MODELING OF POLYMER ADSORPTION AND LOOPING

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Abstract

Understanding the physical adsorption behavior of polymers on surfaces is crucial for advancing materials science and developing smart coatings to enhance the bio-compatibility of implanted devices. Applications, ranging from heart stents to brain-integrated microchips, have been experimentally explored to study the adsorption properties of charged polymers onto diverse surfaces. While experimental observations have indicated the presence of loops in adsorbed polymer chains, there remains a need for a comprehensive theoretical model to consistently predict these phenomena. The proposed self-avoiding walk model aims to elucidate the conformations of polymer chains on a surface lattice, emphasizing the entropic competition between flat adsorption and dangly loops during the adsorption process. Focusing on loops formed by adsorbed polymers, the study aims to determine entropically preferred looping structures. These looping structures are relevant to the biocompatibility of materials. The modeling approach involves relating entropy to partition values generated by different macro-states, with a focus on enumerating micro-states to identify the most entropically preferred behavior of adsorbed polymers.

Dedication

This is dedicated to my partner that spent endless nights supporting me as I did my research and wrote out my results.

Acknowledgements

I would like to thank my supervisors, Professor Neal Madras and Professor Ozzy Mermut. Professor Ozzy Mermut for her vast knowledge in Biophysics, but also her openness to new perspectives, she has been an exceptional role model for myself and the Biophysics community at large. I am grateful to the members of the Department of Mathematics and Statistics as well as the Department of Physics and Astronomy for a memorable experience during my time at York University. Thank you to Professor Esaias J. Janse Van Rensburg and Professor Christopher Bergevin for taking the time to be on my thesis committee and for giving invaluable feedback. Thank you to my family and friends for their endless support throughout my education.

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Notation, Abbreviations, Acronyms and Glossary

1. Introduction

Mer: The building block of polymers, made from individual monomers, which are small molecules [1].

Polymer: A sequence of mers in a series that are linked through covalent bonds [2].

Homopolymer: A polymer, where every individual mer is identical in its geometry and size.

Self Avoiding Walk (SAW): A mathematical model of a homopolymer is that of a self-avoiding walk (SAW), which is a union of a sequence of edges, known as steps, and vertices that correspond to mers (or mer-sites) that follow a path on a lattice that does not intersect with itself [3].

Excluded Volume Effects: The consideration of the limitations posed by solvent molecules and self-avoidance on the conformations of the polymer in the lattice [4].

Microcanonical Partition Function: A function that outputs the number of conformations of size n and energy m [2].

Good Solvent: A solvent where there is no interaction between chain and solvent.

Adsorption: In chemistry, adsorption can be defined as the increase in concentra-

tion of the solute near the solid-liquid interface [5], which we will henceforth refer to as a surface. Specifically to our model, the state at which at least a single mer of a polymer-chain is in contact with a lattice site of the surface.

Proximal Region: The region closest to the surface where the orthogonal distance from the surface z is less than D which is the upper boundary of the proximal region [6, 7, 8].

Distal Region: The region where the orthogonal distance from the surface z is greater than d which is lower boundary of the bulk solution [6, 7, 8].

Central Region: The region where the orthogonal distance from the surface z is greater than D and less than d [6, 7, 8].

Polymer Loop: The contiguous sequence of segments of an adsorbed polymer that is anchored at its two endpoints that allows the majority of the segments of the loops to be free floating constrained only by the two endpoints on the surface [2].

Salt-caps: Salt-ions that occupy sites on the surface rendering a point on the surface-lattice unavailable for adsorption by a mer [9, 10, 11].

Surface Coverage: Fraction of surface sites occupied by mers [9, 10, 11].

Flory-Huggins Mean-Field Model from Chapter 1

$\boldsymbol{N_S}$ **:** Number of spherical molecules of solvent [12].

$\boldsymbol{N_A}$ **:** Number of polymer-chains [12].

$\boldsymbol{N_{vol}}$ **:** Total lattice sites in solution.

$\boldsymbol{n}$ **:** Number of mers for a single polymer chain [12].

$\boldsymbol{A_{ij}}$ **:** Indexation of polymers, where i corresponds to the i^{th} chain currently being placed, and j to the j^{th} mer of that chain being placed [12].

$\boldsymbol{\sigma}$ **:** The symmetry number, has the value 2 if A is a diatomic or triatomic molecule with both ends alike. For longer chains, σ can be put equal to 1 [12].

$\boldsymbol{f_i}$ **:** The number of mers already placed divided by the total number of sites [12].

$\boldsymbol{z}$ **:** The coordination number, the number of neighbours of a site of the lattice [12].

$\boldsymbol{y}$ **:** Equals $z - 1$ [12].

Overview of self avoiding walks in Chapter 1

$\boldsymbol{c_\ell}$: The number of SAWs that start from a specified lattice site ("the origin") and visit a total of $\boldsymbol{\ell}$ sites (including the starting site) [3].

$\boldsymbol{\gamma_3}$: The universal critical exponent for the number of SAWs in three dimensions [3].

$\boldsymbol{A_3}$: The amplitude for computing the number of self avoiding walk in a three dimensional cubic lattice (not to be confused with notation from Flory-Huggins Mean-Field Model above) [3].

$\boldsymbol{\mu_3}$: The connective constant for computing the number of self avoiding walk in three dimensional cubic lattice.

$\boldsymbol{\mathcal{E}_{vol}}$: The partition for the solution volume, for enumerating the walks in a three dimensional lattice.

$[\boldsymbol{RMSD}]$ **:** The root-mean-square-displacement of a random walk [3].

$\boldsymbol{s_{lp}}$ **:** The length of a loop in mers.

$\boldsymbol{N}$ **:** The number of steps [3].

$\boldsymbol{\nu}$ **:** The critical exponent, interpreted loosely as a measure of repulsiveness of the self-avoiding walk [3].

$\boldsymbol{m_v + 1}$ **:** The approximate height of a loop from the surface (Based on number of vacant sites m_v in Chapter 3).

2. One Dimensional Model with Multi-Step Bases and Gaps

$\boldsymbol{r}$: The number of sites in one chain.

$\boldsymbol{r - 1}$: The number of steps in one chain.

$\boldsymbol{n_{surf}}$: Total lattice sites on surface.

$\boldsymbol{n}$: The total number of polymer chains in solution and on the surface.

$\boldsymbol{n_a}$: The count of chains on the surface of adsorption.

$\boldsymbol{n_b}$ **:** The total number of chains in solution.

$\boldsymbol{s_{lp}}$ **:** The number of steps in a single loop.

$\boldsymbol{s_{lp}+1}$ **:** The number of sites in a single loop.

$\boldsymbol{\mathcal{L}}$ **:** The site-length of the adsorbed portion of chain on the surface that includes all the sites in trains and all the sites at the bases of each loop.

$\boldsymbol{\mathcal{L}-1}$ **:** The step-length of the adsorbed portion of chain on the surface that includes all the steps in trains and all the steps at the bases of each loop.

$\boldsymbol{s_{bs}}$ The number of edges between sites at the base of a loop.

$\boldsymbol{s_{bs}-1}$ The number of sites in the base of a loop, excluding the endpoints of the loop which are at the end of the base.

$\boldsymbol{n_{lp}}$ **:** The count of loops on a single chain.

$\boldsymbol{N_{un}}$ **:** The fraction of sites or steps on the surface, that are not occupied by an adsorbed mer

$\boldsymbol{N_{fp}}$ **:** The fraction of sites or steps on the surface that belong to a footprint of a polymer.

$\boldsymbol{N_{gp}}$ **:** The number of sites or steps in gaps between polymers on the surface.

$\boldsymbol{s_{tr}}$ **:** The number of sites or steps in trains on a single polymer

$\boldsymbol{\mathcal{E}_{lp}}$ **:** The enumeration function for the loops

$\boldsymbol{\mathcal{E}_{vol}}$ **:** The enumeration of the solution.

$\boldsymbol{\mathcal{E}_{total}}$ **:** The total enumeration of the system.

Train-positions: The possible positions of placement of train-steps.

Between-loop-positions: The region between two adjacent loops,

End-of-chain-positions: The regions at the ends of the polymer-chain.

$\boldsymbol{TotalTrainPositions}$ **:** The total number of trains on a single polymer, which is

equal to one more than the number of loops and therefore is $(n_{lp} + 1)$.

Self-avoiding Polygon (SAP): A closed self-avoiding walk on a lattice, we use this approach for a loop that is floating in the solution and can arrange itself in three dimensional lattice [13].

$\boldsymbol{B_3}$ **:** In the work by Guttmann, the most commonly used notation for the amplitude of the SAP in a simple cubic lattice (Z^3) [13].

$\boldsymbol{\Psi_{lp}}$ **:** The number of ways to distribute the train-steps amongst the train-positions for a fixed number of total train-steps available.

Gap-positions: The regions on a surface covered in adsorbed polymers surface where gaps can show up.

Between-chain-gap-positions: The positioning of a gap between two adjacent chains.

End-of-surface-gap-positions: The positioning of a gap between a surface-end-point and an adjacent polymer-chain.

3. One Dimensional Periodic Model

$\boldsymbol{m_c}$ **:** sites occupied by mers of an adsorbed polymer.

$\boldsymbol{m_v}$ **:** vacant sites

4. Two Dimensional Surface Model: Unconstrained Approach

$\boldsymbol{N_{lp}}$ **:** The total mers in loops for a single polymer, is calculated through Equation 4.3

$\boldsymbol{k}$ **:** Index of chain being placed on the surface.

$\boldsymbol{\tilde{w}_k}$ **:** The number of ways to place the k^{th} chain with footprint $\mathcal{L}$.

$\boldsymbol{\mathcal{F}(n_a)}$: Flory factor, the product of the number of ways of all n_a chains, without ordering.

$\boldsymbol{q}$ **:** Number of neighbours of each sites in surface lattice.

$\boldsymbol{R_{\mathcal{F}}}$ **:** The ratio of consecutive Flory factors as a function of n_a.

$\boldsymbol{R_{lp}}$ **:** The ratio of consecutive Enumeration functions for the loops as a function of n_a.

5. Two Dimensional Periodic Model with Clustering of Lattice Sites

$\boldsymbol{\mathcal{L}}$ **:** The footprint has an altered definition in this chapter, it is the number of mers in trains on a single polymer, without the distances of the gaps below the loops.

Cluster: Grouping of sites on the surface lattice that are completely unoccupied, or occupied by adsorbed mers of a polymer, or by salt-caps blocking mers from adsorbing to those sites.

$\boldsymbol{n_1}$ **:** The number of consecutive nearest neighbour steps of a SAW before making a loop.

$\boldsymbol{D}$ **:** A measure of distance of the base of the loop using the projection of that loop on the surface.

$\boldsymbol{p}$ **:** The probability of a surface site not being occupied by a salt-cap.

$\boldsymbol{1-p}$ **:** The probability a surface site is occupied by a salt-cap.

Jump: Representation of a loop in this model of a random walk in solution from a full cluster to the nearest empty cluster.

$\boldsymbol{N_{un}}$ **:** The total number of salt-caps on the surface.

$\boldsymbol{N_{tr}}$ **:** The total mers in trains on the surface.

$\boldsymbol{N_{lp}}$ **:** The total mers in loops on the surface.

$\boldsymbol{N_{sm}}$ **:** The total mers in trains and loops on the surface, plus the number of salt-caps.

$\boldsymbol{W_{gp}}$ **:** The weighting factor for salt-caps on the surface, ratio of salt-caps to N_{sm}.

$\boldsymbol{W_{tr}}$ **:** The weighting factor for trains on the surface, ratio of trains to N_{sm}

$\boldsymbol{W_{lp}}$ **:** The weighting factor for loops on the surface, ratio of loops to N_{sm}

$\boldsymbol{H_{lp}}$ **:** The height of loops in mers.

$\boldsymbol{H_{tr}}$ **:** The height of trains in mers.

$\boldsymbol{H_{gp}}$ **:** The height of salt-caps in mers.

$\boldsymbol{\bar{H}_{surf}}$ **:** Average Layer Height of the adsorbed polymer coating on the surface.

$\boldsymbol{\%\, W_{gp+tr}}$ **:** The weighting factor for loops and trains (mers in polymers) on the surface, ratio of loops plus trains to N_{sm}.

$\boldsymbol{\%\, \hat{R}_{lp}}$ **:** Ratio of mers in loops to all mers in a single polymer chain adsorbed on the surface.

$\boldsymbol{\%\, \hat{R}_{tr+gp}}$ **:** Ratio of mers in trains plus total salt-caps under the loops of a single polymer chain adsorbed on the surface to all mers in a single polymer chain adsorbed on the surface.

$\boldsymbol{Ht}$ **:** Approximation of Loop height.

Chapter 1

Introduction

1.1 Molecular Structures of Adsorbed Polymers

We begin with defining and then consequently modeling the polymer itself as a mathematical object and its adsorption onto a surface. The building blocks of polymers are 'mers', made from individual monomers, which are small molecules [1]. All monomers can bond with at least two other monomer molecules. As per [2], we consider linear polymers (as opposed to branched or cross-linked polymers) where a polymer consists of a sequence of monomers in a series that are linked through covalent bonds. In this research we shall focus on homopolymers where every individual mer is identical in its molecular structure, geometry and size.

A good mathematical model of a homopolymer is that of a self-avoiding walk (SAW), which is a union of a sequence of edges, known as steps, and vertices that correspond to mers (or mer-sites) that follow a path on a lattice that does not intersect with itself [3]. The SAW model is an effective tool for modeling the conformational degrees of freedom, and has considerations of excluded volume effects, which is the consideration of the limitations posed by

solvent molecules on the conformations of the polymer in the lattice [4]. The SAW is also an effective way to estimate the polymer entropy, given that the number of total possible paths corresponds to the microcanonical partition function for this type of model, which is a function that outputs the number of conformations of size n and energy m [2]. The above approach works based on the assumption that the only energy being considered is the adsorption interaction between a mer on a chain and the surface. We are assuming that this a good solvent so there is no interaction between chain and solvent which means we can ignore the energy from that interaction. We only consider the energy that makes the mers of the chain stick to the surface which is substantial given that they are indeed adsorbing to the surface. A consequence of this being that if the total number of surface sites at which mers stick is fixed, then in all the allowable configurations the number of contact points is the exact same, and therefore the energy is the same [2].

We are considering a system where each polymer-chain is either free floating in solution or adsorbed to the solid-liquid interface. In order to model this system, one needs to consider the behaviour of the polymers in solution, but also the behaviour of those that are adsorbed to the surface, as those require different computational techniques. Our system will examine the adsorption behaviour of polymers at the solid-liquid interface. In chemistry, adsorption can be defined as the increase in concentration of the solute near the solid-liquid interface [5], which we will henceforth refer to as a surface. In mathematically modeling adsorption, if a polymer resides in solution within a certain proximity to the surface it is considered adsorbed, and as such is termed to be in the proximal region [6, 7, 8]. This is illustrated in Figure 1.1, where some mers of the polymer reside in the region $z < D$ where z is the orthogonal distance of a mer belonging to a polymer from the surface of adsorption and D is the upper boundary of the proximal region.

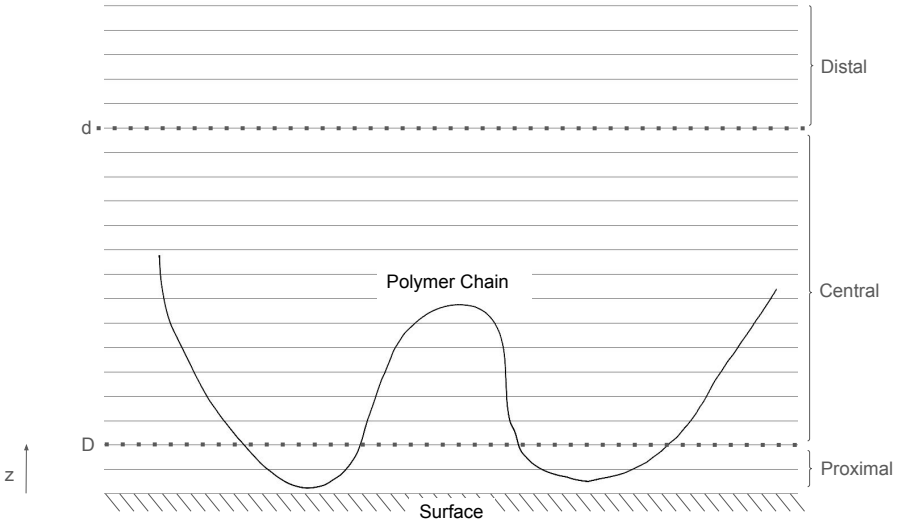


Figure 1.1: Schematic of polymer adsorbed to a surface at proximal, central and distal regions of the solution-surface interface

In our model, adsorption will be defined as the state at which at least a single mer of a polymer-chain is in contact with a lattice site of the surface. Tying the above together, we have a solution of free floating polymers as well as a surface to which typically a fraction of the polymers in solution will adsorb.

Importantly, Figure 1.1 suggests that the adsorbed polymers assemble onto the surface with different molecular architectures. A polymer loop is a a contiguous sequence of segments of an adsorbed polymer that is anchored at its two endpoints as is illustrated in Figure 1.2 below. This allows the majority of the segments of the loops to be free floating constrained only by the two endpoints on the surface.

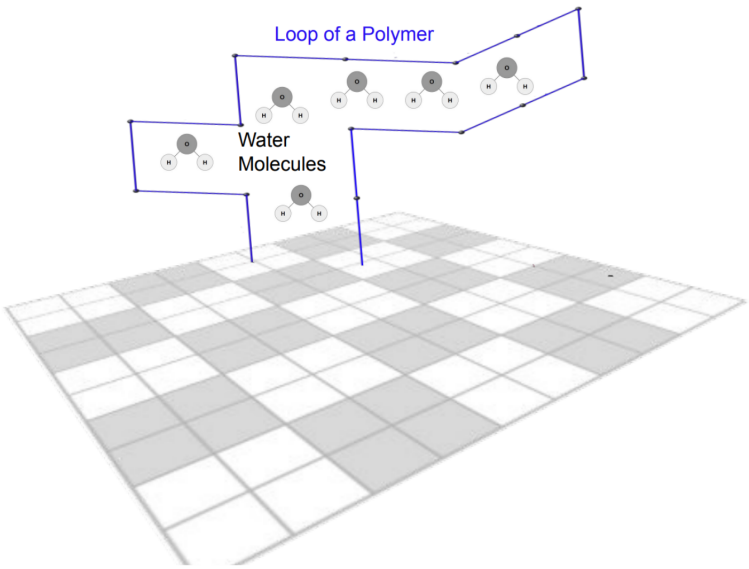


Figure 1.2: Three dimensional approximation of a loop of a polymer trapping water molecules

What is of particular interest to materials scientists and theorists are the emergent physical properties that arise from coating a surface by polymers and the attributes of the coated surface. A recent example is the use of polymer coatings to tune the mechanical properties of a surface, by experimental control of the architectures of the adsorbed polymers on that surface [14]. An interesting consequence of varying the configurations of adsorbed polymers is that one can manipulate the rigidity of the polymer coating at the surface. Controlling mechanical rigidity is important because the existence of many loop-like architectures from the adsorbed polymer can trap water as is illustrated in Figure 1.2 [14, 15]. This control of mechanical properties in a biological water matrix can be very useful to the biomedical industry because the human body is largely composed of water and hydrated biological surfaces [15]. Given appropriate properties, the polymer coating can serve as a biocompatibility layer for foreign materials introduced to the body. Examples of such implantable objects are stents and even microchips for the brain. Coating implants with polymers that modify their surface properties can greatly reduce the risk of rejection of them by the human body [15].

A significant aspect of the above application is to understand what molecular architectures contribute to an increased layer thickness and how that can be controlled [14, 9]. We shall see what has been done to address that in the past with theoretical models to predict layer thickness. We consider the case of adsorption forming a single molecular layer of polymer at the surface, where salt ions called salt-caps occupy sites on the surface rendering a point on the surface-lattice unavailable for adsorption by a mer. Occupying sites of the surface with salt-caps results in adsorbed polymers forming loops over those regions as the mers are unable to attach to those sites, shown in Figure 1.3. Interestingly, under conditions of low surface charge, which means low number of sites occupied by mers, the average layer thickness is increasing to well beyond that of a single mer, sometimes to many tens of mers in thickness [9, 10, 11]. This implies that the single layer is increasing in thickness which implies the existence of loops. Existing theories do not capture this puzzling high thickness regime very well. So in this thesis we attempted to set up a model to try to rationalize under what conditions longer loops might be preferred due to the entropy. For the case of low to medium surface charge, the model we devised predicts an increase in layer height that is in line with experiment [9, 10, 11]. In the case of high surface charge, the theoretical results show a slight increase in height which is not supported by experiment [9, 10, 11].

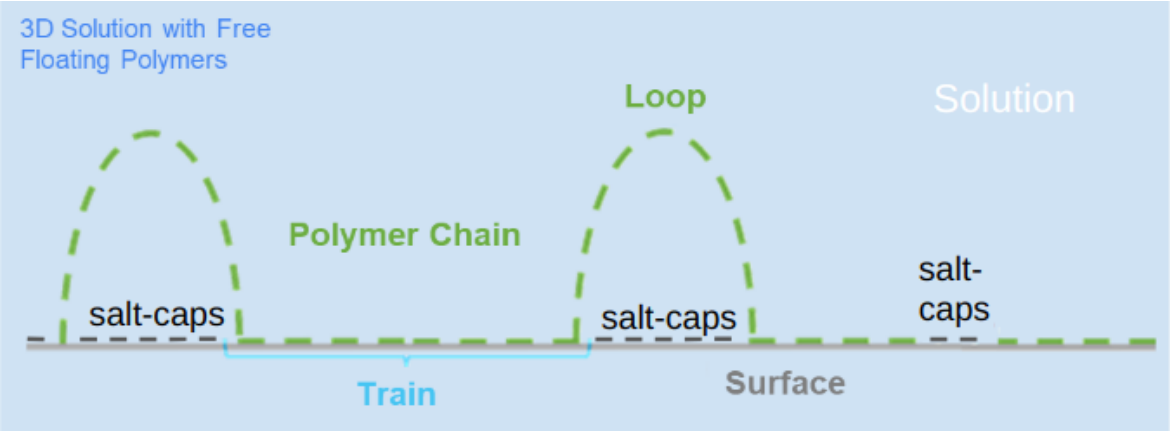


Figure 1.3: One dimensional surface lattice in solution volume. Adsorbed polymer configurations consist of a combination of mers at the surface as trains, loops, salt-caps below loops and the gaps between polymers.

1.2 Hypothesis Statement

Our goal is to show that for lower surface charge, we obtain long loops that are entropically preferred. These loops lead to increased average layer thickness. Low surface charge refers to a large fraction of salt-caps on the surface. Salt-caps occupy sites with a salt ion rendering a point on the lattice unavailable for adsorption by a mer. Using a blend of Fleer and Flory-Huggins enumerational approaches [5, 16, 12], which shall be explained in depth in Section 1.3, we shall attempt to predict the layer thickness for regimes of low surface charge. It is important to note that our model assumes an athermal system with adsorption under static conditions in thermodynamic equilibrium.

1.3 Current Modeling Approach

We assume that polymer self-assembly is driven by entropy which would favour the formation of loops. Based on this assumption, in order to model the structure of the polymer layer on the surface, one must find a way to predict the looping of the polymers on the

surface based on the entropy of the system. We hope the results can help us to understand how the manipulation of salt concentration and surface coverage can impact the preferential formation of long loops which leads to an increased layer thickness [9]. Our model is focused on the experiment [9], where we are holding coverage constant. We assume that interactions are negligible, and as such we do not derive them or incorporate them into our model.

In our model we approximate a solution in terms of a three dimensional lattice in which we have polymers free floating occupying multiple lattice-sites at one time and conforming and arranging themselves in three dimensions. It is important to note that the calculations that are being done are looking at smaller components of the system and enumerating how many ways they can be positioned or arranged in their respective classes of solution, surface, and the class corresponding to the combination of both (i.e loops). We are enumerating the size of the sets of arrangements without necessarily having information about each of the indexed arrangements as a simulation possibly would. In the same way one could enumerate the total arrangements of pieces on a chess board without ever being able to itemize them on a piece of paper exhaustively. In experiments involving sets of microscopic objects like polymers this is extremely useful, as it is currently infeasible to list the total arrangements of even a simple system of homopolymers on a surface, because the values grow exponentially with the length of the polymer.

The model we created is based on two main pillars. The first pillar is based on a model of random mixing of the mers of the polymers with the molecules of the solvent that was proposed by P.J. Flory [17] and Maurice Huggins [12] in the early 1940's. We shall use the Flory-Huggins-type calculation [17, 12] to enumerate what is occurring at the level of a single polymer in the experimental system, and then applying it to all polymers of the system. It would be analogous to zooming in to each polymer and enumerating its possible configura-

tions at that level. The Fleer-type expression [5] will serve as a framework for aggregating all the individual enumerations together. We begin with the Flory-Huggins technique [17, 12], and use the enumeration procedure set out by Maurice Huggins in his 1942 paper [12] as a template to explain the steps.

Let a model solution consist exclusively of N_S spherical molecules of solvent and N_A polymer-chains with n segments (mers, henceforth) which we shall index as A_{ij} where i corresponds to the i^{th} chain currently being placed, and j to the j^{th} mer of that chain being placed. We assume the mers of A are equal in size and shape to a single molecule of type S which is that of the solvent. We assume the volume change on mixing and the heat (or energy) of mixing to be zero [12]. Our system is considered to be athermal and in thermodynamic equilibrium. We treat the solution statistically as if it were a solid solution, having $N_S + nN_A$ sites for both the S solvent molecules and A mers, which corresponds to the total sites in both surface and solution. The A mers are first added (hypothetically) one at a time, then the S molecules, counting the number of different ways in which each solvent molecule or mer (from the polymer chain) can be added and multiplying these numbers together to obtain the total number of configurations [12].

The first mer of the first polymer-chain, i.e., A_{11} can be placed in any of $N_S + nN_A$ sites. Then A_{12} of this polymer chain has a number of alternatives, z. It is worth noting that z can depend on the location of the site as it may differ for the solution and the surface. The parameter z is called the coordination number, and it is the number of neighbours of a site of the lattice. Then, A_{13} has y alternatives, where y equals $z - 1$. Similarly, A_{14} also has y alternatives, and this will apply to all the remaining mers of the polymer-chain A_{1j}, for j greater than 4.

Next we place the mers of the second chain on the lattice, that of A_2. We let N_{vol} be the total lattice sites in solution. The first mer of the second chain, A_{21} has $N_{vol} - n$ sites available. Subsequently, A_{22} has z possible sites, provided A_{21} is not adjacent to any previously occupied sites; it has $z-1$ alternatives if A_{22} is adjacent to one previously occupied site; and it will have $z-2$ alternatives if A_{21} is adjacent to two previously occupied sites, etc. Let f_i be the number of mers already placed divided by the total number of sites. The average number of alternatives for A_{22} is $z\,(1-f_2)$, where f_2 is the chance that any given otherwise available site is already occupied. Mer A_{23} likewise has $y\,(1-f_2)$ alternatives, on the average. In general, for any polymer-chain i, A_{i1} has $N_S + nN_A - (i-1)n$ alternatives, A_{i2} has on average $z\,(1-f_i)$ alternatives, and each of the $n-2$ other mers has $y\,(1-f_i)$ alternatives. To obtain the number of different configurations for the chains, one must divide the total number of configurations, computed in the manner described, by $N_A!$ and by σ_A, where σ is the symmetry number and has the value 2 if A is a diatomic or triatomic molecule with both ends alike. For longer chains, σ can be put equal to 1 [12]. After the addition of all the A polymer-chains, the remaining sites are filled with the S molecules, This addition will have not impact the number of distinguishable configurations.

The way Fleer approached the calculations in [5] for enumerating polymers in solution, on the surface, and in loops, was by splitting the procedure into ever smaller classes of enumeration and aggregating those classes in the end. In this model we will have three main classes of enumeration. Firstly, there is the enumeration of the surface, where we are arranging polymers on a surface of adsorption, which can be two-dimensional or one-dimensional depending on the model, and counting these arrangements. It is worth mentioning that this enumeration only includes trains, which in turn specifies the locations of the endpoints of the loops. Then we also have the enumeration in the solution where we are counting how many ways one could configure the polymers in a solution. Finally, the loops class shares

characteristics of having mers residing in both solution and surface and thus are enumerated in a category of their own.

$$\begin{pmatrix} \text{Surface} \\ \text{Class} \\ \text{Enumeration} \\ \text{Set Size} \end{pmatrix} \times \begin{pmatrix} \text{Solution} \\ \text{Class} \\ \text{Enumeration} \\ \text{Set Size} \end{pmatrix} \times \begin{pmatrix} \text{Loop} \\ \text{Class} \\ \text{Enumeration} \\ \text{Set Size} \end{pmatrix} \tag{1.1}$$

Each of these classes can be separated into sub-classes of a single type of enumeration, reducing the calculations to compartmentalized calculations of each component of the polymer separately. More specifically, as seen in Figure 1.4, a chain on the surface can be enumerated in terms of where its endpoint is placed, but also in terms of enumerations of its random walk on the surface. Additionally, there is the loop that has multiple choices of conformations in three dimensions, but also has a number of ways for the end-points that are adsorbed to the surface to be placed on the polymer chain.

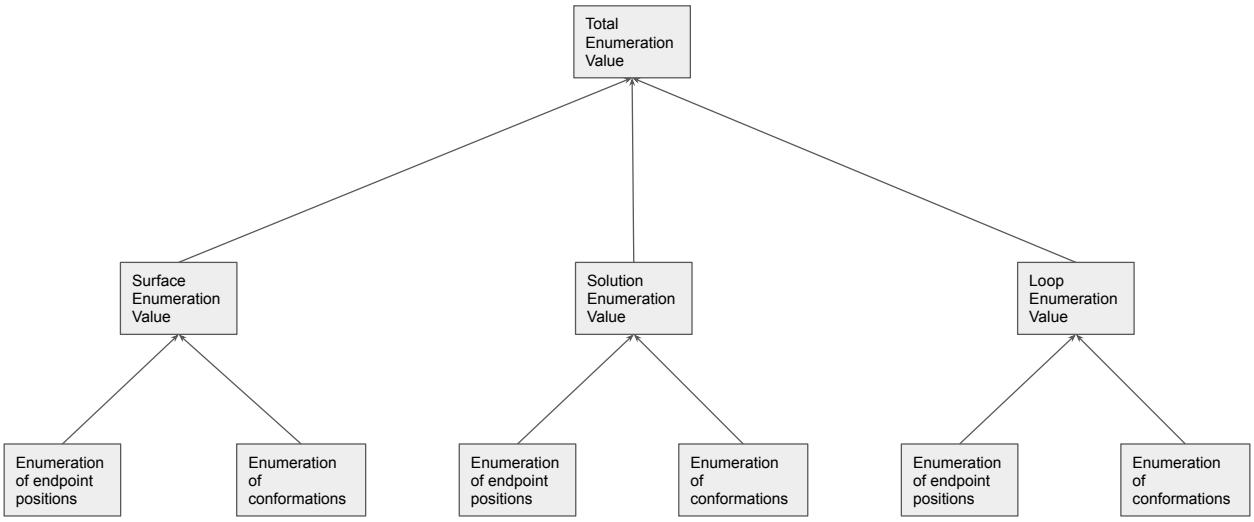


Figure 1.4: Classification of enumeration process of the experimental system

Furthermore, in the approach of counting the configurations of chains and their subcomponents of enumeration, the way we generalize to the enumeration of multiple chains is through raising these calculations to the power of the number of chains being considered for the enumerational process.

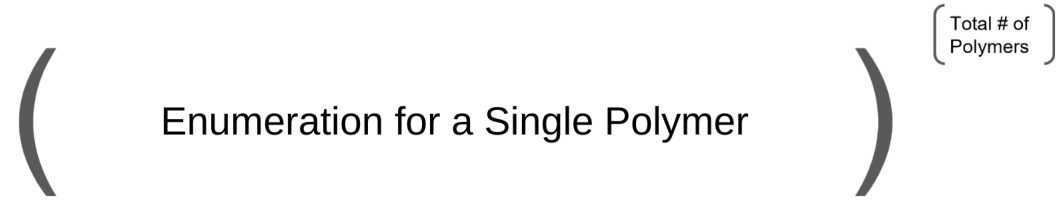


Figure 1.5: Single polymer enumeration being raised to the total population of polymers in that class.

This can be seen for the system as a whole through the below approach where each regime of the system is enumerated and exponentiated by the population of components in question, and then appended to the total multiplication of factors. This all results in a total enumeration of the system, as is seen in Equation 1.2.

$$\left(\begin{array}{c}\text{Factor of}\\ \text{Enumeration}\\ \text{of all Loops}\\ \text{on a Single}\\ \text{Polymer}\end{array}\right)^{\left[\begin{array}{c}\#\\ \text{Polymers}\\ \text{on Surface}\end{array}\right]} \times \left(\begin{array}{c}\text{Factor of}\\ \text{Enumeration}\\ \text{of all}\\ \text{Polymers}\\ \text{on the}\\ \text{Surface}\end{array}\right) \times \left(\begin{array}{c}\text{Factor of}\\ \text{Enumeration}\\ \text{of a}\\ \text{Polymer}\\ \text{in Solution}\end{array}\right)^{\left[\begin{array}{c}\#\text{ of}\\ \text{Polymers}\\ \text{in Solution}\end{array}\right]} \times \frac{\left(\begin{array}{c}\#\text{ of}\\ \text{Sites}\\ \text{in Solution}\end{array}\right)^{\left[\begin{array}{c}\#\text{ of}\\ \text{Polymers}\\ \text{in Solution}\end{array}\right]}}{\left(\begin{array}{c}\text{Factorial of}\\ \#\text{ of Polymers}\\ \text{in Solution}\end{array}\right)} \tag{1.2}$$

The simplest model of polymer adsorption will be that of a one dimensional surface of adsorption where there are mers of polymers in trains on a one dimensional rod and in the case where a sites of the surface is not occupied by a mer, there will be salt-caps occupying that site. This means all sites of the surface will either be occupied by a mer of a polymer or a salt-cap molecule. The salt-caps will be found under the loops and in the sites between neighbouring adsorbed polymers, these shall be defined as gap-sites, as is shown in Figure 1.3.

The next order of complexity of our enumerational model will be that of assuming the surface enumeration to be a two dimensional lattice, and thus providing more degrees of freedom for the self-avoiding walk of the chain on the surface compared to the one dimensional surface in the previous model.

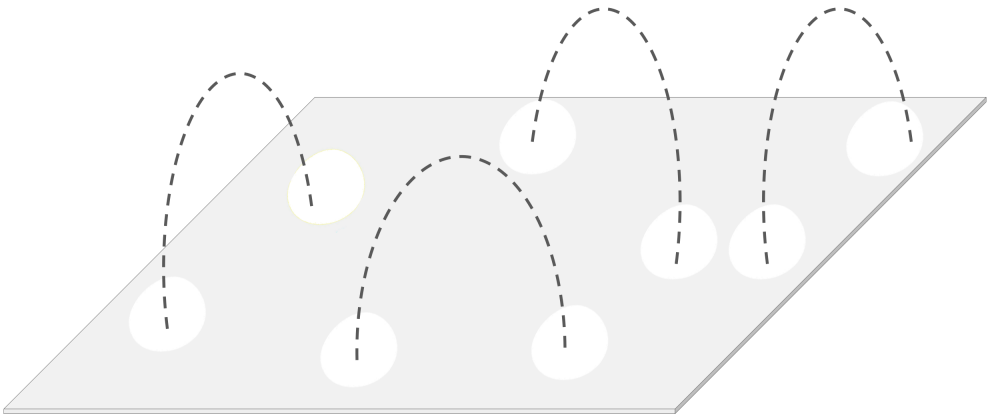


Figure 1.6: Two dimensional surface lattice in solution volume with clusters of self-avoiding walks in trains and loops in the form of jumps between the clusters.

The configuration of a single polymer in a dilute solution is often modeled by a self-avoiding walk (SAW) in a lattice [3], i.e. a path in the lattice that does not visit any site more than once. A fundamental property of SAWs is the following. Let c_ℓ be the number of SAWs that start from a specified lattice site ("the origin") and visit a total of ℓ sites (including the starting site). Then the asymptotic behaviour of c_ℓ on the three-dimensional cubic lattice is [3, 2]

$$c_\ell \;\sim\; A_3\, \ell^{\gamma_3 - 1} \mu_3^\ell \quad \text{as } \ell \to \infty. \tag{1.3}$$

Here μ_3 and A_3 depend on the choice of lattice, but γ_3 is a universal critical exponent that is the same for all three-dimensional lattices. The parameter A_3 is the amplitude and μ_3 is the connective constant, for computing the number of self avoiding walks in a three dimensional

cubic lattice. Their values are known to be approximately[2] [18, 3]

$$\mu_3 \;=\; 4.684, \quad \gamma_3 \;=\; 1.162, \quad \text{and} \quad A_3 \;=\; 0.2573\,. \tag{1.4}$$

The approximation of the enumeration of polymers in solution is calculated via Equation 1.5 below.

$$\mathcal{E}_{vol} = A_3(\mu_3)^r \tag{1.5}$$

For the adsorbed chains, the approach is separated into two categories, the first being that of the portions of the polymer that have all mers occupying a lattice-site on the surface which are aptly named trains for this reason [5, 4]. The other category refers to the portions of the adsorbed polymer that are not occupying lattice-sites on the surface, and because of that can, to a certain degree, free-float in solution while still anchored to the surface. This corresponds to loops which are anchored at both end-points, and tails which are only anchored at one end-point and have the other end-point free-floating in solution. More specifically, trains can be arranged in many ways on the surface and thus have their own method that enumerates their arrangements. Loops and tails are the anchored, but mostly free-floating portions of the chain. A representative model of trains, loops and tails is expanded upon in the book co-authored by some of the leading scientists in the field of polymer modeling, namely Fleer, Stuart, Scheutjens, Cosgrove and Vincent [5].

[2]Estimation in [18] is for the number of SAWs with ℓ *steps* (i.e. $\ell+1$ *sites*), which we write $c_{\ell+1} = (A_3\mu_3)\ell^{\gamma_3-1}\mu_3^{\ell}$; reference [18] obtains $A_3\mu_3 = 1.205$.

1.4 Theoretical Review

In the following paragraphs we shall walk through historical treatments of polymer adsorption onto surfaces. Some techniques share similarities to the approach that we described in Section 1.3, and others will be quite different, but are still worth delving into as it is important to be aware of what has been attempted and what were the results.

Work from Roe in 1974 [19] as well as Scheutjens and Fleer from in the early 1980's [20, 21] led to a model that involved cross-sections of the solution lattice that were parallel to the surface and were numbered 1 through M, with the M-layer residing in the distal region of the solution (z>d). In this approach all sites in a single layer were assumed to be energetically equivalent. This meant that the energy of a mer of a polymer that resided in the k^{th} lattice-layer, could be found by calculating the energy value of the k^{th} lattice layer. The conformation probability was modelled using an assumption of random mixing within each layer.

Scheutjens and Fleer [20, 21] used the above above approach of discretizing the orthogonal distance from the surface into indexed two-dimensional lattices of solution to measure the structure of the polymers adsorbed to the surface by calculating the fractions of mers in each indexed height. They showed that in layers closer to the surface the density of mers that belong to polymers decays exponentially with increasing distance from the surface, but at layers farther from the surface the density decreases at a lower rate. Similarly they found that for loops in specific, the number of mers belonging to loops decreases exponentially with increasing distance from the surface. With the exception of the layers nearest the surface, the contribution of tails is significantly greater than that of loops. Another metric they used was layer thickness, which is a physical height of the adsorbed polymer layer measured in the perpendicular direction from the surface, the main contributors to surface layer thickness

were found to be the mers in tails. The layer thickness was found to be proportional to the square root of the chain length. For very dilute solutions at reasonable adsorption energies, a single chain is found to be flat, where the fraction of chains in trains dominate, the fraction in loops is much smaller in comparison and the fraction from tails is negligible compared to the other two. In very dilute solutions, the length of tails becomes significant, while the length of loops increases and the length of trains decreases [20, 21]. For concentrations that are less dilute, more than a fifth of the segments are predicted to be in tails, with an expected tail size of about 15% of the total polymer-chain length. A chain that has mers occupying the surface is predicted to have two tails of 33% of the polymer-chain length, in layers that lie in the midpoint between surface and bulk, there is a mixture of short trains and longer loops [20, 21].

A more direct approach of computing the number of ways polymers can arrange themselves on a lattice is that of exact enumeration. This technique directly enumerates the exhaustive set of arrangements of the polymers in the system. This is useful, because properties of the adsorbed chain as well as those in the solution can be found directly based on the enumerational results [2]. Enumeration can be done to find the bound fraction of the polymers on the surface, which is the fraction of the lattice sites on the surface that are occupied by mers belonging to adsorbed polymers. Another enumeration is that of volume fraction which is the fraction of the lattice sites in the solution that are being occupied by mers of a polymer. Based on the above, the mean, variance, skewness, and other moments[3] of bound and volume fraction can be computed in order to better describe the overall characteristics of the two quantities above [22, 3].

[3]Most common moments being that of: Mean $E(x) = \mu$, Variance $E((x-\mu)^2) = \sigma^2$, Skewness $\frac{E((x-\mu)^3)}{\sigma^3}$, Kurtosis $\frac{E((x-\mu)^4)}{\sigma^4}$.

A slightly less computationally intensive approach is the Monte Carlo technique, which involves calculating the conformational statistics of the system based on a sampling approach, instead of directly enumerating. In this approach, a randomized algorithm generates a subset of conformations that is representative of the universe of conformations. This is an improvement in terms of computational time from exact enumeration, where modeling a single chain of 100 segments on a cubic lattice could amount to 10^{50} conformations, whereas in the Monte Carlo approach, one could sample a significantly reduced fraction of that set of conformations, and have similar results, as can be seen in the work authored by DiMarzio and McCrackin in 1965 [23]. They used a Monte Carlo method to calculate the average number of contacts of the polymer chain with the surface as well as the distribution of segments with respect to the distance from the surface [23].

The mean-field model derived by De Gennes and Edwards in the 1960s and 70s was a diffusion based approach [24, 25, 26, 27]. The technique assumes that the random conformations of a polymer are very similar to the path followed by a diffusing particle. This led them to compute the conformations of a polymer chain using a diffusion equation where the ranking number in the chain, i.e., the position of the mer segment along the chain, replaces the variable time in a diffusion process [5, 27, 28, 29, 30].

The random walk was a model initially developed to approximate diffusion processes in the physical sciences such as the motion of pollen grains on the surface of water [31], but was later adapted by Flory in 1953 [16] to compute polymer conformations in solution. Around the same time and using a similar approach, Simha, Frish and Eirich [32] treated the polymer in solution as a three dimensional random walk and the polymer on the surface as a two dimensional random walk. They also neglected the excluded volume effects implying steps in all directions were assumed to have the same probability except in the case of the

interface that was modelled similarly to that of a reflective barrier, in other words there is a zero probability of the chains moving through the surface interface. Silberberg in 1962 [33], and DiMarzio in 1965 [34] made improvements to aspects pertaining to the reflecting barrier approach, which resulted in over-counting the number of distinguishable conformations. This approach was also later used by Clayfield and Lumb in 1966 and 1968 [35, 36]. From the perspective of Statistical Mechanical modeling (trains, loops, tails) in 1962 Silberberg authored an approach that modelled a surface layer for the adsorbed mers and an adjacent layer for loops and tails. Each layer corresponded to a different energy state for the mers residing in it, represented by different partition functions, i.e., a partition function for loops, a partition for tails in the bulk and a separate function for the trains on the surface. The model given a constraint of a limited range of possible loop sizes, predicted small loops for all adsorption energy values based on the assumption of equivalence of chemical potential of the macromolecules in the bulk solution and in adsorbed states [33].

In 1965 Hoeve et al. [37] introduced a loop size distribution that found large loops associated with smaller adsorption free energies and more mers in trains for larger adsorption free energies, the later producing more flexible chains. This was incorporated by the modeling of Silberberg 1968 [38] and Hoeve in 1965 and again in 1970 [37, 39] through an accounting of interactions of chains on the surface, and for an environment of high surface coverage. Also incorporated into the model was a treatment for the excluded volume effect which is that of considering limiting the way a polymer can conform based on constraints imposed by the molecules of the solvent. A model that quantified the segment distribution normal to the interface using models of random flights was computed by Hoeve in 1966 [40]. It was shown that the segment density drops exponentially as the distance from the surface is increased with the only exception of the discontinuity of the distribution at the distance equal to the thickness of trains [4]. The segment density distribution of a single tail was developed by

Meier in 1965 [41]. The work of Meier was then further developed by Hesslink between 1960 and 1971, and was able to provide a segment density distribution for single tails as well as single loops in addition to homopolymers and random copolymers [42, 43].

In 1984, Stuart provided theoretical results on layer thickness as a function of adsorbed amount, based on modeling by Scheutjens and Fleer [20, 21, 44]. Although the aspect of multiple layers is not directly related to our work, it is of particular interest to focus in on how they modelled polymer coverage for the first layer of adsorbed polymer. The jump in thickness observed when the fraction of the surface occupied by mers increases to one half, is a similar result to our final model, for low to mid surface charge.

For a low ionic strength solution, Stuart [45] provides a relationship between salt concentration and layer thickness. Their study found that as the weight of the adsorbed polymers increases, the thickness of the layer also increases quite rapidly. This paper compares ionic strength to layer thickness, in a regime of low ionic strength. This research is focuses on thickness as a function of adsorbed polymer mass. It concludes that the increase in thickness can be attributed to a great degree to the existence of tails, whereas our approach considers loops as a contributor to the sudden increase in layer thickness.

Modeling experiments of polyethylene oxides of molecular weights ranging from 25K to 1.3M adsorbed onto polystyrene latex was led by Cosgrove [46] where they presented a relationship between the mass of polymers on the surface and layer thickness. They found that when the adsorbed polymer mass was higher, the thickness also increased. In our model, we also attempt to mimic variable amounts through the surface coverage. In our model, we focus on results associated with layer thickness as a function of surface occupancy in mers. More specifically, both models examine varying thickness as a function of number of mers adsorbed

on the surface whereas the model by Cosgrove [46] they control the mass in different ways. Additionally, their work is focused around proving the existence of tails, whereas ours is centered around loops being the main contributing molecular structure to layer thickness.

Further work was done by Cosgrove in the early 1990s with a model that used a Monte Carlo method, where the focus was more on the volume fraction adsorbed as a function of the layer number [47]. Similar to our work, they provide a comparison of fractions of trains, tails, and loops as a function of surface coverage. In agreement with our model results, they observe more loops in the domain of partial surface coverage by polymers. More specifically, the highest contribution from loops was in the range between 10 and 50 percent surface coverage by mers. Their modeling differs in that they also see a dominant contribution from tails in the volume, whereas our modeling assumes that the tails contribution is negligible.

A model with predictions on layer thickness was devised by Scheutjens in 1986 [48]. Similar to Scheutjens we compare layer thickness and the adsorbed amount as a function of adsorption energy, which we relate analogously to experimentally modulating the available surface sites for adsorption through adjusting the pH [49]. Additionally, the theoretical predictions are in line with ours in terms of increasing thickness as the adsorption energy on the surface is decreased, with the caveat that they hypothesize that the main contributor to anomolously large layer height increase are tails, and determine that this is the case.

Note on Modelling Loop Length In the following chapters, in order to compute the expected properties of loops on the surface, we shall require a way to quantify the loop length using assumptions on the height of the loops. We achieve this though using approximations [3] for the calculation of the mean square distance of a self avoiding walk based on the number of steps, and solved for the number of steps. We have that the mean square distance

can be expressed as the following, where $[RMSD]$ is the root-mean-square-displacement, N is the number of steps and the critical exponent ν could be interpreted loosely as a measure of repulsiveness of the self-avoiding walk [3]. For three dimensional self-avoiding walks, ν is about $\frac{3}{5}$, in two dimensions it is $\frac{3}{4}$, and for the analogue of ordinary random walks, ν is $\frac{1}{2}$ (in any dimension).

$$[RMSD] \ \sim \ [Constant] \times N^{\nu} \tag{1.6}$$

This is quite similar in the case measuring the length of a loop, where the number of steps in a loop is calculated using the orthogonal distance from the surface of adsorption.

$$[RMSD]_{lp} \sim (s_{lp})^{\nu} \tag{1.7}$$

In this work, what shall be of particular interest is the converse, which is the computation of the end-to-end distance in steps of the loop itself. This leads to the following expression.

$$s_{lp} \sim [RMSD]_{lp}^{1/\nu} \tag{1.8}$$

For example, in Chapter 3 we will see expressions similar[4] to the one below where in place of $[RMSD]$ is an approximate height of a loop from the surface, $m_v + 1$.

$$s_{lp} \sim (m_v + 1)^{1/\nu} \tag{1.9}$$

Note on Stirling Approximations We will use Stirling's approximation of the logarithm of the factorial in the numerical computations on the following chapters. We have that the

[4]The expression has been simplified from that of the Chapter 3

Stirling factorial is the following,

$$Stirl(x) = \begin{cases} DNE, & x < 0 \\ 0, & x = 0 \\ 0, & x = 1 \\ x\ \log(x) - x + \frac{1}{2}\log(2\pi x) + \frac{1}{12x}, & O/W \end{cases} \tag{1.10}$$

We derive a function for the approximation of the logarithm of the binomial coefficient in Equation 1.12 based on the binomial coefficient in Equation 1.11 and the Stirling Factorial in Equation 1.10.

$$\binom{Set}{Choose} = \frac{Set}{Choose \times (Set - Choose)} \tag{1.11}$$

$$StirlBin(Set, Choose) = Stirl(Set) - Stirl(Choose) - Stirl(Set - Choose) \tag{1.12}$$

1.5 Topics Overview

1. Introduction Provided in this chapter are definitions of polymer adsorption and loops as well as background on experimental results and theoretical models. All models in the thesis are constructed and analyzed following the general principles described in Section 1.2.

I. One Dimensional Surface Lattice Models

2. One Dimensional Model with Multi-Step Bases and Gaps This chapter is focused on a model with a one dimensional surface and a single expected loop length value, with considerations of loops, trains, gaps, and bases.

3. One Dimensional Periodic Model This chapter is focused on a model with a one dimensional surface with a fixed pattern of salt-caps on the surface dependant only on coverage values with considerations of bases in sites below loops, but no gaps between polymers.

II. Two Dimensional Surface Lattice Models

4. Two Dimensional Surface Model: Unconstrained Approach This chapter is focused on a model with a two dimensional surface of adsorption, using approximations based on Fleer sub-partition methods and Flory-Huggins mean-field approach.

5. Two Dimensional Periodic Model with Clustering of Lattice Sites This chapter is focused on a model with a two dimensional surface of adsorption, using approximations based on Fleer sub-partition methods and Flory-Huggins mean-field approach, with considerations of gaps and loops using clusters of polymer walks and

clusters of salt-caps.

III. Discussions, Conclusions and Future Work

6. Discussion In this chapter a comparison of the models developed and their results is done, as well as a comparison to work of peers in the past. Following that, future considerations for this research are briefly expanded upon.

7. Conclusion Final statement on the outcomes of this research.

Part I

One Dimensional Surface Lattice Models

Chapter 2

One Dimensional Model with Multi-Step Bases and Gaps

We develop a model to enumerate the preferential behaviour of loops on a one dimensional surface, and then provide the intuition behind the placement and enumeration of the polymers in the mean-field model. Subsequently, we describe the major relationships of this model in terms of calculating the number of loops, the length of the portions of the chains that are in trains, and the way we calculate the number of chains on the surface. We then examine derivations related to enumerating the different ways a loop can be anchored at two end-points on the surface. In a similar way, we are able to derive the enumerational approach to counting the positions of the gaps between polymers adsorbed to the surface. Based on the above we then derive partitions for the surface, solution and the loops, and then bring them together in a single calculation. We propose the implementation and calculations needed for the procedure, such as maximum looping condition and bounds of iteration. Finally, we provide the results of this model, plotting entropy as a function of number of mers in loops in a single polymer adsorbed to a surface. This is achieved through evaluating the total

enumeration values for each loop length, and finding the loop length for which the maximum enumeration value corresponds to the maximum entropy.

2.1 Model Intuition

We assume that the surface the polymers will adsorb to is a one dimensional sequence of lattice sites, to which each mer of the polymer can adsorb to a single lattice site. Loops will form in the case when the adsorbed polymer-chains have more mers than available sites. A way to achieve this is through introducing salt-caps to a fraction of surface sites as is explained in detail in Chapter 1. The existence of a certain fraction of salt-caps will constrain the total number of sites the polymers can occupy on the surface, forcing a partial coverage scenario, and as such forcing the mers into loops. The arrangement of both the salt-caps and polymers will be based on entropic preference. There are two ways the salt-caps will impact the arrangement of the polymers on the surface. One way is through the formation of loops above the salt-caps. The other is that of the existence of gaps between adjacent adsorbed polymer-chains on the surface. This combination of gaps, bases, trains and loops, is illustrated in Figure 2.1

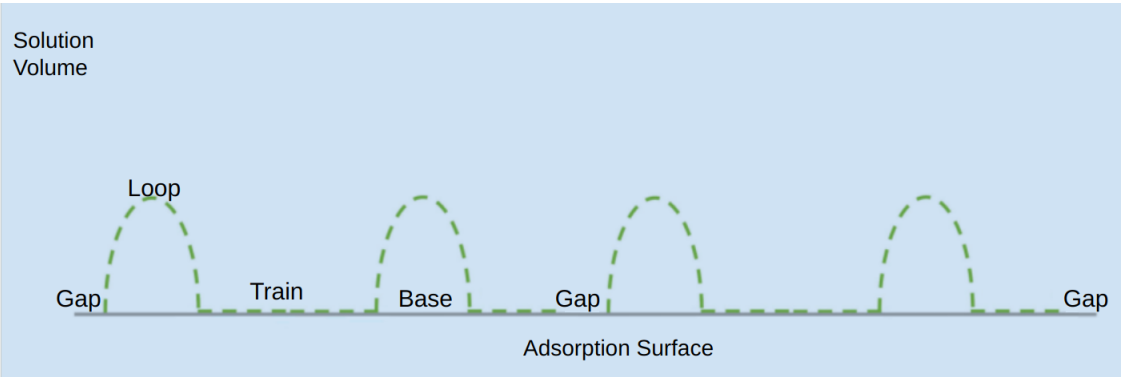


Figure 2.1: One dimensional surface lattice in solution volume. Adsorbed polymer configurations consist of a combination of mers at the surface as trains, loops, salt-caps below loops and the gaps between polymers.

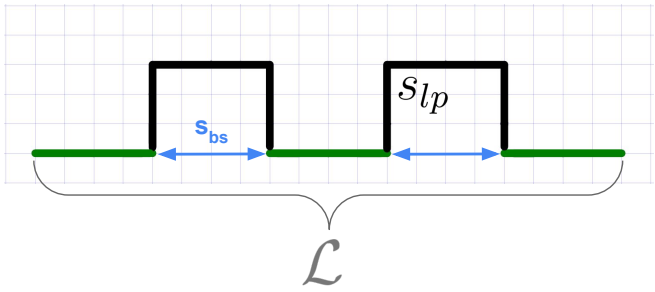


Figure 2.2: Components of a polymer adsorbed to a surface, with base length corresponding to s_{bs} and loop length to s_{lp}

This model has three major sub-tasks of enumeration. The first is that of the solution where the free-floating polymers reside. The second is the surface to which the polymers adsorb to and arrange themselves. Lastly, there is the mixed sub-task for loops, which has aspects of enumeration on the surface and aspects of counting the walks of the free-floating loops in the proximal region of solution.

On a one dimensional lattice, the polymers will be constrained to a single line of contiguous lattice sites, and for that reason there is no considerations of random walks on the surface in the enumeration. The first aspect of the enumeration procedure for loops is that of enumerating all the possible positions a loop can take for a polymer chain. This is best illustrated in Figures 2.3 to 2.5 below, where there is a number of ways to arrange loops on the polymer, if one is provided the number of loops that would occupy that polymer, which in this case for simplicity, is set to be a single loop.

Figure 2.3: Loop over first position

Figure 2.4: Loop over second position

Figure 2.5: Loop over third position

The other enumeration of loops is that of the free-floating mers in the proximal region of the solution. More specifically, a loop can be treated as a polygon that is fixed at two sites, but otherwise can arrange the remaining mers of the loop in multiple ways on a three dimensional lattice. This approach is quantified using methods associated with self-avoiding polygons [13], and more on this will be discussed in detail in Section 2.5.

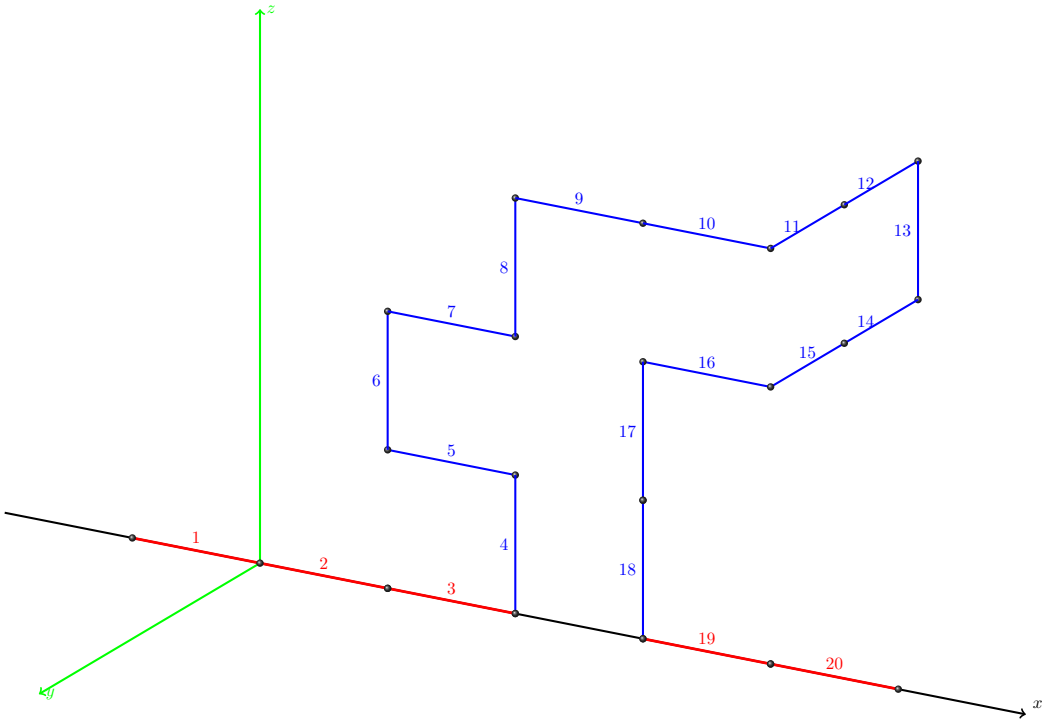


Figure 2.6: A self-avoiding polygon in a solution volume.

2.2 Parameters And Definitions

In this type of model we can quantify our distances in terms of units of sites and steps. Sites can correspond to the vertices on the surface-lattice onto which the mers will adsorb and steps are the edges between two sites on the surface. In this model, our surface is a one-dimensional line with n_{surf} lattice-sites, and the number of sites in one chain is r, and $r-1$ is the number of steps in one chain.

We have n chains of length r, of which n_a are adsorbed onto the surface and n_b are free in solution.

The number of steps in a single loop is s_{lp} and $s_{lp}+1$ is the number of sites in a single

loop.

The footprint measured in sites, $\mathcal{L}$, is the site-length of the adsorbed portion of chain on the surface that includes all the sites in trains and all the sites at the bases of each loop. The footprint measured in steps, $\mathcal{L} - 1$, is the step-length of the adsorbed portion of chain on the surface that includes all the steps in trains and all the steps at the bases of each loop.

These edges at the base are quantified by the parameter s_{bs} and the number of sites in the base excluding the endpoints of the loop which are at the end of the base, by $s_{bs} - 1$.

The count of loops on a single chain is $n_{_{lp}}$. It is important to mention here that the model is set up in such a manner that every chain on the surface is assumed to have the same $n_{_{lp}}$ and loop length s_{lp}.

The number of sites (or steps) on the surface that are not occupied by an adsorbed mer is given by N_{un}.

The number of sites (or steps) on the surface that belong to a footprint of a polymer are $N_{_{fp}}$.

The number of sites (or steps) in gaps between polymers on the surface is given by $N_{_{gp}}$.

The number of sites (or steps) in trains on a single polymer is represented by $s_{_{tr}}$.

In order to differentiate between measures of steps and sites, we will sometimes use the convention of a double subscript. For example $s_{_{tr,st}}$ is steps in trains, where the first subscript is defining the quantity as trains, and the second subscript is the type of unit, which

in this case the subscript "st" corresponds to steps, and "si" to sites.

n_{surf}	number of sites on the two-dimensional square lattice approximation of the surface
r	number of sites in one chain
$r-1$	number of steps in one chain.
n_a	number of polymers adsorbed onto the surface
n_b	number of polymers free-floating in solution
n	number of polymer chains in both solution and adsorbed on the surface
$s_{_{lp}}$	number of steps in a single loop
$s_{_{lp}}+1$	number of sites in a single loop.
$\mathcal{L}$	The footprint measured in sites which is the site-length of the adsorbed portion of chain on the surface that includes all the sites in trains and all the sites at the bases of each loop.
$\mathcal{L}-1$	The footprint measured in steps which is the step-length of the adsorbed portion of chain on the surface that includes all the steps in trains and all the steps at the bases of each loop.
s_{bs}	number of steps at the base of a loop
$s_{bs}-1$	number of sites at the base of a loop, excluding the endpoints of the loop which are at the end of the base
$n_{_{lp}}$	count of loops on a single chain
N_{un}	number of sites (or steps) on the surface that are not occupied by an adsorbed mer
$N_{_{fp}}$	number of sites (or steps) on the surface that belong to a footprint of a polymer
$N_{_{gp}}$	number of sites (or steps) in gaps between polymers on the surface
$s_{_{tr}}$	number of sites (or steps) in trains on a single polymer

Table 2.1: Parameters of the model

2.3 Core Relationships of the Model

This model has a fixed number of total polymers in the system. This means that the number of polymers in solution, n_b, is the difference between the number of polymers and the number of polymers attached to the surface.

$$n_b = n - n_a \tag{2.1}$$

In Figure 2.2, we have a schematic of a polymer adsorbed to the surface with chain-length r. The polymer has loops of length s_{lp} and bases of length s_{bs} in steps.

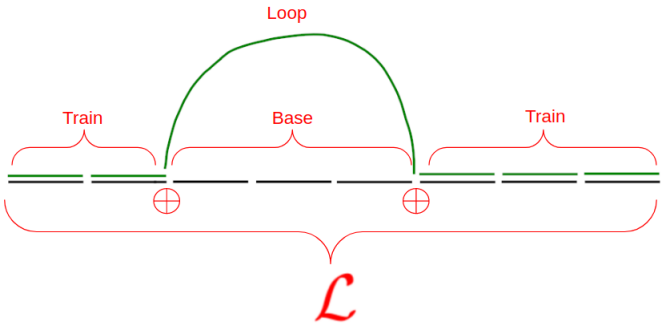


Figure 2.7: Shared end-point sites between base, loop and train

We shall show that the number of loops on a single polymer, n_{lp}, is that of Equation 2.2. The parameter n_{lp} will serve as the index of iteration of the computational procedure of the model, and the below expression will help us in deriving the upper and lower bounds of the range of iterations.

$$n_{_{lp}} = \frac{r - \mathcal{L}}{s_{_{lp}} - s_{_{bs}}} \tag{2.2}$$

We recall from Section 2.2 that the the footprint measured in sites, $\mathcal{L}$, is the site-length of the adsorbed portion of chain on the surface that that includes all the sites in trains and all the sites at the bases of each loop. We recall from Section 2.2 that the the footprint

measured in steps, $\mathcal{L}-1$, is the step-length of the adsorbed portion of chain on the surface that that includes all the steps in trains and all the sites at the bases of each loop. We have that the footprint, $\mathcal{L}$ in terms of sites corresponds to Equation 2.3.

$$\begin{pmatrix}\text{Site-Footprint}\\ \text{of a Single}\\ \text{Polymer Chain}\end{pmatrix} = \begin{pmatrix}\text{Site-Length}\\ \text{of a Single}\\ \text{Polymer Chain}\end{pmatrix} - \begin{pmatrix}\text{Total Contribution from}\\ \text{Sites in Loops for}\\ \text{Single Polymer Chain}\end{pmatrix} + \begin{pmatrix}\text{Total Contribution from}\\ \text{Sites in Bases for}\\ \text{Single Polymer Chain}\end{pmatrix}$$

$$\begin{aligned}\mathcal{L} &= r - n_{lp}\left(s_{_{lp}}+1\right) + n_{lp}\left(s_{_{bs}}+1\right)\\ &= r + n_{lp}\left(s_{_{bs}} - s_{_{lp}}\right)\end{aligned} \tag{2.3}$$

We have that the footprint, $\mathcal{L}-1$, in terms of steps corresponds to Equation 2.4.

$$\begin{pmatrix}\text{Step-Footprint}\\ \text{of a Single}\\ \text{Polymer Chain}\end{pmatrix} = \begin{pmatrix}\text{Step-Length}\\ \text{of a Single}\\ \text{Polymer Chain}\end{pmatrix} - \begin{pmatrix}\text{Total Contribution from}\\ \text{Steps in Loops for}\\ \text{Single Polymer Chain}\end{pmatrix} + \begin{pmatrix}\text{Total Contribution from}\\ \text{Steps in Bases for}\\ \text{Single Polymer Chain}\end{pmatrix}$$

$$\begin{aligned}\mathcal{L}-1 &= (r-1) - n_{lp}\left(s_{_{lp}}\right) + n_{lp}\left(s_{_{bs}}\right)\\ &= (r-1) + n_{lp}\left(s_{_{bs}} - s_{_{lp}}\right)\end{aligned} \tag{2.4}$$

This establishes Equation 2.2. We also defined a total footprint of all chains on the surface. We will use the footprint to derive a formula for n_a that is dependant on n_{lp}.

$$N_{_{fp,si}} = \mathcal{L} \times n_a \tag{2.5}$$

$$= n_{surf} - N_{_{gp,si}} \tag{2.6}$$

$$N_{_{fp,st}} = (\mathcal{L}-1) \times n_a \tag{2.7}$$

$$= (n_{surf}-1) - N_{_{gp,st}} \tag{2.8}$$

Two useful quantities are that of $s_{tr,si}$ which is the number of sites in all trains of a single polymer chain and is calculated using 2.9, and $s_{tr,st}$ which is the same calculation, but in steps with Relation 2.10.

$$s_{tr,si} = \mathcal{L} - (s_{bs} - 1) \times n_{lp} \tag{2.9}$$

$$s_{tr,st} = (\mathcal{L} - 1) - s_{bs} \times n_{lp} \tag{2.10}$$

Using equations 2.6 and 2.8 for total footprint of the chains, leads to the following result for n_a which as we recall from Section 2.2 is the number of polymers on the surface of adsorption.

$$\textbf{Calculation in terms of Sites:} \quad n_a = \frac{n_{surf} - N_{gp,si}}{\mathcal{L}} \tag{2.11}$$

$$\textbf{Calculation in terms of Steps:} \quad n_a = \frac{(n_{surf} - 1) - N_{gp,st}}{(\mathcal{L} - 1)} \tag{2.12}$$

Relation 2.13 calculates the total number of sites in all the gaps on the surface, $N_{gp,si}$, and $N_{gp,st}$ is the same calculation for steps using Relation 2.14.

$$N_{gp,si} = N_{un,si} - (n_{lp} \times (s_{bs} - 1) \times n_a) \tag{2.13}$$

$$N_{gp,st} = N_{un,st} - (n_{lp} \times s_{bs} \times n_a) \tag{2.14}$$

2.4 Development of Loop Occupancy Model

In the single dimensional approach one can leverage methods used in probability for occupancy problems [50]. These are problems of the nature of having multiple indistinguishable objects and distributing varying quantities of them across multiple positions. We observe this in the below graphic where there are 7 objects stacked in the first position (left-endpoint) of the schematic.

Figure 2.8: Distribution of occupancy of multiple indistinguishable objects

The schematic in Figure 2.8 illustrates these train-steps as objects stacked in each position. In the aforementioned example, there are 7 train-steps in the first position (starting from the left), 3 train-steps in the second, 8 train-steps in the third position and 2 train-steps in the last position. These possible positions of placement of train-steps will henceforth be defined as **train-positions**. What is shown in Figure 2.8 is that not only are **between-loop-positions**, which are the regions between two adjacent loops, included in the enumeration, but so is that of **end-of-chain-positions**, which are the segments between an end-point of the polymer-chain and a loop on the opposite side. An example of this can be seen in Figure 2.8, where **end-of-chain-positions** correspond to the first (left end-point of chain) and fourth train-positions (right end-point of chain). This is where the methods used in occupancy problems can be utilized in order to solve the problem. For the case of loops and trains, the problem can be represented in a similar way, using occupancy of train-steps between two adjacent loops as is visualized below in Figures 2.9 to 2.11. It is important to

note that this factor of the model will allow for zero train-steps between adjacent loops, as is shown in the Figure 2.9.

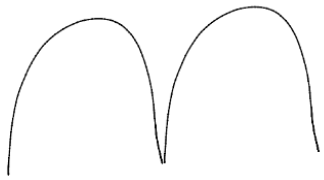


Figure 2.9: Zero train-steps between two adjacent loops

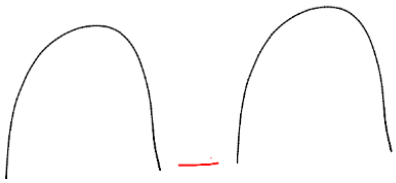


Figure 2.10: One train-step between two adjacent loops

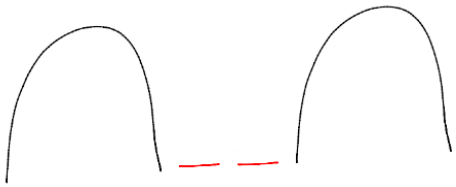


Figure 2.11: Two train-steps between two adjacent loops

Here we have the proposition by Feller [50] of placing of r balls into n cells. Here each event corresponds to a set of occupancy numbers $r_1, r_2, \cdots, r_n$, where r_k stands for the number of balls in the k^{th} cell and every n-tuple of integers satisfying

$$r_1 + r_2 + \cdots + r_n = r \tag{2.15}$$

describes a possible configuration of occupancy numbers [50]. With indistinguishable balls two distributions are distinguishable only if the corresponding n-tuples $(r_1, \cdots, r_n)$ are not

identical [50]. The number of different distributions of Equation 2.15 is

$$A_{r,n} = \binom{n+r-1}{r} = \binom{n+r-1}{n-1} \tag{2.16}$$

More specifically to the context of the model, one could express the total trains being arranged in the positions overall using the following expression of Equation 2.17.

$$\left[\begin{array}{c}\text{Total \# of steps}\\ \text{to be distributed}\\ \text{across all}\\ \text{train-positions}\\ \text{on a single chain}\end{array}\right] = \left[\begin{array}{c}\text{\# of steps on}\\ \text{first train-position}\end{array}\right] + \left[\begin{array}{c}\text{\# of steps on}\\ \text{second train-position}\end{array}\right] + \cdots + \left[\begin{array}{c}\text{\# of steps on}\\ N^{th}\text{ train-position}\end{array}\right] \tag{2.17}$$

The number of solutions to the above equation corresponds to the number of ways to distribute the train-steps amongst the train-positions for a fixed number of total train-steps available. This is expressed through the binomial factor seen in Equation 2.18 and 2.19 to compute the number of combinations of trains and loops.

$$\binom{\left[\begin{array}{c}\text{Total \# of}\\ \text{train-positions on}\\ \text{a single chain}\end{array}\right] + \left[\begin{array}{c}\text{Total \# of steps}\\ \text{to be distributed}\\ \text{across all}\\ \text{train-positions}\\ \text{on a single chain}\end{array}\right] - 1}{\left[\begin{array}{c}\text{Total \# of steps}\\ \text{to be distributed}\\ \text{across all}\\ \text{train-positions}\\ \text{on a single chain}\end{array}\right]} \tag{2.18}$$

$$= \binom{\left[\begin{array}{c}\text{Total \# of}\\ \text{train-positions on}\\ \text{a single chain}\end{array}\right] + \left[\begin{array}{c}\text{Total \# of steps}\\ \text{to be distributed}\\ \text{across all}\\ \text{train-positions}\\ \text{on a single chain}\end{array}\right] - 1}{\left[\begin{array}{c}\text{Total \# of}\\ \text{train-positions on}\\ \text{a single chain}\end{array}\right] - 1} \tag{2.19}$$

We formalize this in the following way, where $\boldsymbol{TotalTrainPositions}$ is equal to one more than the number of loops and therefore is $(n_{lp}+1)$, as can be seen in the number of places

occupying balls in Figure 2.8.

$$\boldsymbol{\Psi}_{lp} = \begin{pmatrix} \boldsymbol{TotalTrainPositions} + \boldsymbol{s}_{tr,st} - 1 \\ \boldsymbol{s}_{tr,st} \end{pmatrix} \tag{2.20}$$

$$= \begin{pmatrix} (n_{lp}+1) + \boldsymbol{s}_{tr,st} - 1 \\ \boldsymbol{s}_{tr,st} \end{pmatrix} \tag{2.21}$$

This can alternatively be written in the following way [50].

$$\boldsymbol{\Psi}_{lp} = \begin{pmatrix} \boldsymbol{TotalTrainPositions} + \boldsymbol{s}_{tr,st} - 1 \\ \boldsymbol{TotalTrainPositions} - 1 \end{pmatrix} \tag{2.22}$$

$$= \begin{pmatrix} (n_{lp}+1) + \boldsymbol{s}_{tr,st} - 1 \\ (n_{lp}+1) - 1 \end{pmatrix} \tag{2.23}$$

We use the case that includes the possibility of zero objects in a position, because in our model this can correspond to the scenario of zero train-steps between two loops or loop and endpoint of the chain. This can be seen in Figure 2.12 where there are no steps between one loop and the next. The other scenario is that of zero trains at the end-point of a chain. Said another way, one of the end-points of a loop happens to be the last mer of a chain. This can be seen in Figure 2.13.

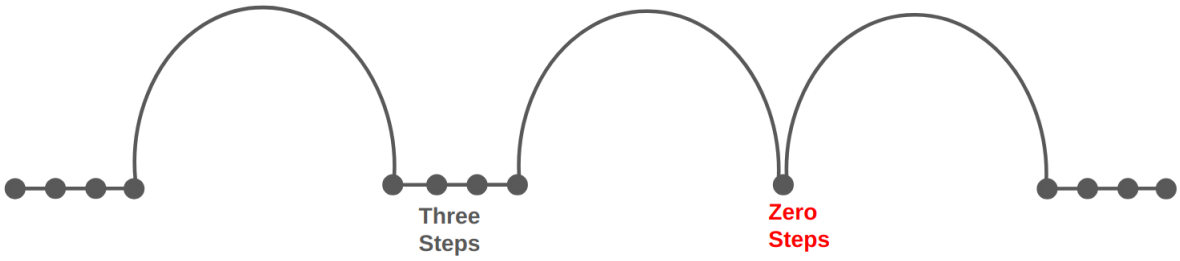


Figure 2.12: Zero train-steps between two adjacent loops

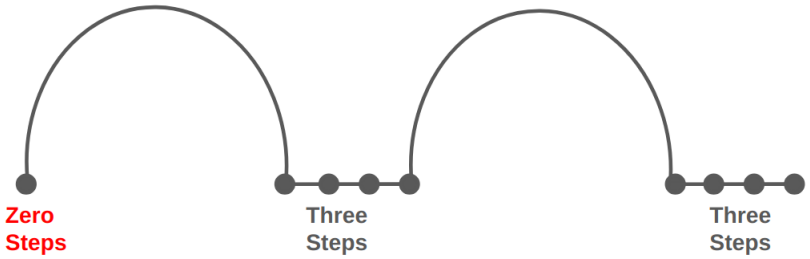


Figure 2.13: Zero train-steps between a loop on the right of the train-position and a surface end-point on its left

2.5 Modelling Loops: Self Avoiding Polygons

For the portion of the loop that is floating in the solution and can arrange itself in three dimensional space we use an approach of self-avoiding polygons (SAP) [13]. In the work by Guttmann, the most commonly used notation for the amplitude of the SAP in a simple cubic lattice (Z^3) is that of B_3 [13]. An interpolation was done based on the values derived by Guttmann in 2009 for asymptotic polygons [13], whereas in our work we shall use it to get an approximate amplitude value for polygons of moderate length, $\mathbf{X} := B_3$, as well as an exponent of s_{lp}, $\mathbf{Y} := \gamma_{lp}$.

$$\left(\mu_3^{s_{lp}} \frac{\mathbf{X}}{\left(s_{lp}\right)^{\mathbf{Y}}}\right)^{n_{lp}} \tag{2.24}$$

Where the interpolated values were found to be $B_3 = 1.1$ and $\gamma_{lp} = 3.7$

$$\left(\mu_3^{s_{lp}} \frac{B_3}{\left(s_{lp}\right)^{\gamma_{lp}}}\right)^{n_{lp}} \tag{2.25}$$

So combining this into one factor describing the overall possible positioning and conformations of loops we have the following.

$$\mathcal{E}_{lp} = \left(\begin{array}{c} \text{Binomial factor of} \\ \text{total arrangements} \\ \text{of trains and loops} \end{array} \right) \times \left(\begin{array}{c} \text{Factor quantifying} \\ \text{\# of ways a single loop} \\ \text{can occupy a 3D space} \end{array} \right)^{\left(\begin{array}{c} \text{Total \# of loops} \\ \text{on one chain} \end{array} \right)} \tag{2.26}$$

More specifically, the above calculations can be formalized in the form of Equation 2.27.

$$\mathcal{E}_{lp} = \Psi_{_{lp}} \times \left(\mu_3^{s_{lp}} \frac{B_3}{\left(s_{_{lp}}\right)^{\gamma_{lp}}} \right)^{n_{lp}} \tag{2.27}$$

2.6 Development of Gap Occupancy Model

We also require a factor that enumerates the number of ways one can arrange the total steps in gap-positions over a specific number of gaps. Important to note is that **gap-positions** corresponds to two different types positions on the surface. There is that of **between-chain-gap-positions**, which is the position between two adjacent chains as is illustrated in Figure 2.14, and also that of **end-of-surface-gap-positions** which are the positions between a surface-end-point and an adjacent polymer-chain, as is shown on Figure 2.15. The aforementioned constraint of a minimum of one gap-step per gap-position applies to both **between-chain-gap-positions** and **end-of-surface-gap-positions**.

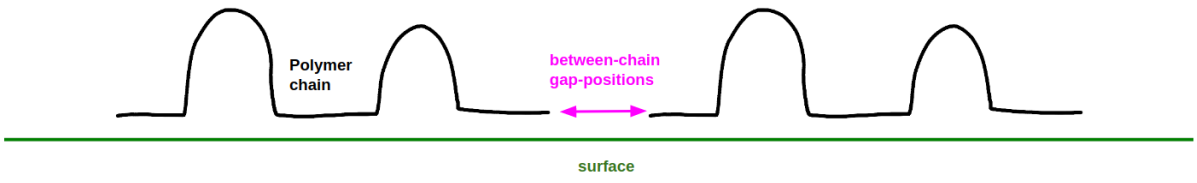


Figure 2.14: Schematic of between-chain-gap positions

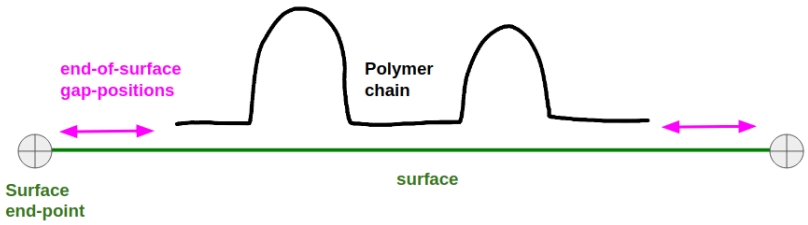


Figure 2.15: Schematic of end-of-surface-gap positions

The enumeration here happens through allocating a fixed amount of gap-steps for the whole system, and distributing their occupancy across all the gap-positions on the surface. A convention of this model is that that the endpoint of a chain is also considered to be a site of the gap.

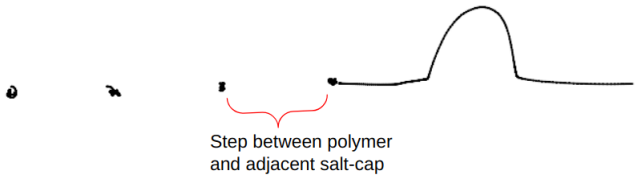


Figure 2.16: Gap-step between a polymer-chain end-point site and a salt-cap site

Figure 2.17: Gap-step step between two nearest neighbour polymer chains

From Feller [51] we have that the number of distinguishable distributions of Equation 2.15 in which no cell remains empty is

$$A_{r,n} = \binom{r-1}{n-1} \tag{2.28}$$

In other words, unoccupied positions do not exist in this enumeration. This leads to the

result of Equation 2.29.

$$\left(\begin{array}{c} \left[\begin{array}{c} \text{Total \# of objects} \\ \text{to be distributed} \\ \text{across all positions} \end{array} \right] - 1 \\ \\ \left[\begin{array}{c} \text{Total \#} \\ \text{of positions} \end{array} \right] - 1 \end{array} \right) \tag{2.29}$$

Adapting this to the specific quantities of the model, the constraint is on the number of gap-steps per gap-position to at least one gap-step. This results in the below concretely defined binomial factor.

$$\left(\begin{array}{c} \left[\begin{array}{c} \text{Total \# of gap} \\ \text{steps allocated} \end{array} \right] - 1 \\ \\ \left[\begin{array}{c} \text{Total \# of} \\ \text{gap positions} \\ \text{on the surface} \end{array} \right] - 1 \end{array} \right) \tag{2.30}$$

The result of Equation 2.30 is formalized in Equation 2.31 below where the total gap positions available correspond to $(n_a + 1)$.

$$\Psi_{gp} = \binom{N_{gp,st} - 1}{TotalGapPositions - 1} \tag{2.31}$$

$$= \binom{\boldsymbol{N_{gp,st}} - 1}{(n_a + 1) - 1} \tag{2.32}$$

2.7 Development of Total Enumeration Methods

The enumeration method for loops on adsorbed polymers is expressed in Equation 2.27.

$$\mathcal{E}_{lp} = \left(\Psi_{_{lp}}\right) \left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3\right)^{n_{lp}} \tag{2.33}$$

The enumeration method for the polymers (or mers) in solution is based on the principles of self-avoiding-walks in a three dimensional lattice, and expressed in Equation 2.34.

$$\mathcal{E}_{vol} = A_3 \ \mu_3^r \qquad \text{from Equation 1.5} \tag{2.34}$$

This leads to the following total enumeration function which will be dependant on $n_{_{lp}}$ and parameterized by $N_{un,st}$.

$$\mathcal{E}_{total} = \left(\Psi_{_{gp}} \ \ \mathcal{E}_{lp}^{n_a} \ \ \mathcal{E}_{vol}^{n_b} \ \ \frac{n_{vol}^{n_b}}{n_b!} \right) \qquad \text{by Equation 1.2} \tag{2.35}$$

2.8 Computational Procedure

To compute the total enumeration of the system we must establish functions to convert quantities from steps to sites. We shall also derive an expression in order to find the maximum loops on single polymer which will serve as the upper bound of the range of $n_{_{lp}}$ values through which the alogorithm for this model shall be iterated. Finally, we will walk through the steps of the computational procedure of the model.

2.8.1 Site-Step Conversion Methods

The above definitions lead to the requirement of the derivation of $N_{_{gp,si}}$ expanded in detail below.

$$N_{gp,si} = N_{un,si} - (n_{lp} \times (s_{bs} - 1) \times n_a) \qquad \text{from Equation 2.13} \tag{2.36}$$

$$N_{gp,si} = N_{un,si} - \left(n_{lp} \times (s_{bs} - 1) \times \frac{(n_{surf}) - N_{gp,si}}{\mathcal{L}} \right) \qquad \text{by Equation 2.11} \tag{2.37}$$

$$N_{gp,si} = N_{un,si} - \frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L}} + \frac{n_{lp} \times (s_{bs} - 1)}{\mathcal{L}} \times N_{gp,si} \tag{2.38}$$

$$N_{gp,si} - \frac{n_{lp} \times (s_{bs} - 1)}{\mathcal{L}} \times N_{gp,si} = N_{un,si} - \frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L}} \tag{2.39}$$

$$N_{gp,si} \left(1 - \frac{n_{lp} \times (s_{bs} - 1)}{\mathcal{L}} \right) = N_{un,si} - \frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L}} \tag{2.40}$$

$$N_{gp,si} \left(\frac{\mathcal{L} - n_{lp} \times (s_{bs} - 1)}{\mathcal{L}} \right) = N_{un,si} - \frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L}} \tag{2.41}$$

$$N_{gp,si} = \left(\frac{\mathcal{L}}{\mathcal{L} - n_{lp} \times (s_{bs} - 1)} \right) \left(N_{un,si} - \frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L}} \right) \tag{2.42}$$

$$N_{gp,si} = \left(\frac{\mathcal{L} \times N_{un,si}}{\mathcal{L} - n_{lp} \times (s_{bs} - 1)} \right) - \left(\frac{n_{lp} \times (s_{bs} - 1) \times n_{surf}}{\mathcal{L} - n_{lp} \times (s_{bs} - 1)} \right) \tag{2.43}$$

The final relation for $N_{gp,si}$ is the following.

$$N_{gp,si} = \frac{\left(\mathcal{L} \times N_{un,si} \right) - (n_{lp} \times (s_{bs} - 1) \times n_{surf})}{\mathcal{L} - (n_{lp} \times (s_{bs} - 1))} \tag{2.44}$$

Additionally, the derivation of $N_{gp,st}$ is expanded in detail below.

$$N_{gp,st} = N_{un,st} - (n_{lp} \times s_{bs} \times n_a) \qquad \text{from Equation 2.14} \tag{2.45}$$

$$N_{gp,st} = N_{un,st} - \left(n_{lp} \times s_{bs} \times \frac{(n_{surf} - 1) - N_{gp,st}}{(\mathcal{L} - 1)} \right) \qquad \text{by Equation 2.12} \tag{2.46}$$

$$N_{gp,st} - \frac{n_{lp} \times s_{bs} \times N_{gp,st}}{(\mathcal{L} - 1)} = N_{un,st} - \frac{n_{lp} \times s_{bs} \times (n_{surf} - 1)}{(\mathcal{L} - 1)} \tag{2.47}$$

$$N_{gp,st} \times \left(1 - \frac{n_{lp} \times s_{bs}}{(\mathcal{L} - 1)} \right) = N_{un,st} - \frac{n_{lp} \times s_{bs} \times (n_{surf} - 1)}{(\mathcal{L} - 1)} \tag{2.48}$$

$$N_{gp,st} \times \frac{(\mathcal{L}-1) - n_{lp} \times s_{bs}}{\cancel{(\mathcal{L}-1)}} = \frac{\big((\mathcal{L}-1) \times N_{un,st}\big) - (n_{lp} \times s_{bs} \times (n_{surf}-1))}{\cancel{(\mathcal{L}-1)}} \tag{2.49}$$

The final relation for $N_{gp,st}$ is the following.

$$N_{gp,st} = \frac{\big((\mathcal{L}-1) \times N_{un,st}\big) - (n_{lp} \times s_{bs} \times (n_{surf}-1))}{(\mathcal{L}-1) - (n_{lp} \times s_{bs})} \tag{2.50}$$

In order to calculate the total enumeration of the system, we will require to convert quantities between steps and sites, as the values can vary depending on which we use. The Equations 2.11 and 2.12 can be combined to create a conversion relation, that is shown in 2.53.

$$\frac{n_{surf} - N_{gp,si}}{\mathcal{L}} = \frac{(n_{surf}-1) - N_{gp,st}}{(\mathcal{L}-1)} \tag{2.51}$$

$$n_{surf} - N_{gp,si} = \mathcal{L} \times \frac{(n_{surf}-1) - N_{gp,st}}{(\mathcal{L}-1)} \tag{2.52}$$

This results in the final expression for $N_{gp,si}$ shown below.

$$N_{gp,si} = n_{surf} - \mathcal{L} \times \frac{(n_{surf}-1) - N_{gp,st}}{(\mathcal{L}-1)} \tag{2.53}$$

$N_{gp,st}$ is expanded in a similar way.

$$\begin{aligned} \frac{n_{surf} - N_{gp,si}}{\mathcal{L}} &= \frac{(n_{surf}-1) - N_{gp,st}}{(\mathcal{L}-1)} \\ \implies (\mathcal{L}-1)\,\frac{n_{surf} - N_{gp,si}}{\mathcal{L}} &= (n_{surf}-1) - N_{gp,st} \end{aligned}$$

This results in the final expression for $N_{gp,st}$ shown below.

$$N_{gp,st} = (n_{surf}-1) - (\mathcal{L}-1) \times \frac{n_{surf} - N_{gp,si}}{\mathcal{L}} \tag{2.54}$$

We then isolate Relation 2.50 for uncovered steps, $N_{un,st}$ which results in the steps followed in Relations 2.55 to 2.59.

$$N_{gp,st} = \frac{\big((\mathcal{L}-1) \times N_{un,st}\big) - (n_{lp} \times s_{bs} \times (n_{surf}-1))}{(\mathcal{L}-1) - (n_{lp} \times (s_{bs}))} \tag{2.55}$$

$$[(\mathcal{L}-1) - (n_{lp} \times (s_{bs}))] \times N_{gp,st} = \big((\mathcal{L}-1) \times N_{un,st}\big) - (n_{lp} \times s_{bs} \times (n_{surf}-1)) \tag{2.56}$$

$$\big((\mathcal{L}-1) \times N_{un,st}\big) = [(\mathcal{L}-1) - (n_{lp} \times s_{bs})] \times N_{gp,st} + (n_{lp} \times s_{bs} \times (n_{surf}-1)) \tag{2.57}$$

$$N_{un,st} = \frac{[(\mathcal{L}-1) - (n_{lp} \times s_{bs})] \times N_{gp,st} + (n_{lp} \times s_{bs} \times (n_{surf}-1))}{(\mathcal{L}-1)} \tag{2.58}$$

$$N_{un,st} = N_{gp,st} + \frac{(n_{lp} \times s_{bs}) \times (n_{surf}-1) - (n_{lp} \times s_{bs}) \times N_{gp,st}}{(\mathcal{L}-1)} \tag{2.59}$$

The final expression is simplified and presented below.

$$N_{un,st} = N_{gp,st} + \frac{n_{lp} \times s_{bs}}{\mathcal{L}-1}\big((n_{surf}-1) - N_{gp,st}\big) \tag{2.60}$$

2.8.2 Maximum Loop Condition

In order to build a procedure of enumerating the system, we will need to know the maximum number of loops that can form on a single polymer. This is dependant on what the model allows in terms of combinations of train-steps between loops. For the case that zero train-steps between adjacent loops is permitted, one can visualize schematically the maximum loop-density as represented in Figure 2.18, which shows a polymer footprint $\mathcal{L}-1$ that consists of a contiguous sequence of loops with one step in trains between each loop.

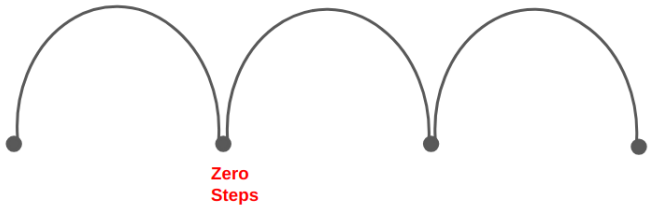


Figure 2.18: Maximum loop density on a polymer with a zero steps in trains between each pair of loops

So this means one could find the maximum number of loops on a single polymer, $max[n_{lp}]$, based on the ratio in Equation 2.61, where we recall that r, s_{bs} and s_{lp} remain fixed.

$$max[n_{lp}] = \frac{min\left[\mathcal{L} - 1\right]}{s_{_{bs}}} \tag{2.61}$$

We have that,

$$\mathcal{L} - 1 = (r-1) + n_{lp}\left(s_{_{bs}} - s_{_{lp}}\right) \qquad \text{by Equation 2.4} \tag{2.62}$$

Now, because all the other quantities are parameters of the model, we get the following result

$$min\left[\mathcal{L} - 1\right] = (r-1) + max[n_{lp}]\left(s_{_{bs}} - s_{_{lp}}\right) \tag{2.63}$$

This leads to,

$$\begin{aligned}
max[n_{lp}] &= \frac{(r-1) + max[n_{lp}]\left(s_{_{bs}} - s_{_{lp}}\right)}{s_{_{bs}}} \\
max[n_{lp}]\ s_{_{bs}} &= (r-1) + max[n_{lp}]\left(s_{_{bs}} - s_{_{lp}}\right) \\
\cancel{max[n_{lp}]\ s_{_{bs}}} &= (r-1) + \cancel{max[n_{lp}]\ s_{_{bs}}} - max[n_{lp}]\ s_{_{lp}} \\
max[n_{lp}]\ s_{_{lp}} &= r-1 \\
max[n_{lp}] &= \frac{r-1}{s_{_{lp}}}
\end{aligned} \tag{2.64}$$

This completes the proof of Relation 2.61.

2.8.3 Implementation

In this model we set the base below the loops to three sites, $s_b = 3$; the connective constant $\mu_3 = 6$ and the amplitude in the three dimensional lattice of the solution to $A_3 = 1$. For the loops the amplitude is $B_3 = 1$. Finally the size of one dimensional lattice of the adsorption surface $n_{surf} = 146200$ lattice-sites [52], and the three dimensional lattice of the volume, $n_{vol} = n_{surf} \times 10^3$ in lattice-sites. The length of a single polymer in mers, based on the long polymers from experiment [52], is $r = 6200$, the total number of polymers in both solution and the surface throughout the model remains fixed at $n = 1000$ and the number of salt-caps on the surface is $N_{un} = 0.18 \times (n_{surf} - 1)$.

There is a step where we convert the uncovered-site to uncovered step, as seen below in Equations 2.65, 2.66 and 2.67.

$$N_{gp,si} = \frac{\left(\mathcal{L} \times N_{un,si} \right) - \left(n_{lp} \times \left(s_{bs} - 1 \right) \times n_{surf} \right)}{\mathcal{L} - \left(n_{lp} \times \left(s_{bs} - 1 \right) \right)} \qquad \text{by Equation 2.44} \tag{2.65}$$

$$N_{gp,st} = (n_{surf} - 1) - (\mathcal{L} - 1) \times \frac{n_{surf} - N_{gp,si}}{\mathcal{L}} \qquad \text{by Equation 2.54} \tag{2.66}$$

$$N_{un,st} = N_{gp,st} + \frac{n_{lp} \times s_{bs}}{\mathcal{L} - 1} \left((n_{surf} - 1) - N_{gp,st} \right) \qquad \text{by Equation 2.60} \tag{2.67}$$

This concludes the process of converting the uncovered steps to sites.

We calculate the number of polymers in solution as this will be needed in the enumeration methods associated to the three dimensional lattice (solution) class of the model.

$$n_b = n - n_a \tag{2.68}$$

An array of n_{lp} values is compiled that is based on the the minimum and maximum possible values based on the chosen s_{lp} as seen in Relations 2.69 and .

$$MIN(n_{lp}) = 0 \tag{2.69}$$

$$MAX(n_{lp}) = \frac{r-1}{s_{lp}} \quad \text{by Equation 2.64} \tag{2.70}$$

The next step is to calculate the logarithm of the binomial factor Ψ_{gp} which is approximated using Stirling factorials which is abbreviated as StirlBin in Equation 2.71 below.

$$\log\left(\ \Psi_{GP}\ \right) = StirlBin\left(\ N_{gp,st} - 1\ ,\ n_a\ \right) \qquad \text{by Equation 2.32} \tag{2.71}$$

The next operation is done on the number of chains adsorbed to the surface, which is calculated using the below function for n_a.

$$n_a = \frac{(n_{surf} - 1) - N_{gp,st}}{(\mathcal{L} - 1)} \qquad \text{from Equation 2.12} \tag{2.72}$$

We will use Stirling's approximation of the factorial in the numerical computations in this chapter. We have that the Stirling factorial is the following,

$$Stirl(x) = \begin{cases} DNE, & x < 0 \\ 0, & x = 0 \\ 0, & x = 1 \\ x\ \log(x) - x + \frac{1}{2}\log(2\pi x) + \frac{1}{12x}, & O/W \end{cases} \tag{2.73}$$

We derive a function for the approximation of the Binomial based on the Stirling Factorial in Equation 2.74.

$$StirlBin(Set, Choose) = Stirl(Set) - Stirl(Choose) - Stirl(Set - Choose) \tag{2.74}$$

In order to do the enumeration of loops, one must first find what the value of the Stirling Binomial factor of the positioning of loops on the polymer.

$$\log\left(\ \Psi_{_{lp}}\ \right) = StirlBin\left(\ \ (n_{lp}+1) + s_{_{tr,st}} - 1\ \ ,\ \ n_{lp}\ \ \right) \qquad \text{by Equation 2.23} \tag{2.75}$$

One can then enumerate the loops.

$$\log \mathcal{E}_{lp} = \log\left(\ \Psi_{_{lp}}\ \right) + n_{lp}\left(s_{_{lp}}\ \log \mu_3\ +\ \log B_3\ -\ 3.7\ \log s_{_{lp}}\ \right) \qquad \text{from 2.27} \tag{2.76}$$

Then we evaluate $\log \mathcal{E}_{vol}$, which is expressed in the following way in the code.

$$\log \mathcal{E}_{vol} = \log\left(A_3\right)\ +\ r\ \log\left(\mu_3\right) \qquad \text{by Equation 1.5} \tag{2.77}$$

Finally the total enumeration $\log \mathcal{E}_{tot}\left(n_{lp};\ N_{_{un,si}}\right)$ is calculated and plotted as a function of number of loops in a single polymer.

$$\begin{aligned}\log \mathcal{E}_{tot}\left(n_{lp};\ N_{_{un,si}}\right) &= \log \Psi_{_{GP}} + n_a \log \mathcal{E}_{lp} \\ &\quad + n_b \log \mathcal{E}_{vol} + n_b \log n_{vol} - Stirl\left(n_b\right) \qquad \text{by Equation 2.35}\end{aligned} \tag{2.78}$$

2.9 Results

In this model procedure we let $s_{_{bs}} = 6, \mu_2 = 3, \mu_3 = 5, A_2 = 1, A_3 = 1, B_3 = 1, n_{surf} = 146200, r = 6200, n_{vol} = n_{surf} \times 100, n = 23$. We fix N_{un} and $s_{_{lp}}$ and iterate through the different values of $n_{_{lp}}$ from the minimum possible to the maximum in order to calculate the logarithm of $\mathcal{E}_{tot}$ based on that. We then repeat this for each value of $s_{_{lp}}$ from 8 to 15. All of the above steps are then executed for different fractions of uncovered sites, which is that of $\%N_{un} = \frac{N_{un}}{n_{surf}}$, with values of 25%, 50% and 75%. We then plotted the $\log \mathcal{E}_{tot}$ as a function of the number of mers in loops. This is a chart of preference for different fractions of mers in loops. From Figures 2.19 to 2.21 it is evident that as one increases the fraction of mers in loops the entropic preference drops. This means that the entropic preference of the system is that of not having polymers and loops and salt caps under those loops. The entropically preferred state is that of all mers being in trains and all salt caps being in gaps between the polymers. This is prediction is not supported by experimental results around thickness as a function of surface charge, which is that the behaviour observed is that of a preference to long loops on the surface. [9, 10, 11]

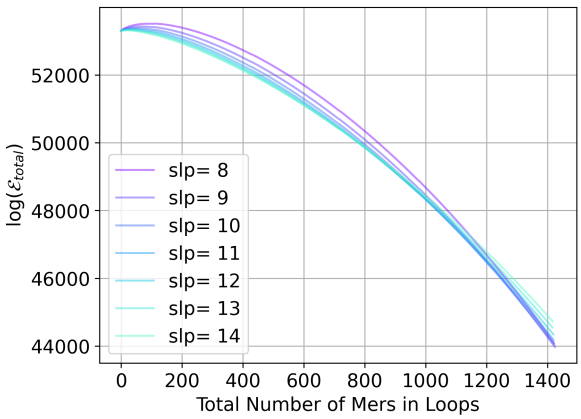


Figure 2.19: Plot of entropic preference as a function of total mers in loops on a single polymer for $\%N_{un} = 25\%$

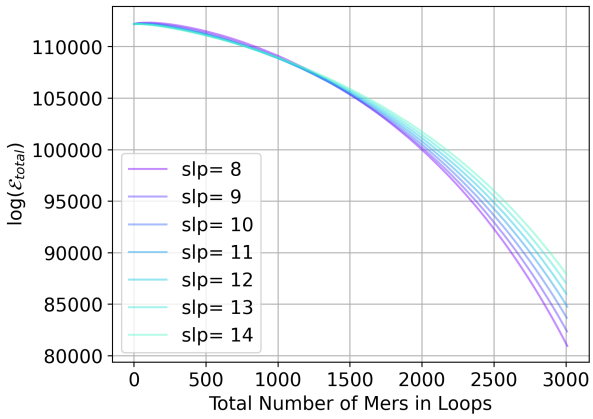


Figure 2.20: Plot of entropic preference as a function of total mers in loops on a single polymer for $\%N_{un} = 50\%$

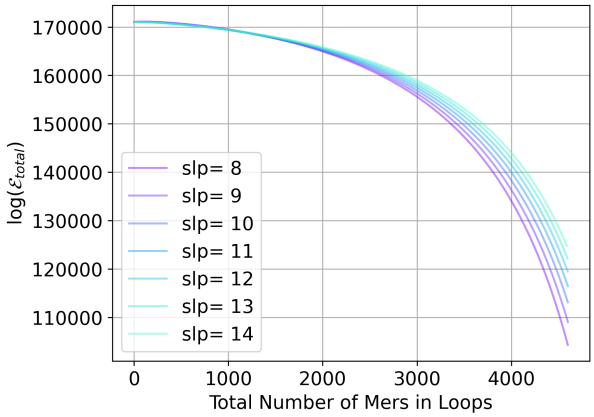


Figure 2.21: Plot of entropic preference as a function of total mers in loops on a single polymer for $\%N_{un} = 75\%$

For this model we assumed self-arrangement of the mers in the presence of salt-caps and the model provided us with information about the most preferred state of that system. The above analysis leads us to inquire what would occur if one was to constrain positioning of the salt ions on the lattice and by extension the positioning of loops. This will be the focus of Chapter 3.

Chapter 3

One Dimensional Periodic Model

In this chapter we develop a one dimensional model of polymers adsorption to the surface and formation of loops wherein positioning of loops are constrained as a function of coverage by polymers on the surface. Below the loops there are salt-caps, but also we find salt-caps on sites between polymer chains. This model differs from the preceding, in that instead of having the positioning of loops to be unconstrained in the model we assumed that the positioning of the salt-caps is determined based on the polymer coverage fraction and as such, so is the positioning of the loops. This means that one can predetermine where on the surface loops and gaps will occur. Due to the single dimension of the surface, this can be modelled using a periodic pattern of vacant and occupiable surface sites. This is achieved by inputting a fraction of occupiable sites to the algorithm. For example 3:7 is the case where every three consecutive salt-caps, 7 consecutive polymer coverage (occupiable) sites shall follow. The goal of this model was to find out which value of s_{lp} yields the largest number of configurations. If the smallest value of s_{lp} is most likely, then that would be the analogue of pancaking, where there are no loops, as all of the mers of the adsorbed polymer are occupying sites on the surface.

3.1 Model Overview

Our surface is a one-dimensional line with n_{surf} sites. We have n chains of length r, of which n_a are adsorbed onto the surface and n_b are free in solution. The term $\left(\mathcal{E}_{vol}^{n_b} n_{vol}^{n_b}\right)/n_b!$ is still valid for the chains in solution, as is done in Equation 2.35. Each loop of length s will have a factor $B_3\mu_3^s \;/\; s^{3.7}$ as before.

We shall use the term "covered site" for a surface site that will be occupied by a mer of an adsorbed chain. We shall use the term "vacant site" for a surface site that will not be occupied by a mer of an adsorbed train. A vacant site could either be under a loop or else in a gap between two chains.

In this model, we shall assume that the surface is covered by alternating segments of m_c covered sites and m_v vacant sites. This pattern repeats periodically for the whole surface. The fraction of covered sites is therefore $m_c/(m_c + m_v)$. For example, for 60% coverage, we could take $m_c = 6$ and $m_v = 4$; or we could take $m_c = 3$ and $m_v = 2$; and so on. We shall assume values of $m_v \leq 19$, as an initial approximation of randomly placed covered and vacant sites.

In the above description, m_v is necessarily the number of sites under a loop, so in our previous notation we have $s_{bs} = m_v + 1$.

We will specify the above definitions and a single loop length (s_{lp}). Since each train has m_c sites and each loop has $s_{lp} - 1$ sites, the number of loops on a single chain must be $\lfloor r/(m_c + s_{lp} - 1)\rfloor$. From this we can compute $\mathcal{L}$ and n_a. So the locations of all the chains on the surface are unambiguously determined (except perhaps for some endpoint effects,

which we shall ignore for now). In this case, the main objective is to count the number of configuration for each loop.

3.2 Relationships of the Model

The below equations are expressions and formulas that were developed in the model from Chapter 2 and now are being used with a more constrained approach. Below are details on how the method has been adjusted and we recall its purpose for the overall model. Here the number of loops is dependent on the number of covered sites m_c, the number of sites in a loop s_{lp} and the chain length, r.

$$n_{lp} = \frac{r}{m_c + s_{lp} - 1} \tag{3.1}$$

In this model the polymer footprint, $\mathcal{L}$, is similar to previous models except that in this sub-model it is also dependent on the number of vacant sites, m_v.

$$\mathcal{L} = r + n_{lp}\left((m_v + 1) - s_{lp}\right) \tag{3.2}$$

The number of polymers on the surface, n_a, is a function of the number of sites on the surface, n_{surf}, the footprint length, $\mathcal{L}$, and the number of vacant sites, m_v.

$$n_a = \frac{n_{surf}}{\mathcal{L} + m_v} \tag{3.3}$$

The number of polymers in solution, n_b, can be found based on a difference between the total polymers overall, n, and the polymers attached to the surface, n_a. This is due to the

fixed value of the total polymers in the system.

$$n_b = n - n_a \tag{3.4}$$

The enumerational method for the loops is shared with the previous chapters. The dependent variable of this function is $n_{_{lp}}$ in this model

$$\log \mathcal{E}_{lp} = n_{lp} \left(s_{lp} \log \mu_3 \ + \ \log B_3 \ - \ 3.7 \log s_{lp} \ \right) \tag{3.5}$$

The enumeration function for the $\mathcal{E}_{vol}$ is a function of parameters associated to the three dimensional lattice of solution, i.e., A_3, μ_3 as is explained in 1.4.

$$\log \mathcal{E}_{vol} = \log \left(A_3 \right) \ + \ r \ \log \left(\mu_3 \right) \tag{3.6}$$

Here we have the total enumeration of the model which in this model is dependent on the number of loops on a polymer, n_{lp}.

$$\log \mathcal{E}_{total}(n_{lp}) = n_a \times \log \mathcal{E}_{lp} + n_b \times \log \mathcal{E}_{vol} + n_b \times \log n_{vol} - Stirling(n_b) \qquad \text{from Equation 1.2} \tag{3.7}$$

3.3 Implementation

The model is now structured into a numerical method where one can find the basic steps followed in the code to calculate the preferred loop length of the experimental system given certain pre-determined constraints on where the salt-caps and loops will reside.

Step 1: Provide constants as well as important parameter-values required to initialize the

model.

- **INPUTS:**
  - The algorithm will iterate through all possible values of the vacant-sites parameter m_v.
    - μ_3 This is the connective constants for three dimensional lattice.
    - A_3 This the amplitude for a three dimensional lattice.
    - B_3 is an amplitude associated with the loops that reside in 3-dimensional solution and their end-points on the 1-dimensional surface.
  - Parameters input into this model are:
    - r chain-length of the polymers
    - n_{surf} the area of the 1-dimensional surface-lattice in units of sites that are the size of a single mer.
    - n_{vol} the volume of the three dimensional solution-lattice in units of sites that are the size of a single mer.
- Using the above quantity m_v, we can now compute the length of the average loop on a chain, s_{lp}. Here the relationship of the number of steps, $(m_v + 1)$ raised to the power ν is the average end-to-end distance for a path of that many steps, which was discussed in detail at the end of Chapter 1. There are three values of ν in this model that we will use, the first is that of the stiff walk which is just the proportionality, i.e., that of $\nu = 1$. The second is that of the Flory exponent of 3/5 and finally that of the random-walk exponent for diffusion of 1/2 [3]. The +2 in the expressions below represent the two end steps, which are not free because they must be perpendicular to the surface.

  - Stiff, with $\frac{1}{\nu} = 1.00$, $s_{lp} = 4 \times (m_v + 1)$.
  - self-avoiding walk with $\frac{1}{\nu} = 1.67$, $s_{lp} = (m_v + 1)^{1.67} + 2$
  - random walk with $\frac{1}{\nu} = 2.00$, $s_{lp} = (m_v + 1)^2 + 2$.

- We need to calculate the number of loops on a single polymer, n_{lp}

$$n_{lp} = \frac{r}{m_c + s_{lp} - 1} \qquad \text{from Equation 3.1} \tag{3.8}$$

- We need to calculate the footprint of the polymers on the surface, $\mathcal{L}$.

$$\mathcal{L} = r + n_{lp}\left((m_v + 1) - s_{lp}\right) \qquad \text{from Equation 3.2} \tag{3.9}$$

- We need to calculate the number of polymers on the surface n_a.

$$n_a = \frac{n_{surf}}{\mathcal{L} + m_v} \qquad \text{from Equation 3.3} \tag{3.10}$$

- We need to calculate the number of polymers in solution n_b based on the number of polymers on the surface n_a.

$$n_b = n - n_a \qquad \text{from Equation 3.4} \tag{3.11}$$

Step 2: Calculate the enumeration function values.

- We then calculate the enumeration function for the loops

$$\log \mathcal{E}_{lp} = n_{lp}\left(s_{lp}\, \log \mu_3 \;+\; \log B_3 \;-\; 3.7\, \log s_{lp}\right) \qquad \text{from Equation 3.5} \tag{3.12}$$

- Finally we compute the enumeration of the solution

$$\log \mathcal{E}_{vol} = \log (A_3) \ + \ r \ \log (\mu_3) \qquad \text{from Equation 3.6} \tag{3.13}$$

Step 3: Output the total enumeration for a specific set of parameters.

$$\begin{aligned} \log \mathcal{E}_{total}(n_{lp}) = & \ Stirling(n) + n_a \times \log \mathcal{E}_{lp} \\ & + n_b \times \log \mathcal{E}_{vol} + n_b \times \log n_{vol} - Stirling(n_b) \qquad \text{from Equation 3.7} \end{aligned} \tag{3.14}$$

3.4 Results and Discussion

Figures 3.1 to 3.9 provide the results we computed on the preference to a specific fraction of mer occupancy on the surface. It is important to recall that the model is setup in such a way that when one increases the vacant sites, the fraction of mers in loops will also grow. The most consistent model here as we increase the surface occupancy by polymers is that of the stiff walk (blue curve), the other two models are a little more irregular, but still provide insights when doing a comparison between larger and smaller loops (s_{lp} as a function of m_v). For surface occupancy greater than 40% we observe a consistent upward trend of entropy as a function of m_v. We also notice that the highest entropy is to the right of the plot where m_v is large, which implies large loops. It is also evident through Figures 3.1 to 3.9 that smaller values of m_v are not the optimal values of entropy. Based on the above, it is suggestive that there is a preference for larger loops as that is where we observe higher entropy values. This means that given the above constraints there is an entropic preference to have large fraction of mers in loops. In other words this model predicts that loops exist and they are preferred entropically.

m_v	s_{lp} Stiff	s_{lp} Self-Avoiding	s_{lp} Random Walk
2	12	8	11
3	16	12	18
4	20	17	27
5	24	22	38
6	28	28	51
7	32	34	66
8	36	41	83
9	40	49	102
10	44	57	123
11	48	65	146
12	52	74	171
13	56	84	198
14	60	94	227
15	64	105	258
16	68	115	291
17	72	127	326
18	76	139	363
19	80	151	402

Table 3.1: Tabulated values of loop length, s_{lp}, as a function of m_v for Stiff, Self-Avoiding and Random Walk.

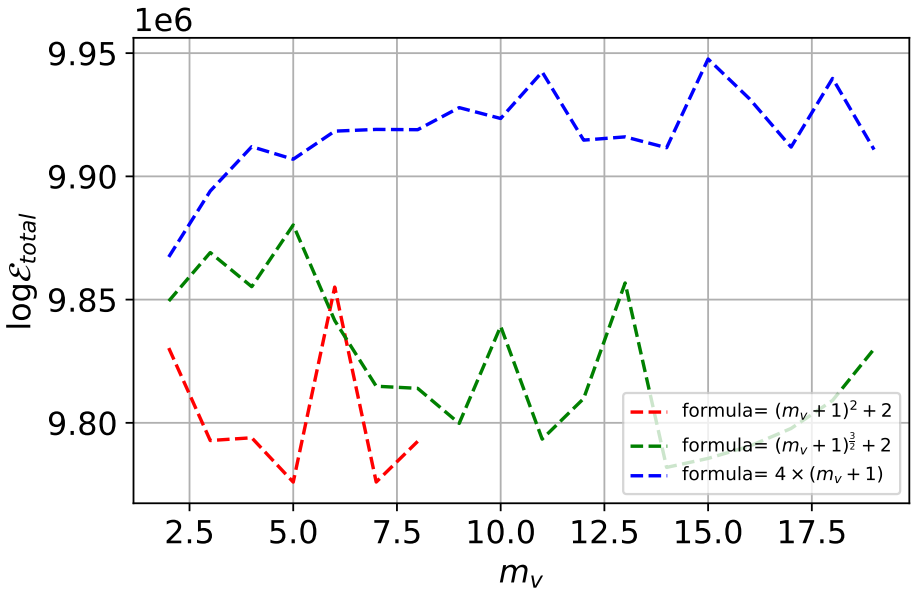


Figure 3.1: Plot of entropic preference as a function of m_v, base-length, for 10% surface occupancy by polymers

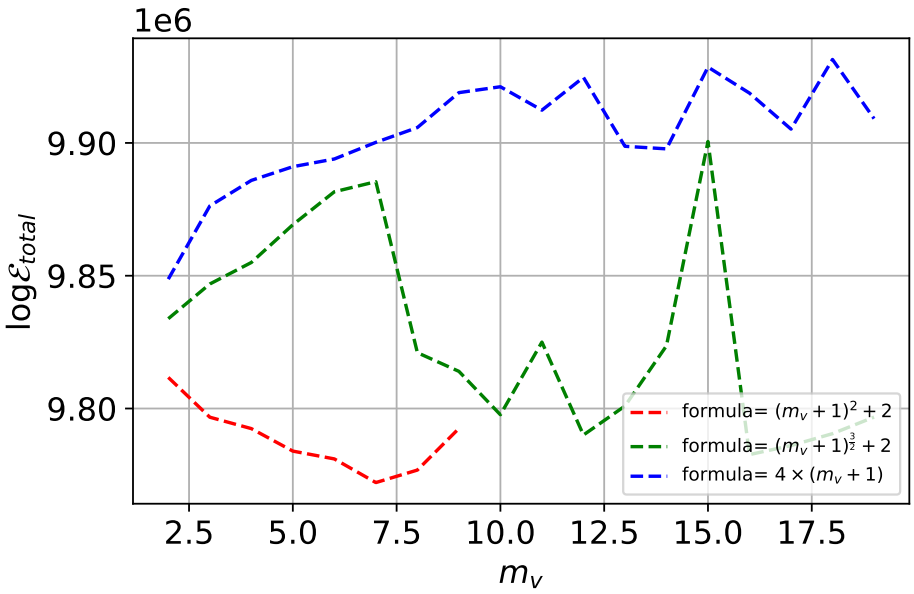


Figure 3.2: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 20% surface occupancy by polymers

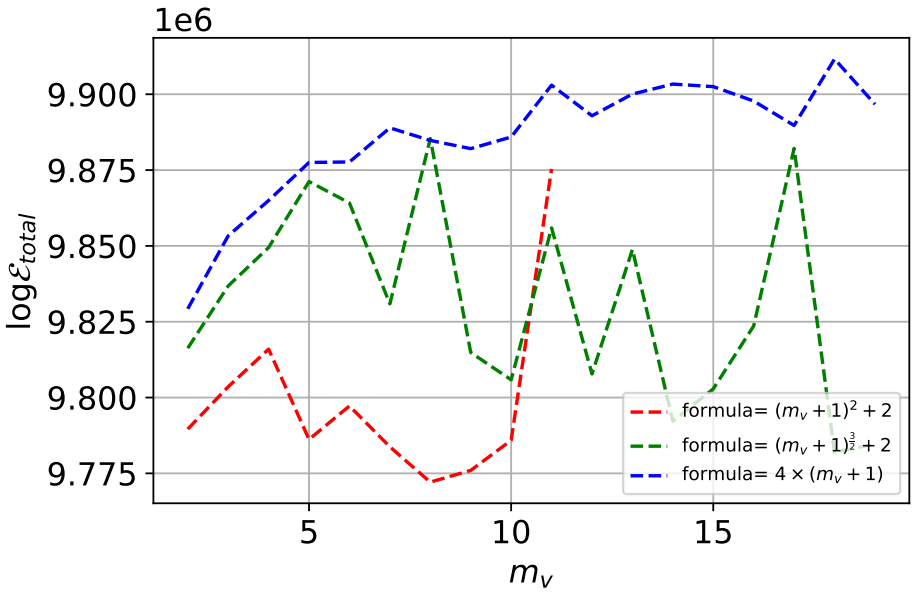


Figure 3.3: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 30% surface occupancy by polymers

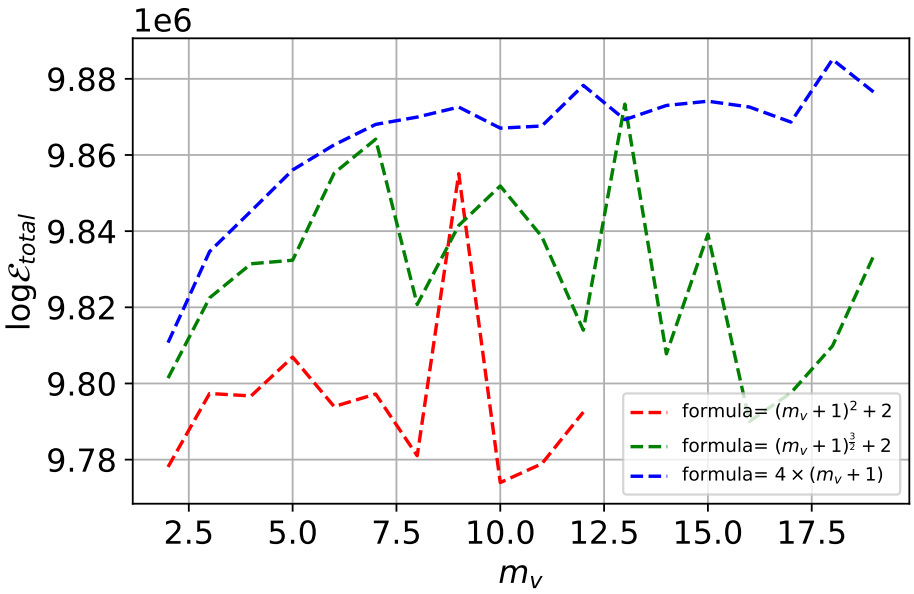


Figure 3.4: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 40% surface occupancy by polymers

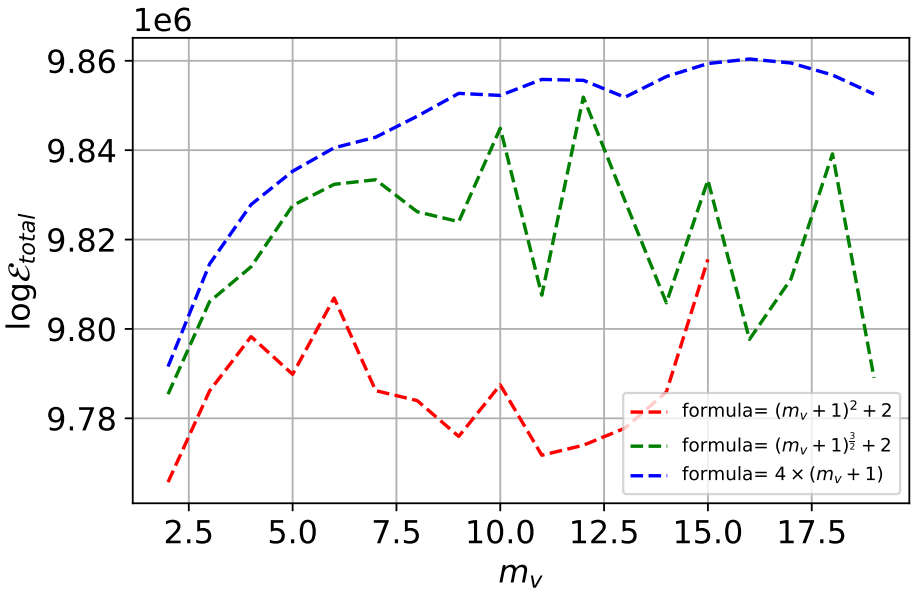


Figure 3.5: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 50% surface occupancy by polymers

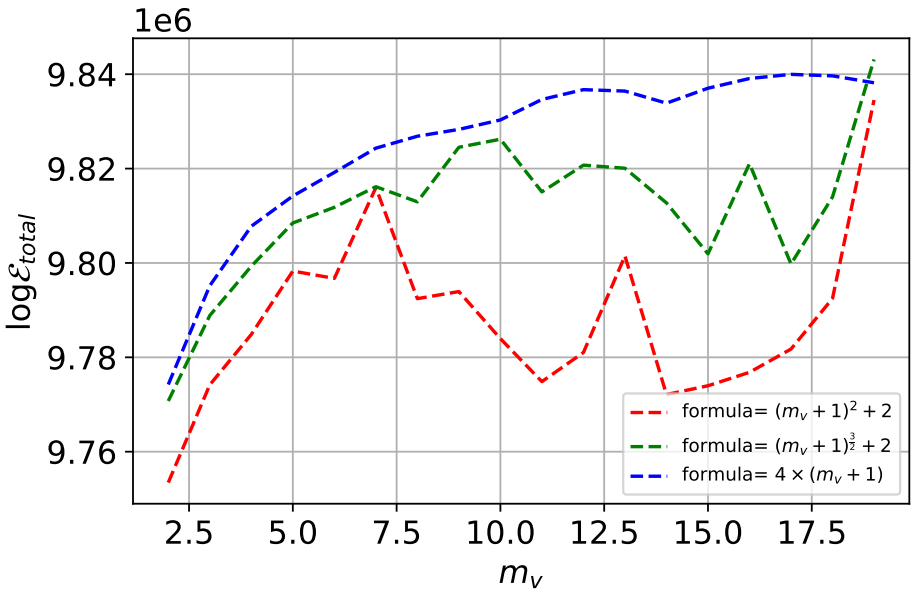


Figure 3.6: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 60% surface occupancy by polymers

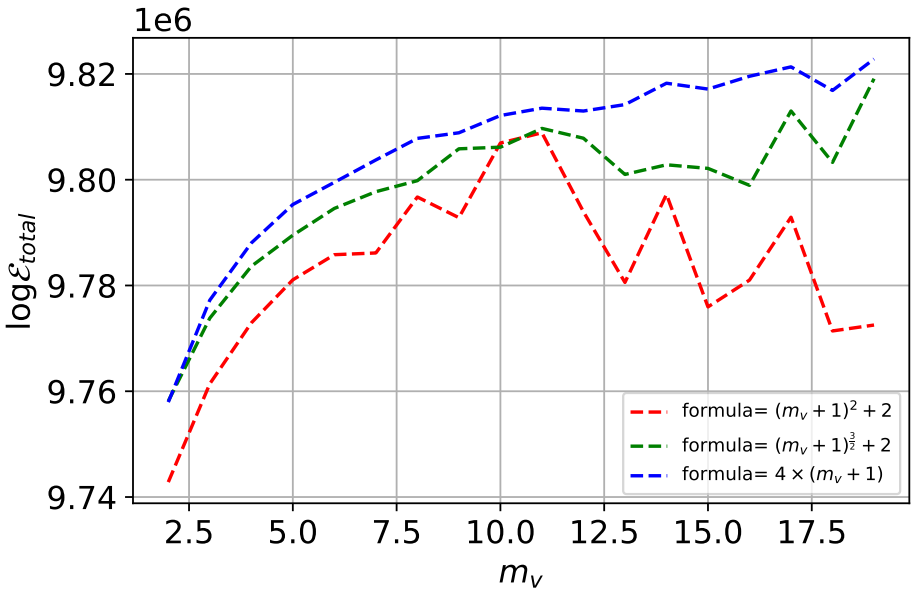


Figure 3.7: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 70% surface occupancy by polymers

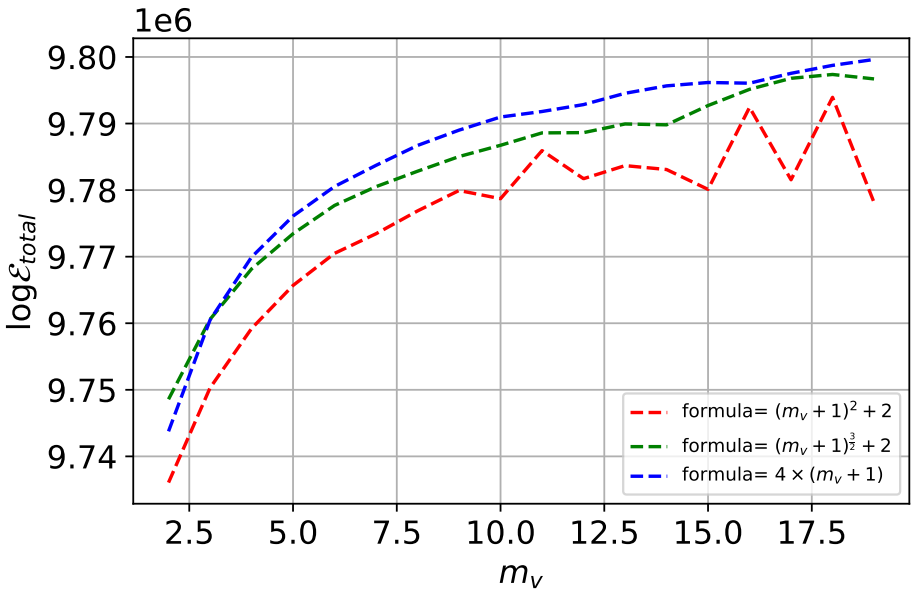


Figure 3.8: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 80% surface occupancy by polymers

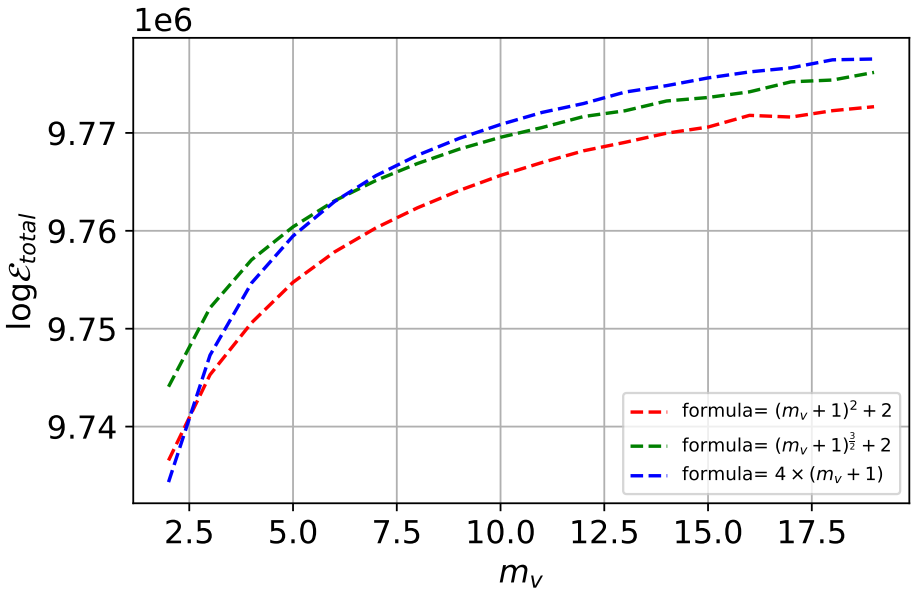


Figure 3.9: Plot of entropic preference $\log \mathcal{E}_{total}$ as a function of base-length in sites m_v, base-length, for 90% surface occupancy by polymers

Part II

Two Dimensional Surface Lattice Models

Chapter 4

Two Dimensional Surface Model: Unconstrained Approach

In this chapter, we develop a model to enumerate the preferential behaviour of loops on a two dimensional surface. The objective of this model is to provide insight into whether loops are an entropically preferred molecular architecture for adsorbed polymers. First, we walk through parameters of the model, namely that of calculating the number of loops, the length of the adsorbed portion of the polymer and the number of chains on the surface, assuming full coverage of the surface by polymers. Subsequently, we describe the Flory-Huggins mean-field approach used in this model for placement of the polymers on the surface [17, 12]. We then cover derivations related to enumerating the different sub-domains of the model. We then provide the discrete approximation of the enumeration function and that of its derivative using divided differences [53]. In order to further verify the mean field model we also developed an asymptotic approach. The steps of the implementations are then explained for the discrete enumeration approximation as well as for the asymptotic approximation. Following that, we provide the results of this model by comparing the

discrete model to the asymptotic approximation, ensuring that there is agreement between two different approaches, and thus providing further confidence in the overarching mean-field model that was developed. Finally, the results are analyzed to find if there is preferential formation of loops and it is found that this is not the case for an unconstrained system such as this one.

4.1 Parameters and Definitions

The parameters and variables of the system we are modelling are the following. The number of sites in one chain is r and $r-1$ is the number of steps in one chain. Our surface is a two-dimensional square lattice with n_{surf} sites. We have n chains of length r, of which n_a are adsorbed onto the surface and n_b are free in solution, with $n = n_a + n_b$. The assumption of full surface coverage means that all n_{surf} surface sites will be occupied by mers of adsorbed polymers independent of the number of polymers adsorbed to the surface, what will vary is how many mers will be forced into loops. The number of sites in a single loop is s_{lp} and $s_{lp}-1$ is the number of steps in a single loop. The footprint measured in sites, $\mathcal{L}$, is the site-length of the adsorbed portion of chain on the surface that includes all the sites in trains and all the sites at the bases of each loop. The footprint measured in steps, $\mathcal{L}-1$, is the step-length of the adsorbed portion of chain on the surface that includes all the steps in trains and all the steps at the bases of each loop. The number of sites at the base is given by s_b and the steps by $s_b - 1$. In this section the number of steps in a base will be fixed to a single step, which is that of $s_b = 2$. The count of loops on a single chain is n_{lp}, and the total mers in loops on a chain overall is N_{lp}. In Figure 4.1, $\mathcal{L}-1$ is the number of red steps from $\boldsymbol{step_{(1)}}$ to $\boldsymbol{step_{(17)}}$ including the green segment. Additionally, the values for $\mathcal{L}$ and $\mathcal{L}-1$ in Figure 4.1 are 7 and 8 respectively.

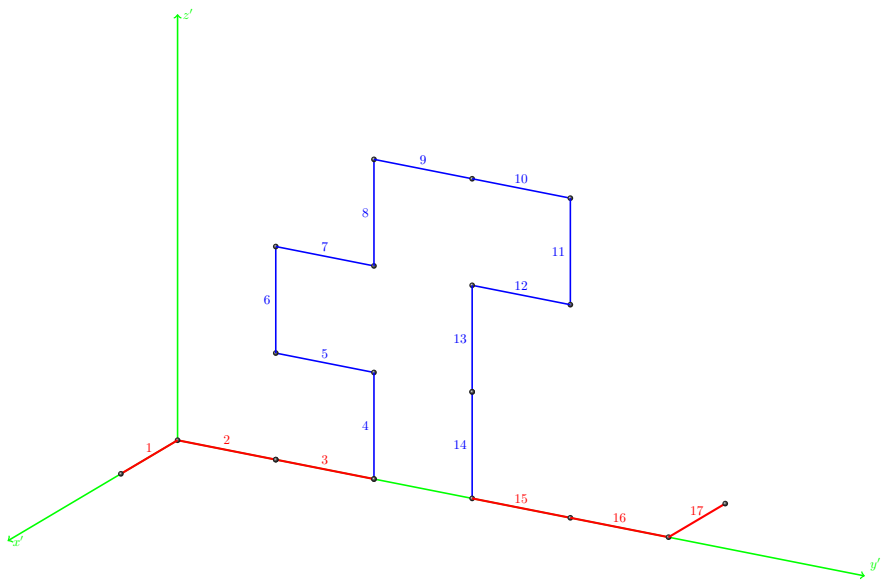


Figure 4.1: Discrete approximation of a loop (blue) and trains (red) on the surface (green x and y axes).

r	number of sites in one chain (polymer chain length)
$r-1$	number of steps in one chain (polymer chain length)
n_{surf}	number of sites on the two-dimensional square lattice approximation of the surface
n	number of polymer chains in both solution and adsorbed on the surface
n_a	number of polymers adsorbed onto the surface
n_b	number of polymers free-floating in solution
$s_{_{lp}}$	number of sites in a single loop
$s_{_{lp}}-1$	number of steps in a single loop.
$\mathcal{L}$	The footprint measured in sites which is the site-length of the adsorbed portion of chain on the surface that includes all the sites in trains and all the sites at the bases of each loop
$\mathcal{L}-1$	The footprint measured in steps which is the step-length of the adsorbed portion of chain on the surface that includes all the steps in trains and all the steps at the bases of each loop.
s_b	number of sites at the base of a loop
s_b-1	number of steps at the base of a loop
$n_{_{lp}}$	count of loops on a single chain is
$N_{_{lp}}$	total number of mers in loops on a chain overall

Table 4.1: Parameters of the model

4.2 Relationships of the Model

Assuming the surface is fully covered in mers that belong to polymers. We recall that there is one step at the base of each loop. the total sites on the surface is product of the number of polymers on the surface and the footprint of one the polymers on the surface in sites.

$$n_{surf} = \mathcal{L}\, n_a \tag{4.1}$$

Solving the above for $\mathcal{L}$ we get one way to calculate the footprint of a single polymer on the surface.

$$\mathcal{L} = \frac{n_{surf}}{n_a} \tag{4.2}$$

The total number of mers loops in a chain, not including the endpoints attached to the surface, is calculated through Equation 4.3.

$$N_{lp} = r - \mathcal{L} = r - \frac{n_{surf}}{n_a} \tag{4.3}$$

The total number of loops in a chain can be found by dividing the number of mers in loops by $s_{lp} - 1$, as is shown in Equation 4.6.

$$n_{lp} = \frac{N_{lp}}{s_{lp} - 1} \tag{4.4}$$

$$= \frac{r - \mathcal{L}}{s_{lp} - 1} \tag{4.5}$$

$$= \frac{r - \frac{n_{surf}}{n_a}}{s_{lp} - 1} \qquad \text{by Equation 4.3} \tag{4.6}$$

Alternatively, the footprint can be found independently of n_{surf} by rearranging Relation 4.5 which results in Equation 4.7 for sites, and in a similar way Equation 4.8 can be found for steps.

$$\mathcal{L} = r - n_{lp}(s_{lp} - 1) \tag{4.7}$$

$$\mathcal{L} - 1 = (r - 1) - n_{lp}s_{lp} + n_{lp} \tag{4.8}$$

Revisiting Self Avoiding Walks Recall from Equation 1.5 that the approximation of the enumeration of polymers in solution is calculated using

$$\mathcal{E}_{vol} = A_3(\mu_3)^r \qquad \text{by Equation 1.5}$$

Revisiting Self Avoiding Polygons For calculating the portion of the loop that is floating in the solution and can arrange itself in three dimensional space we shall use the approach described in detail in Section 2.4. The final expression was found to be that of Equation 2.27, which is the count of all the possible loops on one chain, given the endpoints of all the loops.

$$\left(\mu_3^{s_{lp}} \frac{B_3}{\left(s_{lp}\right)^{\gamma_{lp}}} \right)^{n_{lp}} \tag{4.9}$$

where B_3 is the amplitude for computing the self avoiding polygon in a three dimensional cubic lattice, and γ_{lp} is the exponent of s_{lp}. Recall from Relations 2.24 and 2.25 that the interpolated values were found to be $B_3 = 1.1$ and $\gamma_{lp} = 3.7$.

4.3 Mean Field Approach with Loops

The intuition behind the approach we will follow in the following paragraph is that we perceive the footprint $\mathcal{L}$ as a shorter chain and then later we're going to add loops. For example, if we wanted to add fifteen loops then we're going to pick fifteen steps on the footprint and replace those fifteen bonds on the footprint with a loop, which returns the chain length to its original size r. Based on the derivations in the supplement of [52], we specify that the number of ways to place the k^{th} chain with footprint $\mathcal{L}$ is $\tilde{w}_k$, given the prior information of having already placed $(k-1)\mathcal{L}$ mers on the two dimensional lattice. Let q be the number of nearest neighbours of each site on the surface. Given an arbitrary value n_a, we want to calculate the amount of ways that n_a $\mathcal{L}$-mers could be placed on the surface, without overlapping. We place one polymer at a time. To begin with, there are

$$n_a\mathcal{L} - (k-1)\mathcal{L}$$

available sites for the first monomer. Recall that q is the number of neighbors of each site in the surface lattice. When considering the adsorption of the first chain without any other chains on the surface, there are q choices for the second monomer in the chain, and $q-1$ choices for each monomer after that. More generally, the above value of choices, should on average be reduced by the fraction of the surface that has already been covered. When considering the placement of the second monomer of the chain, there would be

$$n_a\mathcal{L} - (k-1)\mathcal{L} - 1$$

unoccupied sites, which means that each site has probability of being available as

$$\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - 1}{n_a\mathcal{L}}.$$

This results in

$$q\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - 1}{n_a\mathcal{L}}$$

choices for the second monomer. Similarly, after i monomers of the current chain have been placed ($i \geq 2$), the fraction of the surface that has not been covered is

$$\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - i}{n_a\mathcal{L}},$$

So, the choices for the $(i+1)^{th}$ monomer in this chain is

$$(q-1)\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - i}{n_a\mathcal{L}}.$$

choices for the monomer in this chain. The resulting equation is that of 4.10

$$\begin{aligned}\tilde{w}_k &= [n_a\mathcal{L}-(k-1)\mathcal{L}]\times q\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-1}{n_a\mathcal{L}}\right)\\ &\quad\times\prod_{i=2}^{\mathcal{L}-1}(q-1)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-i}{n_a\mathcal{L}}\right)\end{aligned}$$

$$\begin{aligned}&= \frac{[n_a\mathcal{L}-(k-1)\mathcal{L}]!}{[n_a\mathcal{L}-k\mathcal{L}]!}\,q\,\frac{(q-1)^{\mathcal{L}-2}}{(n_a\mathcal{L})^{\mathcal{L}-1}}\\ &= \frac{[n_a\mathcal{L}-(k-1)\mathcal{L}]!}{[n_a\mathcal{L}-k\mathcal{L}]!}n_a\mathcal{L}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_a\mathcal{L}}\right)^{\mathcal{L}}.\end{aligned}\tag{4.10}$$

We then take into account Equation 4.1 which leads to the following simplification,

$$\tilde{w}_k = \frac{[n_{surf}-(k-1)\mathcal{L}]!}{[n_{surf}-k\mathcal{L}]!}n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}.\tag{4.11}$$

For the set of all iterations of coverage fractions of adsorbed mers for up to and including the full coverage scenario we use what will henceforth defined as a Flory factor in Equation 4.12

$$\mathcal{F}(n_a) = \frac{\tilde{w}_1\tilde{w}_2\cdots\tilde{w}_{n_a}}{n_a!}\tag{4.12}$$

To see where the looping will take place in a single chain we have devised a treatment such that the loops will always be atop two adsorbed mers.

The following equations enable calculation of loop placement and the cardinalities of the combinations. Bonds that will belong to the bases beneath the loops are chosen by

$$\begin{pmatrix}\mathcal{L}-1\\ n_{lp}\end{pmatrix}.\tag{4.13}$$

Recall from Relation 4.9 that the number of ways to configure a loop of that size in a three dimensional cubic lattice is computed using the factor in relationship 4.14.

$$\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3\right) \tag{4.14}$$

raised to the power of n_{lp}, the factor of Relation 4.15 is the number of possible loops over all bases for one chain.

$$\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3\right)^{n_{lp}} \tag{4.15}$$

Putting the above factors together into an expression for the loops, we have $\mathcal{E}_{lp}$

$$\mathcal{E}_{lp} = \begin{pmatrix} \mathcal{L} \\ n_{lp} \end{pmatrix} \left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3\right)^{n_{lp}} \tag{4.16}$$

The approximation of the enumeration of polymers in solution (far from the surface) is calculated using Equation 1.5. Combining the above into the enumeration function of Equation 4.17 which is based on the formulation by Fleer [5] on the enumerations of adsorbed polymers on a surface with the consideration of looping. This will serve as the scaffolding on which we will build up our own model. The original consideration of tails, energetic factors as well as the interactions, will be ignored in this model.

$$\mathcal{E}_{total} = n! \left(\mathcal{F}(n_a)\ \mathcal{E}_{lp}^{n_a}\ \mathcal{E}_{vol}^{n_b}\ \frac{n_{vol}^{n_b}}{n_b!}\right) \tag{4.17}$$

4.4 Development of Approximations of Enumeration Functions

The objective of this section is to develop an enumeration function that will then be optimized through inputting different values of loop length s_{lp}, and then iterating through increasing values of polymers on the surface n_a until the critical values (n_a^*, s_{lp}^*) are found such that the enumeration is maximized. When calculating the total enumeration values, the factorials and exponents involved can very quickly grow to such magnitudes that a personal computer is computationally limited. For this reason we develop approximations that are used in the algorithm directly. An approximation function that will be used heavily in this model is Stirling's approximation of the logarithm of a factorial from Equation 1.10.

4.4.1 Logarithmic Approximation of Enumeration

The first step in developing a computable enumeration function is to apply a logarithm throughout the expression and simplify the expression based on logarithmic properties. The logarithmic approximation is described by the following expression.

$$\begin{aligned} \log \mathcal{E}_{total} = Stirling(n) + \log \mathcal{F}(n_a) + \\ n_a \cdot \log \mathcal{E}_{lp} + n_b \cdot \log \mathcal{E}_{vol} \\ + n_b \cdot \log n_{vol} - Stirling(n_b) \qquad \text{by Equation 4.17} \end{aligned} \tag{4.18}$$

We will now proceed to approximate each term in 4.18. The logarithm of the Flory Factor is derived in Equations 4.20 to 4.26.

$$\log \mathcal{F}(n_a) = \log \prod_{k=1}^{n_a} \tilde{w}_k - Stirling(n_a) \tag{4.19}$$

$$= \sum_{k=1}^{n_a} \log \tilde{w}_k - Stirling(n_a) \tag{4.20}$$

Using the formula for w from 4.11, we obtain

$$\sum_{k=1}^{n_a} \log \tilde{w}_k = \sum_{k=1}^{n_a} \log \left\{ \frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!} n_{surf} \frac{q}{(q-1)^2} \left(\frac{q-1}{n_{surf}} \right)^{\mathcal{L}} \right\} \tag{4.21}$$

$$= \left(n_a \log \left[n_{surf} \frac{q}{(q-1)^2} \left(\frac{q-1}{n_{surf}} \right)^{\mathcal{L}} \right] \right) + \left(\sum_{k=1}^{n_a} \log \left[\frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!} \right] \right). \tag{4.22}$$

In Equation 4.23 below, $(\sum_{k=1}^{n_a} \log \tilde{w}_k)$ from 4.22 is substituted into Equation 4.20, enabling the completion of the derivation of $\log \mathcal{F}(n_a)$.

$$
\begin{aligned}
\log \mathcal{F}(n_a) = & \left(n_a \log \left[n_{surf} \frac{q}{(q-1)^2} \left(\frac{q-1}{n_{surf}} \right)^{\mathcal{L}} \right] \right) \\
& + \left(\sum_{k=1}^{n_a} \log \left[\frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!} \right] \right) \\
& - Stirling(n_a) \\
= & \, n_a \times (\log n_{surf} + \log q - 2 \log [q-1] + \mathcal{L} \log [q-1] - \mathcal{L} \log n_{surf}) \\
& + \left(\sum_{k=1}^{n_a} \log \left[\frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!} \right] \right) \\
& - Stirling(n_a) \\
= & \, ((1-\mathcal{L}) \log n_{surf} + \log q + (\mathcal{L}-2) \log [q-1]) \\
& \times \left(\sum_{k=1}^{n_a} [Stirling\left([n_{surf} - (k-1)\mathcal{L}\right) - Stirling\left(n_{surf} - k\mathcal{L}\right)] \right) \\
& - Stirling(n_a) \\
= & \, n_a \times ((1-\mathcal{L}) \log n_{surf} + \log q + (\mathcal{L}-2) \log [q-1]) \\
& + ([Stirling\left(n_{surf}\right) - Stirling\left(n_{surf} - n_a\mathcal{L}\right)]) - Stirling(n_a) \qquad (4.23)
\end{aligned}
$$

The calculation of the logarithm of the enumerational function for loop conformations $\log \mathcal{E}_{lp}$ is derived in Equations 4.24 to 4.25 and results in Equation 4.26.

$$\log \mathcal{E}_{lp} = \log \left\{ \begin{pmatrix} \mathcal{L}-1 \\ n_{lp} \end{pmatrix} \left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3 \right)^{n_{lp}} \right\} \qquad \text{by Equation 1.5} \tag{4.24}$$

$$= \log \left[\frac{\mathcal{L}!}{(n_{lp})!\,(\mathcal{L}-n_{lp})!} \right] + n_{lp} \cdot \log \left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3 \right) \tag{4.25}$$

$$\begin{aligned} \log \mathcal{E}_{lp} = &\{Stirling(\mathcal{L}) - Stirling(n_{lp}) - Stirling(\mathcal{L}-n_{lp})\} \\ &+ n_{lp} \{s_{lp} \cdot \log \mu_3 + \log B_3 - 3.7 \cdot \log s_{lp}\} \end{aligned} \tag{4.26}$$

The logarithm of $\mathcal{E}_{vol}$ is that of Equation 4.27.

$$\log \mathcal{E}_{vol} = \log A_3 + r \cdot \log \mu_3 \tag{4.27}$$

Finally $Stirling(n_b)$ is the following.

$$Stirling(n_b) = (n_b) \cdot \log [n_b] - n_b + \frac{1}{2} \left(\log [2\pi n_b] + \frac{1}{12 n_b} \right) \tag{4.28}$$

This completes the logarithmic approximation of the terms in the enumeration function of Equation 4.18.

4.4.2 Divided Differences of Enumeration Function

The goal is to find the the critical value of surface coverage n_a^* for which the enumeration function is maximized. Recall from calculus [54] that the maximum value of the enumeration function can be found where the derivative is zero and where the enumeration function is

increasing for values less than the critical value and decreasing for value greater than the critical value of n_a^*. Another scenario is that of finding a critical value at boundary of the domain for which there are no greater values of n_a and for values less than n_a^*, the enumeration function is monotonically increasing.

In this model there are finite discrete n_a values, so in place of a derivative, a discrete approximation willl be used, which is that of divided differences [53],

$$\frac{\Delta \log \mathcal{E}}{\Delta n_a} = \frac{\log \mathcal{E}(n_a + 1) - \log \mathcal{E}(n_a)}{n_a + 1 - n_a}$$

which simplifies to $\log \mathcal{E}\,(n_a + 1) - \log \mathcal{E}\,(n_a)$. This is equivalent to $\log\left(\mathcal{E}_{n_a+1}/\mathcal{E}_{n_a}\right)$. This equivalence is useful because there are telescoping products that will cancel out in the ratio of $\mathcal{E}\,(n_a + 1)\,/\mathcal{E}\,(n_a)$ and ultimately further simplify the approximation. In order to make the equations more readable a convention has been used, where a function $f(n_a + 1)$, whose argument n_a has been incremented by 1, will be notated with a superscipted asterisk. The notation is presented in Table 4.2 below.

Function $f(x)$	Representation of $f(n_a)$	Representation of $f(n_a + 1)$
$\mathcal{F}(n_a)$	$\mathcal{F}$	$\mathcal{F}^*$
$\tilde{\omega}_j(n_a)$	$\tilde{\omega}_j$	$\tilde{\omega}_j^*$
$\mathcal{E}_{vol}(n_a)$	$\mathcal{E}_{vol}$	$\mathcal{E}_{vol}^*$
$\mathcal{E}_{lp}(n_a)$	$\mathcal{E}_{lp}$	$\mathcal{E}_{lp}^*$
$\mathcal{E}_{total}(n_a)$	$\mathcal{E}_{total}$	$\mathcal{E}_{total}^*$
$n_b(n_a)$	n_b	n_b^*
$n_{lp}(n_a)$	n_{lp}	n_{lp}^*
$\mathcal{L}(n_a)$	$\mathcal{L}$	$\mathcal{L}^*$

Table 4.2: Representations of functions of n_a and $n_a + 1$

Dividing $\mathcal{E}^*_{total}/\mathcal{E}_{total}$ results in Equation 4.29.

$$\frac{\mathcal{E}^*_{total}}{\mathcal{E}_{total}} = \frac{n!}{n!}\left(\frac{\mathcal{F}^*}{\mathcal{F}}\ \frac{\left(\mathcal{E}^*_{lp}\right)^{n^*_{lp}}}{\left(\mathcal{E}_{lp}\right)^{n_{lp}}}\ \frac{\mathcal{E}^{n^*_b}_{vol}}{\mathcal{E}^{n_b}_{vol}}\ \frac{\frac{n^{n^*_b}_{vol}}{n^{*}_b!}}{\frac{n^{n_b}_{vol}}{n_b!}}\right). \tag{4.29}$$

Let us now derive each term in Equation 4.29 separately, starting with Equation 4.30.

$$\begin{aligned}\frac{\left(\frac{n^{n^*_b}_{vol}}{n^*_b!}\right)}{\left(\frac{n^{n_b}_{vol}}{(n_b)!}\right)} &= \frac{\left(\frac{n^{n_b-1}_{vol}}{(n_b-1)!}\right)}{\left(\frac{n^{n_b}_{vol}}{n_b!}\right)} \\ &= \frac{n^{n_b-1}_{vol}\times n_b!}{n^{n_b}_{vol}\times(n_b-1)!} \\ &= n^{n_b-1-n_b}_{vol} n_b \\ &= \frac{n_b}{n_{vol}}\end{aligned} \tag{4.30}$$

Using a similar manipulation of exponents as that of n_{vol} in Equation 4.30, for $\mathcal{E}^{n^*_b}_{vol}/\mathcal{E}^{n_b}_{vol}$ result in Equation 4.31.

$$\frac{\mathcal{E}^{n^*_b}_{vol}}{\mathcal{E}^{n_b}_{vol}} = \frac{1}{\mathcal{E}_{vol}}. \tag{4.31}$$

Combining the calculations from Equations 4.30 and 4.31

$$R_{vol} := \frac{n_b}{n_{vol}}\ \frac{1}{\mathcal{E}_{vol}} \tag{4.32}$$

The calculation for the ratio of Flory factor is outlined in Equations 4.33

$$\begin{aligned}\frac{\mathcal{F}^*}{\mathcal{F}} &= \left(\frac{\prod_{j=1}^{n_a+1}\tilde{w}_j^*}{(n_a+1)!}\right)\left(\frac{\prod_{j=1}^{n_a}\tilde{w}_j}{n_a!}\right)^{-1} \\ &= \frac{n_a!\left(\prod_{j=1}^{n_a+1}\tilde{w}_j^*\right)}{(n_a+1)!\left(\prod_{j=1}^{n_a}\tilde{w}_j\right)} \\ &= \left(\frac{1}{n_a+1}\right)\left(\frac{\prod_{j=1}^{n_a+1}\tilde{w}_j^*}{\prod_{j=1}^{n_a}\tilde{w}_j}\right)\end{aligned} \tag{4.33}$$

Let $R_{\mathcal{F}}$ be the result of 4.33.

$$R_{\mathcal{F}} := \left(\frac{1}{n_a+1}\right)\left(\frac{\prod_{j=1}^{n_a+1}\tilde{w}_j^*}{\prod_{j=1}^{n_a}\tilde{w}_j}\right) \quad . \tag{4.34}$$

For the factor $\mathcal{E}_{lp}^*/\mathcal{E}_{lp}$, the derivation results in Equation 4.35.

$$\frac{(\mathcal{E}_{lp}^*)}{(\mathcal{E}_{lp})} = \frac{\begin{pmatrix}\mathcal{L}^* \\ n_{lp}^*\end{pmatrix}^{n_a+1}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{2.8}}B_3\right)^{n_{lp}^*\cdot(n_a+1)}}{\begin{pmatrix}\mathcal{L} \\ n_{lp}\end{pmatrix}^{n_a}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{2.8}}B_3\right)^{n_{lp}\cdot n_a}} \tag{4.35}$$

In Equation 4.35 the expression $n_{lp}(n_a+1)\cdot(n_a+1) - n_{lp}(n_a)\cdot(n_a)$ is simplified using

Equation 4.6.

$$\begin{aligned} n_{lp}(n_a+1)\cdot(n_a+1) - n_{lp}(n_a)\cdot(n_a) &= (n_a+1)\frac{r-\frac{n_{surf}}{n_a+1}}{(s_{lp}-1)} - n_a\frac{r-\frac{n_{surf}}{n_a}}{(s_{lp}-1)} \\ &= \frac{r\cdot(n_a+1) - \cancel{n_{surf}} - r\cdot(n_a) + \cancel{n_{surf}}}{(s_{lp}-1)} \\ &= \frac{r}{(s_{lp}-1)}\left(\cancel{n_a}+1-\cancel{n_a}\right) = \frac{r}{(s_{lp}-1)} \end{aligned} \tag{4.36}$$

Substituting the values from 4.36 into Equation 4.35 results in Equation 4.37.

$$R_{lp} := \frac{\begin{pmatrix}\mathcal{L}^* \\ n^*_{lp}\end{pmatrix}^{n_a+1}}{\begin{pmatrix}\mathcal{L} \\ n_{lp}\end{pmatrix}^{n_a}} \left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{2.8}} B_3\right)^{\frac{r}{s_{lp}-1}} \tag{4.37}$$

Combining the above results back into Equation 4.29

$$\frac{\mathcal{E}^*_{total}}{\mathcal{E}_{total}} = R_{\mathcal{F}} \times R_{lp} \times R_{vol} \tag{4.38}$$

We now proceed to the following property of logarithms,

$$\log\left(\frac{\mathcal{E}^*_{total}}{\mathcal{E}_{total}}\right) = \log(E^*_{total}) - \log(E_{total}), \tag{4.39}$$

We let,

$$\log(E^*_{total}) - \log(E_{total}) = \Delta_{n_a \to n_a+1} \log E_{total}. \tag{4.40}$$

This means that,

$$\Delta \log E_{total} = \log\left(R_{\mathcal{F}}\right) + \log\left(R_{lp}\right) + \log\left(R_{vol}\right) \tag{4.41}$$

Similarly to before, we follow a direct approach again where $\log\left[\tilde{w}_j\right]$

$$\begin{aligned} &Stirl\left[n_{surf}-j\mathcal{L}\right]-Stirl\left[n_{surf}-(j+1)\mathcal{L}\right]+\log\left[n_{surf}\right]+\log\left[q\right] \\ &-2\log\left[(q-1)\right]+\mathcal{L}\left(\log\left[q-1\right]-\log\left[n_{surf}\right]\right). \end{aligned} \tag{4.42}$$

and $\log\left[\tilde{w}_j^*\right]$ is,

$$\begin{aligned} &Stirl\left[n_{surf}-j\mathcal{L}^*\right]-Stirl\left[n_{surf}-(j+1)\mathcal{L}^*\right]+\log\left[n_{surf}\right]+\log\left[q\right] \\ &-2\log\left[(q-1)\right]+\mathcal{L}^*\left(\log\left[q-1\right]-\log\left[n_{surf}\right]\right). \end{aligned} \tag{4.43}$$

The calculation of the logarithm of $R_{\mathcal{F}}$ is that of Equation 4.44.

$$\log\left(R_{\mathcal{F}}\right)=\left(\sum_{j=1}^{n_a+1}\log\tilde{w}_j^*\right)-\left(\sum_{j=1}^{n_a}\log\tilde{w}_j\right)-\log\left(n_a+1\right) \tag{4.44}$$

We organize the expression in such a way to seperate the factors of interest,

$$\tilde{w}_k=\left(\frac{[n_{surf}-(k-1)\mathcal{L}]!}{[n_{surf}-k\mathcal{L}]!}\right)\times\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right) \tag{4.45}$$

so that $\prod_{k=1}^{n_a} \tilde{w}_k$ is that of Equation 4.46 using $n_{surf} = n_a\mathcal{L}$.

$$\begin{aligned}\prod_{k=1}^{n_a} \tilde{w}_k = &\frac{[n_{surf}]!}{[n_{surf}-\mathcal{L}]!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)\\ &\times\frac{[n_{surf}-\mathcal{L}]!}{[n_{surf}-2\mathcal{L}]!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)\\ &\vdots\\ &\times\frac{[n_{surf}-(n_a-2)\mathcal{L}]!}{[n_{surf}-(n_a-1)\,\mathcal{L}]!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)\\ &\times\frac{[n_{surf}-(n_a-1)\mathcal{L}]!}{[n_{surf}-n_a\mathcal{L}]!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)\end{aligned}$$

$$\begin{aligned}&= \frac{[n_{surf}]!}{0!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)^{n_a}\\ &= (n_{surf})!\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)^{n_a}\end{aligned} \tag{4.46}$$

Substituting Equation 4.46 into Relation 4.12 results in Equation 4.50, using $n_{surf} = (n_a + 1)\mathcal{L}^* = n_a\mathcal{L}$.

$$\mathcal{F}(n_a) = (n_{surf})! \times \frac{1}{n_a!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)^{n_a} \tag{4.47}$$

$$R_{\mathcal{F}} = \frac{(n_{surf})! \times \frac{1}{(n_a+1)!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}^*}\right)^{n_a+1}}{(n_{surf})! \times \frac{1}{n_a!}\left(n_{surf}\frac{q}{(q-1)^2}\left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}}\right)^{n_a}} \tag{4.48}$$

$$R_{\mathcal{F}} = \frac{1}{(n_a+1)} \times n_{surf} \times \frac{q}{(q-1)^2} \times \frac{\left(\frac{q-1}{n_{surf}}\right)^{(n_a+1)\mathcal{L}^*}}{\left(\frac{q-1}{n_{surf}}\right)^{(n_a)\mathcal{L}}} \tag{4.49}$$

$$R_{\mathcal{F}} = \frac{n_{surf}\, q}{(n_a + 1)(q-1)^2} \tag{4.50}$$

The logarithmic calculation of Equation 4.50 results in Equation 4.51

$$\log\left(R_{\mathcal{F}}\right) = \log\left(n_{surf}\right) + \log\left(q\right) - \log\left(n_a + 1\right) - 2\log\left(q-1\right) \tag{4.51}$$

We now proceed to derive $\log \mathbf{R_{lp}}$ from Equation 4.37.

$$\begin{aligned}
\log\left(R_{lp}\right) &= \left(n_a + 1\right)\log\begin{pmatrix}\mathcal{L}^* \\ n^*_{lp}\end{pmatrix} - \left(n_a\right)\log\begin{pmatrix}\mathcal{L} \\ n_{lp}\end{pmatrix} + \left(\frac{r}{s_{lp}-1}\right)\log\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}\frac{B_3}{\mu_3}\right) \\
&= \left(n_a + 1\right)\log\left(\frac{\mathcal{L}^*!}{\left(n^*_{lp}\right)!\left(\mathcal{L}^* - n^*_{lp}\right)!}\right) - \left(n_a\right)\log\left(\frac{\mathcal{L}!}{\left(n_{lp}\right)!\left(\mathcal{L} - n_{lp}\right)!}\right) \\
&\qquad + \left(\frac{r}{s_{lp}-1}\right)\log\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}\frac{B_3}{\mu_3}\right)
\end{aligned} \tag{4.52}$$

The expression of Equation 4.52 is quite large and in order to reduce the expression we let,

$$\mathscr{S}_{lp} := \log\left(\frac{\mathcal{L}!}{\left(n_{lp}\right)!\left(\mathcal{L} - n_{lp}\right)!}\right) \tag{4.53}$$

and similarly for $\mathscr{S}^*_{lp}$ we let,

$$\mathscr{S}^*_{lp} := \log\left(\frac{\mathcal{L}^*!}{\left(n^*_{lp}\right)!\left(\mathcal{L}^* - n^*_{lp}\right)!}\right) \tag{4.54}$$

After applying the logarithmic properties we have that

$$\mathscr{S}_{lp} = Stirl[\mathcal{L}] - Stirl[n_{lp}] - Stirl[\mathcal{L} - n_{lp}] \tag{4.55}$$

$$\mathscr{S}^*_{lp} = Stirl[\mathcal{L}^*] - Stirl\left[n^*_{lp}\right] - Stirl\left[\mathcal{L}^* - n^*_{lp}\right] \tag{4.56}$$

where the expansion for $\mathscr{S}_{lp}$ is that of Equation 4.57 and $\mathscr{S}^*_{lp}$ is that of Equation 4.58 given that $n_{lp} \neq 0$.

$$\begin{aligned}\mathscr{S}_{lp} = &\left[(\mathcal{L}) \cdot \log\left[\mathcal{L}\right] - \mathcal{L} + \frac{1}{2}\left(\log\left[2\pi\mathcal{L}\right] + \frac{1}{12\mathcal{L}}\right)\right] \\ &- \left[(n_{lp}) \cdot \log\left[n_{lp}\right] - n_{lp} + \frac{1}{2}\left(\log\left[2\pi n_{lp}\right] + \frac{1}{12n_{lp}}\right)\right] \\ &- \left[(\mathcal{L} - n_{lp}) \cdot \log\left[\mathcal{L} - n_{lp}\right] - \mathcal{L} - n_{lp} + \frac{1}{2}\left(\log\left[2\pi\mathcal{L} - n_{lp}\right] + \frac{1}{12\mathcal{L} - n_{lp}}\right)\right], \end{aligned} \tag{4.57}$$

$$\begin{aligned}\mathscr{S}^*_{lp} = &\left[(\mathcal{L}^*) \cdot \log\left[\mathcal{L}^*\right] - \mathcal{L}^* + \frac{1}{2}\left(\log\left[2\pi\mathcal{L}^*\right] + \frac{1}{12\mathcal{L}^*}\right)\right] \\ &- \left[\left(n^*_{lp}\right) \cdot \log\left[n^*_{lp}\right] - n^*_{lp} + \frac{1}{2}\left(\log\left[2\pi n^*_{lp}\right] + \frac{1}{12n^*_{lp}}\right)\right] \\ &- \left[\left(\mathcal{L}^* - n^*_{lp}\right) \cdot \log\left[\mathcal{L}^* - n^*_{lp}\right] - \mathcal{L}^* - n^*_{lp} + \frac{1}{2}\left(\log\left[2\pi\mathcal{L}^* - n^*_{lp}\right] + \frac{1}{12\mathcal{L}^* - n^*_{lp}}\right)\right] \end{aligned} \tag{4.58}$$

This results in the following expression for the ratio of consecutive loop enumerations.

$$\begin{aligned}\log\left(R_{lp}\right) = &\left(n_a + 1\right)\mathscr{S}^*_{lp} - \left(n_a\right)\mathscr{S}_{lp} \\ &+ \left(\frac{r}{s_{lp} - 1}\right)\left[s_{lp}\log\left(\mu_3\right) + \log\left(B_3\right) - \log\left[\mu_3\right] - \left(3.7\right)\log\left(s_{lp}\right)\right] \end{aligned} \tag{4.59}$$

We now calculate the logarithmic approximation of R_{vol} from Equation 4.32 in Equation 4.61.

$$\log\left(R_{vol}\right) = \log\left(\frac{n_b}{n_{vol}\mathcal{E}_{vol}}\right) \tag{4.60}$$

$$= \log\left(n_b\right) - \log\left(n_{vol}\right) - \log\left(\mathcal{E}_{vol}\right) \tag{4.61}$$

4.5 Development of Asymptotic Approximations

In order to validate the mean field model in Section 4.3, we have derived asymptotic approximations that provide information on the expected qualitative bahaviour of the mean field model. This is achieved by assuming that certain parameters of the model that have a very large relative magnitude compared to the rest of the model, will be considered to be infinite in scale. Similarly to the discrete model, we will develop an asymptotic enumeration function and then derive the derivative and compute optimal values in order to find where the enumeration is maximized. In order to develop an asymptotic model, we shall use some results around Stirling's formula [51] that state that if we have two positive sequences a_k and b_k such that

$$b_k < a_k, \tag{4.62}$$

and if

$$\frac{a_k}{k} \to S \tag{4.63}$$

and

$$\frac{b_k}{k} \to T, \tag{4.64}$$

then

$$\binom{a_k}{b_k}^{1/k} \to \frac{S^S}{(T^T(S-T)^{S-T})}. \tag{4.65}$$

We proceed to proving that Relation 4.65 given Conditions 4.62, 4.63 and 4.64.

$$\binom{a_k}{b_k}^{1/k} = \left(\frac{a_k!}{b_k!(a_k-b_k)!}\right)^{\frac{1}{k}} \tag{4.66}$$

$$\tag{4.67}$$

$$= \left(\frac{\sqrt{2\pi\, a_k}\ \frac{a_k^{a_k}}{e^{a_k}}}{\sqrt{2\pi\, b_k}\ \frac{b_k^{b_k}}{e^{b_k}}\ \sqrt{2\pi\,(a_k-b_k)}\ \frac{(a_k-b_k)^{(a_k-b_k)}}{e^{a_k-b_k}}}\right)^{\frac{1}{k}} \tag{4.68}$$

$$\tag{4.69}$$

$$= \left(\frac{a_k^{a_k}}{b_k^{b_k}\,(a_k-b_k)^{(a_k-b_k)}} \times \frac{\sqrt{a_k}\,e^{b_k}}{\sqrt{b_k}\,e^{a_k}\,\sqrt{2\pi}\,\sqrt{a_k-b_k}\,\frac{(a_k-b_k)}{e^{a_k-b_k}}}\right)^{\frac{1}{k}} \tag{4.70}$$

$$\tag{4.71}$$

$$= \left(\frac{a_k^{a_k}}{b_k^{b_k}\,(a_k-b_k)^{a_k-b_k}}\right)^{\frac{1}{k}} \left(\frac{e^{b_k}\,e^{a_k-b_k}}{e^{a_k}}\right)^{\frac{1}{k}} \left(\frac{1}{2\pi}\right)^{\frac{1}{2k}} \left(\left(\frac{a_k}{b_k\,(a_k-b_k)}\right)^{\frac{1}{2}}\right)^{\frac{1}{k}} \tag{4.72}$$

$$\tag{4.73}$$

$$= \underbrace{\left(\frac{a_k^{a_k}}{b_k^{b_k}\,(a_k-b_k)^{(a_k-b_k)}}\right)^{\frac{1}{k}}}_{\text{factor 1}} \underbrace{\left(\cancel{e^{b_k+(a_k-b_k)-a_k}}^{\,e^0=1}\right)^{\frac{1}{k}}}_{\text{factor 2}} \underbrace{\left(\frac{1}{2\pi}\right)^{\frac{1}{2k}}}_{\text{factor 3}} \underbrace{\left(\frac{a_k}{b_k\,(a_k-b_k)}\right)^{\frac{1}{2k}}}_{\text{factor 4}} \tag{4.74}$$

$$= \underbrace{\left(\frac{a_k^{a_k}}{b_k^{b_k}\,(a_k-b_k)^{(a_k-b_k)}}\right)^{\frac{1}{k}}}_{\text{factor 1}} \underbrace{1^{\frac{1}{k}}}_{\text{factor 2}} \underbrace{[\mathbf{\Theta}(CONST.)]^{\frac{1}{k}}}_{\text{factor 3}} \underbrace{[\mathbf{\Theta}(a_k,b_k)]^{\frac{1}{2k}}}_{\text{factor 4}} \tag{4.75}$$

For factor 4, we use the fact that

$$(k)^{\frac{1}{k}} \xrightarrow{k\to\infty} 1 \tag{4.76}$$

For factor 3, the term inside the bracket is a constant, we can state that

$$[CONST.]^{\frac{1}{k}} \xrightarrow{k\to\infty} 1 \tag{4.77}$$

for any positive constant. We return to the proof of Relation 4.65, where we substitute Relation 4.76 and Relation 4.77 into Relation 4.75, and then expand factor 1, which yields Equation 4.78.

$$\binom{a_k}{b_k}^{1/k} = \left(\frac{a_k^{a_k}}{b_k^{b_k}\,(a_k-b_k)^{(a_k-b_k)}}\right)^{\frac{1}{k}} = \frac{a_k^{\frac{a_k}{k}}}{b_k^{\frac{b_k}{k}}\,(a_k-b_k)^{\frac{(a_k-b_k)}{k}}} \quad \frac{k^{\frac{1}{\frac{a_k}{k}}}}{k^{\frac{b_k}{k}}\;k^{\frac{a_k-b_k}{k}}}$$

$$= \frac{\left[\left(\frac{1}{k}\right)^{\frac{a_k}{k}} \quad a_k^{\frac{a_k}{k}}\right]}{\left[\left(\frac{1}{k}\right)^{\frac{a_k}{k}} \quad b_k^{\frac{b_k}{k}}\right]\left[\left(\frac{1}{k}\right)^{\frac{a_k-b_k}{k}} \quad (a_k-b_k)^{\frac{(a_k-b_k)}{k}}\right]}$$

$$= \frac{\left(\frac{a_k}{k}\right)^{\frac{a_k}{k}}}{\left(\frac{b_k}{k}\right)^{\frac{b_k}{k}}\;\left(\frac{a_k-b_k}{k}\right)^{\frac{a_k-b_k}{k}}}$$

$$= \frac{\left(\frac{a_k}{k}\right)^{\frac{a_k}{k}}}{\left(\frac{b_k}{k}\right)^{\frac{b_k}{k}}\;\left(\frac{a_k}{k}-\frac{b_k}{k}\right)^{\frac{a_k}{k}-\frac{b_k}{k}}} \tag{4.78}$$

Based on Relations 4.63 and 4.64, the relation converges in agreement with Relation 4.65.

$$\binom{a_k}{b_k}^{1/k} \to \frac{S^S}{T^T\;(S-T)^{S-T}} \tag{4.79}$$

We have now proven this and shall use the result of 4.79 in our asymptotic model.

In order to find a limit for $\log\left(\mathcal{E}^*_{total}/\mathcal{E}_{total}\right)$, we first look at the core quantities of n_{surf} and n_{vol}. We assume n, n_a and n_b fixed as $r \to \infty$. We also let

$$n_{surf} \to \infty$$

$$n_{vol} \to \infty$$

whilst ensuring that they remain proportional to r, for some positive finite constants C and D we have that,

$$\lim_{n_{surf}\to\infty} \frac{n_{surf}}{r} = C \tag{4.80}$$

and

$$\lim_{n_{vol}\to\infty} \frac{n_{vol}}{r} = D. \tag{4.81}$$

The constant C will be the minimum value of n_a, which in this case is 23, as that is the minimum number of polymers that can be on the surface such that a state of full surface coverage is maintained.

We also get

$$\frac{\mathcal{L}}{r} \to \frac{C}{n_a}. \tag{4.82}$$

We find that Equation 4.6 gives us Relation 4.83.

$$\frac{n_{lp}}{r} \to \frac{1 - \left(\frac{C}{n_a}\right)}{s_{lp} - 1} \tag{4.83}$$

We proceed to calculate the limit of the total enumeration divided by r.

$$\lim_{r\to\infty} \left\{ \left(\frac{1}{r}\right) \mathcal{E}_{total} \right\} \tag{4.84}$$

Obtaining the answer as a function of n_a that only uses logs and algebra, allows one to differentiate the answer and determine what the maximum value of n_a is.

Recall that

$$\frac{n_{surf}}{r} \to C.$$

So for a first approximation,

$$n_{surf} \approx rC.$$

Then

$$\left(\frac{1}{r}\right) log(n_{surf})$$

becomes

$$\left(\frac{1}{r}\right) log(rC) = \left(\frac{1}{r}\right) log(r) + \left(\frac{1}{r}\right) log(C). \tag{4.85}$$

Now the term $\log(C)/r$ in Relation 4.86 goes to zero, because the numerator is constant.

$$\frac{log(C)}{r} \xrightarrow{r\to\infty} 0 \tag{4.86}$$

We can then apply l'Hospital's Rule to the first term in Relation 4.85, obtaining

$$\lim_{r\to\infty} \frac{log(r)}{r} = \lim_{r\to\infty} \frac{\frac{1}{r}}{1} = 0.$$

To make this formalize this further, we write

$$\left(\frac{1}{r}\right) \log(n_{surf}) = \left(\frac{1}{r}\right) \log\left(r\frac{n_{surf}}{r}\right) = \left(\frac{1}{r}\right) log(r) + \left(\frac{1}{r}\right) log\left(\frac{n_{surf}}{r}\right)$$

which converges to $0 + 0$, exactly as above, since

$$\frac{n_{surf}}{r} \xrightarrow{r\to\infty} CONSTANT.$$

Without the logarithm, the reasoning is similar:

$$(n_{surf})^{\frac{1}{r}}$$

is approximately,

$$(rC)^{\frac{1}{r}} = r^{\frac{1}{r}} C^{\frac{1}{r}} \xrightarrow{r\to\infty} 1,$$

The fact that

$$r^{\frac{1}{r}} \xrightarrow{r\to\infty} 1$$

is equivalent to

$$\left(\frac{1}{r}\right)\log(r) \xrightarrow{r\to\infty} 0$$

is because

$$\log\left(r^{\frac{1}{r}}\right) = \left(\frac{1}{r}\right)\log(r).$$

For the calculation of the limits of the enumeration overall, we use Equation 4.17.

$$\mathcal{E}_{total} = n!\left(\mathcal{F}(n_a)\ \mathcal{E}_{lp}^{n_a}\ \mathcal{E}_{vol}^{n_b}\ \frac{n_{vol}^{n_b}}{n_b!}\right) \qquad \text{From Equation 4.17}$$

Taking the limits in order to do the asymptotic analysis we have the following.

$$\lim_{r\to\infty}\{\mathcal{E}_{total}\}^{\frac{1}{r}} = \lim_{r\to\infty}\{n!\}^{\frac{1}{r}} \times \lim_{r\to\infty}\{\mathcal{F}(n_a)\}^{\frac{1}{r}} \times \lim_{r\to\infty}\left\{\mathcal{E}_{lp}^{n_a}\right\}^{\frac{1}{r}} \times \lim_{r\to\infty}\{\mathcal{E}_{vol}^{n_b}\}^{\frac{1}{r}} \times \lim_{r\to\infty}\left\{\frac{n_{vol}^{n_b}}{n_b!}\right\}^{\frac{1}{r}}$$

Now let us look at each of the above factors individually, and begin with the simple quantities first, namely $\{n!\}^{\frac{1}{r}}$, $\left\{\frac{(n_{vol})^{n_b}}{n_b!}\right\}^{\frac{1}{r}}$ and, $\{\mathcal{E}_{vol}\}^{\frac{1}{r}}$

$$\{n!\}^{\frac{1}{r}} \xrightarrow{r\to\infty} 1$$

$\frac{n_{vol}^{n_b}}{n_b!}$, splits into,

$$(n_{vol})^{\frac{n_b}{r}} \approx \left((D\times r)^{\frac{1}{r}}\right)^{n_b} = \left(D^{\frac{1}{r}} \times r^{\frac{1}{r}}\right)^{n_b} \xrightarrow{r\to\infty} 1^{n_b} = 1$$

and,

$$\frac{1}{(n_b!)^{\frac{1}{r}}} \xrightarrow{r\to\infty} 1$$

Lastly $\{\mathcal{E}_{vol}\}^{\frac{1}{r}}$,

$$\{\mathcal{E}_{vol}\}^{\frac{1}{r}} = (A_3 \cdot (\mu_3)^r)^{\frac{1}{r}} \xrightarrow{r\to\infty} \mu_3$$

The factor $\left\{\mathcal{E}_{lp}^{n_a}\right\}^{\frac{1}{r}}$ is more involved and will require further expansion into its respective factors

$$\begin{aligned}
\lim_{r\to\infty}\left\{\mathcal{E}_{lp}^{n_a}\right\}^{\frac{1}{r}} &= \lim_{r\to\infty}\left\{\left[\binom{\mathcal{L}}{n_{lp}}^{\frac{1}{r}}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right)^{n_{lp}}\right]^{n_a}\right\}^{\frac{1}{r}} \qquad \text{From Equation 4.16} \\
&= \lim_{r\to\infty}\left[\binom{\mathcal{L}}{n_{lp}}^{\frac{1}{r}}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right)^{\frac{n_{lp}}{r}}\right]^{n_a} \qquad (4.87)
\end{aligned}$$

From expression 4.82 and 4.83 above, we have that,

$$\frac{\mathcal{L}}{r} \xrightarrow{r\to\infty} \frac{C}{n_a} \qquad (4.88)$$

$$\frac{n_{lp}}{r} \xrightarrow{r\to\infty} \frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1} \qquad (4.89)$$

So using the above relations we calculate the following,

$$\binom{\mathcal{L}}{n_{lp}}^{\frac{1}{r}} \rightarrow \frac{\left(\frac{C}{n_a}\right)^{\frac{C}{n_a}}}{\left[\frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1}\right]^{\left(\frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1}\right)} \times \left[\left(\frac{C}{n_a}\right)-\left(\frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1}\right)\right]^{\left(\frac{C}{n_a}\right)-\left(\frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1}\right)}} \tag{4.90}$$

$$= \frac{\left(\frac{C}{n_a}\right)^{\frac{C}{n_a}}}{\left[\frac{n_a-C}{n_a(s_{lp}-1)}\right]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times \left[\frac{C\,s_{lp}-n_a}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)}} \tag{4.91}$$

$$= \frac{\left(\frac{C}{n_a}\right)^{\frac{C}{n_a}}}{[n_a-C]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times [C\,s_{lp}-n_a]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)} \times \left[\frac{1}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)+\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)}} \tag{4.92}$$

$$= \frac{[(s_{lp}-1)\,C]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)} \times \left(\frac{1}{n_a(s_{lp}-1)}\right)^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)}}{[n_a-C]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times [C\,s_{lp}-n_a]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)} \times \left[\frac{1}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)+\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)}} \tag{4.93}$$

$$= \frac{[s_{lp}-1]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)} \times \left(\frac{C}{n_a(s_{lp}-1)}\right)^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)}}{\left[\frac{n_a}{C}-1\right]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times \left[s_{lp}-\frac{n_a}{C}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)} \times \left[\frac{C}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)+\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)}} \tag{4.94}$$

$$= \frac{[s_{lp}-1]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)}}{\left[\frac{n_a}{C}-1\right]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times \left[s_{lp}-\frac{n_a}{C}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)}} \times \left[\frac{C}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)-\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)-\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \tag{4.95}$$

$$= \frac{[s_{lp}-1]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)}}{\left[\frac{n_a}{C}-1\right]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times \left[s_{lp}-\frac{n_a}{C}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)}} \times \left[\frac{C}{n_a\,(s_{lp}-1)}\right]^{\left(\frac{s_{lp}C-C-C\,s_{lp}+n_a-n_a+C}{n_a\left(s_{lp}-1\right)}\right)} \tag{4.96}$$

$$= \frac{[s_{lp}-1]^{\left(\frac{\left(s_{lp}-1\right)C}{n_a\left(s_{lp}-1\right)}\right)}}{\left[\frac{n_a}{C}-1\right]^{\left(\frac{n_a-C}{n_a\left(s_{lp}-1\right)}\right)} \times \left[s_{lp}-\frac{n_a}{C}\right]^{\left(\frac{C\,s_{lp}-n_a}{n_a\left(s_{lp}-1\right)}\right)}} \times \left[\frac{C}{n_a\,(s_{lp}-1)}\right]^{0} \tag{4.97}$$

The above expression converges to,

$$\binom{\mathcal{L}}{n_{lp}}^{\frac{1}{r}} \rightarrow \left(\frac{[s_{lp}-1]^{\left(s_{lp}-1\right)C}}{\left[\frac{n_a}{C}-1\right]^{n_a-C} \times \left[s_{lp}-\frac{n_a}{C}\right]^{C\,s_{lp}-n_a}}\right)^{\frac{1}{n_a\left(s_{lp}-1\right)}} \tag{4.98}$$

In order to calculate $\{\mathcal{F}(n_a)\}^{\frac{1}{r}}$, we must compute the limit of the quantities, it is comprised of. In this case we have,

$$\mathcal{F}(n_a) := \frac{\tilde{w}_1 \tilde{w}_2 \cdots \tilde{w}_{n_a}}{n_a!}. \tag{4.99}$$

So the quantities are namely, $\{\tilde{w}_k\}^{\frac{1}{r}}$ and, $\{n_a!\}^{\frac{1}{r}}$ The case of $n_a!$ is trivial ie;

$$\{n_a!\}^{\frac{1}{r}} \xrightarrow{r\to\infty} \{n_a!\}^{\frac{1}{r}} = \{n_a!\}^0 = 1 \tag{4.100}$$

Now for $\tilde{w}_k$, we have that,

$$\tilde{w}_k = \frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!} n_{surf} \frac{q}{(q-1)^2} \left(\frac{q-1}{n_{surf}}\right)^{\mathcal{L}} \tag{4.101}$$

Upon examination we determine that,

$$\left(\frac{[n_{surf} - (k-1)\mathcal{L}]!}{[n_{surf} - k\mathcal{L}]!}\right) = \binom{n_{surf} - (k-1)\mathcal{L}}{n_{surf} - k\mathcal{L}}^{\frac{1}{r}} \times \{[n_{surf} - (k-1)\mathcal{L} - (n_{surf} - k\mathcal{L})]!\}^{\frac{1}{r}} \tag{4.102}$$

$$= \binom{n_{surf} - (k-1)\mathcal{L}}{n_{surf} - k\mathcal{L}}^{\frac{1}{r}} \times \{\mathcal{L}!\}^{\frac{1}{r}} \tag{4.103}$$

This means that the limit of the above is the following,

$$\lim_{r\to\infty} \tilde{w}_k^{\frac{1}{r}} = \lim_{r\to\infty} \left\{ \binom{n_{surf} - (k-1)\mathcal{L}}{n_{surf} - k\mathcal{L}} \times \mathcal{L}! \right\}^{\frac{1}{r}} \times \lim_{r\to\infty} \{n_{surf}\}^{\frac{1}{r}} \tag{4.104}$$

$$\times \lim_{r\to\infty} \{q\}^{\frac{1}{r}} \times \lim_{r\to\infty} \left\{ \frac{1}{(q-1)^2} \right\}^{\frac{1}{r}} \times \lim_{r\to\infty} \left\{ (q-1)^{\mathcal{L}} \right\}^{\frac{1}{r}} \times \left\{ \left(\frac{1}{n_{surf}} \right)^{\mathcal{L}} \right\}^{\frac{1}{r}} \tag{4.105}$$

Rearranging the $\mathcal{L}!$ in the first factor and appending it to the final factor we get,

$$\lim_{r\to\infty} \tilde{w}_k^{\frac{1}{r}} = \lim_{r\to\infty} \left\{ \binom{n_{surf} - (k-1)\mathcal{L}}{n_{surf} - k\mathcal{L}} \right\}^{\frac{1}{r}} \times \lim_{r\to\infty} \{n_{surf}\}^{\frac{1}{r}} \tag{4.106}$$

$$\times \lim_{r\to\infty} \{q\}^{\frac{1}{r}} \times \lim_{r\to\infty} \left\{ \frac{1}{(q-1)^2} \right\}^{\frac{1}{r}} \times \lim_{r\to\infty} \left\{ (q-1)^{\mathcal{L}} \right\}^{\frac{1}{r}} \times \lim_{r\to\infty} \left\{ \left(\frac{1}{n_{surf}} \right)^{\mathcal{L}} \times \mathcal{L}! \right\}^{\frac{1}{r}} \tag{4.107}$$

We once more break this expression into its factors and compute them individually,
We shift our focus to $\binom{n_{surf}-(k-1)\mathcal{L}}{n_{surf}-k\mathcal{L}}^{\frac{1}{r}}$ where we have the following relations based on the work in Relations 4.82 and 4.80.

$$\frac{1}{r}\left[n_{surf} - (k-1)\mathcal{L}\right] \xrightarrow{r\to\infty} \left(1 - \frac{k-1}{n_a}\right) \times C \tag{4.108}$$

$$\frac{1}{r}\left[n_{surf} - k\mathcal{L}\right] \xrightarrow{r\to\infty} \left(1 - \frac{k}{n_a}\right) \times C \tag{4.109}$$

Now using the Relation 4.79, we get the following result for $\lim_{r\to\infty} \binom{n_{surf}-(k-1)\mathcal{L}}{n_{surf}-k\mathcal{L}}^{\frac{1}{r}}$.

$$\frac{\left[\left(1 - \frac{k-1}{n_a}\right) \times C\right]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{\left[\left(1 - \frac{k}{n_a}\right) \times C\right]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]} \times \left\{\left[\left(1 - \frac{k-1}{n_a}\right) \times C\right] - \left[\left(1 - \frac{k}{n_a}\right) \times C\right]\right\}^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right] - \left[\left(1-\frac{k}{n_a}\right)\times C\right]}} \tag{4.110}$$

We focus on a significant component here which shows up repeatedly in 4.110.

$$\begin{aligned}\left[\left(1 - \frac{k-1}{n_a}\right) \times C\right] - \left[\left(1 - \frac{k}{n_a}\right) \times C\right] &= C \times \left[\left(1 - \frac{k-1}{n_a}\right) - \left(1 - \frac{k}{n_a}\right)\right] \\ &= C \times \left[\cancel{1} - \cancel{\frac{k}{n_a}} + \frac{1}{n_a} \cancel{-1} + \cancel{\frac{k}{n_a}}\right] \\ &= \frac{C}{n_a}\end{aligned} \tag{4.111}$$

So then Relation 4.110 simplifies as follows.

$$\begin{aligned}
\binom{n_{surf}-(k-1)\mathcal{L}}{n_{surf}-k\mathcal{L}}^{\frac{1}{r}} &\rightarrow \frac{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{\left[\left(1-\frac{k}{n_a}\right)\times C\right]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]}\times\left[\frac{C}{n_a}\right]^{\frac{C}{n_a}}} \\
&\rightarrow \frac{[n_a-(k-1)]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{[(n_a-k)]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]}}\times\left(\frac{C}{n_a}\right)^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]-\frac{C}{n_a}-\left[\left(1-\frac{k}{n_a}\right)\times C\right]} \\
&\rightarrow \frac{[n_a-(k-1)]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{[(n_a-k)]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]}}\times\left(\frac{C}{n_a}\right)^{\frac{C}{n_a}-\frac{C}{n_a}} \quad \text{From Equation 4.111} \\
&\rightarrow \frac{[n_a-(k-1)]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{[(n_a-k)]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]}}\times\left(\frac{C}{n_a}\right)^{0} \\
&\rightarrow \frac{[n_a-(k-1)]^{\left[\left(1-\frac{k-1}{n_a}\right)\times C\right]}}{[(n_a-k)]^{\left[\left(1-\frac{k}{n_a}\right)\times C\right]}} \qquad (4.112)
\end{aligned}$$

Let's briefly focus on, $(\mathcal{L}!)^{\frac{1}{r}}$. Using Stirling's approximation we get,

$$(\mathcal{L}!)^{\frac{1}{r}} \approx \left(\frac{\sqrt{2\pi\mathcal{L}}}{e^{\mathcal{L}}}\times\mathcal{L}^{\mathcal{L}}\right)^{\frac{1}{r}} \qquad (4.113)$$

$$= \left(\frac{\sqrt{2\pi\mathcal{L}}}{e^{\mathcal{L}}}\right)^{\frac{1}{r}}\times(\mathcal{L})^{\frac{\mathcal{L}}{r}} \qquad (4.114)$$

In order to make the below limit on the left hand side of Relation 4.115 computable we further simplify the right-hand-side using $n_{surf} = \mathcal{L}n_a$ and $\mathcal{L}/r \rightarrow C/n_a$. This is all shown

step-by-step in Relations 4.115 to 4.118.

$$\lim_{r\to\infty}\left\{\left(\frac{1}{n_{surf}}\right)^{\mathcal{L}}\times\mathcal{L}!\right\}^{\frac{1}{r}}=\lim_{r\to\infty}\left\{\left(\frac{\sqrt{2\pi\mathcal{L}}}{e^{\mathcal{L}}}\right)^{\frac{1}{r}}\times\frac{\mathcal{L}^{\frac{\mathcal{L}}{r}}}{\mathcal{L}^{\frac{\mathcal{L}}{r}}}\times\left(\frac{1}{n_a}\right)^{\frac{\mathcal{L}}{r}}\right\} \tag{4.115}$$

$$=\lim_{r\to\infty}\left\{\left((2\pi)^{\frac{1}{2r}}\times(\mathcal{L})^{\frac{1}{2r}}\times\frac{1}{e^{\frac{\mathcal{L}}{r}}}\right)\times\frac{\mathcal{L}^{\frac{\mathcal{L}}{r}}}{\mathcal{L}^{\frac{\mathcal{L}}{r}}}\times\left(\frac{1}{n_a}\right)^{\frac{\mathcal{L}}{r}}\right\} \tag{4.116}$$

$$=\left\{\left((2\pi)^{0}\times\left(C^{0}\times\frac{1}{(n_a)^{0}}\right)\times\frac{1}{e^{\frac{C}{n_a}}}\right)\times\frac{\cancel{\mathcal{L}^{\frac{\mathcal{L}}{r}}}}{\cancel{\mathcal{L}^{\frac{\mathcal{L}}{r}}}}\times\frac{1}{(n_a)^{\frac{C}{n_a}}}\right\} \tag{4.117}$$

$$=\left(\frac{1}{e\times n_a}\right)^{\frac{C}{n_a}}. \tag{4.118}$$

So putting all this together we get,

$$\lim_{r\to\infty}\tilde{w}_k^{\frac{1}{r}}\approx\left(\frac{[n_a-(k-1)]^{\left(1-\frac{k-1}{n_a}\right)}}{[(n_a-k)]^{\left[1-\frac{k}{n_a}\right]}}\times\left(\frac{q-1}{e\ n_a}\right)^{\frac{1}{n_a}}\right)^{C} \tag{4.119}$$

$$=\left(\frac{(q-1)\,[n_a-(k-1)]^{(n_a-k+1)}}{(e\ n_a)\,(n_a-k)^{[n_a-k]}}\right)^{\frac{C}{n_a}} \tag{4.120}$$

Here we obtain the subcalculations needed for finding $\mathcal{F}(n_a)$.

$$\lim_{r\to\infty}\{n_{surf}\}^{\frac{1}{r}}=1 \tag{4.121}$$

$$\lim_{r\to\infty}\{q\}^{\frac{1}{r}}=q^{0}=1 \tag{4.122}$$

$$\lim_{r\to\infty}\left\{\frac{1}{(q-1)^2}\right\}^{\frac{1}{r}}=\left\{\frac{1}{(q-1)^2}\right\}^{0}=\frac{1^0}{(q-1)^{2\times0}}=\frac{1^0}{(q-1)^0}=1 \tag{4.123}$$

$$\lim_{r\to\infty}\left\{(q-1)^{\mathcal{L}}\right\}^{\frac{1}{r}}=\{(q-1)\}^{\frac{\mathcal{L}}{r}}=(q-1)^{\frac{C}{n_a}} \tag{4.124}$$

$$\lim_{r\to\infty}\left\{\left(\frac{1}{n_{surf}}\right)^{\mathcal{L}}\times\mathcal{L}!\right\}^{\frac{1}{r}}=\left(\frac{1}{e\times n_a}\right)^{\frac{C}{n_a}}\qquad\text{by 4.114} \tag{4.125}$$

Having computed the above quantities we can proceed to computing $\lim_{r\to\infty}\{\mathcal{F}(n_a)\}^{\frac{1}{r}}$, finally.

$$\begin{aligned}\lim_{r\to\infty}\{\mathcal{F}(n_a)\}^{\frac{1}{r}} &= \lim_{r\to\infty}\left\{\frac{\tilde{w}_1\tilde{w}_2\cdots\tilde{w}_{n_a}}{n_a!}\right\}^{\frac{1}{r}}\\ &= \lim_{r\to\infty}\{\tilde{w}_1\tilde{w}_2\cdots\tilde{w}_{n_a}\}^{\frac{1}{r}}\end{aligned}$$

$$= \left(\frac{(q-1)\,[n_a]^{(n_a)}}{(e\ n_a)\,(n_a-1)^{[n_a-1]}}\right)^{\frac{C}{n_a}}\left(\frac{(q-1)\,[n_a-1]^{(n_a-1)}}{(e\ n_a)\,(n_a-2)^{[n_a-2]}}\right)^{\frac{C}{n_a}}\left(\frac{(q-1)\,[n_a-2]^{(n_a-2)}}{(e\ n_a)\,(n_a-3)^{[n_a-3]}}\right)^{\frac{C}{n_a}}\cdots\left(\frac{(q-1)\,[n_a-[n_a-1]]^{(n_a-[n_a-1])}}{(e\ n_a)\,(n_a-n_a)^{[n_a-n_a]}}\right)^{\frac{C}{n_a}}$$

$$= \left(\frac{(q-1)\,[n_a]^{(n_a)}}{(e\ n_a)\,\cancel{(n_a-1)^{[n_a-1]}}}\times\frac{(q-1)\,\cancel{[n_a-1]^{(n_a-1)}}}{(e\ n_a)\,\cancel{(n_a-2)^{[n_a-2]}}}\times\frac{(q-1)\,\cancel{[n_a-2]^{(n_a-2)}}}{(e\ n_a)\,\cancel{(n_a-3)^{[n_a-3]}}}\cdots\frac{(q-1)\,[n_a-[n_a-1]]^{(n_a-[n_a-1])}}{(e\ n_a)\,(n_a-n_a)^{[n_a-n_a]}}\right)^{\frac{C}{n_a}}$$

$$\begin{aligned}&= \left(\frac{(q-1)^{n_a}}{(e)^{n_a}}\right)^{\frac{C}{n_a}}\\ &= \left(\frac{q-1}{e}\right)^{C}\end{aligned}\tag{4.126}$$

Recall that we have the following function for the enumeration of our system.

$$\lim_{r\to\infty}\{\mathcal{E}_{total}\}^{\frac{1}{r}} = \lim_{r\to\infty}\{\mathcal{F}(n_a)\}^{\frac{1}{r}}\times\lim_{r\to\infty}\left\{\mathcal{E}_{lp}^{n_a}\right\}^{\frac{1}{r}}\times\lim_{r\to\infty}\{\mathcal{E}_{vol}^{n_b}\}^{\frac{1}{r}}$$

We proceed to break this down in the below three factors in order to calculate their respective limits using Relations 4.83, 4.87 and 4.98.

$$\lim_{r\to\infty}\{\mathcal{E}_{vol}\}^{\frac{1}{r}} = \mu_3\tag{4.127}$$

$$\lim_{r\to\infty}\left\{\mathcal{E}_{lp}^{n_a}\right\}^{\frac{1}{r}} = \left[\left(\frac{\left[s_{lp}-1\right]^{\left(s_{lp}-1\right)C}}{\left[\frac{n_a}{C}-1\right]^{n_a-C}\times\left[s_{lp}-\frac{n_a}{C}\right]^{C\,s_{lp}-n_a}}\right)^{\frac{1}{n_a\left(s_{lp}-1\right)}}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right)^{\frac{1-\left(\frac{C}{n_a}\right)}{s_{lp}-1}}\right]^{n_a} \tag{4.128}$$

$$= \left(\frac{\left[s_{lp}-1\right]^{\left(s_{lp}-1\right)C}}{\left[\frac{n_a}{C}-1\right]^{n_a-C}\times\left[s_{lp}-\frac{n_a}{C}\right]^{C\,s_{lp}-n_a}}\right)^{\frac{1}{s_{lp}-1}}\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right)^{\frac{n_a-C}{s_{lp}-1}} \tag{4.129}$$

Finally, we have that $\lim_{r\to\infty}\left\{\mathcal{E}_{total}\right\}^{\frac{1}{r}}$ is equal to,

$$\left[\left(\frac{\left[s_{lp}-1\right]^{\left(s_{lp}-1\right)C}}{\left[\frac{n_a}{C}-1\right]^{n_a-C}\times\left[s_{lp}-\frac{n_a}{C}\right]^{C\,s_{lp}-n_a}}\right)\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right)^{n_a-C}\right]^{\frac{1}{s_{lp}-1}}\times\left(\frac{q-1}{e}\right)^{C}\times\mu_3^{n_b}. \tag{4.130}$$

Let us now proceed to deriving the logarithm of $\left[\lim_{r\to\infty}\left\{\mathcal{E}_{total}\right\}^{\frac{1}{r}}\right]$, starting from the logarithm of the first term of Equation 4.130 the first term above would be the result of 4.131.

$$\begin{aligned}&\left(\frac{1}{s_{lp}-1}\right)\times\log\left(\frac{\left[s_{lp}-1\right]^{\left(s_{lp}-1\right)C}}{\left[\frac{n_a}{C}-1\right]^{n_a-C}\times\left[s_{lp}-\frac{n_a}{C}\right]^{C\,s_{lp}-n_a}}\right)\\ =&\left(\frac{1}{s_{lp}-1}\right)\times\Bigg(\left[\left(s_{lp}-1\right)C\right]\times\log\left[s_{lp}-1\right]\\ &\qquad-\left(n_a-C\right)\times\log\left[\frac{n_a}{C}-1\right]\\ &\qquad-\left(C\,s_{lp}-n_a\right)\times\log\left[s_{lp}-\frac{n_a}{C}\right]\Bigg)\end{aligned} \tag{4.131}$$

Similarly the second term would be found to be that of Relation 4.5.

$$\left(\frac{n_a-C}{s_{lp}-1}\right)\times\log\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}}B_3\right) = \left(\frac{n_a-C}{s_{lp}-1}\right)\times\left(s_{lp}\times\log\mu_3-3.7\times\log s_{lp}+\log B_3\right)$$

The third is computed to be that of Relation 4.132.

$$(n_b) \times \log \mu_3. \tag{4.132}$$

Finally the logarithm of the fourth term is that of Relation 4.133.

$$C \times \log\left(\frac{q-1}{e}\right) = C \times (\log(q-1) - \log(e)) \tag{4.133}$$

This give us,

$$\begin{aligned}
\log\left[\lim_{r\to\infty}\{\mathcal{E}_{total}\}^{\frac{1}{r}}\right] = \left(\frac{1}{s_{lp}-1}\right) \times \Bigg(& [(s_{lp}-1)\,C] \times \log[s_{lp}-1] \\
& - (n_a - C) \times \log\left[\frac{n_a}{C} - 1\right] \\
& - C\left(s_{lp} - \frac{n_a}{C}\right) \times \log\left[s_{lp} - \frac{n_a}{C}\right] \Bigg) \\
& + \left(\frac{n_a - C}{s_{lp}-1}\right) \times (s_{lp} \times \log \mu_3 - 3.7 \times \log s_{lp} + \log B_3) \\
& + C \times (\log(q-1) - \log(e)) \\
& + (n - n_a) \times \log \mu_3
\end{aligned} \tag{4.134}$$

We proceed to differentiating Equation 4.134 which yields Equation 4.135

$$\begin{aligned}
& \frac{d}{dn_a}\left(\log\left[\lim_{r\to\infty}\{\mathcal{E}_{total}\}^{\frac{1}{r}}\right]\right) = \\
& \left(\frac{\not{C}}{s_{lp}-1}\right) \times \left(\frac{1}{\not{C}}\right) \times \left\{-1 - \log\left[\frac{n_a}{C} - 1\right] + 1 + \log\left[s_{lp} - \frac{n_a}{C}\right]\right\} \\
& + \left(\frac{1}{s_{lp}-1}\right) \times (s_{lp} \times \log \mu_3 - 3.7 \times \log s_{lp} + \log B_3) \\
& - \log \mu_3
\end{aligned} \tag{4.135}$$

Simplifying further we get Equation 4.136.

$$\frac{d}{dn_a}\left(\log\left[\lim_{r\to\infty}\{\mathcal{E}_{total}\}^{\frac{1}{r}}\right]\right) = \left(\frac{1}{s_{lp}-1}\right)\times\Bigg(-\log\left[\frac{n_a}{C}-1\right] + \log\left[s_{lp}-\frac{n_a}{C}\right] + s_{lp}\times\log\mu_3 - 3.7\times\log s_{lp} + \log B_3\Bigg) - \log\mu_3 \tag{4.136}$$

We will set the derivative approximation of Equation 4.136 to zero and attempt to calculate the critical point n_a^* for which the enumeration is maximized.

$$\left(\tfrac{1}{s_{lp}-1}\right)\times\left(-\log\left[\tfrac{n_a}{C}-1\right]+\log\left[s_{lp}-\tfrac{n_a}{C}\right]+s_{lp}\times\log\mu_3-3.7\times\log s_{lp}+\log B_3\right)-\log\mu_3=0$$

$$\left(\tfrac{1}{s_{lp}-1}\right)\times\left(-\log\left[\tfrac{n_a}{C}-1\right]+\log\left[s_{lp}-\tfrac{n_a}{C}\right]+s_{lp}\times\log\mu_3-3.7\times\log s_{lp}+\log B_3\right)=\log\mu_3$$

$$\left(-\log\left[\tfrac{n_a}{C}-1\right]+\log\left[s_{lp}-\tfrac{n_a}{C}\right]+s_{lp}\times\log\mu_3-3.7\times\log s_{lp}+\log B_3\right)=\log\mu_3\times(s_{lp}-1)$$

$$-\log\left[\tfrac{n_a}{C}-1\right]+\log\left[s_{lp}-\tfrac{n_a}{C}\right]=-s_{lp}\times\log\mu_3+3.7\times\log s_{lp}-\log B_3+\log\mu_3\times(s_{lp}-1)$$

$$\log\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right]=-s_{lp}\times\log\mu_3+3.7\times\log s_{lp}-\log B_3+\log\mu_3\times(s_{lp}-1)$$

$$\exp\left\{\log\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right]\right\}=\exp\left\{-s_{lp}\times\log\mu_3+3.7\times\log s_{lp}-\log B_3+\log\mu_3\times(s_{lp}-1)\right\}$$

$$\exp\left\{\log\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right]\right\}=\exp\left\{-s_{lp}\times\log\mu_3\right\}\times\exp\left\{3.7\times\log s_{lp}\right\}\times\exp\left\{-\log B_3\right\}\times\exp\left\{(s_{lp}-1)\times\log\mu_3\right\}$$

$$\exp\left\{\log\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right]\right\} = \exp\left\{\log \mu_3^{-s_{lp}}\right\} \times \exp\left\{\log s_{lp}^{3.7}\right\} \times \exp\left\{-\log B_3\right\} \times \exp\left\{\log\left[\mu_3^{(s_{lp}-1)}\right]\right\}$$

$$\exp\left\{\log\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right]\right\} = \exp\left\{\log \mu_3^{-s_{lp}}\right\} \times \exp\left\{\log s_{lp}^{3.7}\right\} \times \exp\left\{\log B_3^{-1}\right\} \times \exp\left\{\log\left[\mu_3^{(s_{lp}-1)}\right]\right\}$$

$$\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right] = \mu_3^{-s_{lp}} \times s_{lp}^{3.7} \times \left(\frac{1}{B_3}\right) \times \left(\mu_3^{(s_{lp}-1)}\right)$$

$$\left[\frac{s_{lp}-\frac{n_a}{C}}{\frac{n_a}{C}-1}\right] = s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)$$

$$\frac{n_a}{C} = s_{lp} - \left\{\left(\frac{n_a}{C}-1\right) \times s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right\}$$

$$n_a = Cs_{lp} - (n_a - C)\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right\}$$

$$n_a = Cs_{lp} - n_a\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right\} + C\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right\}$$

$$n_a + n_a\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right\} = C\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right) + s_{lp}\right\}$$

$$n_a\left\{1 + \left[s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right]\right\} = C\left\{s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right) + s_{lp}\right\}$$

$$n_a^* = \frac{C\left[s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right) + s_{lp}\right]}{1 + \left[s_{lp}^{3.7} \times \left(\frac{1}{\mu_3}\right) \times \left(\frac{1}{B_3}\right)\right]} \tag{4.137}$$

4.6 Numerical Algorithms for Discrete and Asymptotic Model

In the following section we shall list the steps of the numerical algorithm of both the discrete and the asymptotic model. The discrete algorithm will output the enumeration function values as we increase the number of polymers on the surface and additionally provide us with preferential state based on the optimal values of n_a^* and $\mathcal{E}_{total}(n_a^*)$. The asymptotic will provide re-scaled values of $\mathcal{E}_{total}(n_a^*)$, and the curves of the asymptotic enumeration function will be compared to the discrete model as a means to further validate the results, given they are in agreement. The first step for both procedures below is to provide the parameters to the algorithm. In this model we set the connective constant $\mu_3 = 3$, and the amplitude in the three dimensional lattice of the solution $A_3 = 1$. For loops the amplitude is $B_3 = 1$. The size of the one dimensional lattice of the adsorption surface $n_{surf} = 146200$ lattice-sites based on surface of experiment [52], and the three dimensional lattice of the volume was set to $n_{vol} = n_{surf} \times 10^3$ lattice-sites. The length of a single polymer (number of mers) is based on long polymers from previous experiment [52], which is $r = 6200$. The total number of polymers available in the system in both solution and on the surface remains fixed at $n = 1000$. Finally, we set the boundaries of iteration based where $min[n_a] = n_{surf}/r$ which is proven below in Relation 4.138

$$
\begin{aligned}
min[n_{lp}] &= \frac{r - \frac{n_{surf}}{min[n_a]}}{min[s_{lp}] - 1} \\
0 &= \frac{r - \frac{n_{surf}}{min[n_a]}}{0 - 1} \\
r - \frac{n_{surf}}{min[n_a]} &= 0 \\
min[n_a] &= \frac{n_{surf}}{r}
\end{aligned}
\tag{4.138}
$$

For the maximum condition we have that $max[n_{lp}] = min[\mathcal{L}] - 1$, substituting 4.8 into this we get Relation 4.139.

$$\begin{aligned} max[n_{lp}] &= (r-1) - max[n_{lp}]s_{lp} + max[n_{lp}] \\ max[n_{lp}] &= \frac{(r-1)}{s_{lp}} \\ \frac{r - \frac{n_{surf}}{max[n_a]}}{s_{lp} - 1} &= \frac{(r-1)}{s_{lp}} \\ \frac{n_{surf}}{max[n_a]} &= \frac{r\,s_{lp} - r\,s_{lp} + r + s_{lp} - 1}{s_{lp}} \\ max[n_a] &= \frac{(s_{_{lp}} n_{_{surf}})}{(r + s_{_{lp}} - 1)} \end{aligned} \tag{4.139}$$

where each fixed s_{lp} produces a different set of $(min[n_a], max[n_a])$.

4.6.1 Discrete Model Algorithm

We start by taking the Stirling function of n_b where $n_b = n - n_a$ from Equation 4.28.

$$Stirling(n_b) = (n_b) \cdot \log[n_b] - n_b + \frac{1}{2}\left(\log[2\pi n_b] + \frac{1}{12 n_b}\right)$$

The next step is to calculate the value of adjusted chain-length $\mathcal{L}$ from Equation 4.2

$$\mathcal{L} = \frac{n_{surf}}{n_a}$$

Following that we compute the number of loops from a single polymer from Equation 4.6.

$$n_{lp} = \frac{r - \frac{n_{surf}}{n_a}}{s_{lp} - 1}$$

We then compute the logarithm of the Flory factor from Equation 4.23

$$\log \mathcal{F}(n_a) = n_a \times ((1-\mathcal{L}) \log n_{surf} + \log q + (\mathcal{L}-2) \log [q-1]) \\ + Stirling\,(n_{surf}) - Stirling\,(n_{surf} - n_a\mathcal{L}) - Stirling(n_a)$$

We now proceed to the final enumerations, starting with that of $\log \mathcal{E}_{lp}$ from Equation 4.26.

$$\log \mathcal{E}_{lp} = \{Stirling(\mathcal{L}) - Stirling(n_{lp}) - Stirling(\mathcal{L} - n_{lp})\} \\ + n_{lp} \{s_{lp} \cdot \log \mu_3 + \log B_3 - 3.7 \cdot \log s_{lp}\} \qquad \text{by Equation}$$

The next step is to compute the enumeration of the solution volume $\log \mathcal{E}_{vol}$ from Equation 4.27.

$$\log \mathcal{E}_{vol} = \log A_3 + r \cdot \log \mu_3$$

The final step is to compute and plot the total enumeration function as a function of n_a from Equation 4.18.

$$\log \mathcal{E}_{total} = Stirling(n) + \log \mathcal{F}(n_a) + n_a \cdot \log \mathcal{E}_{lp} + n_b \cdot \log \mathcal{E}_{vol} + n_b \cdot \log n_{vol} - Stirling(n_b)$$

4.6.2 Asymptotic Model Algorithm

We start by calculating n_b where $n_b = n - n_a$. We then calculate the Flory factor approximation from Relation 4.131 .

$$\begin{aligned} AsympApprox\left[\mathcal{F}\right] = \left(\frac{1}{s_{lp}-1}\right) \times \Bigg(& \left[\left(s_{lp}-1\right)C\right] \times \log\left[s_{lp}-1\right] \\ & - \left(n_a - C\right) \times \log\left[\frac{n_a}{C} - 1\right] \\ & - \left(C\, s_{lp} - n_a\right) \times \log\left[s_{lp} - \frac{n_a}{C}\right] \Bigg) \end{aligned} \tag{4.140}$$

We then calculate the asymptotic enumeration approximation for the solution volume from Relation 4.132.

$$AsympApprox\left[\mathcal{E}_{volume}\right] = \left(n_b\right) \times \log \mu_3. \tag{4.141}$$

We proceed to the calculation of the asymptotic enumeration approximation for loops from the adsorbed polymer at the surface from Relations 4.5 and 4.133.

$$\begin{aligned} AsympApprox\left[\mathcal{E}_{loops}\right] = \left(\frac{n_a - C}{s_{lp}-1}\right) & \times \left(s_{lp} \times \log \mu_3 - 3.7 \times \log s_{lp} + \log B_3\right) \\ & + C \times \left(\log\left(q-1\right) - \log\left(e\right)\right) \end{aligned} \tag{4.142}$$

In order to find the total enumeration of the system overall we take the summation of all of the above enumeration approximations. We use the covention *AsympApprox* below for the asymptotic approximations we derived in the previous sections.

$$AsympApprox\left[\mathcal{E}_{total}\right] = AsympApprox\left[\mathcal{F}\right] + AsympApprox\left[\mathcal{E}_{volume}\right] + AsympApprox\left[\mathcal{E}_{loops}\right]$$

4.7 Results and Discussion

Using the procedure described in Section 4.6 we computed the corresponding entropic preference value for the range between 23 and 230 polymers on the surface, which is based on the min and max constraints set in Section 4.6. We then plotted the $\log \mathcal{E}_{tot}$ as a function of polymers on the surface, as displayed in Figure 4.2. This plotted function shows the variation of entropic preference as the number of polymers adsorbed to the surface is increased, and by extension also increasing fractions of mers that are pushed into loops.

We then validated the results we from the discrete method, using an asymptotic approach displayed in Figure 4.3. It is evident that as one increases the fraction of mers in loops the entropic preference drops. We also observe the scalings matching up as the enumeration values of Figure 4.3 is approximately $1/r$ that of 4.2. This means that the entropic preference of the system is that of not having polymers in loops and salt caps under those loops. Alternative values of loop length were used to observe if the system behaves any differently with this variation in s_{lp}, but ultimately the system behaves similarly for different values of s_{lp}. Once more the model is showing that the entropically preferred state is that of all mers being in trains. The rationale behind such a result is that without any constraints on the model, there is a preference for the polymers to be flat on the surface of the surface in a state of full surface coverage, effectively maximizing the number of polymers free floating in the solution and by extension the total entropy of the polymers of the experiment.

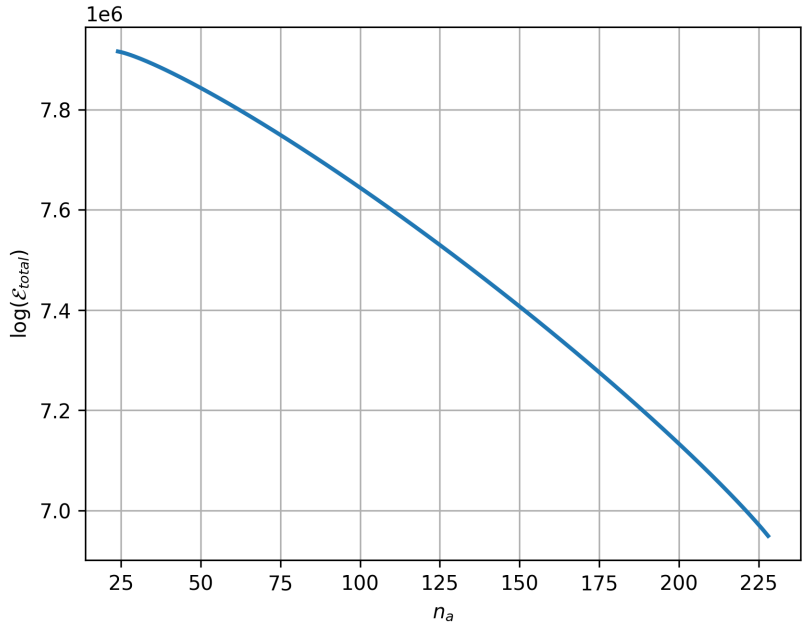


Figure 4.2: Discrete plot of total enumeration of the surface as a function of polymers on the surface n_a for $s_{lp} = 10$

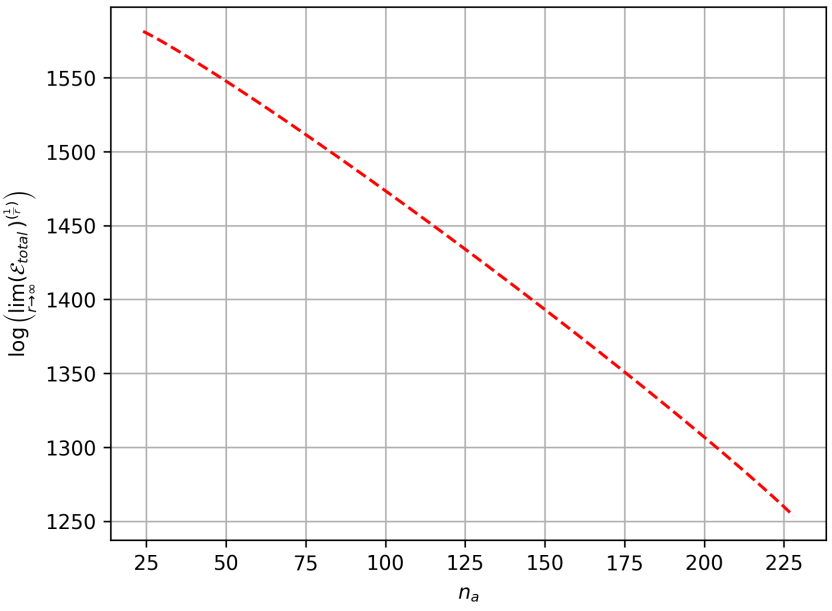


Figure 4.3: Plot of logarithmic asymptotic approximation of enumeration as a function of polymers on the surface n_a for $s_{lp} = 10$

Chapter 5

Two Dimensional Periodic Model with Clustering of Lattice Sites

Here we develop a model to enumerate the preferential behaviour of loops on a surface using an approach that could be best visualized using the concept of clusters of Self Avoiding Walks. First, we explain the intuition of the modelling approach. We then cover derivations related to the positioning of nearest neighbours and to the heuristics that were devised in order to calculate different scenarios of coverage. Subsequently, we describe the major relationships of this model by calculating the number of loops, their footprint, and the number of chains on the surface. Finally, we derive a new version of the Flory-Huggins method for this specific model with considerations of clusters of polymers.

5.1 Parameters and Definitions

Most of the parameters of this model are similar to the previous chapters. It is important to pay attention to how the footprint $\mathcal{L}$ is described in this chapter as it has an altered

definition from previous chapters. The number of repeat mers in a single chain is r, and $r-1$ corresponds to the number of steps (bonds) in one chain. Here n_a is the number of chains on the surface of adsorption, and n_b is the number of chains in the solution, making n the total number of chains in the whole system, i.e., $n = n_a + n_b$. The number of steps in a single loop is s_{lp}, and the number of sites in a single loop, excluding the endpoint sites on the surface is, $s_{lp} - 1$. The quantity $s_{lp} + 1$ is the number of total segments that belong to a loop, including the two end-point sites that are found adsorbed to the surface. Similarly with previous chapters, n_{surf} is the total number of sites on the surface of the colloid, n_{lp} is the number of loops in one chain.

The parameter $\mathcal{L}$ is the number of mers in trains on a single polymer, without the distances of the gaps below the loops. We introduce a new quantity n_1 representing the number of consecutive nearest neighbour steps of a SAW before making a loop, and D is the projection of that loop on the surface. Another new quantity is that of the salt-caps on the surface and the value p will be the probability of a surface site not being occupied by a salt-cap, and $1-p$ is the probability it is occupied by a salt-cap. Finally, coverage is the fraction of mers belonging to polymers over the total number of sites available on the surface.

5.2 Intuition of Cluster Sub-Model

In order to produce a model that had the feature of depleting a certain amount of surface sites in a periodic way similar to the one dimensional periodic model we devised an approach that incorporates a type of clustering of sites that the chain can occupy. In line with the experiments, conditions of partial coverage adsorption is adjusted based on the fraction of salt-caps occupying the surface and thus constraining the number of mers belonging to polymers that adsorb to the the surface sites. Lattice site occupation by salt caps prohibits occupation by mers on the surface. In this model this will be represented through a checker-

board pattern of clusters of salt-caps and clusters of unoccupied sites as seen in Figure 5.1. In Figure 5.1 the grey squares are the salt-caps and the white are the unoccupied spaces where the mers of polymer-chain can attach. Figure 5.2 shows a two dimensional representation of a SAW occuring on the surface, with the grey line being the polymer and the green S's corresponding to the salt-capped sites. The SAW in Figure 5.2 has just enough mers to fit completely in a single cluster.

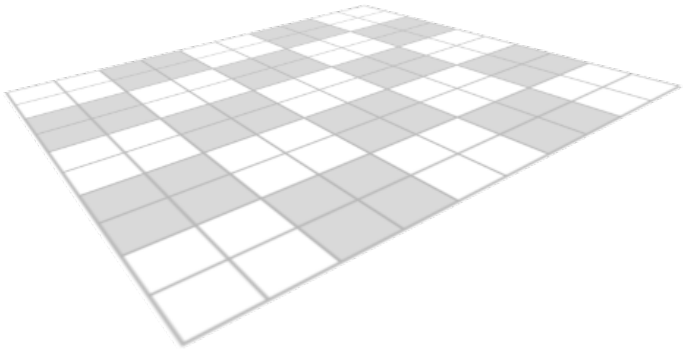


Figure 5.1: Surface of adsorption with salt-cap sites in grey and unoccupied in white

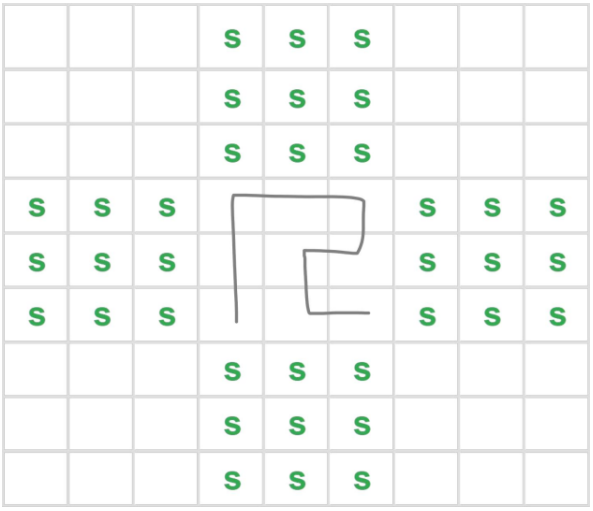


Figure 5.2: Illustration of a SAW in a cluster on a checker-board model lattice

In the case of our model the chain of length r cannot fit on a single cluster, because n_1 is the maximum amount of steps that can fit in a single cluster. In this scenario, it is assumed that the remainder of the chain will do a SAW in the three dimensional lattice of the solution until it has reached a nearest neighbour cluster on the surface that is not occupied by salt-caps as is observed in Figure 5.3. The approach above models the adsorbed polymer chains as a SAW on the surface in trains and when the train runs out of space to do a walk on the surface in that particular cluster, the remainder of the chain will jump to the neighbouring cluster, which is the loop in this model, and will then do a self-avoiding walk in the neighbouring cluster. This alternating process of filling a cluster with trains and then jumping to the neighbouring cluster will repeat until all mers of the chain of length r are in loops and trains. This model can be described as an alternating process between two modes of SAWs, that of an intra-cluster two dimensional SAW of the trains on the surface similar to that of Figure 5.2, and an inter-cluster three dimensional SAW of the jumps of the loops which is illustrated in Figure 5.4.

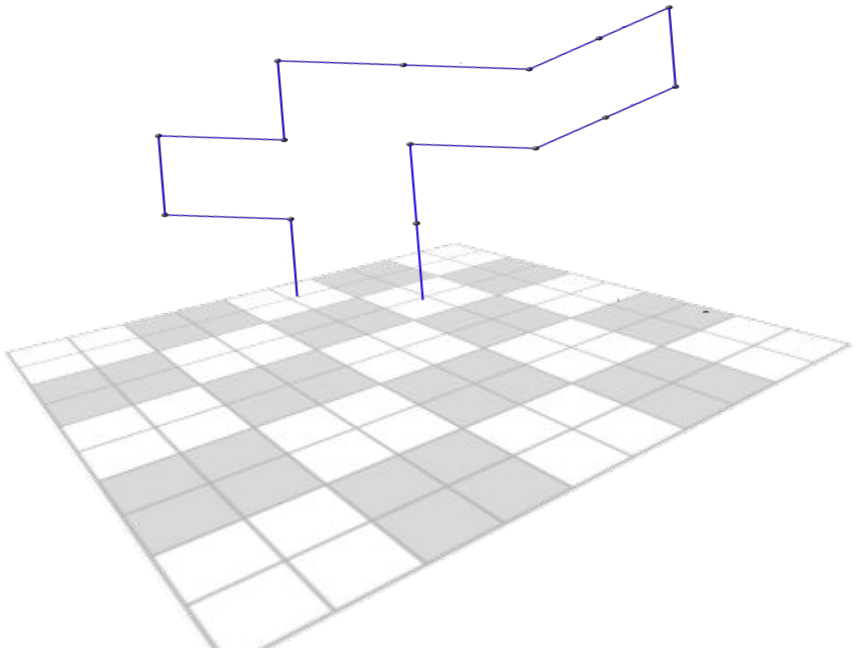


Figure 5.3: A jump of the polymer-chain from one cluster to nearest cluster

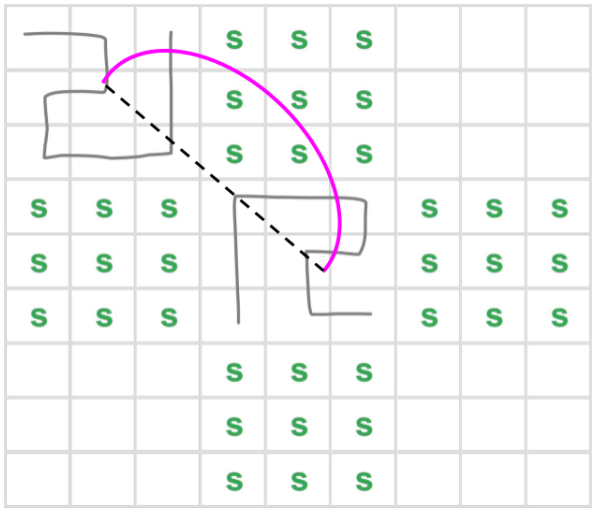


Figure 5.4: Illustration of a nearest cluster jump on a checker-board model lattice

The purpose of this model is to find if the system prefers to arrange itself in many small loops or if on the contrary entropy pushes the system to arrange with only a single long loop for

each chain. Figure 5.5 below shows a way to visualize this with first scenario being that of a chain that has one contiguous SAW on the surface and single long loop in solution (blue) as is represented on the illustration on the left in Figure 5.5, and the alternate scenario of many small SAW clusters and short loops, in an arrangements similar to that of the schematic on the right in Figure 5.5. The key to this approach is to model a relationship between the size of the loops and the number of sites in each cluster.

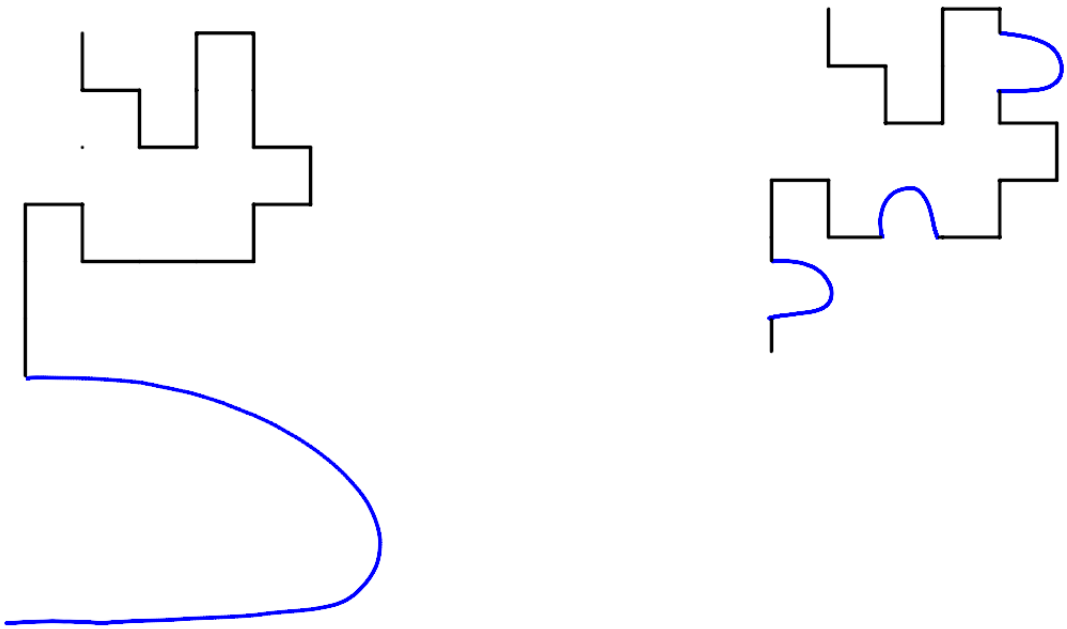


Figure 5.5: **Left:** A two dimensional clustered self avoiding walk followed by a large loop in three dimensions and **Right:** Smaller 2D SAW clusters with smaller loops linking them.

For example, if the surface has 80% coverage, a mer being placed on the surface will have $q-1$ neighbours (If we assume that the preceding site was a neighbour of the current site), but only 80% of them will be available.

The way the loops occur is through a jump to a nearest neighbour clusters. This loop

has a base-length of Distance D, on the surface which is the distance in lattice-sites on the surface one end-point of the loop the other one. This distance D can be represented in a multitude of metrics, below are two such examples.

For the taxicab (L_1) metric, on the square lattice there would be $4D$ possible targets.

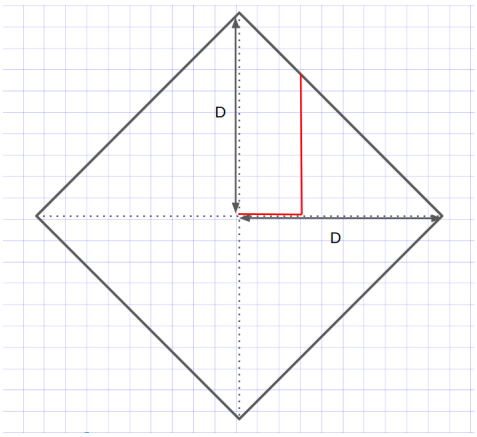


Figure 5.6: nearest neighbour targets - L_1 (taxicab) Metric

For the Euclidean (L_2) metric there would be $2\pi \times D$ targets.

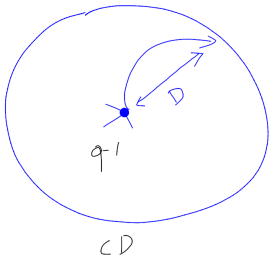


Figure 5.7: nearest neighbour targets - L_2 (Euclidean) Metric

In Figure 5.8 we see a possible scenario of a random jump from one cluster to a nearest neighbour cluster. In this case there are eight choices for that jump.

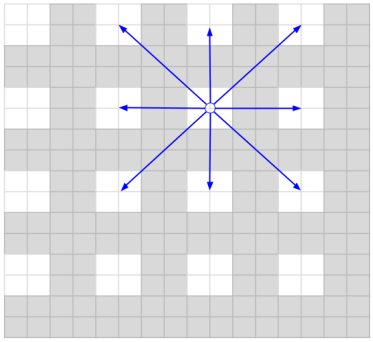


Figure 5.8: Schematic of possible nearest cluster jumps represented by arrows

5.3 Basic Relationships of the Model

In previous chapters we have defined quantities and methods that need to be adjusted to the current model. We start with the way we define the number of loops on a single chain. This calculation is the chain length in mers divided by the summation of the number of mer-sites in a single cluster and the number of mer-sites in a single loop. This computation is achieved through splitting the chain length into all its cluster-loop pairs and counting the number of pairs.

$$n_{lp} := \frac{r}{n_1 + s_{lp}} \tag{5.1}$$

The definition of chain footprint on the surface, $\mathcal{L}$, tends to change a little from model to model. In this model it is defined is the aggregation of all the mers in trains on a single polymer. More specifically we are not considering the distances of the jumps, D.

$$\mathcal{L} = r - n_{lp}(s_{lp} - 1) \tag{5.2}$$

The number of the chains on the surface, n_a, is the ratio of n_{surf} over $\mathcal{L}$ adjusted by probability p. This value is ultimately a function of the size of the clusters and the value of the

coverage parameter, p.

$$n_a = \frac{n_{surf} \times p}{\mathcal{L}} \tag{5.3}$$

5.4 Enumeration of Polymers and Loops on Surface

Our approach is based on the mean-field method devised by P.J. Flory and Maurice Huggins [17, 12]. Here we have adjusted the approach to have considerations of loops on chains and clustering of SAWs. The goal is to create a function that enumerates the number of ways to place $\mathcal{L}$ mers of j chains of length r on the surface. This needs to be done without overlaps and with the consideration of the constraint of the fraction $1 - p$ of total sites that will remain unoccupied by polymer chains given that they are already occupied by salt-caps.

Recall that the surface is approximated by a two-dimensional lattice with coordination number q which is the number of nearest neighbours of each site on the surface. Additionally, there is an assumption that the distance between lattice sites corresponds to the distance between adjacent monomers within a polymer. In the non-reversing model, it is known [3] that after placing the first mer of the chain there would be q choices for the second mer, and finally $q - 1$ choices for each mer after that.

As in Equation 4.10, we have w_k is the number of ways to place the k^{th} chain after $k - 1$ chains have been placed. It is assumed in this model that the number of choices should on average be reduced by the fraction of the surface that has already been occupied by mers [52]. In order to incorporate this assumption into the model it is important to recall the quantities $(k - 1)\ \mathcal{L}$, which is the number of mers that are already on the surface and $n_a\mathcal{L}$ which is the total number of mers on the surface from all adsorbed polymers. This results

in the below two expressions.

$$\begin{pmatrix} \text{Total mer} \\ \text{contribution of} \\ n_a \text{ chains} \end{pmatrix} = n_a\mathcal{L} \tag{5.4}$$

$$\begin{pmatrix} \text{Number of mers} \\ \text{in the first k-1 chains} \\ \text{before we place the} \\ \text{first mer of the kth chain} \end{pmatrix} = (k-1)\mathcal{L} \tag{5.5}$$

Combining the above, it is found that there are $n_a\mathcal{L} - (k-1)\mathcal{L}$ available sites for the first mer of the k^{th} chain on the surface.

$$\begin{pmatrix} \text{Number of available sites} \\ \text{for the first mer} \\ \text{of the } k^{th} \text{ chain} \\ \text{on the surface} \end{pmatrix} = \begin{pmatrix} \text{Total mer} \\ \text{contribution of} \\ n_a \text{ chains} \end{pmatrix} - \begin{pmatrix} \text{Number of mers} \\ \text{in the first k-1 chains} \\ \text{before we place the} \\ \text{first mer of the kth chain} \end{pmatrix} \tag{5.6}$$

$$= n_a\mathcal{L} - (k-1)\mathcal{L} \tag{5.7}$$

This means that there are

$$[n_a\mathcal{L} - (k-1)\mathcal{L} - 1] \tag{5.8}$$

unoccupied sites when placing the second mer of the initial polymer. Subsequently, if the probability p is included in this calculation, then in case of having placed $k-1$ chains on the surface as welll as that of the first mer of the k^{th} chains, we have that there are

$$[n_a\mathcal{L} - (k-1)\mathcal{L} - 1] \tag{5.9}$$

unoccupied sites, where $n_a\mathcal{L} = pn_{surf}$. This means that if one was to pick a site at this point ($k-1$ chains and the first mer of the k^{th} chain on surface) at random, the probability that it is not occupied by a salt-cap and that it is not occupied by a mer that was already placed previously is that of Equation 5.10.

$$p \times \frac{n_a\mathcal{L} - (k-1)\mathcal{L} - 1}{n_a\mathcal{L}} \tag{5.10}$$

This implies that with the above considerations of salt caps there are

$$(q)\,(p)\left(\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - 1}{n_a\mathcal{L}}\right) \tag{5.11}$$

choices for the placement of the second mer of the k^{th} chain. For the case that i monomers of the k^{th} chain have been placed, given a random nearest neighbour site and assuming we already know there is no salt-cap occupying that site, the probability of it not being occupied by a mer is that of Equation 5.12.

$$\left(\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - i}{n_a\mathcal{L}}\right) \tag{5.12}$$

The probability of a site not being occupied by a mer or a salt-cap is that of Equation 5.12.

$$(p)\left(\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - i}{n_a\mathcal{L}}\right) \tag{5.13}$$

so there are

$$(q-1)\,(p)\left(\frac{n_a\mathcal{L} - (k-1)\mathcal{L} - i}{n_a\mathcal{L}}\right). \tag{5.14}$$

choices for the $(i+1)^{th}$ monomer in this chain.

The next step of this process is the consideration of loops, which in this model can be visualized as jumps from the center of one SAW cluster to the center of its nearest cluster. It is important to note that in this model it will be assumed that the first and second steps are not jumps, but walks inside the cluster. Similarly to the previous calculation in Equation 5.14 we have that the radial choices for the other endpoint of the jump can be enumerated using Equation 5.15.

$$(2\pi D) \times (p) \times \left(\frac{n_a \mathcal{L} - (k-1)\mathcal{L} - i}{n_a \mathcal{L}} \right). \tag{5.15}$$

Combining the above factors together and incorporating the rules of placement of the mers of the chain we get the following expression for w_k in Equation 5.16. It is important to note that in the first line of Equation 5.16 there is a product with an upper limit of $\frac{\mathcal{L}-1}{n_1+1}$. This expression and the expression in the numerator of $(n_1+1) \times i$ is referring to the jumps that occur every n_1+1 steps made with the upper limit being that of $i = \frac{\mathcal{L}-1}{n_1+1}$. More specifically, $[n_1+1] \times \left[\frac{\mathcal{L}-1}{n_1+1}\right]$ is the number of the mer at which the final jump that is made, before the

walk runs out of mers.

$$
\begin{aligned}
w_k = & \\
& \prod_{i=1}^{\frac{\mathcal{L}-1}{n_1+1}} (2\pi D)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-(n_1+1)\times i}{n_a\mathcal{L}}\right) && \text{by Equation 5.15} \\
\times\ & n_a\mathcal{L}-(k-1)\mathcal{L} && \text{by Equation 5.8} \\
\times\ & (q)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-1}{n_a\mathcal{L}}\right) && \text{by Equation 5.13} \\
\times\ & \prod_{i=2}^{n_1} (q-1)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-i}{n_a\mathcal{L}}\right) && \text{by Equation 5.14} \\
\times\ & (q)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-(n_1+2)}{n_a\mathcal{L}}\right) && \text{by Equation 5.13} \\
\times\ & \prod_{i=n_1+3}^{2n_1+1} (q-1)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-i}{n_a\mathcal{L}}\right) && \text{by Equation 5.14}
\end{aligned}
$$

$$\vdots$$

$$
\begin{aligned}
\times\ & (q)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}-[\mathcal{L}-(\ n_1+1\ )]}{n_a\mathcal{L}}\right) && \text{by Equation 5.13} \\
\times\ & \prod_{i=\mathcal{L}-(n_1+2)}^{\mathcal{L}-1} (q-1)\,(p)\left(\frac{n_a\mathcal{L}-(k-1)\mathcal{L}\ -i}{n_a\mathcal{L}}\right) && \text{by Equation 5.14} \qquad (5.16)
\end{aligned}
$$

The above calculation is further simplified in the expression below.

$$
\begin{aligned}
w_k = \left(\frac{p}{\mathcal{L}n_a}\right)^{\mathcal{L}-1} & \times (2\pi D\,)^{\frac{\mathcal{L}-1}{n_1+1}} \times\ (\ n_a\mathcal{L}-(k-1)\mathcal{L}\ ) \\
& \times\ (q)^{\frac{\mathcal{L}+n_1}{n_1+1}} \times (q-1)^{\frac{\mathcal{L}+n_1}{n_1+1}(n_1-1)} \times \frac{[n_a\mathcal{L}-(k-1)\mathcal{L}-1]!}{[n_a\mathcal{L}-(k-1)\mathcal{L}-(\mathcal{L})]!} \qquad (5.17)
\end{aligned}
$$

In this step simplifications are done between the numerator ($n_a\mathcal{L} - (k-1)\mathcal{L}$), and the denominator of the factor at the very end of the expression in Equation 5.17 which results in Expression 5.18.

$$w_k = \left(\frac{p}{\mathcal{L}n_a}\right)^{\mathcal{L}-1} \times (2\pi D)^{\frac{\mathcal{L}-1}{n_1+1}} \times (q)^{\frac{\mathcal{L}+n_1}{n_1+1}} \times (q-1)^{\frac{\mathcal{L}+n_1}{n_1+1}(n_1-1)} \times \frac{[n_a\mathcal{L} - (k-1)\mathcal{L}]!}{[n_a\mathcal{L} - k\mathcal{L}]!} \tag{5.18}$$

In order to generalize to all chains, the operator $\frac{1}{n_a!}\prod_{k=1}^{n_a}$ will be applied to Expression 5.18 of w_k.

$$\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k = \frac{1}{n_a!}\left[\left(\frac{p}{\mathcal{L}n_a}\right)^{\mathcal{L}-1} \times (2\pi D)^{\frac{\mathcal{L}-1}{n_1+1}} \times (q)^{\frac{\mathcal{L}+n_1}{n_1+1}} \times (q-1)^{\frac{\mathcal{L}+n_1}{n_1+1}(n_1-1)}\right]^{n_a} \times \prod_{k=1}^{n_a}\frac{[n_a\mathcal{L} - (k-1)\mathcal{L}]!}{[n_a\mathcal{L} - k\mathcal{L}]!} \tag{5.19}$$

In the final factor of Equation 5.19, which is that of Expression 5.20 below, there is a telescoping expansion in which terms cancel out which can be observed below.

$$\begin{aligned}
&\prod_{k=1}^{n_a}\frac{[n_a\mathcal{L} - (k-1)\mathcal{L}]!}{[n_a\mathcal{L} - k\mathcal{L}]!} \qquad (5.20)\\
&= \frac{[n_a\mathcal{L} - 0]!}{[n_a\mathcal{L} - \mathcal{L}]!}\frac{[n_a\mathcal{L} - \mathcal{L}]!}{[n_a\mathcal{L} - 2\mathcal{L}]!}\frac{[n_a\mathcal{L} - 2\mathcal{L}]!}{[n_a\mathcal{L} - 3\mathcal{L}]!} \cdots \frac{[n_a\mathcal{L} - (n_a-2)\mathcal{L}]!}{[n_a\mathcal{L} - (n_a-1)\mathcal{L}]!}\frac{[n_a\mathcal{L} - (n_a-1)\mathcal{L}]!}{[n_a\mathcal{L} - n_a\mathcal{L}]!}\\
&= \frac{[n_a\mathcal{L}]!}{[n_a\mathcal{L} - n_a\mathcal{L}]!}\\
&= \frac{[n_a\mathcal{L}]!}{0!}\\
&= (n_a\mathcal{L})! \qquad (5.21)
\end{aligned}$$

Incorporating the result of the calculation of Expression 5.21 back into 5.19 results in the

below relationship.

$$\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k = \frac{1}{n_a!}\Bigg[\left(\frac{p}{\mathcal{L}n_a}\right)^{\mathcal{L}-1} \times (2\pi D)^{\frac{\mathcal{L}-1}{n_1+1}} \times (q)^{\frac{\mathcal{L}+n_1}{n_1+1}} \times (q-1)^{\frac{\mathcal{L}+n_1}{n_1+1}(n_1-1)} \Bigg]^{n_a} \times (n_a\mathcal{L})! \tag{5.22}$$

The finalized expression for calculating the number of ways to place all chains in the system, can be found after rearranging terms in in Equation 5.23 below.

$$\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k = (n_a!)^{-1}\Bigg[\left(p \times (\mathcal{L}n_a)^{-1} \times (2\pi D)^{\frac{1}{n_1+1}}\right)^{\mathcal{L}-1} \times \left((q) \times (q-1)^{(n_1-1)}\right)^{\frac{\mathcal{L}+n_1}{n_1+1}} \Bigg]^{n_a} \times (n_a\mathcal{L})! \tag{5.23}$$

This function will henceforth be referred to as the Enumeration function for the surface domain of the system, $\mathcal{E}_{surf}$.

Taking the logarithmic of Equation 5.23 gives the below expression

$$\log\left[\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k\right] = \log(n_a\mathcal{L})! - \log(n_a!) + n_a \log\Bigg[\left(p \times (\mathcal{L}n_a)^{-1}(2\pi D)^{\frac{1}{n_1+1}}\right)^{\mathcal{L}-1} \times \left((q) \times (q-1)^{(n_1-1)}\right)^{\frac{\mathcal{L}+n_1}{n_1+1}} \Bigg] \tag{5.24}$$

Using the relationship of the Stirling function in place of logarithmic factorial and distribut-

ing the logarithmic function to the terms inside the large brackets we get Equation 5.25.

$$\log\left[\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k\right] = Stirling\,(n_a\mathcal{L}) - Stirling\,(n_a) + n_a\left[\,(\mathcal{L}-1)\log\left(p\times(\mathcal{L}n_a)^{-1}\times(2\pi D\,)^{\frac{1}{n_1+1}}\right) + \left(\frac{\mathcal{L}+n_1}{n_1+1}\right)\log\left((q)\times(q-1)^{(n_1-1)}\right)\,\right] \tag{5.25}$$

This leads to the final expression for $\log\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k$ which is Equation 5.39 below.

$$\log\left[\frac{1}{n_a!}\prod_{k=1}^{n_a} w_k\right] = Stirling\,(n_a\mathcal{L}) - Stirling\,(n_a) + n_a\left[\,(\mathcal{L}-1)\left(\log p - \log\,(\mathcal{L}n_a) - \left(\frac{1}{n_1+1}\right)\log\,(2\pi D\,)\right) + \left(\frac{\mathcal{L}+n_1}{n_1+1}\right)(\;\log\,(q) - (n_1-1)\log\,(q-1)\;)\,\right] \tag{5.26}$$

This function will henceforth be referred to as the logarithm of the enumeration function for the surface $\log\mathcal{E}_{surf}$.

5.5 Surface Coverage Patterns

Given that most of our results are functions of surface coverage, it is important to visualise what this can actually look like. The coverage scenarios that we will highlight are that of five, twenty and seventy-five percent occupancy of the surface by polymers. The surface coverage corresponds to the fraction of occupancy of the total sites on the surface by mers of polymers adsorbed to the surface. These polymer clusters arrange in patterns that are dependant on the percentage of salt-caps surrounding them. For example, a five percent surface coverage means that five percent of the total surface sites are occupied by mers that belong to trains of adsorbed polymers. For the Figures 5.9-5.11 we chose a simple type of pattern the clusters of salt-caps and polymers could take on, in order to best illustrate what is occurring on the surface. In this pattern nearest neighbours are positioned on the two main axis directions of the square surface. For example, a five percent coverage corresponds to a ratio of mers to salt-caps is that 1:20. This means that for each site occupied by a mer there are twenty sites worth of salt-caps separating it from its nearest neighbour cluster in either axis-directions on the surface. This is what is illustrated in Figure 5.9. A similar logic applies to the case of twenty percent coverage, where the ratio 1:5 corresponds to five steps in either direction, as is illustrated in Figure 5.10. For the case of seventy-five percent Figure 5.11 illustrates the distribution of salt-caps to unoccupied clusters quite effectively, with the main diagonals representing the salt-caps (grey) and the coupled sub-diagonal pairs, corresponding to the now dominant unoccupied clusters (white).

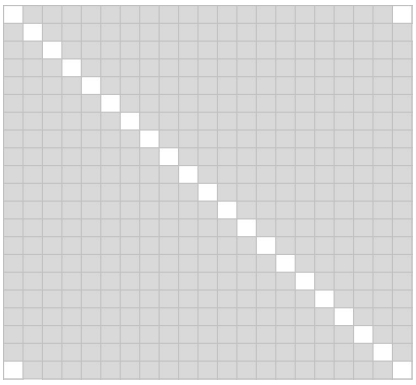


Figure 5.9: Surface pattern for cluster of salt-caps (grey) and mer cluster sites (white) for the case of five percent coverage of mers in trains

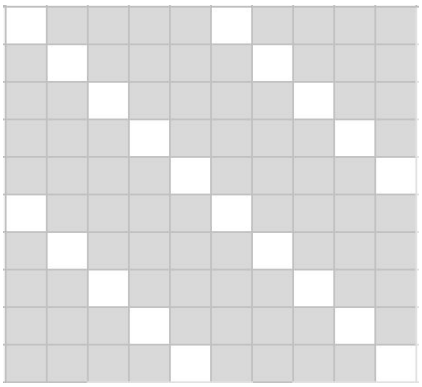


Figure 5.10: Surface pattern for cluster of salt-caps (grey) and mer cluster sites (white) for the case of twenty percent coverage of mers in trains

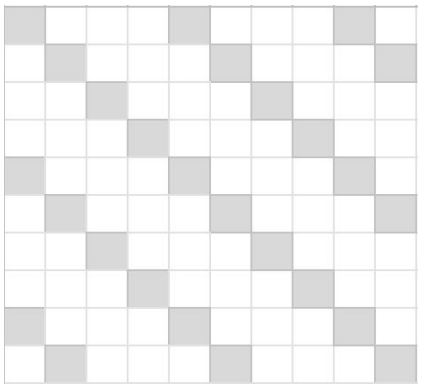


Figure 5.11: Surface pattern for cluster of salt-caps (grey) and mer cluster sites (white) for the case of seventy-five percent coverage of mers in trains

In this model there is a parameter associated with the fraction of salt-caps on the surface, $1-p$. This parameter constrains the distance of nearest clusters from a SAW cluster on the surface. This is because the higher the fraction of salt-caps on the surface, the longer the distances of one polymer cluster to the next. Additionally, depending on this fraction the distribution of clusters on the lattice can vary from one fraction to the next. In this section we will go into detail regarding the consideration of nearest neighbours for different coverage fractions of the surface, which impact the distribution of nearest jump sites for the polymer.

The length of loops s_{lp} is assumed to be dependant on the jump distance, D between two nearest neighbour clusters, with size proportional to n_1. We assume that $D\left(n_1\right) = C_{n_1} \times \sqrt{n_1}$, where value of the coefficient C_{n_1} is dependant on the arrangement of nearest neighbour clusters as was discussed briefly in Section 5.3. Let us first understand how the clusters of salt-caps and unoccupied sites are arranged in this method.

We start with the below arrangement in Figure 5.12, where the blank cells correspond to sites that can be occupied by mers of a polymer and the shaded in cells are the sites that are already occupied by salt-caps. This illustration corresponds to a scenario of $p = \frac{1}{2}$. The clusters of white cells have an area of n_1 sites (here this area is $n_1 = 4$), and this corresponds to sides of length $A = \sqrt{n_1}$

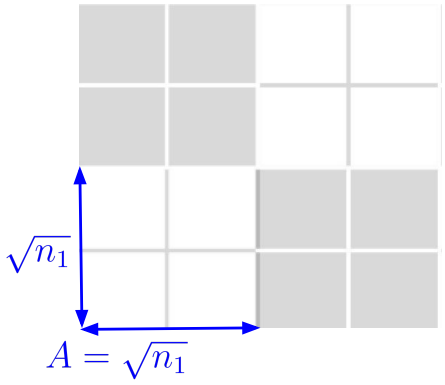


Figure 5.12: SAW cluster measured in distances of length $A = \sqrt{n_1}$

Figure 5.13 illustrates the two different types of jumps that can occur in this scenario of surface coverage ($p = \frac{1}{2}$), which is that of the distances $2A$ and $\sqrt{2}A$. It is often the case that the jump distances will not all be the same, due to the distribution of nearest uncapped sites. We address this in the model by assuming that the expected jump distance is the same for all nearest neighbour clusters. This is accomplished by taking an average of the eight jump distances, and use this averaged value jump distance $\hat{D}$ as the nearest neighbour distance for all targets in Figure 5.14, which is illustrated in Figure 5.15. For this reason an averaging is done over all the distances in order to get a single $\bar{D}$ for all targets below.

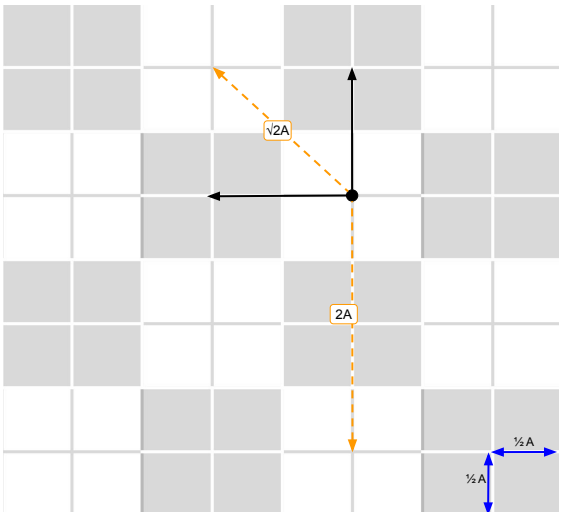


Figure 5.13: Checkerboard setup of lattice of surface with distance measurements for nearest cluster jumps

This averaging process can be done in multiple ways. For example for the simple case of $p = \frac{1}{2}$ we have eight jump targets and those jumps can be either be 2A or $\sqrt{2}A$. In order to address this we average over all eight jump distances, and take into account the frequency of each type of arrow. For example, the above would be 50% of $\sqrt{2}A$ and 50% of $2A$. This is a very neat arrangement, but this won't always be this balanced when it comes to other coverage values p.

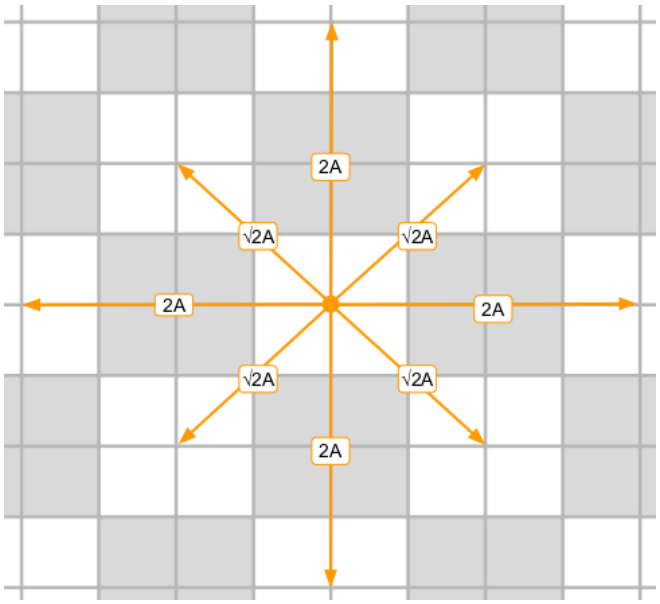


Figure 5.14: Illustration of varying jump distances for $p = \frac{1}{2}$

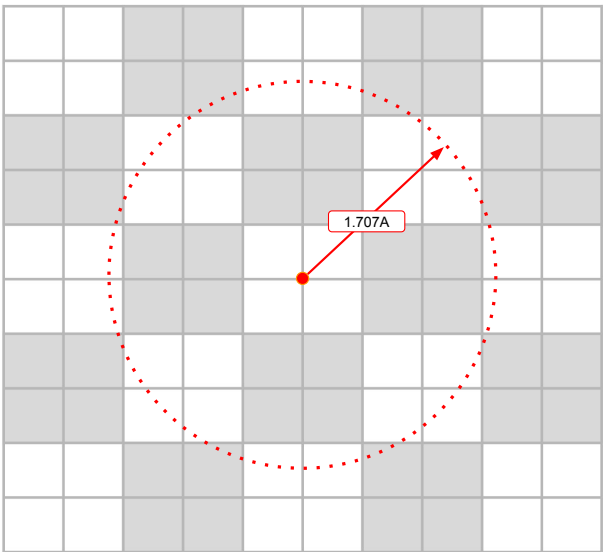


Figure 5.15: Single average jump distance in all directions for $p = \frac{1}{2}$

So the average for the case of all directions would be the below in Equation 5.27.

$$\bar{D}_{p=\frac{1}{2}} = \frac{A}{2}\left[\sqrt{2}+2\right] = \frac{3.414}{2}A = 1.707A = 1.707\sqrt{n_1} \tag{5.27}$$

An alternative to this approach is to only consider the orthogonal axes (x,y), so the average would be of the jump distances of the four targets instead of the eight targets, which is that of $\bar{D}'_{p=\frac{1}{2}} = 2A$. For the case of considering the diagonals instead we have $\bar{D}''_{p=\frac{1}{2}} = \sqrt{2}A$.

Using the above approach we now extend this to coverage values $p < \frac{1}{2}$. Below is an example where the lattice setup is such that the ratio for p is $\frac{1}{5}$. In Figure 5.16 we notice two different diagonal jump distances, $\sqrt{13}A$ and $\sqrt{2}A$, we proceed to take the average $\bar{D}_{\frac{1}{5}}(n_1)$ as seen below in Equation 5.28.

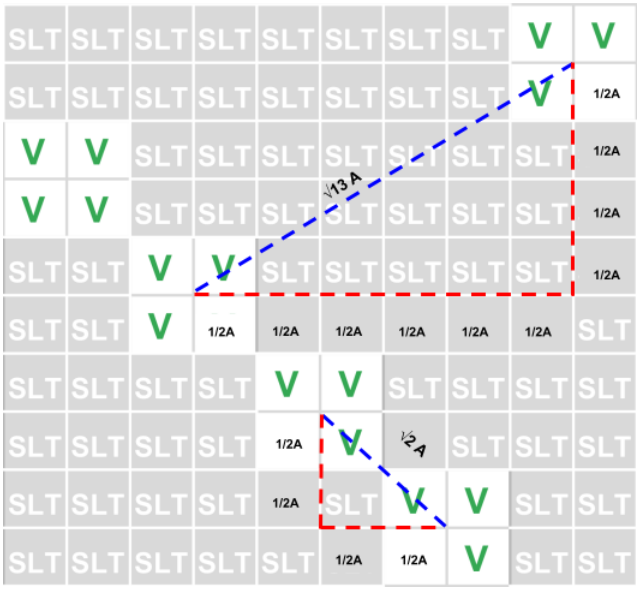


Figure 5.16: Calculation process of nearest neighbour jumps for $p = \frac{1}{5}$

The corresponding calculation of the above approach is the following.

$$\bar{D}_{p=\frac{1}{5}} = \frac{A}{2}\left[\sqrt{13} + \sqrt{2}\right] = \frac{A}{2}\left[3.605 + 1.414\right] = A \times \frac{5.019}{2} = 2.509\sqrt{n_1} \tag{5.28}$$

Similarly, in the case of coverage value of $p = \frac{1}{6}$, the calculation would be the following.

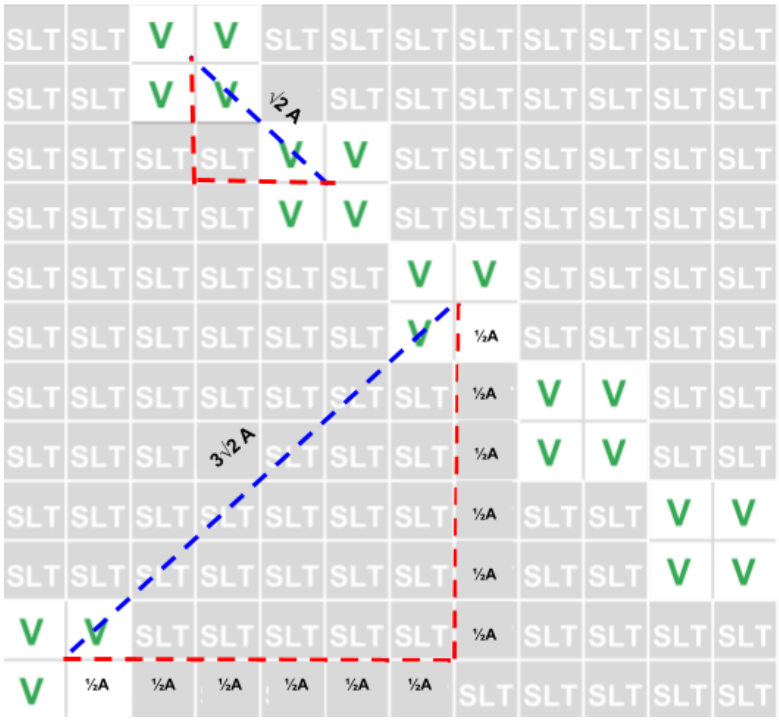


Figure 5.17: Calculation process of nearest neighbour jumps for $p = \frac{1}{6}$

$$\bar{D}_{p=\frac{1}{6}} = \frac{A}{2}\left[3\sqrt{2} + \sqrt{2}\right] = \frac{4\sqrt{2}}{2}A = 2\sqrt{2}A = 2\sqrt{2} \times \sqrt{n_1} \tag{5.29}$$

The above approach can be generalized in order to derive coefficients of $\sqrt{n_1}$ in the calculation of jump distance $D_p(n_1)$ for any possible probability $p < 0.5$, and their corresponding arrangement of clusters[5].

In a similar way to above we will look at the approach for the scenarios for which $p > 0.5$. An example of this is the calculation of $p = \frac{2}{3}$ and $p = \frac{3}{4}$. In Figure 5.18 we see the distances $2\sqrt{2}A, 2A, \sqrt{2}A, 1A$ with frequencies that are the for both schematics. This will enable us to take an average over all arrows just from one of the two schematics in Figure 5.18.

[5]It is important to note that the cluster arrangements are not unique as there could more than one way to arrange the clusters for a single probability parameter.

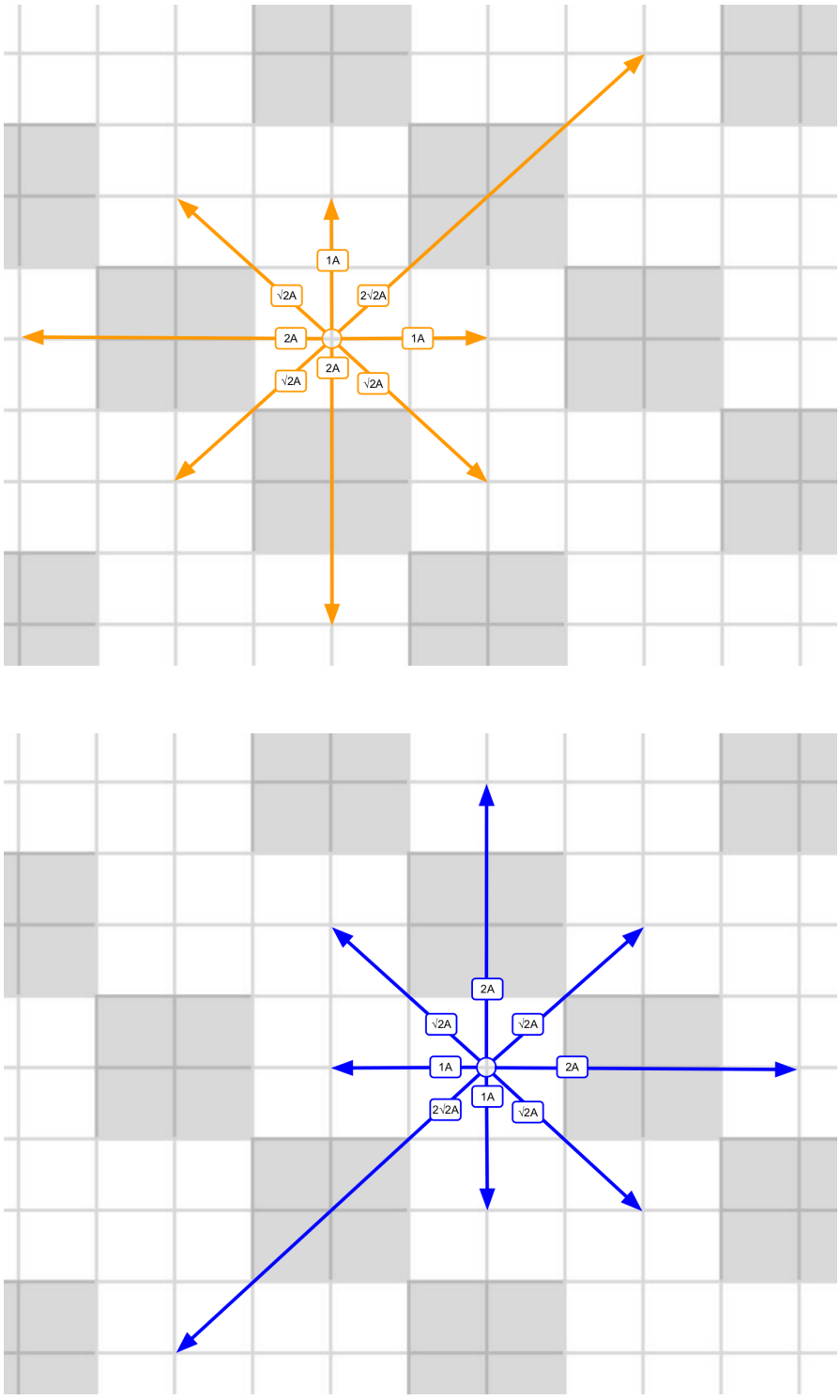
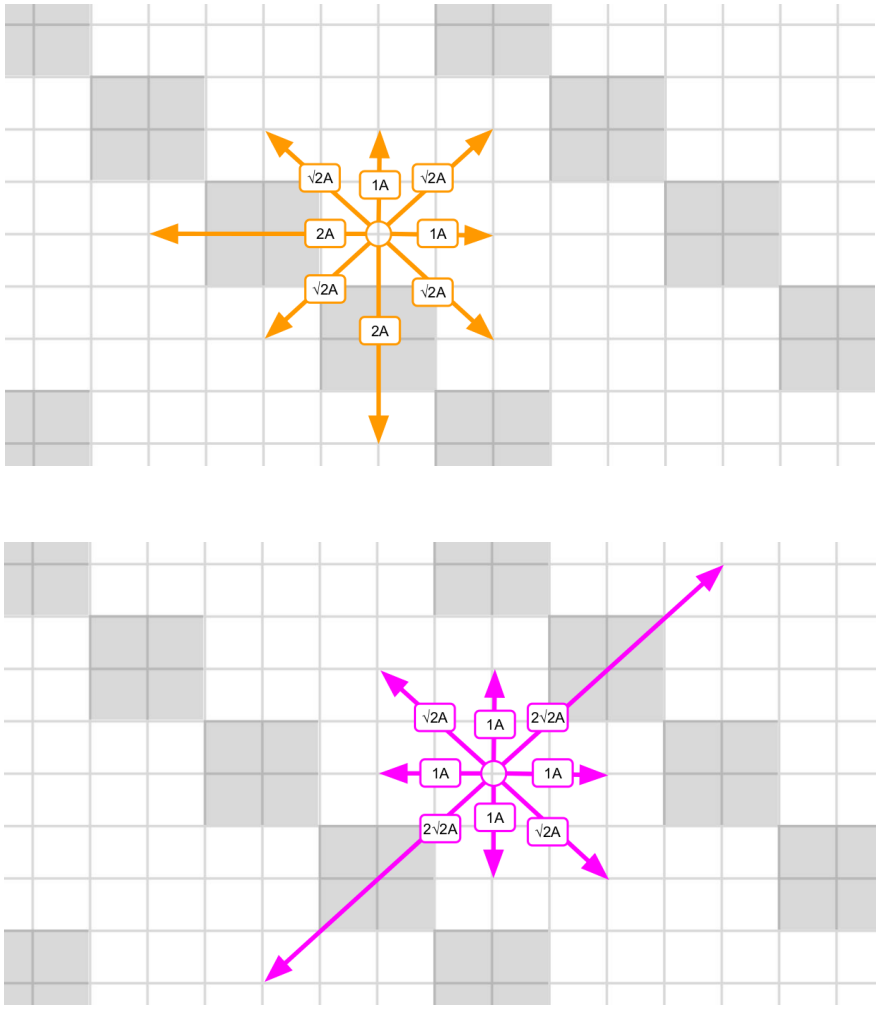


Figure 5.18: Graphical representation of possible jump distances for $p = \frac{2}{3}$

$$\bar{D}_{p=\frac{2}{3}} = \frac{A}{8}\left[\sum_{i=1}^{16} D_i\right] = 1.634A = 1.634\sqrt{n_1} \tag{5.30}$$

In the scenario of $p = \frac{3}{4}$, not all configurations of arrangements of arrows share the same set of jump distances. For this reason we take an average over all distances from all three configurations corresponding to all three schematics in Figure 5.19.



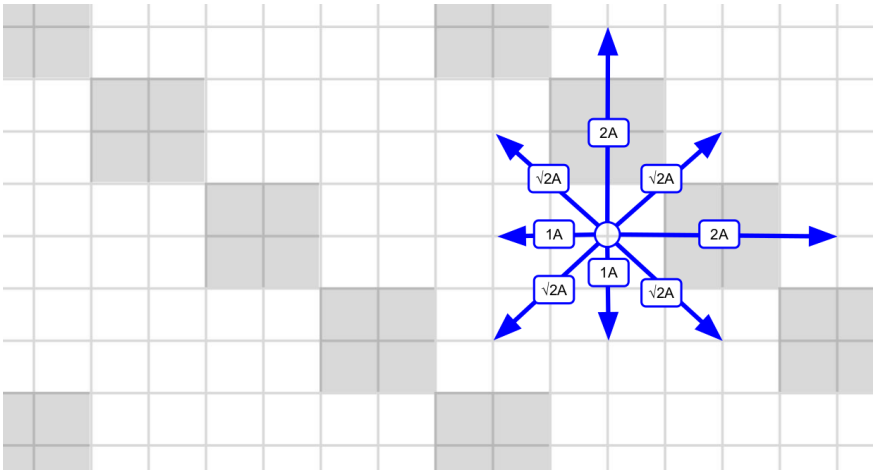


Figure 5.19: Graphical representation of possible jumps for $p = \frac{3}{4}$

$$\bar{D}_{\frac{3}{4}} = \frac{A}{24}\left[\sum_{i=1}^{24} D_i\right] = 1.492A = 1.492\sqrt{n_1} \tag{5.31}$$

Combining the above we have two seperate methods for computing jump distance D. For the case of $p \geq \frac{1}{2}$ we use the below values.

$$D_p = \begin{cases} 1.492 \times \sqrt{n_1} & , p = \frac{3}{4} \\ 1.634 \times \sqrt{n_1} & , p = \frac{2}{3} \\ 1.707 \times \sqrt{n_1} & , p = \frac{1}{2} \end{cases} \tag{5.32}$$

For the case of $p < \frac{1}{2}$ we only consider the diagonals, which results in the below values.

$$D_p = \begin{cases} 2.00 \times \sqrt{n_1} & , p = \frac{1}{3} \\ 2.509 \times \sqrt{n_1} & , p = \frac{1}{5} \\ 2\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{6} \\ 3\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{10} \\ 5.5\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{20} \end{cases} \tag{5.33}$$

5.6 Developing a Total Enumeration Approximation

Taking the relationships developed Section 5.5 as well as Chapter 4, we derive the model of enumerating the system as a whole. The asymptotic behaviour of c_ℓ on the three-dimensional cubic lattice is described extensively in Equations 1.3,1.4. we have that the number of self avoiding walks of a single chain from a specific starting point is approximately the value of the partition function for the solution, $\mathcal{E}_{vol}$, for n_b chains in solution.

$$\mathcal{E}_{vol}^{n_b} \approx (A_3 \cdot (\mu_3)^r)^{n_b} \qquad \text{by Equation 1.5} \tag{5.34}$$

The factor $\left[\left(\mu_3^{s_{lp}}/s_{lp}^{3.7}\right) B_3\right]^{n_{lp}}$ is the number of possible looping configurations in the solution for all of the loops, n_{lp}, and raising the enumeration to n_a in order for it to apply to all chains on the surface,

$$\mathcal{E}_{lp}^{n_a} = \left[\left(\frac{\mu_3^{s_{lp}}}{s_{lp}^{3.7}} B_3\right)^{n_{lp}}\right]^{n_a} \tag{5.35}$$

We have from 5.23 that $\mathcal{E}_{surf}$ was found to be the following expression.

$$\mathcal{E}_{surf} = (n_a!)^{-1} \left[\left(p \times (\mathcal{L} n_a)^{-1} \times (2\pi D)^{\frac{1}{n_1+1}} \right)^{\mathcal{L}-1} \times \left((q) \times (q-1)^{(n_1-1)} \right)^{\frac{\mathcal{L}+n_1}{n_1+1}} \right]^{n_a} \times (n_a \mathcal{L})! \tag{5.36}$$

Below is the aggregation of the enumeration of the surface, the loops as well as the enumeration of the solution including location because of the product of $\mathcal{E}_{vol}^{n_b} \times n_{vol}^{n_b}$. This is following the structure of the partition function from Equation 1.2.

$$\mathcal{E}_{total} = \left(\mathcal{E}_{surf} \ \mathcal{E}_{lp}^{n_a} \ \mathcal{E}_{vol}^{n_b} \ \frac{n_{vol}^{n_b}}{n_b!} \right) \tag{5.37}$$

5.7 Implementation

In this section we outline the functions and methods involved in the computation process of this modelling approach step by step. It is important to note that most of the enumeration is done on a logarithmic scale. This means that in place of logarithmic factorials, the stirling approximation will be used.

$$\log(x!) \approx Stirling(x) = \begin{cases} \text{Does Not Exist}, & x < 0 \\ 0, & x = 0 \\ 0, & x = 1 \\ x \log(x) - x + \frac{1}{2}\log(2\pi x) + \frac{1}{12x}, & \text{Otherwise} \end{cases} \tag{5.38}$$

This extends to taking the logarithm of the binomial coefficient which will be replaced directly with the approximation expression below, which will be defined as the Stirling Binomial Function.

$$\underset{\text{Binomial}}{\text{Stirling}}\left(\ Set \ , \ Choose \ \right) = Stirling(Set) - Stirling(Choose) - Stirling(Set - Choose)$$

Below is the detailed enumeration procedure for the whole system, that is including polymer-chains in solution as well as the the chains adsorbed to the surface in trains and loops.

Step 1: Find the basic quantities of the rest of the model.

- **INPUTS:**
  - The main variable that will drive the rest of the process is the consecutive nearest neighbours, n_1. This parameter is a way to quantify the size of the clusters for the model.
  - The following constants will need to be set before running the process:
    - μ_3 These are connective constants for 3 dimensional lattices.
    - A_3 These are the amplitude for constants 3 dimensional lattices.
    - B_3 is an amplitude associated with the loops that reside in the 3 dimensional lattices anchored to the two dimensional plane at the endpoints.
  - Parameters input into this model are:
    - r: chain-length of the polymers
    - n_{surf}: the area of the two dimensional surface-lattice in units of sites that are the size of a single mer.

  - n_{vol}: the volume of the three dimensional solution-lattice in units of sites that are the size of a single mer.

- The distance of the nearest cluster jumps D_p is computed by iterating through an increasing sequence of values of consecutive nearest neighbours in the cluster n_1.

$$D_p = \begin{cases} 1.492 \times \sqrt{n_1} & , p = \frac{3}{4} \\ 1.634 \times \sqrt{n_1} & , p = \frac{2}{3} \\ 1.707 \times \sqrt{n_1} & , p = \frac{1}{2} \\ 2.00 \times \sqrt{n_1} & , p = \frac{1}{3} \\ 2.509 \times \sqrt{n_1} & , p = \frac{1}{5} \\ 2\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{6} \\ 3\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{10} \\ 5.5\sqrt{2} \times \sqrt{n_1} & , p = \frac{1}{20} \end{cases}$$

- Compute the number of mers in each loop, $s_{lp} = f(D)$, using the above quantity D_p for D using the three separate functions for s_{lp} from Section 3.3.

- Calculate the footprint of the polymers on the surface, $\mathcal{L}$.

$$\mathcal{L} = r - n_{lp}(s_{lp} - 1) \qquad \text{by Equation 5.2}$$

- Find the number of polymers on the surface n_a.

$$n_a = \frac{p \times n_{surf}}{\mathcal{L}} \qquad \text{by Equation 5.3}$$

- Find the polymers in solution, n_b.

$$n_b = n - n_a$$

Step 2: Calculate the enumeration function values.

- Call the logarithmic enumeration function for the surface.

$$\begin{aligned}\log \mathcal{E}_{surf} = & \, Stirling\,(n_a \mathcal{L}) - Stirling\,(n_a) \\ & + n_a \left[\; (\mathcal{L}-1) \left(\log p - \log(\mathcal{L} n_a) - \left(\frac{1}{n_1+1} \right) \log(2\pi D) \right) \right. \\ & \left. + \left(\frac{\mathcal{L}+n_1}{n_1+1} \right) \left(\; \log(q) - (n_1-1)\log(q-1) \; \right) \right] \qquad \text{by Equation 5.36}\end{aligned} \tag{5.39}$$

- Enumerate loop arrangements of the system on a logarithmic scale, $\log \mathcal{E}_{lp}$.

$$\begin{aligned}\log \mathcal{E}_{lp} = & \, StirlingBinomial\,(\mathcal{L}, n_{lp}) \\ & + n_{lp} \left(s_{lp} \log \mu_3 \; + \; \log B_3 \; - \; 3.7 \log s_{lp} \; \right) \qquad \text{by Equation 5.35}\end{aligned} \tag{5.40}$$

- Finally compute the logarithmic enumeration of the solution

$$\log \mathcal{E}_{vol} = \log(A_3) \; + \; r \, \log(\mu_3) \tag{5.41}$$

Step 3: Output the total enumeration for a specific set of parameters.

$$\begin{aligned}\log \mathcal{E}_{total} =& Stirling\,(n) + \log \mathcal{E}_{surf} \\ &+ (n_a \times \log \mathcal{E}_{lp}) + (n_b \times \log \mathcal{E}_{vol}) \\ &+ (n_b \times \log n_{vol}) - Stirling\,(n_b) \qquad \text{by Equation 5.37} \end{aligned} \tag{5.42}$$

Step 4: Look for the values of n_1 that maximize $\mathcal{E}_{total}$.

5.8 Molecular Architecture of Surface and Loops

In the last two sections of this chapter (5.8 and 5.9) we shall present the results of the above periodic model and do an analysis on the molecular architecture of the polymers adsorbed to the surface for varying scenarios of coverage of polymers on the surface. This will be done initially from the macroscopic perspective of the surface overall in terms of the average thickness of the single layer of polymers. Then we will provide more granularity on the different molecular structures on the surface overall. Finally, we shall zoom in to a single polymer of the many on the surface and analyse the molecular architectures at that level. It is important to note that in the previous section we provided three alternate approaches to calculate the length of a loop as a function of its base length D. In this section we will mostly focus on the parameter of ν that corresponds to that of a random walk in three dimensions, namely that of $\nu^{-1} = 2$. The other two approaches, that of the self-avoiding walk which corresponds to $\nu^{-1} = 1.67$ and that of a linear walk of $\nu^{-1} = 1.00$ will be provided as reference data in the appendix. In the immediate three subsections (5.8.1,5.8.2,5.8.3), we have provided a set of possible measures of the height of the polymer layer in terms of the average thickness of the single layer of polymer, approximate loop heights of the loops, as well as the measure of the number of lattice sites occupied by a loop, $s_{_{lp}}$.

5.8.1 Loop Length

A metric that was used to get a sense of the size of the loops was that of loop length, s_{lp}. In the results below of Figure 5.20 we plot the loop length as a function of polymer coverage on the surface. The first thing we notice is high loop lengths for low polymer coverage and smaller loop length for greater polymer coverage. Comparing the different calculation approaches we observe a similar trend of decrease across all calculation approaches, where the non-linear computation has a steeper drop at twenty percent coverage.

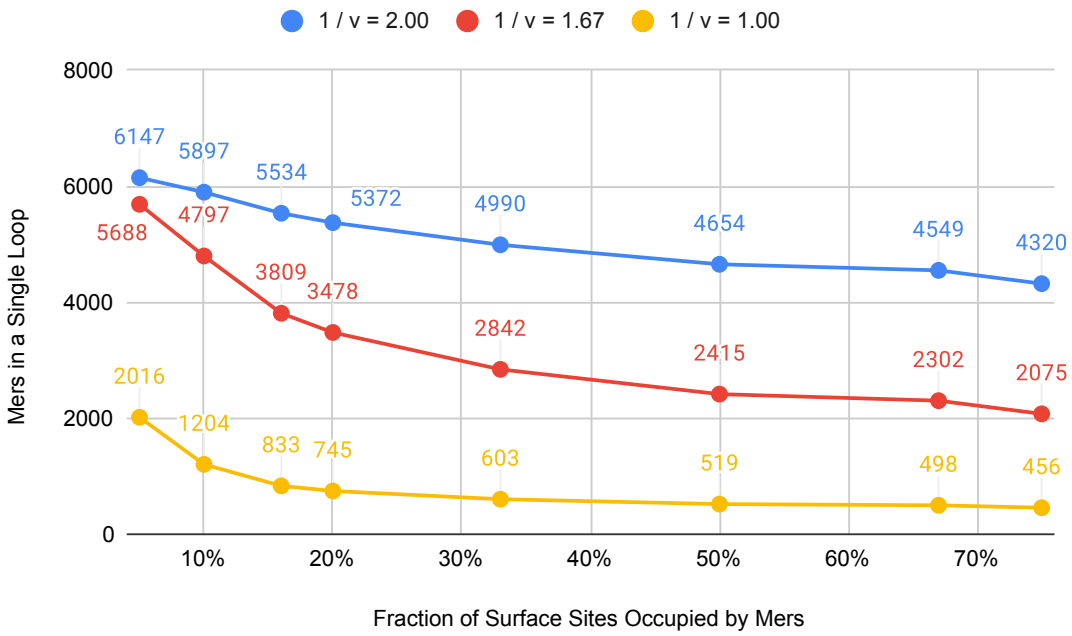


Figure 5.20: Mers in a single loop as a function of fraction of surface-site occupancy by polymers

5.8.2 Base-length of Loop

An alternative way to measure the size of the loops is that of the height of the loop based on the base-length of a loop. In this it is assumed that the height of a loop would be of a similar scale to the base-length. This is because the walk of the loop is assumed to be a

Brownian motion path. This implies that the distance between the endpoints of the loop would be on the same scale as its diameter, which in turn would be on the same scale as the height of the loop. This can be observed in the schematic of Figure 5.21 where the height of the loop (Ht) is equal to base-length (D) and that of Figure 5.22 where the values are not equal ($Ht = \frac{1}{2}D$), but still of similar scaling.[6]

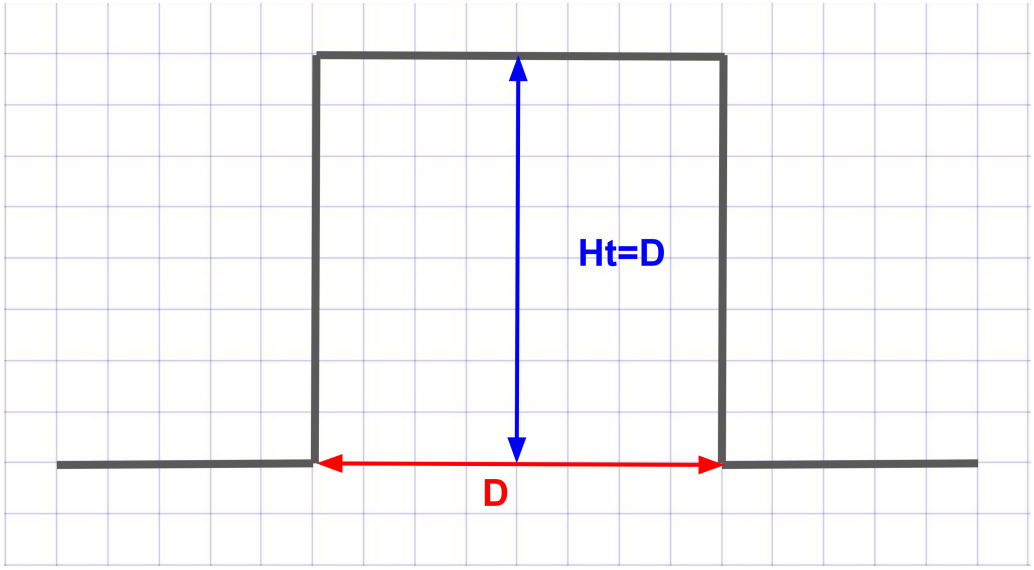


Figure 5.21: Loop height calculation based on the assumption of a square loop shape, where the height would be equal in scale to the base-length in lattice-sites

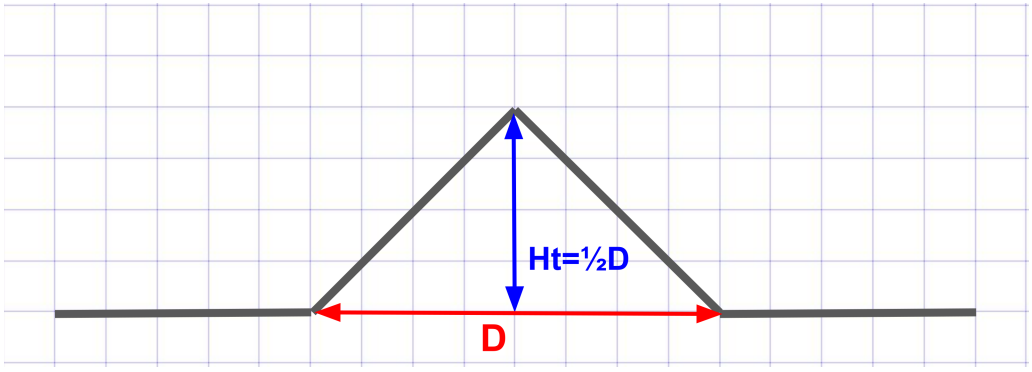


Figure 5.22: Alternative loop height approximation where the height is half the base-length in lattice-sites

[6]Most of this section will use the scaling of $Ht = D$, except in the case of the average surface thickness where $Ht = \frac{1}{2}D$ is used.

Figure 5.23 provides the variation of loop height as polymer coverage on the surface is varied. Given the assumed equality of height to base-length, plot below gives us information both on the height of loops but also their bases. The random-walk calculation ($\nu^{-1} = 2$) is relatively constant, whereas the self-avoiding walk approach ($\nu^{-1} = 1.67$) and linear approach ($\nu^{-1} = 1$) are decreasing functions.

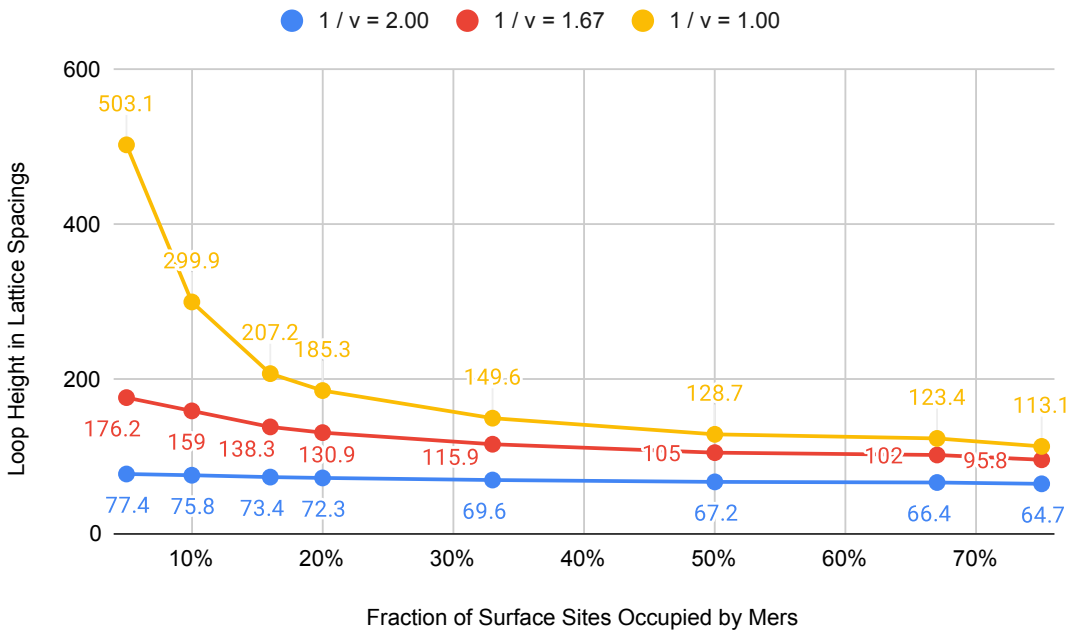


Figure 5.23: Approximate height of loops as a function of fraction of surface-site occupancy by polymers

5.8.3 Average Layer Thickness

Next we compute the average layer thickness, which is a way to come up with a single height value for the layer of polymers adsorbed to the surface overall. This was achieved by using the fraction of mers of loops, trains and salt-caps as weighting factors. We proceeded to calculate the weighted average of the heights of loops, gaps, and trains. More generally, this is the description of what the layer of polymers on the surface would look like if one was to

zoom out and look at the whole surface from a macroscopic perspective. More specifically we devised the following variables and calculations in order to compute the expected layer thickness of the surface. The way we calculated the total mers in salt-caps on the surface is that of multiplying the total lattice-sites on the surface (n_{surf}) by the fraction of mers on the surface ($1-p$).

$$N_{un} = n_{surf} \times (1-p), \tag{5.43}$$

The total mers in trains on the surface is the number of loops in trains on a polymer ($\mathcal{L}$) multiplied by the number of polymers adsorbed to the surface (n_a).

$$N_{tr} = \mathcal{L} \times n_a = p \times n_{surf} \tag{5.44}$$

The total mers in loops on the surface is the total number of mers in loops on a polymer ($(s_{_{lp}} - 1) \times n_{lp}$) multiplied by the number of polymers adsorbed to the surface (n_a).

$$N_{lp} = ((s_{lp} - 1) \times n_{lp}) \times n_a \tag{5.45}$$

The total mers in trains, salt-caps and loops is

$$N_{sm} = N_{lp} + N_{tr} + N_{un}. \tag{5.46}$$

We then converted the above values to weights. The calculation for the weighting factor for salt-caps on the surface is

$$W_{gp} = \frac{N_{un}}{N_{sm}}, \tag{5.47}$$

for the mers in trains on the surface the ratio is

$$W_{tr} = \frac{N_{tr}}{N_{sm}}, \tag{5.48}$$

finally that of the loops on the surface is

$$W_{lp} = \frac{N_{lp}}{N_{sm}}. \tag{5.49}$$

We made the assumption that the height of loops would be equal to half the distance of the base-length of the loop in lattice-sites.

$$H_{lp} = \frac{1}{2} \times D, \tag{5.50}$$

the trains would be one lattice-spacing

$$H_{tr} = 1.0, \tag{5.51}$$

and that of the salt-caps would be zero lattice-spacings

$$H_{gp} = 0. \tag{5.52}$$

The layer thickness calculation ($\bar{H}_{surf}$) would be

$$\bar{H}_{surf} = W_{tr} \times H_{tr} + W_{gp} \times H_{gp} + W_{lp} \times H_{lp}. \tag{5.53}$$

Using the above approach and varying it as a function of mer occupancy on the surface we get the results displayed in Figure 5.24. In the plots below we notice that the curves for which ν is not 1 are decreasing whereas the curve where $\nu = 1$ looks to be increasing. Here the three methods ($\nu^{-1} = 2.00$, $\nu^{-1} = 1.67$, $\nu^{-1} = 1.00$) do not agree in terms of their respective variations of layer height, as mer coverage is increased. The fact there are differences between the linear and the other two non-linear approaches is unsurprising,

because the linear approach describes a stiff constrained walk and the two non-linear are relatively unconstrained random and self-avoiding walks.

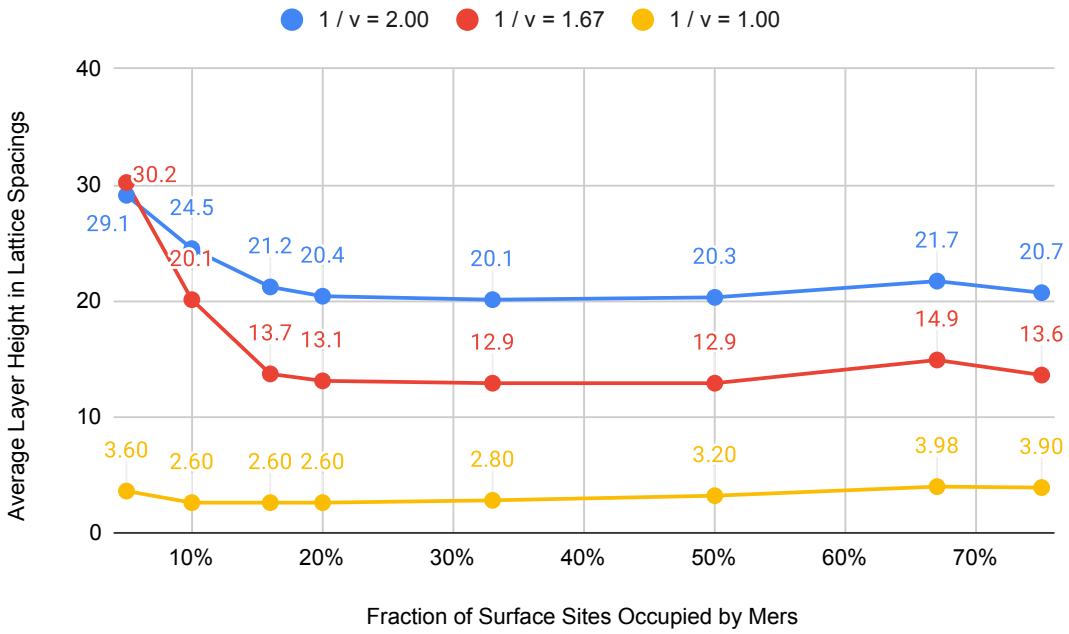


Figure 5.24: Average surface height as a function of fraction of surface-site occupancy by polymers

5.8.4 Surface Contribution Comparison

In this segment we delve into comparing the different categories of molecular architectures based on the fraction of the total mers belonging to polymers being attached to the surface. This was accomplished by taking the lattice-site occupancy ratios from Section 5.8.3 and converting them to a percent contribution. In terms of specific calculations, the percent contribution for trains was that of Equations 5.49 to 5.47. Another calculation is that of pooling of site occupancy of both trains and salt-caps was found to be

$$\%\, W_{gp+tr} = \frac{N_{un} + N_{tr}}{N_{sm}} \times 100\%. \tag{5.54}$$

The above calculations for varying surface coverage scenarios are visualized in Figure 5.25. What is of particular interest here is that the share of mers in loops dominates the share of lattice-site occupancy of trains and salt-caps to such a great degree that there are enough mers in loops in order to cover the surface up to two times over in most of the cases of surface coverage.

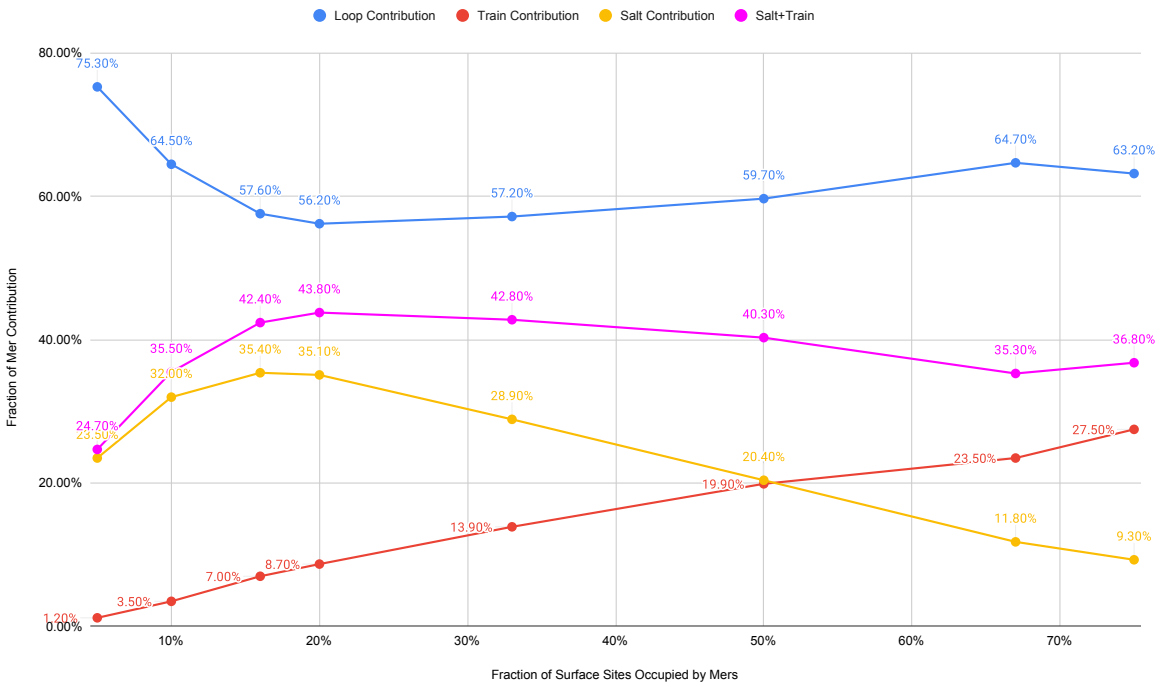


Figure 5.25: Contributions for all polymers on the surface as a function of fraction of surface-site occupancy by polymers, with $\nu^{-1} = 2$

5.8.5 Analysis at the Polymer Level

The calculations up to this juncture were from the perspective of the surface as a whole, but this gives us little insight on the molecular structure of the adsorbed polymer for varying values of surface coverage. In this section we focus on the different molecular structures at the level of a single polymer.[7] Similarly to the previous sections, we calculate the ratios of

[7]This is done while still considering the effects of having n_a polymers adsorbed on the surface.

mer contribution for loops, but in this approach it is instead a fraction of the total mers in a single chain, r,

$$\% R_{_{lp}} = \frac{n_{lp} \times s_{lp}}{r} \times 100\%, \tag{5.55}$$

a ratio is also found for the mers in trains

$$\% R_{_{tr}} = \frac{\mathcal{L}}{r} \times 100\%. \tag{5.56}$$

The two contributions are then compared in Figure 5.26 below, which is a comparison between loop and train contributions for a single polymer.

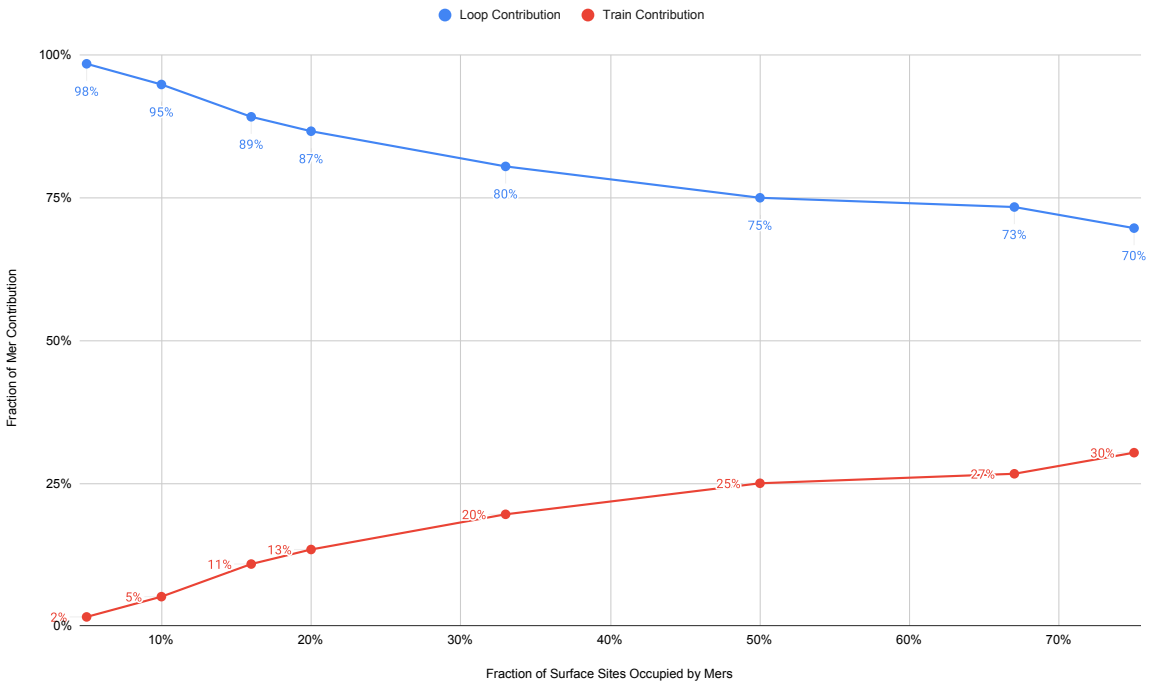


Figure 5.26: Mer contribution ratio for loops and trains for a single polymer as a function of fraction of surface-site occupancy by polymers, with $\nu^{-1} = 2$

The preceding analysis gave us a better understanding of the occupancy of lattice-sites of loops and trains, but could benefit from the introduction from a ratio of occupancy of the salt-caps in the bases of loops, given that salt-caps are what are constraining our model to arrange itself in the ways it does. Below is a more holistic analysis of all three components, that compares the lattice-site occupancy of the mers in loops to that of the aggregate of the salt-caps below loops and that of mers in trains. Here we take the ratio of the lattice-site occupancy for loops

$$\% \hat{R}_{_{lp}} = \frac{n_{lp} \times s_{lp}}{r + (n_{lp} \times D)} \times 100\%, \tag{5.57}$$

a ratio is then computed for the lattice-sites occupied by mers in trains and salt-caps in the bases of the loops, where $\frac{\mathcal{L}}{r+(n_{lp}\times D)}$ corresponds to the fraction of sites occupied by mers in trains and $\frac{n_{lp}\times D}{r+(n_{lp}\times D)}$ is the fraction of sites in bases below loops occupied by salt-caps.

$$\% \hat{R}_{_{tr+gp}} = \left(\frac{\mathcal{L}}{r + (n_{lp} \times D)} + \frac{n_{lp} \times D}{r + (n_{lp} \times D)} \right) \times 100\%. \tag{5.58}$$

The resulting plot of Figure 5.26 presents a comparison of three dimensional lattice site occupancy of mers in loops to that of the surface. The mers in the surface category are the mers in trains and salt-caps below loops. The result is not dissimilar to the previous result of Figure 5.26 that was comparing mers from trains and loops exclusively as coverage was varied. This is because the salt contribution within the context of a chain is very low in relation to the train and loop contribution which is because the only place we find salt-caps in this case is under the loops in bases, the exact quantities can be further examined in the tables provided in Section A.1 of the appendix.

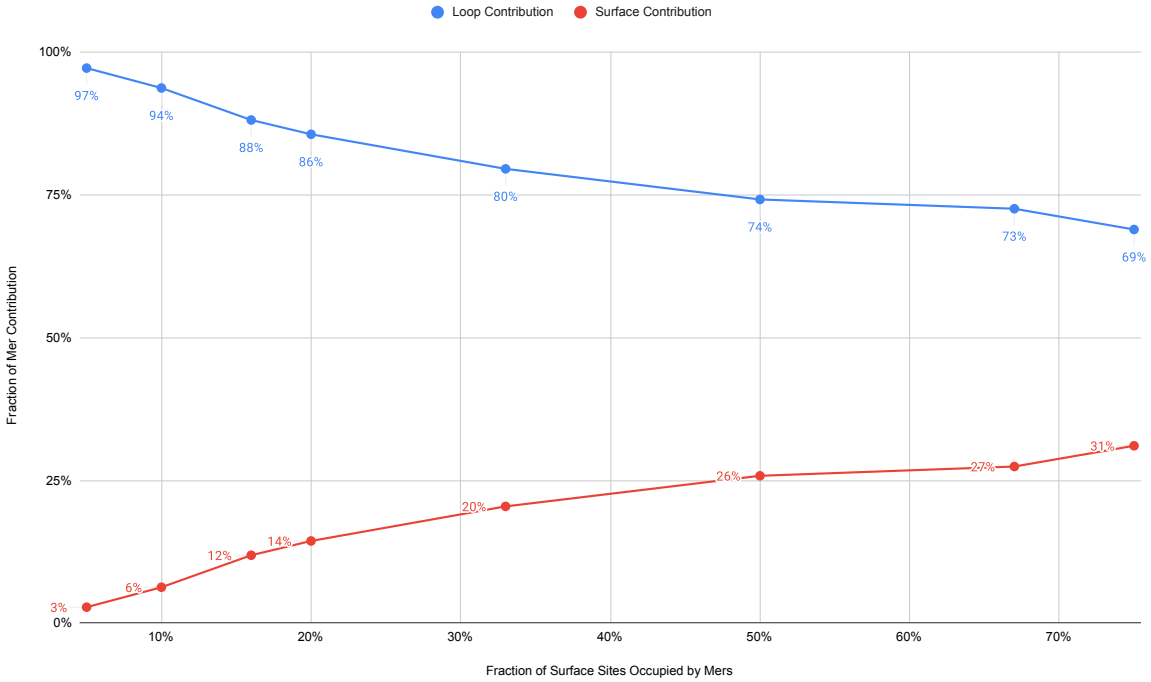


Figure 5.27: Fraction of Lattice-site occupancy for loop and surface sites for a single polymer as a function of surface coverage by polymers, with $\nu^{-1} = 2$

5.9 Visualization of Molecular Structures

We now combine the information from various different aspects of the prior analysis and results from Sections 5.8.2 to 5.8.5, in order to provide a better illustration of what is molecular structure may be formed on the surface at different coverage scenarios and from different spatial scales.

5.9.1 Loop Fraction

For reasons of convenience and simple schematic illustration with reasonable whole number loop counts, we have reduced the surface size (n_{surf}) in the schematics in Figures 5.30 to 5.32 to seven percent its original size. This re-scaling can be perceived as zooming-in to a square that corresponds to seven percent of the whole surface-lattice. We look at how the number of loops on the surface changes as we vary the polymer coverage on the surface, an example of which is displayed in the curve of the plot in Figure 5.28. We found that the number of loops drops approximately sixty percent when polymer coverage is increased from five to twenty percent. This is illustrated as the drop from five loops in Figure 5.30 to approximately two loops in Figure 5.31. Whereas, when we increase polymer coverage to three-quarters of the total surface sites, the number of loops returns to eighty percent of the original number of loops; i.e. a 5:4 ratio of five-percent coverage to that of seventy-five percent illustrated in Figure 5.32. It is also important to note that the height and the base-length of the loops do not vary significantly as is observed from the fairly constant curve of loop height as a function of surface coverage in Figure 5.29.

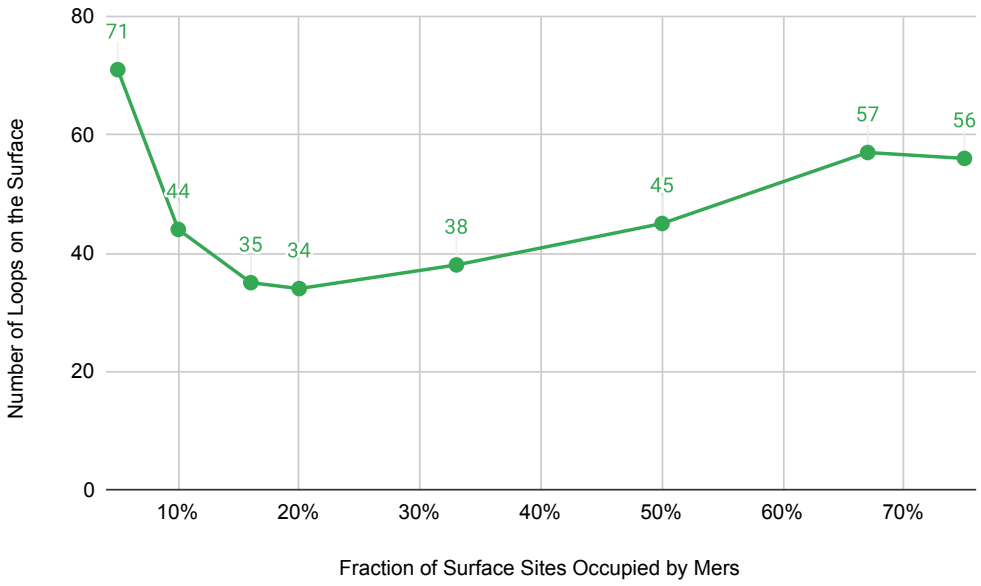


Figure 5.28: Number of loops on the surface as a function of fraction of surface-site occupancy by polymers, with $\nu^{-1} = 2$

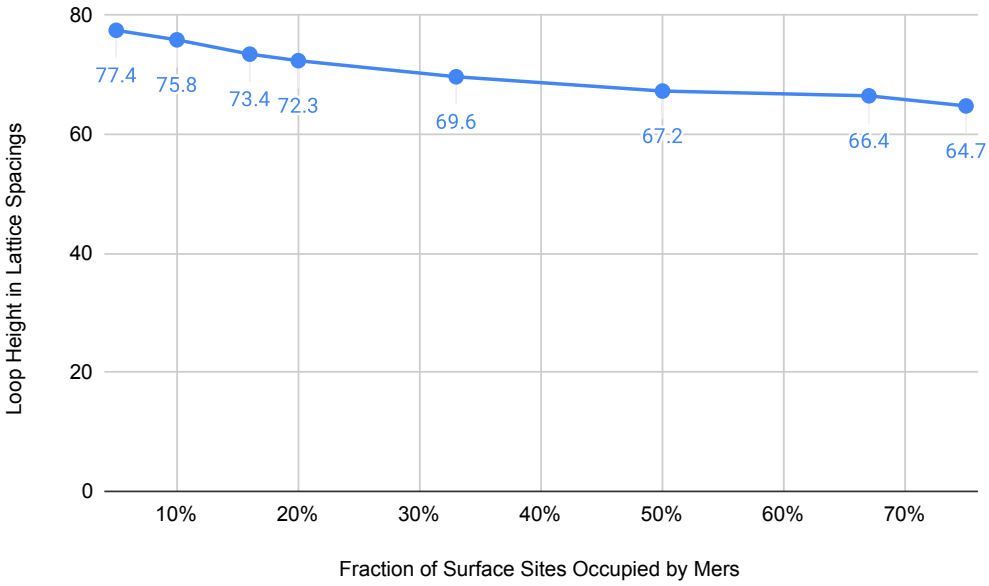


Figure 5.29: Approximate loop height in lattice-spacings as a function of fraction of surface-site occupancy by polymers, with $\nu^{-1} = 2$

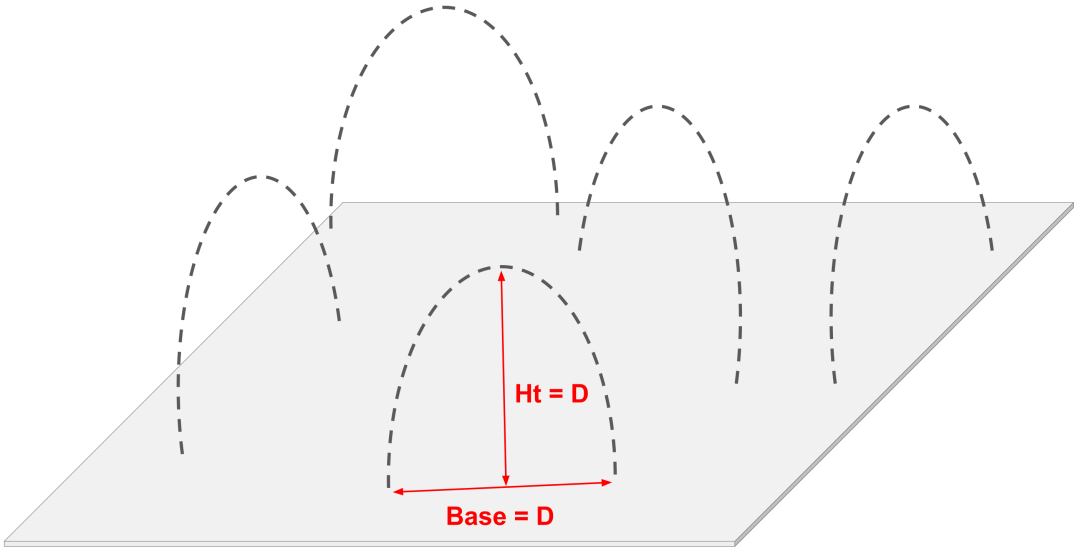


Figure 5.30: For the re-scaled surface[8], there are five loops on the surface in the case of five percent surface occupancy by mers, with $D = 77.4$ Lattice Spacings

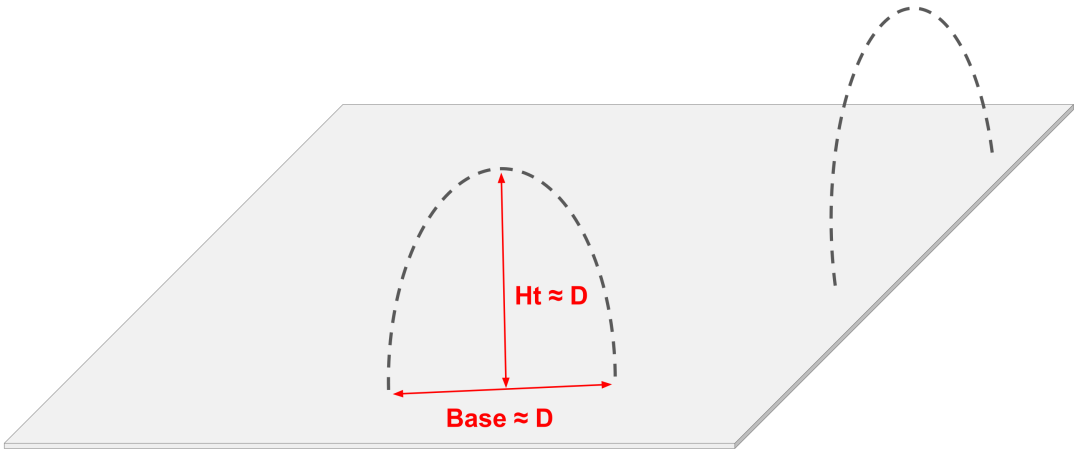


Figure 5.31: For the re-scaled surface, there are two loops on the surface in the case of twenty percent surface occupancy by mers, with $D = 73.4$ Lattice Spacings

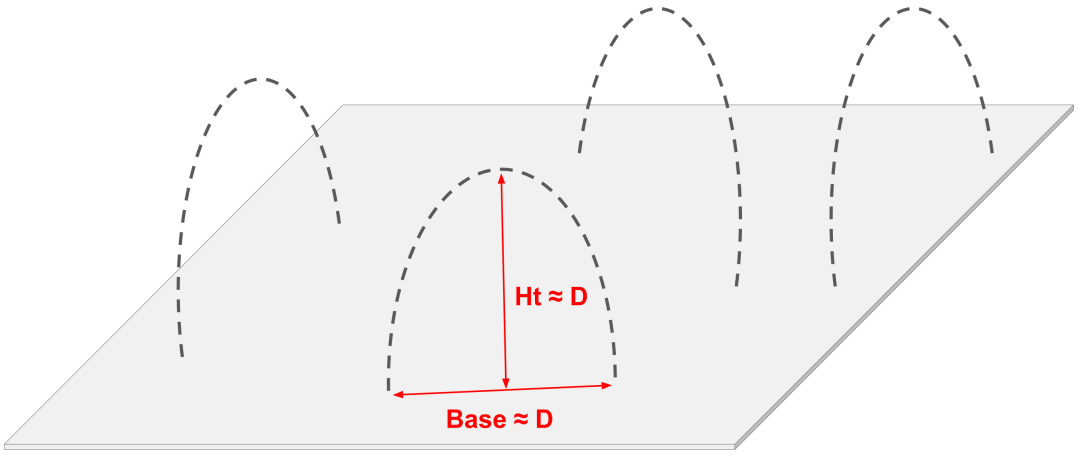


Figure 5.32: For the re-scaled surface, there are four loops on the surface in the case of seventy-five percent surface occupancy by mers, with $D = 64.7$ Lattice Spacings

5.9.2 Layer Thickness

A different characterization of the polymer layer on the surface is to focus on bulk characteristics. For this model we computed the approximate layer thickness. This was done through weighted sums of Equation 5.53. Results of this calculation are presented in Figure 5.33. In this case we observe an initial layer height that is approximately thirty percent greater than the average heights calculated for the other two scenarios of twenty and seventy-five percent coverage.

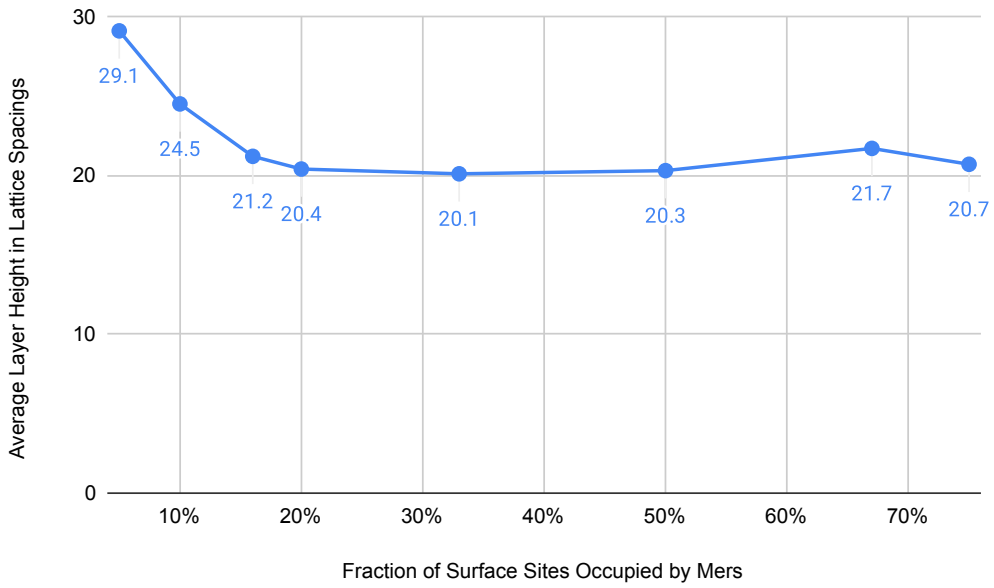


Figure 5.33: Average layer Height as a function of surface site occupancy.

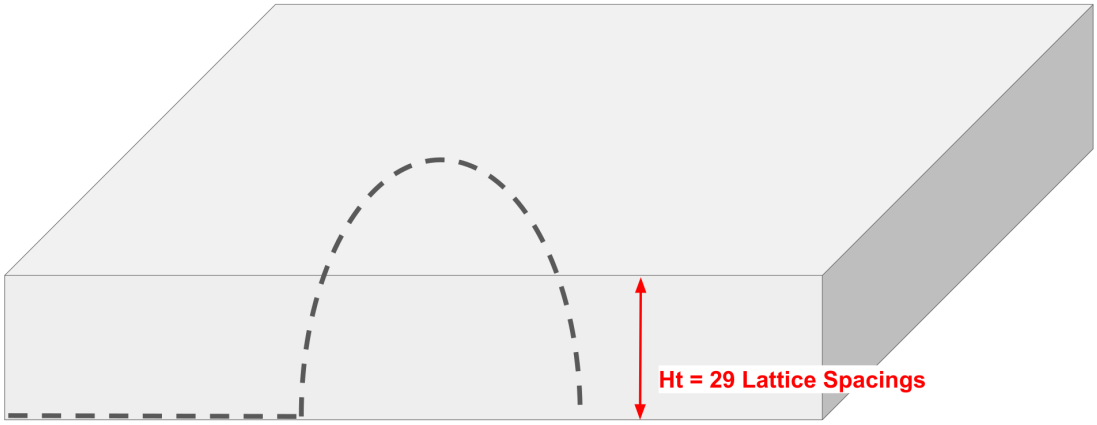


Figure 5.34: Average layer visualization (grey) for the case of five percent lattice-site occupancy by mers in polymer trains

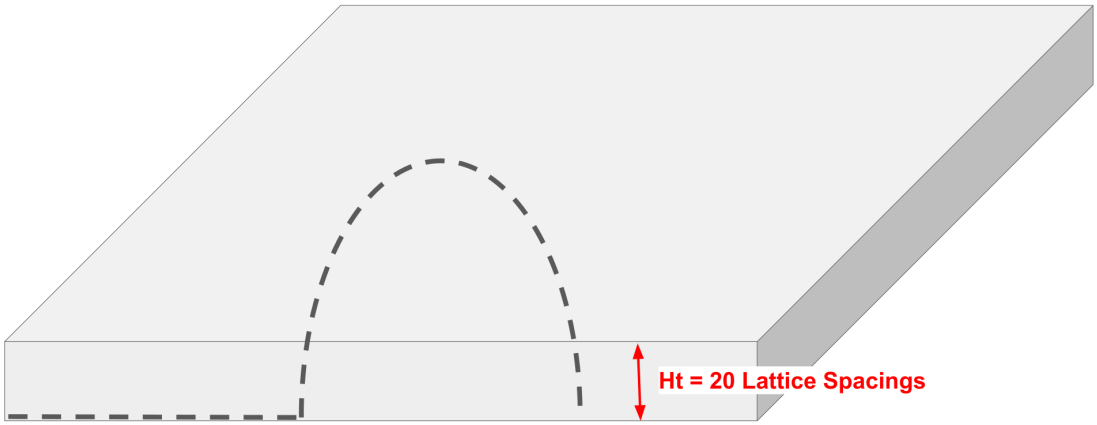


Figure 5.35: Average layer visualization (grey) for the case of twenty percent and seventy-five percent lattice-site occupancy by mers in polymer trains

Part III

Discussions, Conclusions and Future Work

Chapter 6

Discussion

The experiment [9] had shown that for lower surface charge, we have long loops that are entropically preferred, and our goal was to show this using mathematical models. We are now going to discuss those models chronologically.

In all models, all loops have the same length within each allowable configuration. This length differs from configuration to configuration based on surface coverage.

The first model we developed in Chapter 4 had a two dimensional surface of adsorption, with full coverage and a base of one step. We incorporated Flory-Huggins type calculations for the mers on the surface and also used a method of calculation of sub-enumerations developed by Fleer, in order to aggregate the different sub-partitions of the system [16, 12, 5]. We developed approximations of the enumerations of the surface, the solution and the loops, in order to optimize entropy. We also developed asymptotic approximations in order to validate the above results. The result of this model was that the optimal entropic scenario is that of polymers exclusively in trains on the surface. This is not supported by the experimental

observations, which is that of long loops contributing to abnormal increases in layer height [9, 10, 11].

We then developed a one-dimensional surface model, which is the one described in detail in Chapter 2. This model had considerations of gaps and bases, and one dimensional surface of adsorption. This reduction in dimensions of the surface was a way to simplify the calculations. The rationale behind this simplification was to investigate what may be impacting the model such that it was outputting results that contradict experimental observations. For this approach it was assumed that both salt-caps and mers will arrange themselves on the surface lattice based on favoured entropy. Using the procedure described in Chapter 2 we calculated the entropy of different scenarios of salt-fractions on the surface as well as loop lengths, s_{lp}, of the model. The outcome of the procedure was that the preferred state is that of all mers in trains, and all salt-caps belonging to gaps between adsorbed polymers. More specifically, we did not find the existence of loops in this model in contradiction with the experimental results [9, 10, 11].

This led us to change our approach and devise the model described in Chapter 3 with constraints on the positioning of salt-caps and by extension the positioning of the end-points of the loops on the surface. This model forces loops to exist; but lets the system choose between many short loop or few long loops and was used to test if the model would generate larger or smaller loops if the polymers are assumed to be adsorbed on the surface in a specific configuration. In the model, we fixed the number of salt caps on the surface, and observed what type of loops are generated. The the enumerational value corresponding to a scale of entropic preference of this arrangement is then recorded and compared to the results of the preceding iterations of the process. This model showed that the scenarios of mid to high surface coverage corresponded to the entropically optimal arrangements. More specifically,

given fixed ratio of salt-caps on the surface and an assumption that polymers are adsorbed to the remainder of the unoccupied sites, what is found is a preferential existence of long loops.

Given the encouraging results of Chapter 3, we proceeded to develop the two-dimensional model that is described in Chapter 5. It also followed the approach of specified patterning of salt-caps on the surface for each fraction of mers on the surface. This model had a similar scheme of patterning as Chapter 3, but adapted for two dimensions, in the form of salt-cap clusters and unoccupied clusters. Included in the model was a variation of the Fleer method and the Flory-Huggins approach developed in Chapter 4, but with the added consideration of clusters. A sub-model was created in order to calculate nearest neighbour clusters. This sub-model included a piecewise defined function in order to describe the different lengths of jump distances.

When comparing these results to the experimental domain we found that it captures the qualitative results of experiment well, in terms of the clear increase in layer height it exhibits at low surface coverage. For the case of higher coverage it predicts a modest increase in height in comparison to most experiments showing significant increases in thickness. Future work may be concerned with looking into this discrepancy [9, 10, 11].

When reviewing the work done on thickness as a function of coverage we look to the theoretical results presented by Stuart which were based on the models devised by Scheutjens and Fleer [20, 21, 44]. They showed an increase in thickness near the point of occupancy of half the surface by mers, which is captured by our final model from Chapter 5, with the only difference that in their model as the charge density continues to increase the layer thickness drops quite visibly [44]. Further work by Stuart [45] focuses on the increase in layer thickness

and similarly to our approach they focus on scenarios of low coverage of polymers on the surface.

Research work by Cosgrove [46] showed that as the amount of mers of adsorbed polymers increases so too does the layer thickness. This is close to our modelling in the aspect that we are also adding more polymers on the surface and observing thickness variations. Where our models differ is that layer thickness in our model is exclusively a function of mer occupancy of sites on the surface lattice, whereas in their model [46] they can control the mass directly. Additionally, their hypothesis and results are centered around tails being the source of increased layer thickness beyond the expected contribution of each polymer layer, which is in opposition with our work that instead is considering loops as the sources of abnormal layer thickness values and neglects tails completely. A model with predictions by Scheutjens in 1986 [48], measures the layer thickness as a function of coverage. Their theoretical predictions are in line with ours in terms of increasing thickness as the density of the available sites for adsorption on the surface are decreased. Further work was done by Cosgrove that considered multiple chains simultaneously on the surface using Monte Carlo sampling methods [47]. The above models attribute the abnormal increase in layer height in proportion to the increase in mers from adsorbed polymers to the contribution of tails to the layer. The above result the above result differs from ours in part because our approach only considers loops as a contributor to the larger than expected increase in layer thickness.

In terms of future directions the main goal is to find why our results disagree with experiment for higher surface coverage. Additionally, it would be of value to have general values of coverage as opposed to the discrete set of values we have considered. Another consideration that was raised early on in the modelling is the aspect that it is very likely that the direct models do not produce loops, because there is only a single loop-length they

can arrange in. It is suggested that increasing the set of available loop-lengths in the model may increase the preference of looping overall. In future models, we could incorporate a slightly larger range of different size loops and let the model arrange into any one of them based on entropic preference. This model was devised with the ultimate objective of one day predicting the molecular structure multilayers, and is for future consideration of how to make this model more applicable to multilayer experimental results. Finally, a more complex goal is that of considerations of polyelectrolytes in place of the neutral polymers in the current model. In the experiments on which we based our research, these polymers have charge and incorporating this into the model could make it more applicable to experiments and developments of polyelectrolyte multilayer films.

Chapter 7

Conclusion

Previous experimental research has shown a link between the preferential formation of long loops that contribute significantly to layer height and the fraction of surface lattice-sites being occupied by mers that belong to polymers adsorbed to the surface. Theoretical work to explain the above phenomenon is still quite limited. The objective of our model was to find out what the preferential formations of loops look like in terms of height, length, count, but also to be able to characterize the adsorbed layer in terms of average layer height. Although we were not able to get to the point of incorporating modeling considerations of multilayers, as well as multiple loops-lengths on the surface, we were able to show results in the range of low to mid surface coverage that agreed with experimental results. The experiments suggest that increased thickness of a single layer implies the existence of loops. Specifically for the case of low to medium surface charge, we showed an increase in layer height that was in agreement with experiments [9, 10, 11]. The number of microscopic configurations, proportional to entropy, was the prime consideration in our model as we didnt have explicit energy terms due to the fixed coverage on the surface. Future work will be focused on making the model more applicable to real scenarios, in terms of multiple

loop lengths present on the surface, and multilayer considerations. Additionally, the model would benefit from the enhancement of the heuristics used to compute the coverage based on patterns of walks in clusters on the surface lattice.

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Appendix A

Two Dimensional Cluster Model

A.1 Tables

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	99	513	4184
n_{lp}	0.993	1	1
n_a	71	13	1
$\mathcal{L}$	99	514	4185
D	77.4	176.2	503.1
s_{lp}	6147	5688	2016
$\log E_{total}$	9969034	9971888	9980707
Train Contr %	1.2%	3.1%	3.0%
Loop Contr %	75.3%	34.2%	1.4%
Gap Contr %	23.5%	62.7%	95.6%
Avg Surf Height	29.1	30.2	3.6

Table A.1: Coverage 5% with $D_{p=0.05}(n_1) = 5.5\sqrt{2}\times\sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	319	1404	4997
n_{lp}	0.997	1	1
n_a	44	10	2
$\mathcal{L}$	319	1405	4997
D	75.8	159	299.9
s_{lp}	5897	4797	1204
$\log E_{total}$	9955682	9956602	9967815
Train Contr %	3.5%	7.4%	7.1%
Loop Contr %	64.5%	25.2%	1.7%
Gap Contr %	32.0%	67.4%	91.2%
Avg Surf Height	24.5	20.1	2.6

Table A.2: Coverage 10% with $D_{p=0.10}(n_1) = 3\sqrt{2}\times\sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	673	2392	5368
n_{lp}	0.999	1	1
n_a	35	9	4
$\mathcal{L}$	673	2393	5368
D	73.4	138.3	207.2
s_{lp}	5534	3809	833
$\log E_{total}$	9942037	9947225	9947508
Train Contr %	7.0%	12.3%	14.9%
Loop Contr %	57.6%	19.6%	2.3%
Gap Contr %	35.4%	68.1%	82.7%
Avg Surf Height	21.2	13.7	2.6

Table A.3: Coverage 16% with $D_{p=0.16}(n_1) = 2\sqrt{2}\times\sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	830	2724	5455
n_{lp}	1	1	1
n_a	34	10	5
$\mathcal{L}$	831	2724	5456
D	72.3	130.9	185.3
s_{lp}	5372	3478	745
$\log E_{total}$	9936981	9939692	9939751
Train Contr %	8.7%	15.5%	18.8%
Loop Contr %	56.2%	19.7%	2.6%
Gap Contr %	35.1%	64.8%	78.6%
Avg Surf Height	20.4	13.1	2.6

Table A.4: Coverage 20% with $D_{p=0.20}(n_1) = 2.509 \times \sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	1212	3359	5598
n_{lp}	1	1	1
n_a	38	14	8
$\mathcal{L}$	1213	3359	5598
D	69.6	115.9	149.6
s_{lp}	4990	2842	603
$\log E_{total}$	9923907	9923140	9926735
Train Contr %	13.9%	25.8%	30.9%
Loop Contr %	57.2%	21.8%	3.3%
Gap Contr %	28.9%	52.4%	65.8%
Avg Surf Height	20.1	12.9	2.8

Table A.5: Coverage 33% with $D_{p=0.33}(n_1) = 2.00 \times \sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	1550	3786	5682
n_{lp}	0.999	1.000	1.000
n_a	45.0	18.0	12.0
$\mathcal{L}$	1550	3787	5682
D	67.2	105.0	128.7
s_{lp}	4654	2415	519
$\log E_{total}$	9916726	9919237	9919422
Train Contr %	19.9%	37.3%	46.8%
Loop Contr %	59.7%	23.8%	4.3%
Gap Contr %	20.4%	39.0%	48.9%
Avg Surf Height	20.3	12.9	3.2

Table A.6: Coverage 50% with $D_{p=0.50}(n_1) = 1.707 \times \sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	1653	3899	5703
n_{lp}	1	1	1
n_a	57	24	16
$\mathcal{L}$	1653	3900	5703
D	66.4	102	123.4
s_{lp}	4549	2302	498
$\log E_{total}$	9916889	9918384	9920564
Train Contr %	23.5%	47.8%	62.4%
Loop Contr %	64.7%	28.2%	5.4%
Gap Contr %	11.8%	24.0%	32.2%
Avg Surf Height	21.736	14.864	3.982

Table A.7: Coverage 67% with $D_{p=0.67}(n_1) = 1.634 \times \sqrt{n_1}$

s_{lp} method	$(D+1)^2+2$	$(D+1)^{1.67}+2$	$4\times(D+1)$
n_1	1881	4125	5744
n_{lp}	1.000	1.000	1.000
n_a	56.0	25.0	18.0
$\mathcal{L}$	1882	4126	5745
D	64.7	95.8	113.1
s_{lp}	4320	2075	456
$\log E_{total}$	9919744	9922216	9922313
Train Contr %	27.5%	54.1%	70.2%
Loop Contr %	63.2%	27.2%	5.6%
Gap Contr %	9.3%	18.7%	24.2%
Avg Surf Height	20.7	13.6	3.9

Table A.8: Coverage 75% with $D_{p=0.75}(n_1) = 1.610 \times \sqrt{n_1}$

A.2 Plots

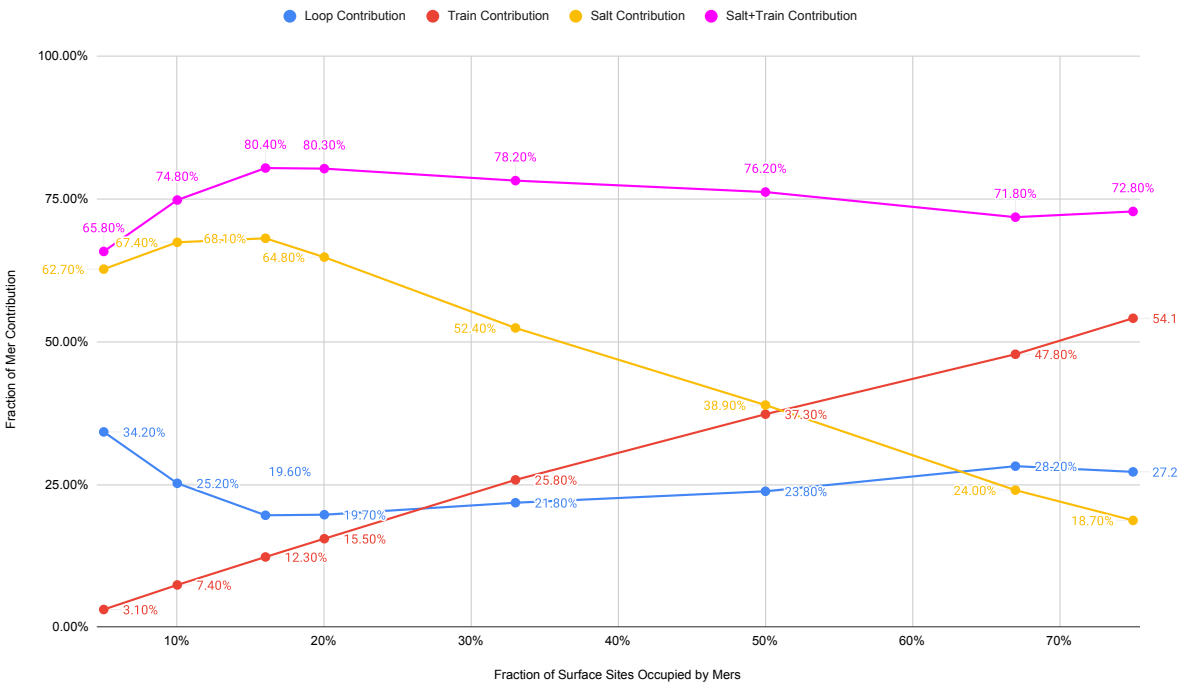

Figure A.1: Contributions for all polymers on the surface as a function of surface coverage using super-linear calculation

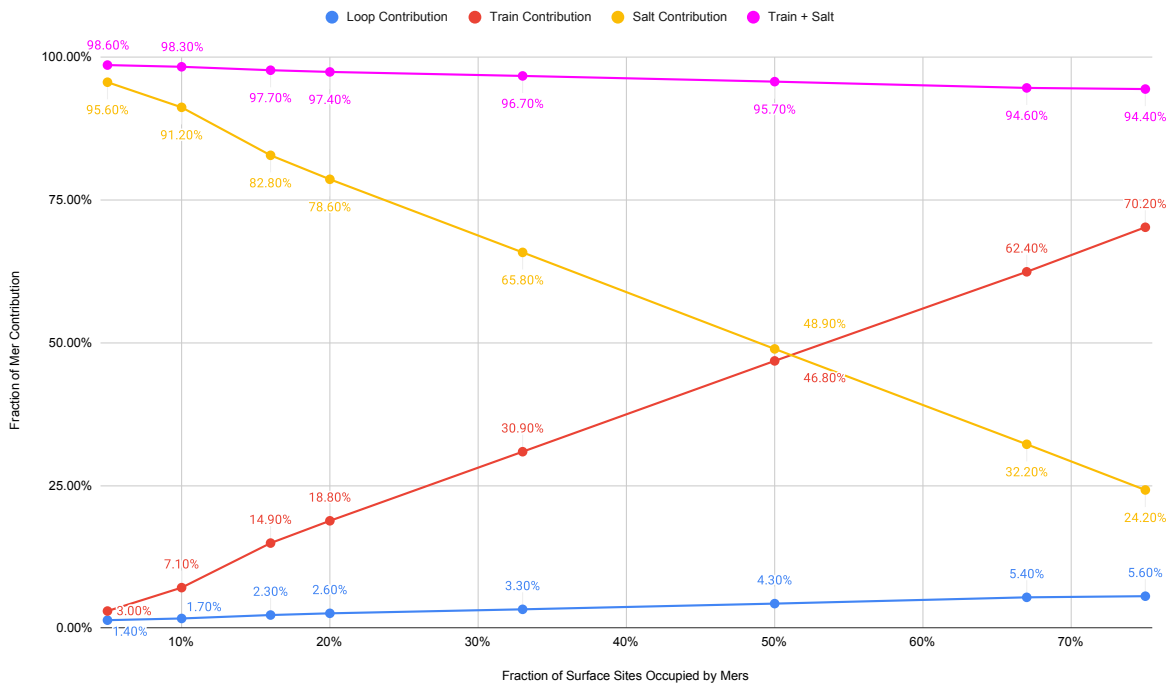

Figure A.2: Contributions for all polymers on the surface as a function of surface coverage using linear calculation

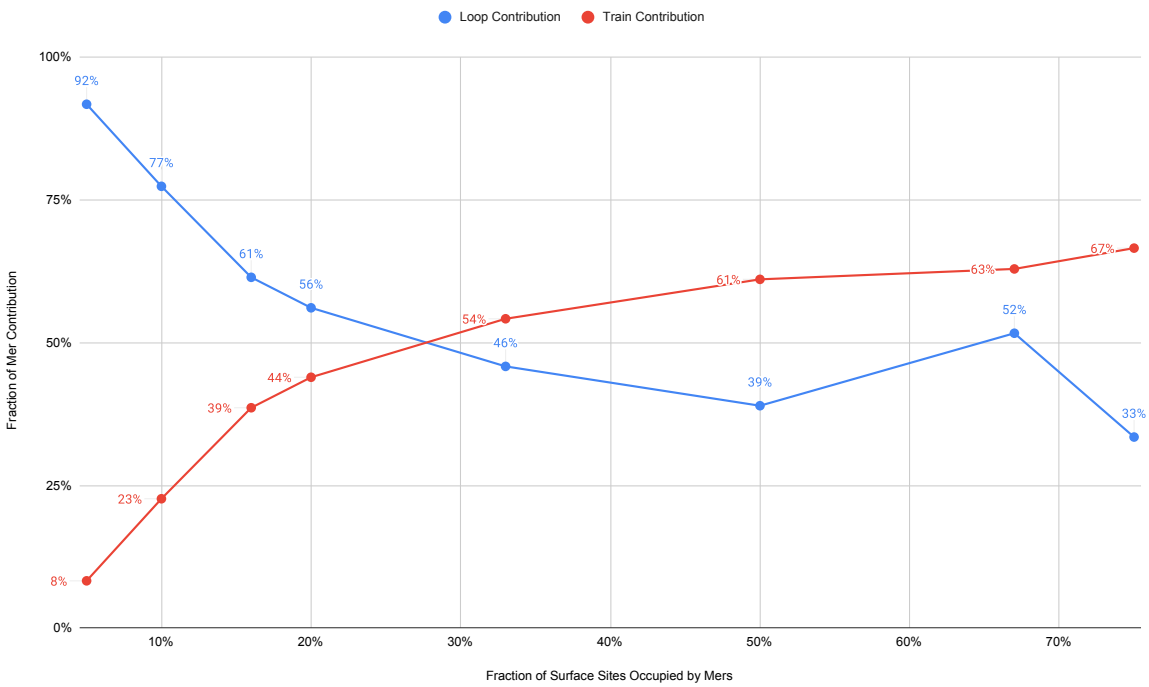

Figure A.3: Mer Contribution Ratio for Loops and Trains for a single polymer as a function of surface coverage using super-linear calculation

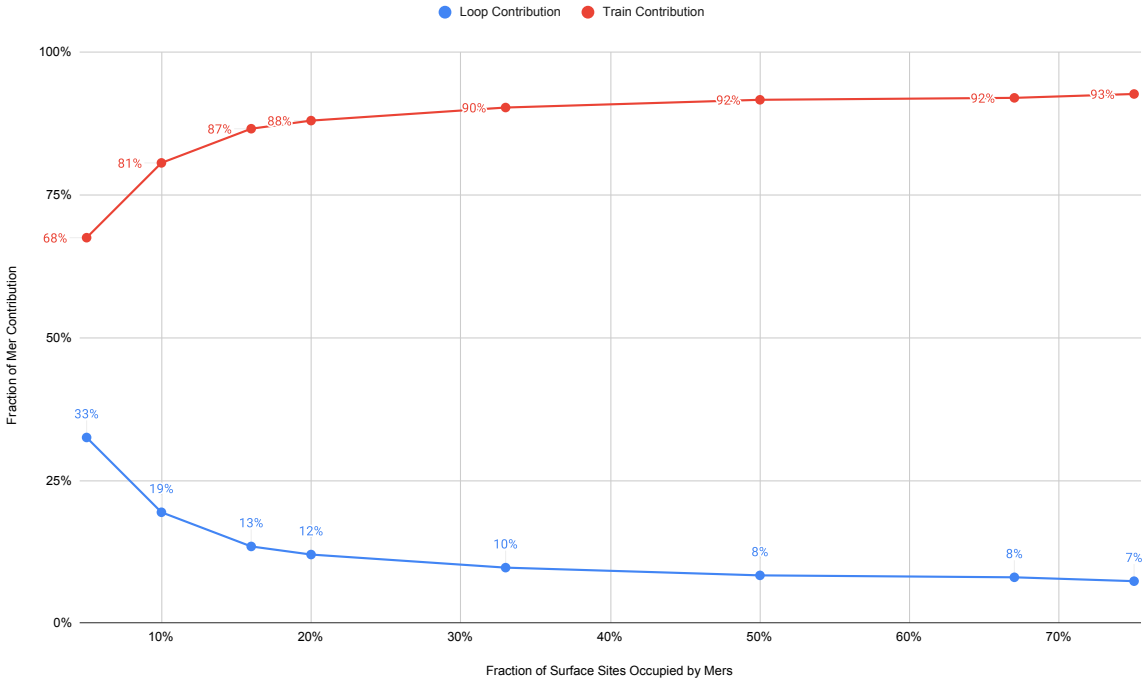

Figure A.4: Mer Contribution Ratio for Loops and Trains for a single polymer as a function of surface coverage using linear calculation

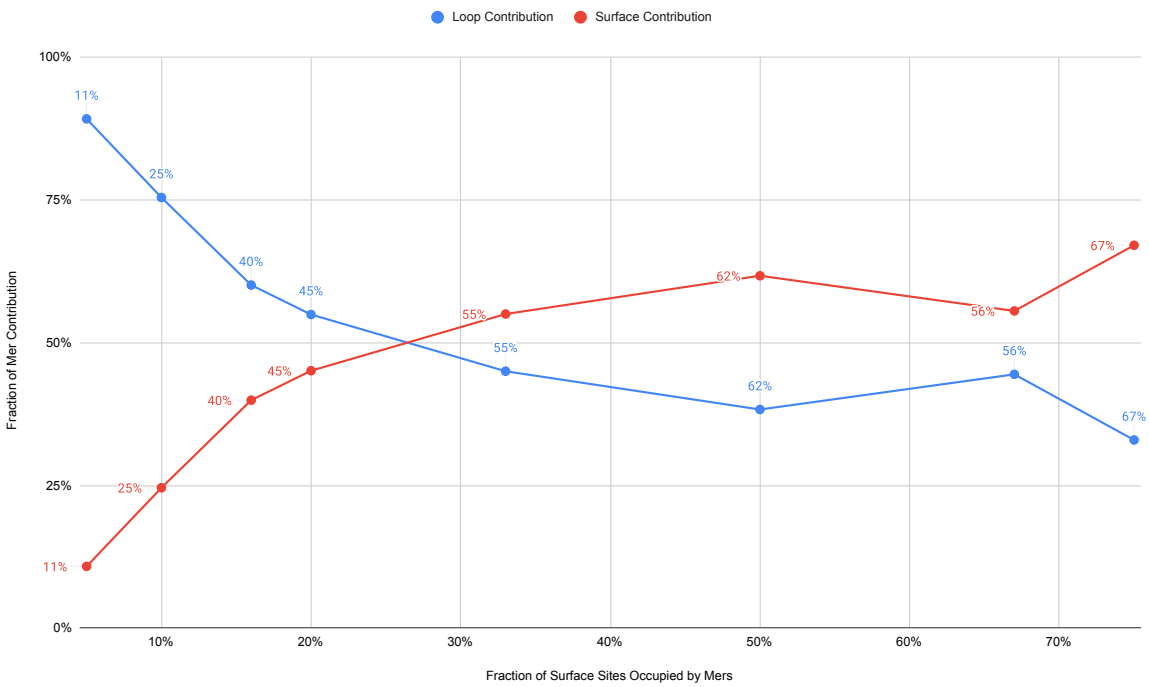

Figure A.5: Mer Contribution Ratio for Loops and Surface Mers Overall for a single polymer as a function of surface coverage using super-linear calculation

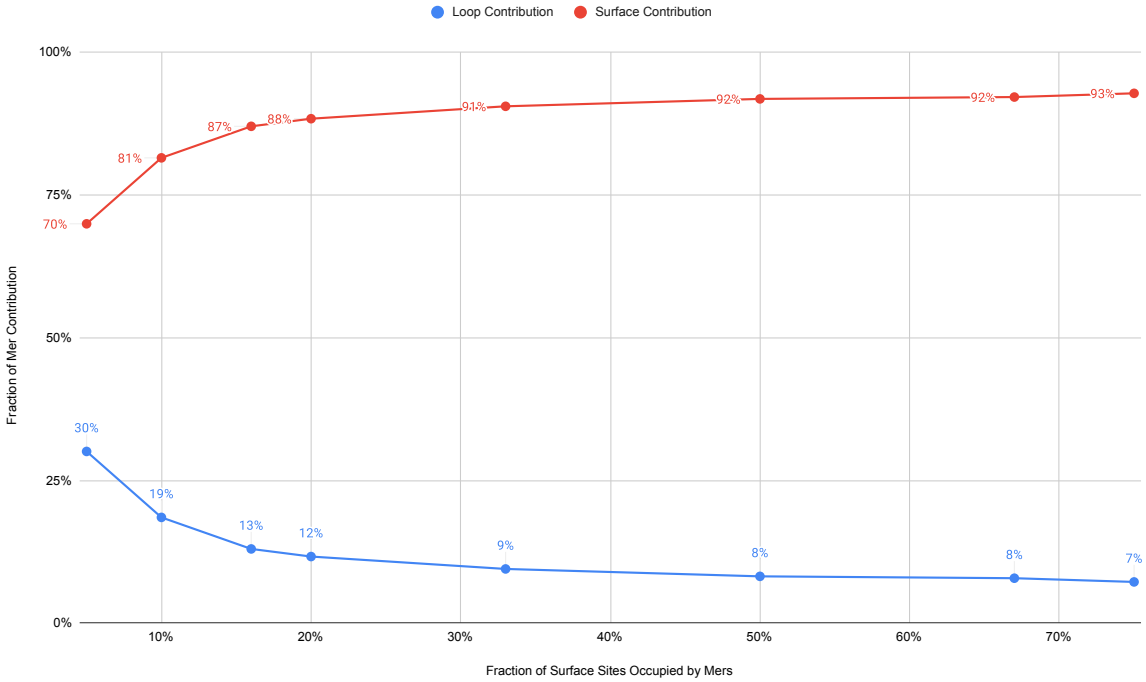

Figure A.6: Mer Contribution Ratio for Loops and Surface Mers Overall for a single polymer as a function of surface coverage using linear calculation