the maximum height, these relationships are described in Eq. 3.10 and Eq. 3.11 respectively.

$$z(\quad) \quad h\cos\left(\frac{}{2}\right) \tag{3.10}$$

$$(z[\quad]) \quad \frac{h}{2}\cos\left(\frac{(\quad 1)}{2}\right) \tag{3.11}$$

In order to satisfy the boundary conditions of the system, it was determined that the height of the brush must be $h \quad 6\,366 \quad 10^{\;8}$ and a corresponding potential of $P_0 \quad 5 \quad 10^{\;15}$. The position of this polymer brush as a function of the chemical index is shown in FIGURE 4 and the number of free chain ends at each position is shown in FIGURE 5.

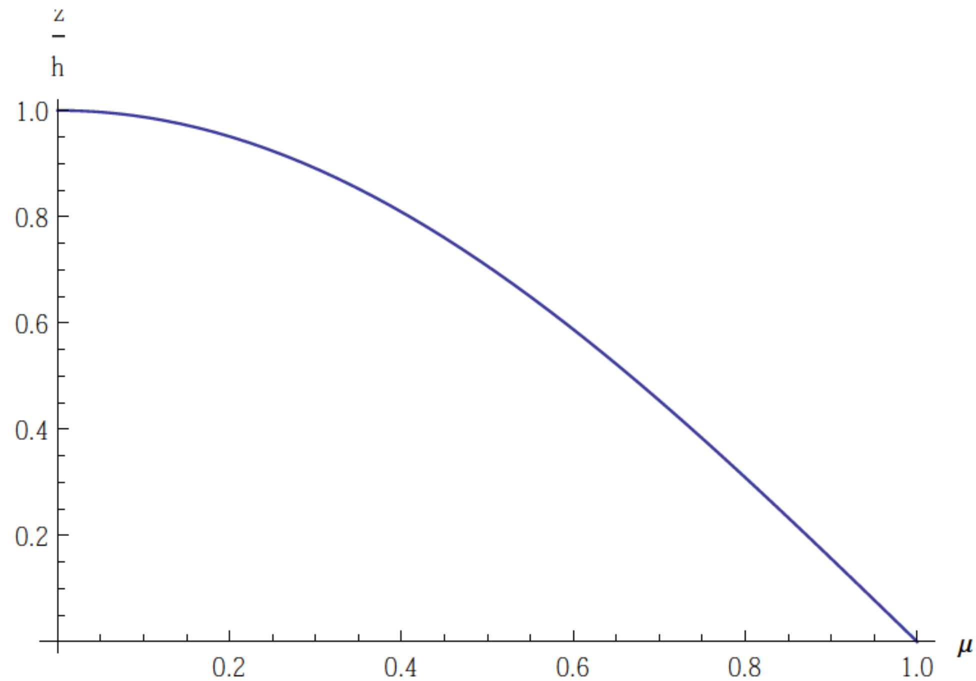

FIGURE 4. The height above the substrate surface for a polymer brush with a weighting function of $f(n) = 1$. A value of $h \approx 6.366 \times 10^{-8}$, and $P_0 = 5 \times 10^{-15}$ in order to satisfy the necessary boundary conditions.

From Eq. 3.7 and Eq. 3.11 it was observed that polymer brushes with the weighting function $f(n) = 1$ must have a vary small maximum height in order to remain attached to the surface substrate.

Case when $b = 1$

When $b = 1$ the weighting function becomes the linear function of $f(n) = n$. An example of a polymer brush with a weighting function of $f(n) = n$ is shown in FIGURE 6.

Eq. 3.3 becomes

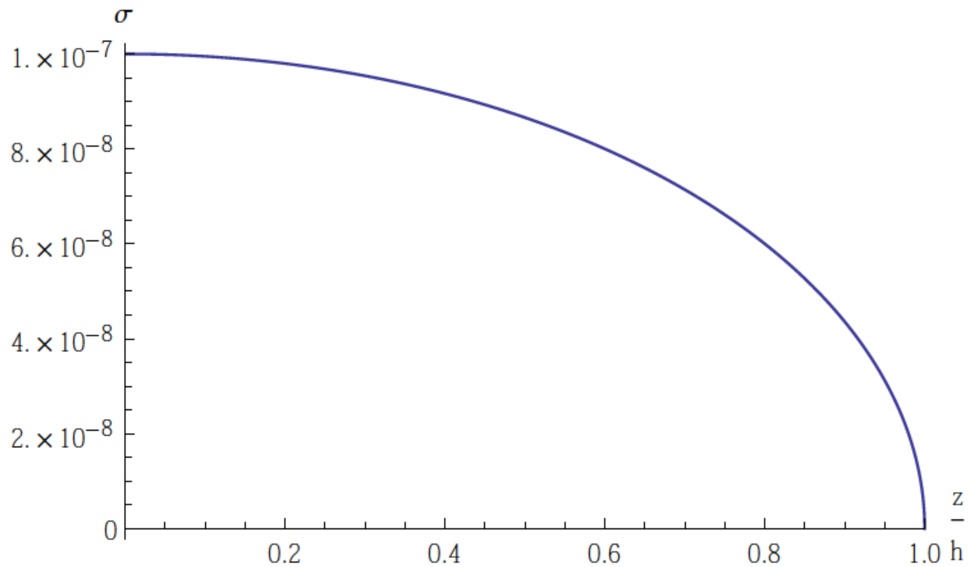

FIGURE 5. The number of free chain ends of a polymer brush with a weighting function of $f(n) = 1$. The polymer brush observed here had a value of $h \approx 6.366 \times 10^{-8}$ and $P_0 = 5 \times 10^{-15}$ in order to satisfy the necessary boundary conditions.

$$\ddot{z}(\mu) + \frac{\dot{z}(\mu)}{\mu} + \frac{2P_0 z(\mu)}{h^2} = 0 \tag{3.12}$$

which was then applied to solved with the boundary condition $z(0) = h$ to obtain the position above the substrate surface in terms of a Bessel function of the first kind (J_0)

$$z(\mu) = hJ_0\left(\frac{\sqrt{2P_0}\mu}{h}\right) \tag{3.13}$$

for the case where $b = 1$

By differentiating Eq. 3.13 with respect to μ

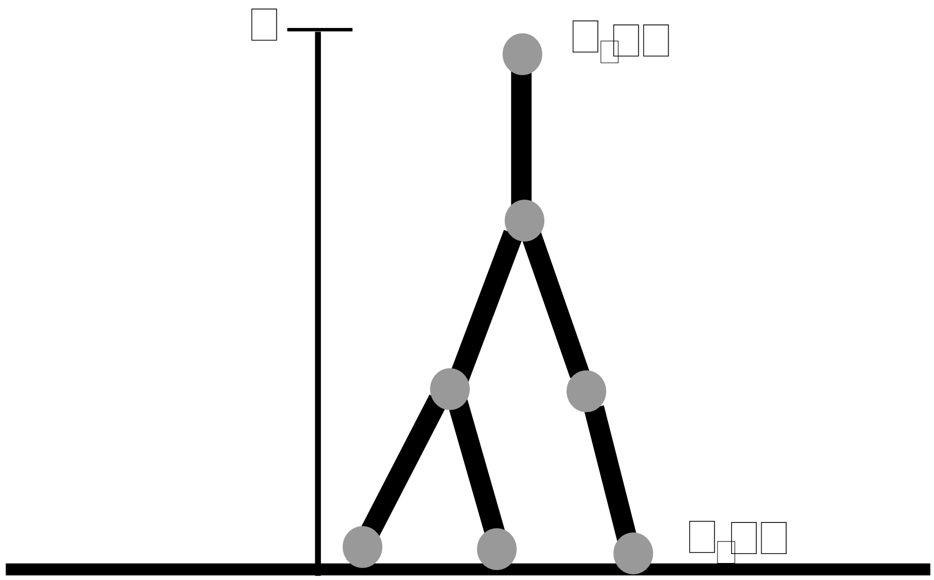

FIGURE 6. A polymer brush attached to a flat surface with a weighting function of $f(n)$ n, a value of N 3, and a maximum height of h.

$$\frac{dz}{d} \qquad \overline{2P_0} J_1 \; \frac{\overline{2P_0}}{h} \tag{3.14}$$

the change in the polymer's structure as a function of the chemical index was obtained.

From Eq.3.13 it is observed that in order for the polymer brush to be attached at the substrate surface, $z($ $1)$ 0, therefore $\frac{\overline{2P_0}}{h}$ $2\ 40483$ since the first order Bessel function has its first zero when $J_0(2\ 40483)$.

Therefore

$$P_0 \quad \frac{(2\ 40483h)^2}{2} \tag{3.15}$$

in order to satisfy Eq. 3.13 at the surface substrate.

Since the number of free chain ends at a given position was determined to be proportional to the change in the polymer's structure in Eq. 2.8, the number of free ends for this polymer was determined to be

$$(z[\quad]) \qquad \frac{dz}{d} \qquad \overline{2P_0} J_1 \ \frac{\overline{2P_0}}{h} \tag{3.16}$$

Using Eq. 3.15 the number of free ends for the system can be written as

$$(z[\quad]) \quad 2\ 40483 h J_1 (2\ 40483\ \ ) \tag{3.17}$$

so that an appropriate value for the height can be found which satisfies the boundary condition at 1. Using Eq. 3.17 it was determined that $h \quad 8\ 0099 \quad 10^{\ 8}$ and $P_0 \quad 1\ 8552 \quad 10^{\ 14}$.

Using Eq. 3.13 and Eq. 3.15 the structure of the polymer brush was determined, this is shown in FIGURE 7.

The number of free chain ends at a given position is shown in FIGURE 8 using the same maximum potential as in FIGURE 7.

From Eq. 3.17 it was observed that the boundary conditions are satisfied and the polymer brush remains attached to the substrate when the brush is very small.

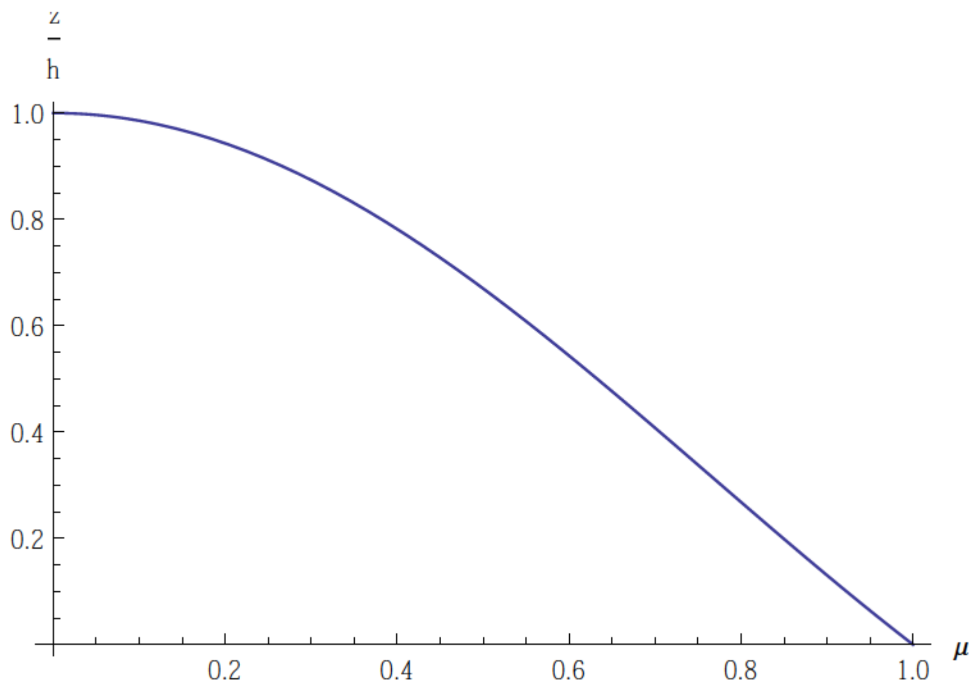

FIGURE 7. The height above the surface substrate for a polymer brush with a weighting function of $f(n) = n$ is described using Bessel functions of the first kind. The polymer brush observed here had a value of $h \approx 8.0099 \times 10^{-8}$ and $P_0 = 1.8552 \times 10^{-14}$ in order to satisfy the necessary boundary conditions.

Case when $b = 2$

When $b = 2$ Eq. 3.3 becomes

$$\ddot{z}(\mu) + \frac{2}{\mu}\dot{z}(\mu) + \frac{2P_0 z(\mu)}{h^2} = 0 \tag{3.18}$$

which was solved with the boundary condition $z(0) = h$ to obtain the equation

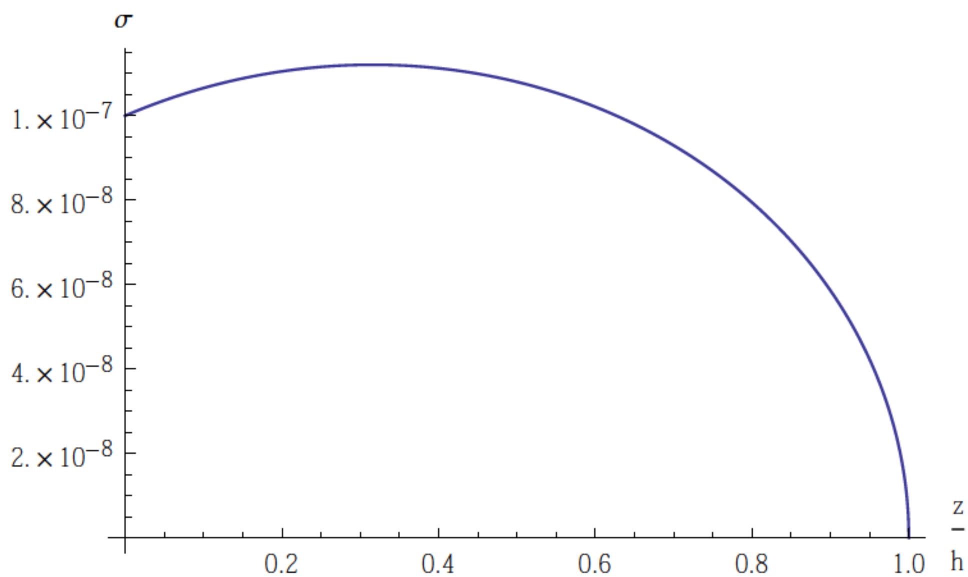

FIGURE 8. Number of free chain ends throughout a branched polymer brush with a weighting function of $f(n) = n$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h \approx 8.0099 \times 10^{-8}$ and a maximum potential of $P_0 = 1.8552 \times 10^{-14}$.

$$z(\mu) = \frac{h^2 \sin\left(\frac{\sqrt{2P_0}\mu}{h}\right)}{\sqrt{2P_0}\mu} \tag{3.19}$$

to describe the structure of the polymer brush. An example of a polymer brush with this weighting function is shown in FIGURE 9.

Differentiating Eq. 3.19 with respect to μ produces Eq. 3.20

$$\frac{dz}{d\mu} = \frac{h}{\mu}\left(\cos\left(\frac{\mu\sqrt{2P_0}}{h}\right) - \frac{h \sin\left(\frac{\mu\sqrt{2P_0}}{h}\right)}{\mu\sqrt{2P_0}}\right). \tag{3.20}$$

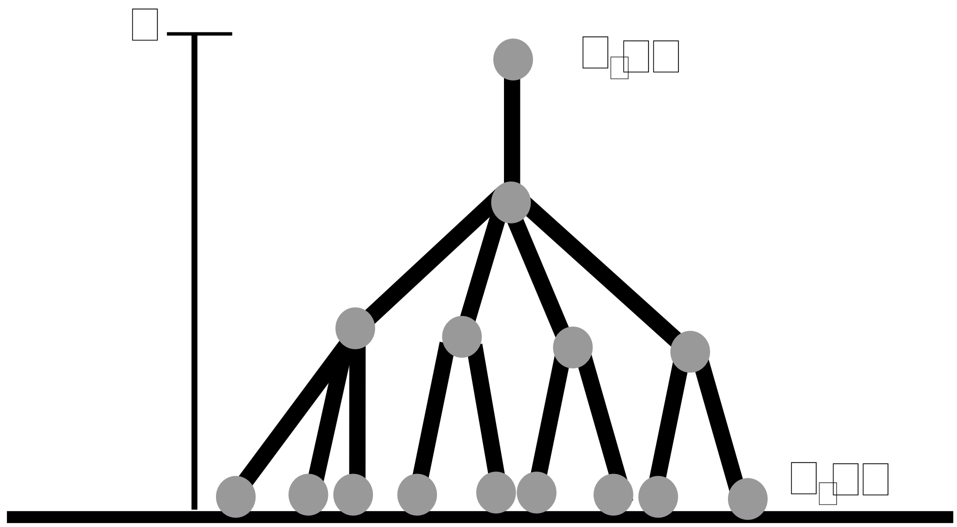

FIGURE 9. A polymer brush attached to a flat surface with a weighting function of $f(n) \quad n^2$, a value of $N \quad 3$, and a maximum height of h.

which was used to solve for appropriate values for P_0 so that the boundary conditions for the polymer brush are satisfied.

Eq. 3.20 was used with Eq. 2.8 to obtain

$$(z[\;]) \quad \frac{h}{\;} \quad \frac{h\sin\frac{\overline{2P_0}}{h}}{\overline{2P_0}} \quad \cos\frac{\overline{2P_0}}{h} \tag{3.21}$$

to mathematically describe the number of free ends for the polymer brush.

Since Eq. 2.6 will return a value of zero regardless of the value of P_0, therefore Eq. 3.19 was used to determine the value of P_0.

From Eq. 3.19 it was observed that

$$z(1) \quad \frac{h^2 \sin \quad \frac{\overline{2P_0}}{h}}{\overline{2P_0}} \tag{3.22}$$

at the substrate's surface, therefore in order for Eq. 3.22 to equal zero the condition $\frac{\overline{2P_0}}{h}$, must be true. The potential can then be expressed as

$$P_0 \quad \frac{(\ h)^2}{2} \tag{3.23}$$

for polymer brushes with a weighting function of $f(n) \quad n^2$.

Using Eq. 3.23 in conjunction with Eq. 3.21 when 1 it was observed that $h \quad 10^{\ 7}$ with a corresponding potential of $P_0 \quad 4\ 9348 \quad 10^{\ 14}$ in order to maintain mechanical equilibrium.

The structure and the number of free chain ends for this brush system are shown in FIGURE 10 and FIGURE 11 respectively.

Using Eq. 3.23 in conjunction with Eq. 3.21 it is observed that the polymer brush must be very small in order to remain attached to the surface substrate and satisfy the necessary boundary conditions.

An analysis of the cases yields the interesting result that all of the electrically neutral polymer brushes studied with a weighting function of the form $f(n) \quad n^b$ must be very small in order to satisfy the boundary conditions.

<u>Case when $b \quad 3$</u>

When $b \quad 3$ the weighting function can be written in terms of the chemical index as $f(\ ) \quad (N\ )^3$. An example of a polymer brush with this weighting function is shown in FIGURE 12.

This weighting function is applied to first applied to Eq. 2.3 and then inserted into Eq. 2.4 to obtain

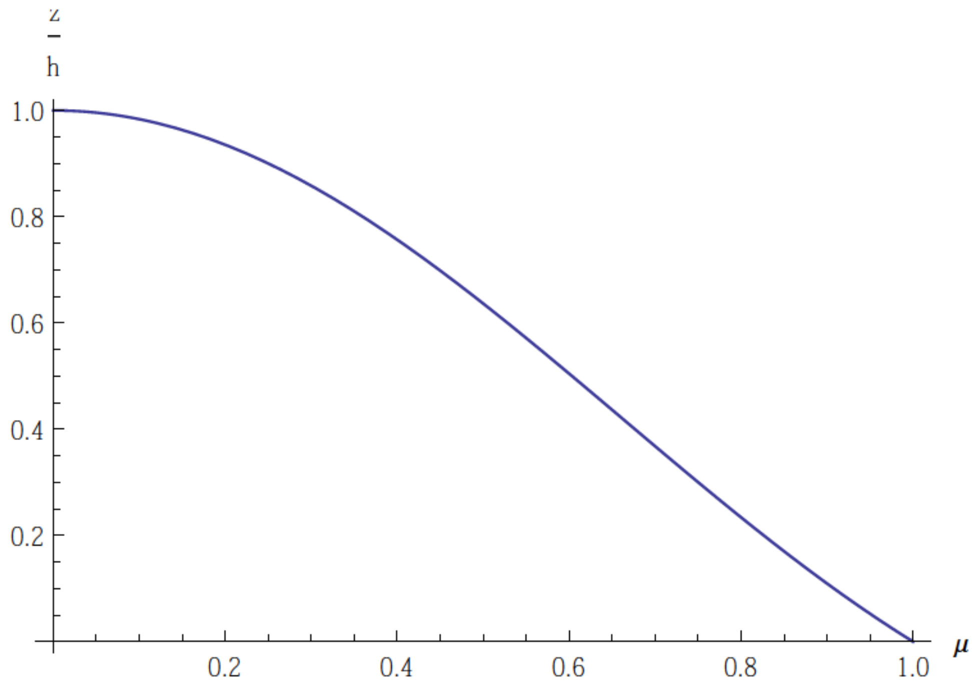

FIGURE 10. Position above the substrate surface for a branched polymer brush with a weighting function of $f(n) = n^2$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 10^{-7}$ and a maximum potential of $P_0 = 4.9348 \times 10^{-14}$.

$$\ddot{z}(\mu) + \frac{3}{\mu}\dot{z}(\mu) + \frac{2P_0 z(\mu)}{h^2} = 0 \tag{3.24}$$

which was then solved with the boundary condition $z(0) = h$ to obtain the equation

$$z(\mu) = \frac{\sqrt{\frac{2}{P_0}}h^2 J_1\left(\frac{\sqrt{2P_0}\mu}{h}\right)}{\mu} \tag{3.25}$$

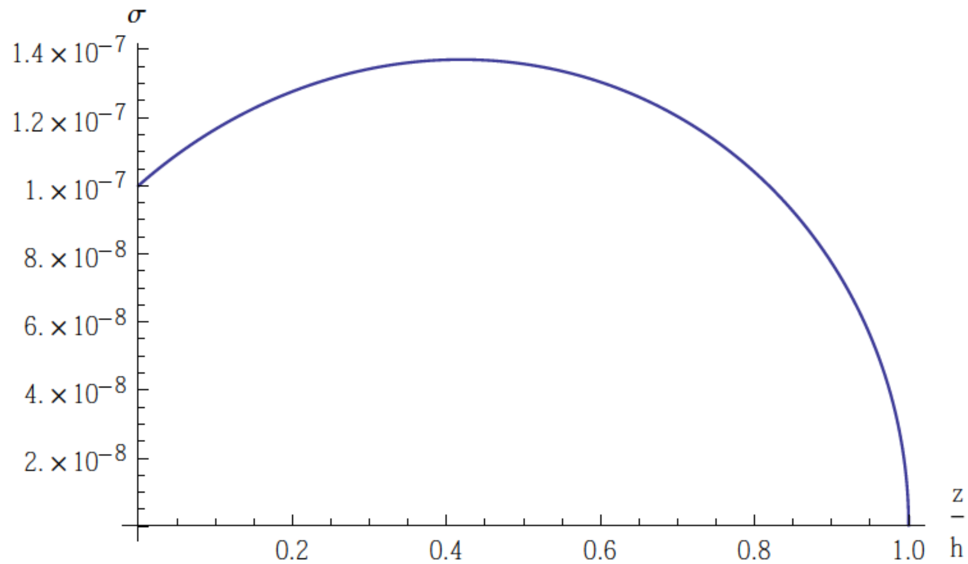

FIGURE 11. Number of free chain ends at throughout a branched polymer brush with a weighting function of $f(n) = n^2$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 10^{-7}$ and a maximum potential of $P_0 = 4.9348 \times 10^{-14}$.

to describe the height of the polymer brush above the surface substrate.

Differentiating Eq. 3.25 with respect to μ produces the equation

$$\frac{dz}{d\mu} = \frac{h}{\mu^2}\left[\mu J_0\left(\frac{\sqrt{2P_0}\mu}{h}\right) - \sqrt{\frac{2}{P_0}}hJ_1\left(\frac{\sqrt{2P_0}\mu}{h}\right) - \mu J_2\left(\frac{\sqrt{2P_0}\mu}{h}\right)\right] \tag{3.26}$$

which was then used with Eq.2.8 to produce

$$\sigma(z[\mu]) = \frac{-h}{\mu^2}\left[\mu J_0\left(\frac{\sqrt{2P_0}\mu}{h}\right) - \sqrt{\frac{2}{P_0}}hJ_1\left(\frac{\sqrt{2P_0}\mu}{h}\right) - \mu J_2\left(\frac{\sqrt{2P_0}\mu}{h}\right)\right] \tag{3.27}$$

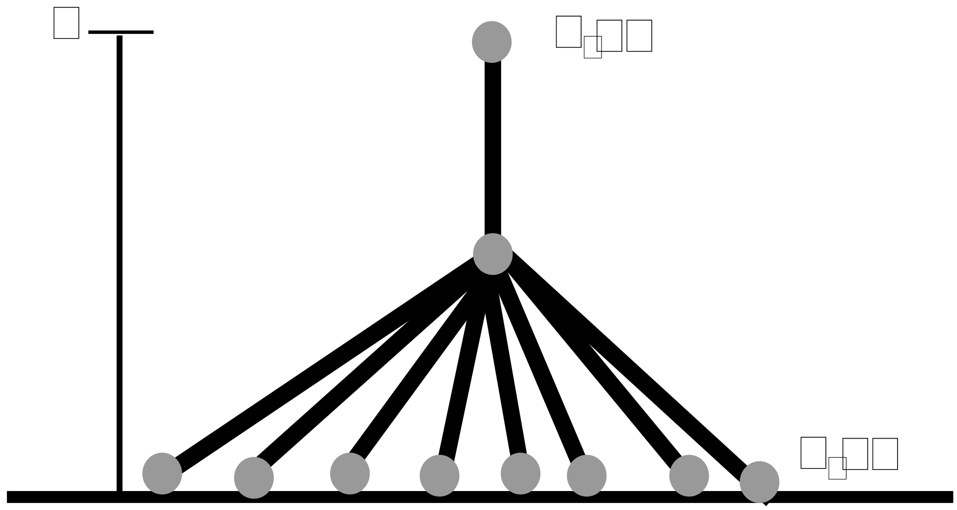

FIGURE 12. A polymer brush attached to a flat surface with a weighting function of $f(n) = n^3$, a value of $N = 2$, and a maximum height of h.

used to describe the number of free chain ends of the polymer brush.

In order to maintain a value of $z(1) = 0$ at the surface substrate, it was observed from Eq.3.25 that $\frac{\sqrt{2P_0}}{h} = 3.8317$. From this result it is evident that the potential of this system can be expressed as

$$P_0 = \frac{(3.8317h)^2}{2} \tag{3.28}$$

From Eq.3.27 it was observed that in order for the boundary condition in Eq.2.5 to be satisfied the maximum brush height must be $h = 1.2414 \times 10^{-7}$ and the potential must be $P_0 = 1.1314 \times 10^{-13}$.

The height above the substrate surface as a function of the chemical index and the number of free chain ends for this polymer brush system are shown in FIGURE 13 and FIGURE 14 respectively.

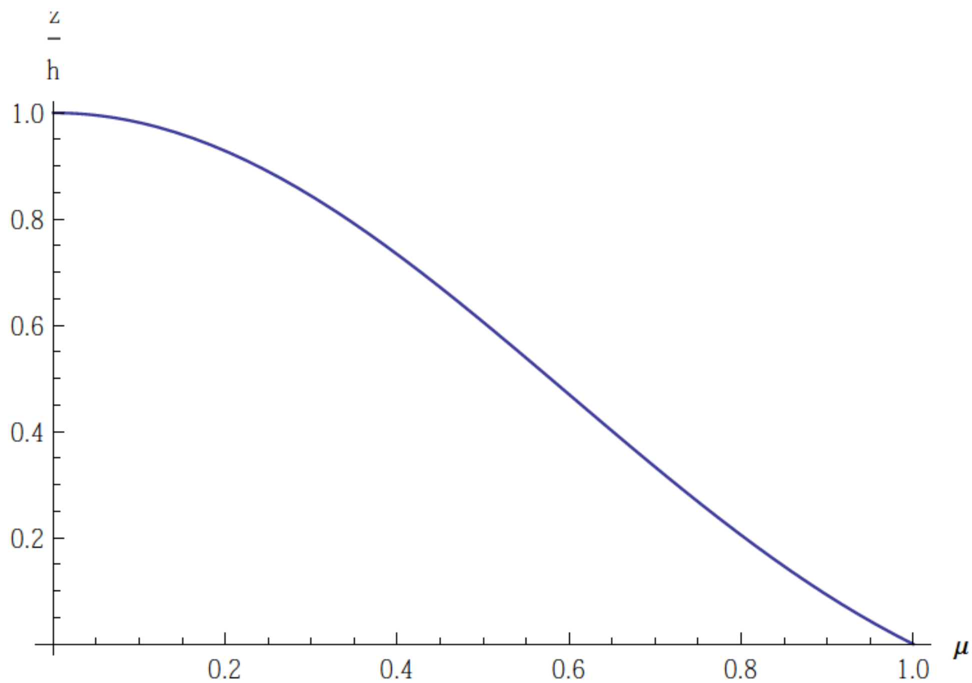

FIGURE 13. Position above the substrate surface for a branched polymer brush with a weighting function of $f(n) = n^3$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 1.2414 \times 10^{-7}$ and a maximum potential of $P_0 \approx 1.1314 \times 10^{-13}$.

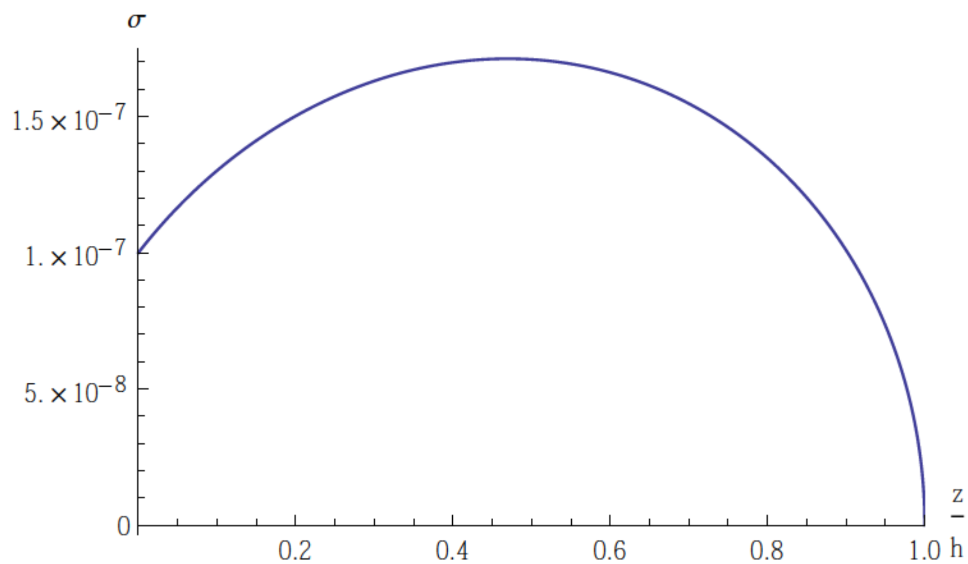

FIGURE 14. Number of free chain ends at throughout a branched polymer brush with a weighting function of $f(n) = n^3$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 1.2414 \times 10^{-7}$ and a maximum potential of $P_0 \approx 1.1314 \times 10^{-13}$.

Comparison of $f(n) = n^b$ cases

When the results for the position for the weighting functions of the form $f(n) = n^b$ are compared to each other, as in FIGURE 15, it was observed that the height of the polymer brush above the substrate surface decreases more rapidly as the magnitude of the weighting function increases.

When the magnitude of the weighting function increases the number of free chain ends increases, this is shown in FIGURE 16.

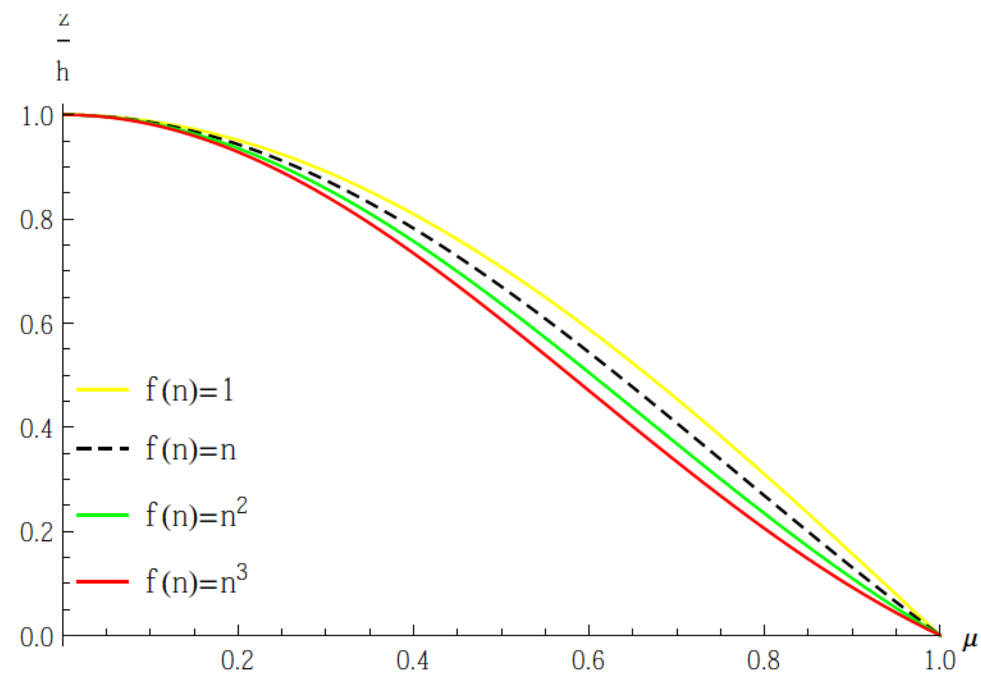

FIGURE 15. For polymer brushes with weighting functions in the form $f(n) = n^b$, the position above the substrate surface decreases more rapidly ss the magnitude of the weighting function increases.

<u>$f(n) = d^{an}$</u>

A polymer brush with a weighting function of $f(n) = d^{an}$ has a Lagrangian of

$$\mathcal{L} = \frac{d^{an}}{2}\left|\frac{dz}{dn}\right|^2 + d^{an}P_0\left(1 - \frac{z(n)^2}{h^2}\right) \tag{3.29}$$

where d and a are constant values.

This can be expressed as

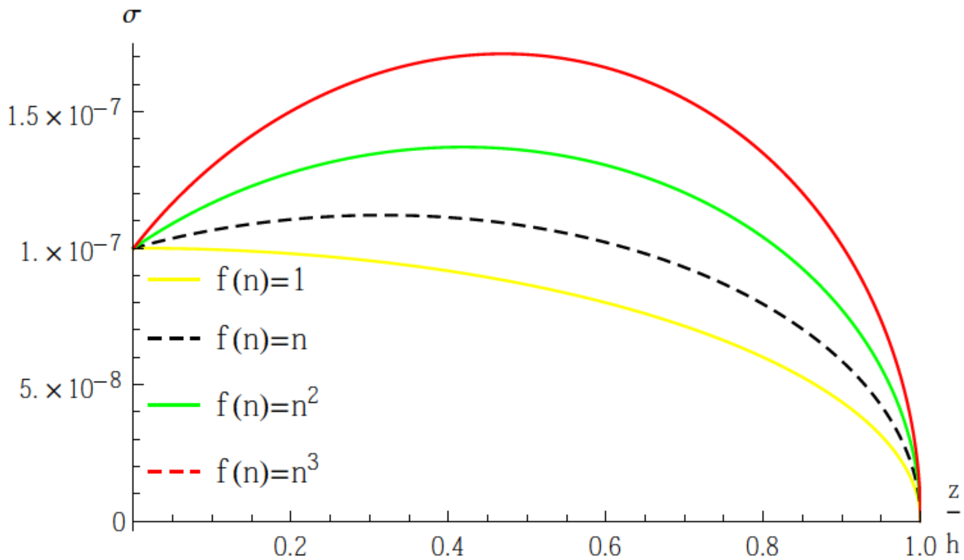

FIGURE 16. For polymer brushes with weighting functions in the form $f(n) = n^b$, the number of free chain ends increases as the magnitude of the weighting function increases.

$$\mathcal{L} = \frac{d^{aN\mu}}{2}\left|\frac{dz}{d\mu}\right|^2 + d^{aN\mu}P_0\left(1 - \frac{z(\mu)^2}{h^2}\right) \tag{3.30}$$

in terms of the chemical index.

This is then used in conjunction with Eq.2.4 to obtain the position of the polymer above the substrate surface

$$z(\mu) = \frac{he^{\frac{(2-\mu)q}{2}}\left(1 - e^{(\mu-1)q}\right)d^{-\frac{a\mu N}{2}}}{e^q - 1} \tag{3.31}$$

where $q = \frac{\sqrt{(ahN\ln(d))^2 - 8P_0}}{h}$.

By di erentiating Eq. 3.31 with respect to , Eq.3.32 is obtained in order to describe the change in the polymer brushes position as a function of .

$$\frac{dz}{d} \quad \frac{he^{(1 \quad \frac{}{2})q} d^{\frac{a \ N}{2}} \quad q \ e^{(\quad 1)q} \quad 1 \quad aN \ln(d) \ e^{(\quad 1)q} \quad 1}{2(1 \quad e^{q})} \tag{3.32}$$

The number of free chain ends for these polymer brushes was then obtained using Eq. 2.8.

$$(z[\ ]) \quad \frac{he^{(1 \quad \frac{}{2})q} d^{\frac{a \ N}{2}} \quad q \ e^{(\quad 1)q} \quad 1 \quad aN \ln(d) \ e^{(\quad 1)q} \quad 1}{2(e^{q} \quad 1)} \tag{3.33}$$

Since the equilibrium condition in Eq. 2.6 returns inconclusive results for the potential, Eq. 2.5 was used to obtain the equation

$$\frac{dz}{d} \quad _1 \quad \frac{hqd^{\frac{aN}{2}} e^{\frac{q}{2}}}{1 \quad e^{q}} \quad 0 \tag{3.34}$$

which was expanded into

$$\frac{dz}{d} \quad _1 \quad \frac{h \frac{\overline{(ahN \ln(d))^2 \quad 8P_0}}{h} d^{\frac{aN}{2}} e^{\frac{\frac{\overline{(ahN \ln(d))^2 \quad 8P_0}}{h}}{2}}}{1 \quad e^{\frac{\overline{(ahN \ln(d))^2 \quad 8P_0}}{h}}} \quad 0 \tag{3.35}$$

Polymer brushes with various values for d and a were examined and are presented in the following sections.

Case when $d \quad 2$ and $a \quad 1$

An example of a polymer brush with a weighting function of $f(n) \quad 2^n$ is shown in FIGURE 17.

For this case the weighting function can be expressed as $f(\ ) \quad 2^N$ and the structure of the polymer brush was found using Eq. 3.31, this obtained Eq.3.36.

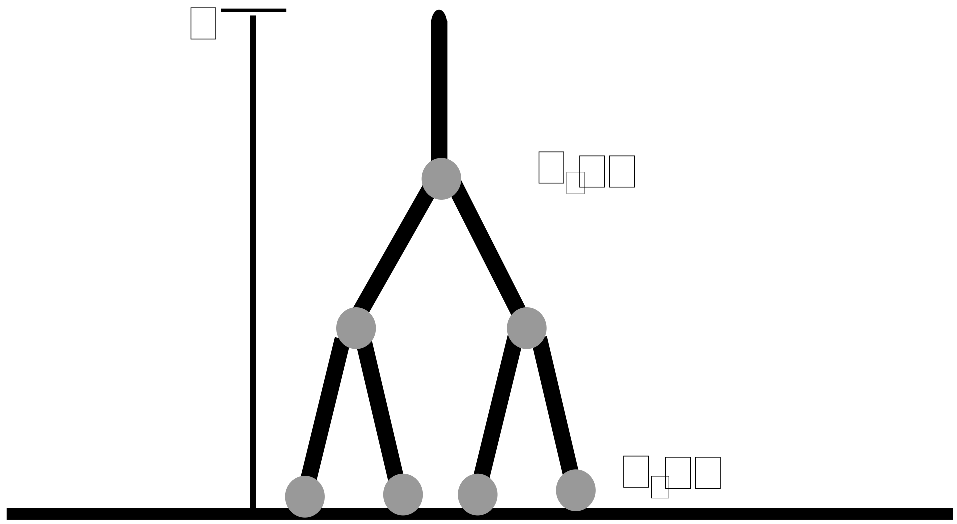

FIGURE 17. A polymer brush attached to a flat surface with a weighting function of $f(n)\quad 2^n$, a value of $N\quad 2$, and a maximum height of h.

$$z(\ \ )\quad \frac{he^{\frac{(2\ \ )q}{2}}\ \ 1\ \ \ e^{(\ \ \ 1)q}\ 2^{\ \frac{N}{2}}}{e^{q}\ \ \ 1} \tag{3.36}$$

Similarly, Eq. 3.33 was used to determine the number of free chain ends for this system. This equation is shown in Eq. 3.37.

$$(z[\ \ ])\quad \frac{he^{(1\ \ \frac{}{2})q}2^{\ \frac{N}{2}}\ q\ e^{(\ \ \ 1)q}\ \ \ 1\ \ \ \ N\ln(2)\ e^{(\ \ \ 1)q}\ \ \ 1}{2\,(e^{q}\ \ \ 1)} \tag{3.37}$$

After thorough numerical analysis it was determined that there was no real positive number for the value of the potential which satisfied the boundary conditions within the desired tolerances. This lead to the conclusion that polymer brushes with this weighting function could not be accurately modeled using the self-consistent mean field theory.

Case when d 2 and a 2

An example of a polymer brush with a weighting function of $f(n)$ 2^{2n} is shown in FIGURE 18.

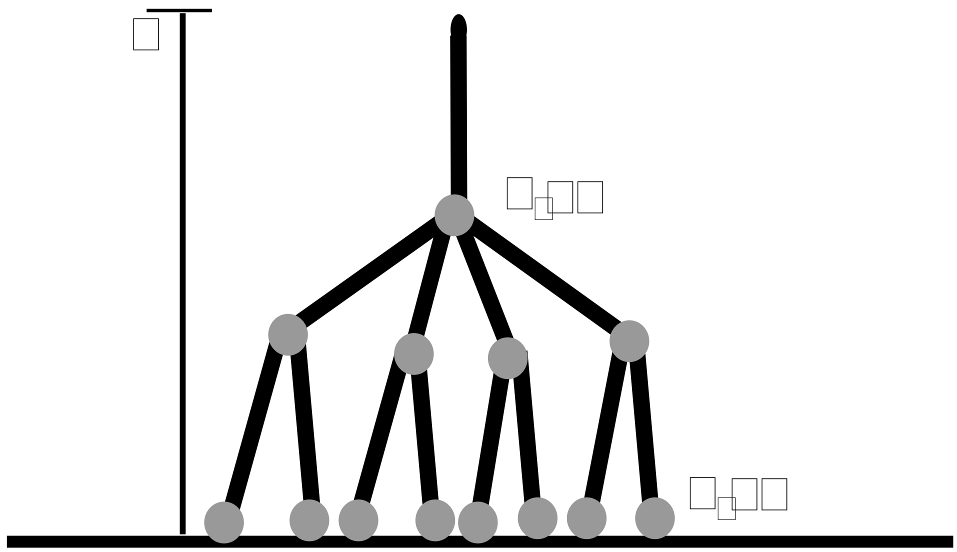

FIGURE 18. A polymer brush attached to a flat surface with a weighting function of $f(n)$ 2^{2n}, a value of N 2, and a maximum height of h.

For a polymer brush with this weighting function the Lagrangian is

$$\frac{2^{2n}}{2}\ \frac{dz}{dn}^{2}\quad 2^{2n}P_0\ 1\quad \frac{z(n)^2}{h^2} \tag{3.38}$$

which was then transformed into

$$\frac{2^{2N}}{2}\ \frac{dz}{d}^{2}\quad 2^{2N}\ P_0\ 1\quad \frac{z(\ )^2}{h^2} \tag{3.39}$$

in terms of the chemical index. This equation was then used with Eq. 2.4 to obtain

$$\ddot{z}(\ )\quad 2N\ln(2)\dot{z}(\ )\quad \frac{2P_0 z(\ )}{h^2}\quad 0 \tag{3.40}$$

Solving this second order di erential equation in order to find the structure of the polymer as a function of the chemical index

$$z(\ )\quad h2^{\ (\ N\ \ 1)}e^{(2\ \ \ )q}\ 1\quad e^{2(\ \ \ 1)q}\ \ \coth(q)\quad 1 \tag{3.41}$$

where $q\quad \frac{\overline{(hN\ln(2))^2\ \ 2P_0}}{h}$. Di erentiating Eq. 3.41 with respect to obtains

$$\frac{dz}{d}\qquad 2^N\ \operatorname{csch}(q)\ \ q\cosh(q(1\qquad))\quad N\ln(2)\sinh(q(1\qquad)) \tag{3.42}$$

which was then used to find the number of free chain ends throughout the system.

$$(z[\ \ ])\quad 2^N\ \operatorname{csch}(q)\ \ q\cosh(q(1\qquad))\quad N\ln(2)\sinh(q(1\qquad)) \tag{3.43}$$

Evaluating Eq. 3.43 at the boundaries of the system for a polymer brush with values of h 1 and N 70 obtains a system in equilibrium with a potential of P_0 1347 967. The structure and number of free ends throughout the polymer brush are shown in FIGURE 19 and FIGURE 20 respectively.

<u>Case when d 3 and a 1</u>

When the values of the constants are d 3 and a 1 the weighting function becomes $f(n)$ 3^n. An example of a polymer brush with a this weighting function is shown in FIGURE 21.

The weighting function $f(n)$ 3^n was then written in terms of , $f(\ )$ 3^N , so that the Lagrangian becomes

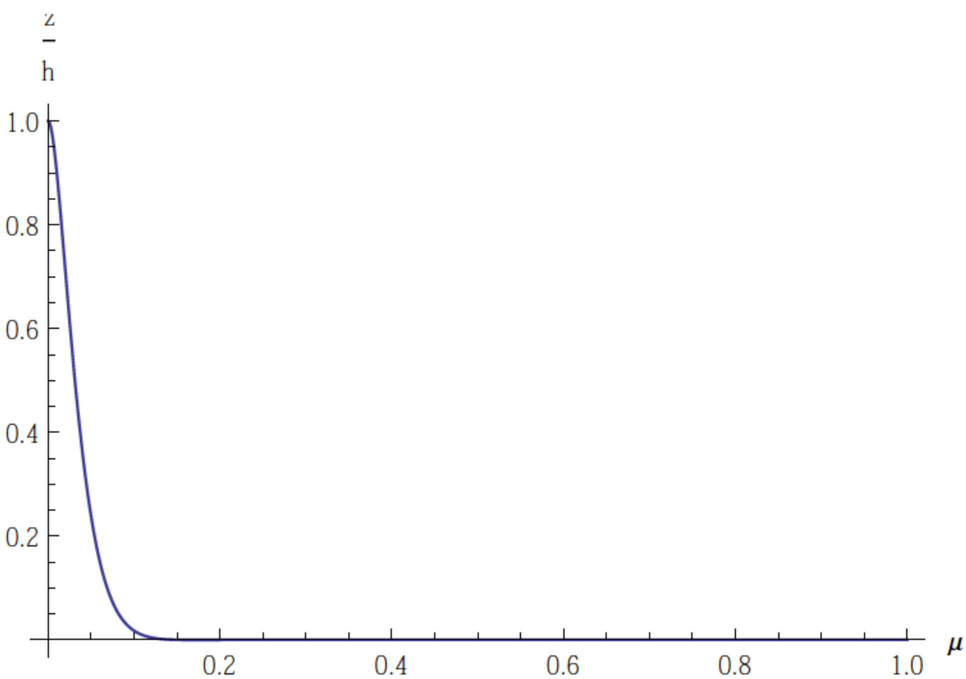

FIGURE 19. The position above the substrate surface for a branched polymer brush with a weighting function of $f(n) = 2^{2n}$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 1$, $N = 70$, and a maximum potential of $P_0 \approx 1347.967$.

$$\mathcal{L} = \frac{3^{N\mu}}{2}\left|\frac{dz}{d\mu}\right|^2 + 3^{N\mu}P_0\left(1 - \frac{z(\mu)^2}{h^2}\right) \tag{3.44}$$

which was used in Eq. 2.4 to produce the equation of motion shown in Eq. 3.45.

$$\ddot{z}(\mu) + N\ln(3)\dot{z}(\mu) + \frac{2P_0 z(\mu)}{h^2} = 0 \tag{3.45}$$

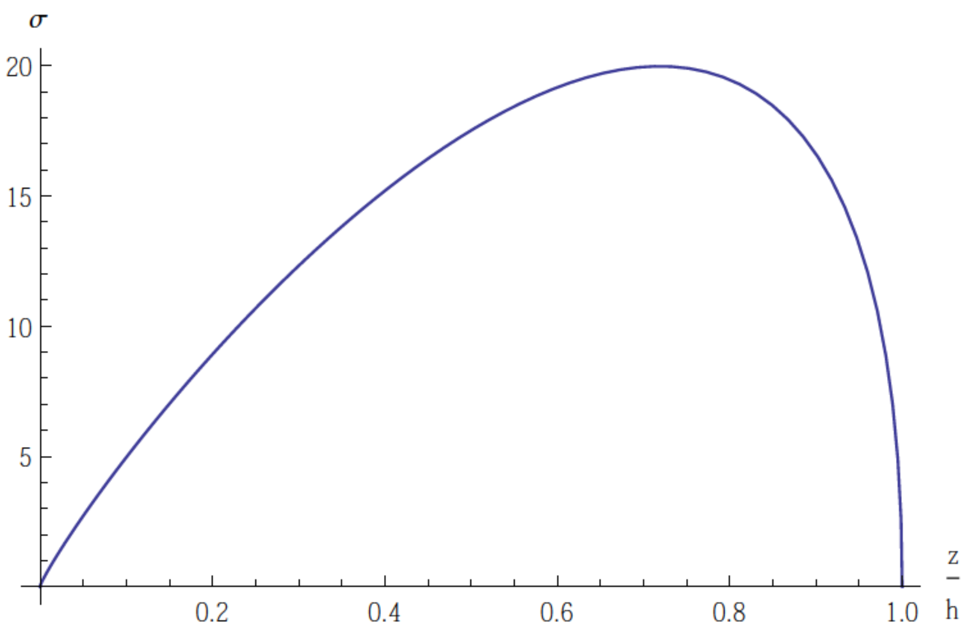

FIGURE 20. Number of free chain ends at throughout a branched polymer brush with a weighting function of $f(n) = 2^{2n}$ as a function of the dimensionless variable μ. The position of the polymer brush has a maximum height of $h = 1$, $N = 70$, and a maximum potential of $P_0 \approx 1347.967$.

From Eq. 3.45 and using the boundary conditions $z(\mu = 0) = h$ and $z(\mu = 1) = 0$, the position of the polymer above the substrate's surface was determined to be

$$z(\mu) = -\frac{h3^{-\frac{\mu N}{2}} e^{\frac{(2-\mu)q}{2}} \left(e^{(\mu-1)q} - 1\right)}{e^q - 1} \tag{3.46}$$

where $q = \frac{\sqrt{(hN\ln(3))^2 - 8P_0}}{h}$. Differentiating Eq. 3.46 with respect to μ obtains

$$\frac{dz}{d\mu} = -\frac{h3^{-\frac{\mu N}{2}} e^{-\frac{\mu q}{2}} \left(e^{\mu q}(q - N\ln(3)) + e^q(N\ln(3) + q)\right)}{2(e^q - 1)} \tag{3.47}$$

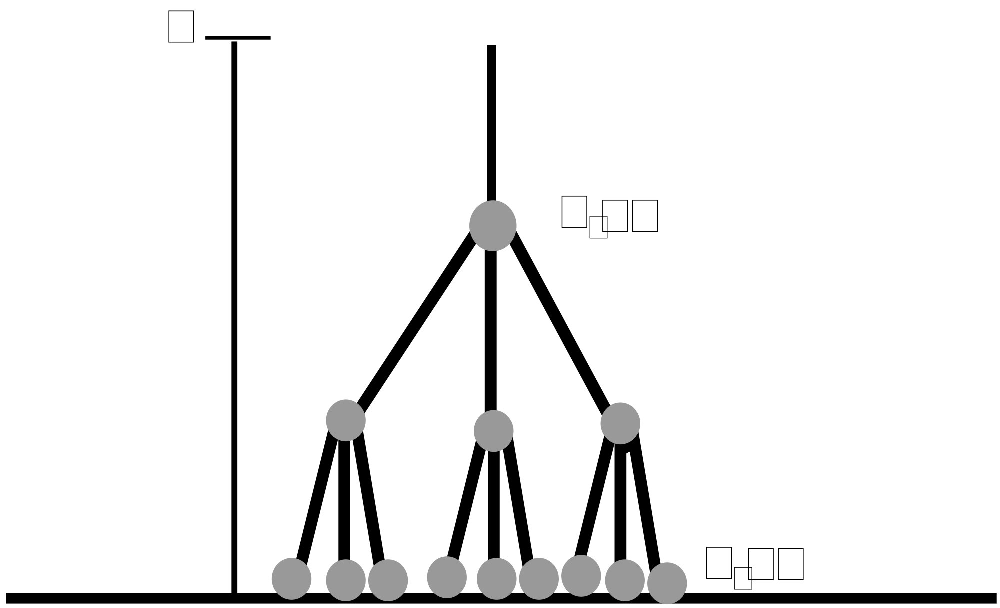

FIGURE 21. A polymer brush attached to a flat surface with a weighting function of $f(n) \quad 3^n$, a value of $N \quad 2$, and a maximum height of h.

which was used with Eq. 2.8 to determine the number of free chain ends throughout the polymer brush. This equation is displayed in Eq. 3.48.

$$(z[\quad]) \quad \frac{h3^{\;\frac{N}{2}}e^{\;\frac{q}{2}}(e^{\;q}(q \quad N\ln(3)) \quad e^{q}(N\ln(3) \quad q))}{2(e^{q} \quad 1)} \tag{3.48}$$

Eq. 3.46 and Eq. 3.47 where then used with the conditions for equilibrium stated in Eq. 2.5 and Eq. 2.6 to determine the value of P_0 for the system.

The position above the substrate for a stable polymer brush system with values of $h \quad 1$, $N \quad 38$, and $P_0 \quad 258\;5075$ is shown in FIGURE 22.

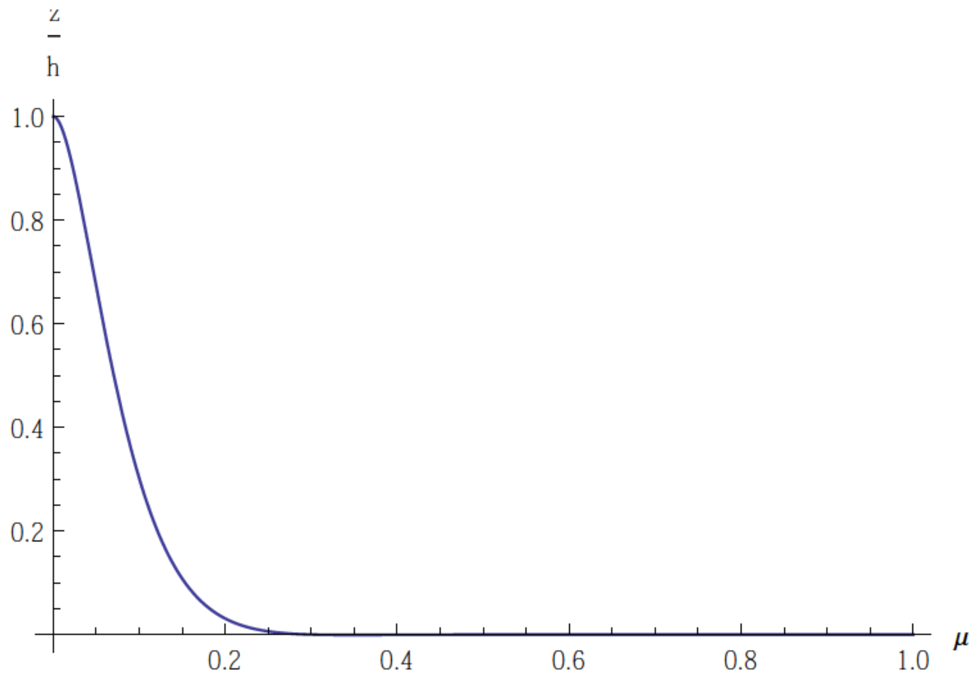

FIGURE 22. The position above the substrate surface for a polymer brush with a weighting function of $f(n) = 3^n$. The polymer brush observed here had a value of $h = 1$, $N = 38$, and $P_0 = 258.5075$ in order to satisfy the necessary boundary conditions.

The number of free chain ends for a stable polymer brush system with values of $h = 1$, $N = 38$, and $P_0 = 258.5075$ is shown in FIGURE 23.

Case when $d = 3$ and $a = 2$

When the constants of the weighting function are $d = 3$ and $a = 2$ the weighting function will be $f(n) = 3^{2n}$, which can be described as $f(\mu) = 3^{2N\mu}$. An example of a polymer brush with this weighting function is shown in FIGURE 24.

From this weighting function it was determined that the Lagrangian of the system was

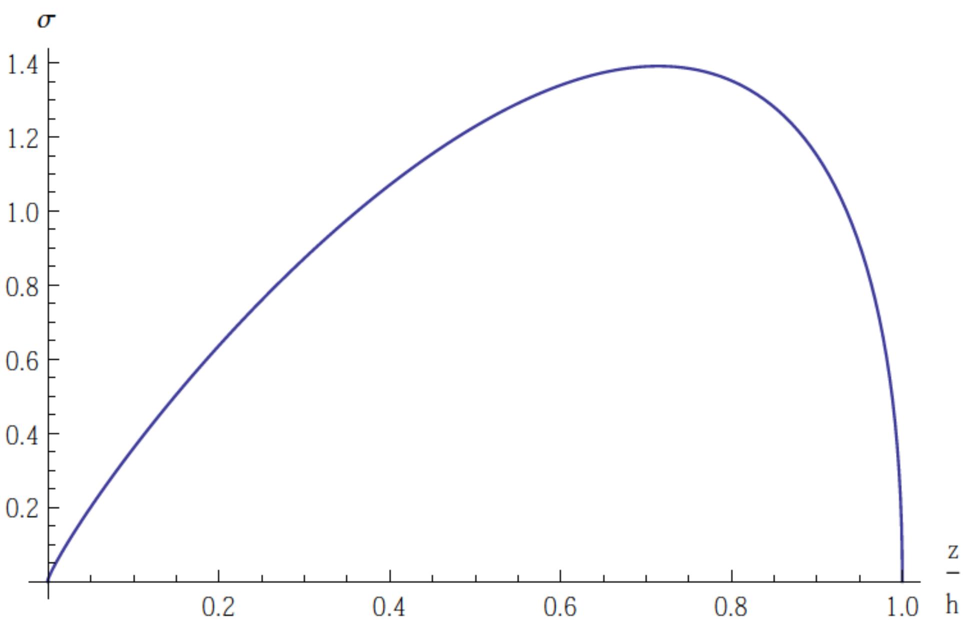

FIGURE 23. The number of free chain ends of a polymer brush with a weighting function of $f(n) = 3^n$. The polymer brush observed here had a value of $h = 1$, $N = 38$, and $P_0 = 258.5075$ in order to satisfy the necessary boundary conditions.

$$\mathcal{L} = \frac{3^{2N\mu}}{2}\left|\frac{dz}{d\mu}\right|^2 + 3^{2N\mu}P_0\left(1 - \frac{z(\mu)^2}{h^2}\right) \tag{3.49}$$

which produced the equation of motion

$$\ddot{z}(\mu) + 2N\ln(3)\dot{z}(\mu) + \frac{2P_0 z(\mu)}{h^2} = 0 \tag{3.50}$$

using Eq. 2.4. When Eq. 3.50 is solved using the boundary conditions $z(\mu = 1) = 0$ and $z(\mu = 0) = h$, the position of the polymer brush above the substrate surface was determined to be described by

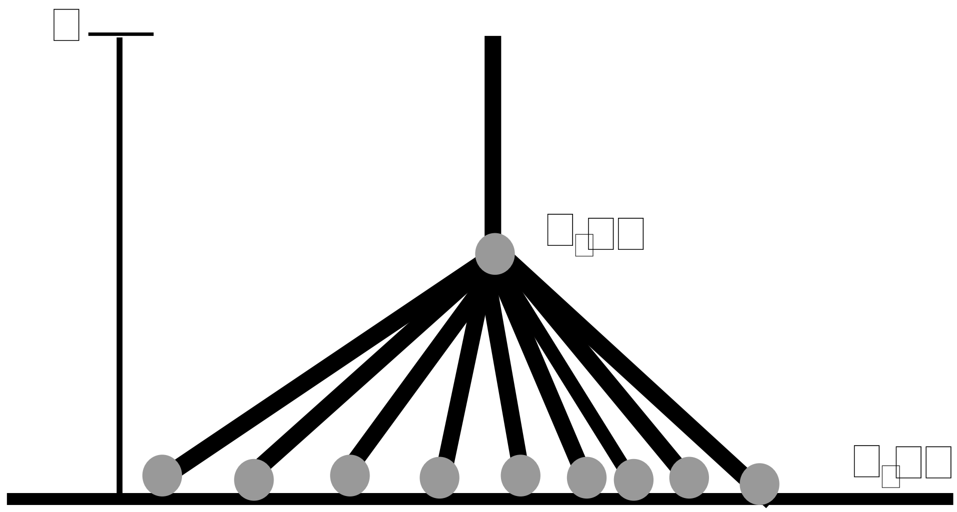

FIGURE 24. A polymer brush attached to a flat surface with a weighting function of $f(n) \quad 3^{2n}$, a value of $N \quad 1$, and a maximum height of h. The number of monomers at each junction increases rapidly as the value of n increases.

$$z(\quad) \quad 3^{\quad N} h\,\mathrm{csch}(q)\sinh(q[1 \quad]) \tag{3.51}$$

where $q \quad \overline{(hN\ln(3))^2 \quad 2P_0}$.

Di erentiating Eq. 3.51 with respect to obtains

$$\frac{dz}{d} \quad h3^{\quad N}\,\mathrm{csch}(q)\,(q\cosh(q[1 \quad])N\ln(3)\sinh(q[1 \quad])) \tag{3.52}$$

which was then used to determine the number of free chain ends throughout the polymer brush

$$\sigma(z[\mu]) = h3^{-N\mu}\text{csch}(q)\,(q\cosh(q[1-\mu])N\ln(3)\sinh(q[1-\mu])) \tag{3.53}$$

Solving for the boundary conditions for a stable polymer brush with a height of $h = 1$ and a value of $N = 42$ obtains a potential of $P_0 \approx 1368.149$. The position of the polymer as a function of the chemical index and the number of free chain ends for this system are shown in FIGURE 25 and FIGURE 26 respectively.

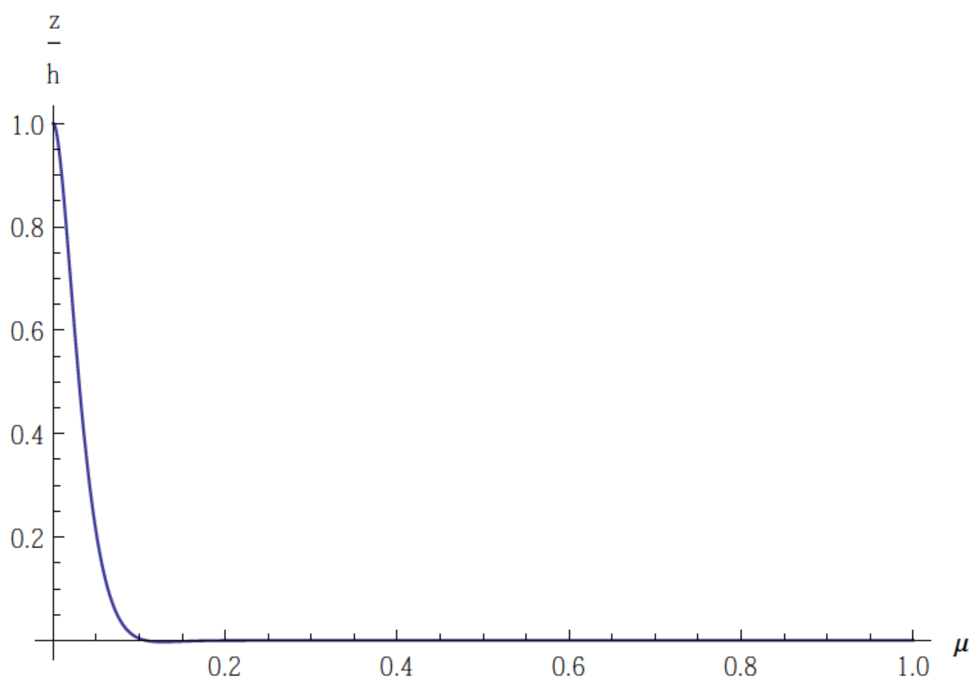

FIGURE 25. The position above the substrate surface for a polymer brush with a weighting function of $f(n) = 3^{2n}$. The polymer brush observed here had a value of $h = 1$, $N = 42$, and $P_0 \approx 1368.149$ in order to satisfy the necessary boundary conditions.

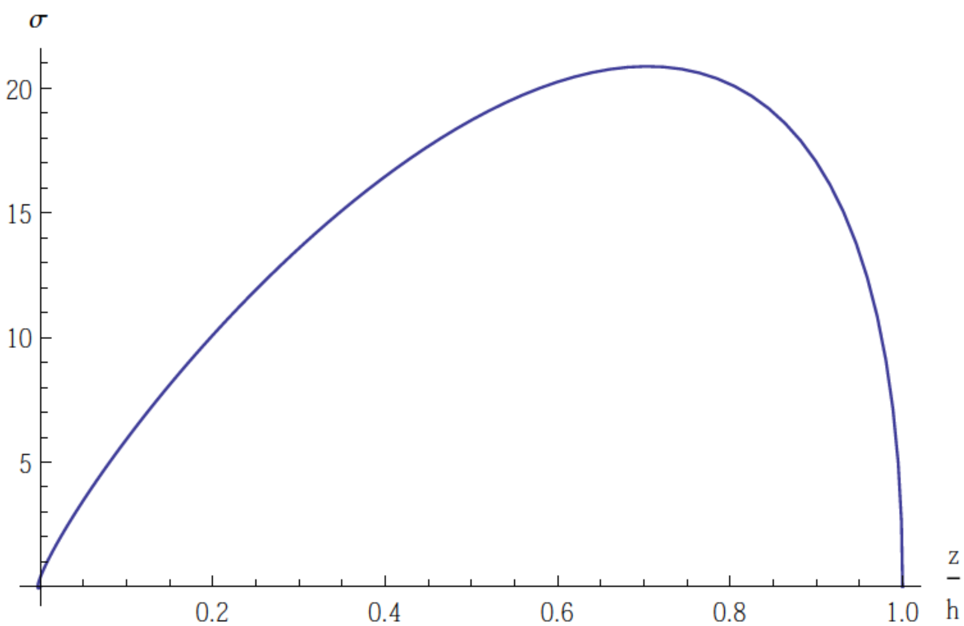

FIGURE 26. The number of free chain ends for a polymer brush with a weighting function of $f(n) = 3^{2n}$. The polymer brush observed here had a value of $h = 1$, $N = 42$, and $P_0 \approx 1368.149$ in order to satisfy the necessary boundary conditions.

Comparison of $f(n) = d^{an}$ cases

Analysis of these cases obtains the result that once the weighting function has a value of a large enough, the brush will be in equilibrium and satisfy the boundary conditions. As the value of a increases for the weighting function, the potential P_0 of the brush will increase. In addition to this increase in the potential, the height of the polymer brush above the substrate surface is shown to decrease rapidly as the value of a increases. This result is shown in FIGURE 27.

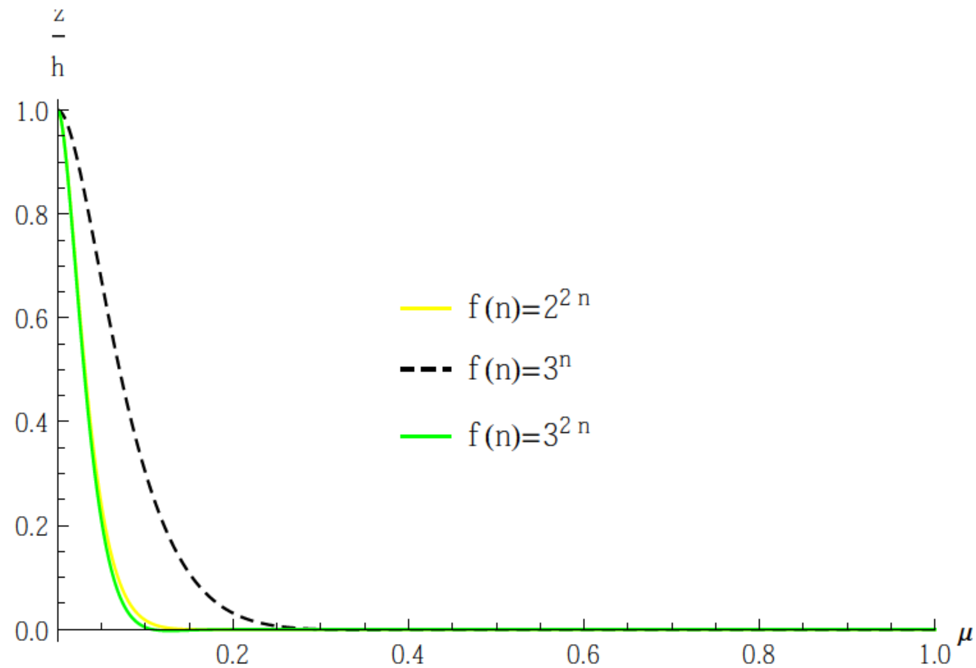

FIGURE 27. For polymer brushes with weighting functions in the form $f(n) = d^{an}$, the position above the substrate surface decreases was shown to decrease as the value of a increased.

It was also observed that as the value of a increased that the number of free chain ends increased dramatically, these results are shown in FIGURE 28.

$$f(n) = 2^{\frac{(N-n)G}{N}}$$

An example of a polymer brush with a weighting function of $f(n) = 2^{\frac{(N-n)G}{N}}$, where G is the number of generations of functional junctions is shown in FIGURE 29.

Polymer brushes with this weighting function have a Lagrangian of

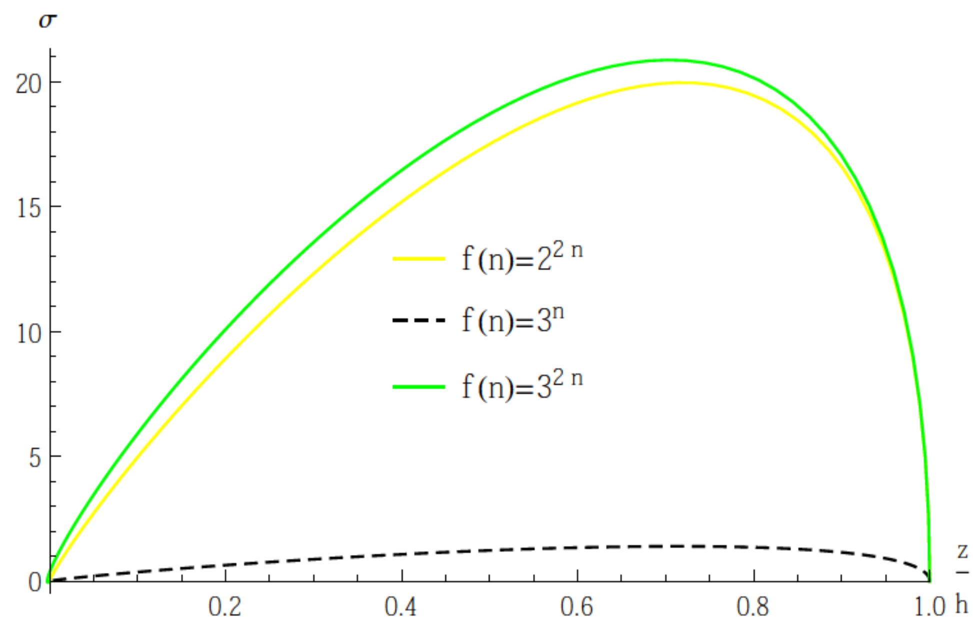

FIGURE 28. For polymer brushes with weighting functions in the form $f(n) = d^{an}$, the number of free chain ends in the system increased dramatically as the value of a increased.

$$\mathcal{L} = 2^{\frac{(N-n)G}{N}-1}\left|\frac{dz}{dn}\right|^2 + 2^{\frac{(N-n)G}{N}} P_0\left(1-\frac{z^2}{h^2}\right) \tag{3.54}$$

which can be expressed as

$$\mathcal{L} = 2^{G(1-\mu)-1}\left|\frac{dz}{d\mu}\right|^2 + 2^{G(1-\mu)} P_0\left(1-\frac{z^2}{h^2}\right) \tag{3.55}$$

in terms of the chemical index. The position of the polymer above the surface's substrate is found by inserting Eq. 3.55 into Eq. 2.4. This obtains the equation

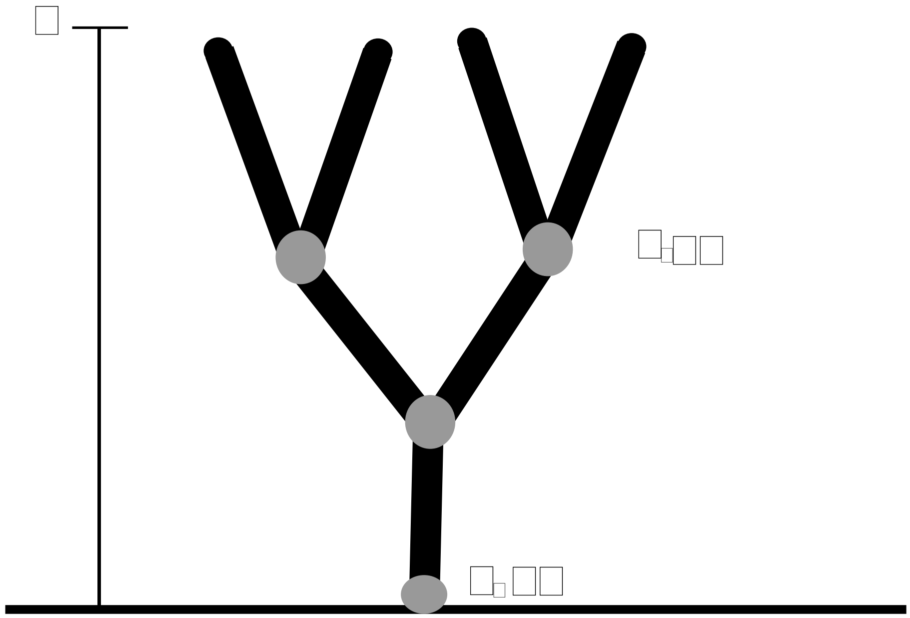

FIGURE 29. A polymer brush attached to a flat surface with a weighting function of $f(n) \quad 2^{\frac{(N \quad n)G}{N}}$, a value of $N \quad 2$, and a maximum height of h. The number of monomers at each junction decreases as the value of n increases.

$$z(\quad) \qquad \frac{h2^{\frac{G}{2}} e^{\frac{q}{2}} (e^{q} \quad e^{q} \quad)}{1 \quad e^{q}} \tag{3.56}$$

where $q \qquad \frac{\overline{(Gh\ln(2))^2 \quad 8P_0}}{h}$

By di erentiating Eq. 3.56 with respect to , the equations for $\frac{dz}{d}$ and $\frac{d^2z}{d^{\ 2}}$ where obtained.

$$\frac{dz}{d} \qquad \frac{h2^{\frac{G}{2} \quad 1} e^{\frac{(\ q)}{2}} (e^{q}(G\ln(2) \quad q) \quad e^{\ q}(G\ln(2) \quad q))}{e^{q} \quad 1} \tag{3.57}$$

$$\frac{d^2z}{d\ ^2} \quad \frac{h2^{\frac{G}{2}\ \ 2}e^{\ \frac{1}{2}(\ q)}\ e^q(q \quad G\ln(2))^2 \quad e^{\ q}(G\ln(2) \quad q)^2}{e^q \quad 1} \tag{3.58}$$

Using Eq. 3.57 and Eq. 2.8 it is seen that the number of free chain ends is described by

$$(z[\ \ ]) \qquad \frac{dz}{d} \quad \frac{h2^{\frac{G}{2}\ \ 1}e^{\ \frac{q}{2}}(e^{\ q}(G\ln(2) \quad q) \quad e^q(q \quad G\ln(2)))}{e^q \quad 1} \tag{3.59}$$

for polymer brushes with weighting functions of the form $f(n) \quad 2^{\frac{(N \quad n)G}{N}}$.

Eq. 2.6 was used in an attempt to find an appropriate value for the potential, but no positive, real values were found which would satisfy the boundary conditions of the system. From this result it was determined that stable electrically neutral polymer brushes with a weighting function of the form $f(n) \quad 2^{\frac{(N \quad n)G}{N}}$ did not have a su ciently high molecular weight to be accurately described using the self-consistent mean field theory.

<u>$f(n) \quad e^{bn}$</u>

A polymer with a weighting function of $f(n) \quad e^{bn}$, where b is a constant value, has a Lagrangian of

$$\frac{e^{bn}}{2}\ \frac{dz}{dn}^{\ 2} \quad e^{bn}P_0\ \ 1 \quad \frac{z^2}{h^2} \tag{3.60}$$

which can be expressed as

$$\frac{e^{bN}}{2}\ \frac{dz}{d}^{\ 2} \quad e^{bN}\ \ P_0\ \ 1 \quad \frac{z^2}{h^2} \tag{3.61}$$

in terms of the chemical index.

The position of the polymer above the surface's substrate is found by inserting Eq. 3.61 into Eq. 2.4. This obtains the equation

$$z(\quad) \quad \frac{h \; 1 \quad e^{(\quad 1)w} \quad e^{\frac{1}{2}((2 \quad)w \;\; b \;\; N)}}{e^{w} \quad 1} \tag{3.62}$$

where $w \quad \frac{\overline{(bhN)^2 \quad 8P_0}}{h}$.

The first and second derivative of Eq. 3.62 were obtained in order to obtain the number of free chain ends as well as the potential of the system in order to satisfy the necessary boundary conditions. This produced the equations

$$\frac{dz}{d} \quad \frac{he^{w \;\; \frac{1}{2} \;\; (bN \;\; w)} \quad e^{(\quad 1)w}(w \quad bN) \quad bN \quad w}{2(e^{w} \quad 1)} \tag{3.63}$$

and

$$\frac{d^2z}{d \;\; ^2} \quad \frac{he^{\frac{1}{2}(w \;\; b \;\; N)} \quad b^2N^2 \quad w^2 \;\; \sinh \; \frac{1}{2}(\quad 1)w \quad 2bNw\cosh \; \frac{1}{2}(\quad 1)w}{2(e^{w} \quad 1)} \tag{3.64}$$

for the first and second derivatives of Eq. 3.62 respectively.

Eq. 3.62 - 3.64 were then inserted into Eq. 2.6 in order to determine the necessary values in order to maintain mechanical equilibrium at the substrate surface. Eq. 2.6 was expanded out to

$$f(\quad)\frac{d^2z(\quad)}{d \;\; ^2} \quad \frac{df(\quad)}{d} \; \frac{dz(\quad)}{d} \quad \frac{2P_0z(\quad)}{h^2}f(\quad) \quad 0 \tag{3.65}$$

which was then evaluated when $\quad 1$ at the substrate surface. Since $z(\quad 1) \quad 0$, and it is observed that $f(\quad 1)\frac{d^2z(\;)}{d \;\; ^2} \;\; _1 \quad \frac{df(\;)}{d} \;\; _1 \; \frac{dz(\;)}{d} \;\; _1$, Eq. 3.65 will be unable to provide reliable values for P_0 in order to maintain mechanical equilibrium when $\quad 1$. In order to provide accurate results, Eq. 2.5 was used to find an approximate value of P_0 where there are no free ends at a position greater than h. Using Eq. 3.63, it was observed that

$$\frac{dz}{d\mu}|_{\mu=1} = \frac{-hwe^{\frac{w-Nb}{2}}}{e^w - 1} \tag{3.66}$$

for polymer brushes with a weighting function of $f(\mu) = e^{Nb\mu}$. Using numerical analysis it was determined that for a polymer brush with values of $b = 1$, $h = 100$, and $N = 50$ that the system was at mechanical equilibrium at the surface substrate when $P_0 \approx 3.8589 \times 10^6$. The structure of this system as a function of μ is shown in FIGURE 30.

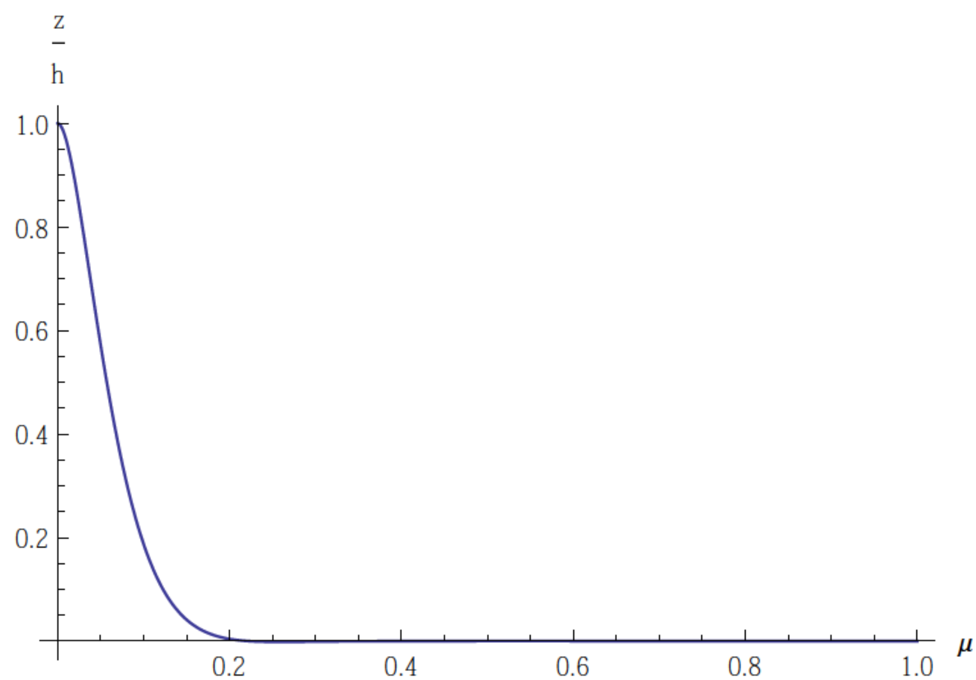

FIGURE 30. The structure of a polymer with a weighting function of $f(n) = e^{bn}$. The polymer brush has a maximum height of $h = 100$, a value of $b = 1$, a value of $N = 50$, and $P_0 \approx 3.8589 \times 10^6$.

Using Eq. 2.8 it was determined that the number of free chain ends throughout the polymer brush is described with Eq. 3.67.

$$\sigma(z[\mu]) = \frac{h e^{w-\frac{1}{2}\mu(bN+w)}\left(e^{(\mu-1)w}(w-bN)+bN+w\right)}{2(e^{w}-1)} \tag{3.67}$$

For the system previously examined in FIGURE 30, the number of free chain ends at each position on the polymer brush is shown in FIGURE 31.

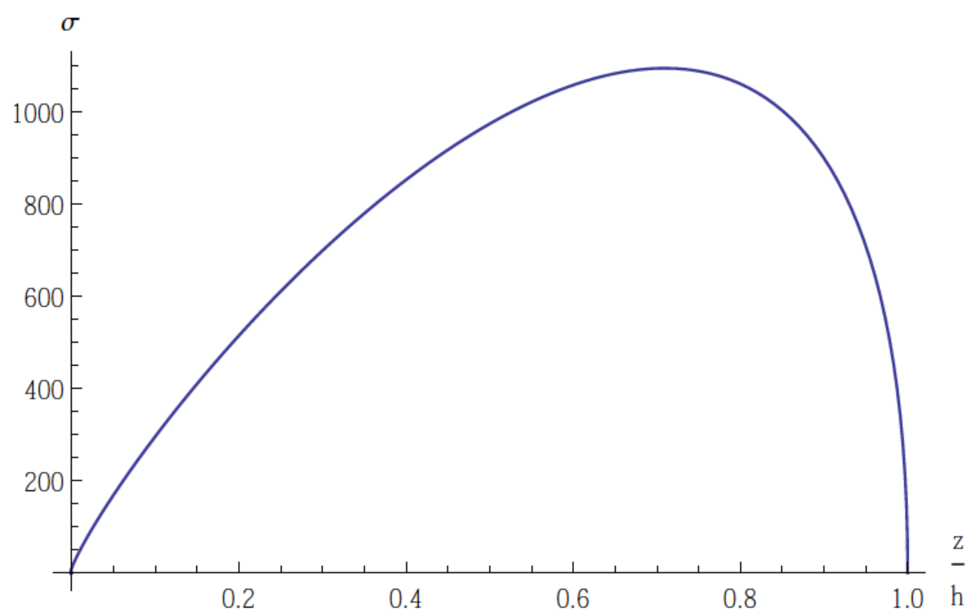

FIGURE 31. The number of free chain ends for a polymer with a weighting function of $f(n) = e^{bn}$. The polymer brush has a maximum height of $h = 100$, a value of $b = 1$, a value of $N = 50$, and $P_0 \approx 3.8589 \times 10^6$.

In order to determine the relationship between the polymer brush and a change in its weighting function the case of $f(n) \quad e^{2n}$ was examined. Numerical analysis of this system determined that the structure of the brush can be expressed as

$$z(\ ) \quad \frac{h}{2}e^{\quad N} \quad e^{\frac{(2\quad)\quad \sqrt{h^2N^2 \quad 2P_0}}{h}} \quad e^{\frac{\sqrt{h^2N^2 \quad 2P_0}}{h}} \quad \coth \frac{\sqrt{h^2N^2 \quad 2P_0}}{h} \quad 1 \tag{3.68}$$

with an equation for the number of free chain ends of

$$(z[\ ]) \quad e^{\quad N}\operatorname{csch} \frac{\sqrt{h^2N^2 \quad 2P_0}}{h} \quad \sqrt{h^2N^2 \quad 2P_0}\cosh \frac{(\quad 1)\quad \sqrt{h^2N^2 \quad 2P_0}}{h} \quad hN\sinh \frac{(\quad 1)\quad \sqrt{h^2N^2 \quad 2P_0}}{h} \tag{3.69}$$

Eq. 3.68 and Eq. 3.69 where then used to determine the potential for a stable polymer brush that would satisfy the necessary boundary conditions. For a polymer brush with values of $h \quad 100$ and $N \quad 40$ a potential of $P_0 \quad 9\ 696 \quad 10^6$ was obtained. FIGURE 32 and FIGURE 33 show the structure and number of free chain ends of this system respectively.

<u>Comparison of $f(n) \quad e^{bn}$ cases</u>

When the height of the polymer brushes for the cases observed with the weighting functions $f(n) \quad e^n$ and $f(n) \quad n^{2n}$ are compared to each other, see FIGURE 34, it was observed that the height above the surface substrate decreases more rapidly as increase for increasing values of b.

It was also observed from FIGURE 35 that the number of free chain ends for these polymer brushes increased as the value of b increased.

An analysis of these polymer brushes showed that as the value of b increases the allowed potential of the system increases and stable brushes can be found with smaller values of N.

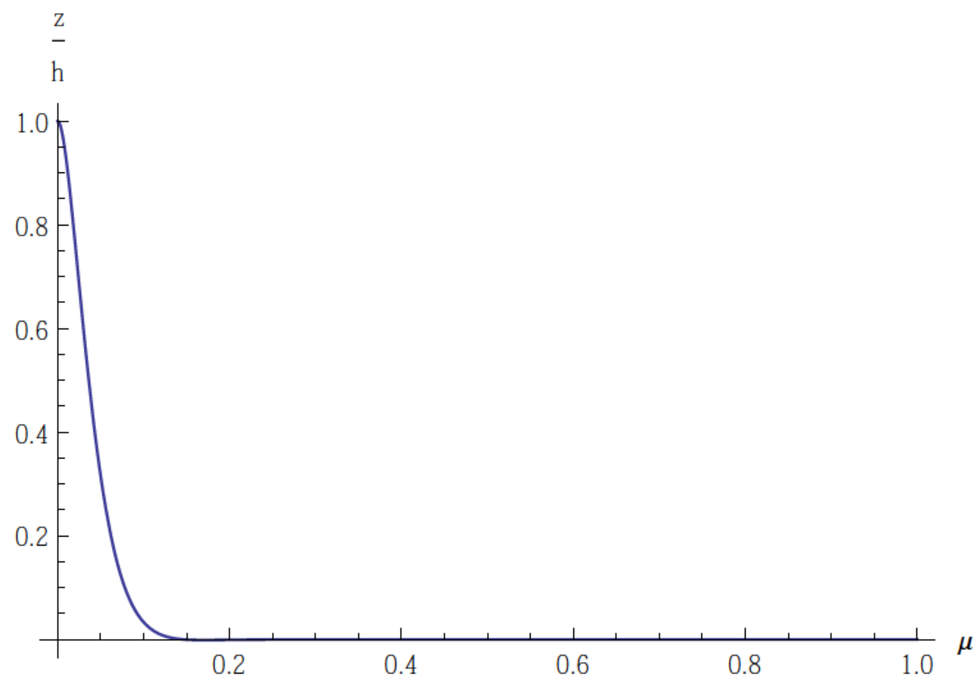

FIGURE 32. The structure of a polymer with a weighting function of $f(n) = e^{2n}$. The polymer brush has a maximum height of $h = 100$, a value of $N = 40$, and $P_0 \approx 9.696 \times 10^6$.

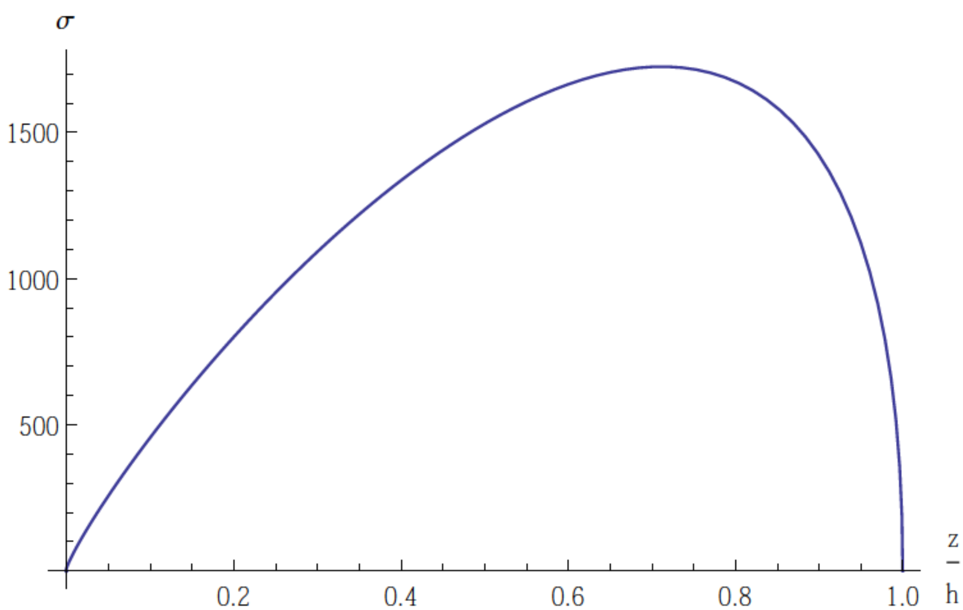

FIGURE 33. The number of free chain ends for a polymer with a weighting function of $f(n) = e^{2n}$. The polymer brush has a maximum height of $h = 100$, a value of $N = 40$, and $P_0 \approx 9.696 \times 10^6$.

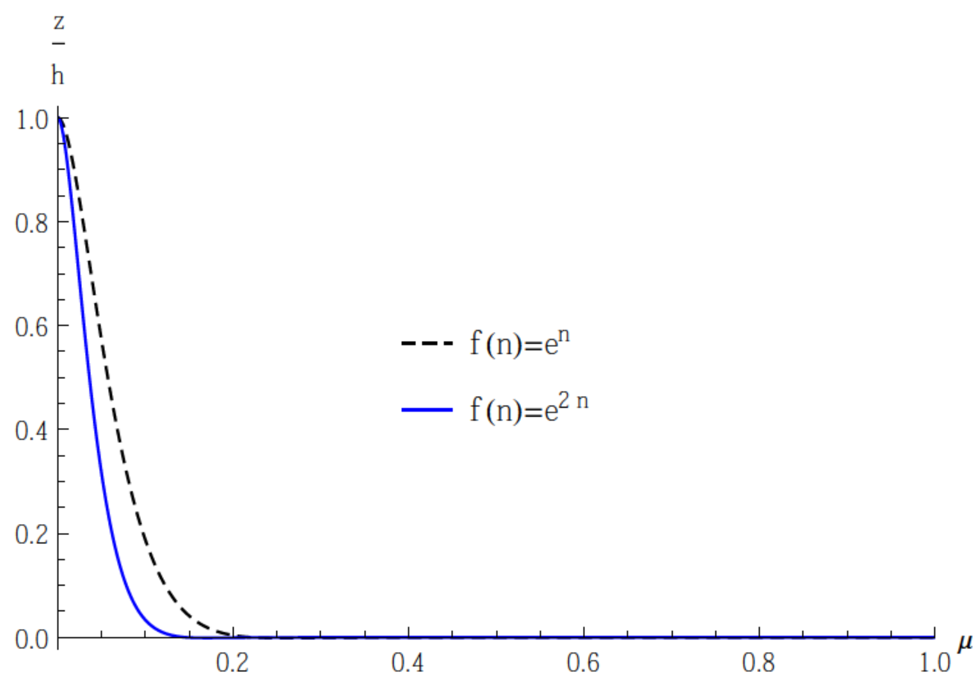

FIGURE 34. For polymer brushes with weighting functions in the form $f(n) = e^{bn}$, the position above the substrate surface decreases was shown to decrease as the value of b increased.

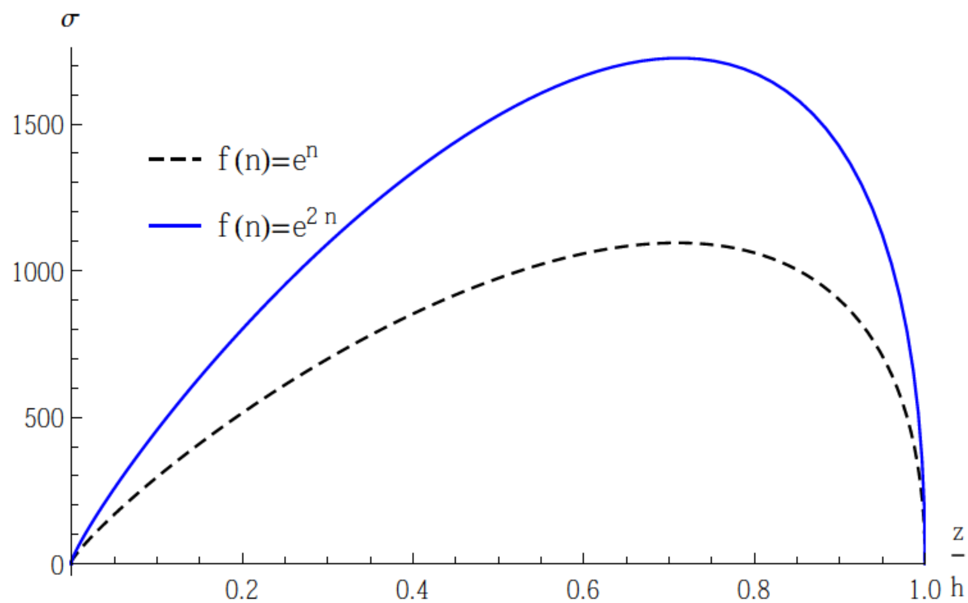

FIGURE 35. For polymer brushes with weighting functions in the form $f(n) = e^{bn}$, the number of free chain ends increases as the value of b increases.

CHAPTER 4

CONCLUSION

Using this variation of the self-consistent field theory it was shown that various regularly branched polymer brushes could be accurately modeled. The polymer brushes with a weighting function of the form $f(n) \quad n^b$ were determined to remain stable only when the brushes themselves remained very small.

Brushes with weighting functions of the form $f(n) \quad d^{an}$ were determined to be stable for $f(n) \quad 2^{2n}$, $f(n) \quad 3^n$, and $f(n) \quad 3^{2n}$, but not for the case $f(n) \quad 2^n$. As the value of a increased for these functions, the allowed potential for stability increased.

Since no real, positive values for the potential were found for weighting functions of the form $f(n) \quad 2^{\frac{G(N \; n)}{N}}$ these polymer brushes were determined to be unstable.

For the polymer brushes with the exponential weighting function $f(n) \quad e^{bn}$ it was determined that the brush would remain stable. As the value of b increased, the allowed potential of the system increased. Similarly, as the value of b increased for the polymer brush, the value of N necessary for the brush to remain in equilibrium decreased.

BIBLIOGRAPHY

BIBLIOGRAPHY

[1] W. J. Brittain and S. Minko, J. Polym. Sci. A Polym. Chem. **45**, 3505 (2007).

[2] L. M. Hall, A. Jayaraman, and K. S. Schweizer, Current Opinion in Solid State and Materials Science **14**, 38 (2010).

[3] G. H. Fredrickson, V. Ganesan, and F. Drolet, Macromolecules **35**, 16 (2001).

[4] O. Azzaroni, J. Polym. Sci. A Polym. Chem. **50**, 3225 (2012).

[5] A. N. Semenov, D. Vlassopoulos, G. Fytas, G. Vlachos, G. Fleischer, and J. Roovers, Langmuir **15**, 358 (1999).

[6] P. E. Theodorakis, A. Avgeropoulos, J. J. Freire, M. Kosmas, and C. Vlahos, J. Phys.: Condens. Matter **19**, 466111 (2007).

[7] J. Roovers, L. L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou, and N. Hadjichristidis, Macromolecules **26**, 4324 (1993).

[8] K. Gong, B. D. Marshall, and W. G. Chapman, The Journal of Chemical Physics **139**, 094904 (2013).

[9] K. N. Plunkett, X. Zhu, J. S. Moore, and D. E. Leckband, Langmuir **22**, 4259 (2006).

[10] W. Senaratne, L. Andruzzi, and C. K. Ober, Biomacromolecules **6**, 2427 (2005).

[11] M. Welch, A. Rastogi, and C. Ober, Soft Matter **7**, 297 (2011).

[12] A. Mizutani, A. Kikuchi, M. Yamato, H. Kanazawa, and T. Okano, Biomaterials **29**, 2073 (2008).

[13] N. Ayres, Polym. Chem. **1**, 769 (2010).

[14] D. Leckband, S. Sheth, and A. Halpern, Journal of Biomaterials Science – Polymer Edition **10**, 1125 (1999).

[15] Jacob, Klein, Kumacheva, Eugenia, Mahalu, Diana, Perahia, Dvora, and Fetters, Lewis J., Nature **370**, 634 (1994).

[16] U. Raviv, S. Giasson, N. Kampf, J.-F. Gohy, R. Jrme, and J. Klein, Nature **425**, 163 (2003).

[17] M. E. Welch and C. K. Ober, J. Polym. Sci. Part B: Polym. Phys. **51**, 1457 (2013).

[18] T. C. Zook and G. T. Pickett, Phys. Rev. Lett. **90**, 015502 (2003).

[19] P. G. de Gennes, Macromolecules **13**, 1069 (1980).

[20] G. T. Pickett, Macromolecules **34**, 8784 (2001).

[21] G. E. Rios and G. T. Pickett, Macromolecules **36**, 2967 (2003), wOS:000182361700058.

[22] G. T. Pickett and T. A. Witten, Macromolecules **25**, 4569 (1992).

[23] M. Murat and G. S. Grest, Macromolecules **22**, 4054 (1989).