Tunable Surface Interactions In Adsorbing Polymer Solutions

Sorour Hosseini
University of Texas at El Paso, shosseini@miners.utep.edu

Follow this and additional works at: https://digitalcommons.utep.edu/open_etd
Part of the Physical Chemistry Commons, and the Physics Commons

Recommended Citation
https://digitalcommons.utep.edu/open_etd/1454

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact lweber@utep.edu.
TUNABLE SURFACE INTERACTIONS IN ADSORBING POLYMER SOLUTIONS

SOROUR HOSSEINI
Master’s Program in Physics

APPROVED:

______________________________
Marian Manciu, Ph.D., Chair

______________________________
Felicia Manciu, Ph.D.

______________________________
Giulio Francia, Ph.D.

______________________________
Charles H. Ambler, Ph.D.
Dean of the Graduate School
DEDICATION

To my beloved parents, Nasrin and Adib, and my love Aria, people who taught me that understanding, compassion, and love are not just notions in a book. My life means more because I have you.
TUNABLE SURFACE INTERACTION IN ADSORBING POLYMER SOLUTIONS

by

SOROUR HOSSEINI, B.S.

THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Physics
THE UNIVERSITY OF TEXAS AT EL PASO
August 2018
ACKNOWLEDGMENTS

Firstly, I would like to express my genuine appreciation to my advisor Dr. Marian Manciu from the department of Physics at The University of Texas at El Paso for the continuous support, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of my master's studies also research and writing of this thesis.

I would also like to acknowledge members of my thesis committee Dr. Felicia Manciu from Department of Physics and Dr. Giulio Francia from the Department of Biology for their support and devoting their valuable time.

Lastly, I would like to thank my family for their endless love and motivation, without whom any of my success would be possible. Thank you for encouraging me in all of my pursuits and inspiring me to follow my dreams. I always knew that you believed in me and wanted the best for me.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ v

TABLE OF CONTENTS ........................................................................................................ vi

LIST OF FIGURES ............................................................................................................. vii

CHAPTER 1: INTRODUCTION ................................................................................................. 1

CHAPTER 2: THE RANDOM WALK PROBLEM ....................................................................... 7
  2.1 Simple 1D Random walk ......................................................................................... 7
  2.2 Mean values of the random walk problem .......................................................... 9
  2.3 Random walk in presence of reflecting and adsorbing surfaces ................. 11

CHAPTER 3: FLORY-HUGGINS THEORY ........................................................................... 13
  3.1 Lattice model of polymer solutions ................................................................ 13
  3.2 The mixing Entropy in the Flory-Huggins model ........................................... 15
  3.3 The mix of polymer solution energy in the Flory-Huggins model ......... 17

CHAPTER 4: THE PROBABILITY OF LOOPS, TAILS, AND BRIDGES FOR NON-
INTERACTING GRAFTED POLYMER ........................................................................... 20

CHAPTER 5: THEORETICAL MODEL OF Bridging INTERACTION OF
ADSORBING POLYMERS ............................................................................................... 22

CHAPTER 6: RESULTS AND DISCUSSION ....................................................................... 29
  6.1 Bridging interactions in dilute polymers solutions ..................................... 29
  6.2 Bridging interactions in interacting polymers solutions ....................... 34

CHAPTER 7: CONCLUSIONS ............................................................................................... 42

VITA .................................................................................................................................... 49
LIST OF FIGURES

Figure 1. Polymer, solvent and solution fractions (MIT Open Course Ware 2005).......................14

Figure 2. Probabilities of first return to the surface (loops) / first reaching the other surface (bridges) after “i” steps, for a non-interacting random walk, for various separation distances $D$ between surfaces, between 4 and 100 Kuhn lengths (in steps of 2 Kuhn lengths). ...25

Figure 3. Probabilities of loop/ bridge formation after “i” steps, for a separation distance of $D=100$ Kuhn lengths between surfaces, and various adsorption energies for monomers on surfaces, between $0.01 \, kT$ and $0.1 \, kT$ (in steps of $0.01 \, kT$). .................................................................28

Figure 4. Number of bridges formed by one polymer of length $N=1000$ Kuhn segments, as a function of the distance between surfaces, and various adsorption energies (between $0.01 \, kT$ and $0.4 \, kT$, in steps of $0.01kT$). At $D =100$, the number of bridges formed decreases with $A$ by about 10 orders of magnitude. .................................................................30

Figure 5. Attractive forces between surfaces (arbitrary units), as a function of the distance between surfaces, for various $A$ values. At large separations, large $A$ values correspond to lower forces, but at small separations smaller $A$ values provides also lower forces.........................31

Figure 6. Attractive forces between surfaces as functions of $A$ (and various distances $D$) shows that an optimal value of $A$ exists for each separation distance. .................................................32

Figure 7. Adsorption energy that provides the maximum force, as a function of the distance at which this force is measured. The strongest long-range bridging attraction (at $D =100$) requires a value of $A$ of about $0.06 \, kT$..............................................................................................................33
Figures 8. Number of loops (a) and bridges (b) as a function of the separation distance for various average segment volume densities $\phi_0$ (0.01 , red $< \phi_0 < 0.1$, blue)........................................36

Figure 9. Distribution of the segment density between the plates (0.01 blue $< \phi_0 < 0.1$ red)......37

Figure 10a. Force between the plates (0.01 $< \phi_0 < 0.1$) obtained as a derivative of the free energy of adsorption with respect to the separation between plates. At larger separations, the attraction increases monotonically with increasing monomer density. ..........................................................39

Figure 10b. Force between the plates (0.01 $< \phi_0 < 0.1$) obtained as a derivative of the total Flory-Huggins free energy, with respect to the separation between plates. The steric repulsion increases monotonically with increasing monomer density. ..........................................................40

Figure 10c. Total force between the plates (0.01 $< \phi_0 < 0.1$).........................................................40
CHAPTER 1: INTRODUCTION

Polymers are a very crucial category of materials without which life would be impossible. They are being employed in many different applications as synthesized materials, e.g., plastic, adhesives, resins, and rubber. Yet, many polymers have existed in nature since the beginning of life and many large molecules such as DNA, RNA, and proteins play a key role in animal and plant life. From ancient times, humans had been utilizing some natural polymers as their materials to make housing, equipment, weapons, clothing and other life requirements. Nevertheless, modern polymer industry is originated from an early nineteenth century after the industrial revolution (Aftalion 2001).

Polymers are a distinctive type of macromolecule. The “Polymer” term is composed of two parts come from Greek words: poly (i.e., numerous) and meres (i.e., repeating components, typically called monomers). Therefore, polymers are very large molecules with high molecular weight, which are built up by joining a large number of small molecules (the monomers), which might be all of one kind or of different kinds (such as DNA). The reaction of combining monomers to form a polymer is known as polymerization (Gowariker 2005).

Polymer is a universal name to a broad range of materials. These materials are uncountable due to the vast difference in the type of monomers, chemical structure, physical properties, thermal reaction, and so on. Polymers can be classified in many different ways expressed as follows:

(1) one of the well-known classifications is to categorize all polymers into two main groups based on their monomers (Gosh 2008):

- **Homopolymer**: which is a polymer comprised of identical monomer units.
- **Copolymer**: which is a polymer created from different monomers (i.e., two or more monomer units are deployed).
(2) Polymers can be also categorized based on their origins:

- **Natural:** Polymers which exist in nature also known as biopolymers such as silk, cellulose, proteins, DNA, etc.

- **Semi-synthetic:** Natural polymers which are chemically modified such as cotton and some other fabrics.

- **Synthetic:** Polymers which are man-made and synthesized in the laboratories. Examples of which are Nylon and Teflon.

There are many more classifications which have been omitted here in this study; for instance, polymers can be classified using their polarization or their line structure defined as linear or branched (Gosh 2008; Jones 2002)

Covalent bonds are the main intermolecular force that holds the polymer molecule together. Other intermolecular forces, e.g., hydrogen bonds, dipole-dipole interactions, London forces, etc., hold the assembled structures of the molecules together. Polymers are also called “Macromolecules” indicating that large or long molecules are assembled together. There is a difference between the two. Even though polymers are macromolecules; all macromolecules are not polymers. For instance, proteins are not made of one or two repeating unites. Protein unites are among 20 existing amino acids. Each protein is made of a specific repetitive pattern selected from those 20 amino acids. They are thus macromolecules but not polymer (Hiemenz and Lodge 2007).

Considering the size of polymer molecules, two main features are taken into account: (1) the number of repeated unites, and (2) its molecular weight. Assume that molecular weight of a polymer is $M$, which is in the scale of $10^3$-$10^7$ (g/mole) or more, and the molecular weight of one monomer is considered to be $M_0$. Therefore, the degree of polymerization ($N$) defined as the
The number of repeated units in a molecule can be expressed as the ratio of the molecular weight of the polymer divided by the molecular weight of one monomer as:

\[ N = \frac{M}{M_0} \]  

(1.1)

Even though one of the main features of a polymer structure is having a large number of monomers (Cosgrove 2005), the structure might be broken up owing to the stress made along the units. In other words, the longer the chain, the more likely the chain to be broken up. Indeed, significant features and properties of different types of polymers (e.g., being strong and long-lasting, cheap, and easy to fabricate) come from the chain length. The applications of polymers can be seen in almost every aspect of human life including clothes, sports, building materials, artificial joints and so on. Some of the aforementioned applications are documented in (Flory 1953; Huang, Kotaki and Ramakrishna 2003; Ramasubramaniam et al. 2003; Zou and Shen 2008; Gueguen et al. 2010; Gilardi et al. 2017; Bossi et al., 2018).

Performance of polymers depends on the type of solvent they are interacting with. Two different behavior can be usually observed. When the polymer is compatible with the solution, the chains would be unfolded and stretched out through the solvent (the polymer "prefers" the solvent), which is a result of a better interaction with the solvent. In the opposite case (the polymer does not "like" the solvent) it would be clumped into a smaller shape.

Grafted polymer brushes, which are made by attaching one end of each chain to a surface, have been often used to stabilize colloidal dispersions, because of the steric repulsion that develops when two brushes are overlapping (Napper 1983). This is a consequence of the increase in the free energy of the system because of the increase in the local monomer density, similar to the hard-sphere repulsion.
However, if the monomers are adsorbing on the surfaces (the monomers are attracted by the surface), the opposite effect, namely an attraction between surfaces might also occur – because a polymer “bridge” may reach the other surface and therefore lowers the free energy of the system (Iler 1971). This “bridging” interaction has been already used to induce flocculation of colloidal particles in water purification systems (Everett 1988), and might also play a role in various biological processes, such as the attachment of biological cells on foreign surfaces. Because bridging requires interdigitating of brushes, it is more difficult to be understood in terms of simple theoretical models, than the steric interaction.

The lattice model of Scheutgens and Fleer (Scheutgens and Fleer 1979) for the adsorption of a polymer molecule on a single plate have been extended to the attractive interaction between plates by Li and Ruckenstein (Ruckenstein and Li 1997). The self-consistent field theory (for adsorption on one plate) of Varoqui (Varouqi, Johner and Elaissari 1991) has been used to calculate the bridging interactions between two plates by Podgornik (Podgornik 1992), and was extended to polyelectrolytes by Borukhov et al. (Borukhov, Andelman and Orland 1999). Additional van der Waals interactions have been accounted for, in this framework, by Huang and Ruckenstein (Huang and Ruckenstein 2004). Whereas these self-consistent field theories can provide a general description of the system (e.g. the monomer distribution in overlapping brushes or the forces between plates), they cannot provide microscopic information (such as the number of bridges formed, and their dependence on the monomer-surface interaction).

The approximation of a polymer confined between walls as a random walk on a lattice is usually treated in a matrix formalism suggested by DiMarzio and Rubin (Di Marzio and Rubin 1971), which allows one to calculate the fraction of loops, bridges, and trains, and consequently the polymer-mediated interaction between plates as functions of the separation between plates and
the adsorption energy. It was later shown (Van Opheusden, Nijs and Wiegel 1985) that the interaction between plates depends critically on the value of the adsorption energy, $\theta_c = \frac{A}{kT}$, with $A$ being the adsorption energy of a Kuhn segment on the surface, $k$ the Boltzmann constant and $T$ the absolute temperature. If $\theta < \theta_c$, the interaction between plates was shown to be repulsive (because of the repulsion generated by the entropic confinement of the polymer), at $\theta = \theta_c$ there is no interaction, whereas for $\theta > \theta_c$ the attraction increases monotonically with decreasing plate separation (the formalism does not take into account the steric repulsion due to monomer volume exclusion effect). When $\theta$ is large, the attraction is actually decreased, because the polymer collapses on one surface and less bridges are formed.

The configuration of a polymer grafted on the interface can be described in terms of short configurations (loops, trains, and tails), for which the probability of occurrence can be easily calculated. The "loops" represent chains that have both ends on the surface, "trains" are chains for which all monomers remain in the vicinity of the surface and "tails" are chains with one end attached to the surface and the other in the solvent.

It was recently shown that, if the interaction energy of the short configurations can be estimated, the probability of the configurations in the polymer brush can be calculated via a constrained (Lagrange) minimization (Manciu and Ruckenstein, Simple model for grafted polymer brushes. 2004). The idea of this model is based on the fact that it is very simple to calculate the entropy of a non-interacting polymer in the absence of any interactions (the entropy of a random walk) and subsequently to calculate the probability of formation of loops, trains, and tails. If the energy of these configurations can be estimated, a constrained minimization can be employed to calculate the brush configuration corresponding to the minimum energy. The energy of a small
configuration should include all the interactions within the configurations (between monomers), as well as the interactions with the rest of the polymer, the solvent, and the surface.

The aim of this work is to extend the model for the interactions between surfaces with (adsorbing) grafted polymer chains, in which bridges between surfaces occurs, in addition to the loops, tails, and trains. We expect that based on the parameters of the system (the grafting density, the polymer length, the quality of the solvent, the electrolyte concentration, the interactions between the monomers and the surface) we will be able to "tune" the interactions such as they become either attractive or repulsive at any desired distance. The solution to this problem is of general interest for many applications in colloidal and biological sciences, from designing selective molecular filters in water purifications to understanding (and preventing) the attachment of metastasis cancerous cells on tissues (Manciu and Hosseini 2016). The dilute polymer is approximated by a 1D non-interacting random walk starting on one surface, for which the probabilities of reaching the other surface or returning to the initial surface can be obtained as functions of the number of steps (the size of the bridges and loops, respectively). The monomer-monomer and monomer-solvent interactions are taken into account via the commonly used, mean-field Flory-Huggins interactions, and the adsorption on monomer on the surfaces is modeled by a decrease in the free energy of the system.
CHAPTER 2: THE RANDOM WALK PROBLEM

2.1 SIMPLE 1D RANDOM WALK

A random walk is a sequence of random steps by which moving particles wander away from some initial point. The random walk is formed by the summation of independent and identically scattered variables (Lawler and Limic 2010). In this distribution, each particle is free to move with steps of equal length. The steps of equal length are taken with the probability \( p \) and \( q \) \((p+q=1)\) toward the left or right direction (or forward and backward).

In many cases, the binomial distribution describes the behavior of a variable. It is appropriate to summarize a set of independent observations by the number of observations in the group that represent one of two outcomes. The simple random walk can be thus assumed as a binomial distribution of steps. Ransom walk is a binomial distribution if the following conditions are taken into consideration (Collani and Drager 2001):

- Each step is independent.
- The number of steps \( N \) is known.
- Each step shows only one of two results (e.g., "forward" or "backward").
- The probability of "forward" \( p \) is the same for each result.

Imagine a particle starts a movement at \( x=0 \) and performing some steps in one dimension if the length of each step is \( l \) and total of \( N \) steps has been done, the location of the particle is:

\[
x = ml
\]  

(2.1.1)

Where \( m \) is an integer between
\[ -N \ll m \ll N \]  \hspace{2cm} (2.1.2)

Determining the probability of finding the particle at the point \( x = ml \) after \( N \) steps, follow the steps are required to be implemented. First, we need to define \( n_1 \) as the number of steps to the right and \( n_2 \) as the corresponding number of steps to the left. Where we know:

\[ N = n_1 + n_2 \]  \hspace{2cm} (2.1.3)

The net displacement to the right in terms of units of steps is:

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

Now, considering the total steps \( N \) and total steps to the right \( n_1 \):

\[ m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N \]  \hspace{2cm} (2.1.5)

The Equation (2.1.5) indicates that if the total steps \( N \) is even; as a result, the value of \( m \) must be even too. On the other hand, if \( N \) is odd, the value of \( m \) must be odd as well.

In order to calculate the probability of step outcomes \( p \) and \( q \) (left and right) multiplication rule of probability is used due to the independency of each step (Bowler and Sanchez 2000). The probability of any \( n_1 \) steps to the right and \( n_2 \) steps to the left can be calculated by multiplying the respective probabilities as follows:

\[ (p..p) (q..q) = p^{n_1} q^{n_2} \]  \hspace{2cm} (2.1.6)

There are so many ways of distributing \( n_1 \) and \( n_2 \) steps in a total of \( N \) steps. A number of distinct possible ways of taking \( N \) steps where \( n_1 \) of them is to the right and \( n_2 \) to the left is expressed as:

\[ \frac{N!}{n_1!n_2!} \]  \hspace{2cm} (2.1.7)
By multiplying equations 2.1.7 and 2.1.8 the probability \( \omega_N \) of taking \( n_1 \) steps to the right and \( n_2 \) steps to the left of a total of \( N \) steps can be calculated as:

\[
W_N(n_1) = \frac{N!}{n_1!n_2!} p^{n_1} q^{n_2} \tag{2.1.8}
\]

Equation (2.1.8) indicated that Random walk is binomial distribution and it is derived from the binomial expansion.

\[
(p + q)^N = \sum_{n=0}^{N} \left( \frac{N!}{n!(N-n)!} \right) p^n q^{N-n} \tag{2.1.9}
\]

It is already known that the particle is taking \( n_1 \) steps to the right and reaches the displacement \( m \). Thus, this statement shows that the probability \( p_N(m) \) of finding the particle at position \( m \) after taking total \( N \) steps is equal to the probability \( W_N(n_1) \) of finding the particle after the random walk taking \( n_1 \) steps to the right.

\[
p_N(m) = \omega_n(n_1) \tag{2.1.10}
\]

Now, by considering Equations (2.1.3 and 4) we can show:

\[
n_1 = \frac{1}{2} (N + m), \quad n_2 = \frac{1}{2} (N - m) \tag{2.1.11}
\]

By plugging Equations (2.1.11) into the equation (2.1.8) the following equation can be drawn:

\[
p_N(m) = \frac{N!}{[(N+m)/2]![N-(m)/2]!} p^{(N+m)/2} (1 - p)^{(N-m)/2} \tag{2.1.12}
\]

### 2.2. Mean Values of the Random Walk Problem

One of the critical points is to calculate the mean value of steps of the random walk problem. First, the normalization of the probability \( \omega_N(m) \) should be verified (Rief 2008).

\[
\sum_{n_1=0}^{N} \omega(n_1) = 1 \tag{2.2.1}
\]
When \( W(n_1) \) is normalized, it states that the probability of taking any number of right steps between 0 and \( N \) have to be unity. Now, substituting the equations (2.1.8) and (2.1.13) will verify the results.

\[
\sum_{n_1}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} = (p + q)^N \\
= 1^N = 1 \tag{2.2.2}
\]

Using the normalization condition and doing the summation of the probabilities multiplied by the function, average of the function can be determined.

\[
\overline{f(u)} = \sum_{i=1}^{M} P(u_i) f(u_i) \tag{2.2.3}
\]

To determine the mean number of \( n_1 \) steps to the right, the \( w_N \) probability equation can be used to get:

\[
\overline{n_1} = \sum_{n_1=0}^{N} (n_1) n_1 = \sum_{n_1=0}^{N} \left( \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} \right) n_1 \tag{2.2.4}
\]

Now, considering two random parameters \( p \) and \( q \) and doing some differentiation formula we can simplify the Equation (2.2.4) to:

\[
\overline{n_1} = Np \tag{2.2.5}
\]

Also, we can get the same results for the left steps:

\[
\overline{n_2} = Nq \tag{2.2.6}
\]

Subtracting the average values of \( n_1 \) and \( n_2 \) will result in average displacement (\( m \)) of the particle:

\[
\overline{m} = N(p - q) \tag{2.2.7}
\]
Obviously, Equation (2.2.7) implies that if the probability of the two intended outcomes, in this case, left and right steps, are equal \((i.e., p=q)\) then the average displacement is 0.

The last important parameter is how to determine the average scattering \((\Delta n_1)^2\) around the average value:

\[
(n_1)^2 \equiv (n_1 - \bar{n_1})^2 = n_1^2 - \bar{n_1}^2
\]

we already know \(\bar{n_1}\) therefore, to get the scattering equation we just need to calculate \(n_1^2\):

\[
\bar{n_1}^2 \equiv \sum_{n_1=0}^{N} W(n_1)n_1^2 = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} n_1^2
\]

Using the same random parameters \(p\) and \(q\) and using the same differentiation method as before we can get to the simplified form of the scattering of \(n_2\):

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

2.3. **Random walk in presence of reflecting and adsorbing surfaces**

To study the random walk with two adsorbing interfaces the characteristic function needs to be determined. Assume \(X\) is an arbitrary variable then the characteristic function of \(X\) is defined by (Rief 2008):

\[
\varphi(t) = E(e^{itX})
\]

Characteristic functions are mainly used to simplify the long summation equations; they can be used to either change from a huge summation into the simplified characteristic function or go from the characteristic function into the long summation.
Calculating the characteristic function of the random walk problem we need to determine the probabilities which:

- The particle returns to the initial point \( x=0 \) at \( t=2n \) for the first time.
- The particle gets to the point \( x=1 \) at time \( t=2n+1 \).
- The particle reaches \( x=b \) for the first time at \( t=n \) and never gets to the point \( x=-a \) before the time \( t=n \).
CHAPTER 3: FLORY-HUGGINS THEORY

Flory-Huggins solution theory is thermodynamics mathematical model of polymer solutions. This theory concerns molecular size variations in mixing entropy (Sperling 2005). Flory-Huggins model developed based on of free energy of mixing polymer solutions using the statistical approach on a regular lattice. Deploying this model phase stability and phase diagrams of polymer solutions could be described (Sperling 2005).

3.1. LATTICE MODEL OF POLYMER SOLUTIONS

Lattice models are the graining forms in which only the most important molecules of a system are maintained in their statistitical mechanics model (Lau and Dill 1989). This method can be used as a powerful tool to predict the complex behavior of materials. In other words, the input parameters utilized in this method are trained to predict the final product in form of a mathematical equation. An extensive literature have been implemented using such predictive models to find reliable relationships in complex related problems in several fields of study such as pharmacy, biomedical engineering, chemical enegineering, material science, pavement engineering and so on, as documented in (Lau and Dill 1989, Vanderzande 1998, Marro and Dickman 2005, Teif and Rippe 2010, Tirado et al. 2017, Fleer 2018, and Fathi et al. 2018). It is worth to mention that sensitivity analysis techniques can be deployed in accordance with predictive models to get a better insight into the final product to see how the predicted value can be contributed to the involving parameters. Similar to the predictive models, sensitivity analyses techniques are widely used in different fields. Examples of which can be found in Neubert et al. 2000; Marino et al. 2008; and Lemus et al. 2018. This study benefits local sensitivity methods that would be discussed in the following sections.
Free energy of mixing for polymer solutions can be derived based on Flory-Huggins theory (Dill and Bromberg 2003).

where \( n_p \) is a number of polymer chains, \( N \) is the number of segments in a chain, \( N_s \) is the number of solvent molecules, and \( M \) is the total number of lattice sites which is equal to \( n_s + N n_p \).

Lattice sites are points on the lattice grain added together repeated to form the whole lattice and each can take only up to one molecule of either solvent or one segment of the polymer.

The equation below shows the volume fraction of the polymer:

\[
\varphi_p = \frac{V_p}{V_p + V_S} = \frac{N n_p}{M} \quad (3.1.1)
\]

Now, the Volume fraction of the solvent can be determined as:

\[
\varphi_s = \frac{V_s}{V_p + V_S} = \frac{n_s}{M} \quad (3.1.2)
\]
The simplifying assumptions were taken into consideration in Equations (3.1.1) and (3.1.2) are as follows:

- All molecules are mixed subjectively.
- Molecules of the same type are indiscernable.
- One solvent molecule and one piece of the polymer chain are equal to one lattice site.

Now, to determine the thermodynamic behavior of a polymer solution, the expression of the free energy (Gibbs free energy $G$) of mixing for polymer solutions could be used in a closed system at constant pressure and temperature:

$$
\Delta G^{Mix} = \Delta H^{Mix} - T \Delta S^{mix}
$$

(3.1.3)

where $\Delta G$ is the Gibbs free energy, $\Delta H$ is enthalpy of the mixing, $\Delta S$ is entropy of it and $T$ is the temperature of the the mixing solution (Brazel and Rosen 1971).

$$
\Delta S_{Small \ molecule} \gg \Delta S_{polymer}
$$

$$
\Delta G_{small \ molecule} \ll \Delta G_{polymer}
$$

↓  ↓

Easy to dissolve  Difficult to dissolve

3.2. **The mixing Entropy in the Flory-Huggins model**

Considering $(p)$ as the number of polymer molecules initially placed on a lattice; the $i^{th}$ polymer, i.e., $(p+1)$, can be set on the lattice by calculating using different ways. To determine the Placement of the first segment of polymer $(p+1)$ we have:

$$M-n_p = \text{number of remaining lattice sites} = \text{number of ways to place the first segment}. $$
For placement of the second segment of the polymer \((p+1)\), \(K\) is defined as the coordinate number of the lattice:

\[
K = \frac{M-n_p}{M} \tag{3.2.1}
\]

The Equation (3.2.1) is the number of possible ways to set the second segment of the polymer on the lattice.

Moving on to the \(p\)th molecule, the probability of placing the last segment of the polymer on the lattice is expressed as (Brazel and Rosen 1971):

\[
p_p = K(K - 1)^{n-2} M \binom{M-n(p-1)}{M}^n \tag{3.2.2}
\]

Following the same procedure used for the single chain polymer, a number of possible configurations for the total set of \(n_p\) chains can be determined. (Dill and Bromberg 2003). First, we need to start setting the first segment of all \(n_p\) polymer chains into the lattice sites. The number of possible configurations of first segments of all \(n_p\) polymers is derived as \(\omega_1\):

\[
\omega_1 = M(M - 1)(M - 2)(M - 3) \ldots \left(M - (n_p - 1)\right) = \frac{M!}{(M-n_p)!} \tag{3.2.3}
\]

The number of configurations for the \((n-1)\) remaining polymer segments of all the chains is \(\omega_2\):

\[
\omega_2 = \left(\frac{K-1}{M}\right)^n p_{n-1} \frac{(M-n_p)!}{(M-Nn_p)!} \tag{3.2.4}
\]

Now, adding the \(\omega_1\) and \(\omega_2\) equations together, the total number of configurations for all the segments \((N)\) of all the polymer chains \((n_p)\) could be calculated:

\[
W = \frac{\omega_1 \omega_2}{n_p!} \tag{3.2.5}
\]
It should be pointed out that, as all the polymer chains are indistinguishable, the \( n_p \) denominator eliminates over-counting.

To determine the entropy of the mixing polymer solution the implementation of the following steps are required (Jaynes 1965):

\[
\Delta S_{\text{mix}} = S_{\text{solution}} - S_{\text{unmixed}} = S_{\text{solution}} - (S_{\text{pure solvent}} + S_{\text{pure polymer}})
\]

\[= S_{\text{solution}} - S_{\text{pure polymer}} \tag{3.2.6}
\]

Considering the Boltzmann entropy formula accounts for:

\[
\Delta S_{\text{mix}} = k_b \ln \frac{(z-1)^{n_p(N-1)} M!}{n_s! n_p!} = k_b \ln \frac{(N n_p)^{n_p(N-1)} M!}{(N n_p)! n_s!} \tag{3.2.7}
\]

where \( k_b \) is Boltzman constant (\( k_b = 1.38065 \times 10^{-23} \text{ Jk}^{-1} \)).

Now, by applying Sterling approximation (\( \ln x! \approx x - x \ldots \)) the final result can be made as:

\[
\Delta S_{\text{mix}} = -k_b [n_s \ln \varphi_s + n_p \varphi_p] \tag{3.2.8}
\]

### 3.3. The Mix of Polymer Solution Energy in the Flory-Huggins Model

Generally, molecules are having all sorts of interactions with one another such as polar, or Van der Waals and electrostatic interactions (attraction and repulsion). All these forms of interaction are playing their own role in changing the internal energy of the system (Hirschfelder and Meath 2007).

To get a better insight into the interactions in a lattice model, the enthalpy \( (\Delta H) \) of the mixing polymer solution should be determined. At constant pressure \( (P) \), the enthalpy equation is linked to the internal energy of the polymer solution mix \( (U) \) as:
\[ \Delta H \equiv U + PV \quad (3.3.1) \]

\[ \Delta H_{\text{mix}} = \Delta U_{\text{mix}} + PV_{\text{mix}} \approx \Delta U_{\text{mix}} \quad (3.3.2) \]

In Equation (3.3.2), the change in volume of mixing is zero; thus, the second term can be simplified as: \[ \Delta H_{\text{mix}} = \Delta U_{\text{mix}}. \]

To find the internal energy of the solution, the number of contacts and interactions between the molecules on the lattice should be taken into account (Brazel and Rosen 1971).

- \( m_{ij} \) = number of \( i-j \) contacts between molecules in the polymer solution
- \( E_{ij} \) = energy per each contact
- \( U_{\text{solution}} = \Sigma (\text{number of contacts})(\text{energy/contacts}) \)

The number of contacts made between solvent molecules or the polymer segments is related to the coordination number \((K)\) and the contact numbers \( n_{ij} \):

A number of polymer segment contacts:

\[ Nn_pK = 2m_{pp} + m_{ps} \]

\[ m_{pp} = \frac{KKn_p - m_{ps}}{2} \quad (3.3.3) \]

where \( m_{pp} \) is the number of polymer-polymer bonds and \( m_{ps} \) is the number of polymer-solution contacts.

A number of solvent contacts is expressed:

\[ n_sK = 2m_{ss} + m_{ps} \]

\[ m_{ss} = \frac{Kn_s - m_{ps}}{2} \quad (3.3.4) \]
where $m_{ss}$ is the number of solvent-sovent bonds and $m_{ps}$ is the number of polymer-solvent contacts.

The final expression for the internal energy of the solution is as:

$$U_{solution} = m_{pp}E_{pp} + m_{ss}E_{ss} + m_{ps}E_{ps} \quad (3.3.5)$$

$$U_{solution} = \frac{K_N n_p}{2}E_{pp} + \frac{K_n s}{2}E_{ss} + (E_{ps} - \left(\frac{E_{pp}+E_{ss}}{2}\right))m_{ps} \quad (3.3.6)$$

The unmixed internal energy is as follows:

$$U_{unmixed} = (#solvent - solvent bonds)E_{ss} + (# polymer - polymer bonds)E_{pp} \quad (3.3.7)$$

The internal energy of unmixed could be shown as:

$$U_{unmixed} = \left(\frac{K_n s}{2}\right)E_{ss} + \left(\frac{K_N n_p}{2}\right)E_{pp} \quad (3.3.8)$$

Combining the mixed and unmixed equations will result in final expression for internal energy:

$$\Delta U_{mix} = U_{solution} - U_{unmixed} \quad (3.3.9)$$

which equals to:

$$U_{mix} = (E_{ps} - \left(\frac{E_{ss}+E_{pp}}{2}\right))m_{ps} \quad (3.3.10)$$
CHAPTER 4: THE PROBABILITY OF LOOPS, TAILS, AND BRIDGES FOR NON-INTERACTING GRAFTED POLYMER

A non-interacting grafted polymer can be accurately described by a random walk. The probability of occurrence of loops, tails, and trains (configurations much shorter than the polymer) in the brush can be calculated exactly, either for one or for two surfaces. If the polymer interacts only with the surface (attraction/repulsion), the probabilities of occurrence of loops, tails, and trains can also be calculated exactly via a constrained optimization. The minimum energy of a short configuration (a loop, tail or train) can be estimated via mean-field (Flory Huggins) theory, and when they are sufficiently short, their minimum energy can be obtained via ab-initio calculations.

In the case of only one surface, the probability of return to the origin was shown to be provided by the Catalan numbers (Chandrasekhar 1943):

\[ P_i^\infty = \frac{1}{(2i)!} \left( \frac{2}{i(i+1)} \right) \]

(4.1)

where \( P_i^\infty \) represent the probability of first return to the surface after \( 2i \) steps of a random walk of infinite length, which, for large values of \( i \), can be approximated by:

\[ P_i^\infty = \frac{1}{2i-1} \sqrt{\frac{2}{(2i-1)\pi}} \exp\left(-\frac{1}{2(2i-1)}\right) \]

(4.2)

an accurate approximation for large \( i \) values, for which the use of Equation (4.1) becomes too time consuming.
The case of two adsorbing surfaces for the non interacting random walk is more difficult to be studied. In the case that both the origin and the opposite surface are adsorbing (namely, the random walk is considered to create either a loop or a bridge, depending on which surface reach up first), it was shown (Goldman 1970) that the probability of first passage can be obtained from the generating function

\[ U(z, c) = \sum_{n=0}^{\infty} u_n(c)z^n = (2pz)^{l-c} \frac{(1+\sqrt{1-4pqz^2})^c + (1-\sqrt{1-4pqz^2})^c}{(1+\sqrt{1-4pqz^2}) + (1-\sqrt{1-4pqz^2})} \]  

(4.3)

From the previous formula, the probability of occurrence of loops, trains, tails & bridges can be calculated exactly from:

1. The probability of reach the surface at "D" steps away:

\[ \sum_{i=1}^{\infty} P_{b_i}z^i = z^{D-1} \frac{(1+\sqrt{1-z^2})-(1-\sqrt{1-z^2})}{(1+\sqrt{1-z^2})^{D-1}(1-\sqrt{1-z^2})^{D}} \]  

(4.4)

2. The probability of return to origin:

\[ \sum_{i=1}^{\infty} P_{l_i}z^i = z^{D-1} \frac{(1+\sqrt{1-z^2})^{D-1}-(1-\sqrt{1-z^2})^{D-1}}{(1+\sqrt{1-z^2})^{D}-(1-\sqrt{1-z^2})^{D}} \]  

(4.5)

By expanding the second terms in Taylor series and identification of the coefficients.
CHAPTER 5: THEORETICAL MODEL OF BRIDGING INTERACTION OF ADSORBING POLYMERS

The polymer is considered composed of Kuhn segments, that can have orientations independent of each other, and the segment distribution for non-interacting segments is provided by a random walk. Furthermore, any configuration of a polymer can be described by a combination of a number of nli loops (random walks that returns to the same surface from which they departed after “i” steps), nbi bridges (random walks that reach the opposite surface after “i” steps) and one tail (a random walk that ends up without reaching any surface). The partition function of such a polymer is therefore given by:

\[ Z = \sum_{j=1}^{N} \exp \left( -\frac{U_j}{kT} \right) = \sum_{[nli,nbi]} \exp \left( -\frac{U_{nli,nbi}}{kT} \right) \]  \hspace{1cm} (5.1)

where the sum over “j”, that runs over all the N Kuhn segments is replaced by a sum over all possible configurations of nli loops, nbi bridges and one tail, compatible with a polymer composed of N Kuhn lengths. The energy \( U \) associated with the configuration energy should account for the interactions between monomers and surfaces, monomers and monomers and monomers and solvent. A mean field approximation, in which a minimum energy is associated with each individual loops, tails, and bridges was proposed recently (Manciu and Ruckenstein 2004) (Manciu, Bosse and Ruckenstein 2013). However, if the solvent is neutral and the polymer solution dilutes, the largest contribution to the energy comes from the interactions between monomers and surfaces, which can be calculated exactly:

\[ U_{[nli,nbi]} = -A \sum_i (nl_i + nb_i + 1) = -A(n_s + 1) \]  \hspace{1cm} (5.2)
Where one considers that the interaction energy between segments and surface is equal to 
\(-A\) if the segment is adsorbed on the surface and zero otherwise, the sum is over the number of 
loops and bridges that contain “\(i\)” segments, and \(n_S\) is the total number of loops and bridges. The 
probability for a “loop” or a “bridge” to occur in a configuration, when there are two parallel 
surfaces at a distance of \(D\) Kuhn segments (where \(D\) is an integer) and the interaction energy 
\(U=0\), is provided by the probability that a random walker, that departs from a surface, will return 
to the same surface or reach the opposite one after “\(i\)” steps, without having reached any of the 
two surfaces before. A random walker starting at a surface makes the first step away from the 
surface, and then either returns to the initial surface after 2, 4, 6…steps or reaches the other surface 
after \(D, D+2, \) \(D+4\) steps, where the number of steps should be smaller than the length \(N\) of the 
polymer (a random walk that after \(N\) steps does not reach any surface is a “tail”).

The probabilities of the “first return” to the origin after “\(i\)” steps of a random walk, that 
start at a distance of \(c\) steps from the origin have been calculated by Chandrasekhar for both a 
reflecting and an absorbing wall (Chandrasekhar 1943). The presence of the second surface at a 
distance \(D\) (on which the walker can be also adsorbed) complicates the problem, although it was 
shown long ago by Huygens that the probability of reaching either wall (regardless of the number 
of steps) is inverse proportional to the distance to the wall (the “gambler’s ruin” problem) 
(Goldman 1970). The probability of reaching for the first time a surface at a distance \(D\), without 
having reached the surface at 0, can be calculated as follows (Goldman 1970). Assuming that the 
probability of a step forward is equal to the probability of a step backward, the probability to reach 
a point at a distance \(c\) after \(i+1\) steps is provided by:

\[
p_{t+1}(c) = \frac{1}{2}p_t(c - 1) + \frac{1}{2}p_t(c + 1)
\]  

\[\text{(5.3)}\]
By multiplying with a variable $z^{i+1}$ and summing over “$i$”, one obtains:

$$\sum_{i=0}^{\infty} p_i(c)z^i = G(z, c) = \frac{z}{2} G(z, c + 1) + \frac{z}{2} G(z, c - 1)$$  \hspace{1cm} (5.4)

When “$c$” represents the starting point of the walk, the generating function $G$ of the probabilities to reach the surface at $D$ in “$i$” steps for the first time, without returning to the origin, obeys the boundary conditions:

$$G(z, D) = 1 \hspace{1cm} (5.5a)$$
$$G(z, 0) = 0 \hspace{1cm} (5.5b)$$

Which simply state that a walker starting at $D$ always reaches first the surface at $D$ and never reaches first the surface at $0$. The solution of Eq.(5.4) subject to the boundary conditions (5) is unique and provided by:

$$\sum_{i=0}^{\infty} p_i(c)z^i = z^{D-c} \frac{(1+\sqrt{1-z^2})^c-(1-\sqrt{1-z^2})^c}{(1+\sqrt{1-z^2})^D-(1-\sqrt{1-z^2})^D} \hspace{1cm} (5.6)$$

The probability that a random walker starting from a surface to reach the other surface after “$i$” steps, hence to form a bridge (since the first step is always away from the surface), is therefore given by:

$$\sum_{i=0}^{\infty} p_b i z^i = z^{D-1} \frac{(1+\sqrt{1-z^2})^{D-1}-(1-\sqrt{1-z^2})^{D-1}}{(1+\sqrt{1-z^2})^D-(1-\sqrt{1-z^2})^D} \hspace{1cm} (5.7a)$$

and the probability of first return to the origin, hence forming a loop, by:

$$\sum_{i=1}^{\infty} p_l z^i = z \frac{(1+\sqrt{1-z^2})^{D-1}-(1-\sqrt{1-z^2})^{D-1}}{(1+\sqrt{1-z^2})^D-(1-\sqrt{1-z^2})^D} \hspace{1cm} (5.7b)$$

Where $D$ represents the minimum number of steps required to reach the opposite surface (the distance between surfaces, measured in Kuhn lengths). These probabilities can be calculated
as usual, by expanding in a series the generating functions from Eqs. (5.7a) and (5.7b) and identifying the terms of $z$ powers. In Figure 2, the probabilities to return to the initial surface or to reach the other surface are plotted for the first 1000 steps, for a separation $D$ between plates of 100 Kuhn lengths.

Figure 2

![Figure 2](image-url)

**Figure 2.** Probabilities of first return to the surface (loops) / first reaching the other surface (bridges) after “$i$” steps, for a non-interacting random walk, for various separation distances $D$ between surfaces, between 4 and 100 Kuhn lengths (in steps of 2 Kuhn lengths).
The partition function becomes:

\[ z = \sum_j \exp \left( -\frac{U_j}{kT} \right) = \sum nj_i b_i \exp \left( \frac{n_s}{nl_i \times nb_i \times \cdots \times p_{l_1} \times p_{b_1} \times \cdots} \right) \exp \left( \frac{A}{kT} (n_s + 1) \right) \]  

(5.8)

Subject to the constraint that the sum of the segments in the loops, bridges and in the tail to be equal the total number \( N \) of the Kuhn segments of the polymer:

\[ \sum_i (inl_i + inb_i) = N \]

(5.9)

Where the values \( i < N \) belong to a loop or bridge and the values \( i > N \) to a tail (walks that need more than \( N \) steps to reach a surface). The equations for the most likely configuration are provided by the derivative of the logarithm of the partition function Equation (4.6) subject to the constrain (4.7), with respect to all \( nl_i \) and \( nb_i \):

\[ \frac{d}{dnl_i} \left( \ln \left( \frac{n_s}{nl_i \times nb_i \times \cdots} \right) p_{l_1} \times p_{b_1} \times \cdots \exp \left( \frac{A(n_s + 1)}{kT} \right) \right) - \lambda (N - \sum_i (inl_i + inb_i)) = 0 \]  

(5.10a)

\[ \frac{d}{dnb_i} \left( \ln \left( \frac{n_s}{nl_i \times nb_i \times \cdots} \right) p_{l_1} \times p_{b_1} \times \cdots \exp \left( \frac{A(n_s + 1)}{kT} \right) \right) - \lambda (N - \sum_i (inl_i + inb_i)) = 0 \]

(5.10b)

After employing the Sterling approximation, \( \ln(n!) = n \ln(n) - n \), equations (3.10) become:

\[ nl_i = n_s (p_{l_i} \exp \left( \frac{A}{kT} - i\lambda \right)) \]

(5.11a)

\[ nb_i = n_s (p_{b_i} \exp \left( \frac{A}{kT} - i\lambda \right)) \]

(5.11b)

Where \( \lambda \) is a Lagrange multiplier, which can be obtained from the condition that the sum over all possible \( i \) values to be equal to \( n_s \):

\[ \sum_i (nl_i + nb_i) = \sum_i n_s (p_{l_i} + p_{b_i}) \exp \left( \frac{A}{kT} - i\lambda \right) \]

(5.12)

Which, because \( n_s = \sum (nl_i + nb_i) \), reduces to:
\[
\sum_i (p_l \exp\left(\frac{A}{kT} - i\lambda\right) + p_b \exp\left(\frac{A}{kT} - i\lambda\right)) = 1
\] (5.13)

Which can provide \(\lambda\). Once \(\lambda\) is known, \(n_S\) can be determined from the constrain equation (5.9).

The terms \(p_l \exp\left(\frac{A}{kT} - i\lambda\right)\) and \(p_b \exp\left(\frac{A}{kT} - i\lambda\right)\) represent the new probabilities of loops and bridges formation, in the presence of short-range (adsorption) interactions between monomers and the surface. They are plotted in Figure 3, for \(D=100\), and various adsorption energies -\(A\).

Figure 3
Figure 3. Probabilities of loop/bridge formation after \( t \) steps, for a separation distance of \( D=100 \) Kuhn lengths between surfaces, and various adsorption energies for monomers on surfaces, between 0.01 \( kT \) and 0.1 \( kT \) (in steps of 0.01 \( kT \)).
CHAPTER 6: RESULTS AND DISCUSSION

6.1 BRIDGING INTERACTIONS IN DILUTE POLYMERS SOLUTIONS

The number of bridges for a polymer with \( N=1000 \) is plotted vs. the separation distance between surfaces in Figure 4, for various values of \( A \). One can see that the number of bridges decreases drastically with increasing adsorption, because a larger adsorption increases the number of short loops (the polymer being almost completely adsorbed on one surface). This implies that the attractive force between surfaces does not vary monotonically with \( A \): for \( A=0 \) (no adsorption energy), the attractive force vanishes. The attraction force is also negligible for strong adsorption interactions, because in this case the adsorbing polymer collapses on one surface, and does not reach the other one.
Figure 4. A number of bridges formed by one polymer of length \( N=1000 \) Kuhn segments, as a function of the distance between surfaces, and various adsorption energies (between 0.01 \( kT \) and 0.4 \( kT \), in steps of 0.01\( kT \)). At \( D =100 \), the number of bridges formed decreases with \( A \) by about 10 orders of magnitude.

The attractive force between plates (calculated as the derivative with respect to the distance between the plates of the total energy of the most likely polymer configuration, measured in units of \( kT \) divided by the Kuhn length, is plotted in Figure 5 as a function of distance, for various \( A \) values. At large separations, the force is large for low \( A \) values (because of a drastic decrease in
the number of bridges with increasing $A$), while at low separations the force is in general larger for larger $A$ values. In the extreme case, when the separation between the surfaces is only 2 Kuhn segments, the probability of a loop or a bridge formation become equal and independent of $A$. At this distance, the attraction increases monotonically with $A$.

Figure 5

![Graph showing attractive forces between surfaces](image)

**Figure 5.** Attractive forces between surfaces (arbitrary units), as a function of the distance between surfaces, for various $A$ values. At large separations, large $A$ values correspond to lower forces, but at small separations smaller $A$ values provides also lower forces.
In general, for larger distances, the force as a function of $A$ exhibits a maximum which depends on the distance between surfaces, as shown in Figure 6.

**Figure 6.** Attractive forces between surfaces as functions of $A$ (and various distances $D$) shows that an optimal value of $A$ exists for each separation distance.

The value of that maximum, as a function of distance, is represented in Figure 7. This maximum shows that the long-range attractive force between surfaces, due to dilute polymers, can be tailored by changing the nature of the polymer (e.g., the adsorption energy of monomers on
surfaces), in such a manner that the flocculation of colloidal suspensions becomes optimal. A too weak adsorption energy, as well as a too strong adsorption energy, do not generate a significant bridging force.

Figure 7

![Graph showing the adsorption energy that provides the maximum force as a function of the distance at which this force is measured. The strongest long-range bridging attraction (at $D = 100$) requires a value of $A$ of about $0.06 \ kT$.]

**Figure 7.** Adsorption energy that provides the maximum force, as a function of the distance at which this force is measured. The strongest long-range bridging attraction (at $D = 100$) requires a value of $A$ of about $0.06 \ kT$. 
6.2 BRIDGING INTERACTIONS IN INTERACTING POLYMERS SOLUTIONS

In this section we will take into account the monomer-monomer and monomer-solvent interaction (which have been neglected in the precedent section) via the common mean-field Flory-Huggind energy density:

\[ U_{FH} (z) = \frac{kT}{\alpha^z} \left( -\frac{1}{2} \tau \phi^2 + \frac{1}{6} \psi \phi^3 \right) \]  \hspace{1cm} (6.2.1)

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, the Kuhn segment length, \( \phi \) is the monomer volume fraction, \( \tau \) is a dimensionless excluded volume parameter (\( \tau = (2\chi - 1) \) with \( \tau < 0 \) for a good solvent and \( \tau > 0 \) for a poor solvent) and \( \psi \) is the third virial coefficient, which is positive and typically of the order of unity. Under these conditions, the partition function of the polymer becomes:

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

\[ = \sum_{n_1,n_2,...} \frac{n_s!}{n_1!n_2!...} P_1^{n_1} P_2^{n_2} ... P_i^{n_i} ... \exp \left( -\frac{\sum_{i} n_i U_{FH} (i)}{kT} - \frac{(n_s + 1)A}{kT} \right) \]  \hspace{1cm} (6.2.2)

and constrained minimization under the condition that the total number of segments add up to \( N \)

\[ \frac{d}{dn_i} \left( \log \left( \frac{n_s!}{n_1!n_2!...} \left( P_i \exp \left( -\frac{U_{FH} (1)}{kT} \right) \right)^{n_i} \exp \left( -\frac{A(n_s + 1)}{kT} \right) \right) - \lambda \left( N - \sum_{i} 2i n_i \right) \right) = 0 \]  \hspace{1cm} (6.2.3)

leads to the equation:

\[ n_i = n_s P_i \exp \left( -\frac{U_{FH} (1)}{kT} \right) \exp \left( -\frac{A}{kT} - 2i \lambda \right) \]  \hspace{1cm} (6.2.4)
which, under the constrain:

\[
\sum_i P_i \exp\left(-\frac{U_{FH}(1)}{kT}\right) \exp\left(-\frac{A}{kT} - 2i\lambda\right) = 1
\]  

(6.2.5)

can be solved for \(\lambda\).

The increase in the energy due to monomer overlap (excluded volume interactions) in a good solvent (\(\tau=1, w=1\)) raises the free energy of compacted brush, and, as expected, increases the probability of formation of large loops (Figure 8a). This in turns increases the probability of formation of bridges (Figure 8b).
Figures 8. Number of loops (a) and bridges (b) as a function of the separation distance for various average segment volume densities $\phi_0$ (0.01, red $< \phi_0 < 0.1$, blue).

Consequently, the distribution of the segments between the plates can be calculated as a function on monomer density at any separation distance between plates:
As expected, the excluded volume effects push the monomers at larger distances from each surface; when the monomer density is low, the brushes are almost collapsed on one surface, and therefore are unlikely to generate bridges. This leads to a paradoxical effect, namely that exclusion volume forces, which are expected to increase the steric repulsion, might also increase the attraction at certain distances. These distances can be calculated for a given distribution of
parameters; alternatively, the parameters required to maximize the attraction or the repulsion at certain distances can be calculated.

The interaction between surfaces can be calculated in the usual manner, as the change in the free energy with respect to the distance between surfaces. The attractive force between plates due solely to the attractive interaction between monomers and surfaces (the adsorption energy) is depicted in Figure 10a:
**Figure 10a.** The force between the plates (0.01 < \( \phi_0 \) < 0.1) obtained as a derivative of the free energy of adsorption with respect to the separation between plates. At larger separations, the attraction increases monotonically with increasing monomer density.

The steric force (due to Flory-Huggins free energy) is plotted in Figure 10 b, which shows that it increases monotonically with increasing monomer density at any separation distance:
**Figure 10b.** The force between the plates ($0.01 < \phi_0 < 0.1$) obtained as a derivative of the total Flory-Huggins free energy, with respect to the separation between plates. The steric repulsion increases monotonically with increasing monomer density.

The total force between plate, calculated as the derivative of the total free energy of the system with respect to the separation distance, is plotted in Figure 10 c:

**Figure 10c.** Total force between the plates ($0.01 < \phi_0 < 0.1$)
At short separation distances, and low monomer densities, the interaction is attractive; however, at large monomer densities the interaction becomes repulsive. The grafting density, therefore, can tailor whether the interactions between brushes is attractive or repulsive. At larger separations, the situation is more complex (see the inset in Figure 10 c); depending on the balance between adsorption free energy, solvent quality, polymer length and grafting density, the interaction can be tailored to be attractive or repulsive at any desired distance.
CHAPTER 7: CONCLUSIONS

Polymers that adsorb on colloidal particle surfaces can create bridges between adjacent particles, and generate long range attractions between them, leading to their flocculation. However, if the attractive short-range adsorption energy for monomers on a surface is too strong, the polymer collapses on one surface, and create very few bridges between surfaces; if it is too weak, then the long-range attractive forces between colloidal surfaces are also weak. Increasing the density of grafted polymers increases the free-energy of the system (via excluded-volume interaction); however, these interactions might lead to the extension of brushes and therefore increasing the chance of bridge formation. Consequently, somewhat counterintuitively, larger exclusion volume repulsion might increase the bridging interactions between particles. Therefore, the surfaces with grafted adsorbing polymers are very complex system and either attractions or repulsion can be obtained at any separation distances, depending on the parameters of the system.

A formalism to calculate the bridging interactions between particles with grafted adsorbing polymer brushes was suggested, based on the calculation of the probability of occurrence of the possible polymer configuration; the free energy associated with a polymer configuration was approximated by the minimum one.

For dilute solutions of polymers (for which monomer-monomer and monomer-solvent interactions are negligible), it was shown that the long-range attractive forces between colloidal particles exhibit a maximum, as a function of the adsorption energy between monomers and the surface, which depends on the separation between adjacent particles. The optimal adsorption energy, which maximizes the bridging force at various separation distances, was consequently calculated. When the monomer-monomer and monomer-solvent interactions are taken into account via a Flory-Huggins mean field approach, a complex behavior of the system was obtained.
By changing the parameter of the system (grafting density, length of the polymer, solvent quality adsorption energy, we showed that attractive or repulsive interactions can be tailored at any desired distance.
REFERENCES


46


VITA

Sorour Hosseini completed graduate work in Physics under advisory of professor Manciu at Physics Department at The University of Texas at El Paso (UTEP). She has worked as a Graduate Teaching Assistant of Physics labs and workshops to get a better understanding and enhance mastery of different subjects. Her research interests include Bio-printing, Tissue Engineering, Polymer Science, Statistical Data Analysis, and Bio-Material. During her master’s studies, she was a coauthor of two conference papers and one journal article, and she has two other publications under review from her master.

Her undergraduate degree was in Radiology Technology and Health Physics. She starts her Ph.D. in Biomedical Engineering (BME) as a Doctoral Research Associate in the Biomedical Device, Delivery, and Diagnostic Lab (B3D) in August 2018 at UTEP.

This thesis/dissertation was typed by Sorour Hosseini.