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Research Article

Investigating the Static and Dynamic Aspects of Polymer Adsorption on Wave-like Surface

Adugna Terecha Furi[1], * [iD]**, Gutu Dereje Mekonen[2]** [iD]**, Solomon Negash Asfaw[3], Diriba Gonfa Tolosa[4]** [iD]

[1]Department of Physics, Gambella University, Gambella, Ethiopia

[2]Department of Physics, Mizan Tepi University, Tepi, Ethiopia

[3]Department of Physics, Jimma University, Jimma, Ethiopia

[4]Department of Physics, Asosa University, Asosa, Ethiopia

Abstract

This study investigates the adsorption of linear polymers onto wave like surfaces using Monte Carlo simulations on 2D lattice. Using the bond fluctuation model (BFM), we analyzed the behavior of polymer chains of length (N) near a surface. We computed the mean-square end-to-end distance ‹R^2› and mean-square radius of gyration ‹Rg^2› for polymer by varying chains lengths (N). Interestingly, the scaling behavior of these properties with chain length deviates from the expected universal relationships due to the wave like surfaces. The number of adsorbed monomers, the fraction of adsorbed monomers, and the adsorption energy were determined for polymer chains of different lengths on a corrugated surface. The influence of interaction strength on adsorption energy was also investigated. Our findings indicate that the longest chains exhibit the highest surface coverage of adsorbed monomers. Shorter chains, however, display the maximum average adsorbed monomer fraction and optimal surface coverage. The factors affecting polymer adsorption onto surfaces include the strength of polymer-surface interactions, surface properties, length of the polymer chains, and the adsorption energy. For adsorption to occur, the energetic benefit gained from binding to the surface must exceed the loss in conformational freedom of the polymer chain. The influence of surface topography on polymer adsorption has been extensively studied using wave-like surfaces as a model system. Molecular simulations have been used to explore the effects of these surfaces on polymer behavior.

Keywords

Linear Polymer, Adsorption, MC, BFM, Wave Like Surface

1. Introduction

Polymer adsorption involves the adhesion of polymer chains to a substrate. This process can be weak, leading to easy desorption of the molecules from the surface [1]. Understanding and controlling polymer adsorption onto curved surfaces is essential for many technological applications [2]. Numerous technological fields, including drug formulation, paint, detergent, cosmetic, adhesive, deposition, lubrication, surface-wetting, printing ink,

ceramic processing, food stabilization, DNA, packaging, chromatography, and artificial membrane synthesis, involve polymer adsorption onto surfaces [3, 4]. Biological applications utilize the mapping of biopolymer adsorption, such as mucus in saliva or other proteins, to determine their structure and function. The adsorption of polymer chains onto wave like surfaces is crucial in various biological and industrial processes [4]. The adsorption of polymers is used to modify the surfaces of medical implants. The interfacial behavior of these macromolecules plays a crucial role in biomedical applications like artificial heart valves and joint prostheses [5, 6]. Polymer adsorption can lead to the creation of new materials with beneficial properties. To understand this phenomenon, we must investigate the behavior of polymer chains, their interactions with their surroundings, and how these factors influence the macroscopic properties of the interface. Factors like solvent quality, polymer size, chain dimensions, and radius of gyration have been extensively studied at the molecular level for the past four decades. The theory of polymer-solid interactions remains complex [7]. This complexity increases when considering corrugated surface structures with varying interaction types and surface energies. As the production of rough surfaces becomes more prevalent, the technological applications of polymer adsorption are influenced [8-10]. Thermodynamically, polymers minimize their energy by maximizing the number of monomer-surface interactions. However, this process results in a loss of entropy due to the reduced availability of free monomers for forming new conformations [11, 12]. The binding energy of certain regions on the surface, depending on the surface structure, is strong enough to overcome the entropic penalty of polymer adsorption. In contrast, other regions have insufficient binding energy to compensate for this entropic penalty [13, 14]. Polymers are typically studied in fields like biophysics, macromolecular science, and polymer science, including polymer physics. Polymer physics is concerned with the structure and properties of polymeric materials [15]. A statistical approach, drawing an analogy between polymers and Brownian motion or other random walks, is often used in polymer physics. Polymers are characterized by their static properties, such as chain size and shape [4, 16]. The properties of polymers, including end-to-end distance (R), radius of gyration (Rg), adsorbed monomers, average adsorbed monomer fraction, and adsorption energy, are important considerations [17, 18]. A variety of simulation methods have been used to calculate these properties. Molecular Dynamics (MD) and Monte Carlo (MC) are two common simulation techniques for polymers. These methods correspond to time and ensemble averaging in statistical mechanics. Monte Carlo simulations involve generating and probabilistically accepting or rejecting possible polymer conformations. In Molecular Dynamics (MD), Newton's laws of motion are used to integrate the positions and velocities of atoms over

time [19, 20, 21]. We have focused on Monte Carlo simulations of linear polymer adsorption.

2. Methodology

Computer simulations link theory and experiments. They validate theoretical predictions and replicate experimental systems like polymer solutions, melts, and networks. Molecular Dynamics (MD) and Monte Carlo (MC) are the two primary simulation techniques for polymers. These methods correspond to time and ensemble averaging in statistical mechanics [7, 19, 22]. We have chosen to use the Monte Carlo (MC) method for our simulations. To balance computational efficiency and accuracy for long-time, large-scale phenomena like translocation, we opted for a coarse-grained lattice-based MC simulation. This model simplifies the ring polymer structure by eliminating microscopic degrees of freedom, retaining only essential features like chain connectivity and short-range excluded-volume interactions. This model is well-suited for investigating general and universal properties of linear polymer chains. The Monte Carlo simulation method involves generating and probabilistically accepting or rejecting possible conformations. A mechanism is required for generating and evaluating these conformations to determine their acceptance or rejection during each move. In our simulations, the Bond Fluctuation Method (BFM) will be used to accomplish this task. The details of our model and method are presented below.

2.1. Lattice-Based Bond Fluctuation Model

To capture the fundamental physics of a problem, simplified models that preserve universal properties are often employed. The self-avoiding walk (SAW) on a lattice, a common lattice model representation of macromolecular configurations, is one such model. Each lattice site occupied by the walk represents a monomer. The bond length between consecutive steps of the walk equals the lattice constant, and the bond angles are constrained by the lattice geometry and the repulsive hard-core interaction between monomers. Lattice model simulations of polymers can be conducted on various lattice geometries, including the square lattice geometry used in our simulations. While the choice of lattice geometry is somewhat arbitrary, it does not influence universal properties, which depend solely on the lattice's dimensionality. Specific algorithms, such as the bond fluctuation method (BFM), are used to generate self-avoiding walk (SAW) conformations of a given polymer configuration on a particular lattice. The BFM is a widely used lattice model simulation method that provides an algorithm for analyzing dynamic properties in all dimensions and is more ergodic. The Bond Fluctuation Method (BFM) has been widely used to study the structure and dynamics of various polymer systems. To ensure self-avoiding walk (SAW)

conditions, each lattice site can only be occupied by a single monomer. In our model, each monomer occupies four vertex sites of a square area on the lattice. Monomers are connected to their nearest neighbors by a predefined set of bond vectors. The bond length between neighboring monomers must be within a specific range, $2 \leq bl \leq \sqrt{13}$ [7, 19], where bl is the bond length. To preserve topology and prevent bond crossings, bond lengths are restricted to the set $\{2, \sqrt{5}, \sqrt{8}, 3\sqrt{10}, \sqrt{13}\}$ [23]. All spatial distances are measured in units of the lattice spacing constant. The minimum distance of 2 ensures the excluded volume effect. The Bond Fluctuation Method (BFM) involves a local move where a randomly selected monomer is attempted to be displaced by one lattice constant in a randomly chosen direction. This move is accepted only if it satisfies both bond length constraints and the excluded volume interaction.

2.2. Simulation Techniques of Polymer Adsorption

We conducted a Monte Carlo simulation using the Bond Fluctuation Method (BFM) to study polymer chains on a 2D square lattice with periodic boundary conditions. We initialized the simulation by randomly placing non-concatenated polymer chains symmetrically within the simulation box, ensuring that each monomer was connected to two neighbors and there were no free ends. The excluded volume property was enforced by restricting each lattice site to be occupied by at most one monomer. To equilibrate the system, we performed a series of Monte Carlo steps, randomly selecting monomers and attempting to displace them to neighboring lattice sites. These moves were accepted or rejected based on the Bond Fluctuation Method constraints, which ensured that the polymer chains remained connected and self-avoiding. During the simulation, bond breaking and formation were allowed for monomers at chain ends, enabling chain growth or shrinkage. However, the order of monomers within the chain was maintained.
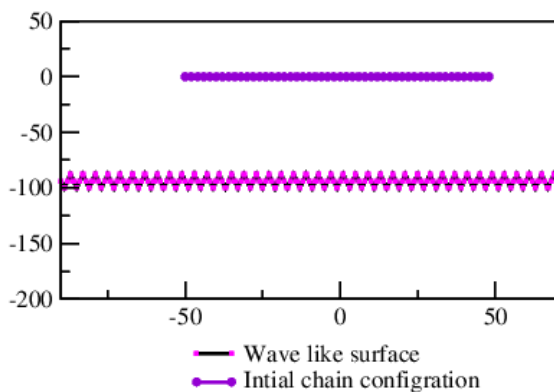

Figure 1. Initially configuration for linear polymer adsorption on wave like surface.

Wave like surface is defined by its wave height amplitude (ht) and maximum height (H_{max}). The value of ht is 6, and H_{max} is calculated as 2 times the absolute value of h(3), where h(3) is the absorption at the surface height at a horizontal distance of 3. This formula creates a sinusoidal surface. To generate a smooth surface, both H_{max} and ht should be 0. To indicate; wave like surface, initial chains configuration, relax configured chain and absorbing configured chain in to created surface which illustrated on figure 1, figure 2, figure 3 respectively.
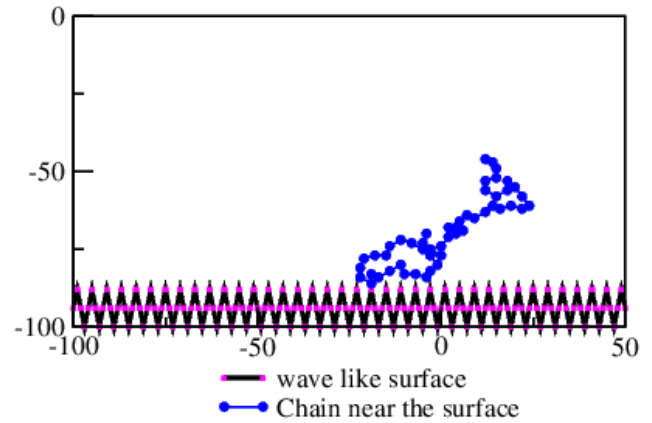
Figure 2. Configuration of linear polymer adsorption near wave like surface.
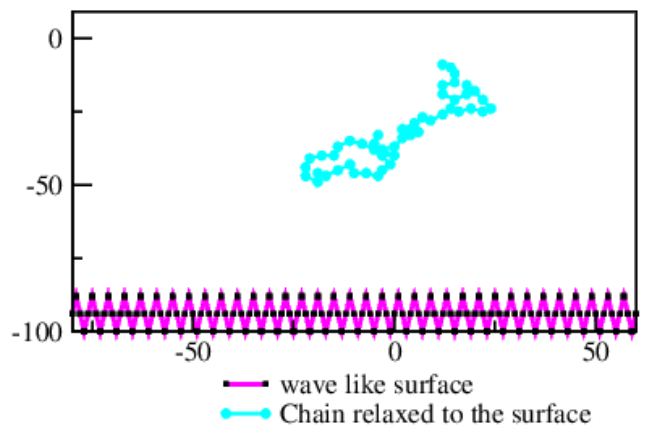
Figure 3. Relaxed linear polymer adsorption near wave like surface.

So, after reaching equilibrium the simulation; data was collected and then, we created wave like surface because no material can come into being without creating a surface or interface. Finally initially conformance chain relaxed to surface to adsorb on surface due to free energy of the system were shown in (figure 4).
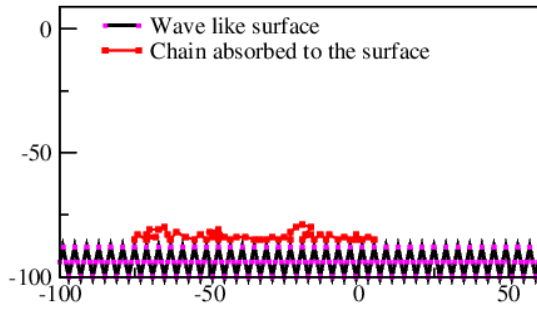
Figure 4. *Absorbed linear polymer on the wave like surface.*

3. Results and Discussion

3.1. Static Properties of Linear Polymer Adsorption on Wave Like Surface

The adsorption of linear polymers onto wavy surfaces differs significantly from that on flat surfaces. Polymer chain behavior on such undulating substrates with either regular or irregular patterns is influenced by the surface's topography, affecting how the polymer conforms, binds, and distributes itself. Understanding these static properties (conformation, adsorption strength, and spatial arrangement) is key to comprehending polymer-surface interactions.

3.2. Mean Square End-to-end Distance ($\langle R^2 \rangle$) of Linear Polymer

The net displacement of the chain, or the end-to-end vector R, can be calculated for an ideal chain. This vector connects the starting and ending points of the random walk, which are the end monomers. The universal scaling exponent that relates the mean square end-to-end distance to the chain length can be expressed as:

$$\langle R^2 \rangle \sim N^{2\nu} \tag{1}$$

The scaling parameter is also influenced by the spatial dimension (d).

$$\nu = \frac{3}{2+d} \tag{2}$$

In polymer physics, the scaling dimension (d) is known to be 2 for chains perfectly adsorbed onto a surface and 3 for chains freely suspended in bulk. However, our simulations involving sinusoidal or smooth surfaces reveal a surprising deviation. The scaling parameter (ν) observed in these simulations significantly deviates from the expected values for both adsorbed and bulk scenarios. This suggests that the presence of these non-ideal surfaces significantly impacts the behaviour of the polymer chains. The slope of our study was 2.13 for a wave like surface which implies that variation from expected value and the

universal scaling exponent of mean square end-to-end distance with chain length of $\langle R^2 \rangle \sim N^{2\nu}$ is influenced by wave like surface which is agree with reference [24].
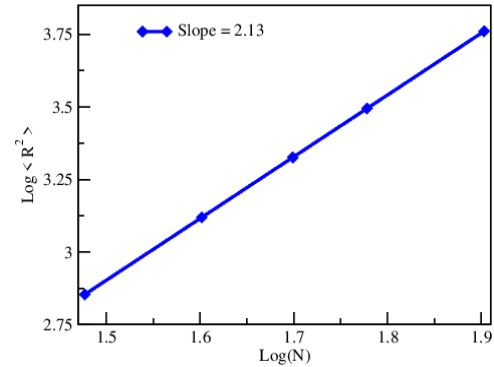

Figure 5. *Log-log plot of mean square end-to-end distance with respect to number of monomers of linear polymer adsorption on wave like surface.*

3.3. Radius of Gyration ($\langle R^2 \rangle$) for Linear Polymer

The radius of gyration, which is a measure of a polymer chain's size and shape, tells us how the chain tends to align with the surface. The square radius of gyration is an average value calculated from all possible conformations the chain can take. While this average suggests a spherical shape, the chain doesn't always adopt this exact form. This important static property, which depends on the number of monomers in the polymer chain, provides valuable information about the chain's behaviour. The plot of the mean polymer size $\langle Rg^2 \rangle$, against degree of polymerization N, on wave like surface represented on figure 6. Ideal polymer models have shown that the power−law scaling relation between these two quantities as $\langle Rg^2 \rangle \sim N^{1/2}$ *and* the universal scaling exponent is broken due to the conformations of the polymer is distorted or inhibited by the wave like surface which is Comparable finding obtained by [24].
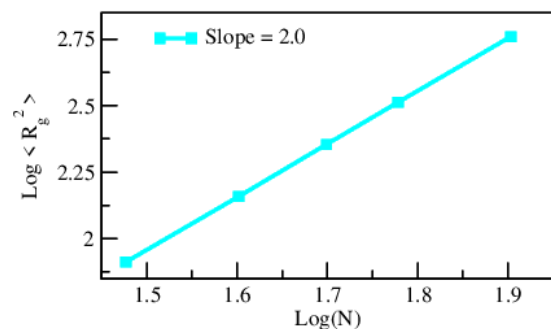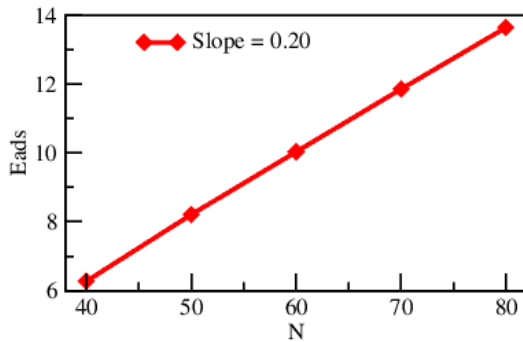

Figure 6. *Log-log plot of mean square radius of gyration with respect to number of monomers of linear polymer adsorption on wave like surface.*

While the degree of polymerization remained constant, varying the surface type and maximum height of the wave-like surface (s) significantly impacted the adsorption of monomers and the resulting chain conformation within the simulation box.

3.4. Adsorbed Monomer

Longer polymer chains tend to exhibit stronger adsorption to surfaces compared to shorter chains. This enhanced adsorption is attributed to the ability of longer chains to overcome the entropic penalty associated with conformational restrictions, facilitated by increased enthalpy interactions arising from the larger number of monomers. Consequently, the average adsorbed monomer fraction of linear polymers on the wave-like surface, as represented on figure 7 by slope of the graph (0.20), demonstrates a positive correlation with chain length. The average adsorbed monomer fraction, calculated from the slope of the average adsorbed monomer as a function of chain length, is associated with a higher probability of achieving the maximum number of adsorbed monomers on the wave-like surface.

varying interaction strength at a fixed chain length. The relationship between these variables can be inferred from their definitions as follow.

$$E_{adsorption} = N_{adsorbed} \times \varepsilon\varsigma \tag{4}$$

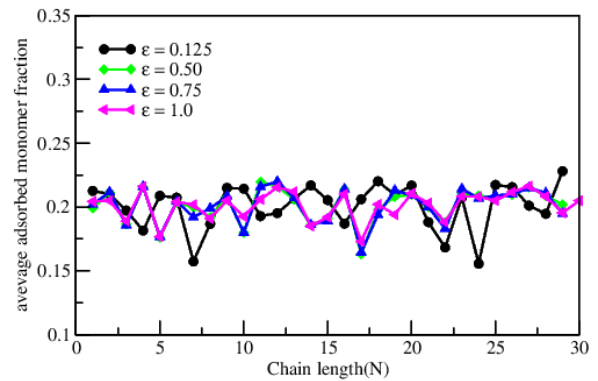$$N_{adsorbed} = \frac{E_{adsorption}}{\varepsilon\varsigma} \tag{5}$$

Where $N_{adsorbed}$ is adsorbed monomer, $E_{adsorption}$ is adsorption energy and $\varepsilon\varsigma$ is interaction strength that expressed in terms of KT. From equation (3) probability of adsorption can be expressed as:

$$P_{ads} = \frac{Nadsorbed}{Nmonomer}$$

But, $N_{adsorbed}$ is given by: $\frac{E_{adsorption}}{\varepsilon\varsigma}$ and $\varepsilon\varsigma = KT$

$$P_{ads} = \frac{E_{adsorption}}{Nmonomer \times \varepsilon\varsigma} \tag{6}$$

The impact of varying interaction strength on a polymer chain (constant monomer) is shown in the following graph.

Figure 7. Adsorbed energy as function of chain length.

3.5. Average Monomer Adsorption Fraction

The average adsorbed monomer fraction was determined for various chain lengths on wave like surfaces. The effects of changing interaction strength of the wave like surface were also investigated. The probability distribution of the average adsorbed monomer fraction can be calculated as follows:

$$P_{ads} = \frac{Nadsorbed}{Nmonomer} \tag{3}$$

Where P_{ads} = probability of adsorbed monomer, $N_{adsorbed}$ = number of adsorbed monomers and $N_{monomer}$ = total number of monomers in the simulation. Probability distribution of adsorbed monomer fraction examined with its relation; in the case of wave like surface. We calculated the probability distribution of average adsorbed monomer fraction by

Figure 8. A plot showing the likelihood of different probability distribution of average adsorption levels.

This graphical representation suggests the probability distribution for interaction strength 0.125KT, 0.5KT and 0.75KT and 1KT. This schematic graphical illustration expresses the probability distribution of average adsorbed monomer fraction decreased with increased interaction strength. Additionally, the probability distribution for the average adsorbed monomer fraction on the wave-like surface reveals that longer chains exhibit a higher average adsorbed monomer fraction compared to shorter chains.

4. Conclusion

We developed and tested a Monte Carlo simulation algorithm to investigate the adsorption of linear polymers

onto wave like surface. Our static property analysis revealed that the scaling relationships between the mean-square end-to-end distance $\langle R^2 \rangle$ and the mean-square radius of gyration $\langle R_g^2 \rangle$ with chain length (N) deviate from the universal scaling exponents.

Additionally, adsorbed monomers, averaged adsorbed monomers fraction and adsorption energy as the function of chain length for the wave like surface are investigated. Large Chain length was largest surface coverage because of enthalpy contribution of polymer surface contacts was the optimum and the system losses less configurational entropy arising from the confinement to the surface. We calculated the probability distribution of average adsorbed monomer fraction by varying interaction strength at a fixed chain length. The probability distribution for the average adsorbed monomer fraction on the wave-like surface reveals that longer chains exhibit a higher average adsorbed monomer fraction compared to shorter chains. The chain increases the averaged adsorbed monomer fraction was decreased.

Abbreviations

EV	Excluded Volume
MC	Monte Carlo
MD	Molecular Dynamics
SAW	Self Avoiding Walk
BFM	Bond Fluctuating Method
R	End-to-End Distance
Rg	Radius of Gyration

Author Contributions

Adugna Terecha Furi: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation , Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft

Gutu Dereje Mekonen: Methodology, Project administration, Resources, Supervision, Visualization, Writing – original draft, Writing – review & editing

Solomon Negash Asfaw: Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft

Diriba Gonfa Tolosa: Software, Visualization, Writing – original draft, Writing – review & editing

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Data Availability Statement

The data is available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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