MONTE CARLO SIMULATION STUDY OF POLYMER ADSORPTION ON ROUGH SURFACES

A THESIS SUBMITTED TO THE GRADUATE STUDIES OF JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS (STATISTICAL PHYSICS)

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DECLARATION

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Abstract

In this work we have presented Monte Carlo simulations of linear polymer adsorption on rough surfaces in a two dimensional $(2D)$ lattice. To this end we used the bond fluctuation model (BFM) to study the adsorption process of a polymer chain length N. We have calculated the average mean-square end-to-end distance $\langle R^2(N) \rangle$ and the mean-square radius of gyration $\langle R_g^2(N) \rangle$ as a function of chain length N. We found that the scaling relation of both the mean square end-to-end distance and the radius of gyration as a function of chain length N are non universal due to the effect of surface roughness. On the other hand, the adsorbed monomers, averaged adsorbed monomers, averaged adsorbed monomers fraction, adsorption energy and averaged adsorption energy were measured as function of chain length N, surface roughness height(h) and adsorption energy with the interaction(ϵ_s). Our results show that the longest chain length $N = 85$ has maximum surface coverage of adsorbed monomers and averaged adsorbed monomers. Also for a given, chain length as the surface roughness height(h) increases the adsorbed monomers, averaged adsorbed monomers, averaged adsorption energy, adsorption energy and averaged adsorbed monomers fraction were decreased. Short chain length$N = 30$ has maximum averaged adsorbed monomers fraction and optimum surface coverage. Adsorption energy was optimum for the strongest interaction strength (ϵ_s) and longer chain length.

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1

Introduction

1.1 Background of study

Polymer adsorption is the adhesion and bonding of molecules which stick together and weakly held by a substrate that easily slip down from the surface. An interface polymer adsorption is a phenomenon which is a great importance in a number of areas in our everyday life. In many technological applications, understanding and controlling polymer adsorption onto solid surfaces is essential to the outcome of a product. Such technological areas may comprise formulations of drugs, paints, detergents, cosmetics, adhesion, deposition, lubrication, surface-wetting, printing inks, ceramic processing, food stabilizers, DNA, packing, Chromatography and synthesis of artificial membranes all involve polymer adsorption on to a surface. Biological aspects include mapping the adsorption of bio-polymers, such as musing in the saliva or other proteins, to determine their structure and function. The adsorption of polymer chains on a solid surface is important in biology, tribology and industrial process. Coating semiconductor substrates with mono-dispersed polymer is one method for increasing the performance of semiconductor or metals in detection of gases such as hydrogen. Another application is in optics and biosensors, where polymers can pattern to different specific wave lengths of light[2, 13]. Recently the sensitivity property of polymer has been shifted to a new era of applications which is in the biomedical field[3]. Polymer chains have been employed to increase the efficiency of injection and drugs in terms of speed and coverage. Basically, drugs molecule will attach to a polymer chain and that helps the drug to identify the target cells faster and more efficiently than with the regular approach[4]. Adsorbed polymers are also used to surface modification of medical implants the inter-facial be-

havior of macro molecules plays an important role in biomedical applications such as artificial heart valves and joint prostheses. Polymers are highly sensitive and responsive to environment via their configurations and they are well known as a smart materials.

Polymers on a surface effectively give rise to new materials with potentially useful properties. To understand this we need to study the nature, the application of polymer chain and its environment to determine the macroscopic properties of the interface. Factors such as solvent quality the size of macro-molecules, end-to-end vectors and radius of gyration length have been extensively explored at the molecular level the last four decades[1,25].

In general, the theory of the polymer-solid interaction is very complex[1]. This will become more complicated when we consider corrugated surface structures with different kinds of interactions and surface energies. When the production of surface roughness increases the technological application of polymer adsorption was decreased. From thermodynamic point of view, polymers will minimize their energy by maximizing the number of adsorbed monomer-sites, but this leads to entropy loss, due to the reduction of free available monomer for building new conformation. From a surface structure point of view, there are some region on the surface with binding energies that can overcome the loss of entropy of an adsorbed polymer, whereas in other areas the entropy loss of the polymer chain is greater than binding energy. In practice most of the surfaces are inherently heterogeneous, so the study of the statistical and dynamical behavior of polymers near a heterogeneous surface is crucial. In 1953, the first discovery of the change in conformation of a polymer chain in the presence of a reflecting wall was made by Simha, Frisch and Eirich. They studied the properties of a single semi-flexible chain tethered to a planar surface with a long- range attractive potential by means of Monte Carlo simulations. They employed the bond fluctuation lattice model and the Wang-Landau sampling technique to find the adsorption isotherm. Their discovery led to finding the thickness of the adsorbed layer of monomers at a point which was proportional to the square root of the molecular weight of the polymer. However, in 1960 DiMarzio et al. proved that the total number of distinct conformations had been overestimated. They applied a new method for conformation of a polymer chain in a

periodic cubic box. One monomer will change its place; however, chains never take backward steps, but rather always press forward. The polymer chain continues its displacement until their last monomer hits the other side of the wall of the simulation box. They showed that the evaluation of the conformation of the polymer chain must be considered one step before hitting the wall. Their calculation was consistent with their experimental result. Also, there were some diverse studies regarding the thermodynamic interaction parameters, applying scaling theory of polymer adsorption and finding the thickness of the layer of adsorbed segments around that time. The contribution of entropy to free energy is proportional to the temperature, when temperature increases entropy increases or temperature decreases entropy decreases. The consequence of high temperature and short chain length dominate the adsorption amount on the rough surface and the adsorption energy will dominate entropy penalty at long chain and low temperature. Once the polymer chain recognizes the attractive pattern for adsorption (fully recognition of pattern by polymers means, when the polymer can self-assemble it self based on the pattern) another phase of the system will occur.

Generally, polymers are studied in the fields such as biophysics, macro-molecular science and polymer sciences which include polymer physics. Polymer physics deals with the description of the structure and the resulting properties of polymeric materials. The statistical approach of polymer physics is based on an analogy between a polymer and a Brownian motion or some other type of random walk (RW) [5,15,19].

In polymer physics [1, 19], polymers are usually classified by topology, sources and composition. Polymers are characterized by their static properties of the polymer chain size and shape [2,22]. Like end-to-end distance(R) and radius of gyration (R_g). On the other hand, adsorbed polymers are characterized by the parameter like the adsorbed monomers, averaged adsorbed monomers, the averaged adsorbed monomers fraction, adsorption energy and averaged adsorption energy[3,25].

So far, in order to determine these properties many simulation methods are employed. The two prominent approaches used to simulate polymers are Molecular Dynamics (MD) and Monte Carlo (MC) methods[26]. These approaches are analogous to time and ensemble averaging in statistical mechanics. Monte Carlo simu-

lation method involves generating and accepting or rejecting of possible conformations (states) stochastically and Molecular Dynamics (MD) the fundamental idea of the molecular simulation is to use Newton's laws of motion to integrate the positions and velocities of the atoms in the system as a function of time [4,10, 17].

1.2   Statement of the problem

Polymer-substrates of interfaces have been extensively studied for a number of years due to scientific significance and their wide applications in technological importance. The number of polymer-surface interaction sites and distribution of interaction strength will depend on surface structure. The fact that polymer adsorption are important in our daily life and technological application mostly being used, the static properties and surface structure of polymer are remained with great debates. In particular the physical properties of polymer adsorption on rough surfaces still not fully addressed. In addition less attention has been paid the influence of rough surface on the adsorption behavior of linear polymer chains. This study focused on Monte Carlo simulation of the effect of surface roughness on the adsorption behavior of linear polymer chains. In this context, this statement of the problem expected to answer the following basic question

1. What is the scaling behavior of end-to-end distance and radius of gyration with chain length N?

2. How can we examine the adsorbed monomers and averaged adsorbed monomers of linear polymer with chain length N and surface roughness height(h)?

3. How can we determine the averaged adsorbed monomers fraction of linear polymer with chain length N and surface roughness height(h)?

4. How can we determine the adsorption energy and averaged adsorption energy of linear polymer with interaction strengths (ϵ_s) and surface roughness height (h)?

1.3 Objectives

1.3.1 General objective

- To investigate the effect of surface roughness on the adsorption behavior of linear polymer chains.

1.3.2 Specific objectives of this thesis were:-

- To determine the scaling behavior of end-to-end distance and radius of gyration with chain length N.

- To examine the adsorbed monomers and averaged adsorbed monomers of linear polymer with chain length N and surface roughness height(h).

- To determine the averaged adsorbed monomers fraction of linear polymer with chain length N and surface roughness height(h).

- To determine the adsorption energy and averaged adsorption energy of linear polymer with interaction strengths (ϵ_s) and surface roughness height(h).

1.3.3 Significance of the Study

The application of linear polymer adsorption in our daily life and for industrial technological areas may comprise formulations of paints, detergents, cosmetics, adhesion, deposition, lubrication, coating, surface-wetting, painting inks, surface modification of medical implants the inter-facial behavior of macro molecules plays an important role in biomedical applications such as artificial heart valves, joint prosthesis, increase the efficiency of injection, food stabilizers and drugs in terms of speed and coverage. This study used to determine the effect of surface roughness height, influence of chain length and interaction strengths (ϵ_s) in technological application of linear polymer adsorption on rough surface. Also the information can be used as a base for the other researchers about Monte Carlo simulation of linear polymer adsorption on rough surface.

2

Review of Related Literature

2.1 Polymer and polymerization

Since most materials are polymeric and most of the recent advances in science and technology involve polymers, some have called the polymer age. Actually, we have always lived in polymer age. The ancient Greeks classified all matters as animal, vegetable and mineral[6,11]. The word Polymer came from two Greek words:- poly means many and mer means unit or part. The term polymer is defined as very large molecules having high molecular mass. The repeating structural units are derived from some simple and reactive molecules known as **monomers**. They linked to each other by bonded with hydrogen or covalent forces. This process of formation of polymers from respective monomers is called **polymerization**. Polymers consisting of identical and repeating monomers are called **homo polymers**, if units or blocks of monomers of different species are combined in a repeating fashion, these are named **block co-polymers** and if different units are connected in completely random fashion these are called **hetero-polymers** which shown in Figure 2.1. Although, natural polymers do exist (e.g. natural rubber), most polymers are synthesized by polymerization of monomers from the Petrochemical industry. Real examples of polymer chains include DNA molecules or proteins. DNA molecules are very important for life, their primary structures are linear (multiple chemical units) composed of monomers (single chemical units), called nucleotide, as are proteins which consist of amino acids (monomers). The basic properties of polymers are a consequence of the size of the polymer chain and the size of monomers (which correspond to the volume of space excluded by the monomers). This controls other characteristics of the polymer chain such as extensivity, flexibility, and

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conformation of the polymer. A polymer chain in solution can change its shape dynamically and its instantaneous shape is called a conformation. The number of monomers
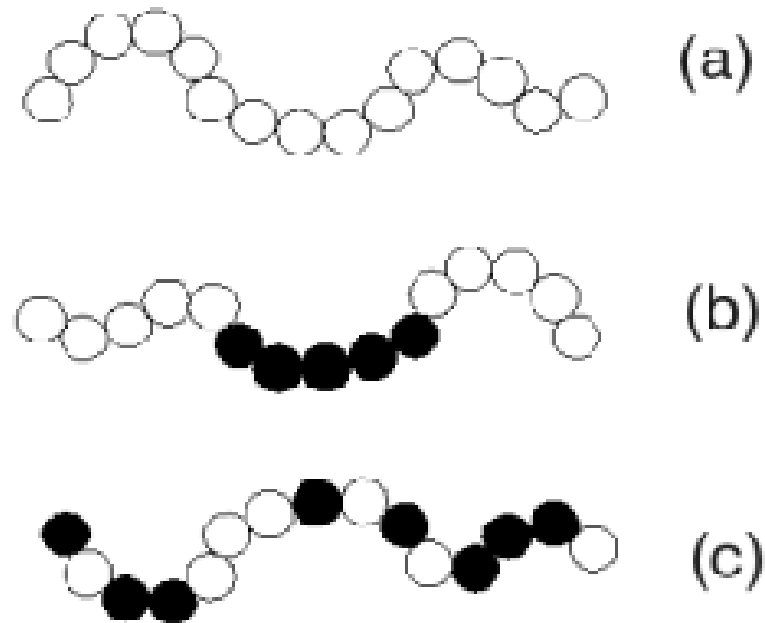
Figure 2.1: Classes of polymers which depend on the physical relations of the monomer composition of a polymer (a)homo-polymer, (b) block co-polymer and (c) hetero-polymer[18]

in Polymer is called **its degree of polymerization** N [7, 2, 20]. The molar mass M_N of polymer is equal to its degree of polymerization N times the molecular weight M_{mol} of its chemical monomer.

$$M_N = N \times M_{mol} \tag{2.1}$$

Where N is degree of polymerization, M_N is moral mass of polymer molecule N and M_{mol} is molecular weight of monomer. Another important feature controlling the properties of polymeric systems is polymer architecture. Types of polymer architecture include linear, comb, star, ring, randomly branched and network as sketched in Figure 2.2 [8,11,22].
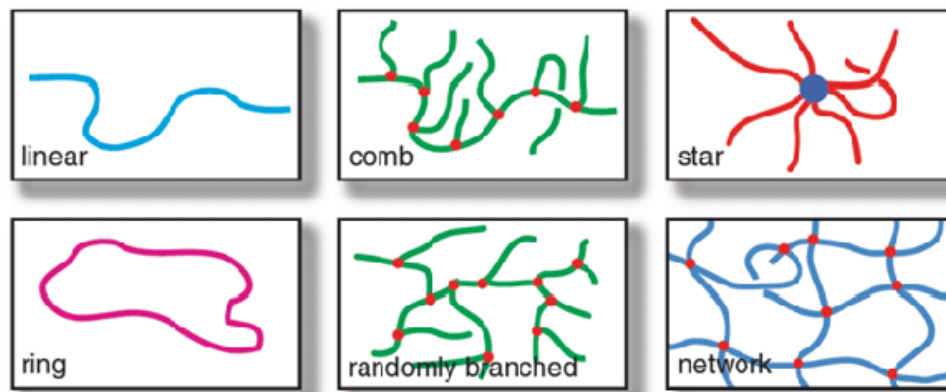
Figure 2.2: Examples of polymer architectures (a) linear, (b) comb, (c) star, (d) ring, (e) randomly branched and (f) network [18]

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2.2 Static properties of linear polymer

Now we discus the static properties of ideal polymers like chain size and shape (end-to-end distance and radius of gyration).

2.2.1 Ideal chain

The most important shortcoming of the concept of an ideal chain is the neglect of long range interaction. Apart from the local constraints which basically only affect the statistical length, there are no restrictions on the ideal chain configuration. In particular, chain segments are allowed to overlap. Let us start with a very simple model, freely jointed chain (FJC) model, which consists of mass less points connected by bonds with a constant length l and freely rotate angles. This model is analogous to the random walk in two dimensions in which the length step of l.

Here, the bond vector is represented by

$$\vec{r_n} = \vec{R_{n+1}} - \vec{R}n \tag{2.2}$$

$$\vec{R_n} = \Sigma_{i=1}^{N}\vec{r_i} \tag{2.3}$$

$\vec{R_n}$, is the position of the nth monomer and

$|\vec{r_n}|$, is for all n end-to-end vectors.

In this model the ensemble average of end-to-end distance $\langle \vec{R} \rangle$ can written as

$$\langle \vec{R} \rangle = \langle (\Sigma_{i=1}^{N} \vec{r_i}) \rangle = 0 \tag{2.4}$$

And ensemble average of squared end-to-end distance is

$$\langle \vec{R^2} \rangle = \langle \vec{R}^2 \rangle = \langle (\Sigma_{i=1}^{N} \vec{r_i})(\Sigma_{j=1}^{N} \vec{r_j}) \rangle \tag{2.5}$$

$$= \Sigma_i^N \Sigma_j^N l^2 \cos \theta ij \tag{2.6}$$

$$= Nl^2 + 2l^2 \Sigma_i^N \Sigma_{i>j}^N \cos \theta^{i,j}, where\ 2l^2 \Sigma_i^N \Sigma_{i>j}^N \cos \theta^{i,j} \binom{i=j=1}{i=j=0} \tag{2.7}$$

$$\langle R^2 \rangle = Nl^2 \tag{2.8}$$

The end-to-end distance is a well-defined observable for a linear polymer as shown in
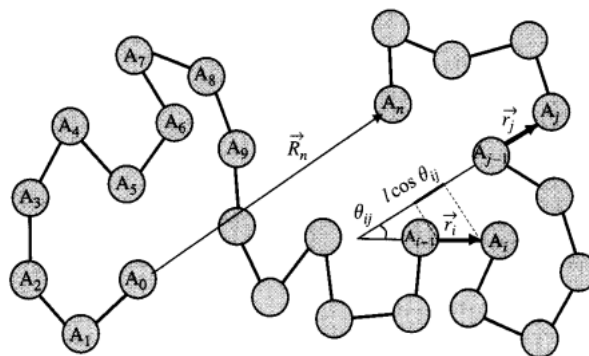
Figure 2.3: Schematic description of Free Joint Chain (FJC) [19]

Figure 2.3, but it cannot characterize the size of branched and ring polymers, because they either have too many ends or no ends at all .

The mean square end-to-end distance $\langle R^2(N) \rangle$, where $\vec{R}$ is the simply the vector distance between the first and last monomers and the brackets depict an ensemble average over all possible states of the system. So end-to-end distance describes the static property of polymer. Mathematical can be described in short and precise from the above equation.

$$\langle R^2(N) \rangle = \langle (\vec{r_1} - \vec{r_N})^2 \rangle \tag{2.9}$$

Where $\vec{r_1} - \vec{r_n}$ is the distance between the first and the last monomer of the chain respectively.

Radius of gyration:- since all polymers posses a radius of gyration, it can characterize the whole size of polymers of any architecture as shown in Figure 2.4. **The mean square radius of gyration** is defined as the average square distance between monomers in a given conformation (position vector R_i) and the polymers centre of mass (position vector R_{cm}) . Conformation is the instantaneous shape of polymer in the solution [18] . The molecules mean square of the radius of gyration $\langle R_g^2(N) \rangle$, which is an average of every monomers square distance from the polymer center of masses.
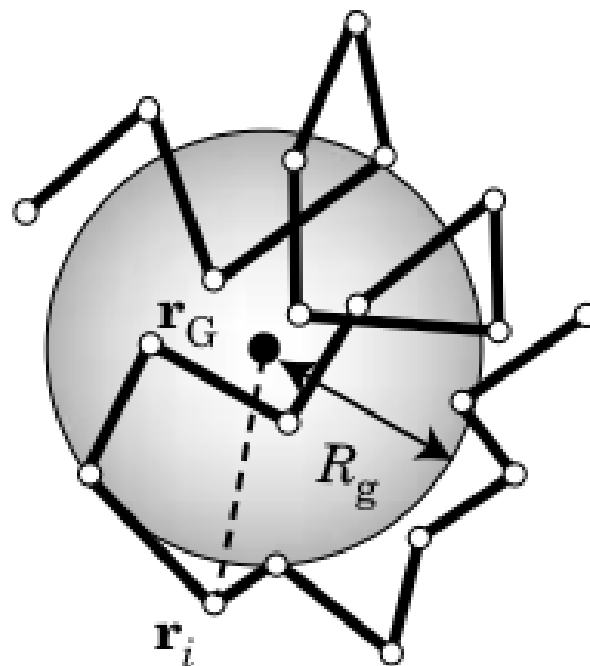
Figure 2.4: Center of mass (r_G), position vector (r_i) and the radius of gyration (R_g) in the bead-stick model [21]

$$\langle R_g^2(N) \rangle = \Sigma_{i=1}^N (Ri - \vec{Rcm})^2 \tag{2.10}$$

$$\vec{Rcm} = \frac{1}{N}\Sigma_{j=1}^N \vec{Rj} \tag{2.11}$$

Where $\vec{R}_i$ and $\vec{R}_{cm}$ are the position of the ith monomer and the position of the polymer's center of mass respectively. The position of center of mass of the polymer is the number of average of all monomer position vectors.

$$R_g^2 = \frac{1}{N}\Sigma_{i=1}^N (\vec{R}_i^2 - 2\vec{R}_i\vec{R}_{cm} + \vec{R}_{cm}^2) \tag{2.12}$$

$$R_g^2 = \frac{1}{N}\Sigma_{i=1}^N [\vec{R}_i^2\frac{1}{N}\Sigma_{j=1}^N 1 - 2\vec{R}_i\Sigma_{j=1}^N\vec{R}_j + (\frac{1}{N}\Sigma_{j=1}^N\vec{R}_j)^2] \tag{2.13}$$

$$R_g^2 = \frac{1}{N^2}\Sigma_{i=1}^N\Sigma_{j=1}^N (\vec{R}_i - \vec{R}_j)^2 \tag{2.14}$$

$$\langle R_g^2 \rangle = \frac{1}{N^2}\Sigma_{i=1}^N \langle (\vec{R}_i - \vec{R}_{cm})^2 \rangle \tag{2.15}$$

$$\langle R_g^2 \rangle = \frac{1}{N^2}\Sigma_{i=1}^N\Sigma_{j=1}^N \langle (\vec{R}_i - \vec{R}_j)^2 \rangle, where \; \langle (\vec{R}_i - \vec{R}_j)^2 \rangle = \frac{1}{2}(i - j)b^2 \tag{2.16}$$

$$\langle R_g^2 \rangle = \frac{1}{2N^2}\Sigma_{i=1}^N\Sigma_{j=1}^N (i - j)b^2 \tag{2.17}$$

Now change summation in to integration

$$\langle R_g^2 \rangle = \frac{b^2}{2N^2}\int_{i=1}^N di \int_{j=1}^N dj(i - j) \tag{2.18}$$

Now we going to evaluate the second integral

$$\int_o^N (dj)(i - j) = 2\int_o^i (dj)(i - j) \tag{2.19}$$

$$= 2(ij - \frac{j^2}{2}) \overset{i}{0} \tag{2.20}$$

$$= 2(i^2 - \frac{i^2}{2}) = 2(\frac{i^2}{2}) = (i^2) \tag{2.21}$$

$$= \frac{b^2}{2N^2} \int_o^N (i^2)di \tag{2.22}$$

$$= \frac{b^2}{2N^2}[\frac{i^3}{3} / \overset{N}{0}] \tag{2.23}$$

$$= \frac{N^3b^2}{6N^2} = \frac{Nb^2}{6} \tag{2.24}$$

$$\langle R_g^2 \rangle = \frac{Nb^2}{6} \tag{2.25}$$

$$\langle R_g^2 \rangle = \frac{\langle R^2 \rangle}{6} \; where \; \langle R^2 \rangle = Nb^2 \; and \; \frac{\langle R^2 \rangle}{\langle R_g^2 \rangle} = 6 \tag{2.26}$$

This indicates that the ratio of mean square end-to-end distance and mean square radius of gyration is 6.

2.3 Real chain and excluded volume (EV)

The interactions between monomers of a chain with finite lateral dimensions at the real polymer chains and these interactions can alter the size of the polymer. Therefore, it is important to see such constraints and their effects on the static behaviors of polymer chains. Real chains have a finite molecular volume and will exclude overlapping configurations. On a lattice this can be implemented by allowing empty sites for each subsequent segment only. Such configurations are known as **Self Avoiding Walk (SAW)**.

SAW is a random walk in which points are not revisited, as shown in Figure 2.5. This inter molecular excluded volume effect leads to an expansion of the chain with respect to the corresponding ideal chain, since the excluded volume effect is proportional to the segment density which is highest at the center of the chain. A real polymer chain of excluded volume was analyzed by Flory[8]. The Flory Calculation of the Flory Expo-
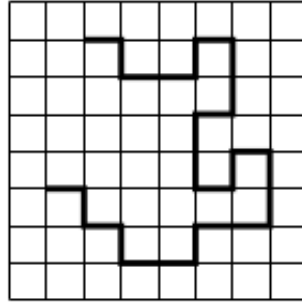
Figure 2.5: Self Avoiding Walk (SAW)

nent (ν). For N monomers, Flory [8] considered that the monomers are uniformly distributed within the total volume of the chain with neglecting correlation between them and represented the polymer coil a d-dimensional sphere with radius R filled with the polymer segments with mutual repulsive interaction. The repulsive energy is [12]

$$F_{repulsive}(N, \vec{R}) = KBTvex\frac{N^2}{R^d} \tag{2.27}$$

The probability of distribution is given

$$P(N, \vec{R}) = (2\pi N l^2 \frac{1}{d})^{\frac{-d}{2}}(exp(\frac{-d\vec{R}^2}{2Nl^2})) \tag{2.28}$$

Hence, the F entropic (N; R) becomes

$$F_{entropic}(N, R) = -TS(N, \vec{R}) \approx -KBT \ln P(N\vec{R}) = \frac{dKBT\vec{R}^2}{2Nl^2} \tag{2.29}$$

Hence,the force of repulsive(N;R) and force of entropic gives the total free energy

$$F(N, R) =F_{rep}(N, R) + F_{entropic}(N, R) \approx KBT(V_{ex}\frac{N^2}{R^d} + \frac{dR^2}{2l^2N}) \tag{2.30}$$

The equilibrium radius corresponds to the minimum total free energy leads to gives

$$\frac{dF}{dR}(N, R) = 0 \tag{2.31}$$

$$\frac{d}{dR}(KBT(V_{ex})\frac{N^2}{R^d} + \frac{dR^2}{2l^2 N}) = 0 \tag{2.32}$$

$$A_2(R^{d+2}) = A_1(N^3) \tag{2.33}$$

$$R \sim N^V$$

Now we substitute N^ν in terms of R for the following equation.

$$A_2 N^{v(d+2)} = A_1(N^3) \tag{2.34}$$

$$N^{v(d+2)} = N^3 \tag{2.35}$$

$$v = \frac{3}{d+2} \tag{2.36}$$

Where A_1 and A_2 are constants similarly or equal ν is Flory exponent , d is dimension and N is chain length of polymer. An important result from Flory's theory for a polymer in good solvent is that it yields a universal power-law dependence of polymer size R for ideal chains $\nu = 1/2$. $\langle R^2 \rangle \sim N^{2\nu}$ and $\langle R_g^2 \rangle \sim N^{2\nu}$ for mean square end-to-end distance and mean square of radius of gyration respectively he concluded the scaling exponent for real chains to be for two and three dimensions $\nu = 3/4$ and $\nu = 3/5$ respectively[8].

2.4 Linear polymer adsorption

Surface roughness can be characterized by a non uniform distribution of atoms. Polymer-substrate interfaces have been extensively studied because of their technological importance. Accordingly, the polymer adsorption has got attention to study. Ji and Hone [13] considered adsorption on curve surfaces from good solvents and found that inter-facial tension is dependent on curvature (inner/outer surfaces of a sphere) and that for sinusoidal grating, although kinetically hindered, it is favorable for the polymer

to fill the deep holes or valleys on rough surface. The existence of either state (adsorption on peaks or valleys) was determined by interaction potential.

Douglas[27] theoretically investigated the effect of surface roughness on the interactions between the polymer and the surface. The polymers were modeled as Gaussian chains, and surface roughness was characterized and checked by adsorbed polymer. The model assumed that the probability of intersection between the polymer and the surface. Baumgartner and Muthakumar [16] studied the effect of surface roughness on the adsorption characteristics of an isolated chain using scaling arguments and Monte Carlo simulations. Edwards and Muthukumar[19] developed an analytical model that described the size of a polymer chain in a random media. Specifically, they investigated the equilibrium behavior of Gaussian chain in the presence of a random medium.

Xu et al [6] and Hone et al [7] studied a sinusoidal surface profile theoretically, and calculated adsorption of an infinitely long Gaussian chain with ground state dominance approximation. Gottstein et al [14] investigated the adsorption of single chain polymer structured surface using bond-fluctuation model. Vilgis and Coworkrs [24] considered various theoretical models for the adsorption of single ideal polymer chain on disorder surfaces and showed that adsorption was always enhanced with respected to flat surfaces. There are very few experimental works that systematically investigated homo polymer adsorption on rough surface while considered the effect of surface roughness Shu etal [3]. Topological modification of surface includes random roughness of the surface cases surface energy. The surface roughness influences the technological application or significance process of polymer adsorption. Understanding the behavior of polymers at surface and interface is necessary condition to control the properties of polymer surface systems and to develop new techniques for their preparations and efficient function of a range of materials manufacturing composite process and device fabrication technologies[23]. when long chain molecules interact with surfaces and interfaces there is high adsorption involved and there is greater interaction between the conformational degrees of freedom of the chains of the interaction between the monomers and surface sites [8, 25]. Free energy of the polymeric system has a key role

in determining the conformational transitions of molecules in a system and reveals the balance between entropy and adsorption energy that controls adsorption the importance of this idea was first discussed by Flory [8]. He also introduced the minimization of the free energy of polymer adsorption on to surface in the lattice space, which combines the mean field theory and lattice models of polymer chains. Polymer can be adsorbed in high amounts when the adsorption energy of surface is greater than entropy loss of the molecules leaving in the solution. He used the free energy minimization approach for single chain in a solution, where its degree of scaling ν corresponding the density of the monomer with end-to -end vector of the scaling ν is ($\nu = 3/5$)for 3D and ($\nu = 3/4$)for 2D.

First the adsorption of a single chain at interfaces can be understood using well developed methods from statistical mechanics. Polymer adsorption on both regular and random surfaces is governed by the same mechanism, the delicate balance between the entropic losses and enthalpic gains originated from the encounters of polymers with adsorbed surface. It is intuitively clear that for any surface potential the balance between the above entropic and enthalpic competitive contributions must substantially depend on the relation the length scales involved the radius of gyration of the polymers and characteristic size of surface pattern[25]. The basic physical origin of the criteria of adsorption of polymer chains is the competition between the gain in internal energy informing by monomers by binding to surface and the loss in entropy associated with reduction in the number of possible chain configuration of the adsorbed chains in comparison with that of desorbed chain(free joint chain). Broad molecular distribution showed greater adsorption than narrow distributions at rough surface[25]. As number of beads in molecule decreases chains are less likely to interact with the surface. Adsorbed polymers are characterized by averaged adsorbed monomer fraction and topologies evaluated by radius of gyration which related with chain length and the structure of the surface.

The same is true for the understanding for adsorbed polymer chains were excluded volume effects lead to strong stretching of the individual chains in the direction of adsorption of polymers to the surface [17]. The surface roughness height influences the

polymer adsorption and averaged adsorbed monomer fraction[29].

2.4.1 Adsorbed monomer, averaged adsorbed monomer fraction and adsorption energy

The macro structure information such as surface coverage, adsorption amount or adsorbed monomers and averaged adsorbed monomers fraction are characterized the adsorption behavior of polymer. Adsorbed monomers and averaged adsorbed monomers fraction as the function of chain length of the polymer at the surfaces[28]. The energetic interaction of polymer with surface which determine by the enthalpic interaction energy with the surface and the loss of entropic penalty[24]. Negative values balance between entropic losses and enthalpic gains originated from the encounters of polymer chain length with adsorbing surface. We measure the probability of averaged adsorbed monomer fraction with the number of monomers in contact with surface or adsorbed monomer over the total number of monomers of the chain length$N$. The p_{ads} is the probability of averaged adsorbed monomers fraction [14]. The interaction strengths(ϵ_s) of adsorbed monomers with the surface is describes by adsorption energy .

Performed numerical simulations of Monte Carlo method of Metropolis algorithm was employed a $2D$ lattice model to study the adsorption of self-avoiding walk of polymers and for the further investigations concern the effect of surface roughness on linear polymer chains by considering for static properties end -to-end distance and radius of gyration with respect to chain length N. All these studies were aiming at conclusively determining the scaling exponent and amount of adsorption. Most of these studies use extensive numerical simulations based on the bond fluctuate model (BFM). The polymer adsorption on rough surface factors and $R \sim N^\nu$ for a self-avoiding polymer, where ν is the Flory exponent ($\nu = 3/4$ and $3/5$ in two-dimensional (2D) and three-dimensional (3D) respectively)[8]. On the other hand, adsorbed monomers, averaged adsorbed monomers, averaged adsorption energy, averaged adsorbed monomers fraction with chain length N, surface roughness height(h) and adsorption energy in addition with interaction strengths (ϵ_s) are parameters to characterize linear polymer adsorption on rough surfaces.

3

Methodology

The detail concept of Monte Carlo simulation and bond fluctuation method (BFM) were described below.

3.1 Monte Carlo simulation

Among the two well known simulation methods, Monte Carlo method (MC) and Molecular dynamics (MD), we have selected to use MC method. Then we have to make a further decision, whether to do the MC simulation on a lattice. Monte Carlo method an estimate of property is made by randomly sampling states of the system and averaging of the value of overall states[4,12]. The choose of appropriate model and simulation method for the problem we wanted to study enable us to reach the meaningful conclusion. For long time and large-scale phenomena like adsorption detailed model would require too much computer time and memory. Computer simulations not only link analytic, theory and experiment in order to test theories, but can also be used as an exploratory tool in computer experiments under conditions which would be unfeasible, too expensive, or too dangerous for real experiments in the laboratory. In general the Metropolis algorithm of Monte Carlo method is the probability of generating with accepting or rejecting the states stochastically(randomly). We used Monte Carlo method to generate a random walk, and reject it if it violates self avoid walk(SAW). During our simulation Monte Carlo algorithm produced each N-step self avoid walk with equal probability. Note that if an attempted state is rejected, the old state is counted again for the averaging, bond length constraints and self avoid walk are violated.

We needed a way of generating and evaluating for accepting or rejecting the conformations forwarded along each steps (moves).

3.2 **Bond fluctuation model**

Bond-fluctuation model (BFM) was proposed [4] as an alternative to a (single-site) SAW model, which retains the computational efficiency of the lattice without being plagued by severe ergodicity problems. If bond fluctuation model(BFM) is an efficient lattice Monte Carlo (MC) algorithm for coarse-grained polymer chains where each monomer occupies exclusively a certain number of lattice sites on a simple square lattice [5, 12]. The key idea is to increase the size of a monomer which now occupies, instead of a single site, a whole unit cell of the lattice (for example, a square for the $2D$ square lattice). To satisfy the SAW condition, each lattice site can only be part of a single monomer. Each monomer on the model occupies 4 vertex sites of a square area on the lattice. Then each monomer connected to its nearest neighbor monomer by a predetermined set of bond vectors. Two neighbor monomers on a chain must be within a certain bond distance, which is to vary in the range $2 \leq bl \leq \sqrt{13}$ [4, 1], where bl is the bond length between two consecutive beads. The resulting sets of allowed bond vectors are $(2,0), (2,1), (2,2), (3,0), (3,1)$ and $(3,2)$ or the lengths of the bonds are allowed to fluctuate, they have to belong to the set of lengths $2, \sqrt{5}, \sqrt{8}, 3, \sqrt{10}, \sqrt{13}$. All spatial distances are measured in units of the lattice spacing constant. The minimum distance 2 to guarantees the excluded volume effect and the upper limits $\sqrt{13}$ to guarantees bond crossing a bond length less than 2 violate self avoidance condition. We restrict to bond length (bl) less than 4 [4, 1] prevents bonds from crossing each other. Such restrictions
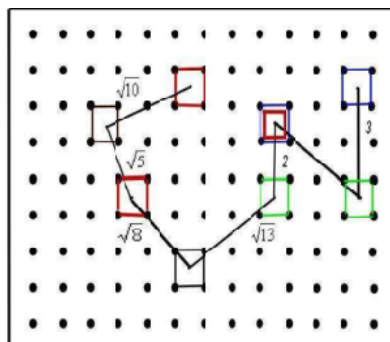

Figure 3.1: Abound fluctuating lattice polymer with all possible bond lengths less than 4 lattice units are depicted [4]

on the bond lengths are topology-preserving. The BFM allows a local move which con-

sists of selecting a monomer at random and of attempting a displacement by one lattice constant in a randomly chosen lattice direction. If the attempted displacement satisfies both the bond length constraints and the excluded volume interaction, the move is accepted. Lattices with the same color represent equal bond lengths as shown in Figure 3.1.

Implementation of bond fluctuation model proceeds as follows.

step 1 start with an initial state of self-avoiding conformation of polymer chain consisting of N monomers.

step 2 Select a monomer randomly and select one of the four lattice directions.

Step 3 Move the selected monomer in selected direction by one lattice spacing. Call this, a trial move.

Step 4 Check if the trial move violates self-avoidance(excluded volume) and bond length constraints if it does, then reject the trial move by returning the monomer to its earlier lattice position and go to step 2.

Metropolis Algorithm:- Since we want to model the adsorption energy of polymer chains we introduce an energy penalty for moves which are allowed under the above scheme, but which involve an energy change of U for interaction strength(ϵ_s). For this we use the Metropolis algorithm to determine the transition probability of acceptance.

Step 5 Calculate the energy change (U) between the new and the old configurations of the system, and if $E < 0$ the move is accepted, otherwise.

step 6 Generate a random number r such that $0 < r < 1$.

step 7 If $r < epx - \frac{\Delta U}{K_{BT}}$, accept the move, otherwise.

step 8 Go to the second step.

N elementary moves define one Monte Carlo time step.

Simulation Procedures of polymer adsorption are mentioned below

We executed our simulation by distributing the polymer chain in each system. We applied x-y reflective boundary condition in the square lattice($2D$). Again the methods that we used was computational approach using Monte Carlo simulation and Bond fluctuation Method or Model (BFM). For each time step, we selected one monomer randomly and after checking the bond fluctuation method we displaced it to new cell. Since the order of the monomers in a chain is important to use, only the same type of monomers can swap their places, otherwise, the new trial will be rejected. Furthermore, we checked whether one end of the polymer chain close to the neighbours of selected monomer or not. As a trial conformation we selected one monomer randomly and then we checked whether constraint condition of the bond fluctuation method to retain the condition. The trial conformation will be accepted if the random monomer generated. If that is the case, the monomer could make a new bond with that end and subsequent monomer becomes the last or first monomer of the chain and that end plays the role of a new neighbours for that monomer. This method could dramatically increased the speed of the evolution of the systems with adsorption sites. The situation was more complicated when some monomers are adsorbed on the surface, while their neighbours are free to make a local move. The system could transit from one conformation to another, if the strength of the surface was such that adsorbed monomer couldn't leave the adsorption sites then their neighbours could only move with a certain distance which was obeying the bond fluctuation model assumption. Now N became the $(i+1^{th})$ monomer and the previous neighbours will became the last monomer. Where i is the number of iteration and N is the monomer in chain length then attempt a trial move of one lattice unit and it is accepted if it doesn't violated the excluded volume, chain connectivity and chain uncrossablity constraints. Since we used lattice for our simulation purpose the first thing that we prepared the lattice it self. Thus two dimensional ($2D$) square simulation box with square lattice 100×100 for our simulation for five different chain length of polymers ($30, 42, 52, 75$ and 85) and these chain length to been determined polymer adsorption and according with the long and short chain length and to been compared the effect of chain length in each run, 5000 Monte

Carlo time steps were used, we used different surface roughness height$(h) = 2, 5, 7, 10, 30$ and 40 with constant chain length $N = 30$ to been determined polymer adsorption and according with the longest height (h) and the shortest (h) in each run 2500 Monte Carlo time steps were used and lastly we used for different interaction strengths$(\epsilon_s) = 1KT, 0.5KT, 0.25KT$ and $0.125KT$ with constant chain lengths of $N = 30$ and $N = 85$ to been determined adsorption energy according with the strong interaction strength(ϵ) and the weak interaction strengths (ϵ_s) and in order to been compared the strongest adsorption energy on two chain lengths in each run 3500 Monte Carlo time steps were used. We selected these chain length by two cases one was if we selected below thirty the entropy penalty was the highest in adsorption and the other if we selected above eighty five the computational cost was the most expensive. We selected two dimensional lattice because it is ideally suited to the purpose for two reasons that excluded volume effects are more apparent and computational times are shorter than three dimensional case. The length of bonds between neighbors monomers were set as bond fluctuation model (BFM) on $2D$ allowed starting from the initial polymer configuration many moves are made until the polymer is equilibriated. Figure 3.2 shows that initial polymer configuration which at the center of surface. To generate such an equilibriated configuration the chain is allowed to relax by attempting local moves as shown in Figure 3.3. Averages were calculated over simulation runs of 10^5 cycles to obtain fully equilibriated configuration Monte Carlo times steps per monomer (MCS) were allotted. After equilibration we have measured distribution of ploymer adsorption on rough surfaces as shown in Figure 3.4. Polymer chain was also found not to relax after adsorption and remain fixed to the surface at or enclose proximity to, their initial contact point. Monte Carlo simulations of long polymer chains to study the adsorption on to rough surface were computationally very expensive due to the fact that the relaxation and desorption occurred only after long times. Finally adsorption on rough surfaces were determined by the Metropolis algorithm of Monte Carlo simulation. We have used this procedures to investigate the effect of surface roughness on adsorption behavior of linear polymer chains. The results were discussed in the next chapter.
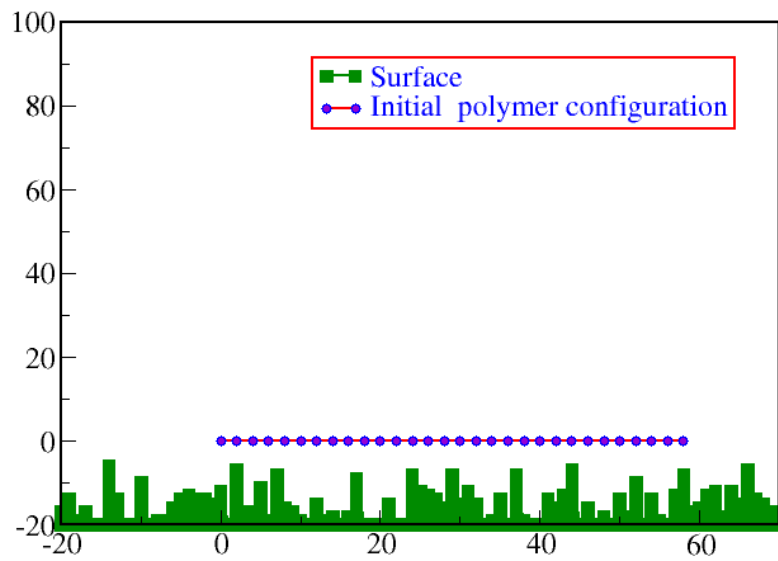
Figure 3.2: Schematic representation of initial configuration of linear polymer chain $N = 30$.
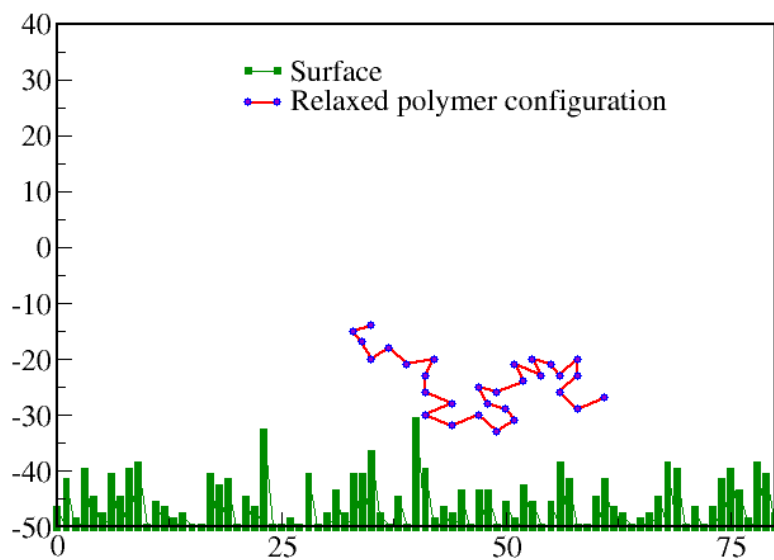

Figure 3.3: Schematic representation of relaxed configuration of linear polymer chain $N = 30$.
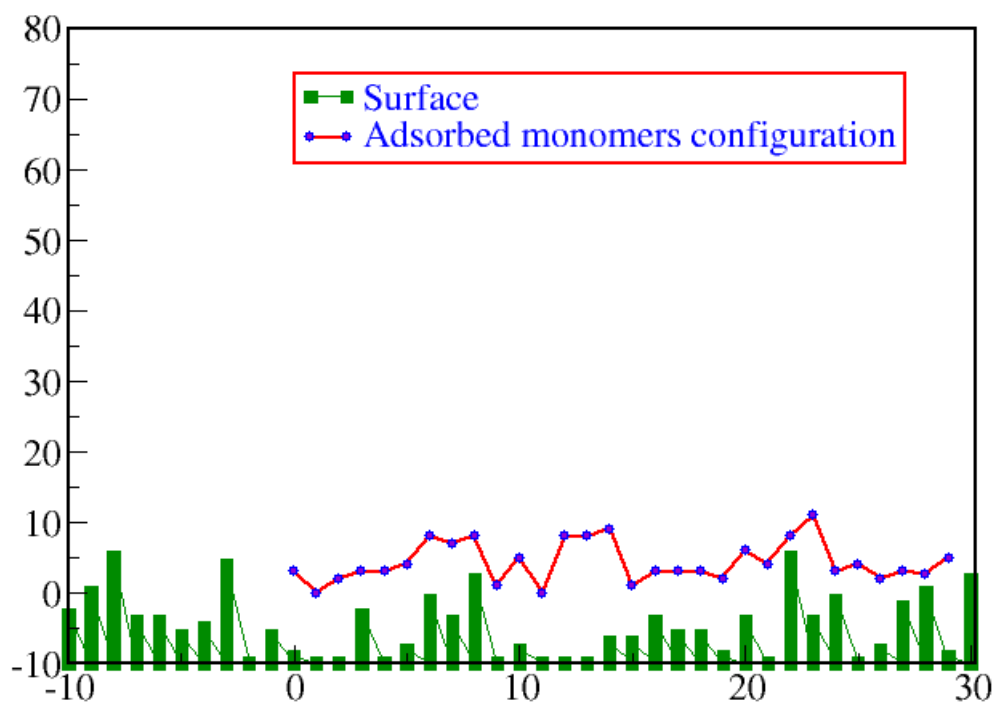
Figure 3.4: Schematic representation of adsorbed monomer of linear polymer chain $N = 30$.

4

Results and Discussion

4.1 Results and discussion

The chains were permitted to adsorbed on rough surfaces in the simulation and after equilibration of the system the structure and chain statistics were investigated.

4.1.1 Static properties of linear polymer adsorption on rough surface
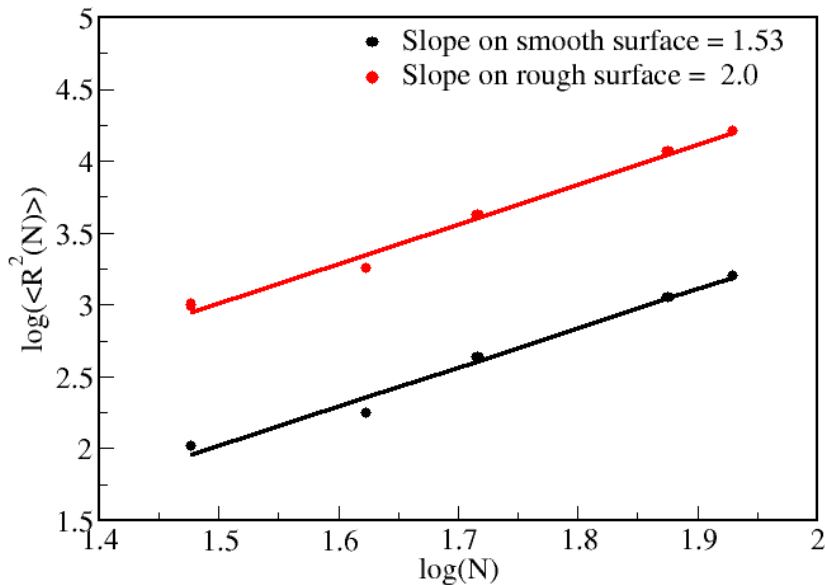
4.1.2 End-to-end distance

Figure 4.1: Log-log plot of end-to-end distance $\langle R^2(N) \rangle$ versus chain length N. The chain length considered are $N = 30, 42, 52, 75$ and 85.

The mean-square end-to-end distance on smooth and rough surfaces were plotted

25

as a function of the chain length as shown in Figure 4.1. This plot is obtained from five different number of monomers of chain length $N = 30, 42, 52, 75$ and 85. The scaling exponent of our study was 2.0 which the expected value of slope was greatly vary from universal scaling exponent of mean square end-to-end distance with chain length $\langle R^2 \rangle \sim N^{2\nu}$ which shown that the universal scaling exponent is broken due the surface roughness. The surface roughness closes to monomer beads to stretch polymers conformation in agreements result with in reference[7].

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4.1.3 Radius of gyration

Figure 4.2 shows the mean square radius of gyration on smooth and rough surfaces as the function of chain length. The scaling exponent of our study was 1.78 which the
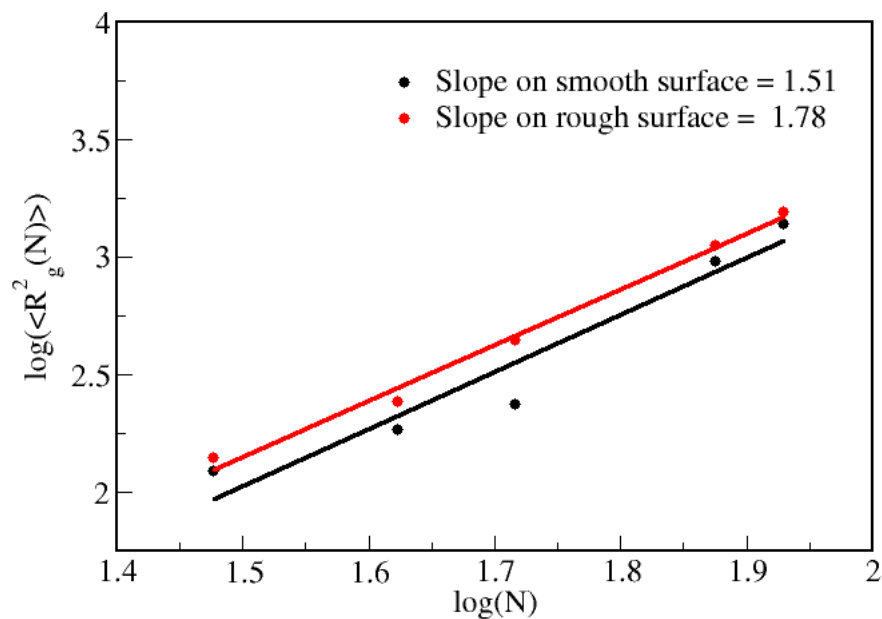

Figure 4.2: Log-log plot of radius of gyration $\langle R_g^2(N) \rangle$ versus chain length$N$. The chain length considered are $N = 30, 42, 52, 75$ and 85.

expected value of slope was greatly vary from the universal scaling exponent of mean square radius of gyration with chain length $\langle R_g^2 \rangle \sim N^{2\nu}$ which shown that the universal scaling exponent is broken due to the conformations of the polymer is distorted or

inhibited by the surface roughness in consistent result with reference[7].

4.2 Adsorbed monomer

An important information about the polymer adsorption can be obtained from the adsorbed monomers as a function of chain length is depicted in Figure 4.3. As expected long polymer chains tend to stay closer to the surface or adsorbed on to the surface better than short chains as they are able to overcome the loss in configurational entropy easily as compared to a shorter chains, due to greater enthalpic interactions arising in the number of monomer beads. The averaged adsorbed monomers were calculated as the sum of overall (total) adsorbed monomers in a chain length per total monomers in chain length for each and individual chain length independently which is given by in equation 4.1 and the result is shown in Figure 4.4 our result in agreement with reference[25]. Chain length $N = 85$ was the longest, maximum adsorbed monomers and
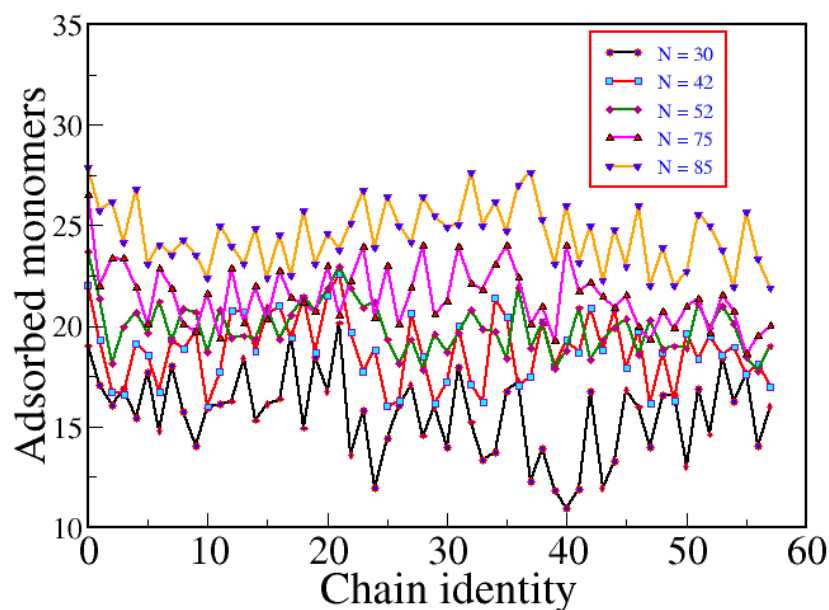

Figure 4.3: Adsorbed monomers versus chain identity. The chain length considered are $N = 30, 42, 52, 75$ and 85. Obtained from 5000 runs for each chain.

averaged adsorbed monomers. The number of monomer beads on it was the broadest for enthalpic contribution of polymer surface contacts so, as we have mentioned above the less loss of configurational entropy arising from the confinement to the surface it

covers more optimum surface than the other lower chains our result is in consistent with reference[25].

$$Average\ adsorbe\ monomers = \frac{Total\ number\ of\ adsorbed\ monomers\ in\ chain\ lengh}{Total\ number\ of\ monomers\ in\ chain\ length} \quad (4.1)$$
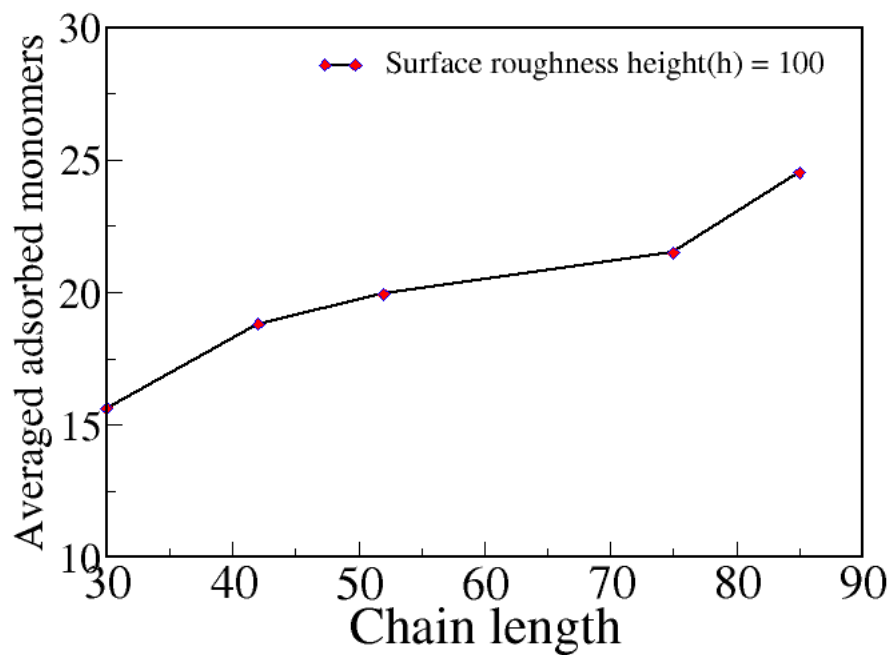

Figure 4.4: Averaged adsorbed monomers versus chain length. The strength of averaged adsorbed monomer with chain length $N = 30, 42, 52, 75$ and 85.

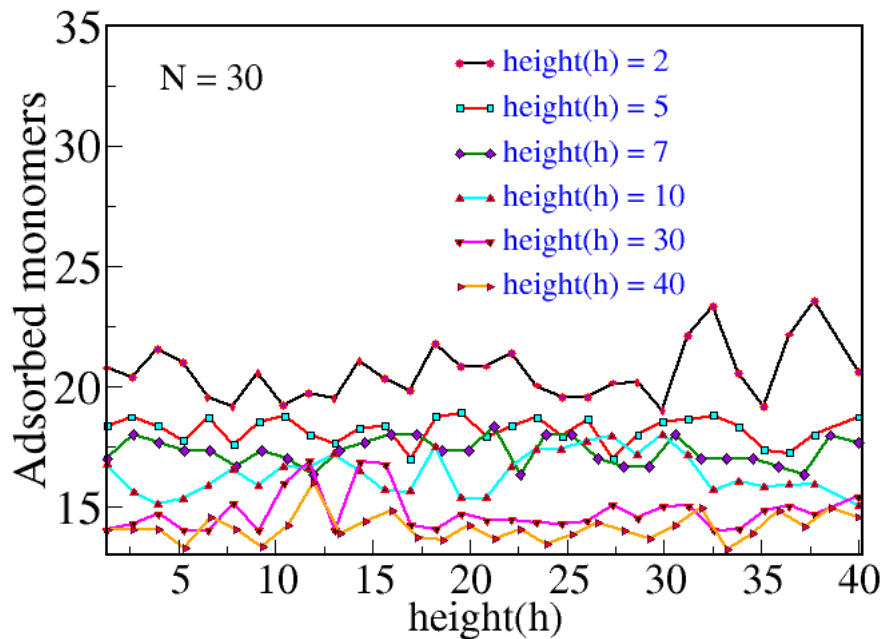The adsorbed polymer also characterized by the surface roughness height. A sur-

Figure 4.5: Adsorbed monomers versus surface roughness height(h). The height of surface roughness are $h = 2, 5, 7, 10, 30$ and 40 where h is surface roughness height. Obtained from 2500 runs for each surface roughness height(h)

face roughness height(h) were increased monomers are less likely to interact with surface. A short surface roughness height(h) showed greater adsorption than long surface roughness height(h) for a given, chain length. AS the height of surface roughness increases both the adsorbed monomers and averaged adsorbed monomers were decreased because the loss of configurational entropy arising from the confinement to the surface was maximum, while at short height system has less loss of configurational entropy arising from the confinement to surface and chain length tends to become stable as a consequence there were maximum adsorbed monomers and averaged adsorbed monomers termed in the total surfaces as shown in Figures 4.5 and 4.6 respectively our result is can be defined as reference [29].
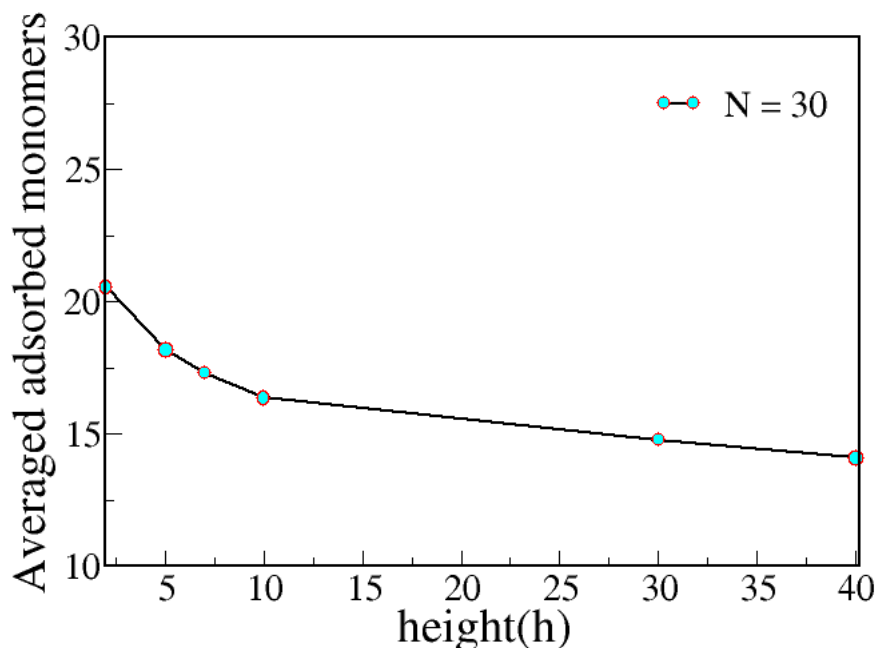
Figure 4.6: Averaged adsorbed monomers versus surface roughness height(h). The surface roughness height(h) are $= 2, 5, 7, 10, 30$ and 40.

4.2.1 Averaged adsorbed monomer fraction

Probabilities of adsorbed monomer fraction are calculated by measuring the number of adsorbed monomers per the total number of monomers in the chain length ($\frac{N_{adsorbed}}{N_{mono}}$) for each chain length in the system.

$$p_{ads} = \frac{number\ of\ adsorbed\ monomers\ in\ contact\ with\ surface}{Total\ number\ of\ monomers\ in\ the\ chain} = \frac{N_{adsorbed}}{N_{mono}} \qquad (4.2)$$

Where p_{ads} is probability of adsorbed monomer fraction [14]. Thus, the overall averaged adsorbed monomers fraction which can also be considered as the sum of overall adsorbed monomers fraction values weighted by their population, it was smaller for long chain length, so it was surprising to observe that the total averaged adsorbed monomers fraction decreases with the increases of chain length as shown in Figure 4.8. Averaged adsorbed monomers fraction at equilibrium varies with the chain length of the adsorbed monomers fraction species and this trend is systematically maintained over the five different chain lengths distribution as shown in Figure 4.7.

Finally, Figure 4.7 indicates that even for the relatively short chain length studied
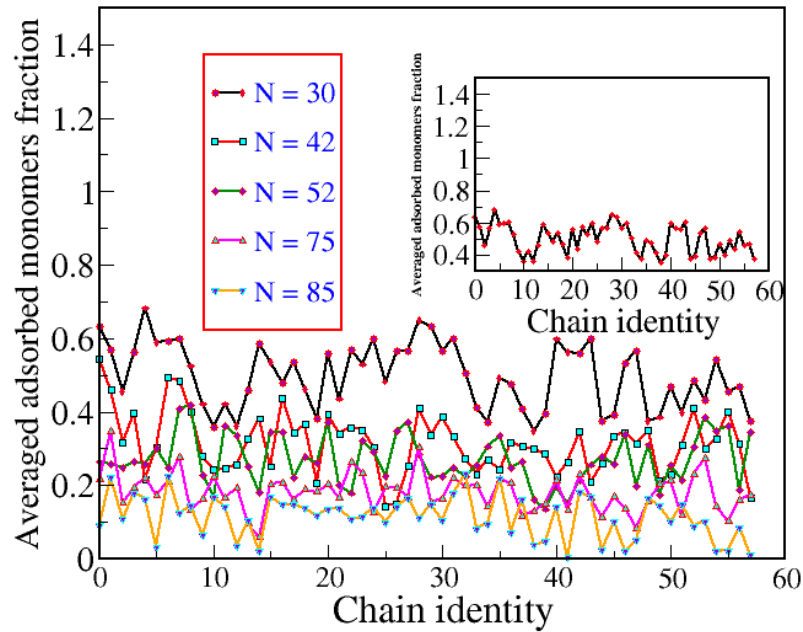
Figure 4.7: Averaged adsorbed monomers fraction versus chain identity. The chain length considered are $N = 30, 42, 52, 75$ and 85.

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here, a rich variety of configurations is displayed, indicated by the broad distributions of adsorbed monomers fraction which shown that each and individual chain length influence on averaged adsorbed monomers fraction as the function of chain length.

Chain length 30 was the maximum averaged adsorbed monomers fraction and surface coverage from other four chain lengths our result is consistent with the reference[28].

The averaged adsorbed monomer fraction also characterized by the surface roughness height(h). It is interesting to observe that the height of surface roughness increase the averaged adsorbed monomers fraction were decreased because loss of configurational entropy arising from the confinement to the surface was highest for longest surface roughness height, so the high entropy of the system does not let the polymer chain to become close to the surface, whereas the less configurational entropy permits the optimum averaged adsorbed monomers fraction for the shortest surface roughness height as shown in Figures 4.9 and 4.10 our result in agreement with the reference[29].
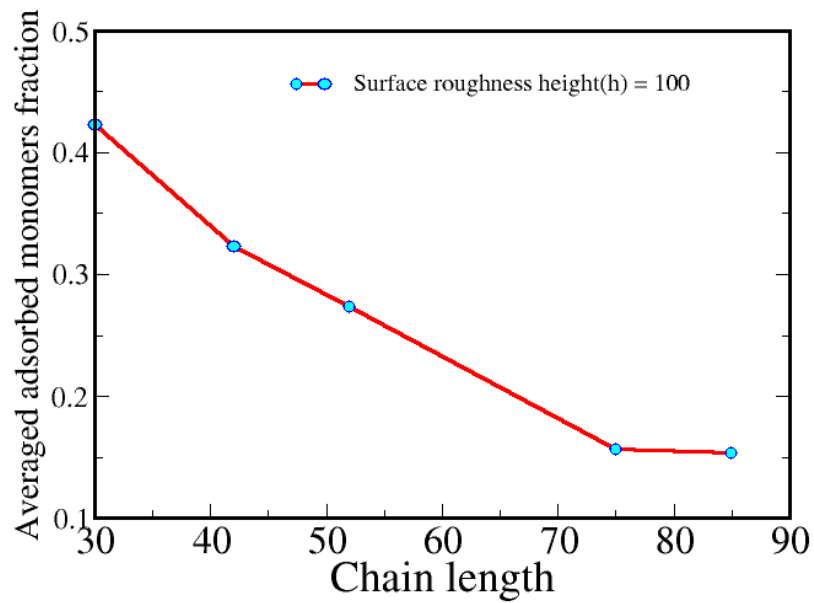
Figure 4.8: Averaged adsorbed monomers fraction versus chain length It shows the influence of chain length $N = 30, 42, 52, 75$ and 85.
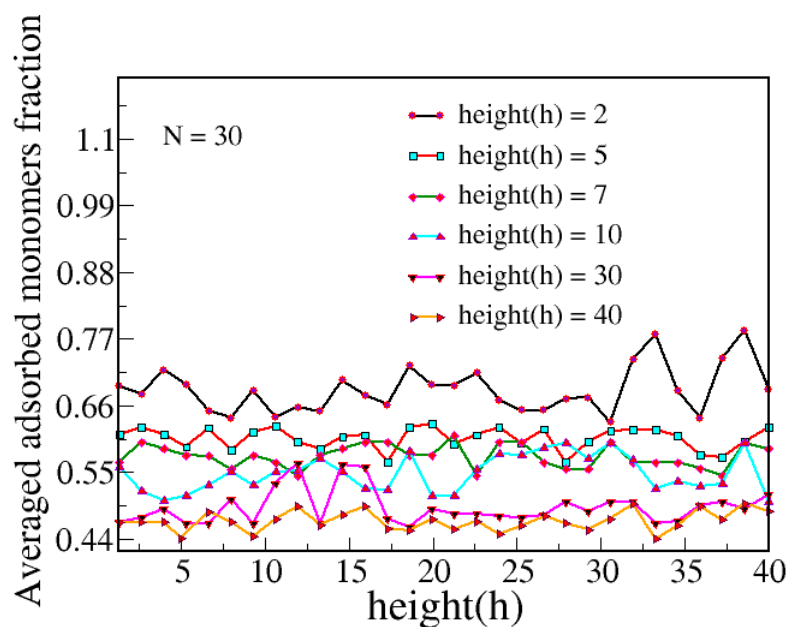
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Figure 4.9: Averaged adsorbed monomer fraction versus surface roughness height(h). The height of surface roughness are $h = 2, 5, 7, 10, 30$ and 40. Where h is roughness surface height.
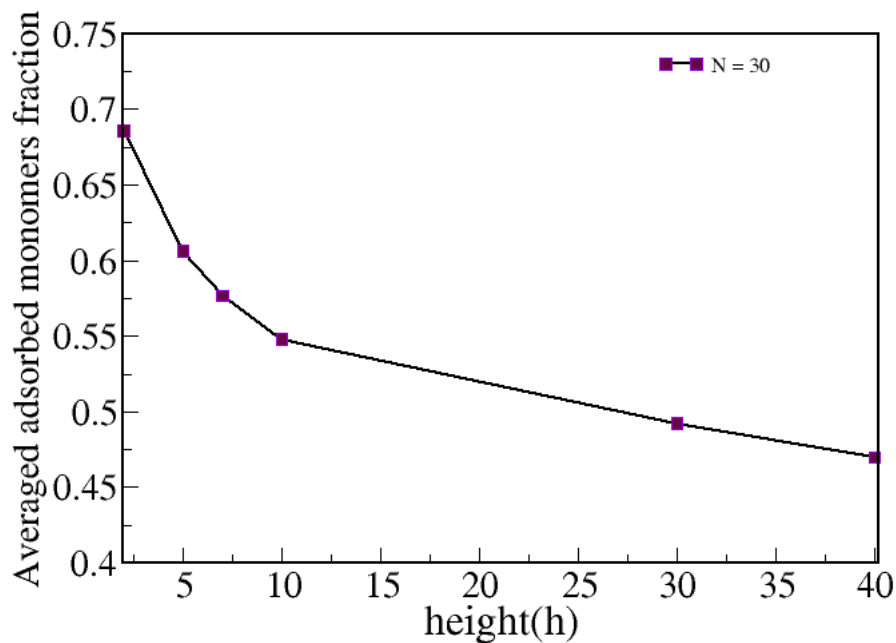
Figure 4.10: Averaged adsorbed monomer fraction versus surface roughness height$(h) = 2, 5, 7, 10, 30$ and 40 in order to show the average value of each height.

4.2.2 Adsorption energy of linear polymer

The degree of interaction between a polymer and a surface may be modified with monomer surface interaction strength it has significant impact on the degree of adsorption energy.

$$E_{ads} = N_{adsorbed} \times \epsilon_s \tag{4.3}$$

Where E_{ads} is adsorption energy, $N_{adsorbed}$ is the number of adsorbed monomer , ϵ_s is the interaction strengths with unit of kT is Boltzmann constant and temperature[25].

In case of $1kT$ interaction strength(ϵ) chain lengths were found to be strong enough adsorbed to the surface. Figure 4.11 shows the effect of interaction strengths(ϵ_s) both on $N = 30$ and 85 it is interesting to observe that chain length $N = 85$ was maximum adsorption energy. The interaction strengths(ϵ_s) with $0.5kT, 0.25kT$ and $0.125kT$ seemed the most chain lengths were weakly adsorbed polymer our result in consistent with the reference[25].

It is also interesting to see that the surface roughness height influence the adsorp-
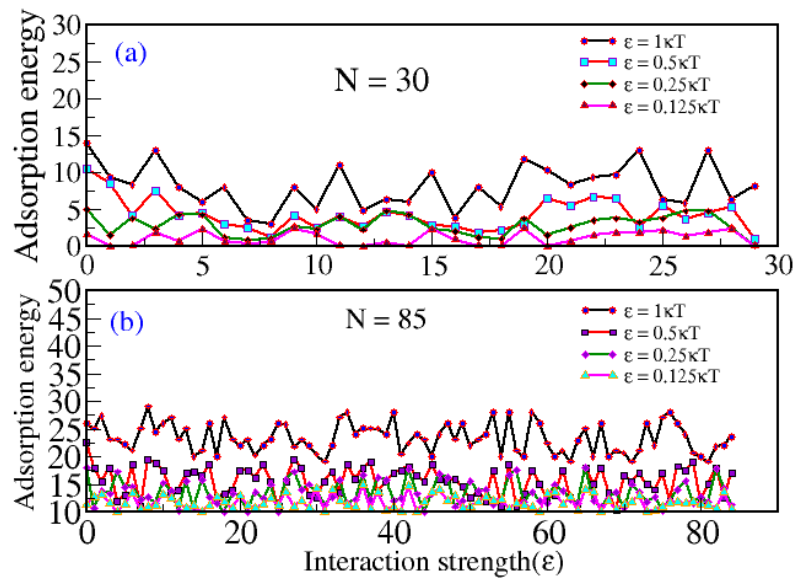
Figure 4.11: Adsorption energy versus interaction strength (ϵ_s) a) Chain length $N = 30$ b) Chain length $N = 85$ and which related with interaction strength (ϵ_s). Obtained from 3500 runs for each interaction strength (ϵ)

tion energy of the polymer. We measured adsorption energy based on the coverage
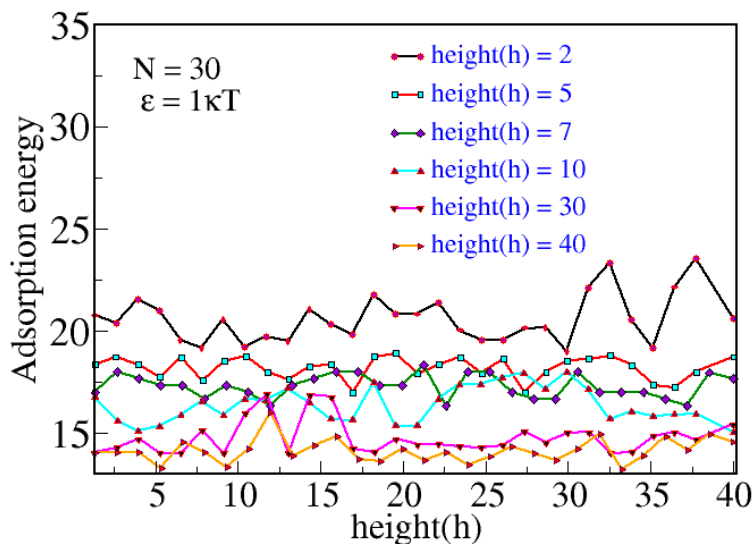

Figure 4.12: Adsorption energy versus surface roughness height(h) .Then height $(h) = 2, 5, 7, 10, 30$ and 40.

of surface by adsorbed monomers. When surface roughness height $h = 2$ adsorption energy and averaged adsorption energy were optimum. With constant interaction

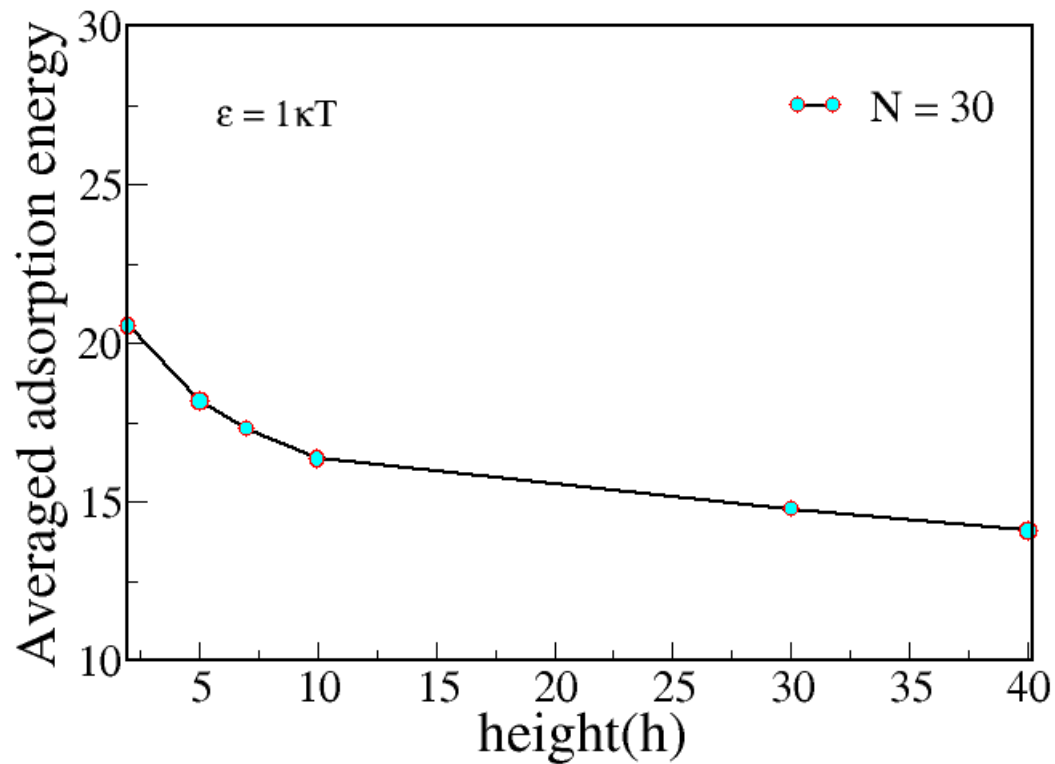Figure 4.13: Averaged adsorption energy versus surface roughness height$(h) = 2, 5, 7, 10, 30$ and 40 .

strength$(\epsilon) = 1KT$ and chain length $N = 30$ as shown in Figures 4.12 and 4.13 respectively our result in consistent with the reference[29].

5

Conclusion

We presented and tested a Monte Carlo simulation algorithm of linear polymer adsorption on rough surfaces. In static properties the scaling exponent of mean-square end-to-end distance $\langle R^2 \rangle$ and mean-square radius of gyration $\langle R_g^2 \rangle$ corresponds with chain length N and their scaling exponents were 2.0 and 1.78 respectively. The slopes were non universal due to the roughness of surfaces closes to the monomer beads that cases the end-to-end distance of polymers conformation to extended or stretch and radius of gyration of polymer conformation was distorted or inhibited.

On the other hand, adsorbed monomers, averaged adsorbed monomers, averaged adsorbed monomers fraction, averaged adsorption energy and adsorption energy as the function of chain length and surface roughness height in addition to the adsorption energy with the interaction strength (ϵ_s). Chain length 85 was largest surface coverage because of enthalpic contribution of polymer surface contacts was the optimum and the system losses less configurational entropy arising from the confinement to the surface. The chain increases the averaged adsorbed monomers fraction were decreased. Chain length $N = 30$ was maximum averaged adsorbed monomers fraction. Adsorbed monomers, averaged adsorbed monomers, averaged adsorbed monomers fraction, averaged adsorption energy and adsorption energy were maximum for shortest surface roughness height (h) $= 2$, for a give chain length $N = 30$ and strong interaction strength(ϵ_s). Adsorption energy was maximum for the strongest interaction strength(ϵ_s) and longer chain length.

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